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## In situ HT-XRD study of the $\text{UO}_2\text{-PuO}_2\text{-Pu}_2\text{O}_3$ sub-system

R. Vauchy, Renaud C. Belin, Christine Gueneau, Thibaut Truphemus, Michal Strach, Alexis Joly, Jean-Christophe Richaud

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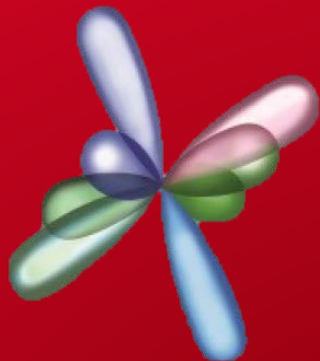
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The Science 2016  
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# *In situ* HT-XRD study of the $\text{UO}_2\text{-PuO}_2\text{-Pu}_2\text{O}_3$ sub-system

Romain VAUCHY<sup>1</sup>

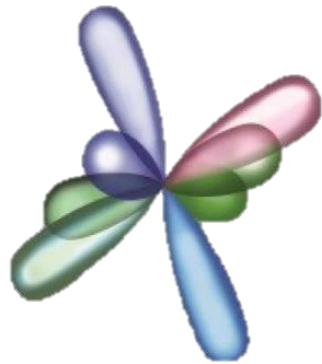
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Thibaut TRUPHEMUS<sup>2</sup>, Michał STRACH<sup>1</sup>,  
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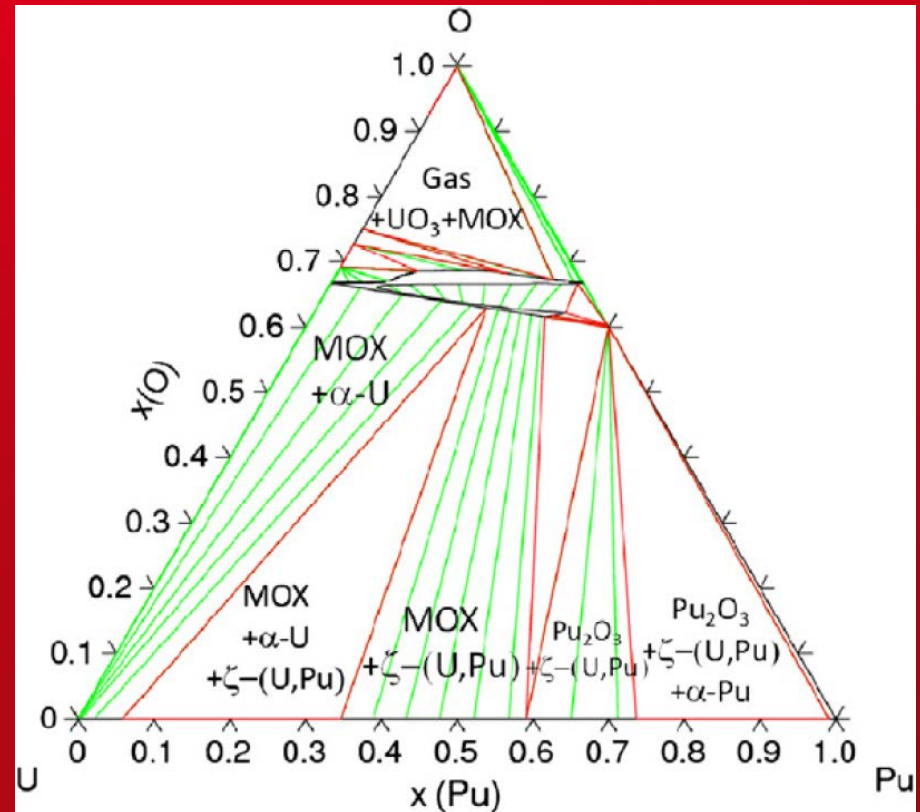
<sup>3</sup>CEA, DEN, DANS, DPC, Saclay F-91191 Gif-sur-Yvette Cedex, France

- U-Pu-O : literature review
  - A phase diagram
  - $\text{UO}_2$ - $\text{PuO}_2$ - $\text{Pu}_2\text{O}_3$  at room temperature
  - $\text{UO}_2$ - $\text{PuO}_2$ - $\text{Pu}_2\text{O}_3$  at high temperature
- Studying  $\text{UO}_2$ - $\text{PuO}_2$ - $\text{Pu}_2\text{O}_3$  *in situ* by HT-XRD
  - Our setup
  - Limitations of the setup
  - Selected samples and conditions
- Experimental results
  - Phase separation temperatures
  - How evaluating the O/M ratio
- Conclusions



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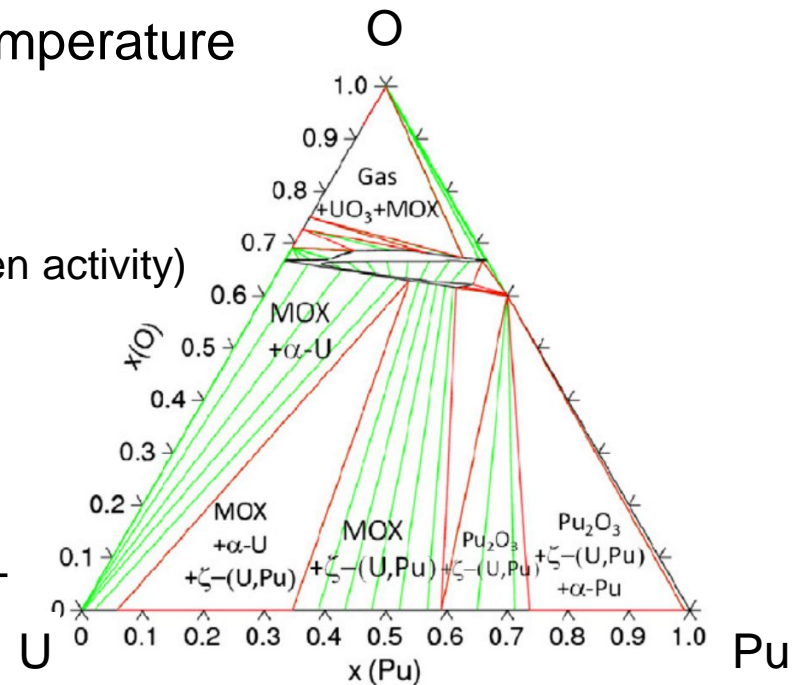
# U-Pu-O literature review



# A phase diagram

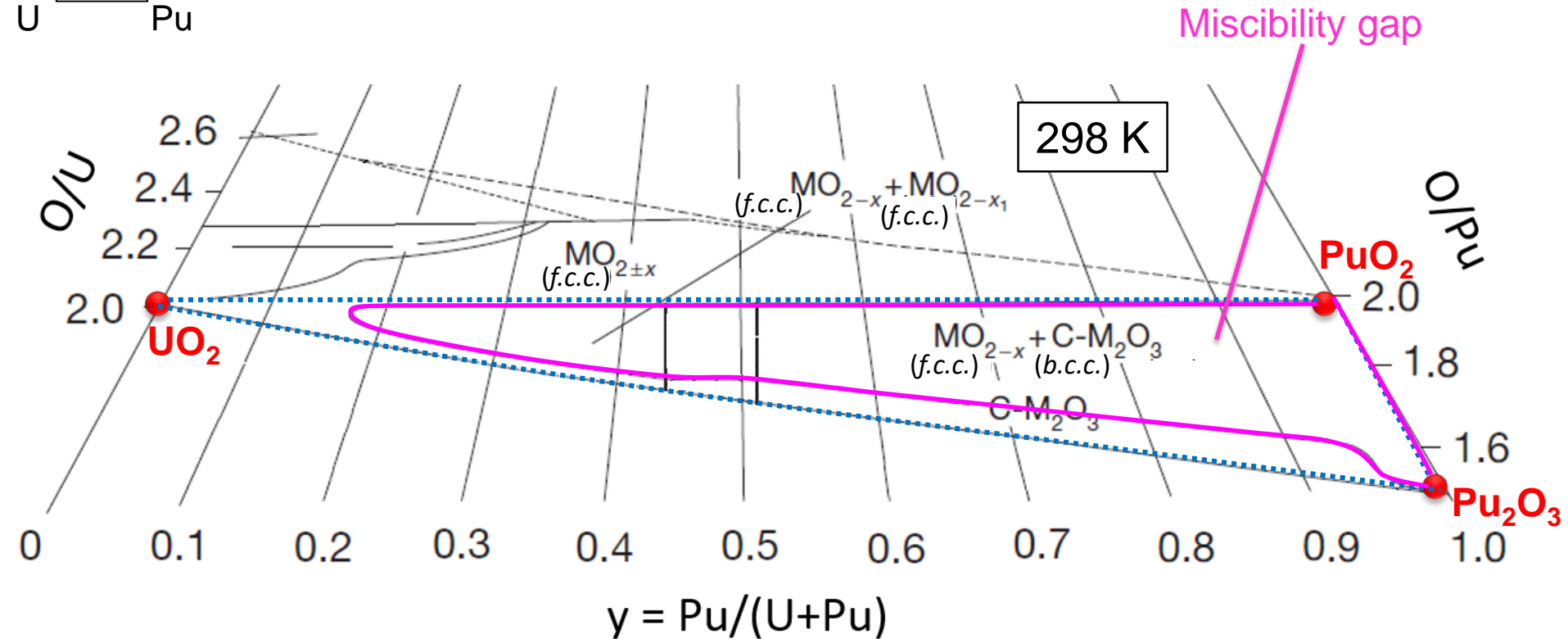
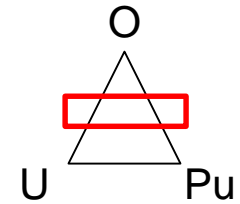
- Chart depicting phases **at equilibrium**
- Each point has composition and temperature coordinates
- HT-XRD ➔ crystal structure and temperature
- In oxide samples, two variables :
  - Oxygen/Metal ratio (related to oxygen activity)
  - Temperature

