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INSPYRE

Investigations Supporting MOX Fuel Licensing in ESNII Prototype Reactors

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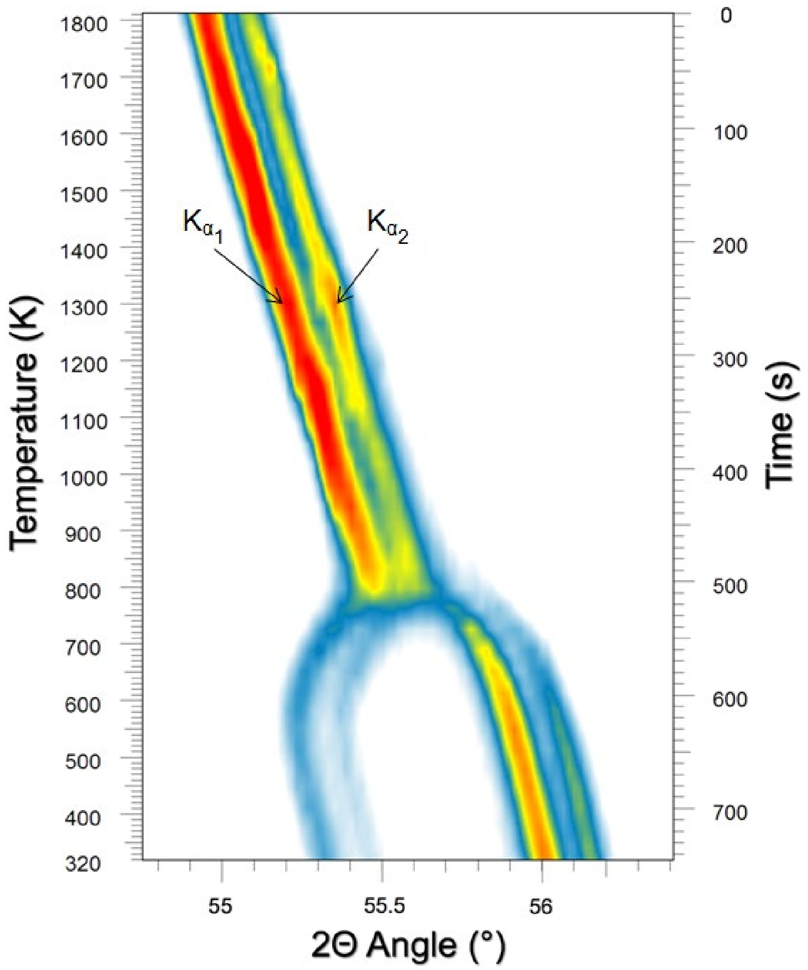
Case study
SFR fuels : O/M ratio

Romain VAUCHY

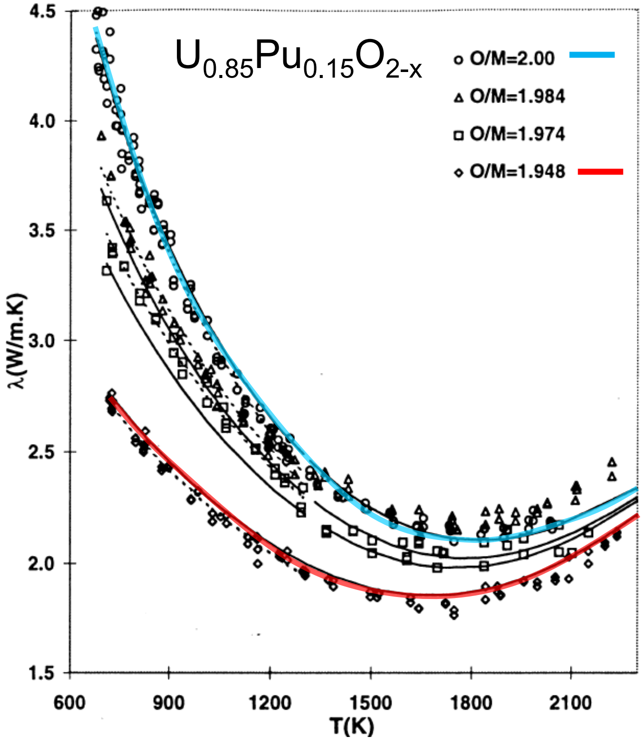


16 May, 2019 Delft – The Netherlands

Fuels for Na fast reactors – O/M ratio

- **O**xygen/**M**etal ratio : key specified parameter for the nuclear fuel behaviour under irradiation
  - Oxidation of the cladding → O/M ratio < 2.00
  - Melting temperature : $T_{melting} = f(O/M)$
  - Thermal conductivity : $\lambda_{th} = f(O/M)$

  (the last two) → O/M ratio > 1.94



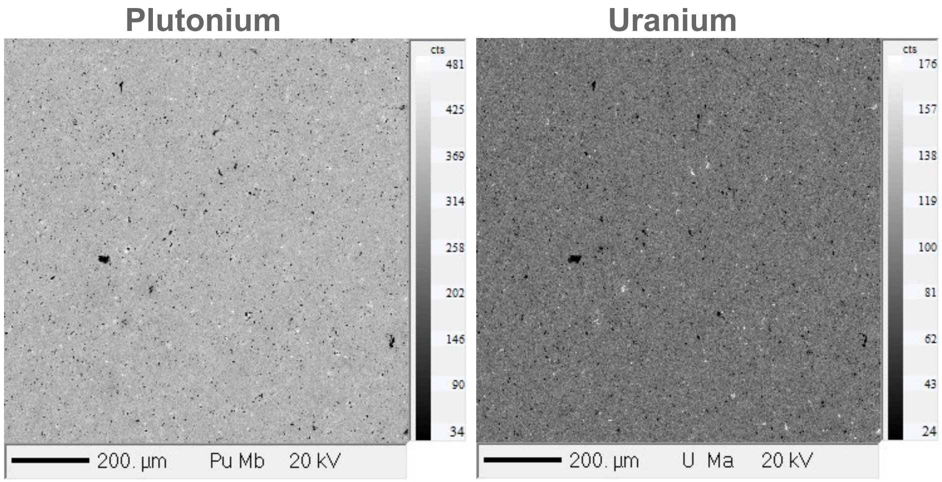
Duriez et al., JNM, 277, 2000, 143-158

Sample manufacturing

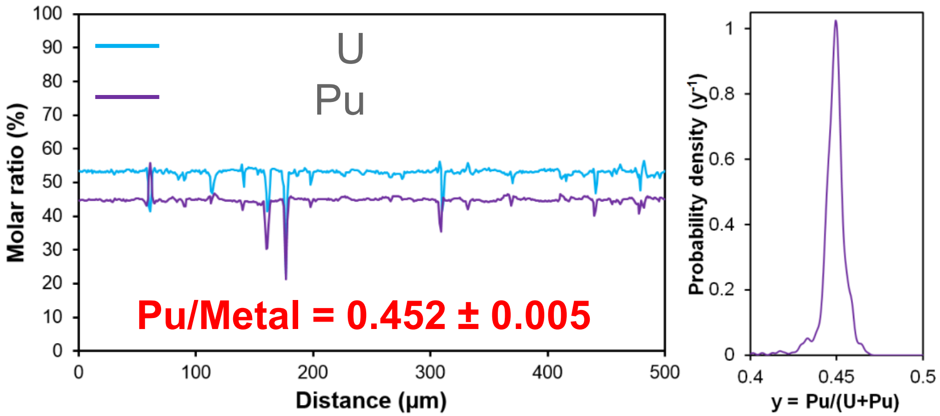
Sample manufacturing

- **Manufacturing of $U_{0.55}Pu_{0.45}O_2$ pellets by powder metallurgy** [1]

Objective #1 : homogeneous U-Pu distribution

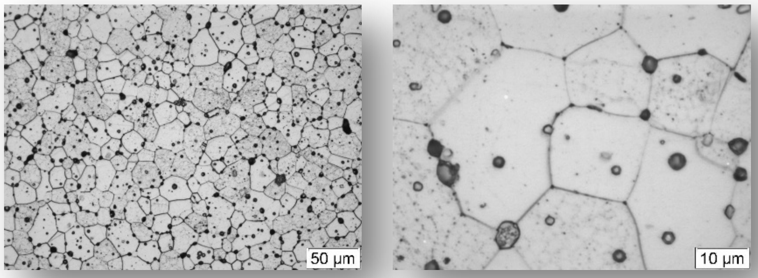


EPMA X-ray mapping in gray levels of Pu and U in $U_{0.55}Pu_{0.45}O_2$ [2]



Elementary U and Pu profils over 500 µm and integrated Pu/M [2]

Objective #2 : dense pellets with big grains for diffusion study

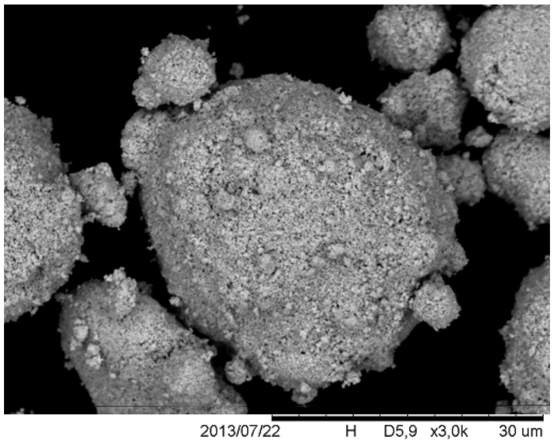


$\rho_{apparent}$ (% ρ_{theo})	Grain size (µm)
95.6(3)	30-40

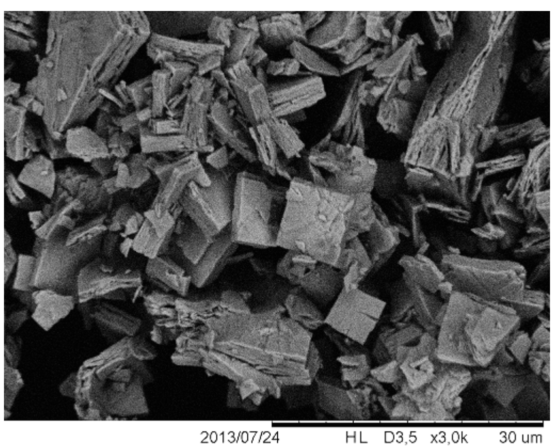
[1] *Vauchy et al.* ***Ceram. Int.***, *40(7B), 2014, 10991-10999*
[2] *Vauchy et al.* ***JNM***, *456, 2015, 115-119*

Optimized ceramic processing

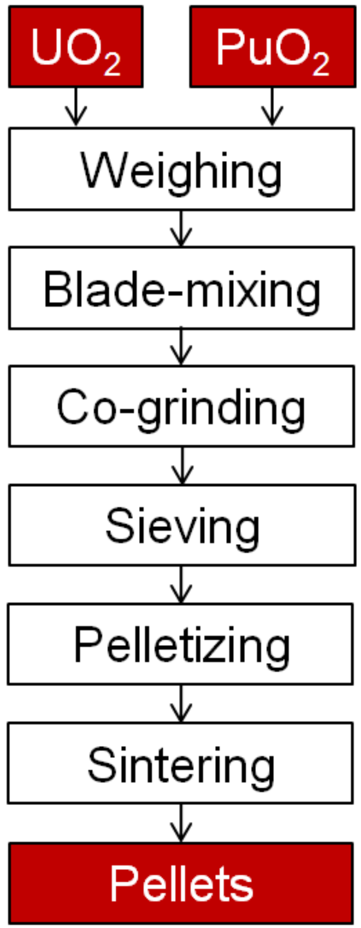
- Optimization of a powder metallurgy process [1]



SEM on raw UO_2 powder [2]



SEM on raw PuO_2 powder [2]



Blade-mixing: Tank : 40 rpm; Blades : 3000 rpm; 30 min

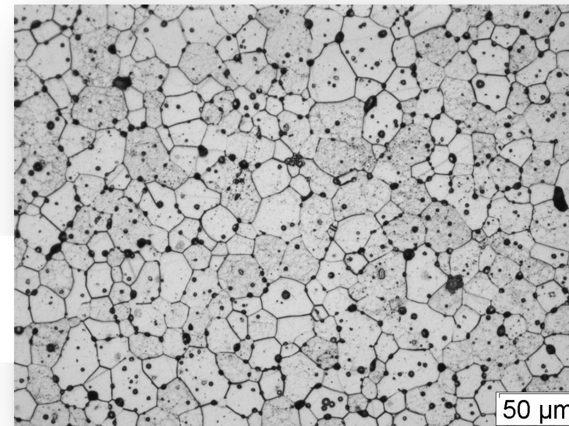
Co-grinding: Ball-mill; 300 min

Sieving: 160 µm

Pelletizing: Automatic, uni-axial, mono-punch press; ~300 MPa

Sintering: 2023 K, 24 h; ↗100 $K.h^{-1}$ ↘50 $K.h^{-1}$; Ar + 5% H_2 + 1500 ppm H_2O

Pellets: Apparent density> 95% ρ_{theo}; Homogeneous U-Pu distribution

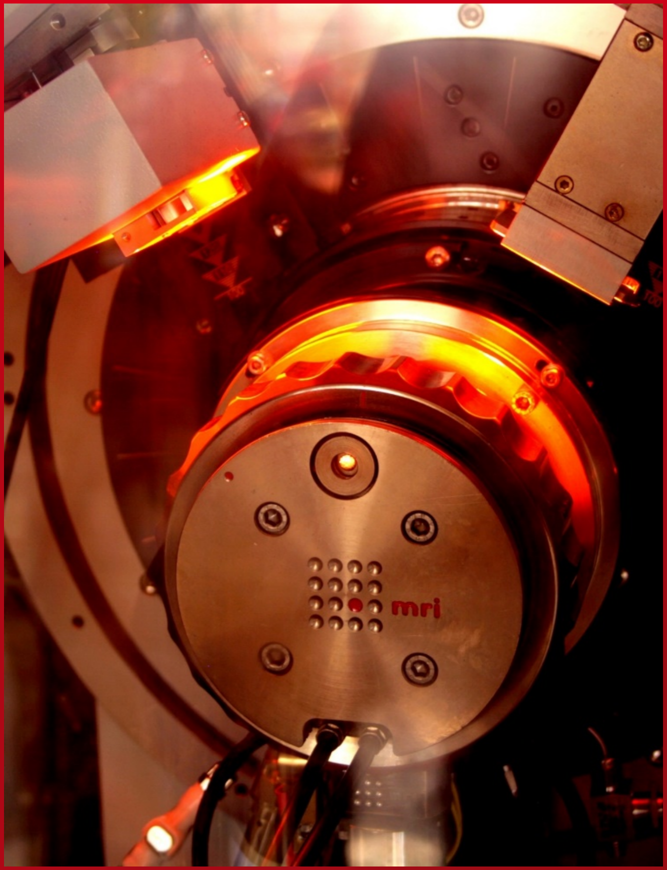


Optical micrography of $U_{0.55}Pu_{0.45}O_{2.000}$ after chemical etching

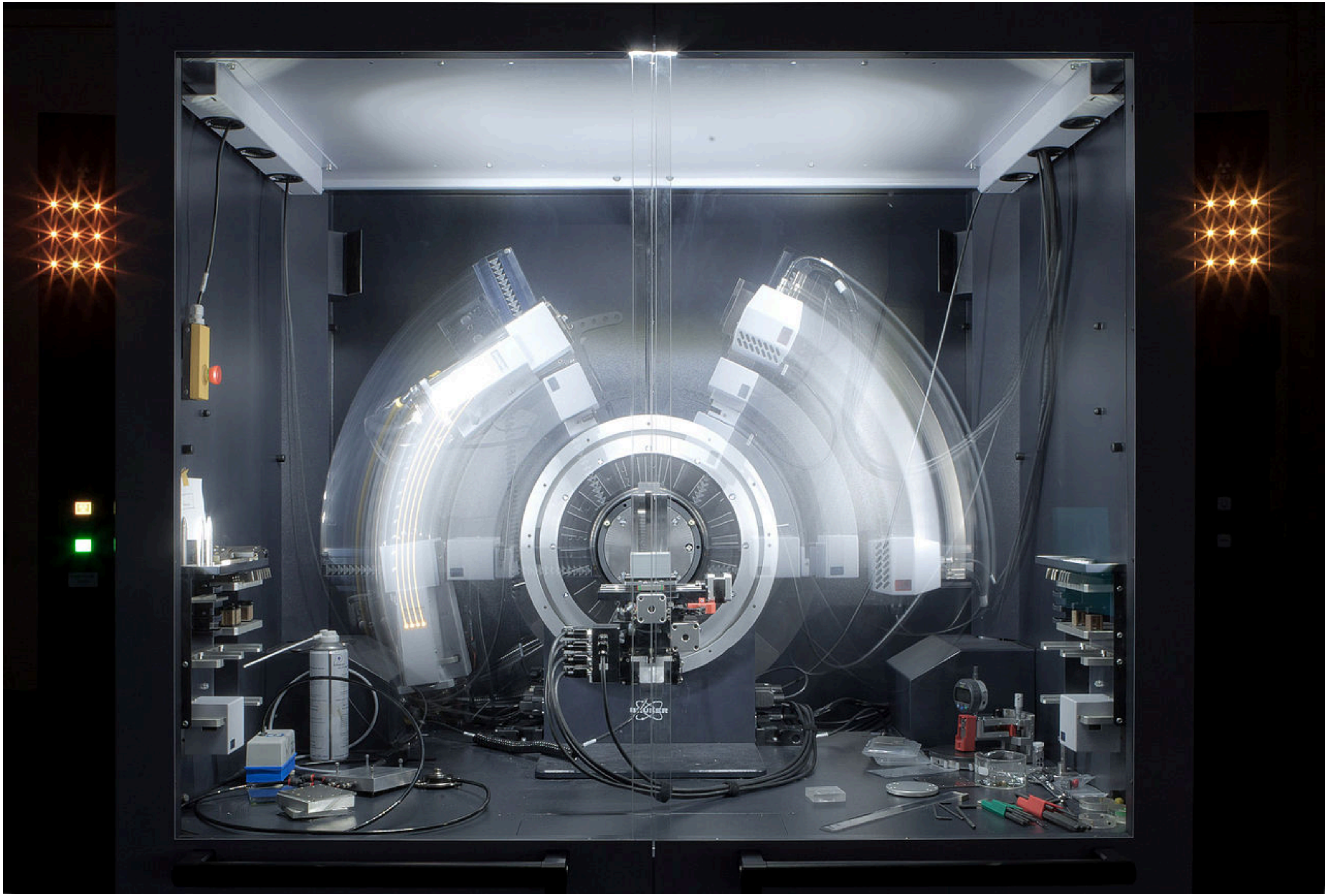
$\rho_{apparent}$ (%ρ_{theo})	Grain size (µm)
95.6(3)	30-40

