FROM RESEARCH TO INDUSTRY

# New types of Pu fuel and targets for actinide transmutation

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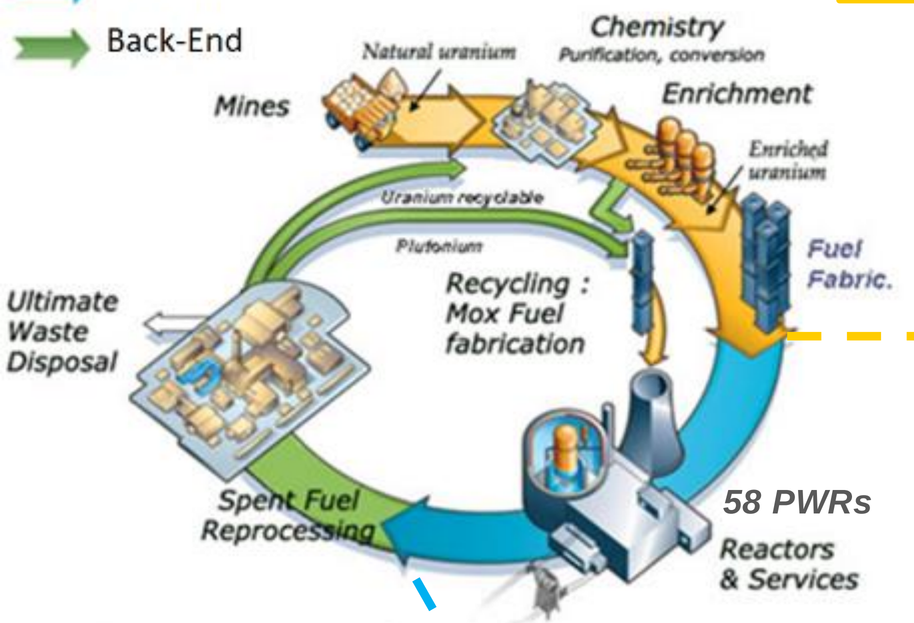
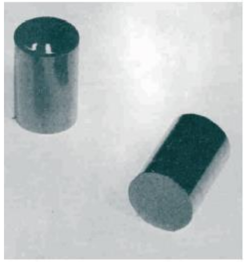
# INTRODUCTION: NUCLEAR FUEL CYCLE

Front-End
Reactor
Back-End

*In France:*

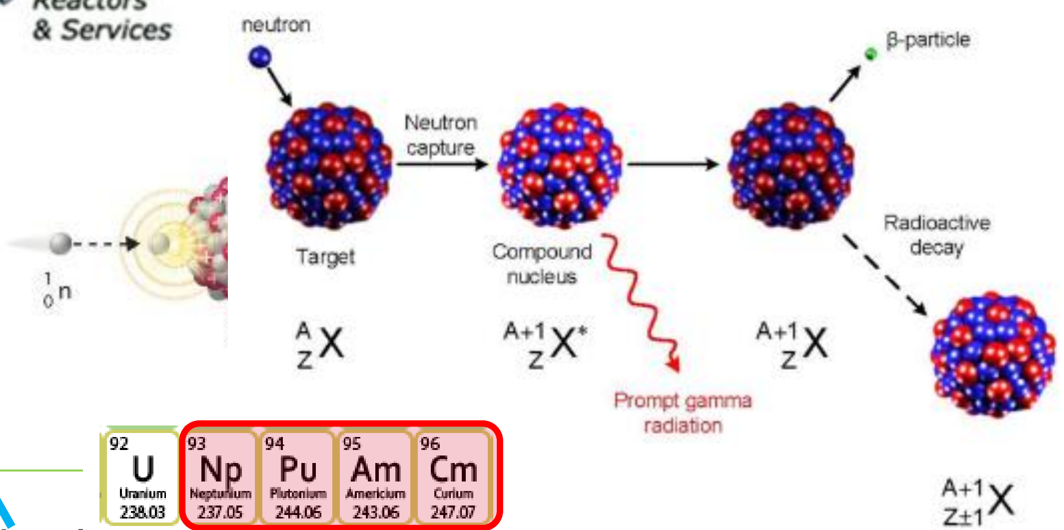
**UOX**: enriched $UO_2$
**MOX**: $(U,Pu)O_2$



Evolution of the chemical composition:
- Nuclear fissions (FPs)
- Neutron captures & radioactive decays (MAs)

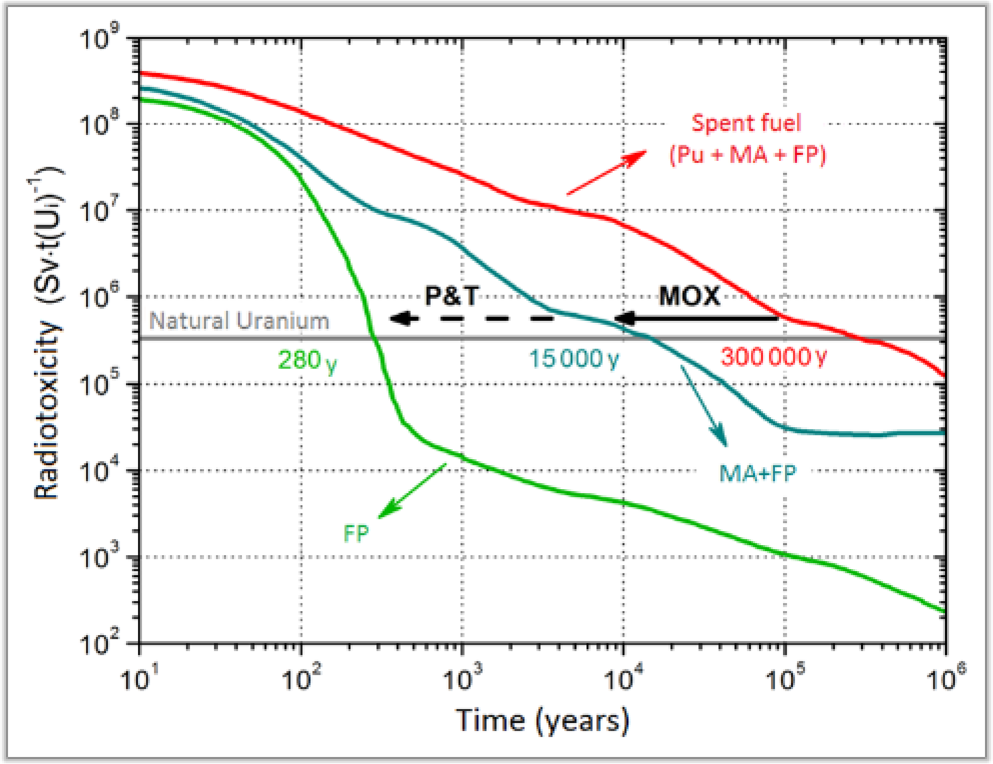
**Spent fuel*:**
- U~ 95 wt.%
- FPs ~ 3.9 wt.%
- Pu ~ 1 wt.%
- **MAs ~ 0.1 wt.%**




*UOX fuel, b.u =33 GW·d·t$^{-1}$

# INTRODUCTION: PARTITION & TRANSMUTATION

- Spent fuel: long-term **radiotoxicity** due to
  - ❑ **Pu**
  - ❑ MAs, in particular $^{241}$**Am**
- Pu → already recovered to produce MOX

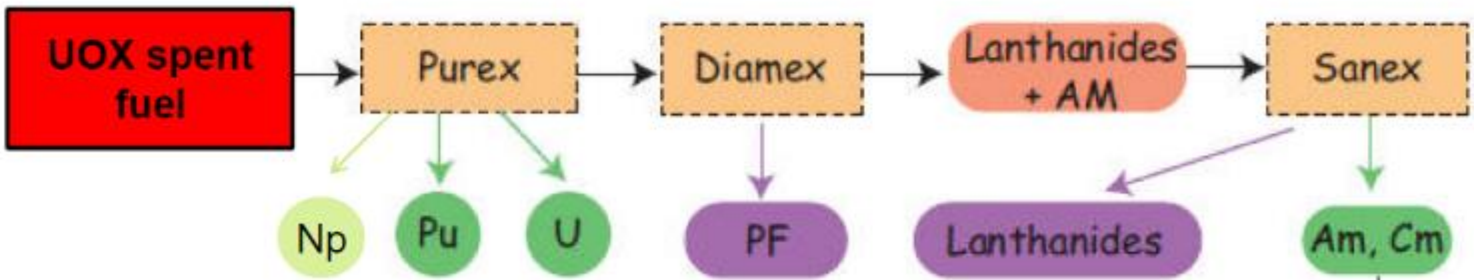


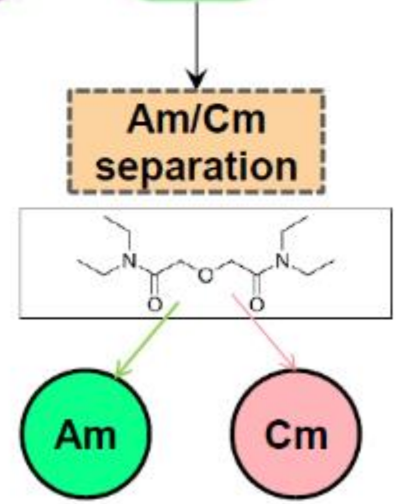

- Next step for a sustainable **nuclear fuel cycle**:

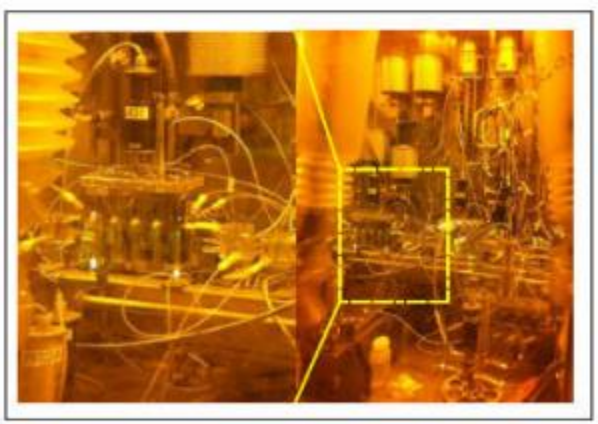
**Partition & Transmutation of MAs**

# INTRODUCTION: MA EXTRACTION

➢ Selective liquid-liquid extraction – advanced steps



*Purex - 2014 Atalante*

# INTRODUCTION: PARTITION & TRANSMUTATION

**MA are considered separately:**

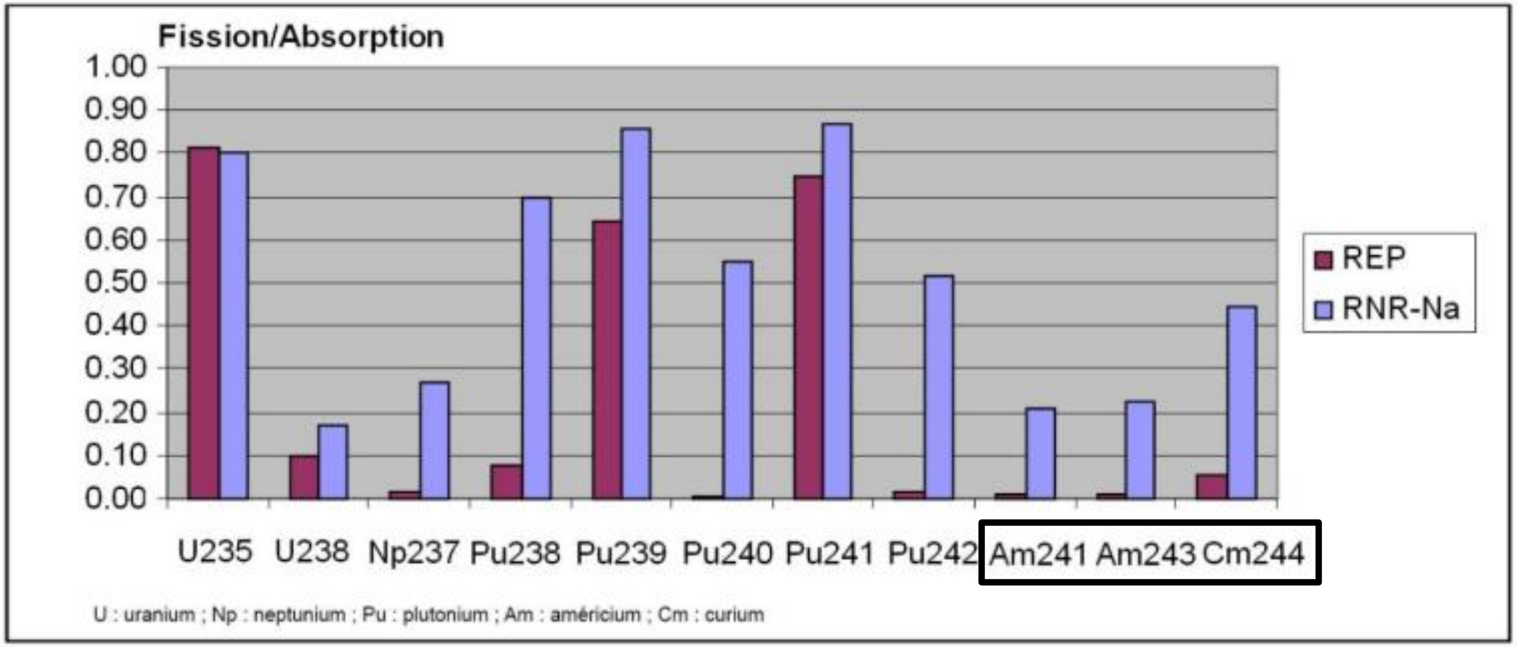
- Priority to americium ($^{241}$Am and $^{243}$Am) : Relative abundance + high radiotoxicity
- Curium : $^{244}$Cm very active but disappears after 100 years
  - **radioprotection constraints**: Gloves box not efficient (neutronic + thermal emission))
- Neptunium ($^{237}$Np) : less active

| Isotope | $^{237}$Np | $^{241}$Am | $^{243}$Am | $^{244}$Cm | $^{245}$Cm |
|---|---|---|---|---|---|
| Half-life (year) | $2.14\times10^{6}$ | 433 | 7370 | 18.1 | 8500 |
| Activity ($Bq.g^{-1}$) | $2.6\times10^{7}$ | $1.3\times10^{11}$ | $7.4\times10^{9}$ | $3.0\times10^{12}$ | $6.4\times10^{9}$ |
| Quantity in spent fuel ($g.TWhe^{-1}$)* | 1700 | 1160 | 540 | 190 | 16 |

* After 5 years cooling time

# INTRODUCTION: TRANSMUTATION

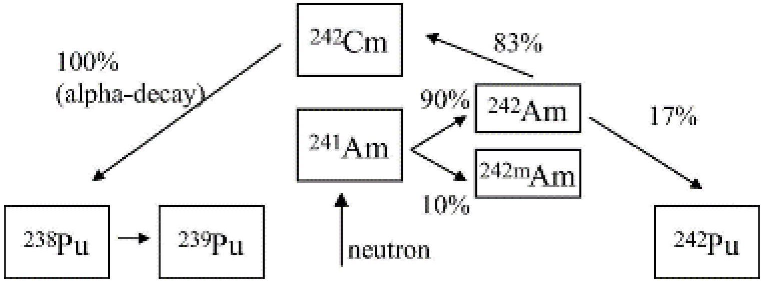
Competition between fission (heat + FP) and capture (heavier element) for actinide elements in PWR (thermal neutrons) and Na-FR