Calculated U-Pu-O phase diagram at RT



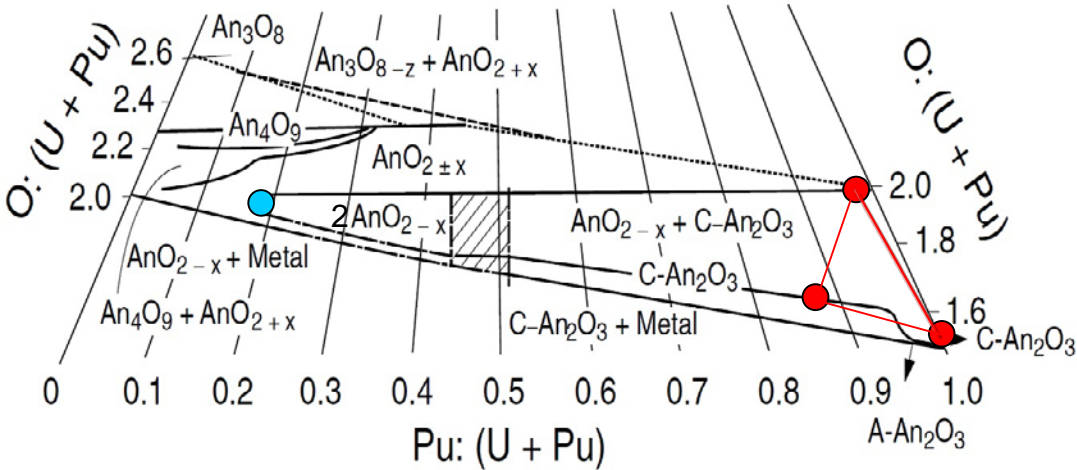
Guéneau *et al.*, *Journal of Nuclear Materials* 419 (2011) 145-167

# UO<sub>2</sub>-PuO<sub>2</sub>-Pu<sub>2</sub>O<sub>3</sub> at room temperature

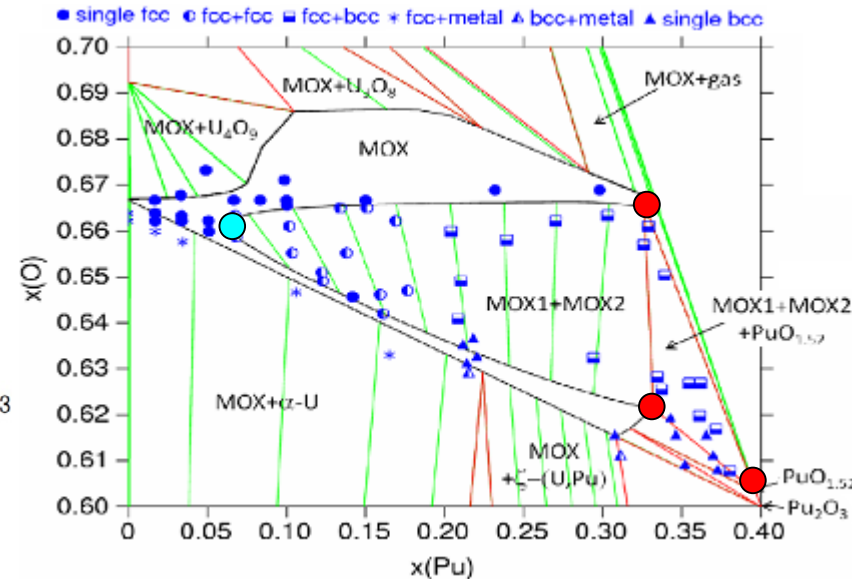


Sari *et al.*, *Journal of Nuclear Materials* 35 (1970) 267-77

# Experiment vs. Modeling



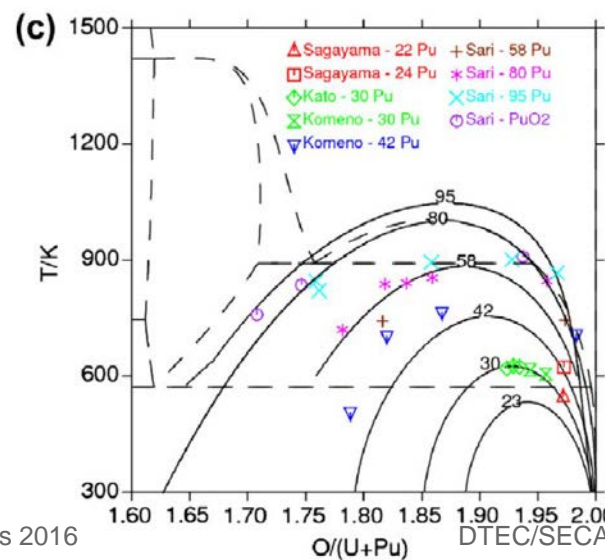
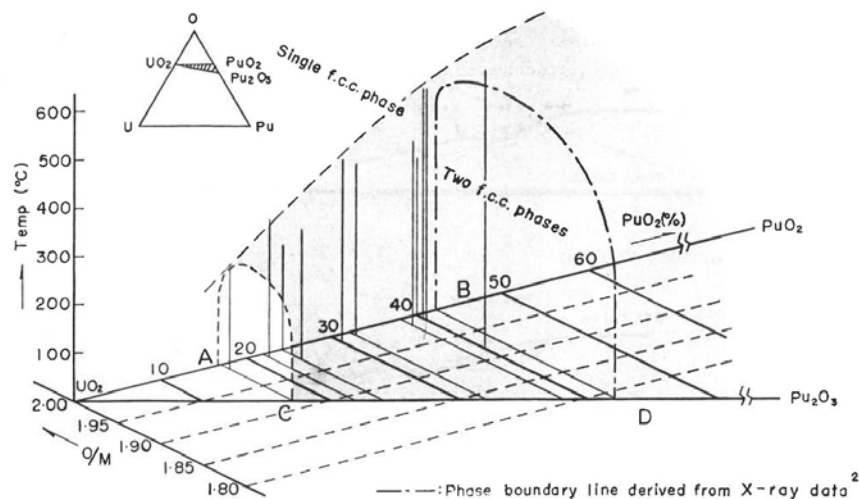
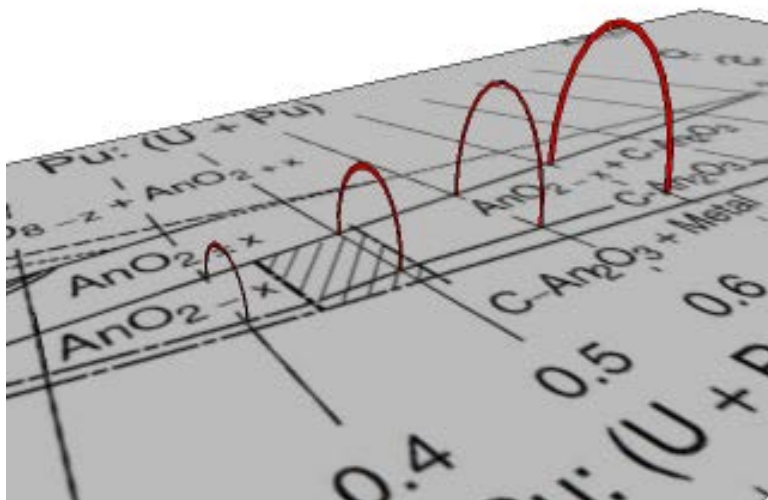
Sari et al., *Journal of Nuclear Materials* 35 (1970) 267-77



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

- Experiment and modeling in good agreement
- Same **low Pu content limit** for the miscibility gap (~17% Pu)
- Biphasic domain  $MO_{2-x} + M_2O_3$  not modeled
- Existence of a **triphasic domain**  $2MO_{2-x} + M_2O_3$
- Calculated composition range far from the hatched area of Sari

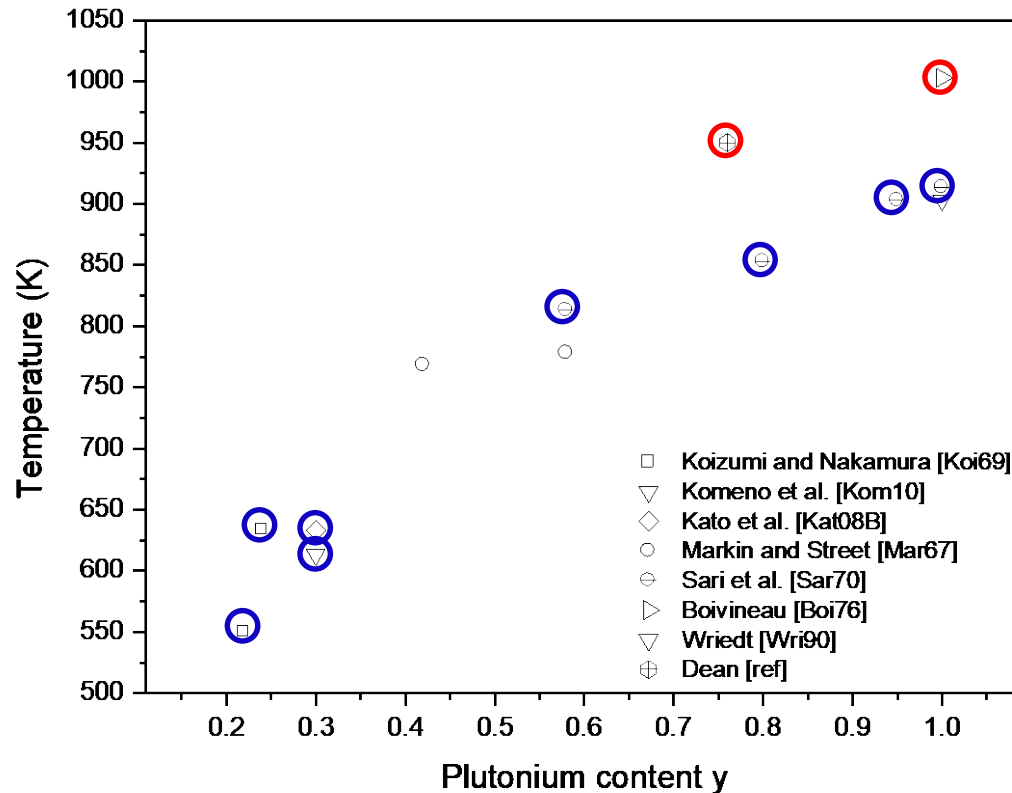
# UO<sub>2</sub>-PuO<sub>2</sub>-Pu<sub>2</sub>O<sub>3</sub> at HT