[1] *Vauchy et al., Ceram. Int. 40, 2014, 10991-10999*
[2] *Berzati, PhD thesis, 2013*

High-temperature X-ray diffraction



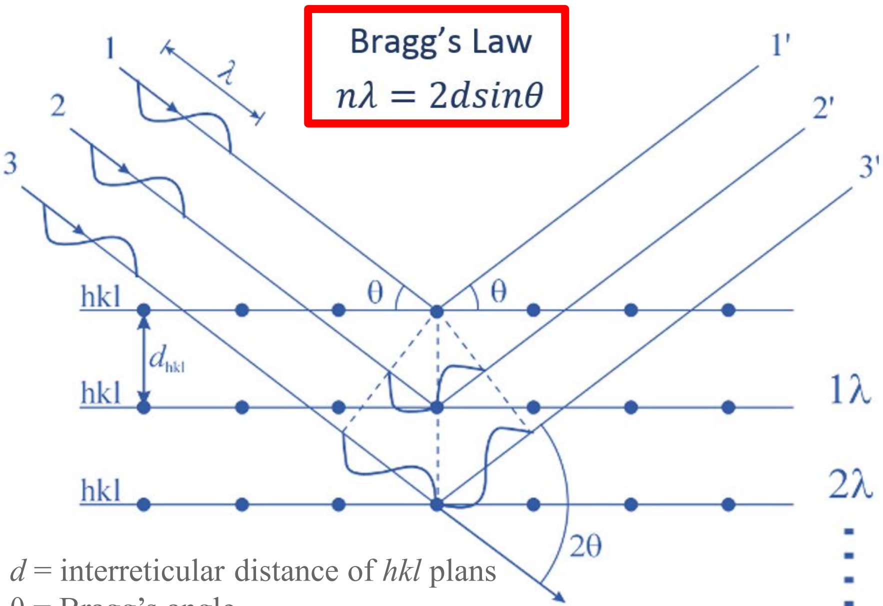
Principle of X-ray diffraction



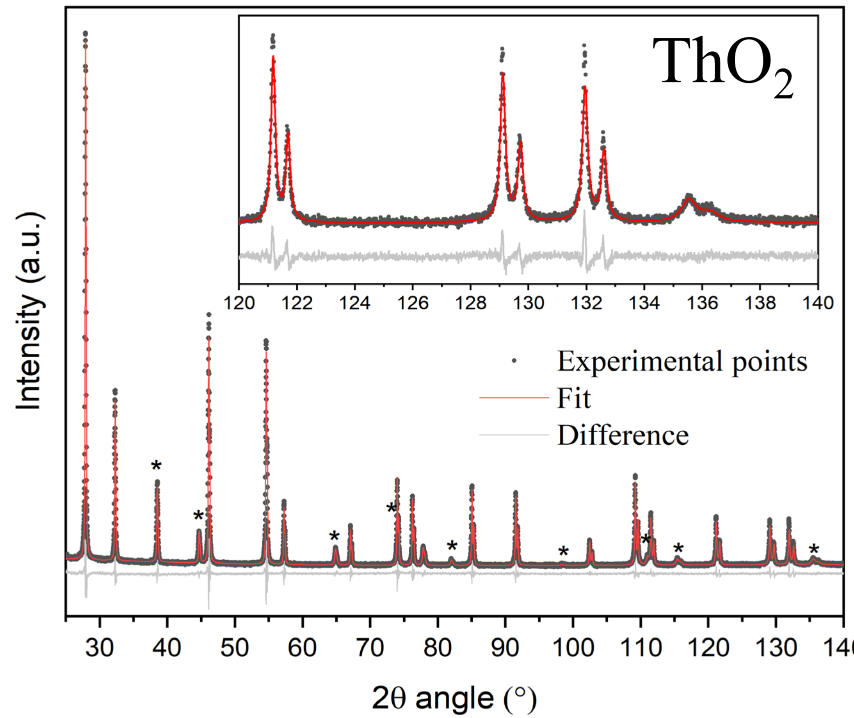
- **X-ray diffraction (XRD) of crystal structure**

  - Monitoring the scattered intensity of an X-ray beam illuminating a sample (the electrons of the atoms it contains because λ of X-rays similar to interreticular distances) as a function of incident and scattered angle, wavelength, *etc*.

  - Gives information on long-range crystal structure (symmetry → phases), size of crystallites, cell parameters, *etc*.



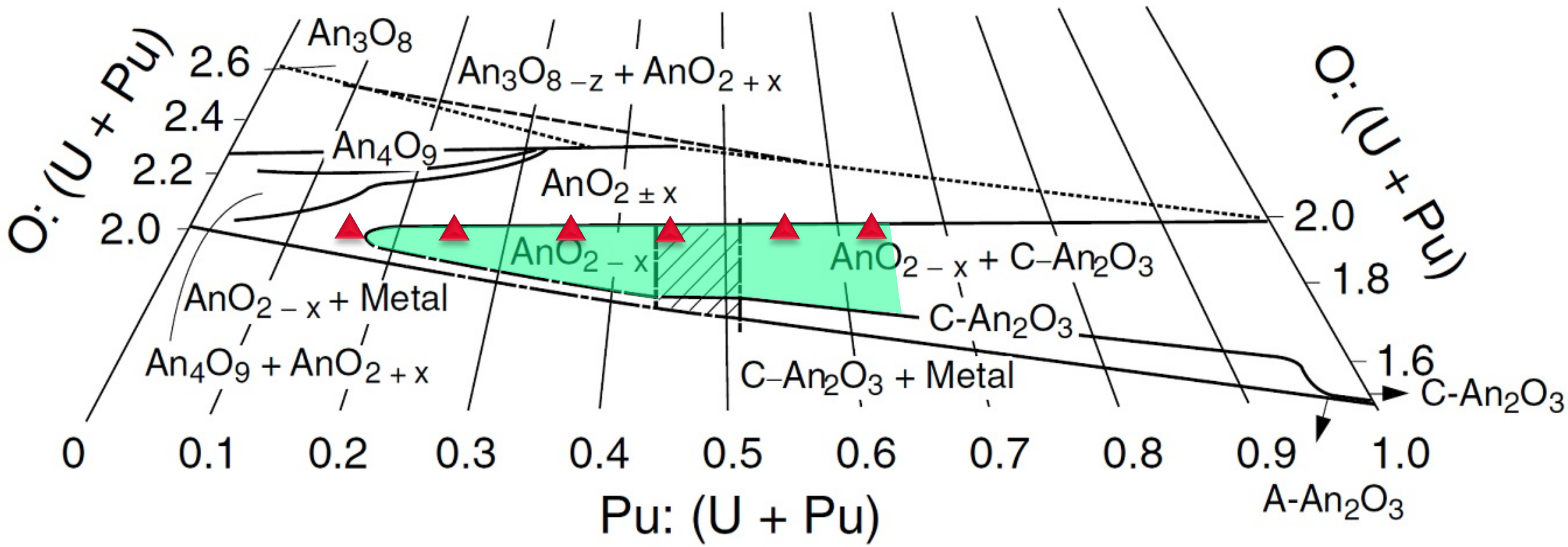
d = interreticular distance of *hkl* plans
θ = Bragg's angle
n = diffraction order
λ = wavelength of X-rays



Fouquet-Métivier *et al. to be published*

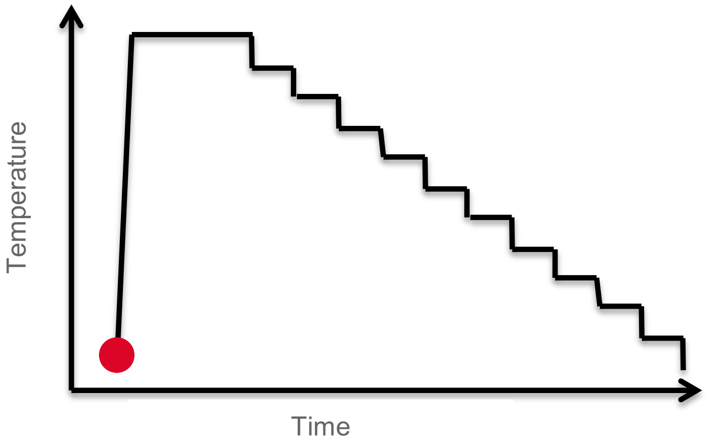
Samples and conditions

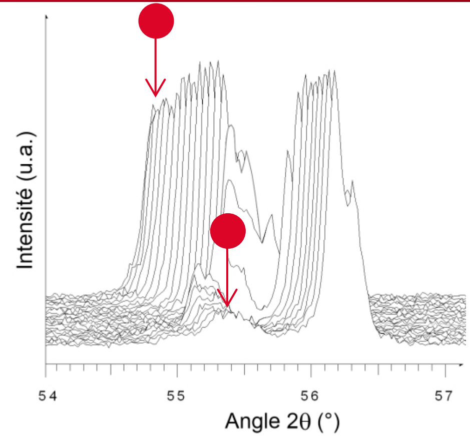
- 6 Pu contents : **14** to **62% Pu**
- Initially stoichiometric samples (**O/M ratio = 2.00**)

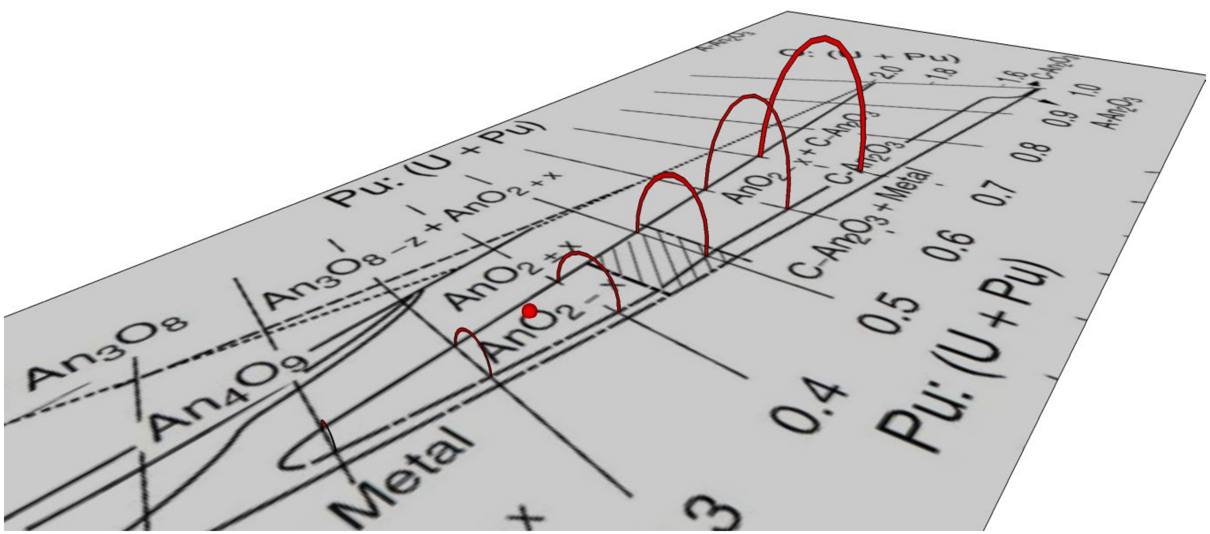


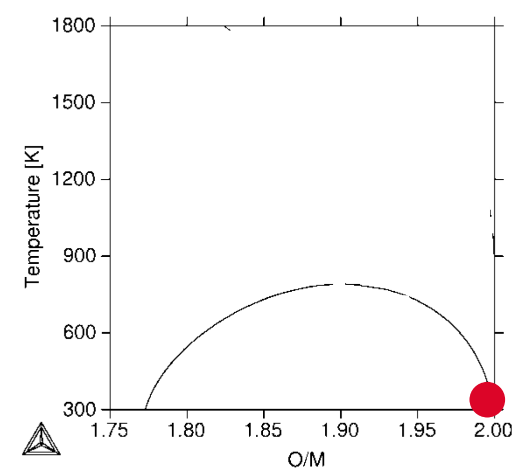
***In situ* reduction experiments under He + 5% H_2**