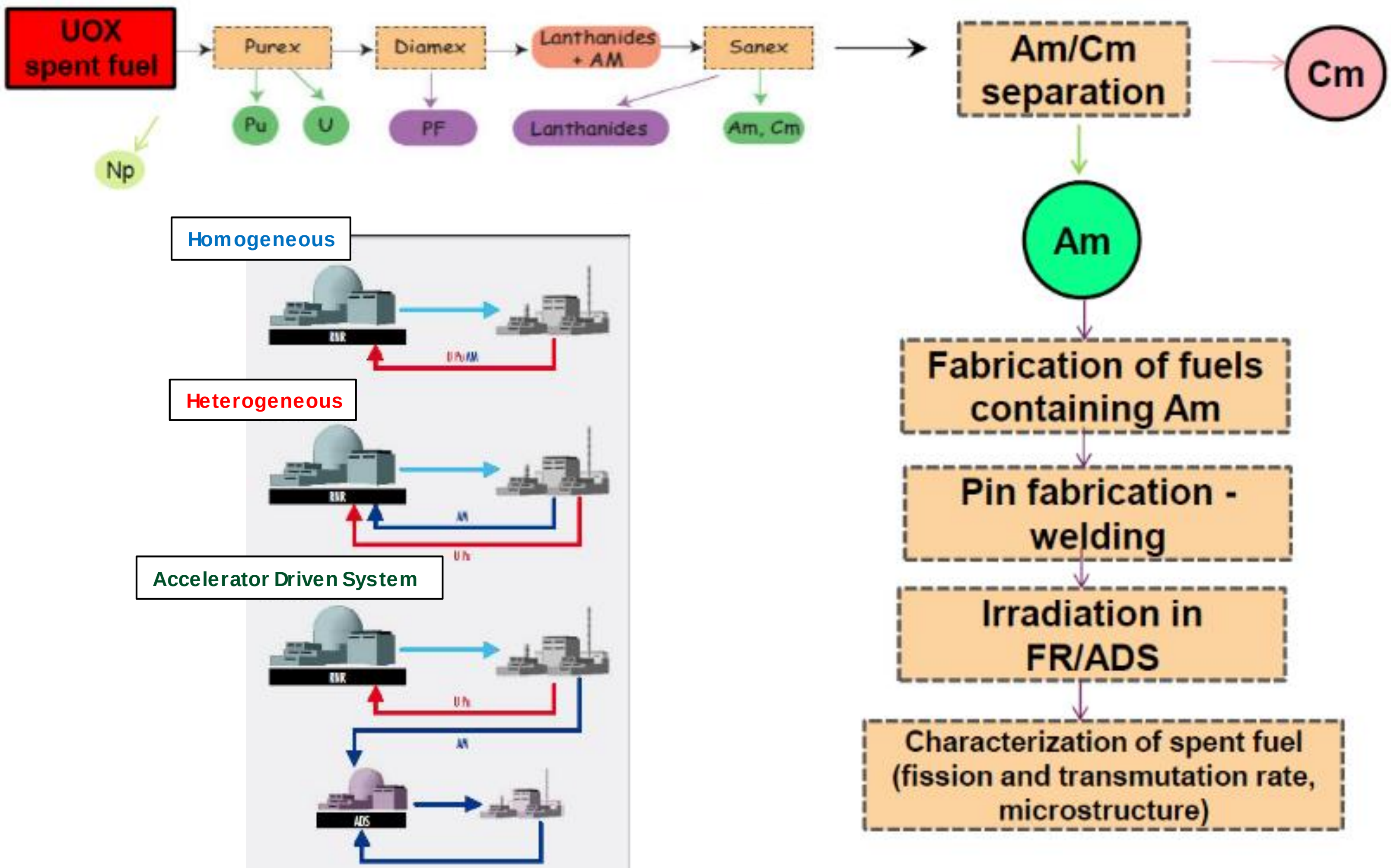

FNR advantages:

- MA $\sigma_f > \sigma_c$ compared to PWR
- positive neutron balance for Am/Cm/Np

**Transmutation in FN reactors**

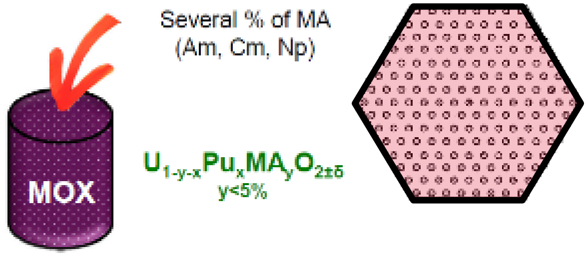


# INTRODUCTION: TRANSMUTATION




CEA Report « Avancées des recherches sur la séparation-transmutation et le multi-recyclage du plutonium dans les réacteurs à flux de neutrons rapides, juin 2015, France.

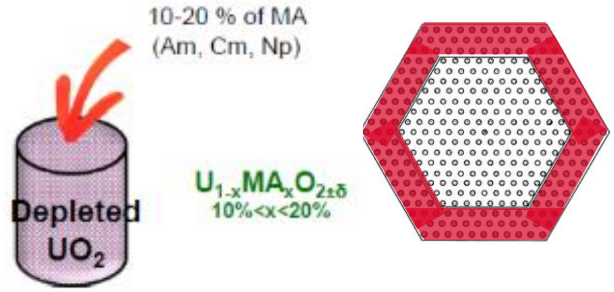
# INTRODUCTION: TRANSMUTATION SCENARIOS




## Homogeneous

### MA-MOX fuel

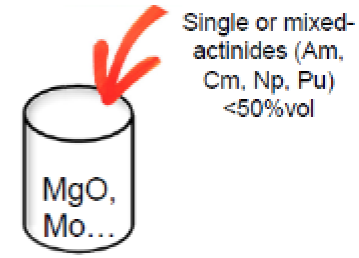
- MAs (few %) diluted in the fuel
- Low quantity to minimize impact on reactor safety (thermal properties)
- High neutron flux
- Drawbacks :
  - Irradiation time
  - MA inventory on all fuel elements ➔ technological constraints on the whole fuel cycle




## Heterogeneous

### MABB (Minor Actinide bearing Blanket)

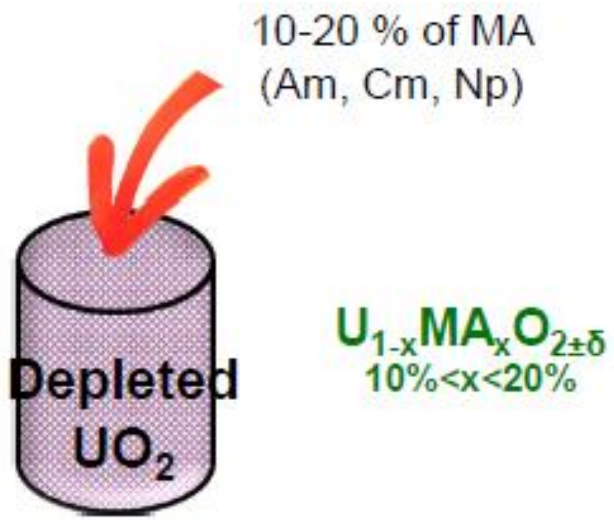
- MA concentrated in dedicated assemblies located at the periphery of the core (blanket)
- Higher MA content (10-20 %)
- No impact on operating reliability of the reactor
- Independent management of MABB and spent fuel
- Drawbacks:
  - 2 production lines
  - MABB must stay longer than core fuel




### ADS (Accelerator Driven System)

- System dedicated to transmutation
- Electricity production and transmutation are independent
- Subcritical core => high MA charge up to 50% vol. (Pu, Np, Am, Cm).
- Drawbacks:
  - Necessity of a particle accelerator.
  - Dedicated production line

# TRANSMUTATION BY HETEROGENEOUS MODE



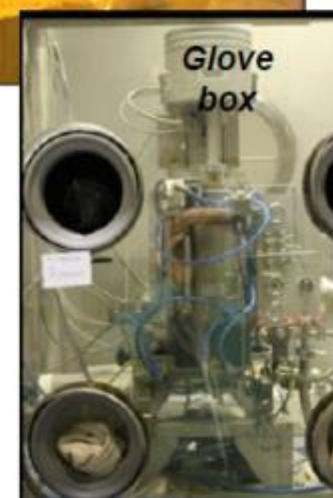

**MANUFACTURING AND PROPERTIES OF $U_{1-x}Am_xO_{2\pm\delta}$ OR MABB (Minor Actinide Bearing Blanket)**

# HETEROGENEOUS MODE: MANUFACTURING CONDITIONS

## Fabrication : working conditions in Atalante (CEA Marcoule)

- Fabrication of pellets in hot cell with remote handling
- Characterization in shielded glove boxes/hot cell


Shielded hot cell




**Objective**: development of simple and reliable process limiting dissemination of highly radioactive fine particles

# HETEROGENEOUS MODE: EXPERIMENTAL IRRADIATION PROGRAMS

| Experiment | SUPERFACT –high MA content | MARIOS | DIAMINO | MARINE |
|---|---|---|---|---|
| Irradiation date | 1986-1988 | 2011-2012 | 2014-2015 | 2015-2016 |
| Test reactor | PHENIX | HFR | OSIRIS | HFR |
| MABB | $(U_{0,60}Am_{0,19}Np_{0,21})O_{2-x}$ | $(U_{0,85}Am_{0,15})O_{2-x}$ | $(U_{0,925}Am_{0,075})O_{2-x}$ $(U_{0,85}Am_{0,15})O_{2-x}$ | $(U_{0,86}Am_{0,14})O_{2-x}$ |
| Fabrication route | Internal gelation | Powder metallurgy | Powder metallurgy | Internal gelation |
| Geometry | Pellet | Disc | Disc | pellet |
| % theoretical density | 96 | 88 ; 92 | 82-85 ; 96-97 | 94 |

**CEA Report 2015** « Avancées des recherches sur la séparation-transmutation et le multi-recyclage du plutonium dans les réacteurs à flux de neutrons rapides, juin 2015, http://www.cea.fr/multimedia/Documents/publications/rapports/avancees-recherches-separation-transmutation-et-multirecyclage-pu-rnr.pdf

# HETEROGENEOUS MODE: FABRICATION GENERAL SCHEME

**Powder metallurgy**

Raw powder(s)

↓

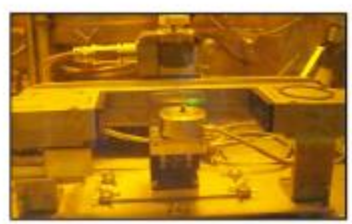
Preparation (milling, sieving, mixing)

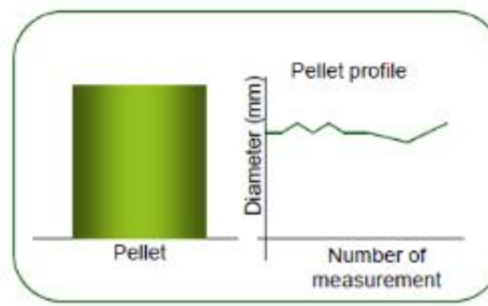
↓

Uniaxial pressing

↓

Sintering






↓

*Contraction Φ-15/20%*

# FABRICATION OF DENSE $U_{1-x}Am_{X}O_{2\pm\delta}$

# FABRICATION OF DENSE $U_{1-x}Am_xO_{2\pm\delta}$: PROCESSES DEVELOPED AT CEA

FROM RESEARCH TO INDUSTRY — cea den

**2010** — **2011** — **2013**

**Reactive sintering between $UO_2$ and $AmO_2$**

$UO_2$ | $AmO_2$

Simplicity

Incomplete densification <92%

*Irradiation program: MARIOS*

D. Prieur *et al.*, *J. Nucl. Mater.* **414** (2011) 503

**UMACS, adding of a step dedicated to solid solution formation**

$UO_2$ | $AmO_2$

High densities >95%

Dust production

*DIAMINO*

T. Delahaye et al., French patent 11–60597, 2011 // *J. Nucl. Mater.* 432 (2013) 305

**Use of $U_{1-x}Am_xO_{2\pm\delta}$ CO-CONVERTED powder as a precursor**

Solid solution $(U,Am)O_2$

High densities >95%
Reduced sintering temperature

Reduced dust production

*AmBB-1*

D. Horlait *et al.*, *J. Nucl. Mater.* **444** (2014) 181
*L. Ramond et al., JECS 36 (2016) 1775*

**Calcined Resin Microsphere pelletizing**

Impregnation of resin microspheres with U/Am nitrate

High densities >95%

Highly reduction of dust production

*AmBB-1*

E. Remy *et al.*, *J. Nucl. Mater.* **453** (2014) 214

→ Improvment of the densification

→ Reduction of dust generation, increase of reactivity

| PAGE 17

# FABRICATION OF DENSE $U_{1-x}Am_xO_{2\pm\delta}$: REACTIVE SINTERING

**2010**

**Reactive sintering**

$UO_2$ | $AmO_2$

↓

Ball-milling

↓

Pelletizing

↓

Reactive sintering
2023K-4h

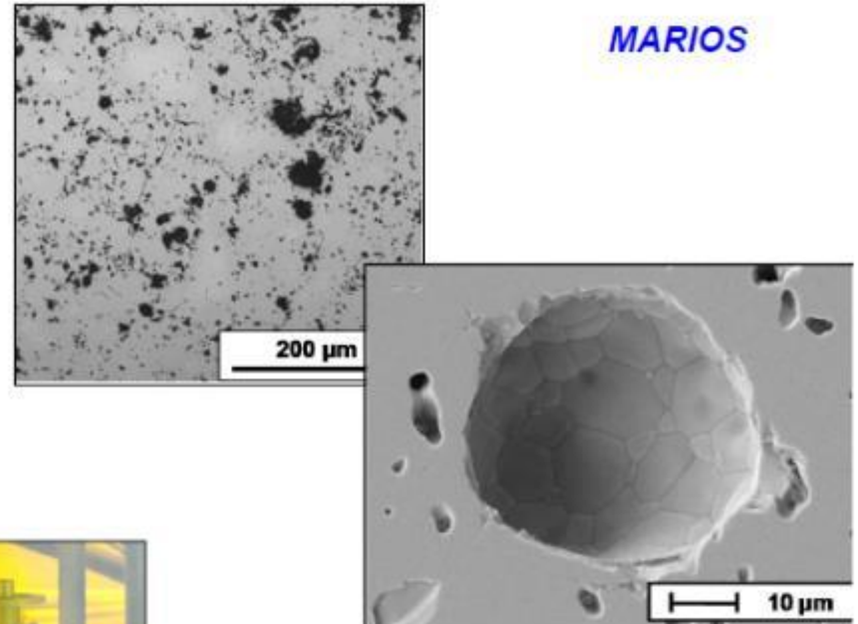
↓

$(U,Am)O_2$ pellet
**<92%TD**

**Simplicity**

**Incomplete densification**

*MARIOS*




- Solid Solution $U_{0.85}Am_{0.15}O_{2\pm\delta}$
- Density $D_f$ < 92 %TD
- Heterogeneous microstructure

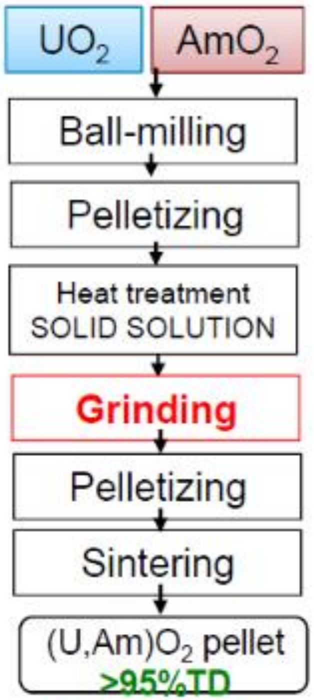
D. Prieur *et al.*, *J. Nucl. Mater.* 414 (2011) 503