# UO<sub>2</sub>-PuO<sub>2</sub>-Pu<sub>2</sub>O<sub>3</sub> at HT

Experimental values for the critical temperature of phase separation found in the literature using DTA and HT-XRD



The critical T progressively increases with Pu content

At low Pu content, only DTA results  
Scattering confirms the difficulties in measuring at low Pu content

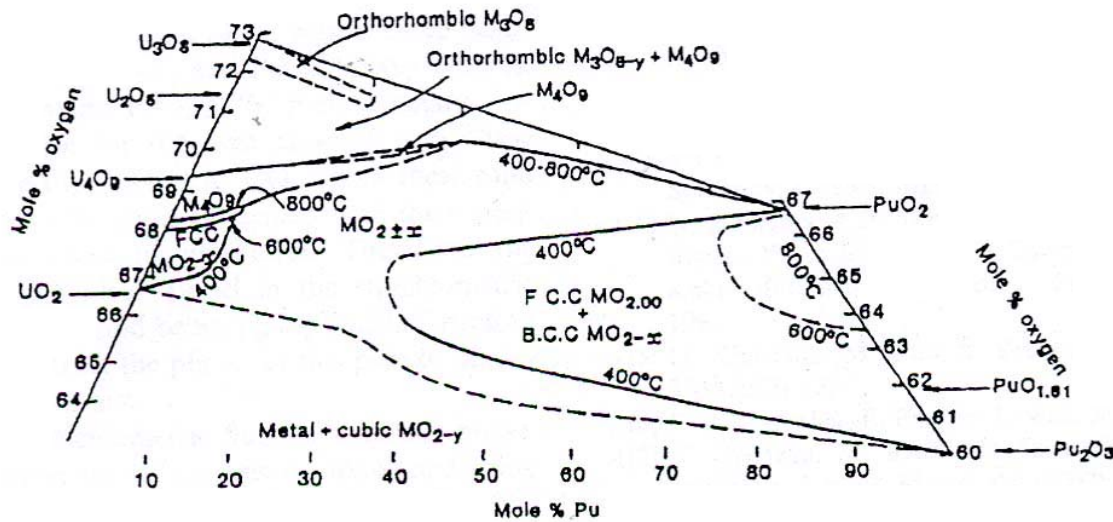
At higher Pu content, T of phase separation obtained with DTA are lower than those obtained with HT-XRD

At y=1 (PuO<sub>2</sub>), HT-XRD value (1000 K) in agreement with the description of the Pu-O phase diagram

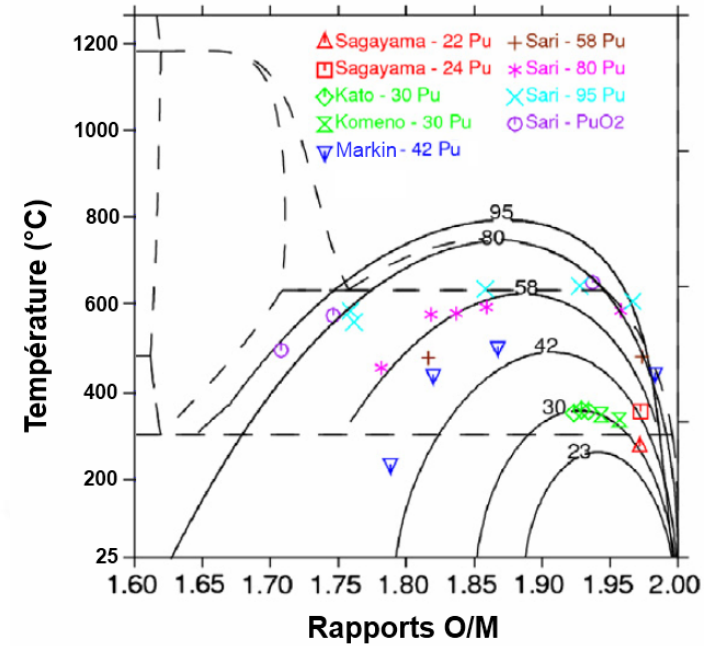
DTA data underestimate the T

HT-XRD provides a large amount of experimental data that lead to reliable T

# Experiment vs. Modeling



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

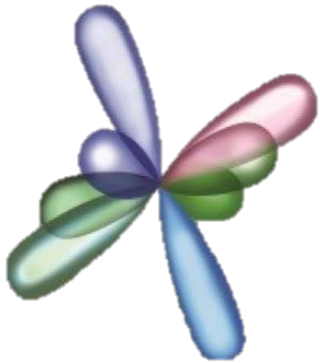


Guéneau *et al*, *Journal of Nuclear Materials* 419 (2011) 145-167

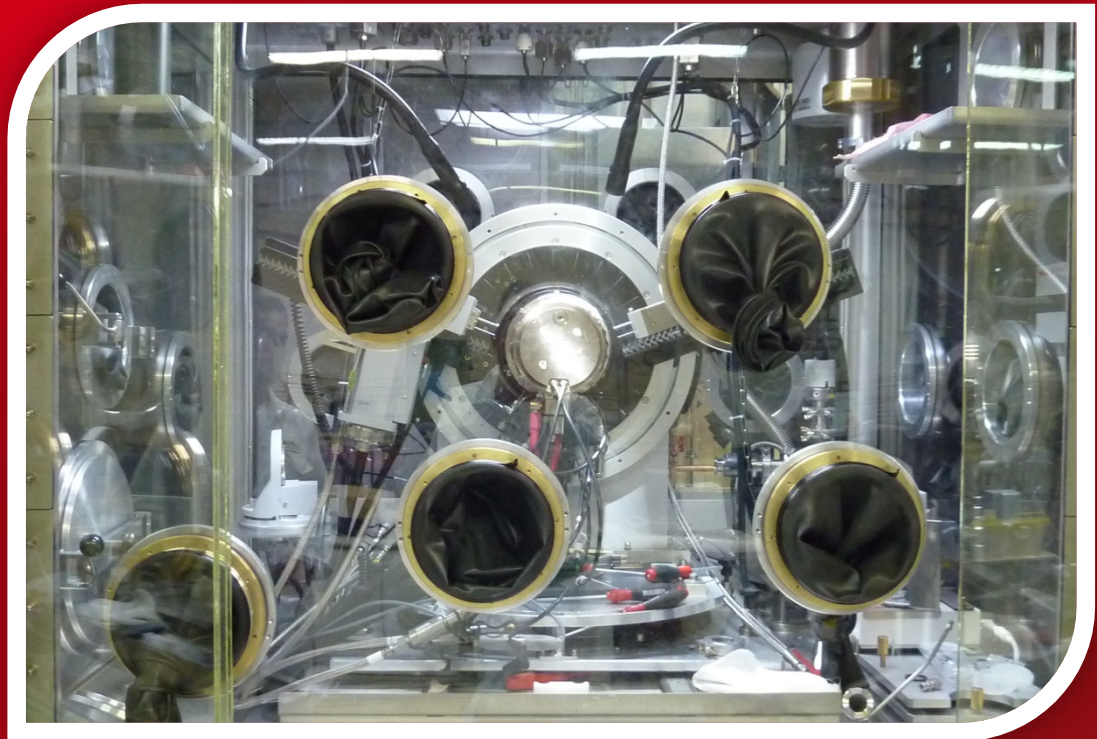
- Good agreement between experimental and modeling for  $y \leq 0.40$
- Difference for  $y > 0.40$  : calculations overestimate  $T_{\text{separation}}$

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

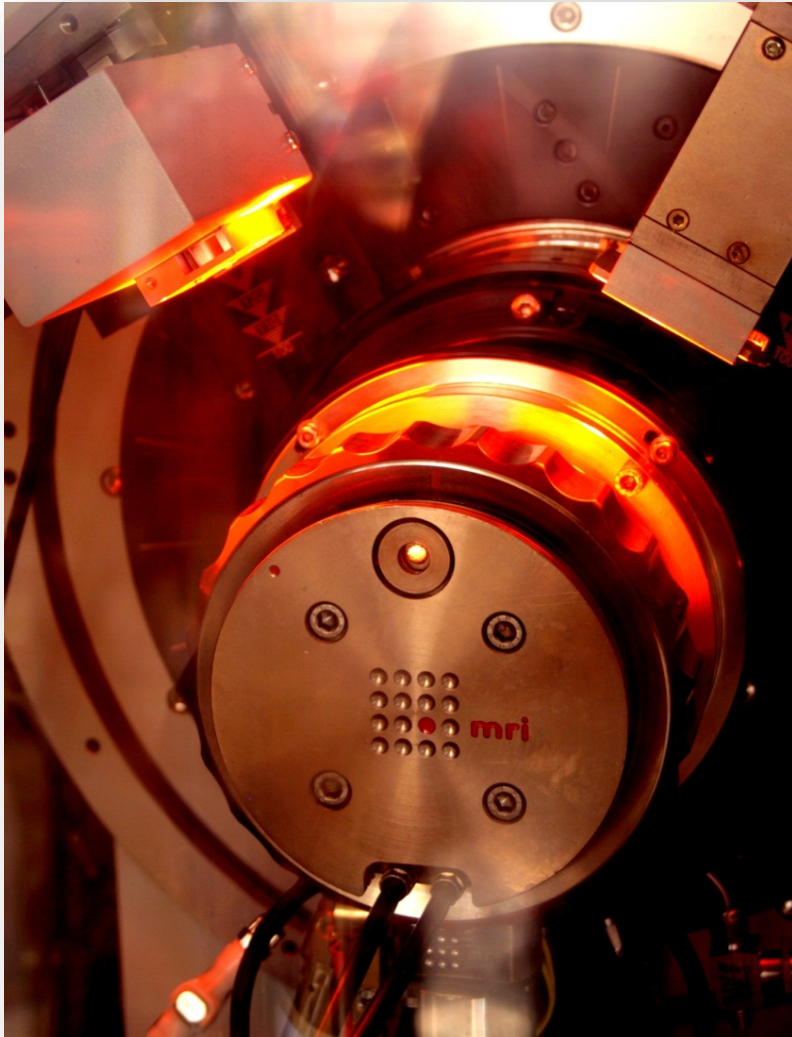
# Studying $\text{UO}_2\text{-PuO}_2\text{-Pu}_2\text{O}_3$ *in situ* by HT-XRD