In situ observation of phase separation

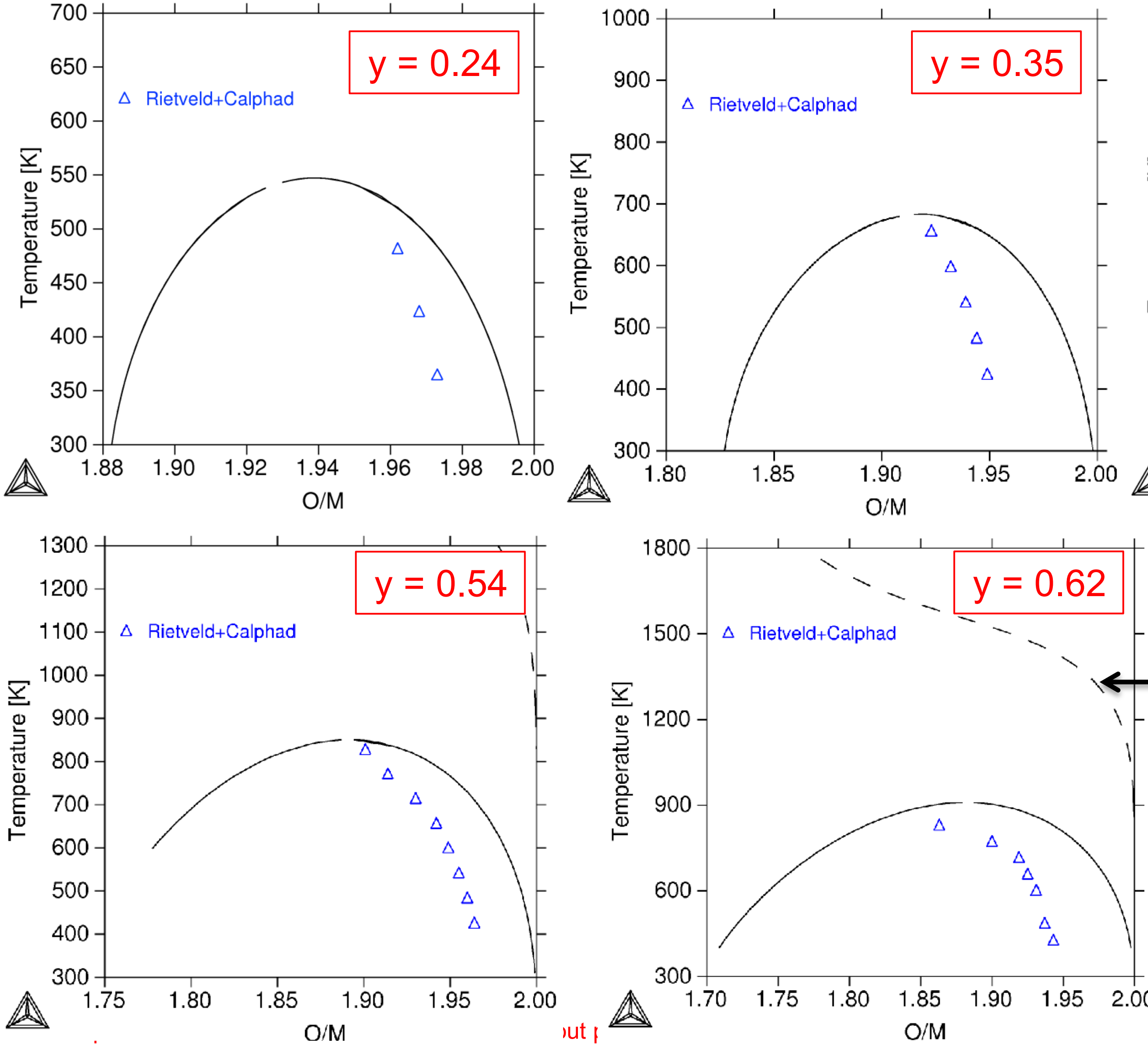






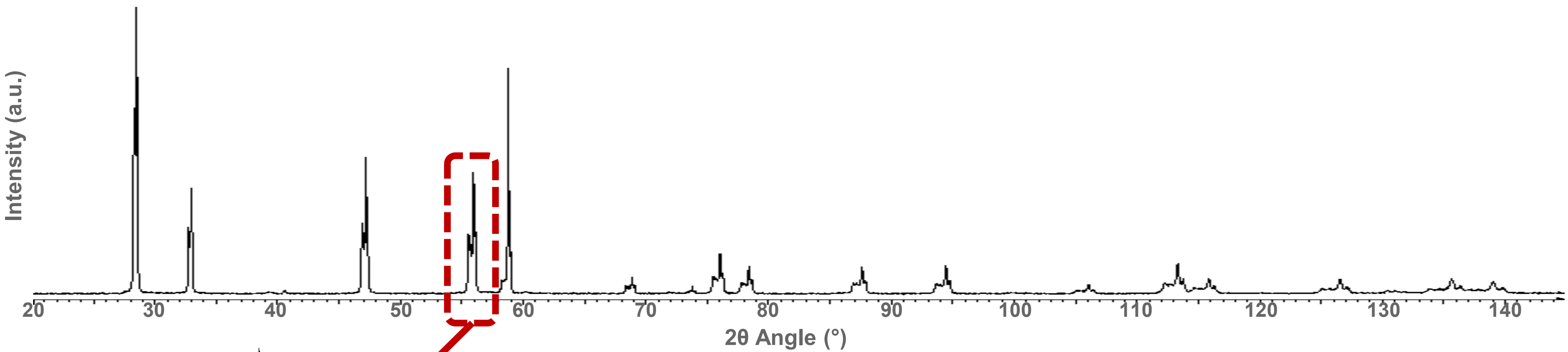


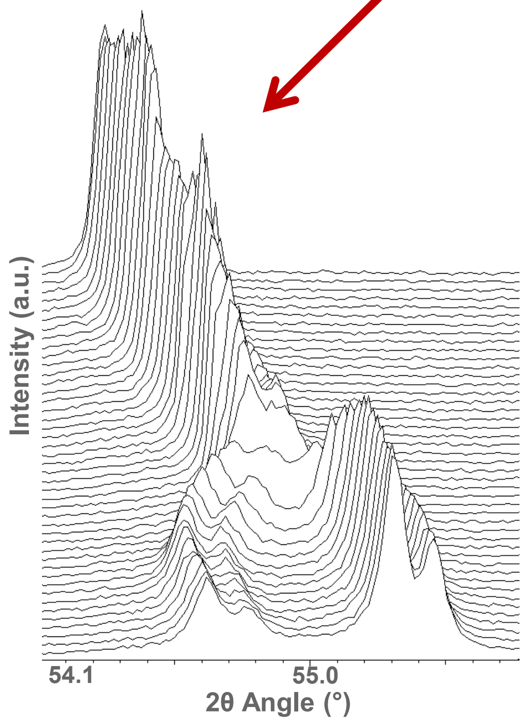
Rietveld + CALPHAD

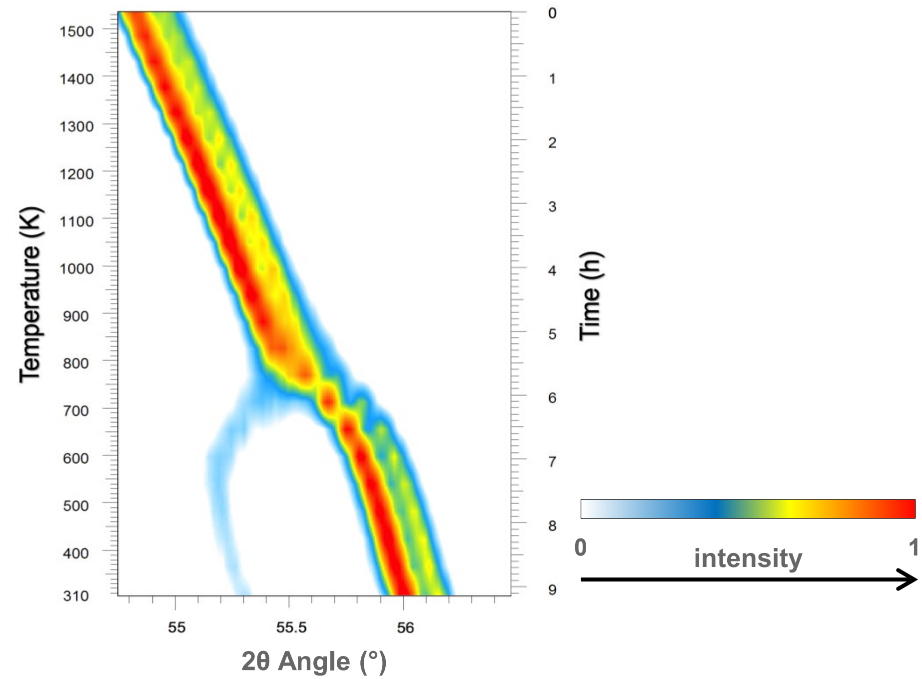


Calculated equilibrium between sample and gas for He/5%H_2 + 15 vpm H_2O

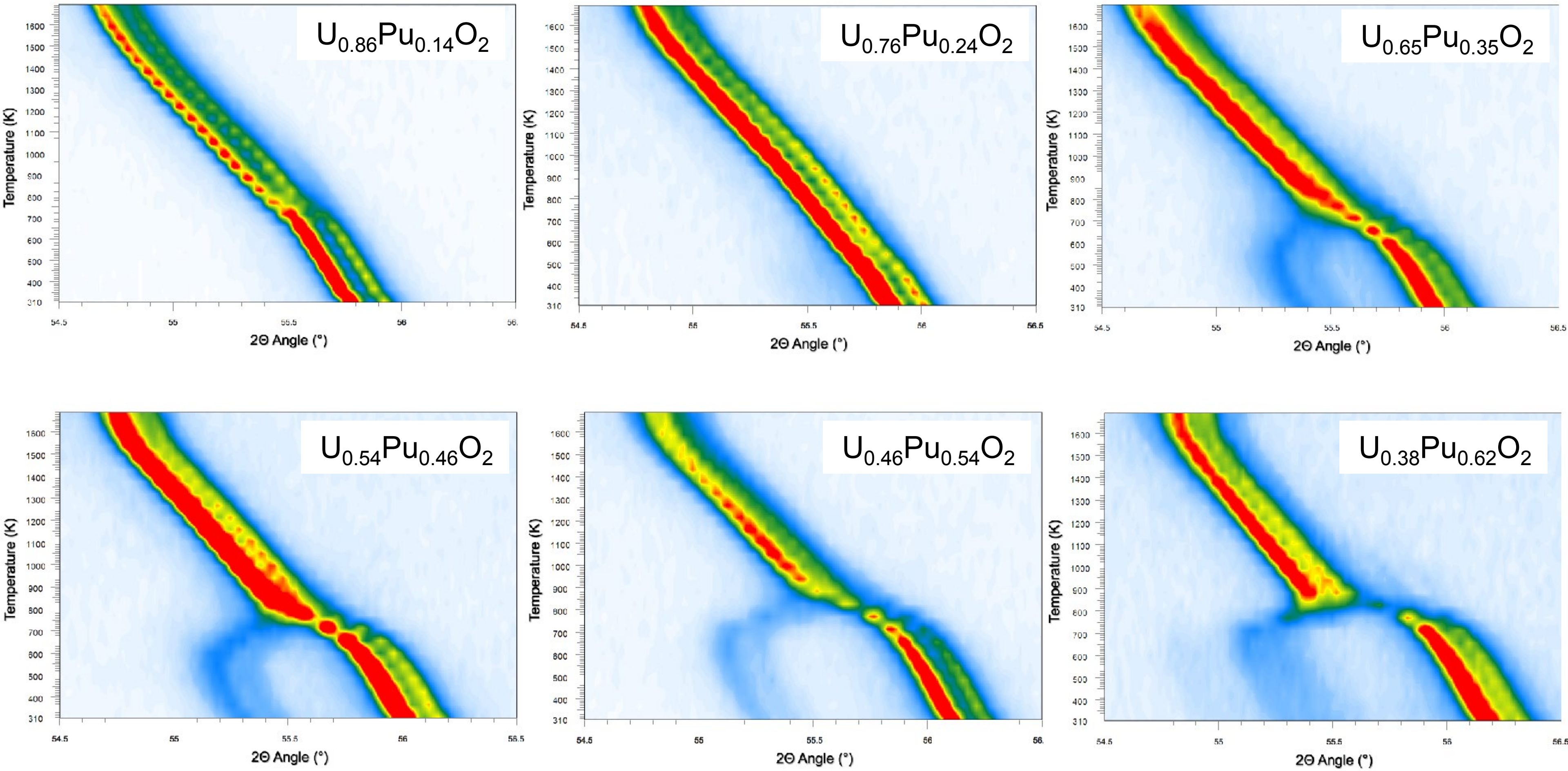
How to read the data : iso-intensity map





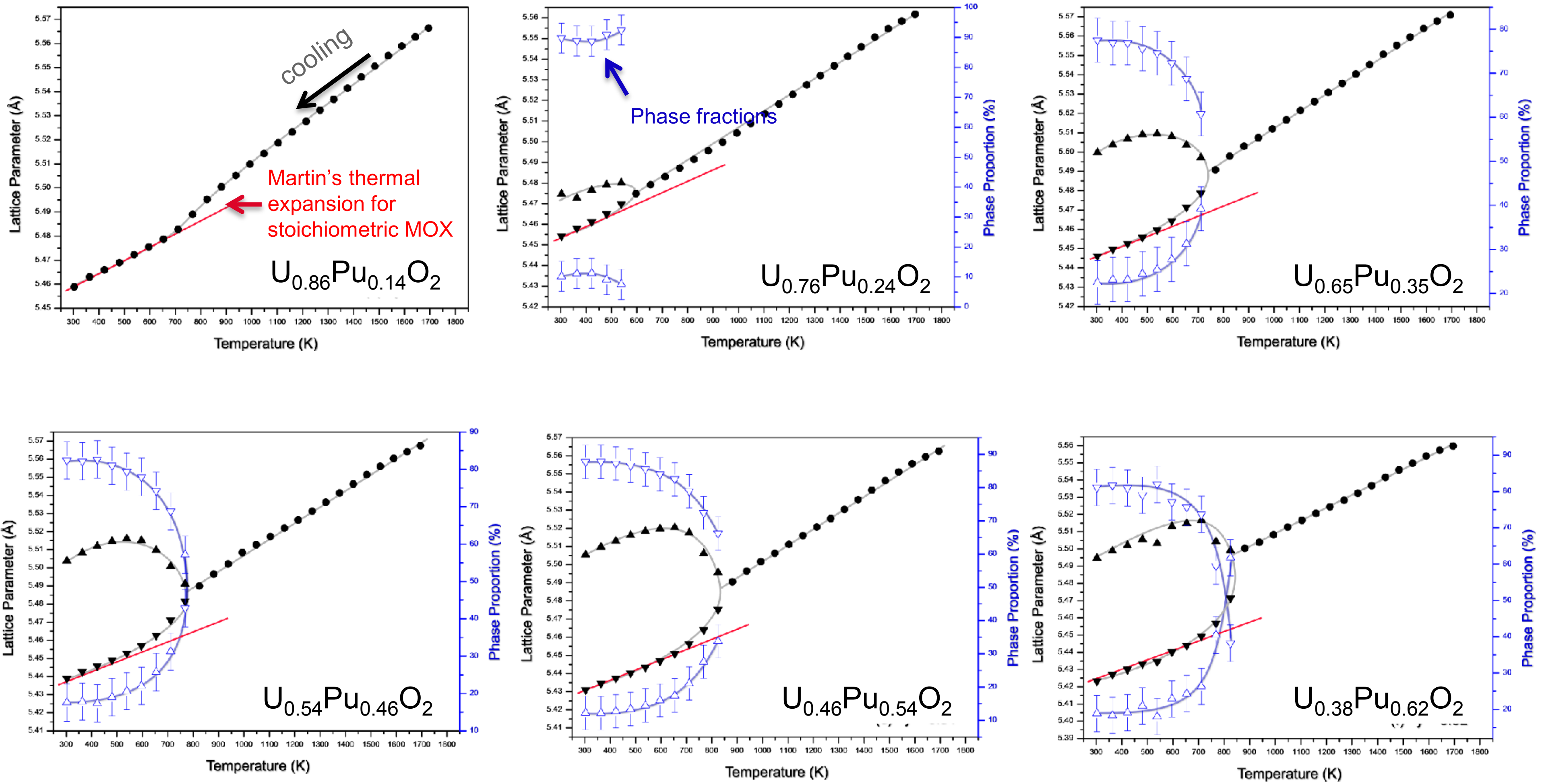


XRD iso-intensity maps



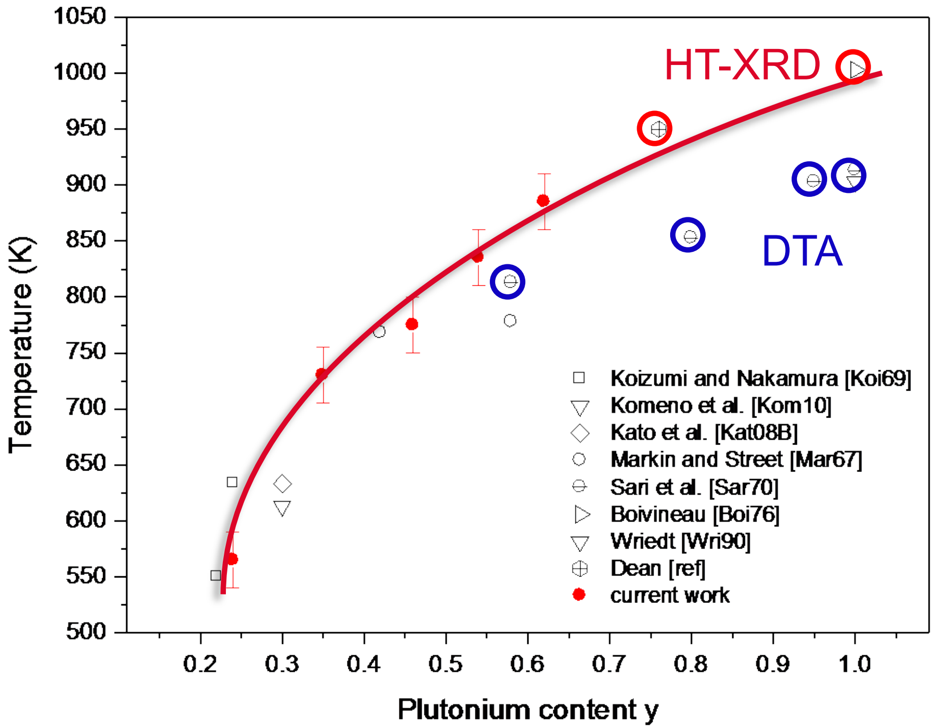
Belin *et al.* *JNM* 465, 2015, 407-417

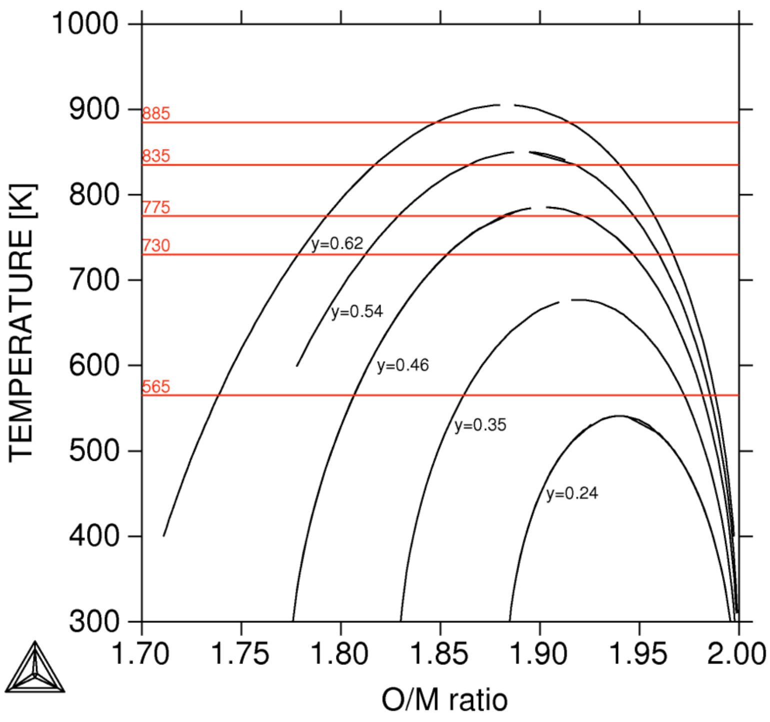
Lattice parameters and phase fractions



Belin *et al. JNM* 465, 2015, 407-417

Temperature of demixtion

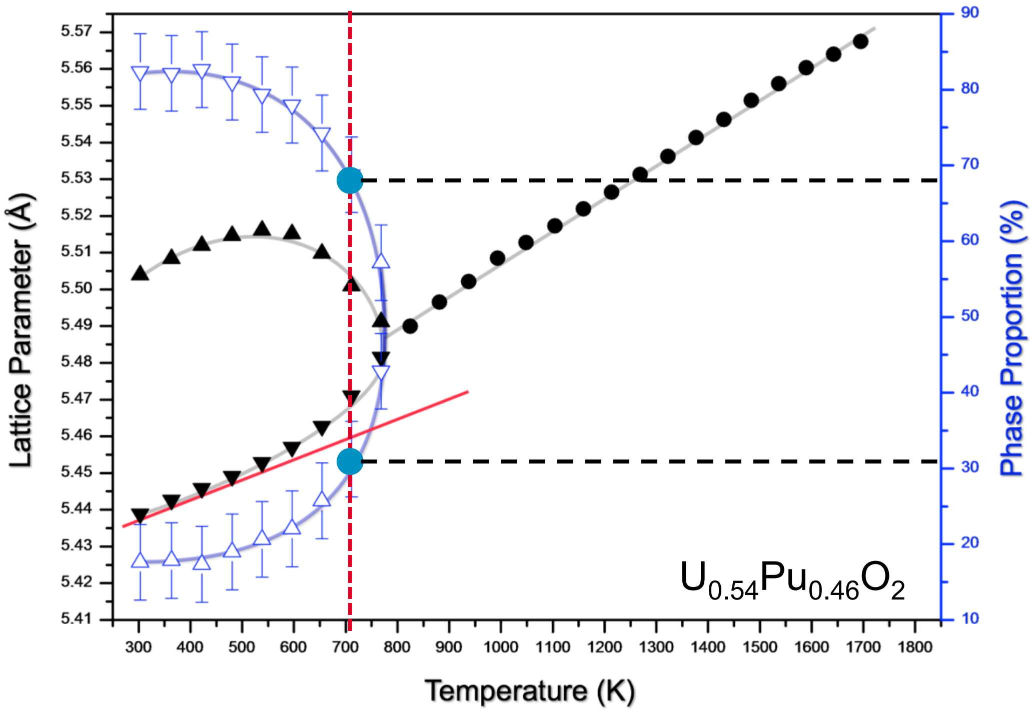


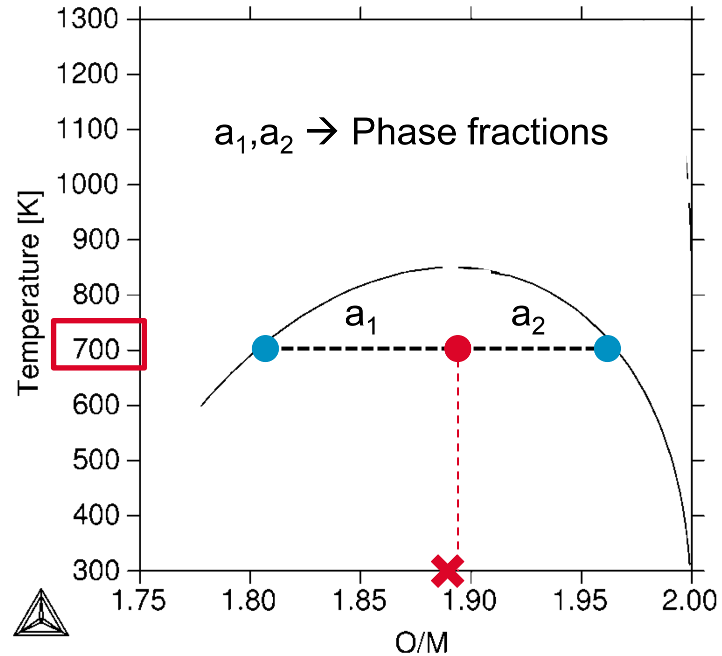


Evaluation of the O/M ratio ?