**Competition between densification and formation of the solid solution ➔ incomplete densification**

# FABRICATION OF DENSE $U_{1-x}Am_xO_{2\pm\delta}$: UMACS PROCESS

**2011**

**UMACS, adding of a step dedicated to solid solution formation**




**High densities**

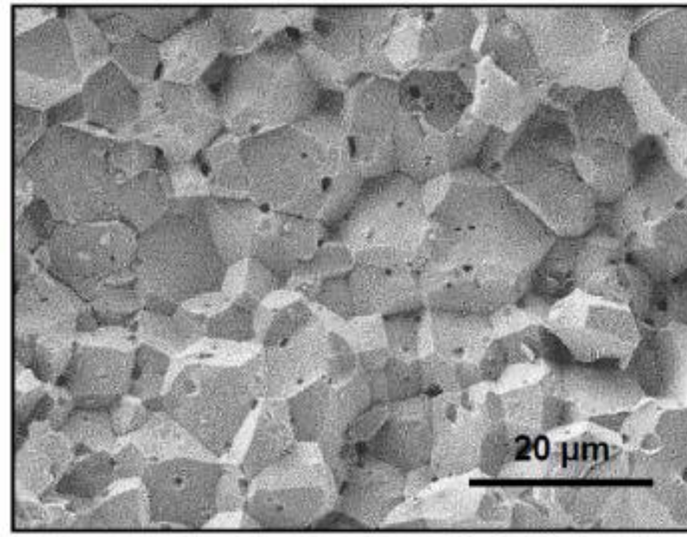
**Dust producing**

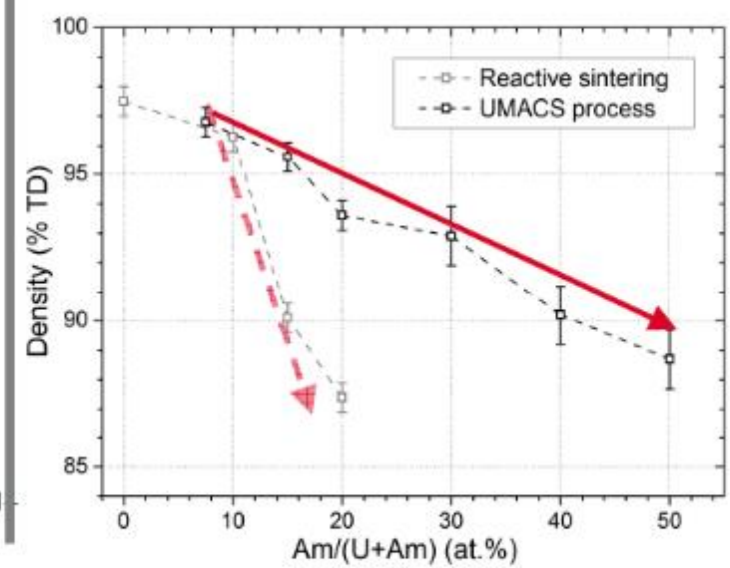
T. Delahaye et al., French patent 11-60597, 2011 // *J. Nucl. Mater.* **432** (2012) 305

***DIAMINO***

**Final pellets :**

- Complete formation of ideal solid solution for 0.075 ≤ x ≤ 0.7.
- Low residual porosity (for x<30%) high densification




Final density ↘when Am content ↗

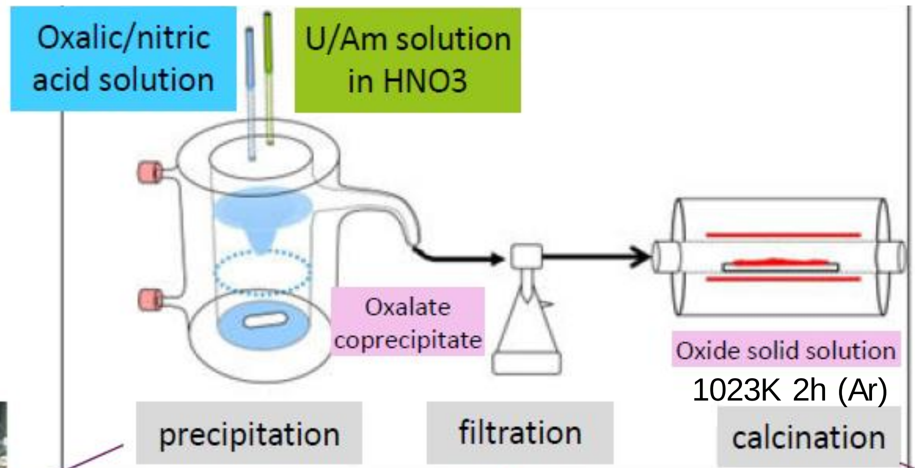
…but this loss of density is less important with UMACS than reactive sintering

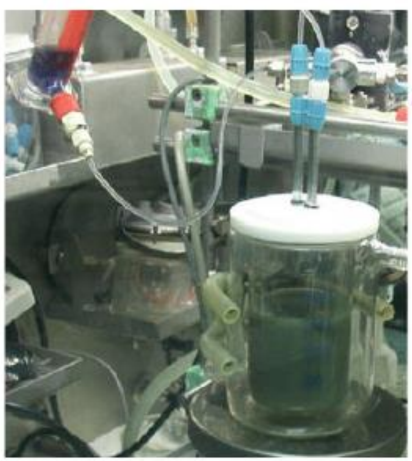
# FABRICATION OF DENSE $U_{1-x}Am_xO_{2\pm\delta}$: OXALIC CO-CONVERSION

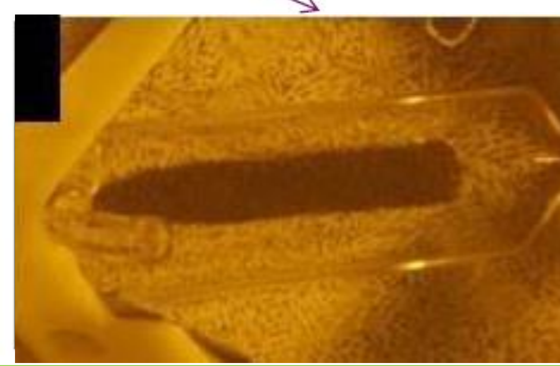
**2013** — Feasibility demonstrated at Atalante - $\mathbf{U_{1-x}Am_xO_{2\pm\delta}}$

- 15 g of $(U_{0.90}Am_{0.10})O_{2\pm\delta}$ and $(U_{0.85}Am_{0.15})O_{2\pm\delta}$ powders
- Reduced number of steps BUT presence of powders (dissemination risk!)

Solid solution $(U,Am)O_2$
↓
Pelletizing
↓
Sintering
↓
$(U,Am)O_2$ pellet **>95%TD**

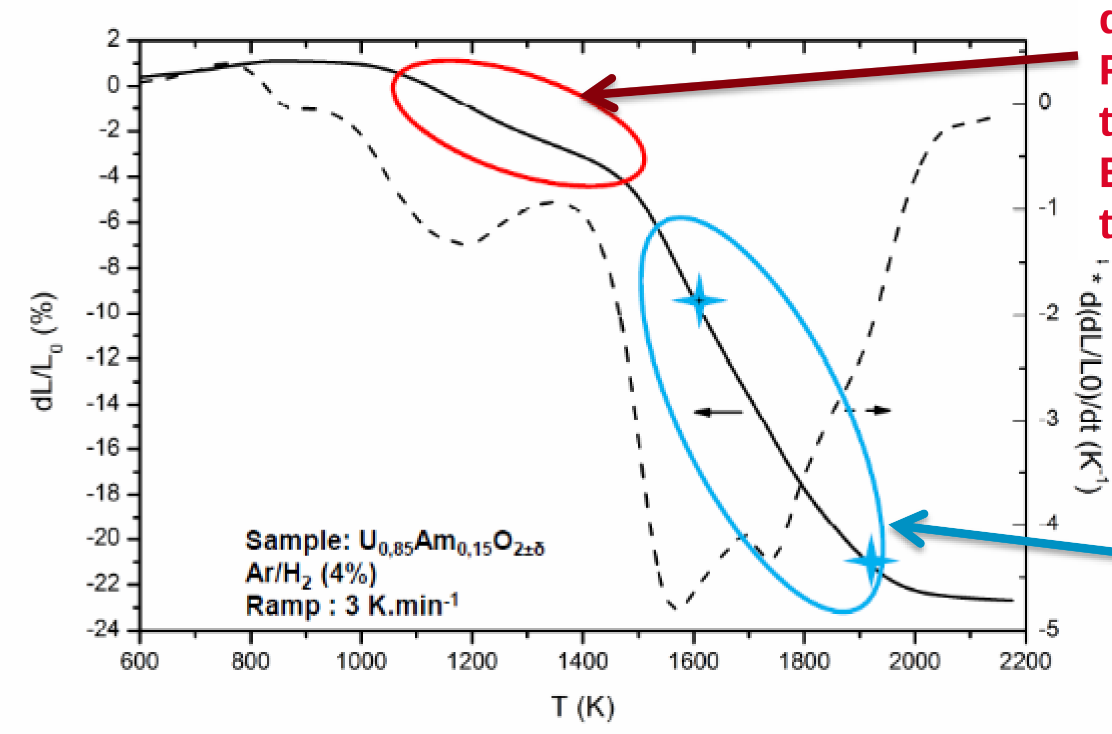


# FABRICATION OF DENSE $U_{1-x}Am_xO_{2\pm\delta}$: OXALIC CO-CONVERSION: SINTERING STEPS

- Understanding and optimization of the sintering of the co-converted $(U,Am)O_{2\pm\delta}$ powder
- Identification of the 2 phenomena: shrinkages 4% and 18%




**$dL/L_0 = -4\%$**
**First shrinkage linked to a microstructural Effect ➔ pre-sintering of the finest particles**

**dL/L0 = -18%**
**Strong shrinkage of about 18%**
**➔ sintering of an oxide ceramic materials**

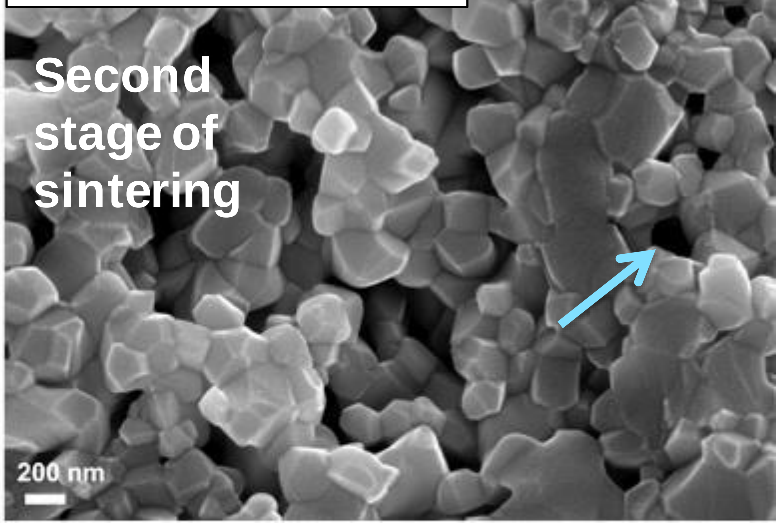
Dilatometry curve of the co-converted $U_{0.85}Am_{0.15}O_{2\pm\delta}$ compound, heat-treated at 1023K-3h under argon

L. Ramond et al. Journal of the European Ceramic Society. 36 (2016) 1775–1782. doi:10.1016/j.jeurceramsoc.2016.01.028.

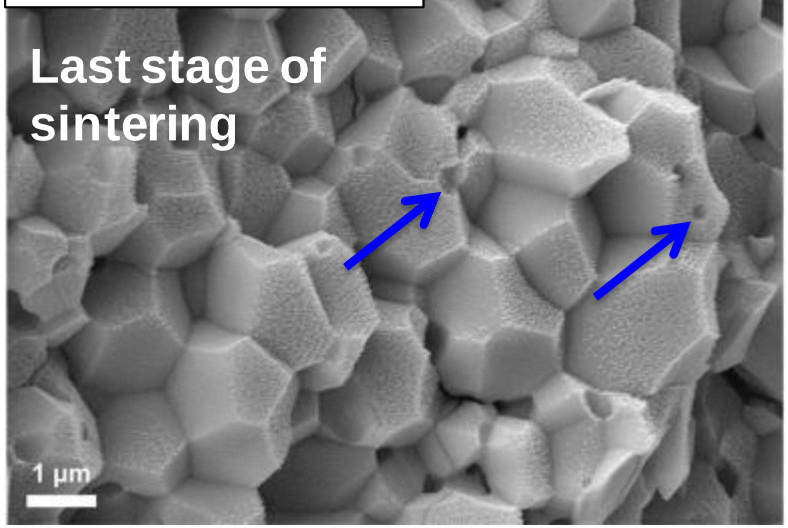
# FABRICATION OF DENSE $U_{1-x}Am_xO_{2\pm\delta}$: OXALIC CO-CONVERSION: SINTERING STEPS

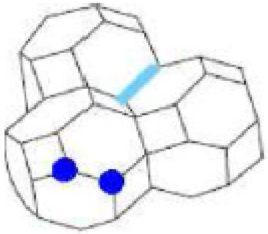
SEM micrographs (secondary electron mode) of sintered $U_{0.85}Am_{0.15}O_{2\pm\delta}$ pellets prepared with powder obtained by calcination 3h at 1023 K under Ar then heat treated 1h at 1373 K under Ar+4%$H_2$

1.5 h at 1610K – D~77 %




4 h at 1900K – D~95%



Open porosity

Closed porosity

➔ **Second shrinkage on dilatometry curve due to densification steps**

L. Ramond et al. Journal of the European Ceramic Society. 36 (2016) 1775–1782. doi:10.1016/j.jeurceramsoc.2016.01.028.

# FABRICATION OF DENSE $U_{1-x}Am_xO_{2\pm\delta}$: CRMP ⇔ MICROSPHERE SYNTHESIS

FROM RESEARCH TO INDUSTRY

**2013**

Calcined Resin Microsphere Pelletizing

Impregnation of resin spheres with U/Am nitrate

↓

Calcination

↓

Pelletizing

↓

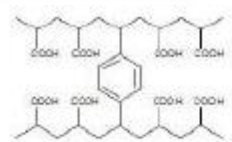
Sintering

↓

$(U,Am)O_2$ pellet
**>95%TD**

**Drastic reduction of dust production**

Resin → Sieving - washing → Fixation → Drying → Carbonisation Under Air



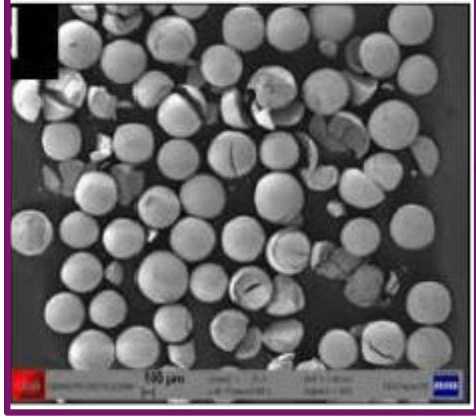


E. Remy et al. Journal of Nuclear Materials. 453 (2014) 214–219. doi:10.1016/j.jnucmat.2014.06.048.

$(U,Am)_3O_8$

Reductive treatment under $Ar\text{-}4\%H_2$

$(U_{0.90}Am_{0.10})O_{2\pm\delta}$ microspheres

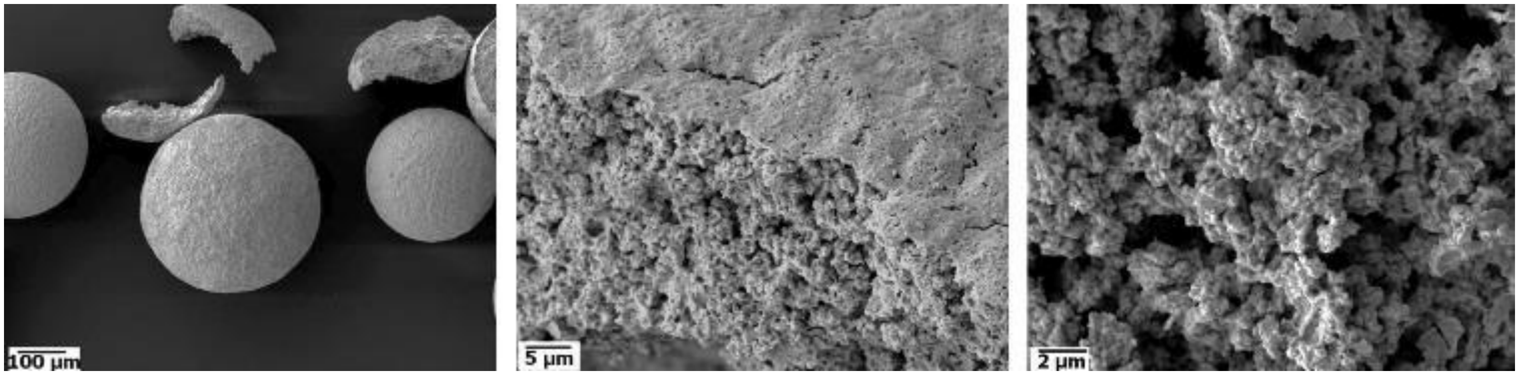


- Porous microspheres (density ~25%) constituted by submicronic particles.
- Φ ~375±50 µm