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# The High-Temperature X-Ray Diffraction setup



## X-ray diffraction technical details

Goniometer in dedicated a **shielded glove-box**

XRD type : Bragg-Brentano  $\theta$ - $\theta$

Brand : BRUKER® D8 Advance XRD

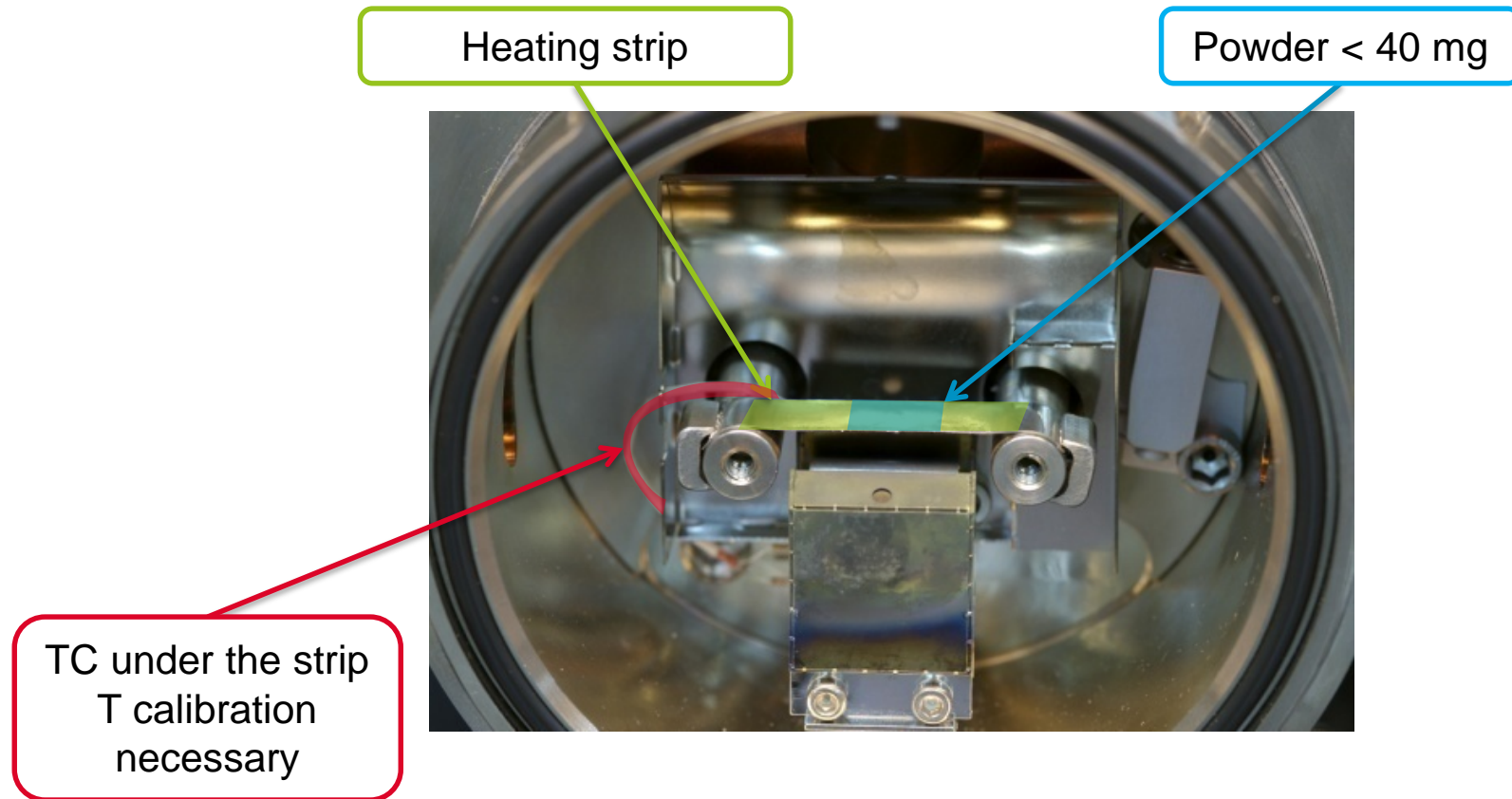
Source : copper radiation ( $K\alpha_1 + K\alpha_2$  radiation :  
 $\lambda = 1.5406$  and  $1.5444 \text{ \AA}$ ) at 40 kV and 40 mA

Detector : LynX'Eye PSD **fast-counting detector**

Heating stage : MRI®, Mo or W strip and Ta radiant heater  
**up to 2273 K on powders** and **1273 K**  
on bulk samples

Control of oxygen activity and  
temperature required

# Controlling the temperature



Calibration : W powder (ALDRICH® 99.999%)

↳ ±20 K between RT and 1973 K

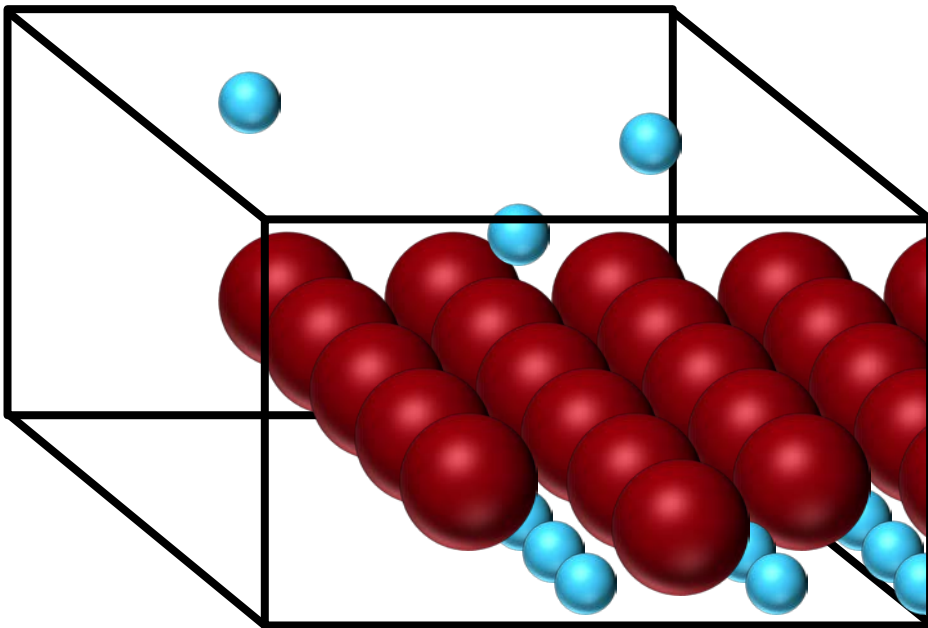
Prompt cooling/heating rates + fast counting detector

↳ Suited for kinetics studies

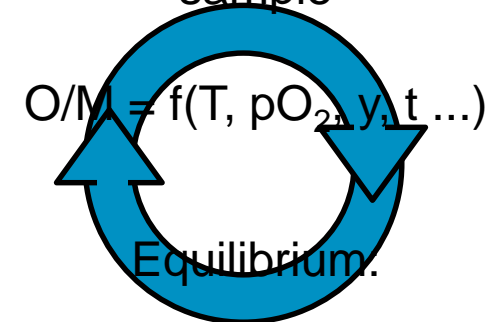
# Controlling the oxygen activity : 2 approaches

Sample in a closed container (crucible)

Fixed oxygen activity  
(constant O/M)