O/M determination : biphasic domain

- Biphasic domain : Rietveld refinement + CALPHAD





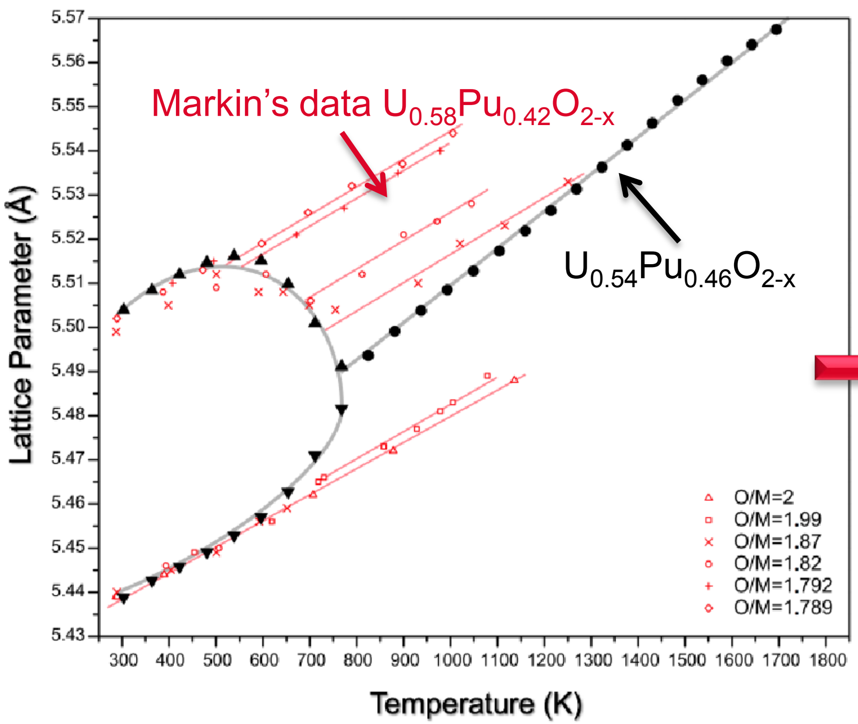
Experimental phase fractions (Rietveld)

Phase fractions are positioned on the calculated miscibility gap

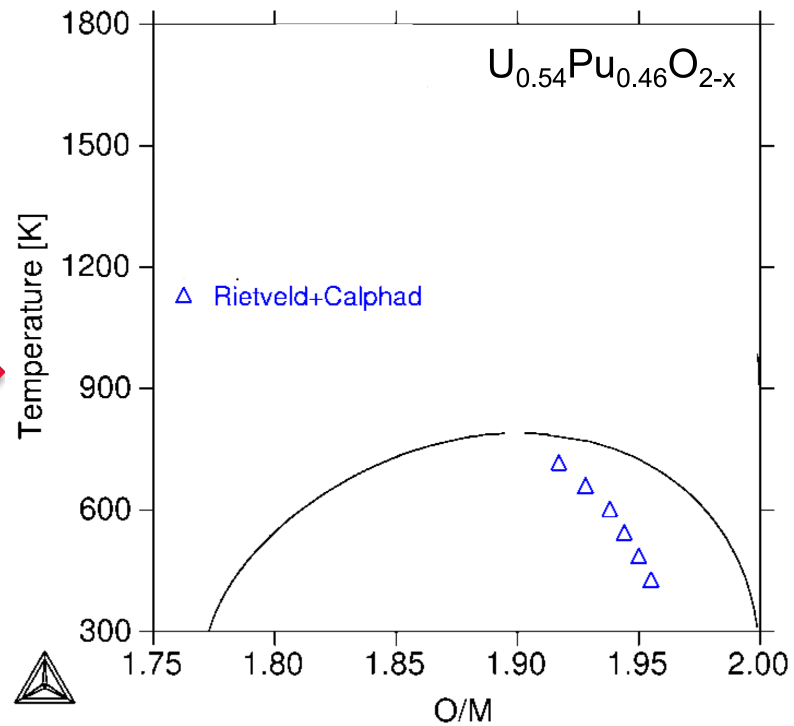
O/M ratio at each temperature

O/M determination : single phase domain

- Single phase domain → comparison with literature



Markin & Street. *Journal of Inorganical Nuclear Chemistry* 29 (1967) 2265-2280

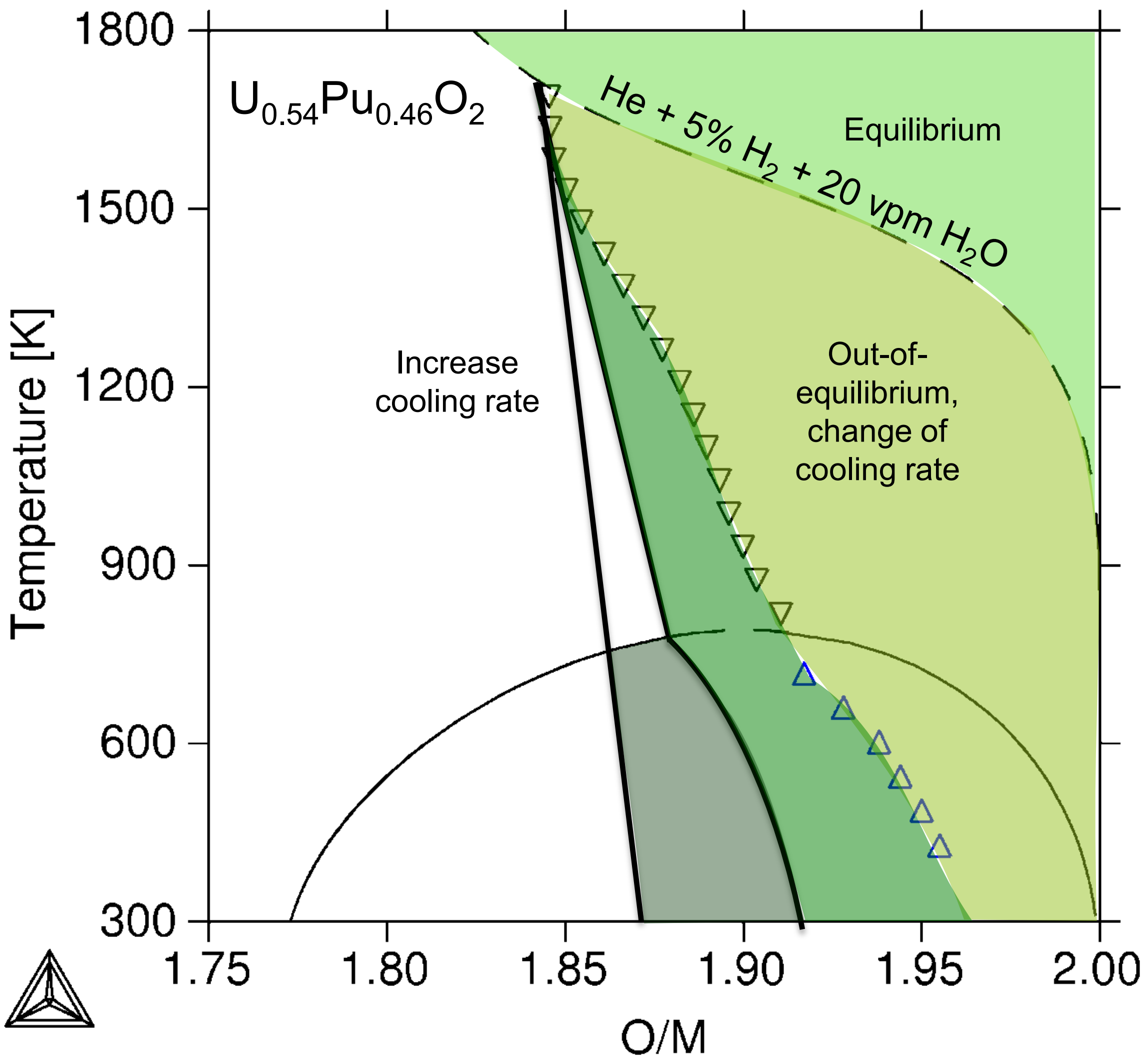


$$\frac{O}{M} = 21{,}3075 + 22{,}78 * 10^{-5} * T - 3{,}565 * a$$

O/M ratio at each temperature

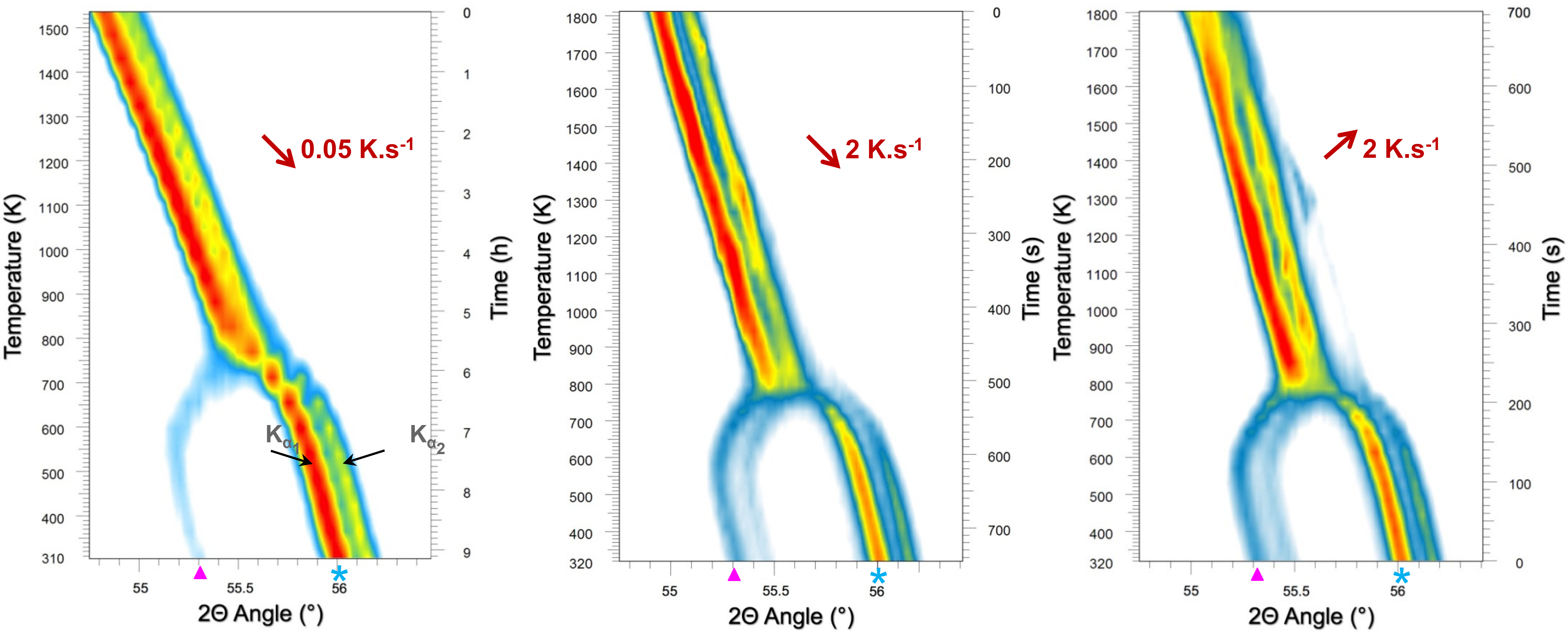
Belin *et al. JNM* 465, 2015, 407-417

To be or not to be at equilibrium ?



Effect of cooling rate on demixtion

- $U_{0.55}Pu_{0.45}O_{2-x}$, He + 5% H_2 + 20 vpm H_2O, various cooling/heating rates (from 0.05 to 4 $K.s^{-1}$)



▲ Low-oxygen phase (O/M << 2.0) ***a* = 5.495(1) Å** * High-oxygen phase (O/M ≈ 2.0) ***a* = 5.439(1) Å**

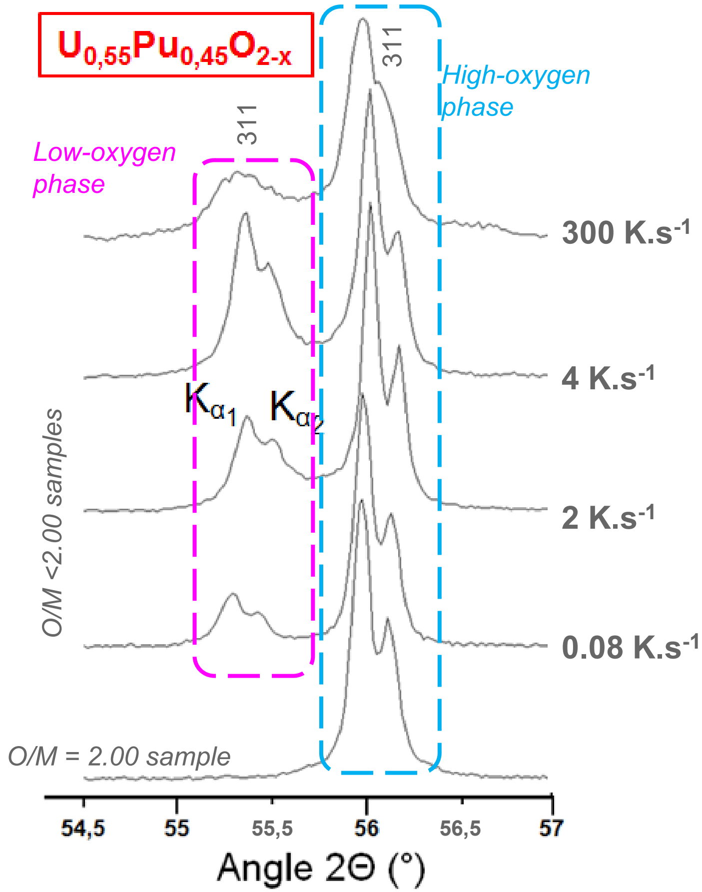
Lattice parameters and $T_{demixtion/recombination}$ identical regardless of cooling/heating rates !!!