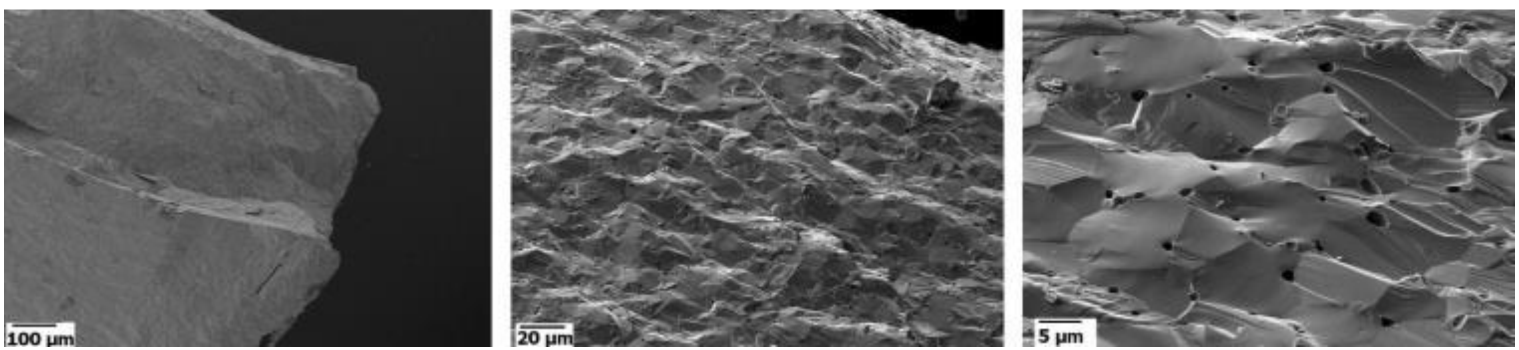
# FABRICATION OF DENSE $U_{1-x}Am_xO_{2\pm\delta}$: CRMP

**SEM observations in secondary electron mode**

Reduced oxide microsphere morphology and internal microstructure




After pelletizing & sintering at 1750 °C (Ar + 4% H2)




➔ D ~ 95% DT

E. Remy et al. Journal of Nuclear Materials. 453 (2014) 214–219. doi:10.1016/j.jnucmat.2014.06.048.

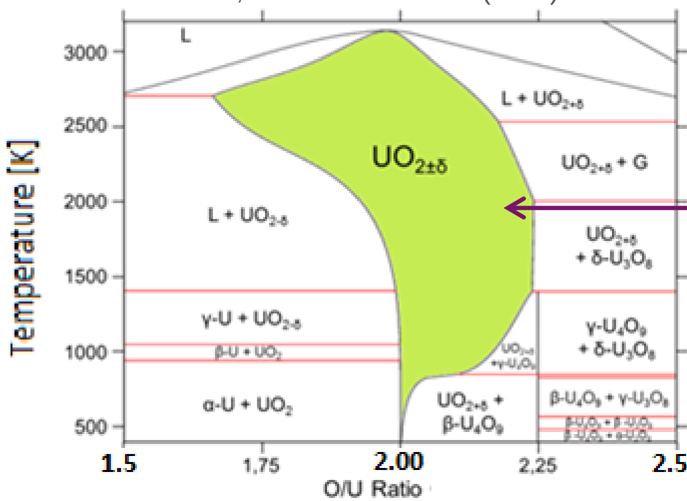
# PECULIAR STRUCTURAL PROPERTIES OF $(U,Am)O_{2\pm\delta}$
# ⬄
# IMPACT ON MELTING POINT

# PECULIAR STRUCTURAL PROPERTIES OF $(U,Am)O_{2\pm\delta}$

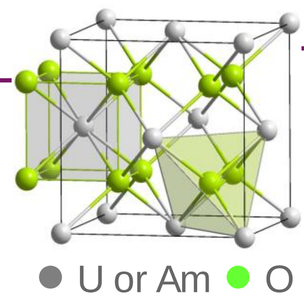
## The U-O and Am-O systems

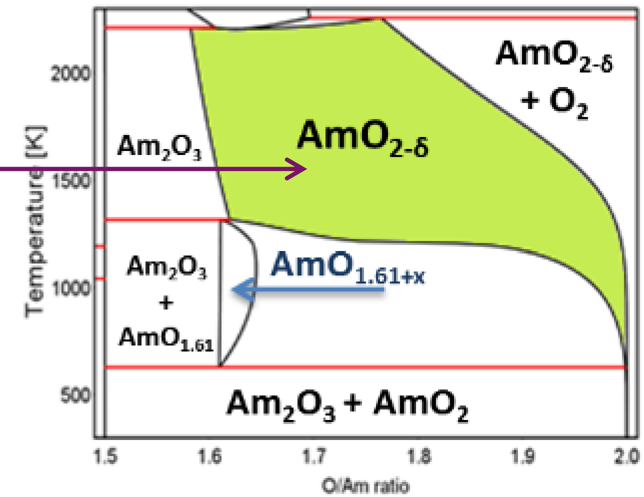
1. C. Guéneau *et al.*, *J. Nucl. Mater.* 419 (2011) 145-167

*2. E. Epifano et al., Inorg. Chem. 56 (2017) 7416–7432*




Fluorite structure




- U oxidation state between +3 and +6
  - ❑ Large existence domain of **$UO_{2\pm\delta}$**
  - ❑ *Hyper-stoichiometric* phases ($U_4O_9$, $U_3O_8$…)
- Am oxidation states between +3 and +4
  - ❑ Large existence domain of **$AmO_{2-\delta}$**
  - ❑ *Hypo-stoichiometric* phases

$UO_{2\pm\delta}$ and $AmO_{2-\delta}$ have different thermodynamic properties ⬄ Oxygen/Metal **(O/M)** ratio

**$(U,Am)O_{2\pm\delta}$ solid solution stability ?**

# PECULIAR STRUCTURAL PROPERTIES OF $(U,Am)O_{2\pm\delta}$

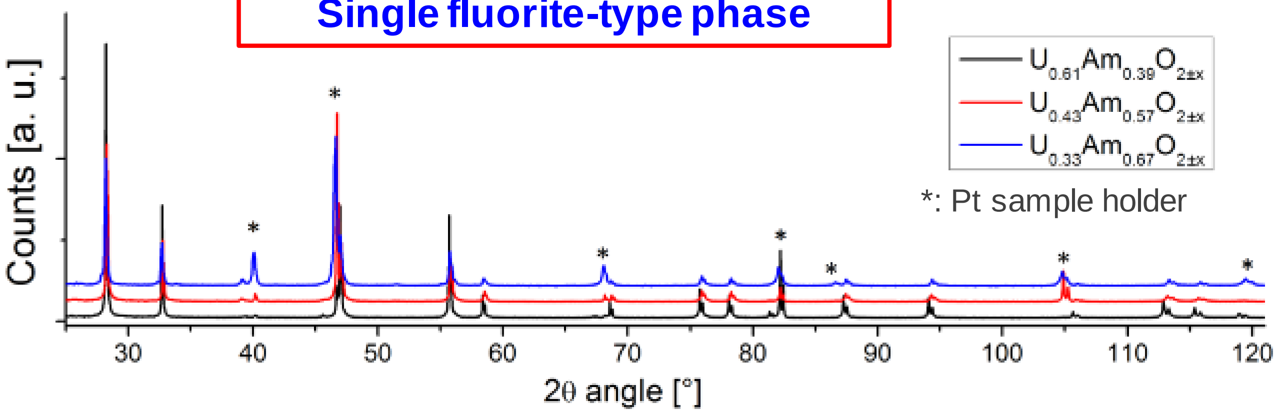
- **Dense $(U, Am)O_{2\pm x}$** pellets manufactured with the UMACS[7] process

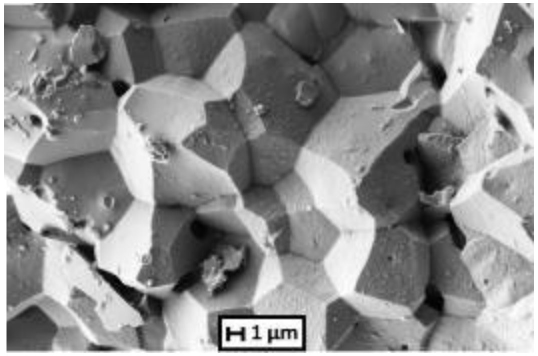
7. T. Delahaye et al, *J. Nucl. Mater.* 432, (2013), 305-312

- Different Am contents: 7 ≤ Am/(Am+U) ≤ 70 mol.%

- **Characterizations:**
  - **TIMS:** measured Am/(Am+U) ratios
  - **SEM**: expected **microstructure**, well-faceted grains of 5-10 µm
  - **XRD: homogeneity of the powdered samples**

**Single fluorite-type phase**




**O stoichiometry ⇔ O/(U+Am) ratio ?**

E. Epifano, "Study of the U-Am-O ternary phase diagram", Université Paris-Saclay, 17/112017.

# PECULIAR STRUCTURAL PROPERTIES OF $(U,Am)O_{2\pm\delta}$

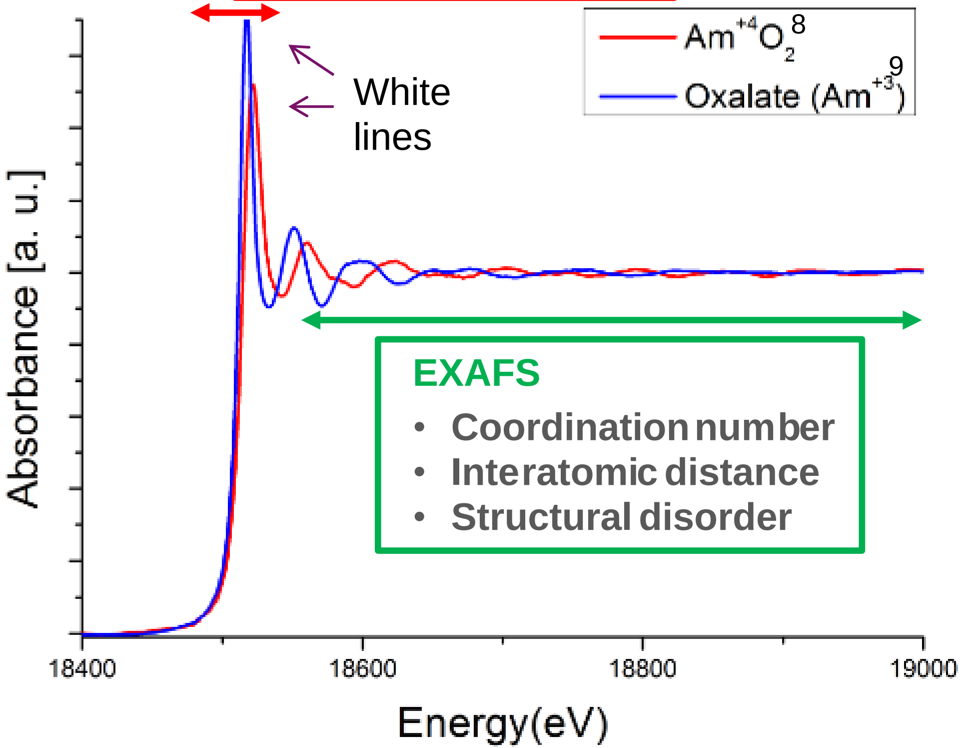
## X-ray Absorption Spectroscopy (XAS)

- **U $L_{III}$, U $L_{II}$** and **Am $L_{III}$** edges
- Measurements at **15 K** on **1 mg** samples

8. R. Belin et al., Inorg. Chem 52, (2013), 2966
9. B. Arab-Chapelet et al., Dalton Trans. 45 (2016) 6909

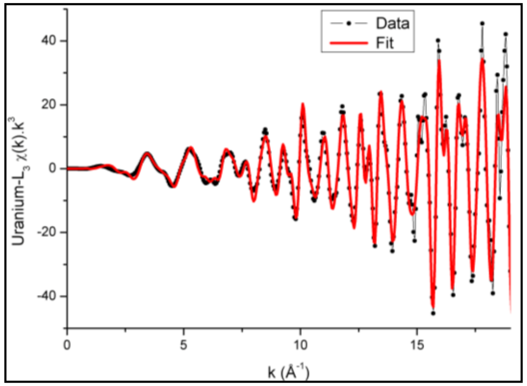
**Am-$L_{III}$**

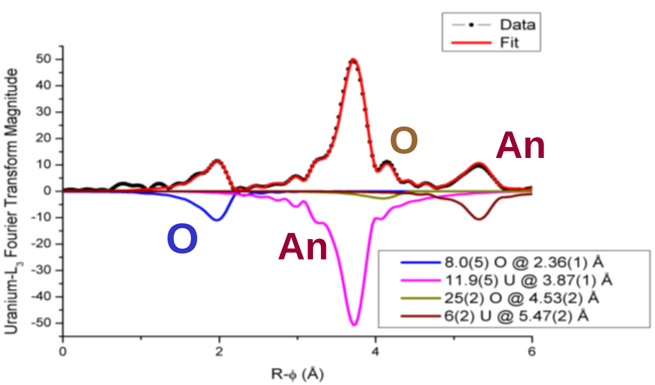
**XANES**
- Oxidation states
- Symmetry



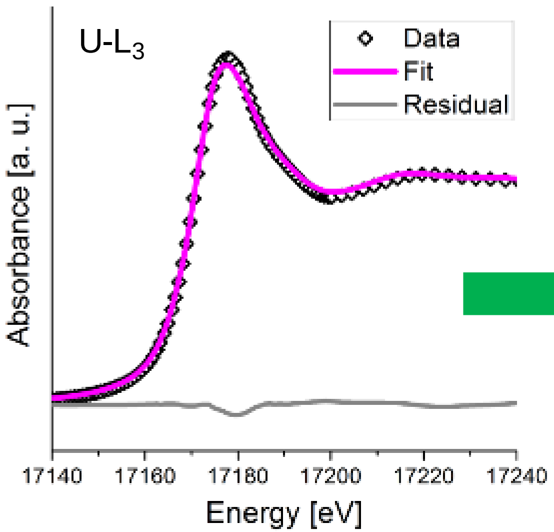

**EXAFS**
- Coordination number
- Interatomic distance
- Structural disorder

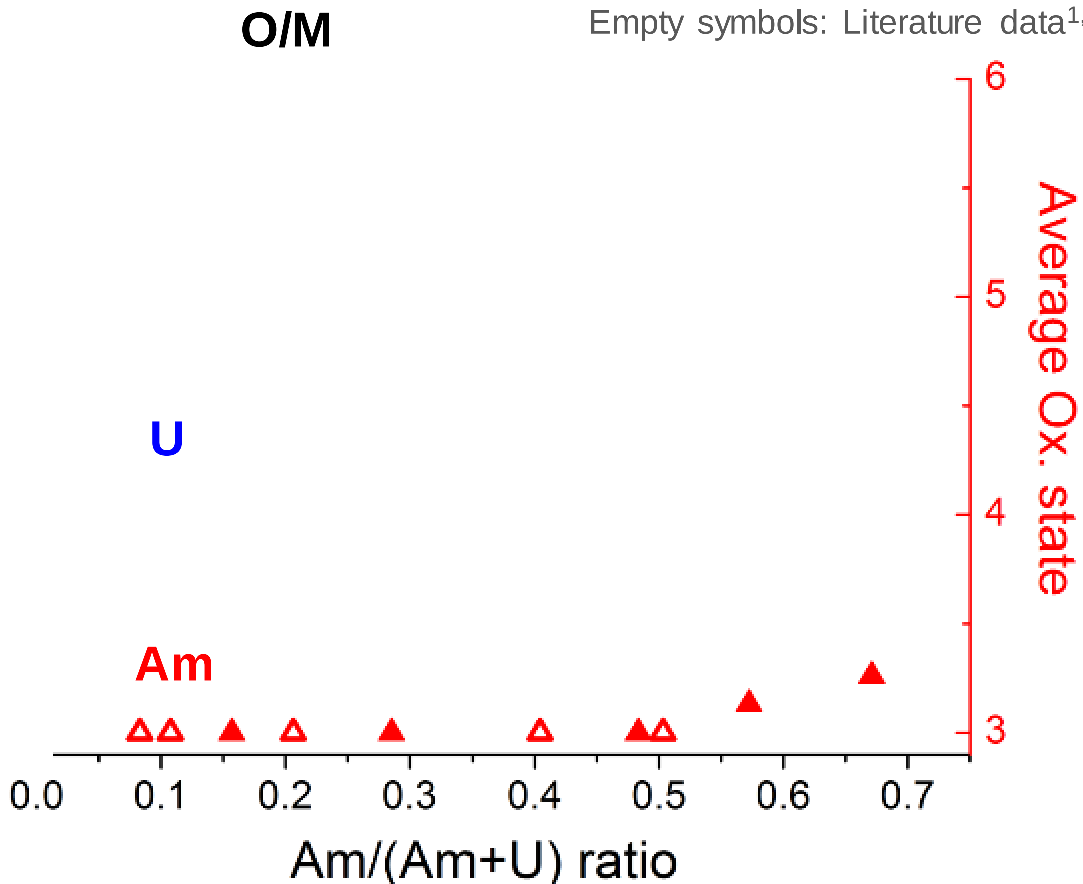
**$AnO_2$**



# PECULIAR STRUCTURAL PROPERTIES OF $(U,Am)O_{2\pm\delta}$




**Linear combination fit**

➔ U & Am oxidation states
➔ O/M ratios

- **High stability of $Am^{+3}$**
- **$Am^{+4}$** present for **Am/(Am+U) > 0.50**
- Increase of **U oxidation state** with the Am content
- **O/M<2** for Am/(Am+U)≥ 0.40