Free exchange allowed  
between gas and  
sample

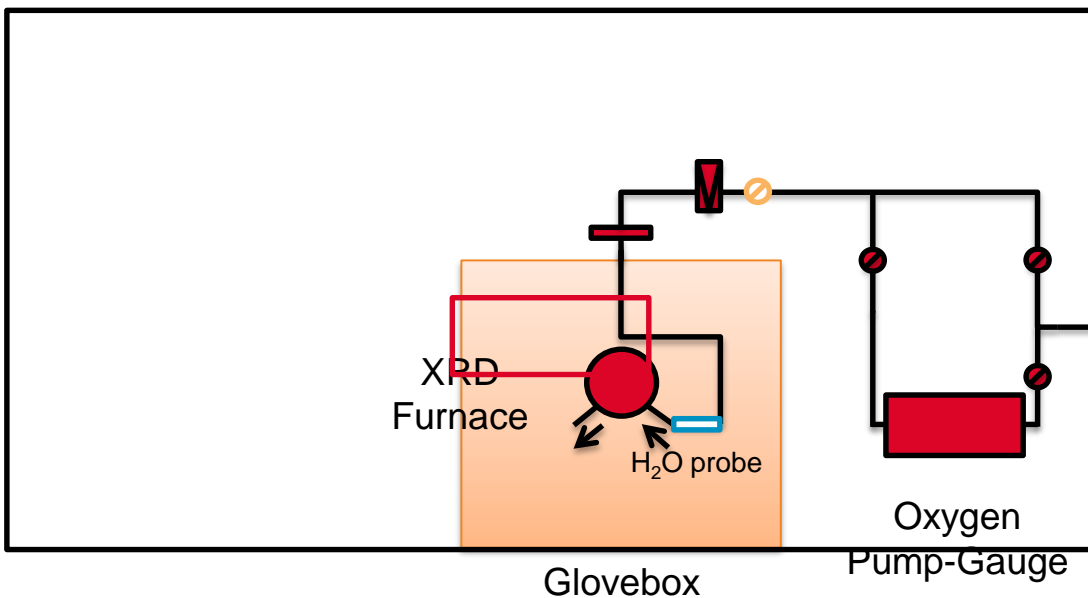


$O_2$  chemical  
potential in  
the sample



$O_2$  chemical  
potential in  
the gas

# Controlling the oxygen activity

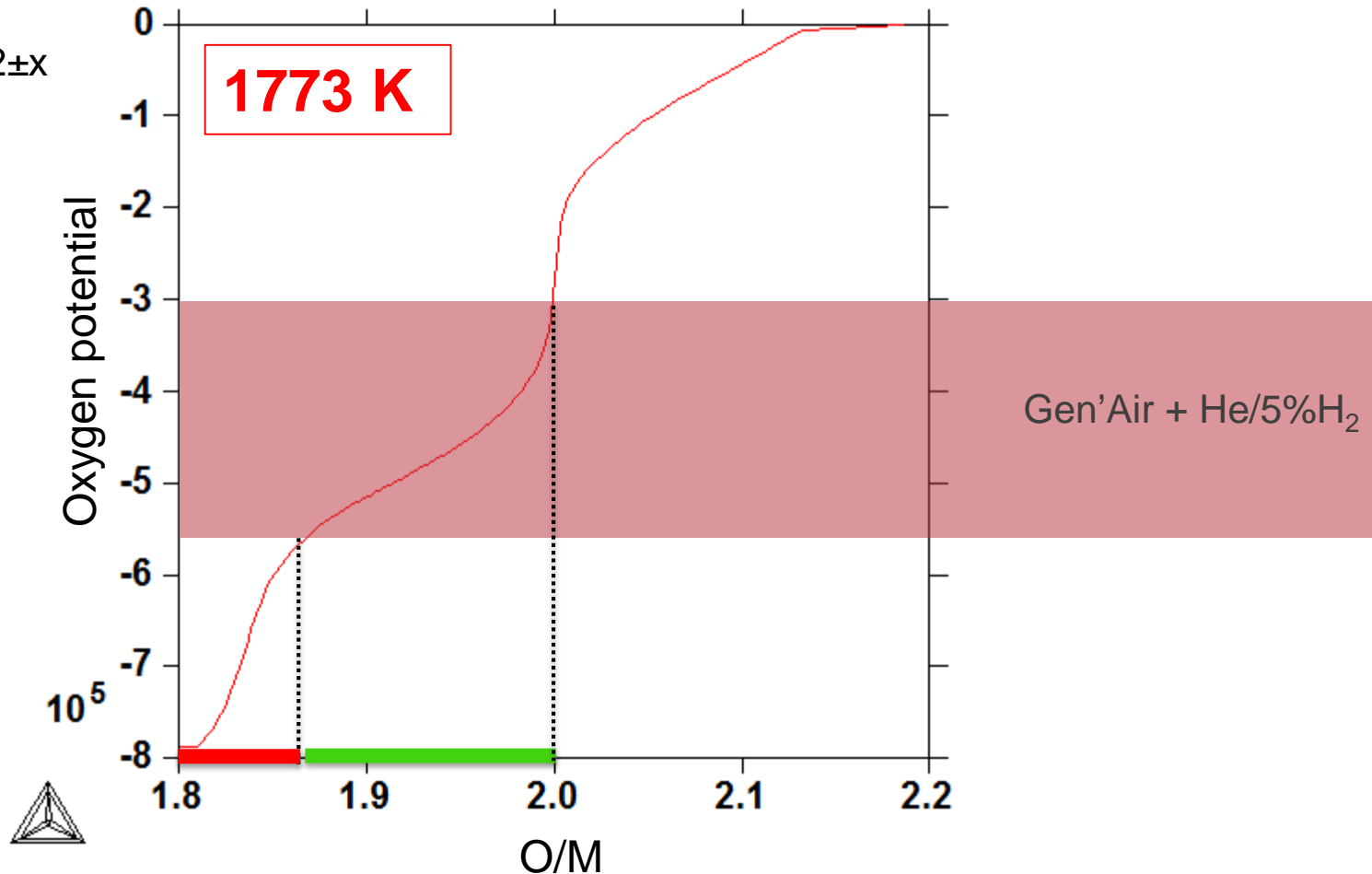
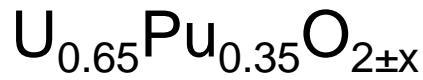


- Precise flow and pressure control
- Calibration of the probe
- Susceptibility of the probe to hydrogen-containing gas mixtures

- Certain species in the used gas might react with the studied sample
- H<sub>2</sub> rises security issues
- Direct measurement of pO<sub>2</sub> in the vicinity of the sample is (usually) impossible
- The pipeline needs particular attention

Control of oxygen activity is challenging

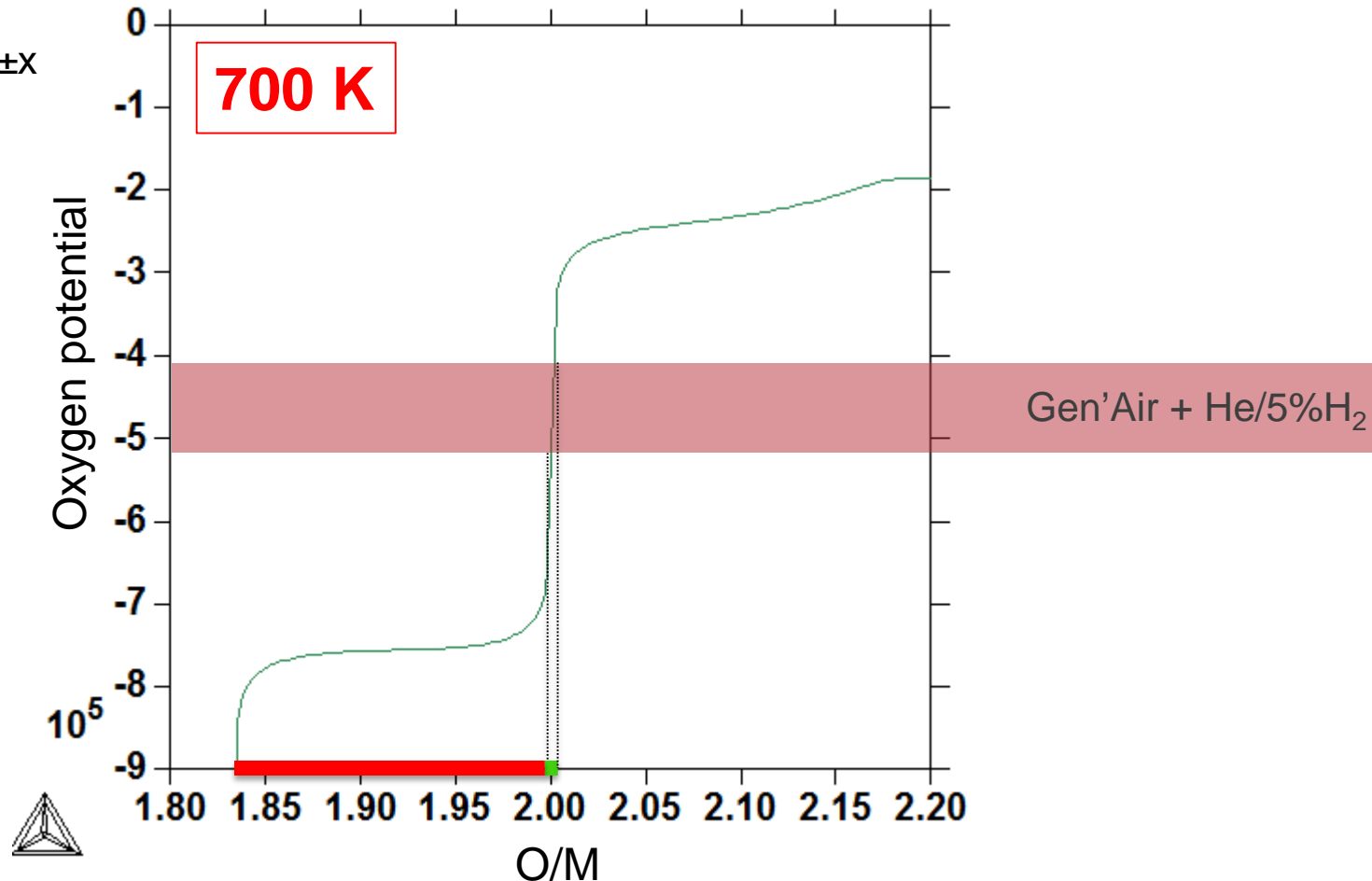
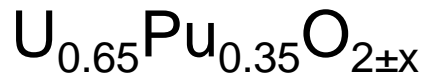
# Controlling the oxygen activity



- Relatively wide range of **achievable O/M ratios**
- Sample can reach low O/M ratios at equilibrium with the gas mixture