$T_{demixtion/recombination}$ = 770 ± 20 K

Vauchy *et al. JECS* 34, 2014, 2543-2551

Effect of cooling rate on demixtion

- Elaboration of dense, stoichiometric (x=0) $\mathbf{U_{0.55}Pu_{0.45}O_{2-x}}$ samples [1]
- Room-temperature XRD on $\mathbf{U_{0.55}Pu_{0.45}O_{2-x}}$ samples cooled from 1773 K from **0.08 K.s^{-1}** to **300 K.s^{-1}** under dry (~20 vpm H_2O) **Ar(He) + 5% H_2** [2]



Cooling rate (K.s^{-1})	Lattice parameter (Å) *		Phase fraction (%) **	
300	5.502(5)	5.441(5)	27(5)	73(5)
4	5.498(1)	5.439(1)	42(1)	58(1)
2	5.495(1)	5.439(1)	30(1)	70(1)
0.08	5.505(1)	5.439(1)	17(1)	83(1)

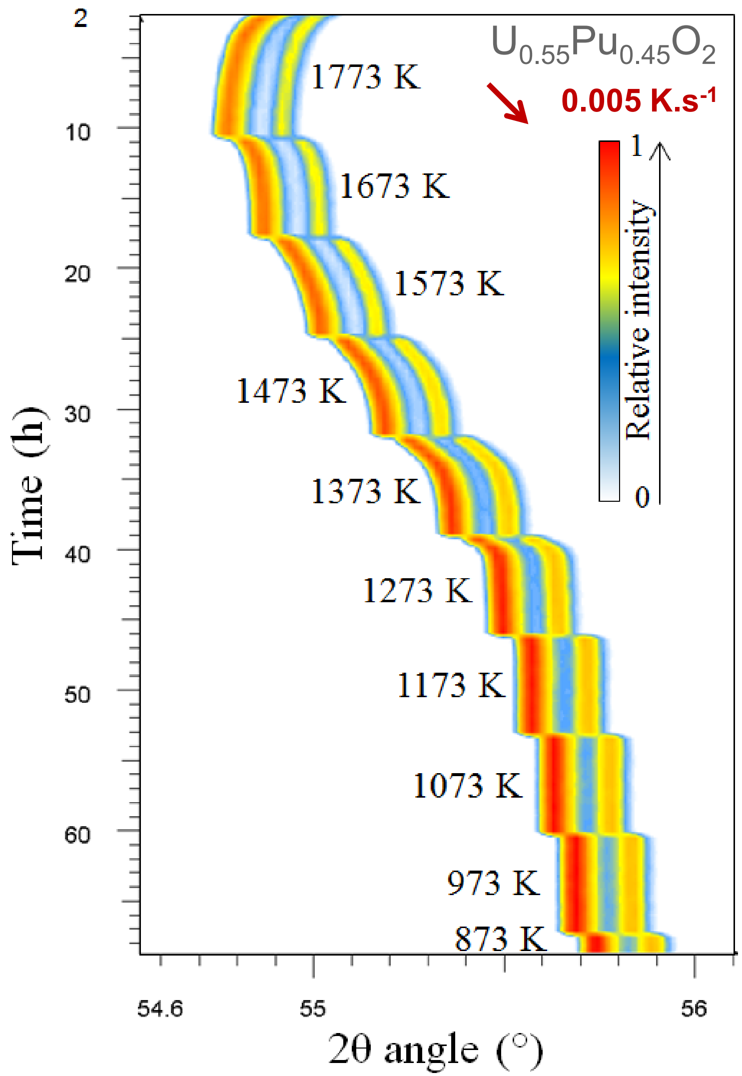
** Pawley refinement* *** Rietveld refinement*

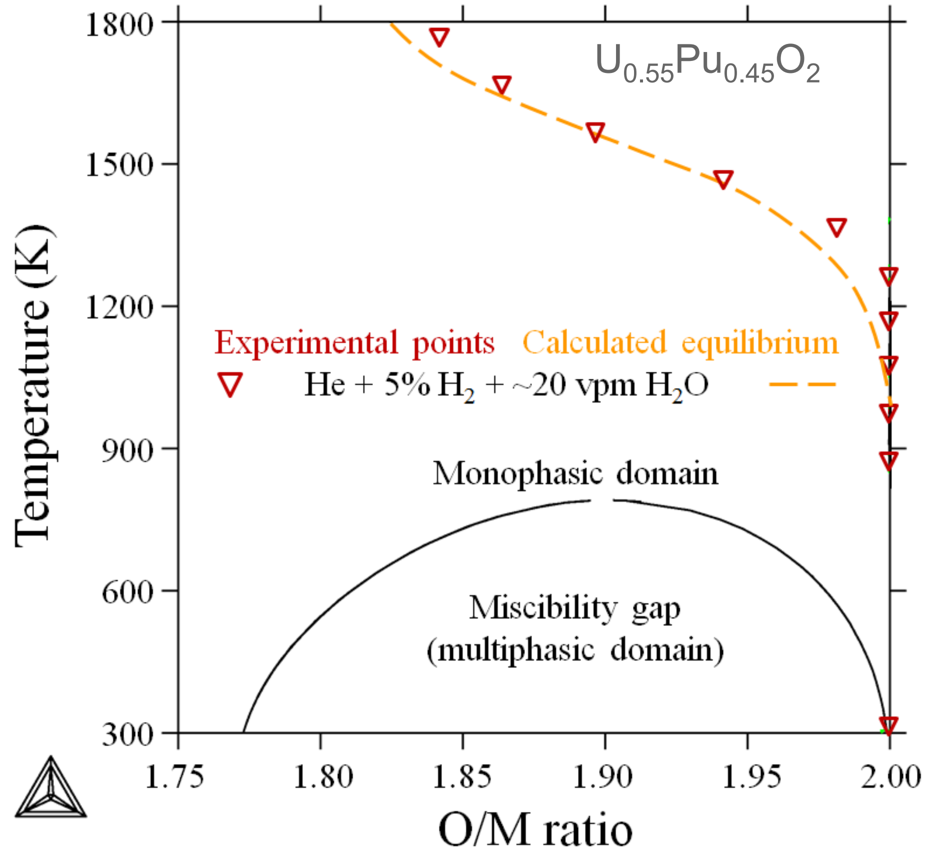
Phase separation occured for all the studied cooling rates

Increasing the cooling rate increases the amount of reduced phase (O/M << 2.0)

[1] *Vauchy et al. Ceram. Int. 40, 2014, 10991-10999*
[2] *Vauchy et al. JECS 34, 2014, 2543-2551*

Extremely slow cooling rate



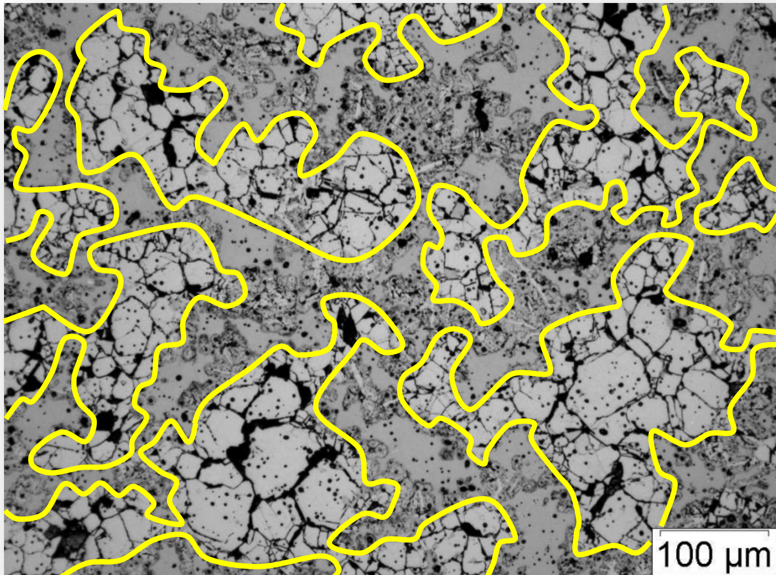


No demixtion
Experiment = calculation
Equilibirum reached !

Vauchy *et al.* *JNM* 469, 2016, 125-132

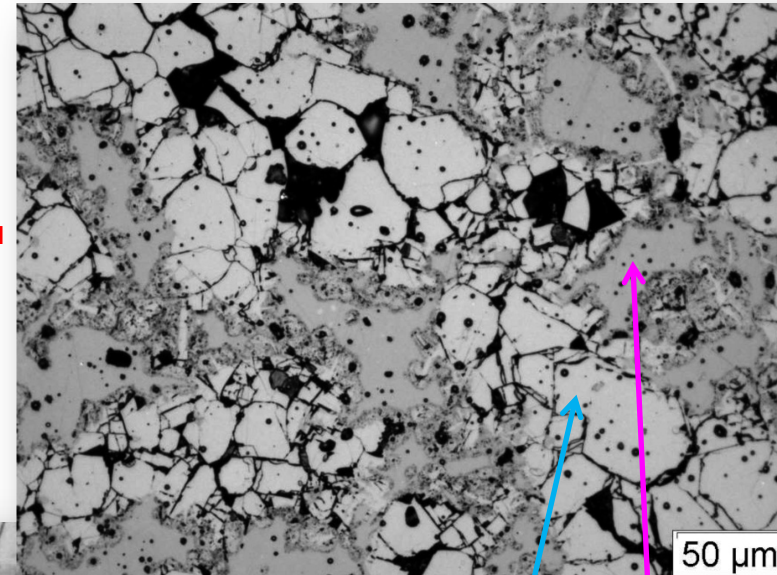
Cooling rate (O/M ratio) & microstructure

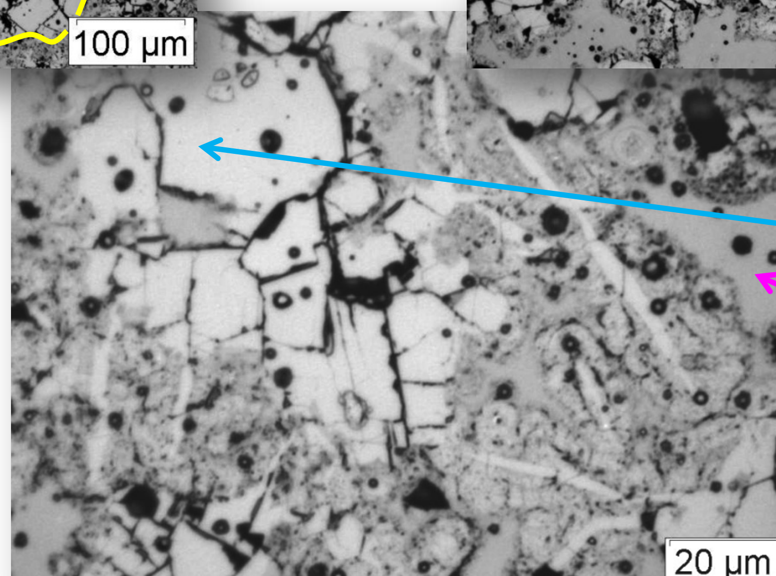
Microstructural effects of demixtion - $U_{0.55}Pu_{0.45}O_{2-x}$



Ar + 5% H_2

↘ ~0.05 $K.s^{-1}$





High-oxygen phase (O/M≈2.0)

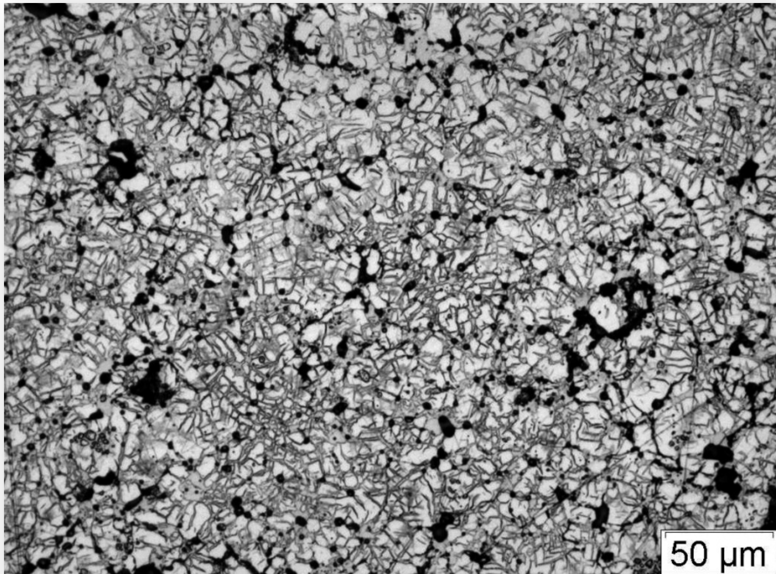
Low-oxygen phase (O/M<<2.0)

Two distinct zones **even before** chemical etching

Related to the **two phases** observed by XRD

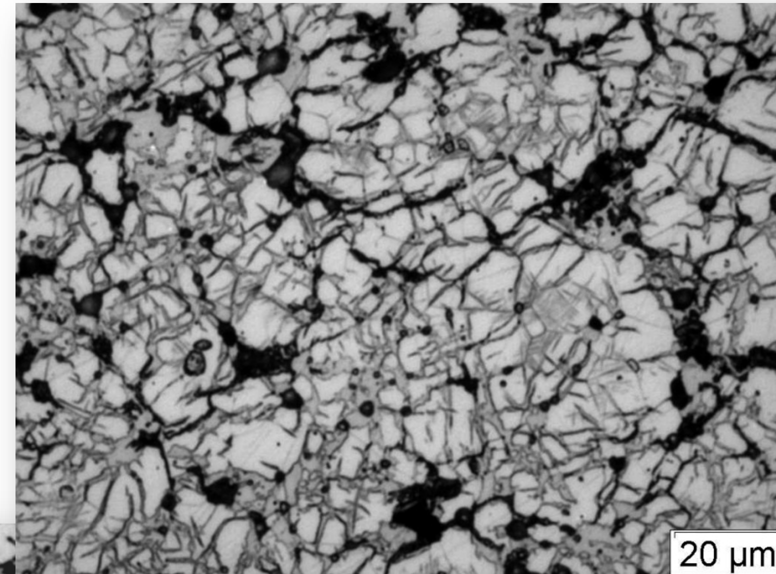
Damaged microstructure (cracks) owing to mechanical strains induced by the phase separation

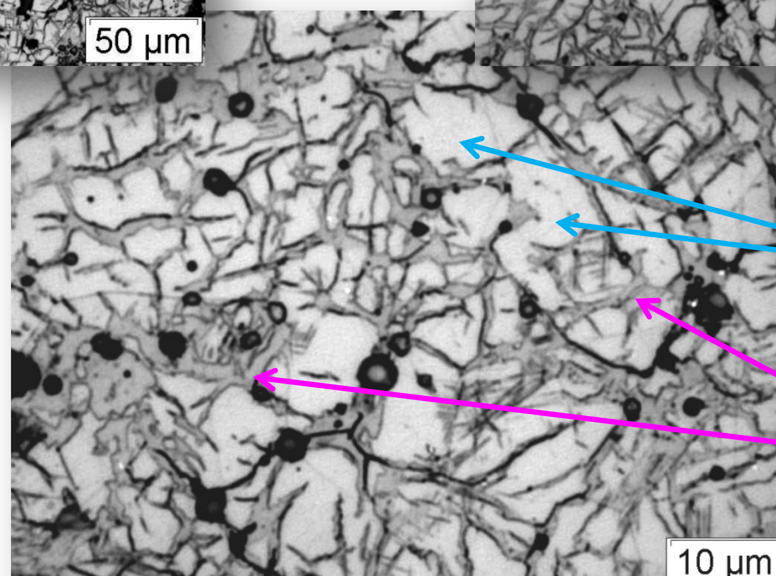
Microstructural effects of demixtion - $U_{0.55}Pu_{0.45}O_{2-x}$



Ar + 5% H_2

↘ ~300 $K.s^{-1}$





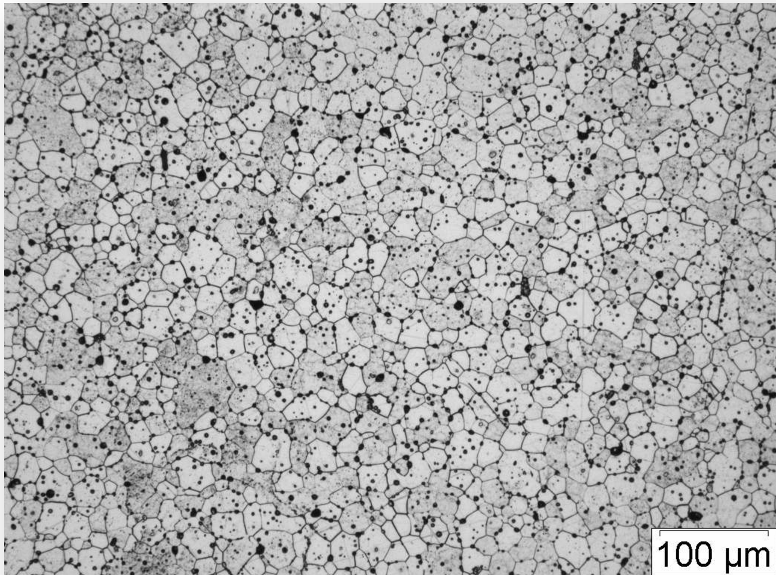
High-oxygen phase (O/M≈2.0)

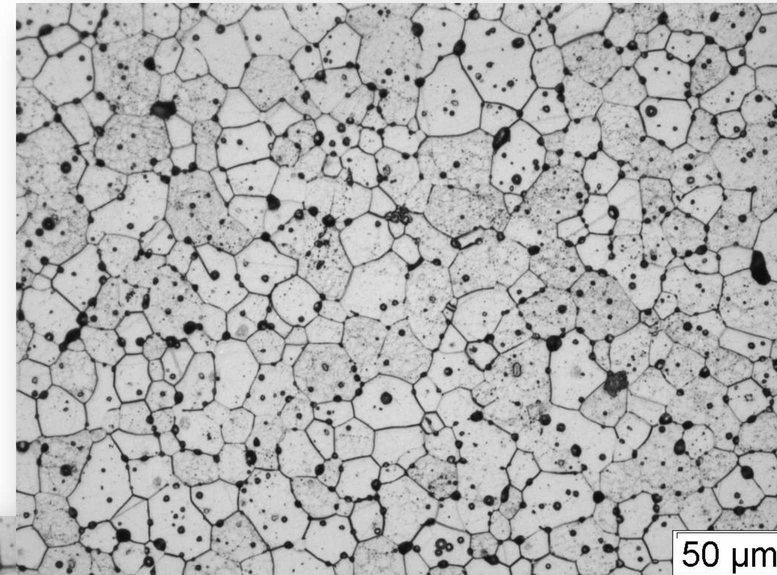
Low-oxygen phase (O/M<<2.0)

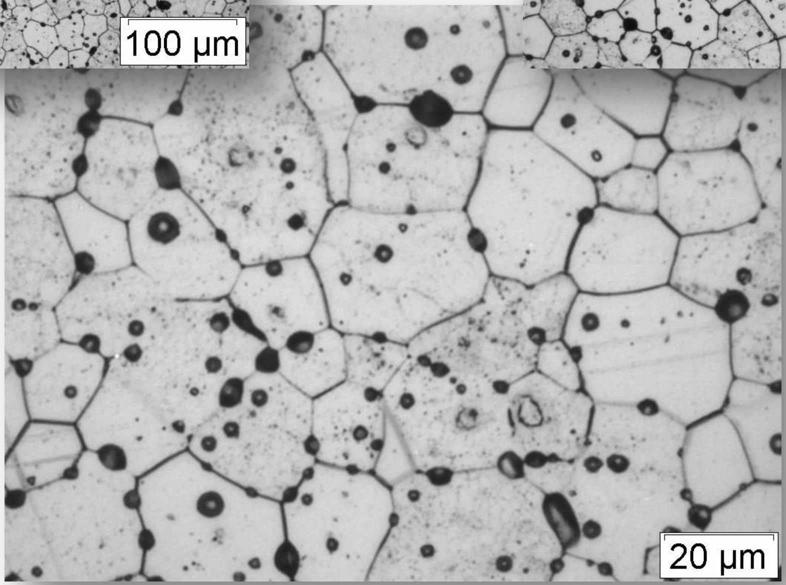
Two zones clearly visible **after** chemical etching and at a **different scale** than the slowly cooled sample

Damaged microstructure by cracks (not visible here)