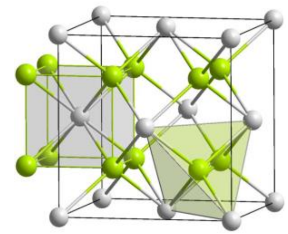
*E. Epifano, "Study of the U-Am-O ternary phase diagram", Université Paris-Saclay, 17/112017.*

1. F. Lebreton, *Synthèse et caractérisation d'oxydes mixtes d'uranium et d'américium* (PhD thesis), Limoges 2014
2. D. Prieur, *Elaboration de combustible à base d'oxydes d'uranium et d'americium: modelisation thermodynamique et propriétés des materiaux* (PhD thesis), Limoges 2011

# PECULIAR STRUCTURAL PROPERTIES OF $(U,Am)O_{2\pm\delta}$

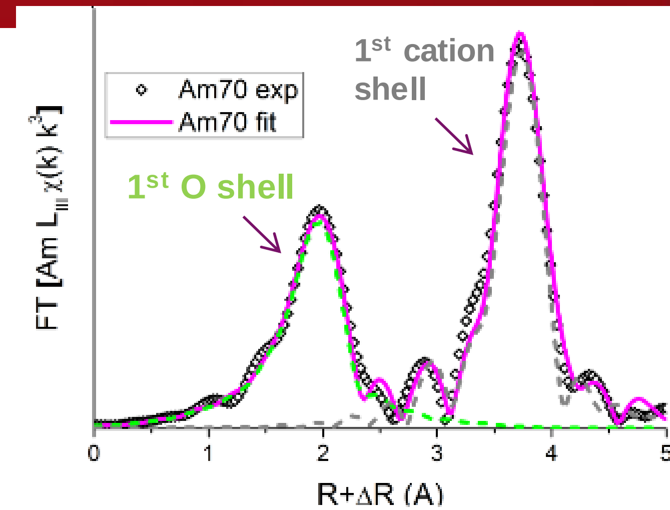
## Am-$L_3$ EXAFS fit:

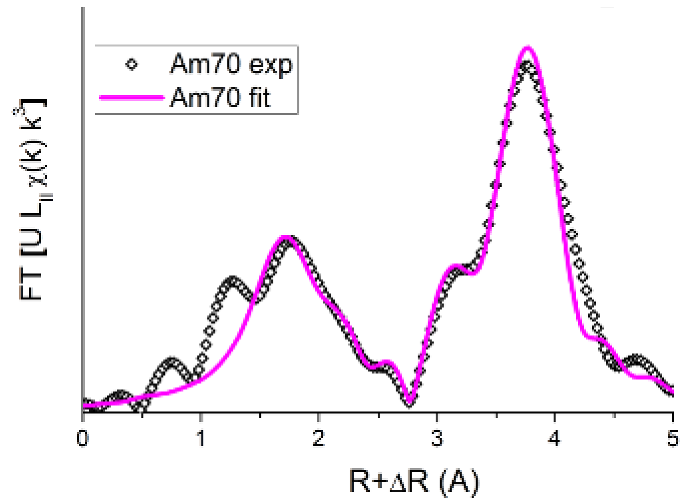
- Fluorite structure model
- Am/(Am+U) > 0.5, the fit shows oxygen vacancies

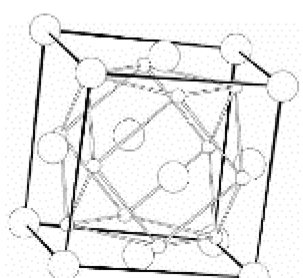


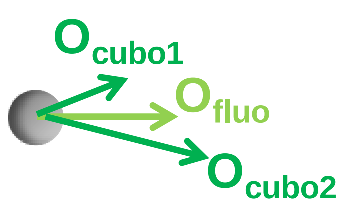

## U-$L_2$ EXAFS fit:

- For **Am/(Am+U) ≤ 0.30,** fluorite structure model
- For **Am/(Am+U) ≥ 0.50**:
  - ❑ Fail of the fluorite structure
  - ❑ Model based on the **β-$U_4O_9$** structure[1]
    - Cation sublattice unaffected
    - **Cuboctahedral O cluster→ Additional U-O distances**






**Sample Am70**

| | R (Å) |
|---|---|
| Ocubo1 | 2.17(1) |
| Ofluo1 | 2.29(1) |
| Ocubo2 | 2.82(1) |

*E. Epifano, "Study of the U-Am-O ternary phase diagram", Université Paris-Saclay, 17/112017.*

1. Cooper-Willis, *Acta Cryst A* 60, (2004), 322-325

# FABRICATION OF DENSE $U_{1-x}Am_xO_{2\pm\delta}$: PECULIAR STRUCTURAL PROPERTIES OF $(U,Am)O_{2\pm\delta}$

- New structural data acquired on $(U,Am)O_2$ with $0.15 \leq Am/M \leq 0.70$ *(E.. Epifano, "Study of the U-Am-O ternary phase diagram", Université Paris-Saclay, 17/112017).*

- First structural data on **$U_{0.4}Am_{0.6}O_{2-x}$** & **$U_{0.3}Am_{0.7}O_{2-x}$**
  - **$Am^{+4}$** presence
  - Increasing U oxidation state
  - **O/M ratio < 2**

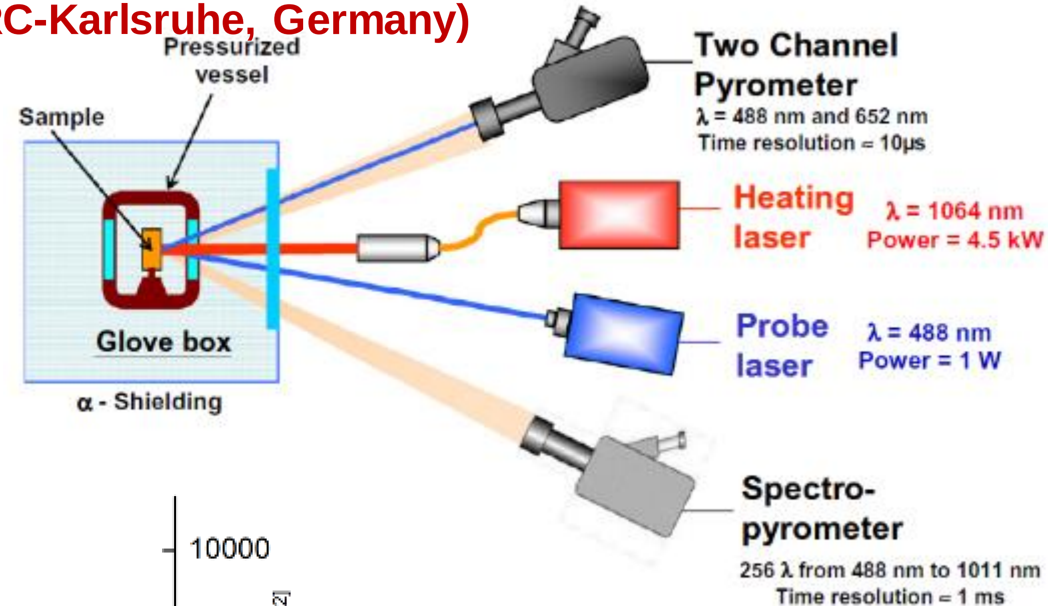
Fluorite-type structure

- Unaffected cationic sublattice
- Oxygen vacancies around Am
- Complex defects in the O sublattice around U

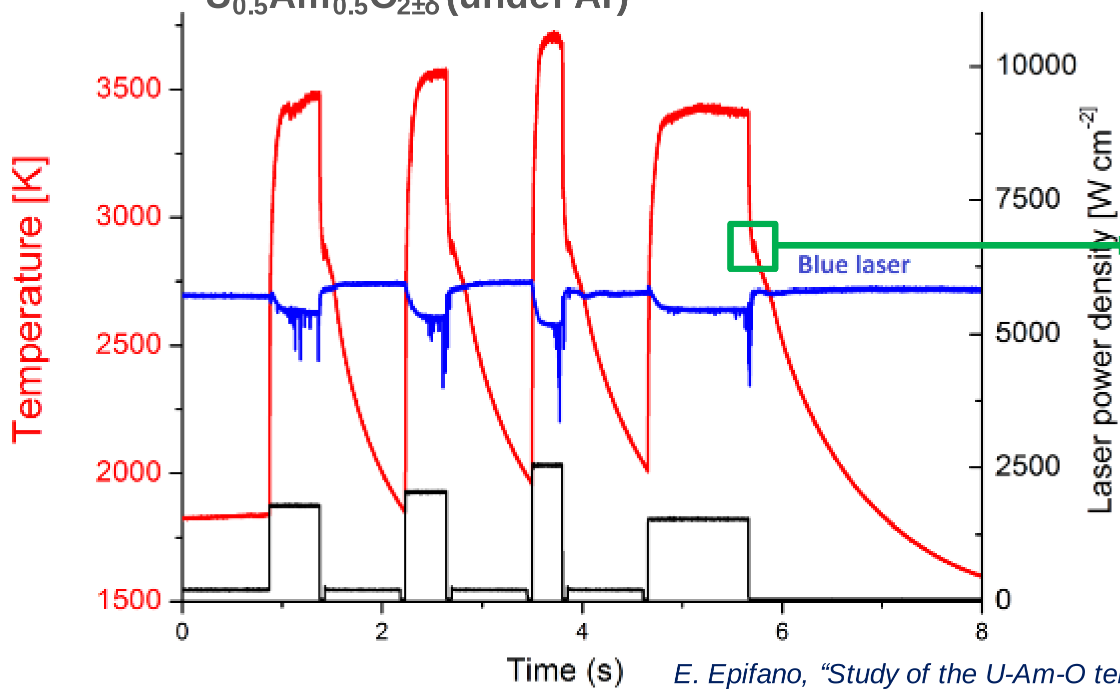
# FABRICATION OF DENSE $U_{1-x}Am_xO_{2\pm\delta}$: MELTING POINT

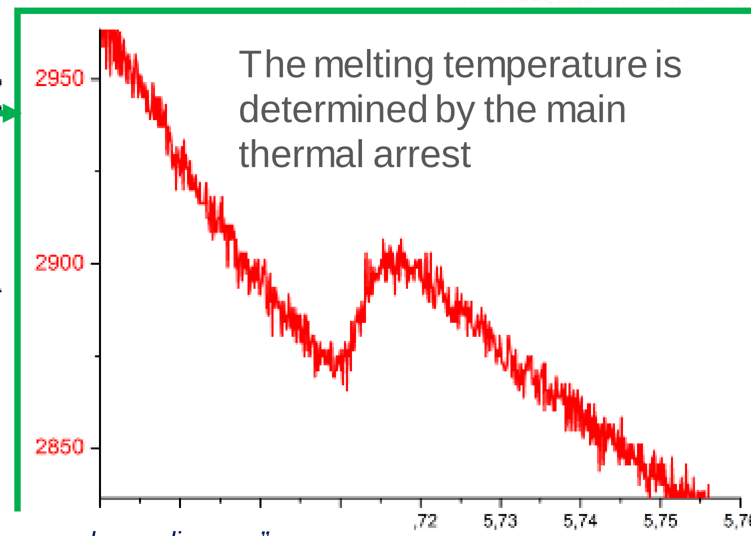
## Experimental set-up & procedure (EC JRC-Karlsruhe, Germany)

- ❑ Nd:YAG Heating laser (~4.5 kW) ⬄ melting
- ❑ *Fast* Pyrometer ⬄ thermogram acquisition
- ❑ Probe Laser ⬄ Reflected Signal Technique to detect the melting
- ❑ Spectro-pyrometer (check on the ε value)




Example:




The melting temperature is determined by the main thermal arrest

*E. Epifano, "Study of the U-Am-O ternary phase diagram", Université Paris-Saclay, 17/112017.*