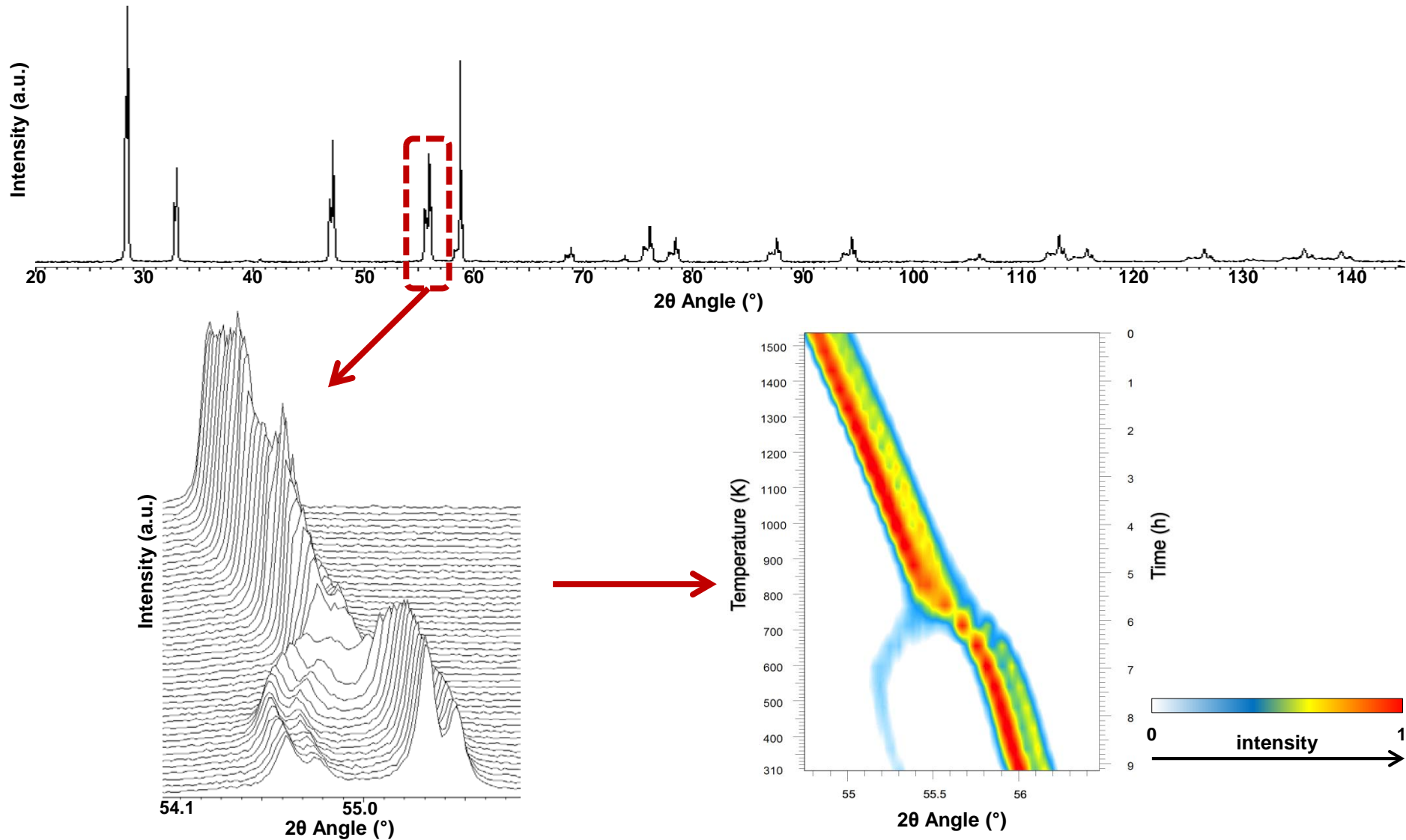
# Controlling the oxygen activity



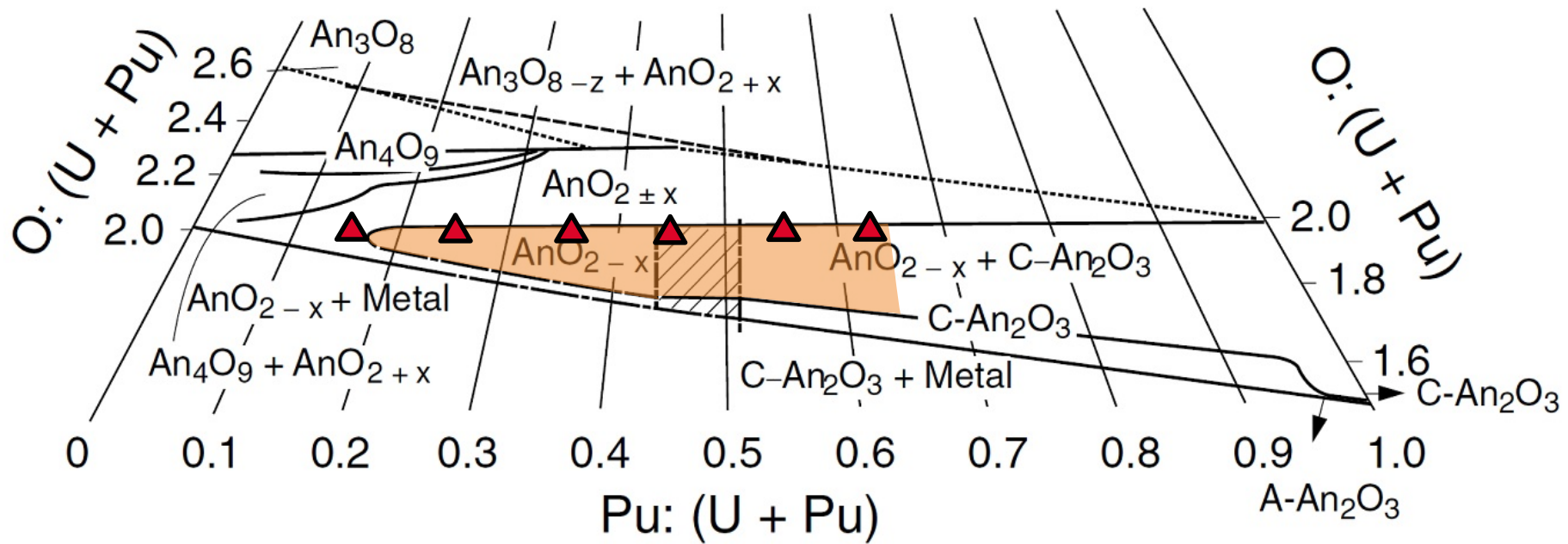
Gen'Air + He/5% $\text{H}_2$

- **Very restricted** achievable O/M ratios
- Sample can not reach low O/M ratios at equilibrium with the gas mixture

# How to read the data : iso-intensity map

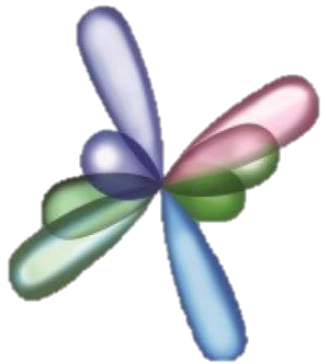


# Samples and conditions



Reduction experiments under He + 5% H<sub>2</sub>

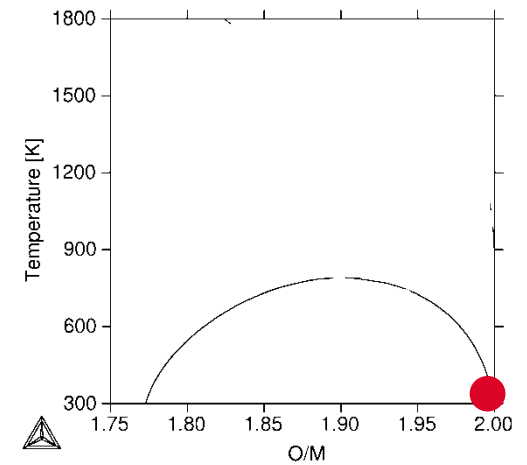
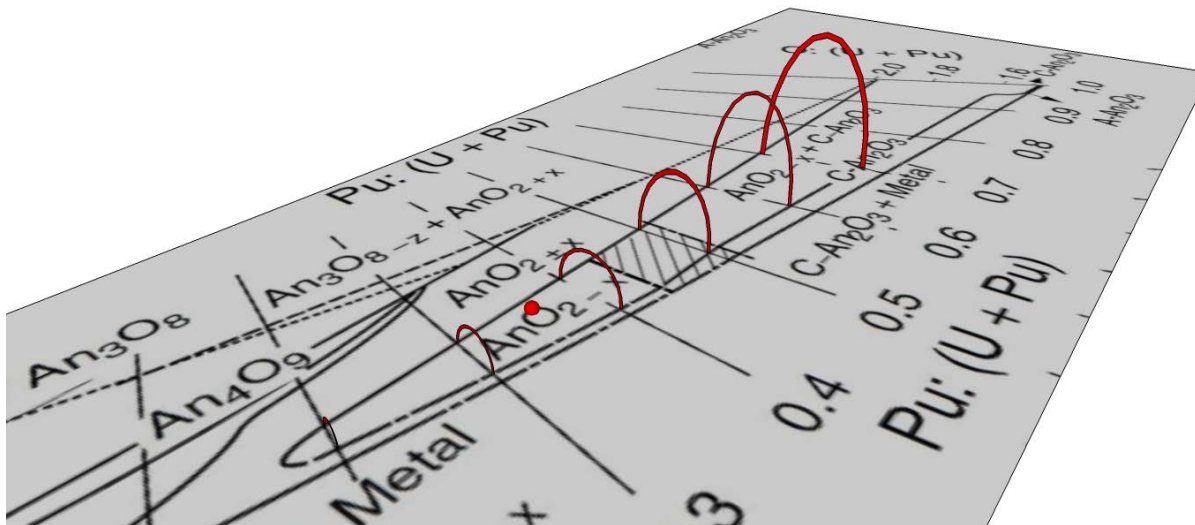
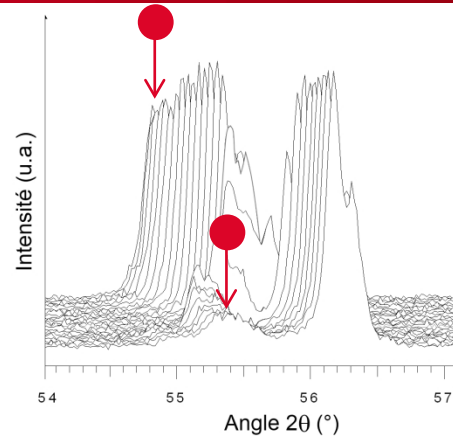
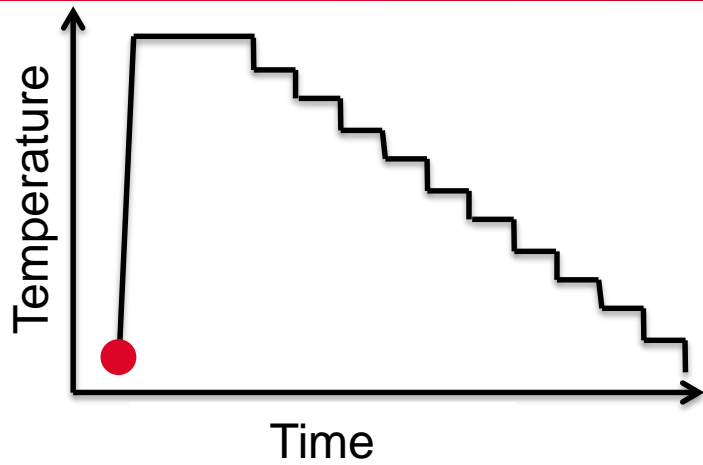
# Experimental results