Microstructural effects of demixtion - $U_{0.55}Pu_{0.45}O_{2-x}$







$U_{0.55}Pu_{0.45}O_{2.00}$

Monophasic

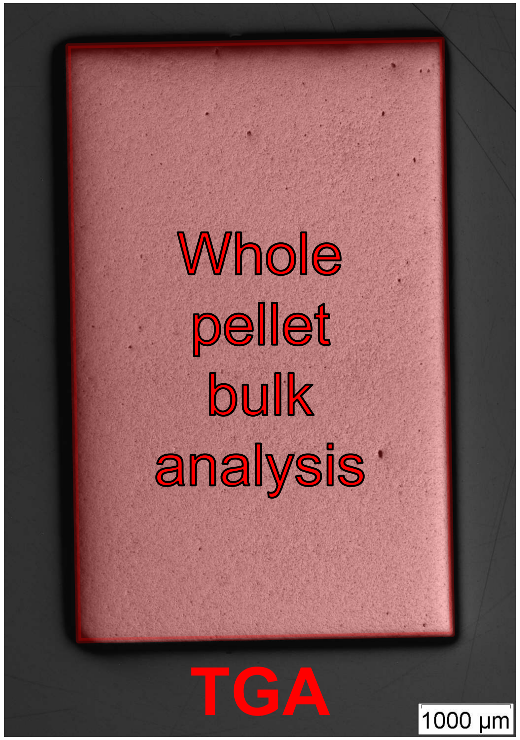
Damage-free microstructure

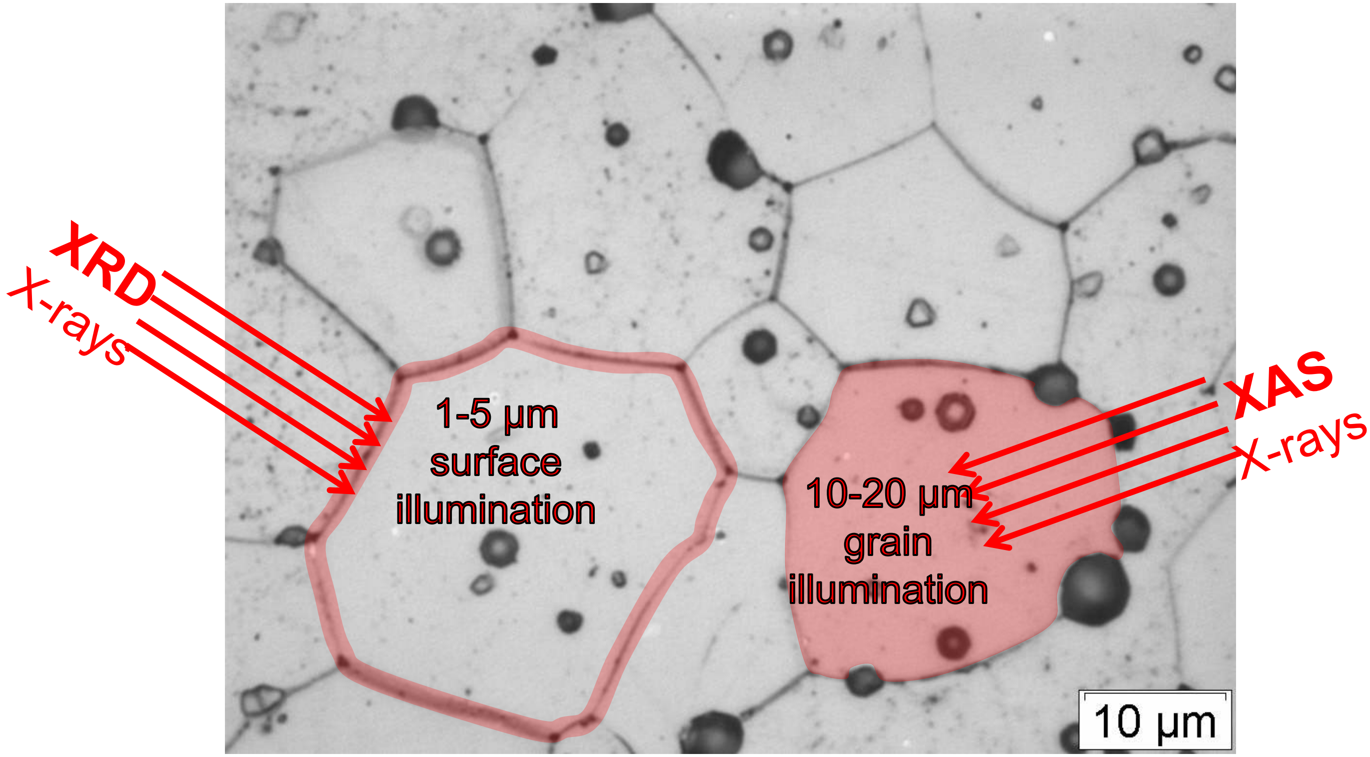
Grains visible after chemical etching

Vauchy *et al.*, *Ceram. Inter.* 40 (7B) (2014) 10991-10999

Room-temperature oxidation

Variation of the O/M ratio at room temperature



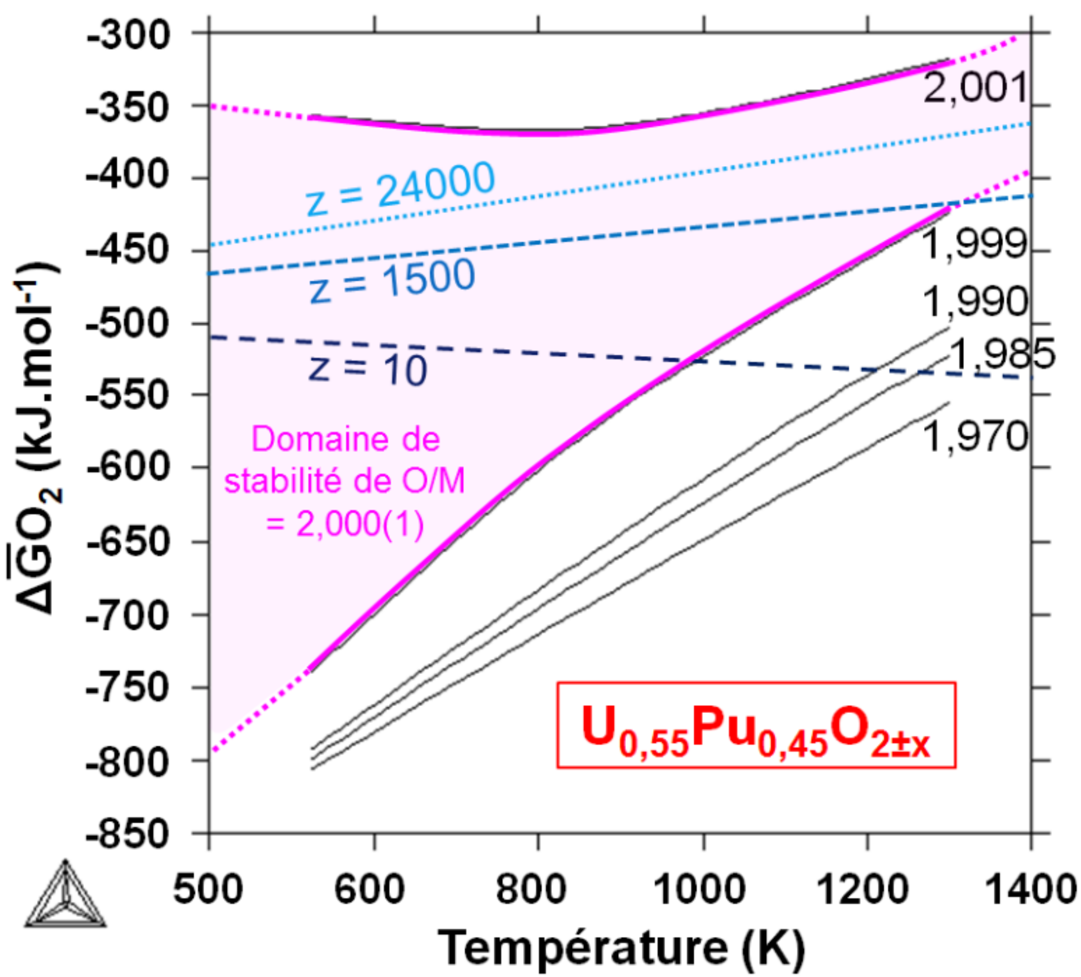


Variation of the O/M ratio at room temperature

- Variation at the pellet scale (TGA) [1]

Glove box atmosphere : N_2 + ~30 vpm O_2 + ~50 vpm H_2O

Storge duration	O/M ratio of $U_{0.55}Pu_{0.45}O_{2-x}$ mesured by TGA
t_0	1.927(1)
t_0 + 3 months	1.938(1)
t_0 + 9 months	1.976(1)



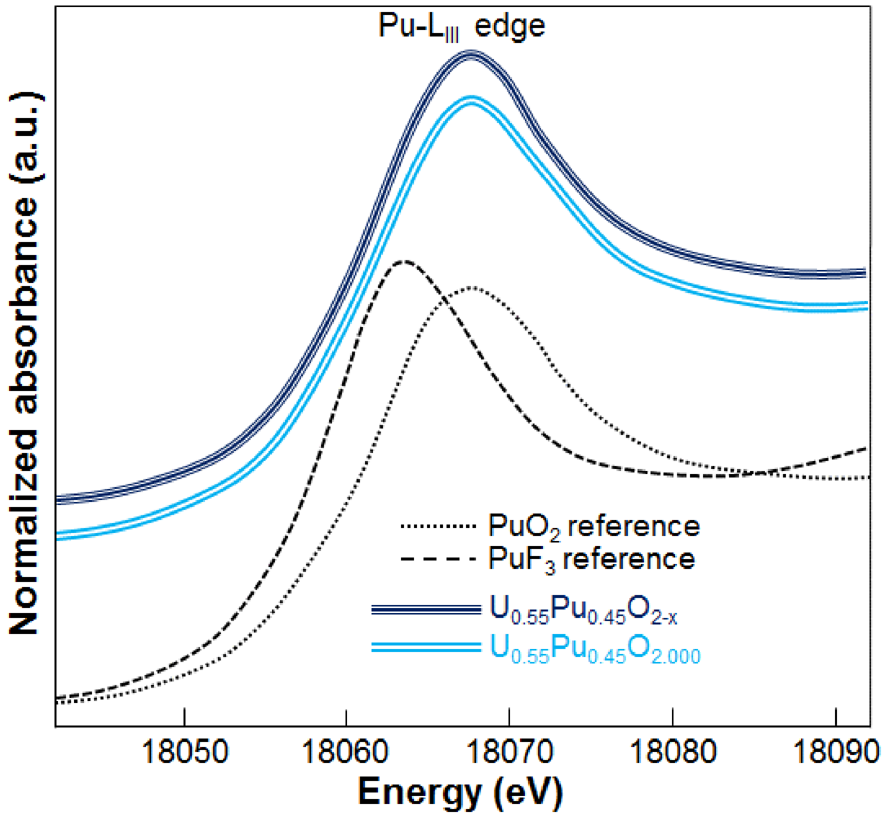
Significative oxidation at the pellet scale in N_2

[1] *Vauchy et al., JNM 465 (2015), 349-357*

Variation of the O/M ratio at room temperature

- Variation at the grain scale (XAS) [1]

Glove box atmosphere : N_2 + ~30 vpm O_2 + ~50 vpm H_2O



- Powders (grains 30-40 µm)
- X rays penetrate tens of µm in $U_{1-y}Pu_yO_2$

Sample	%UO_2	%U_4O_9	%PuO_2	Calc. O/M ratio
$U_{0.55}Pu_{0.45}O_{2-x}$	96(2)	4(2)	100	2.01(1)
$U_{0.55}Pu_{0.45}O_{2.000}$	94(2)	6(2)	100	2.01(1)

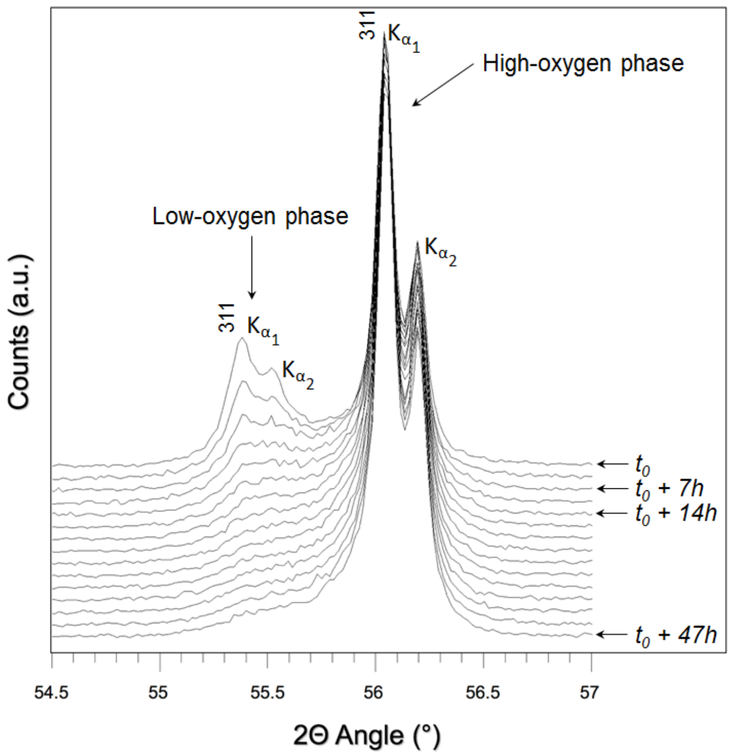
Complete oxidation at grain scale (30-40 µm) in meantime between preparation and analysis (3 months)

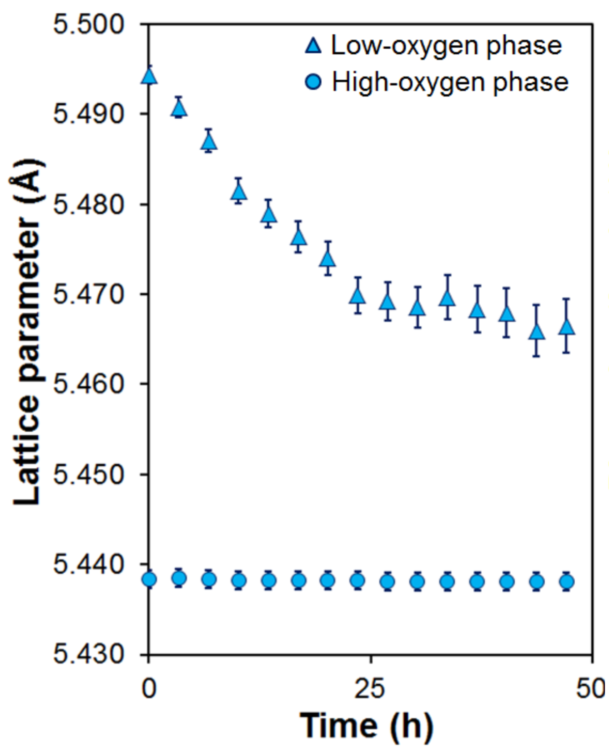
[1] *Vauchy et al., JNM 465 (2015), 349-357*

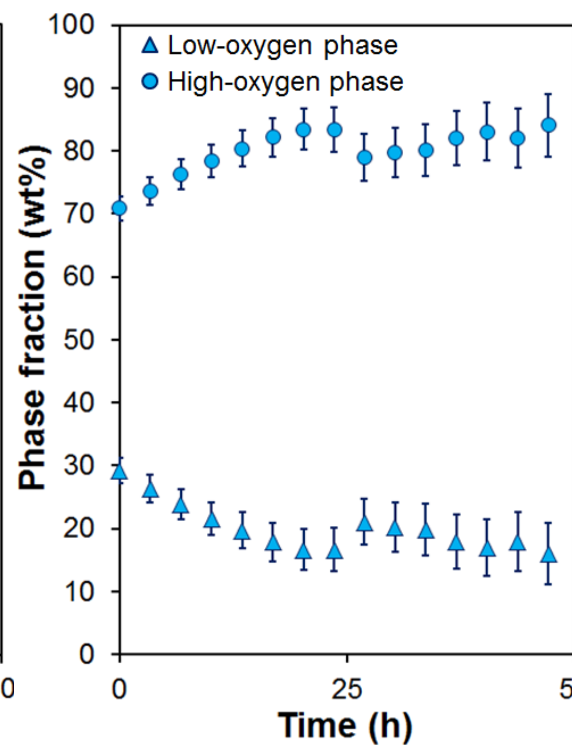
Variation of the O/M ratio at room temperature

- Variation at the scale of the surface of grains (XRD) [1]