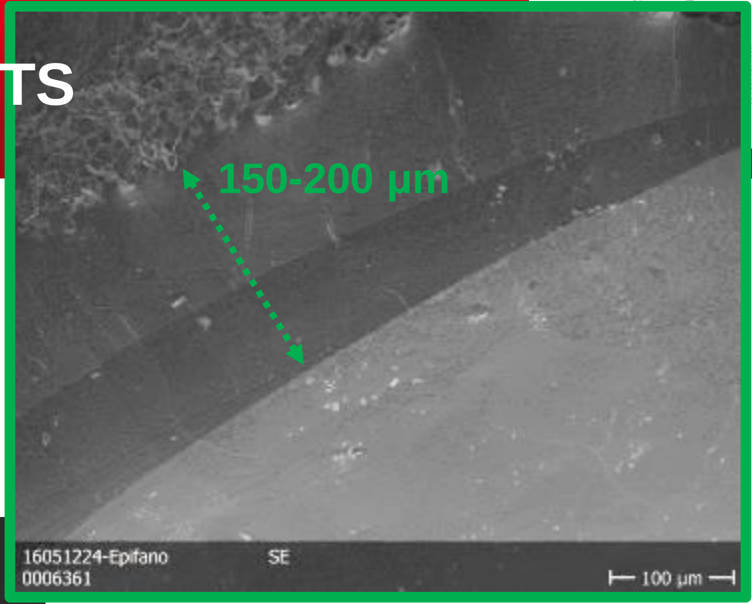
# MELTING-T MEASUREMENTS

**Laser heating advantages:**

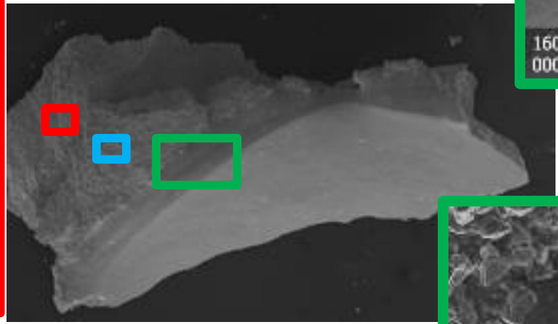
- ❑ Short measurement duration

*Far* **region**

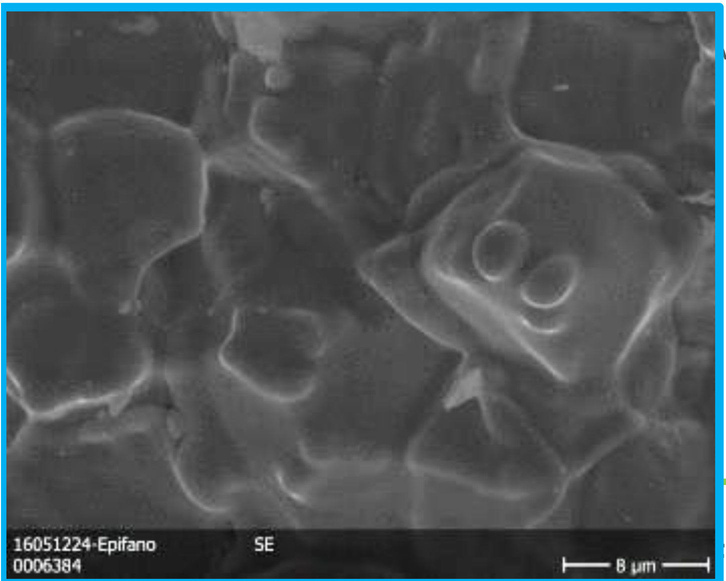
**Melted region**



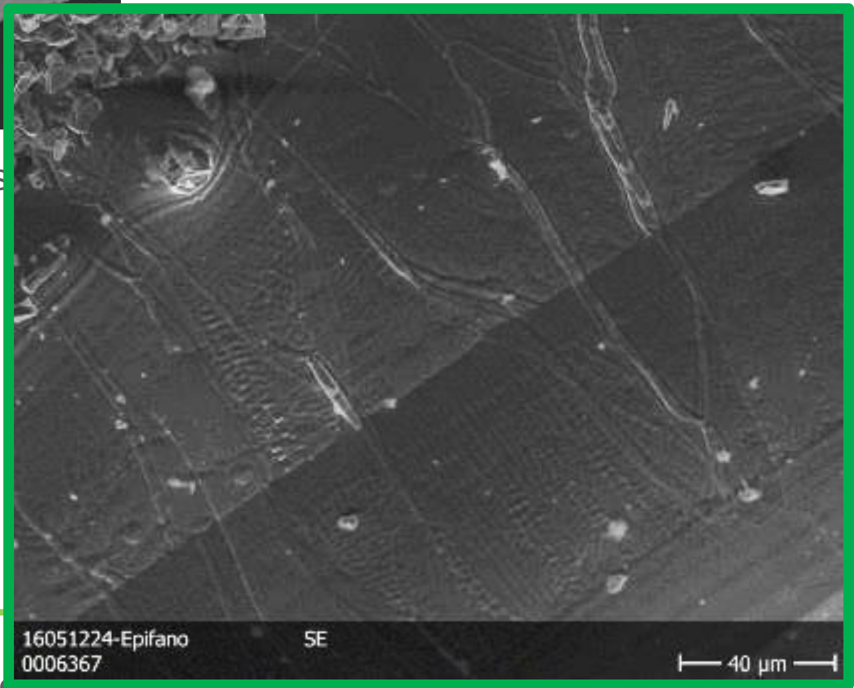




...M image of a melted s...




***Intermediate* region**

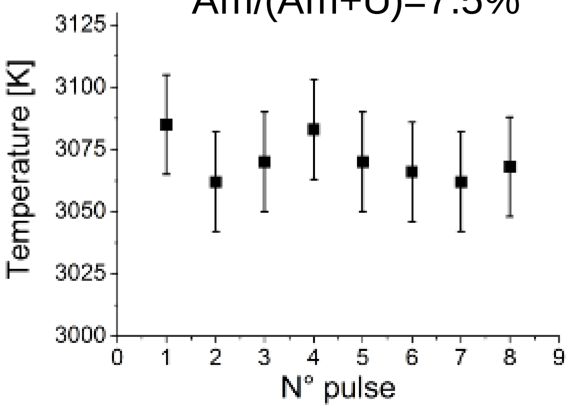


# FABRICATION OF DENSE $U_{1-x}Am_xO_{2\pm\delta}$: MELTING POINT

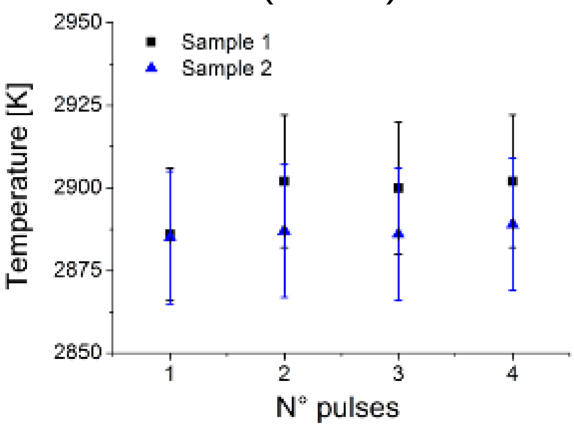
## Argon

**Repeatability** of all the measurements

Am/(Am+U)=7.5%




Am/(Am+U)=50%

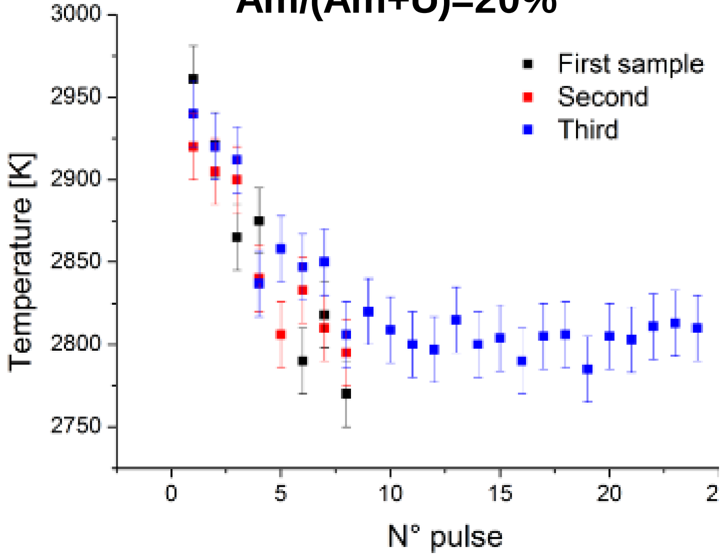



## Air

**7.5% ≤Am/(Am+U) ≤ 20%**

**Initial decrease of $T_m$**

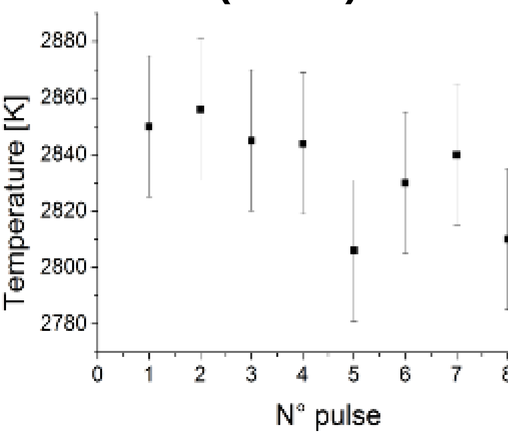
**Am/(Am+U)=20%**




**Am/(Am+U) = 30%, 50%**

Discrete **repeatability** of the measurements, but higher data dispersion

**Am/(Am+U)=50%**




Exception: Am/(Am+U)=70%, only 1 measurement under air (technical difficulties)

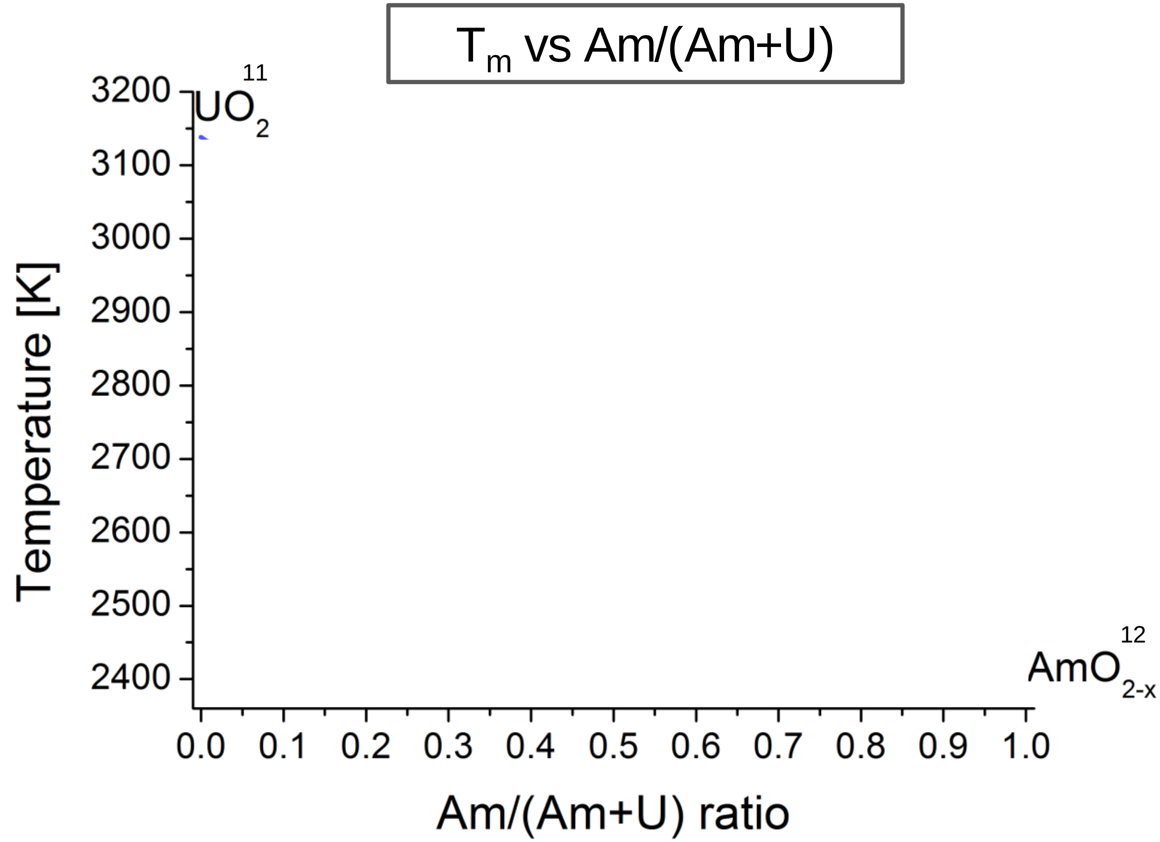
# FABRICATION OF DENSE $U_{1-x}Am_xO_{2\pm\delta}$: MELTING POINT

## Under argon

- almost **linear decrease of $T_m$** with the Am/(Am+U) ratio

## Under air

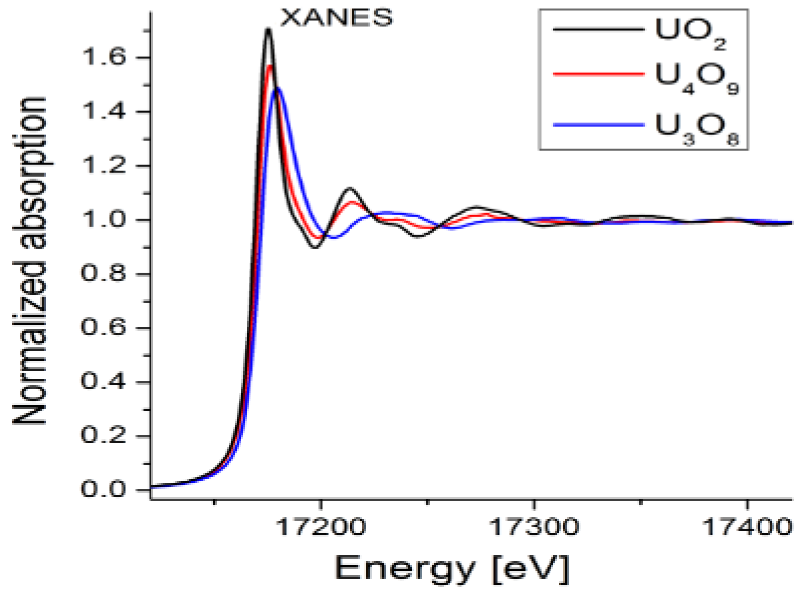
- **Lower $T_m$** than in Ar
- No monotonic variation with Am/(Am+U) ratio
- Highest $T_m$ for Am/(Am+U) = 0.3 and 0.5, with similar values in Ar and in Air




**➔ Variation of the composition: need for characterizations**

*11. D. Manara et al, J. Nucl. Mater. 342 2005)148 ; 12 R. McHenryl, Trans. Am. Nucl. Soc. 8(1965)75 ; D. Prieur et al., J. Chemical Thermodynamics.97(2016)244.*

# FABRICATION OF DENSE $U_{1-x}Am_xO_{2\pm\delta}$: MELTING POINT



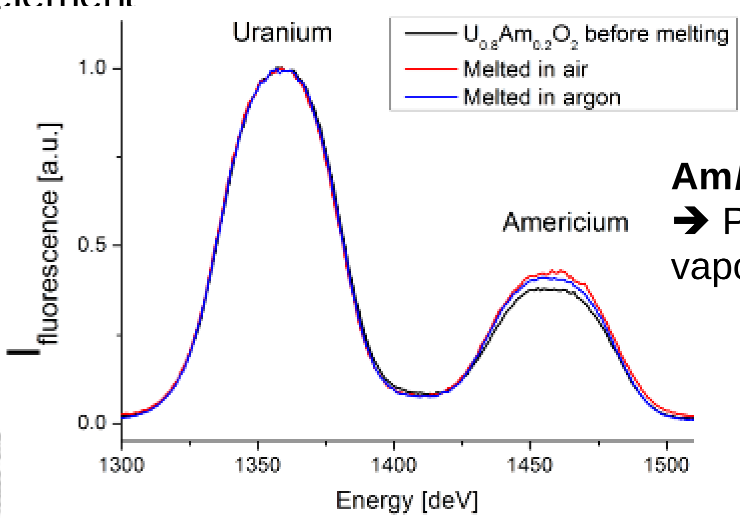

- Characteristic of the element
- Absorption edge is dependent on the **oxidation state**