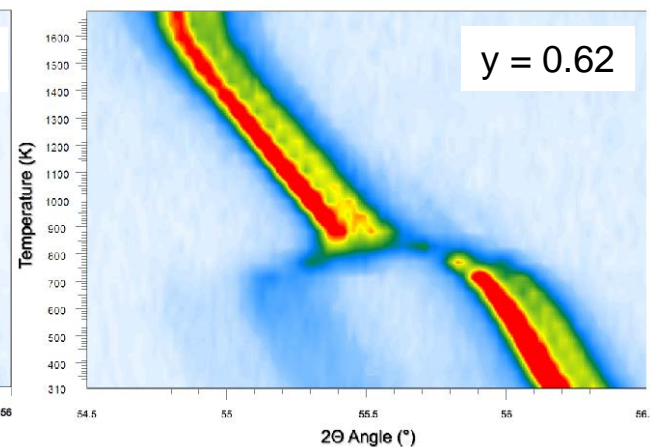
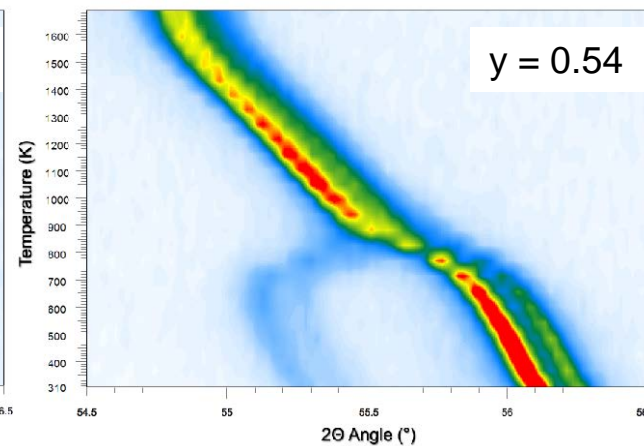
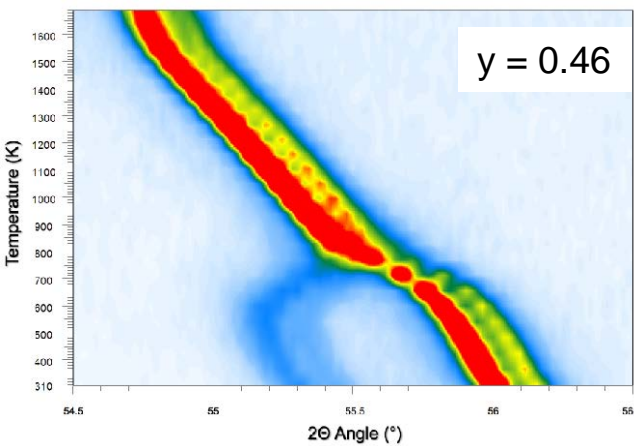
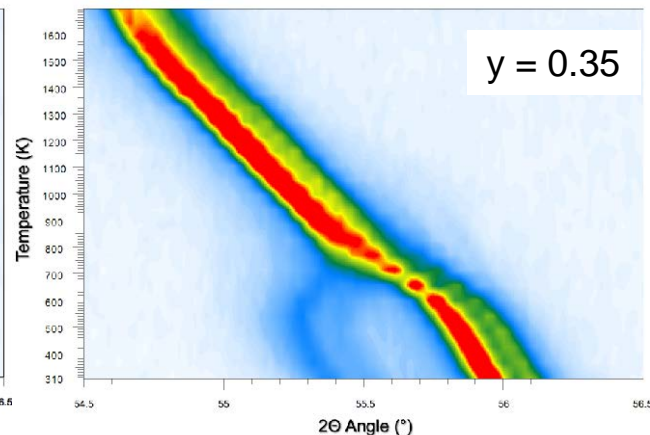
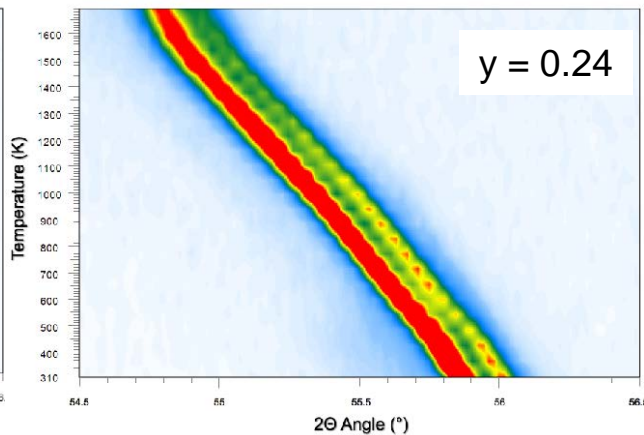
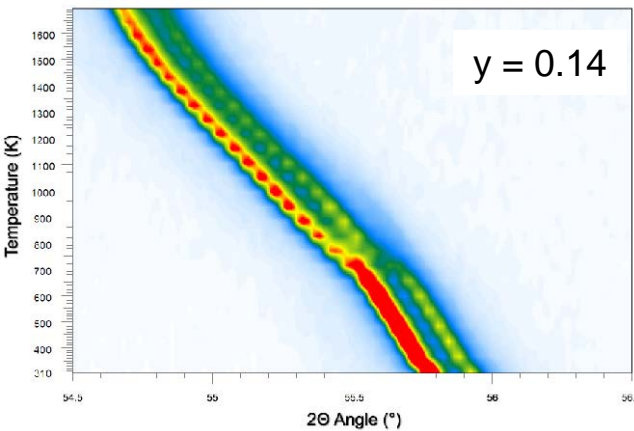
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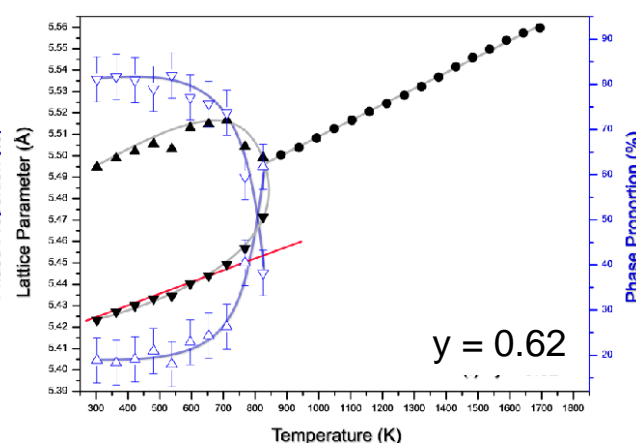
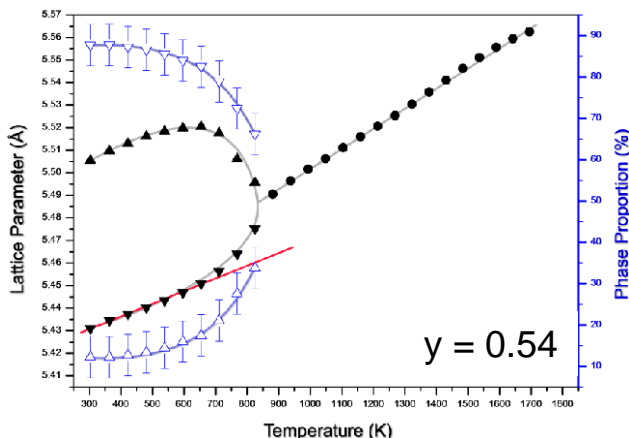
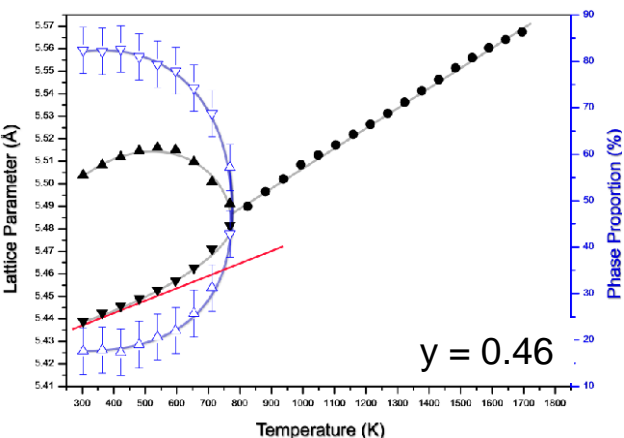
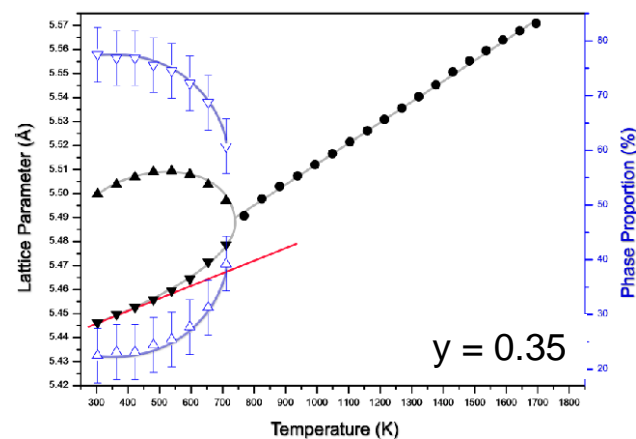
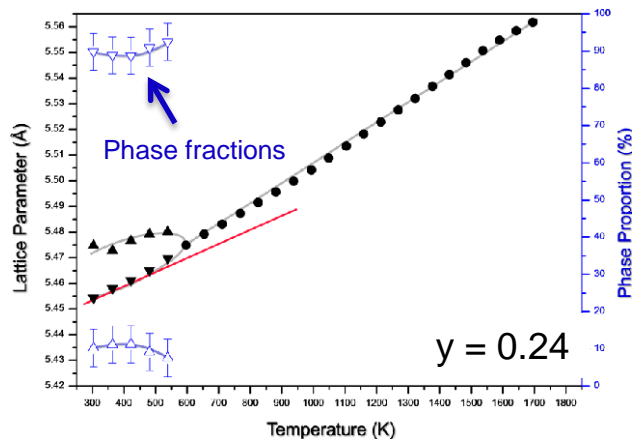
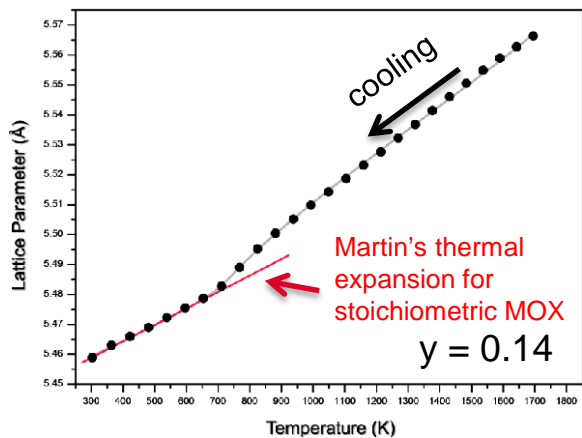
# In situ observation of phase separation