Glove box atmosphere : N_2 + ~30 vpm O_2 + ~50 vpm H_2O







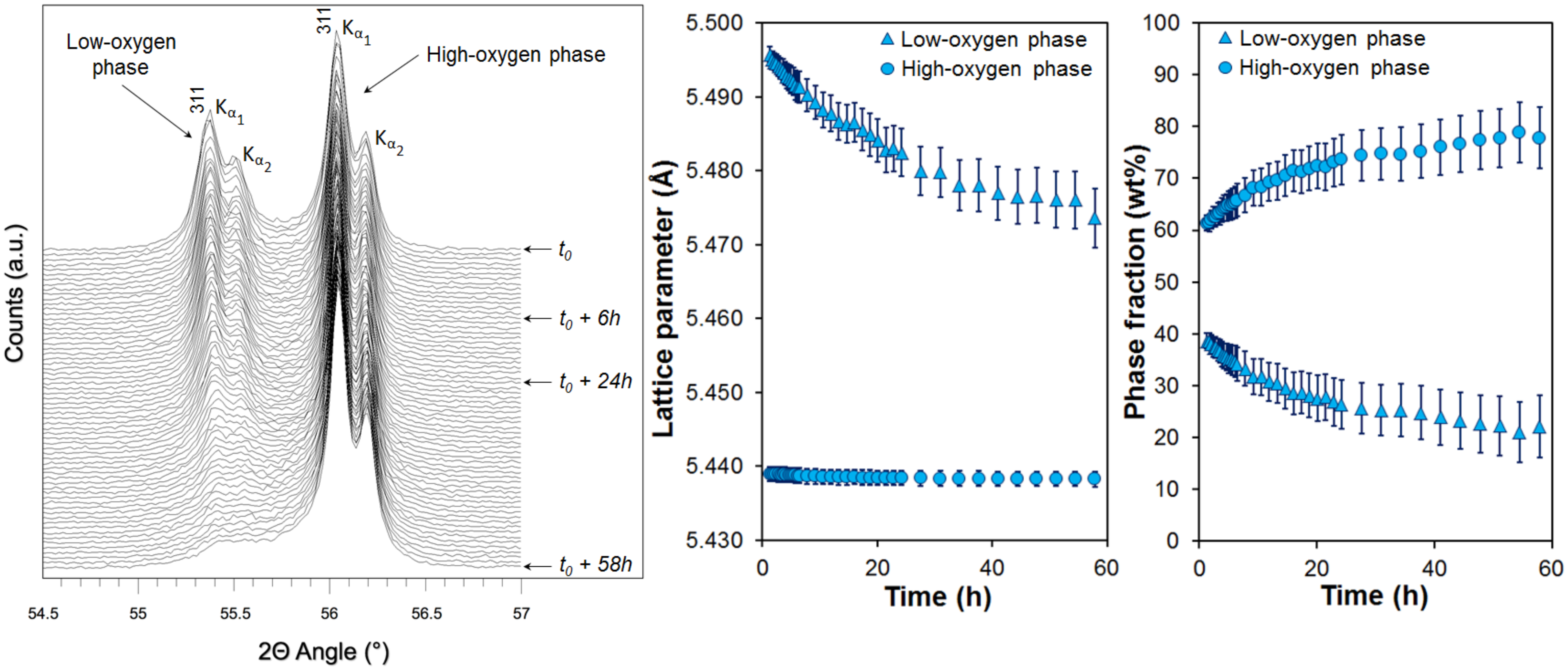
- Low-oxygen phase : lattice parameter & fraction vary
- High-oxygen phase : fraction varies

[1] *Vauchy et al., presented at Pu Futures 2014, Las Vegas, USA*

[2] *Vauchy et al., JNM 465 (2015), 349-357*

Variation of the O/M ratio at room temperature

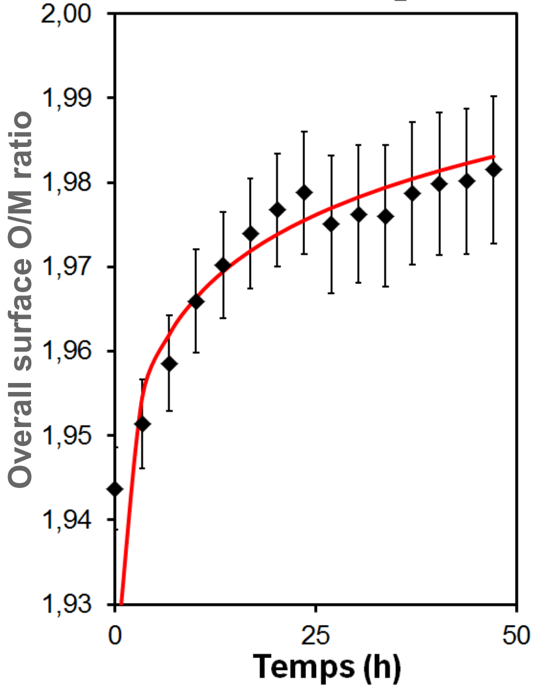
Reconstituted air : N_2 + 21% O_2 + ~5 vpm H_2O



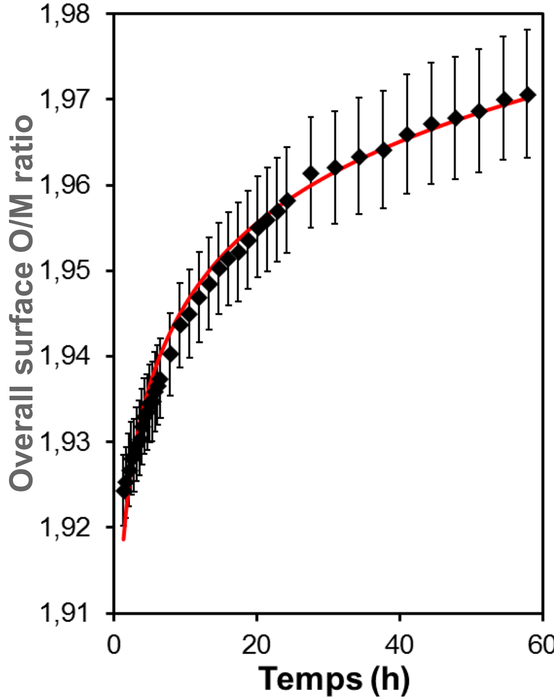
Similar trend than in glove-box atmosphere

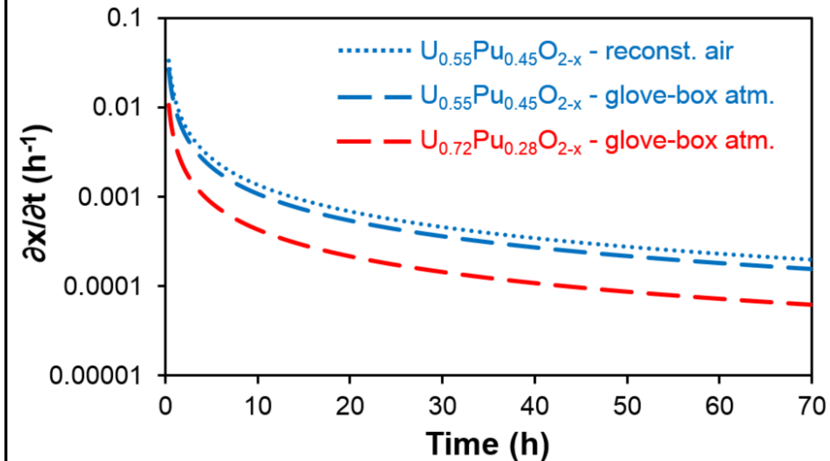
Variation of the O/M ratio at room temperature

Glove-box atm.
N_2 + ~30 vpm O_2 + ~50 vpm H_2O



Reconstituted air
N_2 + 21% O_2 + ~5 vpm H_2O





Oxidation rates of ***$U_{0.72}Pu_{0.28}O_{2-x}$*** *and* ***$U_{0.55}Pu_{0.45}O_{2-x}$*** *as a function of time and atmosphere*

Surface oxidation
- Significant
- Fast
- Similar oxydation rates

H_2O seems responsable for oxidation [1]

[1] *R.E. Woodley et al., HEDL-SA-592, 1973*

Conclusions

O/M ratio of $U_{1-y}Pu_yO_{2-x}$ fuel depends upon :

- U and Pu composition
- Impurities (ex. Am)
- Sintering conditions (dwell temperature, dwell time, atmosphere)
- Cooling rate
- Storage conditions (temperature, atmsophere, time)
- Could be influenced by isotopic composition (ex. [^{238}Pu])

Control of the OM ratio of $U_{1-y}Pu_yO_{2-x}$ fuel during both manufacturing and storage is challenging

Thank you for your attention

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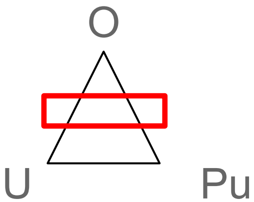
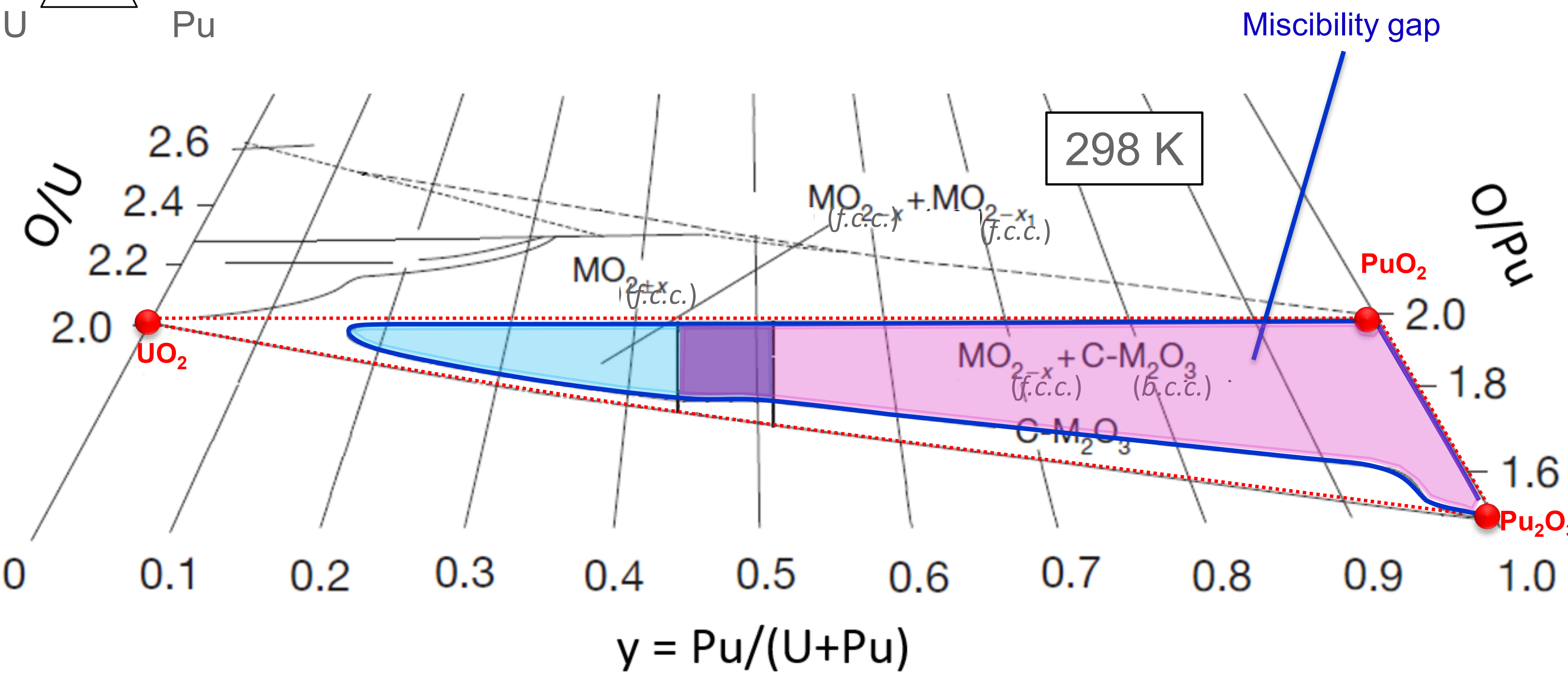
Nuclear Energy Division
Research Department on Mining and Fuel Recycling Processes
Department of Process Engineering of Actinide Materials Manufacturing

Microstructural effects of demixtion - $U_{0.55}Pu_{0.45}O_{2-x}$

UO_2-PuO_2-Pu_2O_3 at room temperature

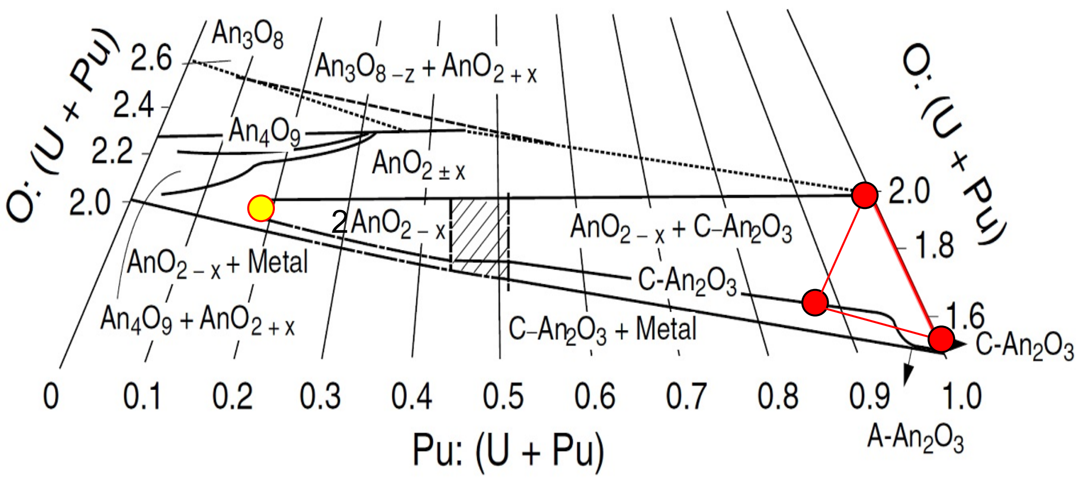




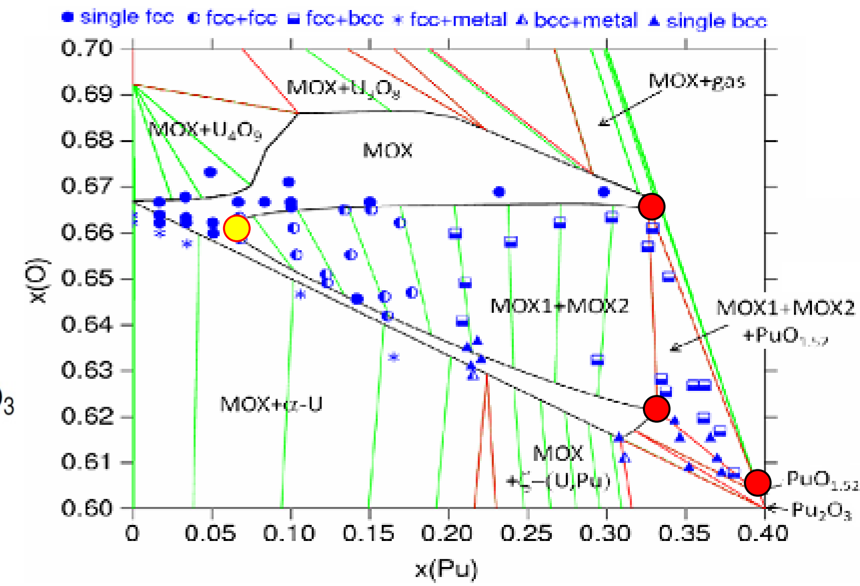
Sari et al., Journal of Nuclear Materials 35 (1970) 267-77

2 x *f.c.c.* phases 2 x *f.c.c.* + *b.c.c.* phases *f.c.c.* + *b.c.c.* phases

Experiment vs. Modeling



Sari *et al.*, *Journal of Nuclear Materials* 35 (1970) 267-77

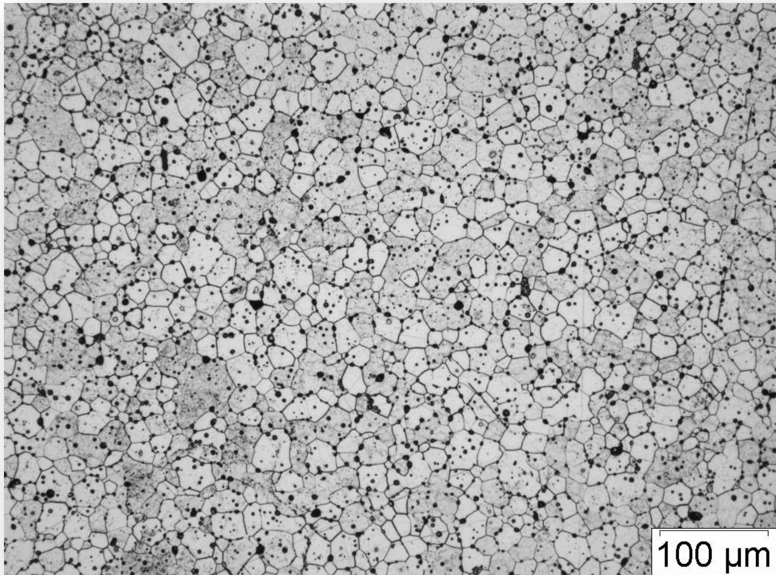


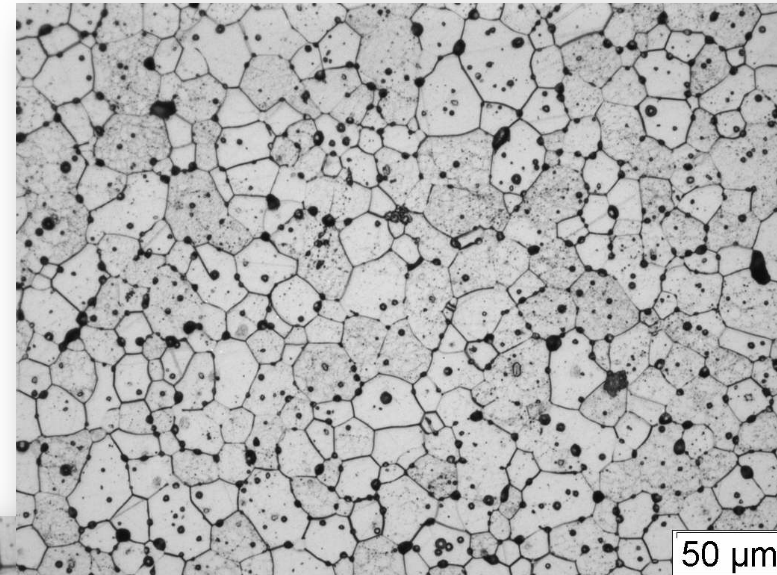
Guéneau *et al.*, *Journal of Nuclear Materials* 419 (2011) 145-167