**U, Am oxidation state** (using reference materials)

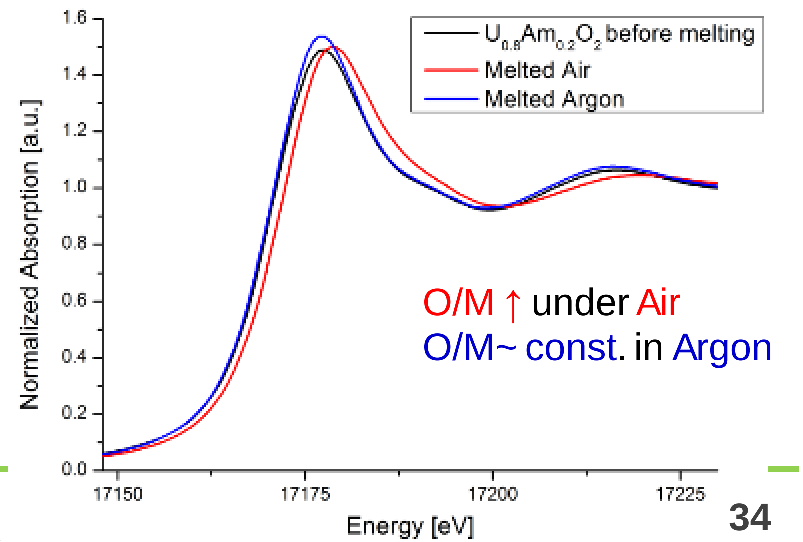
→ **O/M ratio**

**Am/(Am+U) ratio**

E>> $E_{edge}$ → $I_f$ is proportional to the mass of element



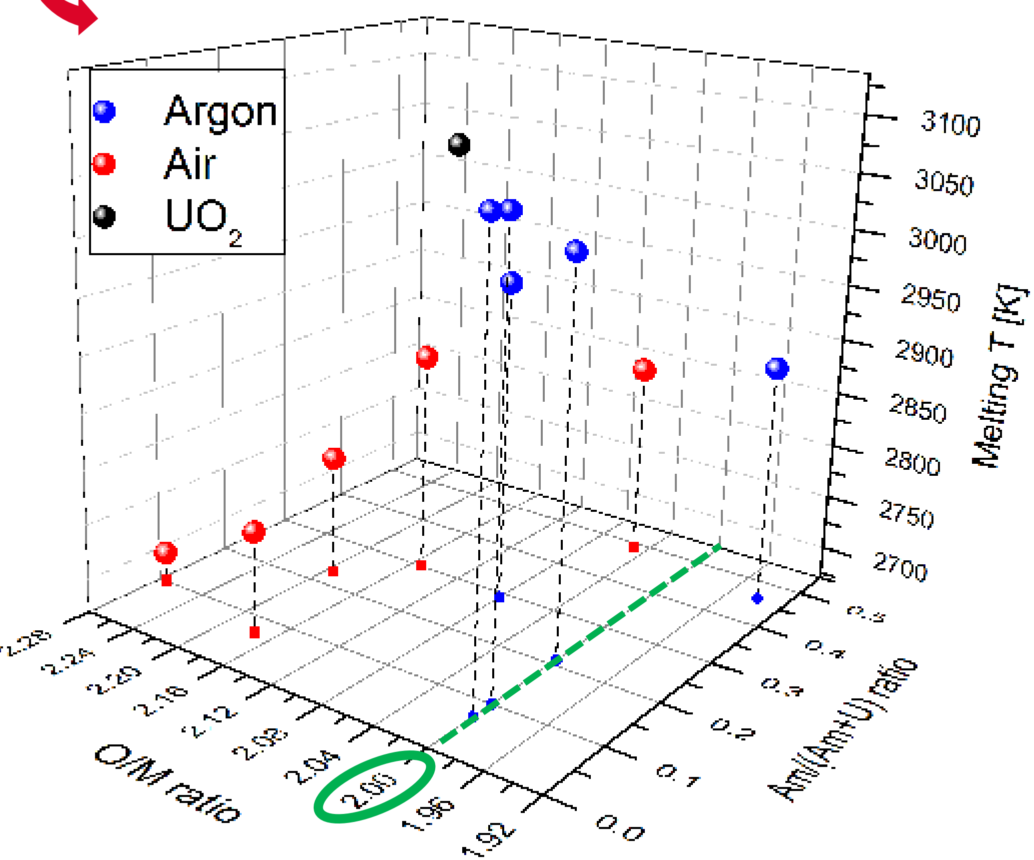

**Am/(Am+U)** ↑
➔ Preferential vaporization of U

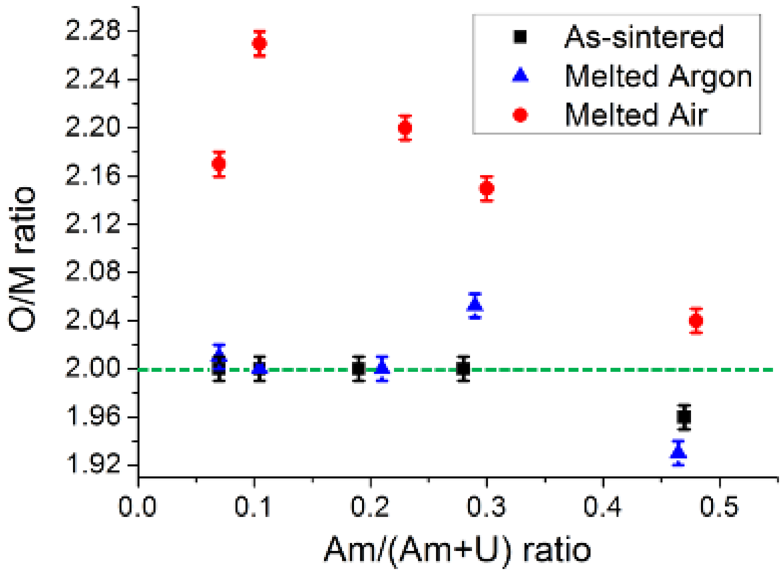


# FABRICATION OF DENSE $U_{1-x}Am_xO_{2\pm\delta}$: MELTING POINT

- Fluorescence X-ray spectroscopy → **Am/(Am+U)** → **minor variations**
- XANES → **O/M → important variations**!!!

Associate a composition to each $T_m$



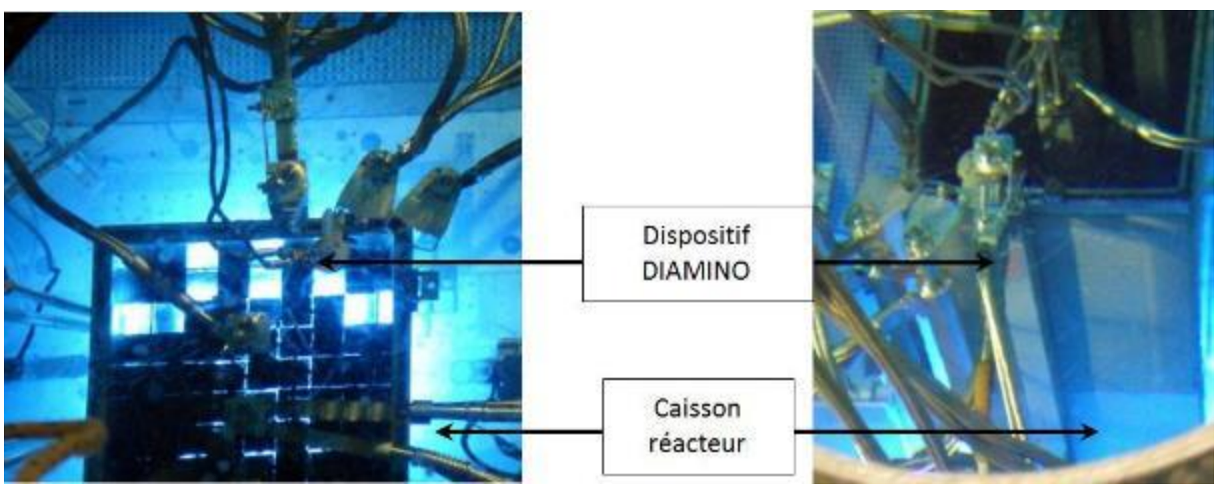




- For **O/M ~ 2, $T_m$ ↓ when Am/M ↑**
- The **oxidation** is more important for the low Am/M oxides
- **Stabilization of the fluorite structure toward the oxidation with the Am content**

# FABRICATION OF POROUS $U_{1-x}Am_xO_{2\pm\delta}$

# FABRICATION OF POROUS $(U,Am)O_{2\pm\delta}$ MABB

- **Assess the influence of the fuel microstructure on the <u>helium release</u>**
  - ➢ Comparison between **dense / tailored porosity** pellets.
- **Porous pellet**
  - ➢ favored He release during irradiation by creating open porosity network ⬄ interconnection between pores = fission gases release under irradiation.
- **Test of minor actinide bearing fuels behavior:**
  - ➢ **MARIOS :** 15% Am porous (88%) and dense (92%)
  - ➢ **DIAMINO :** 7.5 & 15 % Am porous (82-85%) and dense (96-97%)

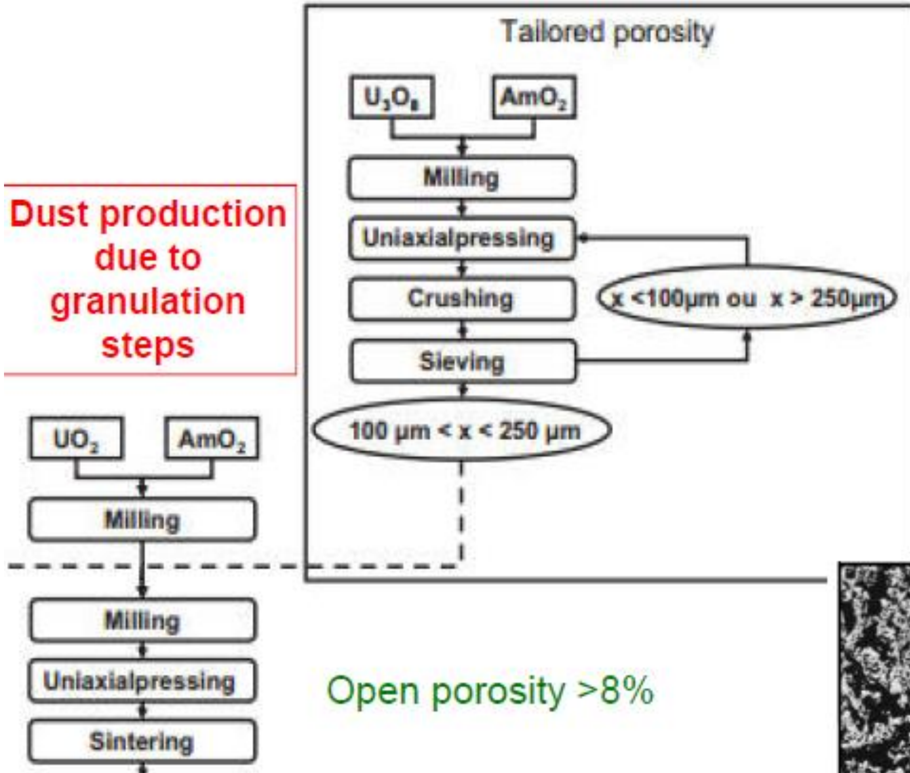



OSIRIS (Paris, France) reactor pool

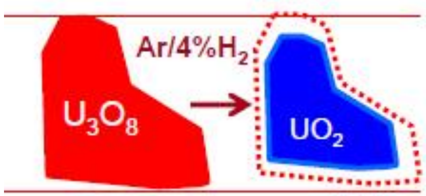
**CEA Report 2015 (Cf slide 12)**

# FABRICATION OF POROUS $(U,Am)O_{2\pm\delta}$ MABB: REACTIVE SINTERING BETWEEN $UO_{2+\delta}$, $U_3O_8$ AND $AmO_{2-\delta}$

Dust production due to granulation steps



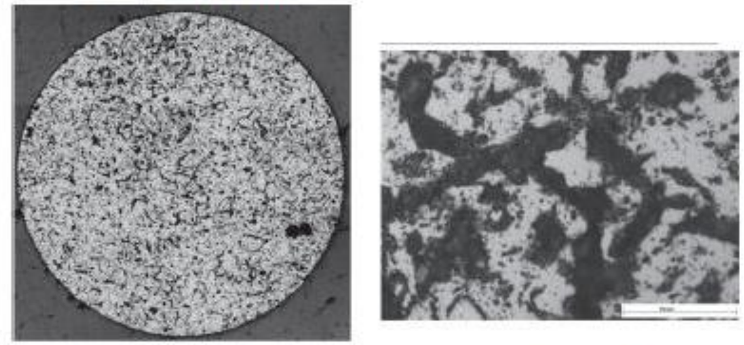

Open porosity >8%



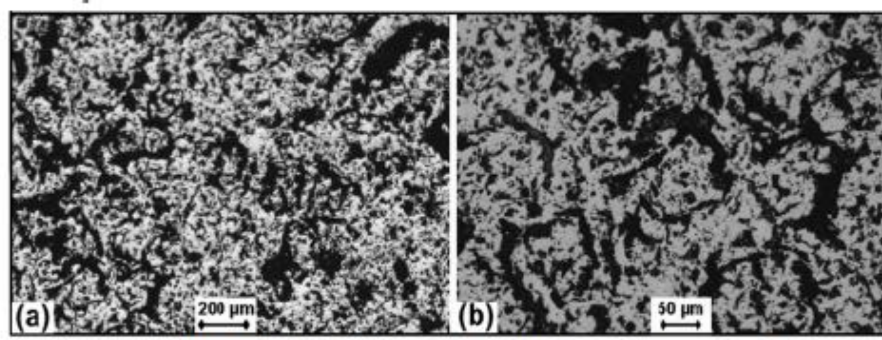

$U_3O_8$ : inorganic pore-former.
Creation of porosity with the structure change ($U_3O_8$-> $UO_2$)

D. Prieur *et al.*, *J. Nucl. Mater.* **414** (2011) 503
T. Delahaye, J. Nucl. Mater. 432 (2013) 305

*Tailored porosity microstructure*



*MARIOS Fabrication $U_{0.85}Am_{0.15}O_{2\pm\delta}$*




*DIAMINO Fabrication $U_{0.925}Am_{0.075}O_{2\pm\delta}$*

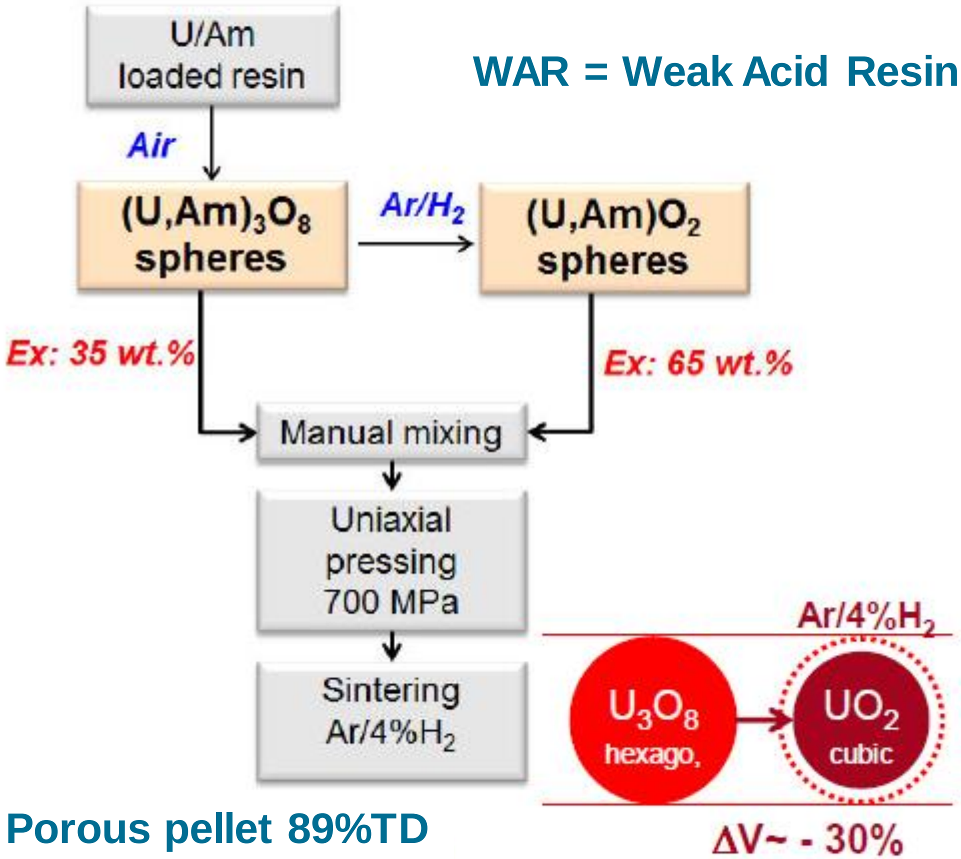
Porous volume : very wide and elongated-shape pores (5 to 60µm), interconnected and creating open porosity network

# FABRICATION OF POROUS $(U,Am)O_{2\pm\delta}$ MABB: WAR + CALCINED RESIN MICROSPHERE PELLETIZING

**2016**

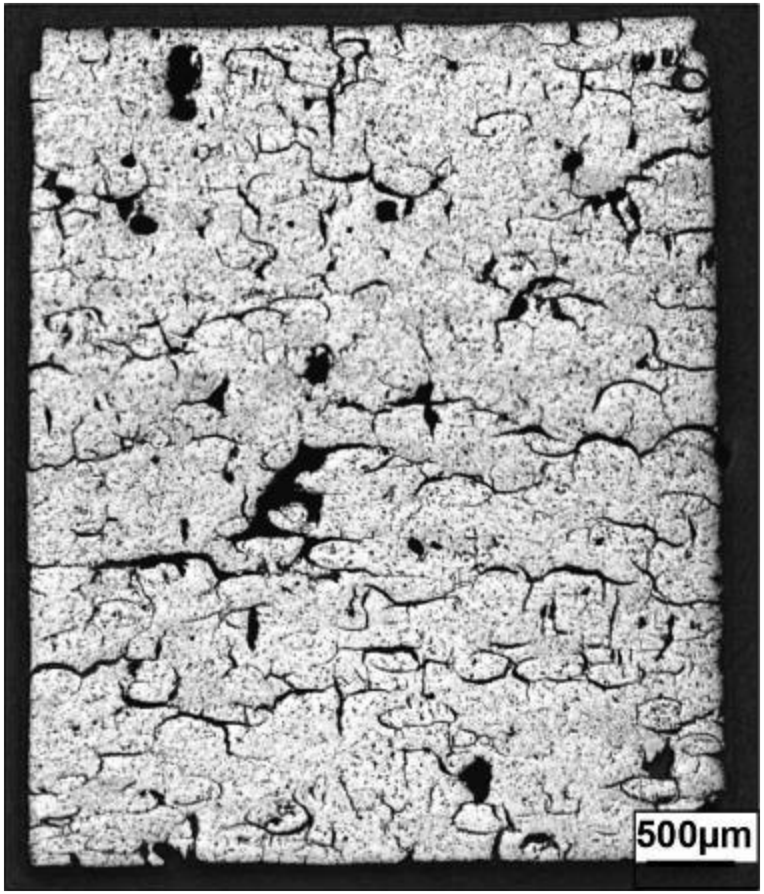
**Calcined Resin Microsphere pelletizing**