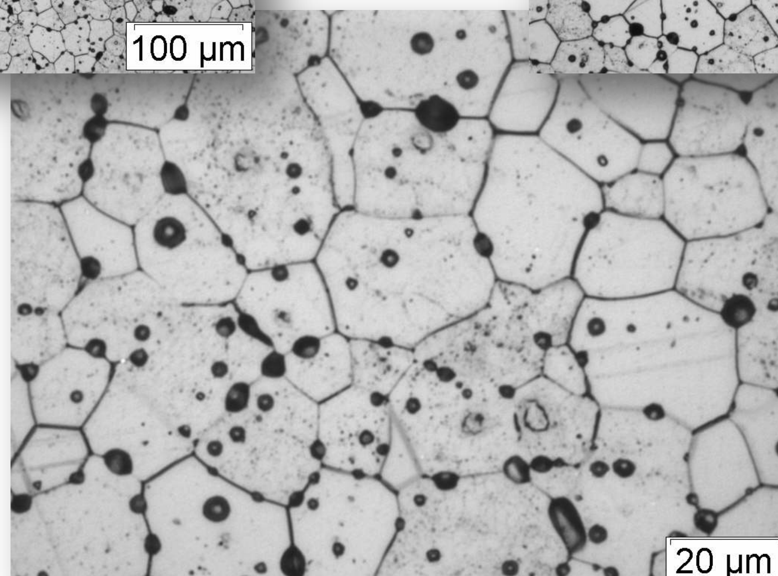
- Generally : experiment and modeling in good agreement
- Same low Pu content limit for the miscibility gap (~17% Pu)
- Some differences :
  - ➢ Biphasic domain MO_{2-x} + M_2O_3 not modeled
  - ➢ Existence of a three-phases domain 2 x MO_{2-x} + M_2O_3

    Calculated composition range far from the hatched area of Sari

High Pu content : microstructures & O/M ratios







$U_{0.55}Pu_{0.45}O_{2.00}$

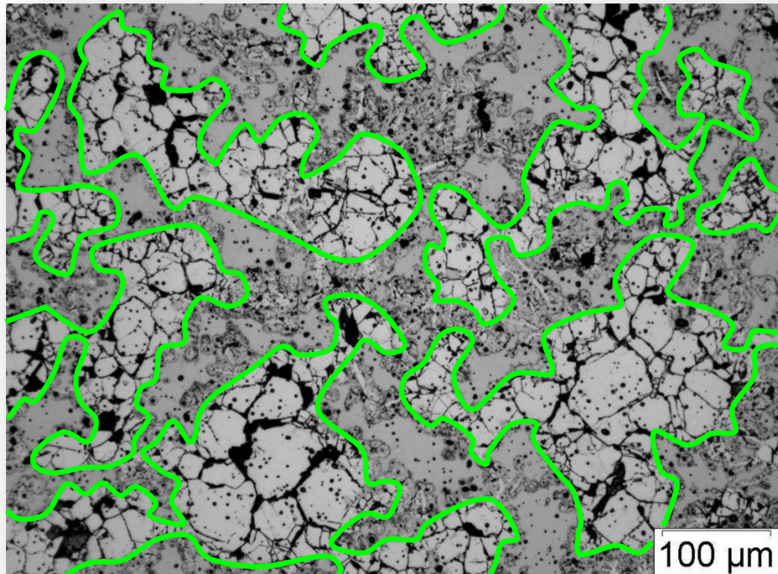
Vauchy *et al.*, *Ceram. Inter.* 40 (7B) (2014) 10991-10999

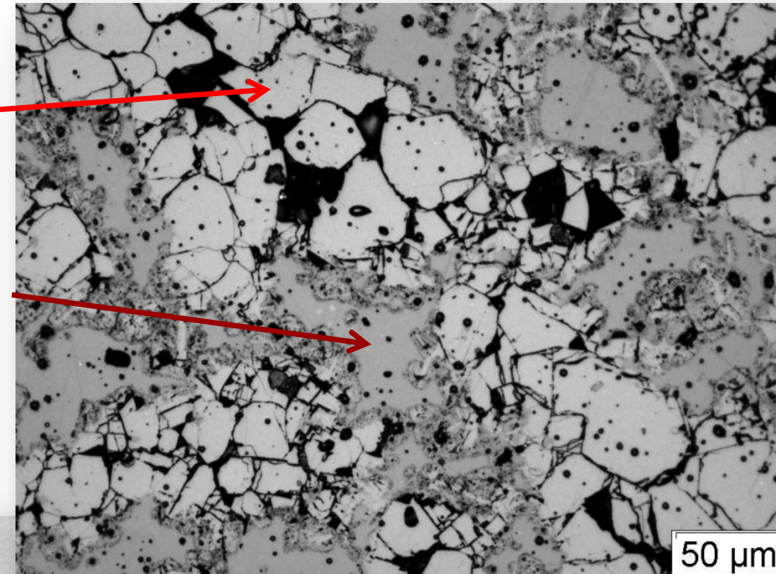
Monophasic

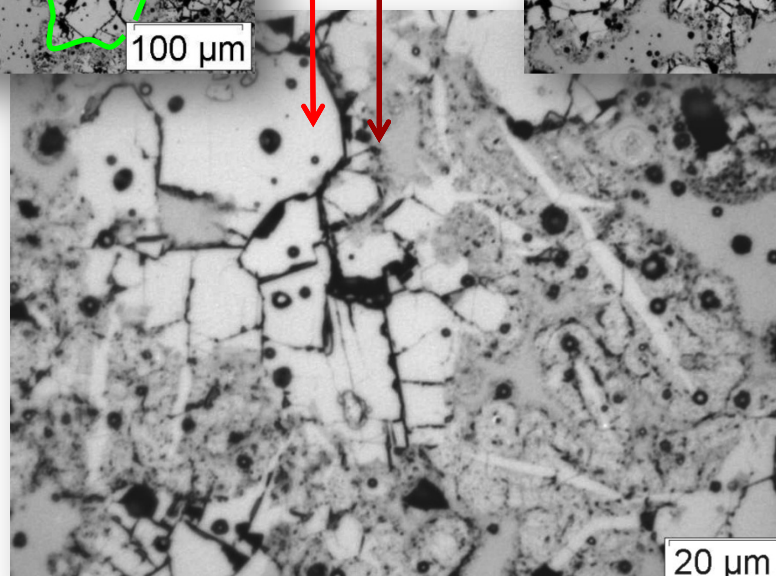
Damage-free microstructure

Grains visible after chemical etching

High Pu content : microstructures & O/M ratios







$U_{0.55}Pu_{0.45}O_{1.93}$

Vauchy *et al., J. Eur. Ceram. Soc. 30 (10) (2014) 2543-2551*

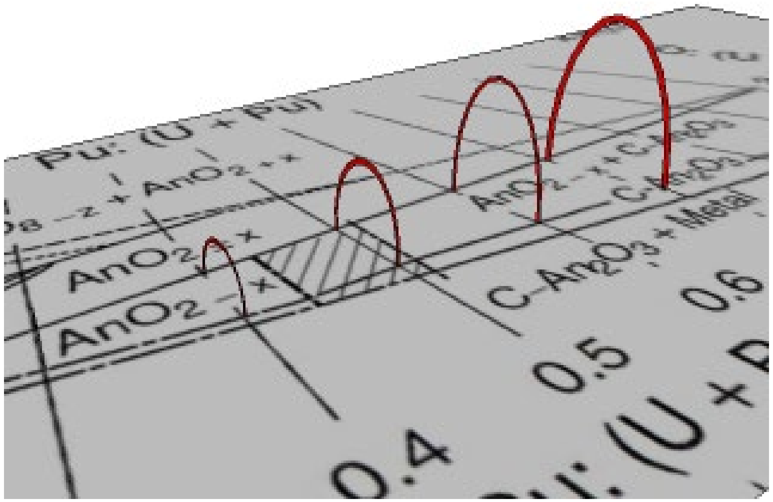
Damaged microstructure (cracks)

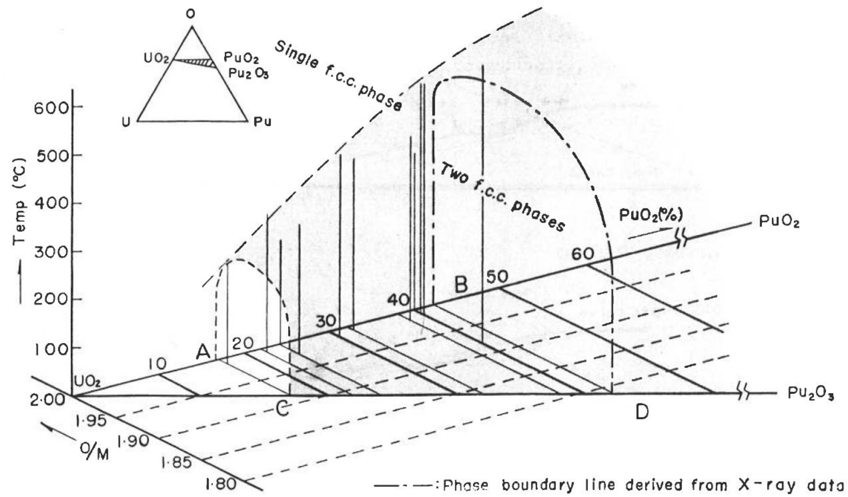
Two **distinct** zones

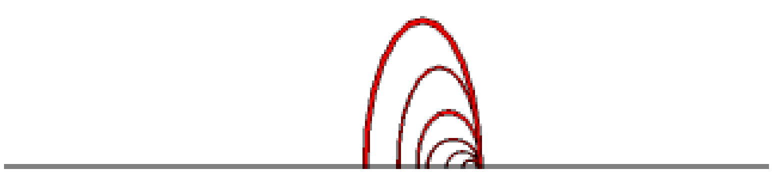
⇓

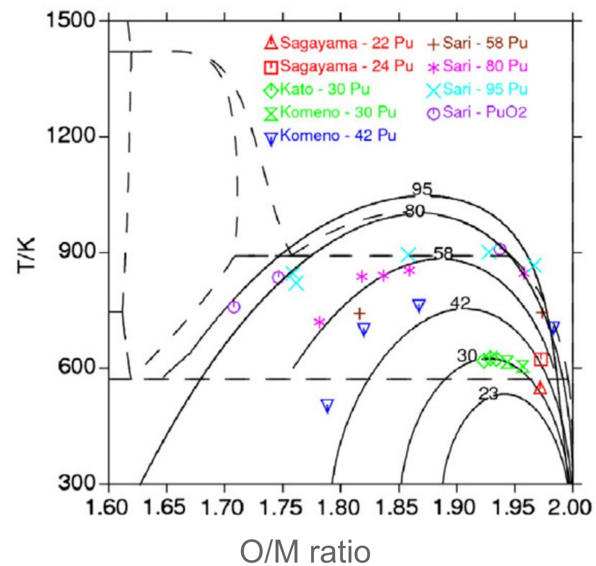
T**wo phases** observed by XRD

UO_2-PuO_2-Pu_2O_3 at HT



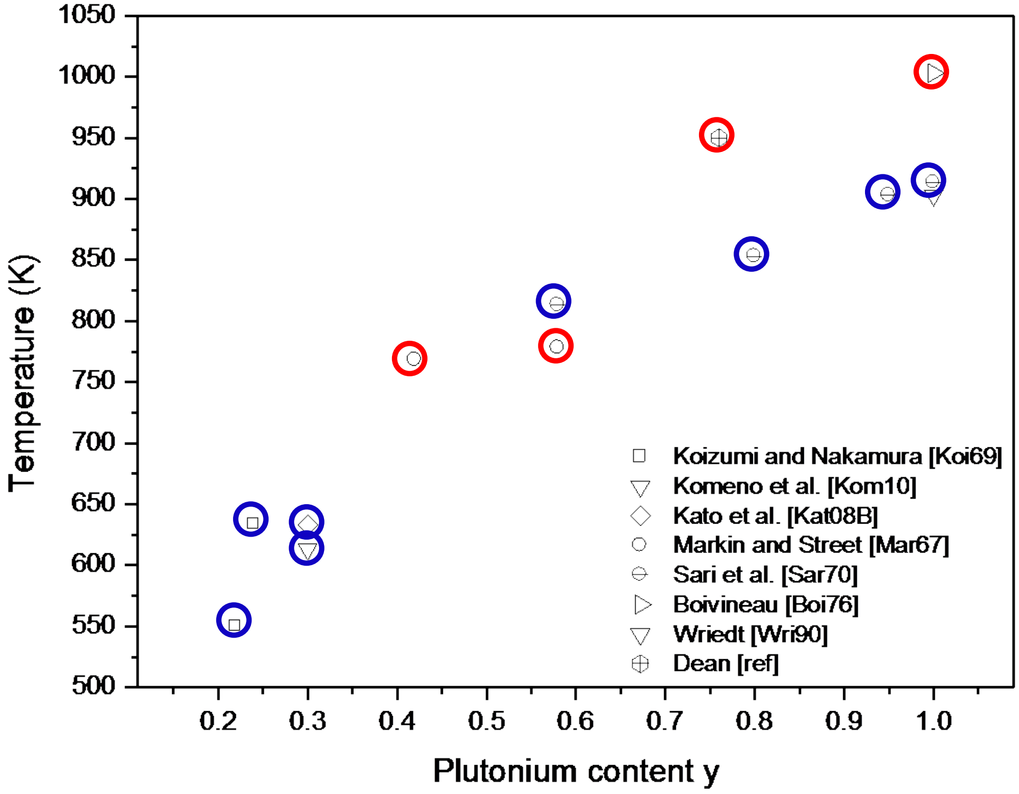






UO_2-PuO_2-Pu_2O_3 at HT

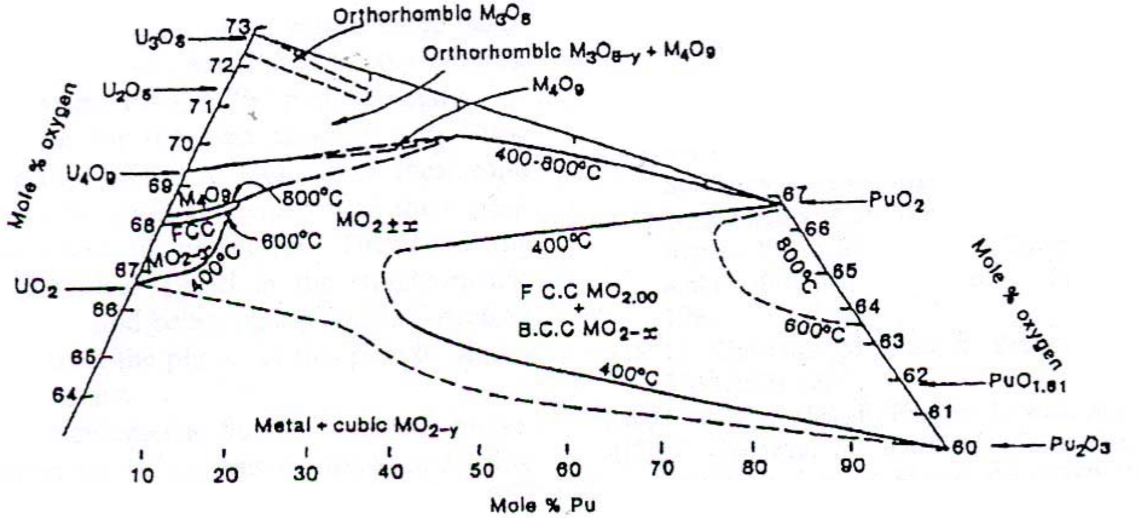
Experimental temperatures of phase separation (DTA, HT-XRD)
→ Entering in the miscibility gap



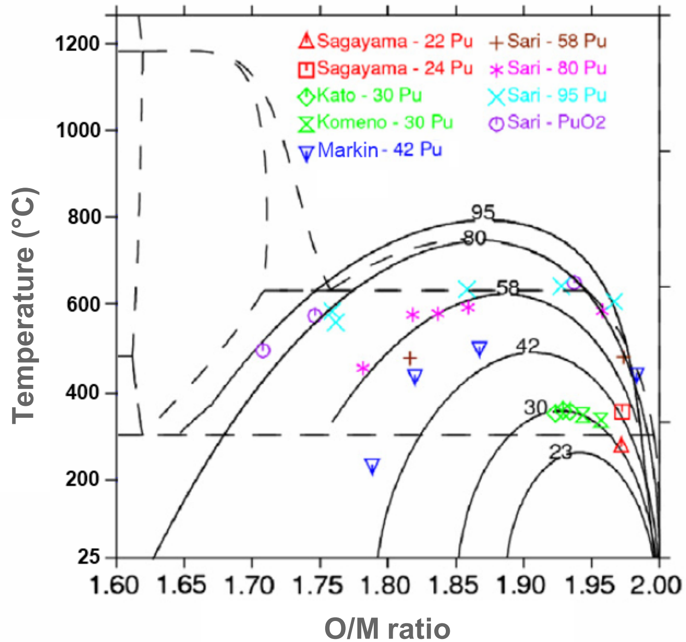
- T increases with Pu content
- Low Pu : only DTA results → scattering confirms the difficulties in measuring at low Pu content
- High Pu : T obtained with DTA lower than with HT-XRD
- PuO_2 : HT-XRD value (1000 K) in agreement with description of Pu-O

Very few experimental results

Experiment vs. Modeling



Markin & Street. *Journal of Inorganical Nuclear Chemistry* 29 (1967) 2265-2280



Guéneau *et al. Journal of Nuclear Materials* 419 (2011) 145-167

- Experiment and calculations agree for $y \leq 0.40$
- Difference for $y > 0.40$: calculations overestimate $T_{separation}$

New HT studies are required to better describe the phase separation phenomenon

Conclusions

Conclusions

- Main specifications :
  - ✓ Pu content > 20 % (about 30%)
  - ✓ 1.94 < O/M ratio < 2.00
  - ✓ Dense pellets (95% Dth)

- Fabrication by powder metallurgy :
  - ✓ Direct co-milling of UO_2 + PuO_2
  - ✓ Sintering : key step → densification + formation of solid solution + control of O/M ratio

↳ Challenging because of high Pu content and O/M specifications

↓

At high Pu content : **possible demixtion** (phase separation) during cooling step (sintering)

The higher the Pu content, the more difficult the control of O/M ratio

↓

Thursday 16/05 16h00-16h30→ case studies: mixed oxide fuels in fast reactors