**WAR = Weak Acid Resin**




**Porous pellet 89%TD**
**Open porosity = 9%**

L. Ramond et al. Journal of Nuclear Materials. 492 (2017) 97–101. doi:10.1016/j.jnucmat.2017.05.005.




Fabrication $U_{0.90}Am_{0.10}O_{2\pm\delta}$

Interconnected hemispherical porosity

➔ open porosity network supposed to facilitate helium and FG release

# TRANSMUTATION BY HOMOGENEOUS MODE


Several % of MA
(Am, Cm, Np)

$U_{1-y-x}Pu_xMA_yO_{2\pm\delta}$
$y<5\%$

**Core of the reactor = MA-MOX**

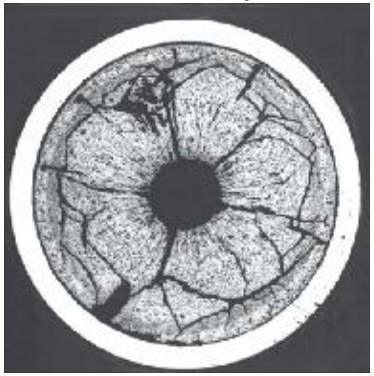
# HETEROGENEOUS MODE: EXPERIMENTAL IRRADIATION PROGRAMS

| Experiment | SUPERFACT 1 | Am1 | AFC- 2C & 2D | SPHERE |
|---|---|---|---|---|
| Irradiation date | 1986-1988 | 2008 | 2008-2010 | 2013-2015 |
| Test reactor | PHENIX | JOYO | ATR | HFR |
| **Pu content (mol. %)** | **24** | **29** | **20** | **21** |
| **Am content (mol. %)** | **2** | **2-5** | **3** | **3** |
| **Np content (mol. %)** | **2** | **0-5** | **2** | **-** |
| **O/M ratio** | **1.97** | **1.98-1.95** | **1.98-1.95** | **1.98** |
| **Fabrication route** | **Internal gelation** | **Powder metallurgy** | **Powder metallurgy** | **Internal gelation** |
| Burn up max. (at. %) | 6.8 | 10 min & 24 h | 6-19 | ~5 |
| Liner power ($W.cm^{-1}$) | 350-385 | 430 | 220-320 | ~300 |

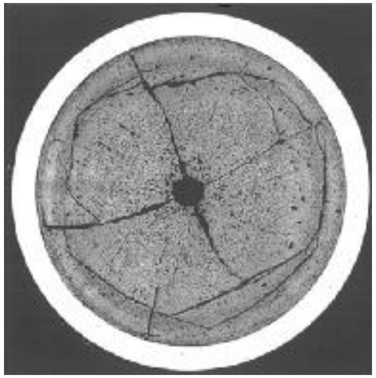
**CEA Report 2015** « Avancées des recherches sur la séparation-transmutation et le multi-recyclage du plutonium dans les réacteurs à flux de neutrons rapides, juin 2015, http://www.cea.fr/multimedia/Documents/publications/rapports/avancees-recherches-separation-transmutation-et-multirecyclage-pu-rnr.pdf

# HETEROGENEOUS MODE: SUPERFACT-1 RESULTS

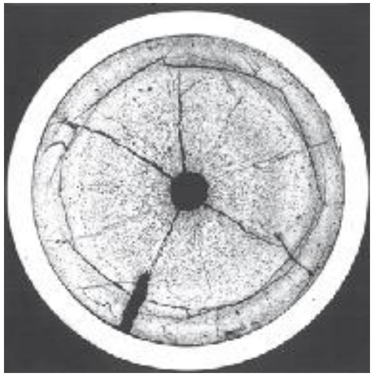
- Driver MOX fuels including several % of MA in all the core of the reactor
- GOAL experiment : study the effect of MA adding on the fuel behavior under irradiation
  - Modification of thermal properties (decrease of thermal conductivity and melting temperature?)
  - Production of He : could lead to fuel swelling and weakening of the cladding
- First integral experiment (1980-1988) : SUPERFACT (ITU and CEA) in Phénix reactor
  - 6.8% at.% / 70 GWj/t max.: MA transmutation rate of ~30%
  - PIE: No anomaly in the road containing MA, just a higher production of He release -> no consequences on the cladding



Standard fuel / pin n° 8
$(U_{0.75}Pu_{0.25})O_{1.98}$
350-400 W.cm$^{-1}$



Am doped / pin n°4
$(U_{0.74}Pu_{0.24}Am_{0.02})O_{1.96}$
350-380 W.cm$^{-1}$



Np doped / pin n°7
$(U_{0.74}Pu_{0.24}Np_{0.02})O_{1.967}$
350-385 W.cm$^{-1}$

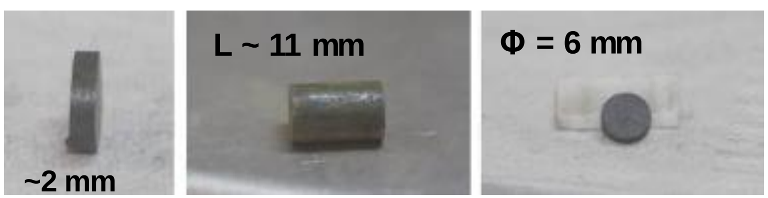
CEA Report 2015
(Cf slide 12)

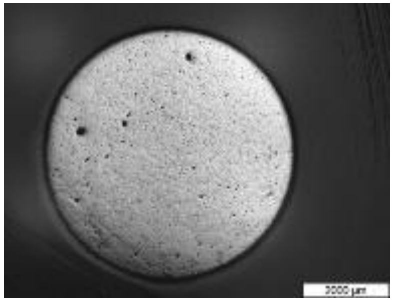
Drawback : limited linear power (<400 W.cm$^{-1}$) & burn-up ➔ more experiment needed to conclude about the technical feasibility of the transmutation in homogeneous mode

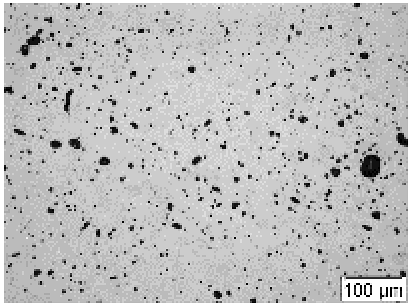
# HETEROGENEOUS MODE: GACID PROGRAM

- GACID (Global Actinides Cycle International Demonstration) program (DOE / JAEA / CEA) from 2007 in the framework of GEN-IV International Forum
- Fabrication by powder metallurgy process (co-milling of powders, pressing and sintering) at the LEFCA facitlity (CEA Cadarache, France)
  - $(U_{0.81}Pu_{0.19})O_{2-x}$ (TD ~97-98 %)
  - $(U_{0.77}Pu_{0.19}Am_{0.03}Np_{0.01})O_{2-x}$ (TD ~95 %)
- Irradiation will be performed in the JOYO reactor (Japan)

$(U_{0.77}Pu_{0.19}Am_{0.03}Np_{0.01})O_{2-x}$ samples






- Ongoing experimental program CEA-JRC-Karlsruhe to determine effect of MA addition on fuel thermal properties: thermal conductivity, Cp, melting point, vapor pressure ➔ safety aspects

# CONCLUSIONS

- Transmutation of MAs in FNR and particularly Am would allow reducing long term radiotoxicity of ultimate nuclear wastes

- Several experimental irradiations (heterogeneous and homogeneous modes) have demonstrated:
  - The feasibility of Am transmutation
  - The good behavior of MA doped fuel and transmutation blankets

- On going work about the impact of Am addition on $(U,Pu)O_{2-x}$ properties (thermal, structural, …).

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# Thank you for your attention

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Research Department on Mining and Fuel Recycling Processes

# O/M DETERMINATION ⇔ XANES $L_3$ VS $M_4$ HERFD

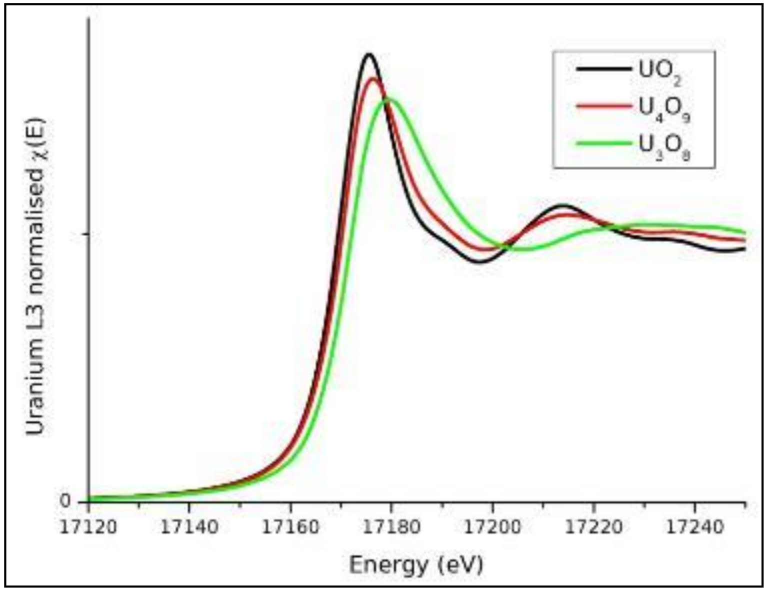
Hypo-stoichiometric Mixed oxide (O/M<2.00)

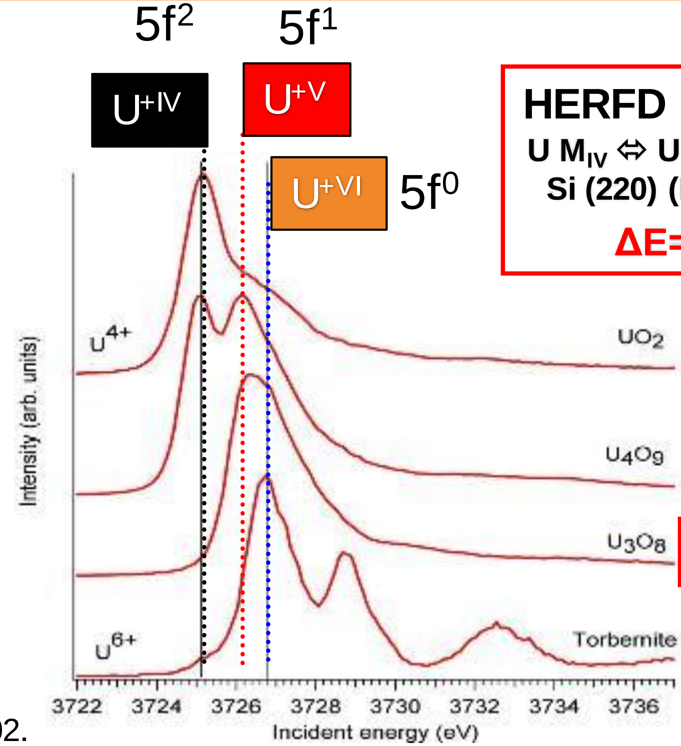
**$An^{+III}/An^{+IV}$ « easy » to observe as ΔE~4eV and single-valence compounds are available**

Hyper-stoichiometric Mixed oxide (O/M>2.00)

**Identification of $U^{+IV}/U^{+V}/U^{+VI}$ in $UO_{2+x}$ compounds is more complex**
**⇔ mixed valence in $U_4O_9$ or $U_3O_8$ have to be clearly identified ⇔ ionic model**

**U $L_3$** (ROBL-ESRF)




**HERFD** (ID26 – ESRF)
**U $M_{IV}$ ⇔ U Mβ = 3336 eV**
**Si (220) (R=1m) θ=75°**
**ΔE=0.7 eV**

[1]

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

# U VALENCE STATE ⇔ XANES $L_3$ VS $M_4$ HERFD

A.L. Smith, et al. **A New Look at the Structural Properties of Trisodium Uranate $Na_3UO_4$**, Inorg. Chem. 54 (2015) 3552–3561.

A.L. Smith et aL, **Structural Properties and Charge Distribution of the Sodium Uranium, Neptunium, and Plutonium Ternary Oxides: A Combined X-ray Diffraction and XANES Study**, Inorg. Chem. 55 (2016) 1569–1579

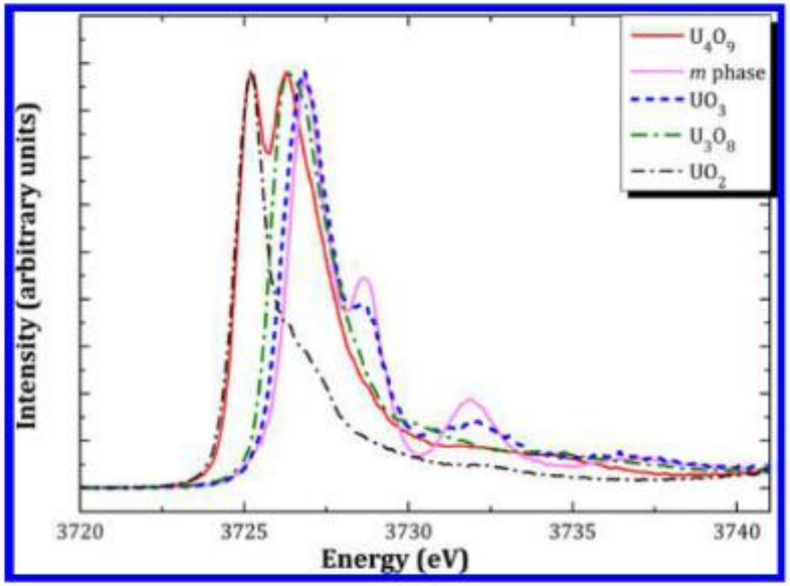



Figure 1. XANES spectrum of the *m* phase measured at the U-$M_4$ edge and comparison with the reference spectra of $UO_2$, $U_4O_9$, $U_3O_8$, and $UO_3$.[29]

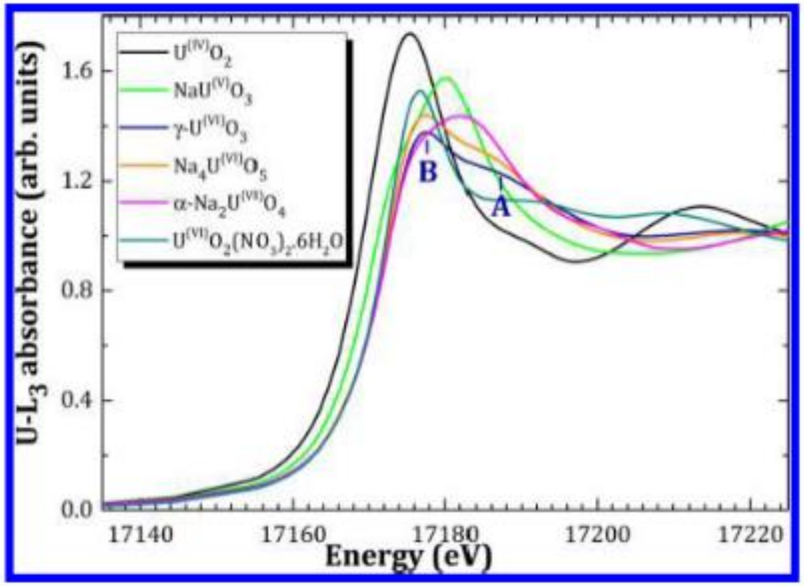



Figure 3. Normalized XANES spectra of $UO_2(NO_3)_2{\cdot}6H_2O$, α-$Na_2UO_4$ (present work), $NaUO_3$, $Na_4UO_5$, together with $UO_2$ and $UO_3$ reference materials.[5]