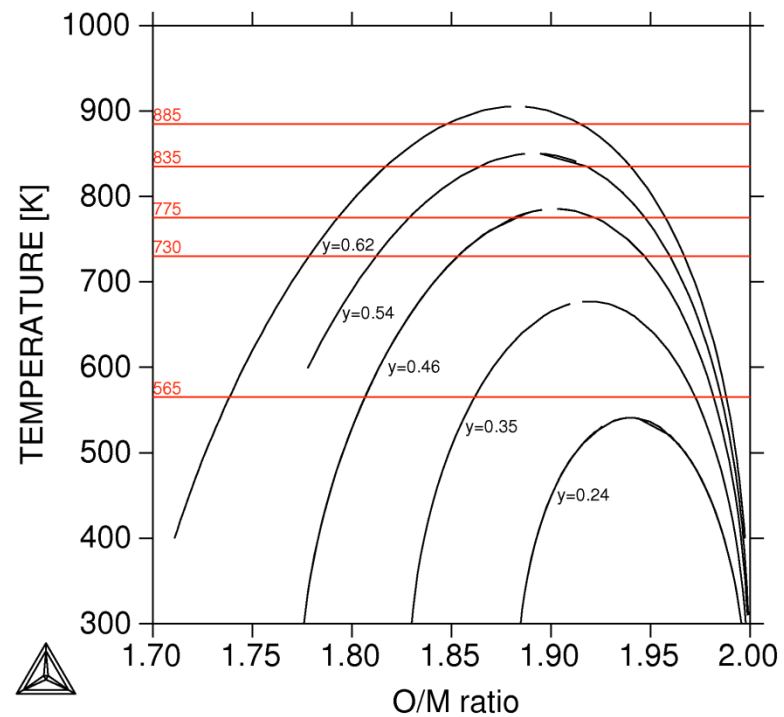
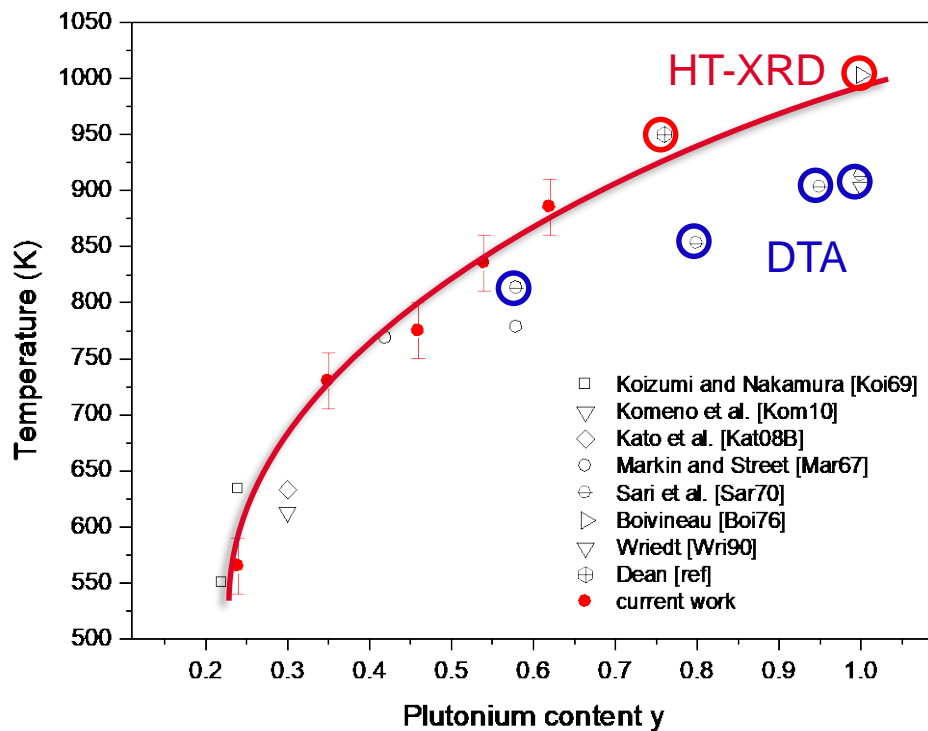
# XRD iso-density maps



# Lattice parameters and phase fractions



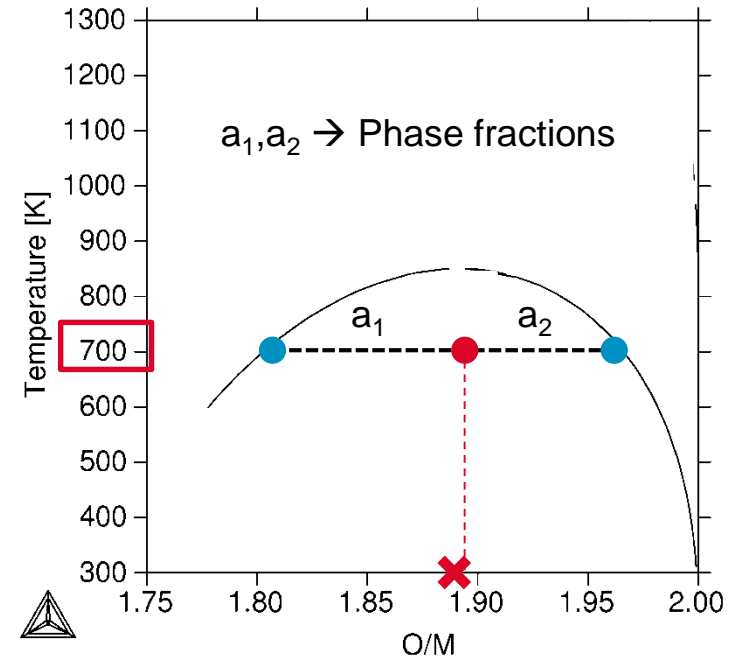
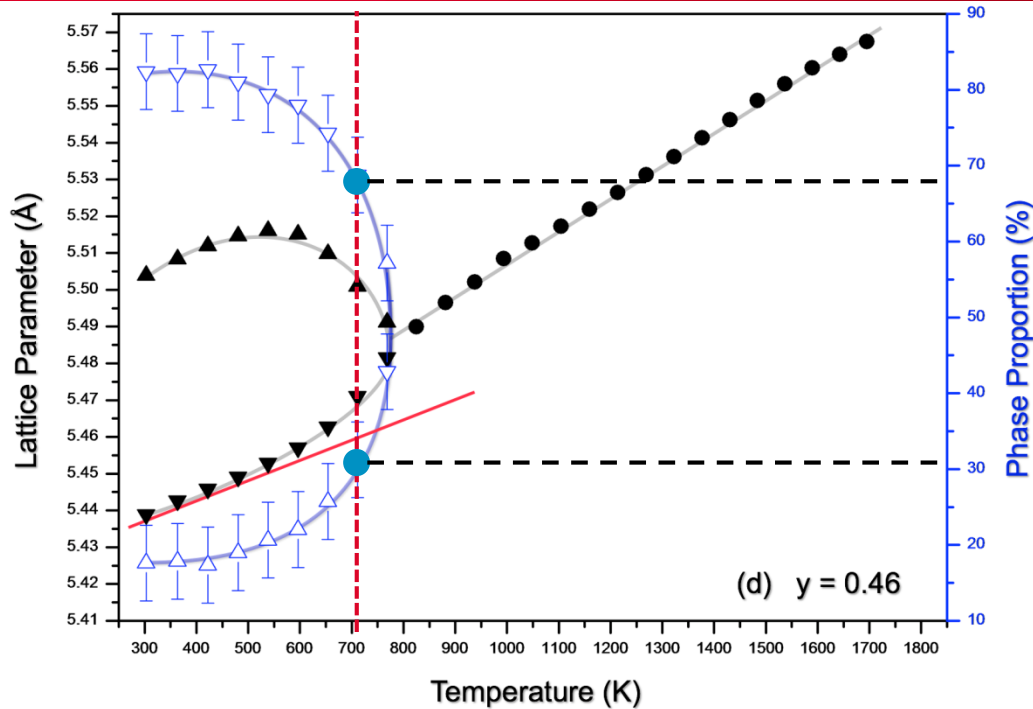
# Temperature of phase separation



Evaluation of the O/M ratio ?



# O/M determination : Calculations to overcome limitations



Determination of O/M is possible in certain cases:

- Biphasic domain  $\rightarrow$  Rietveld refinement + CALPHAD

Phase fractions from experiments  
(peak intensities, Rietveld refinement)

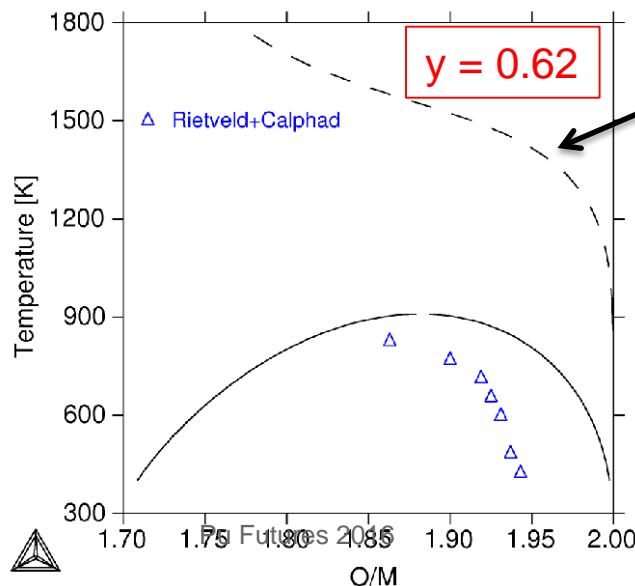
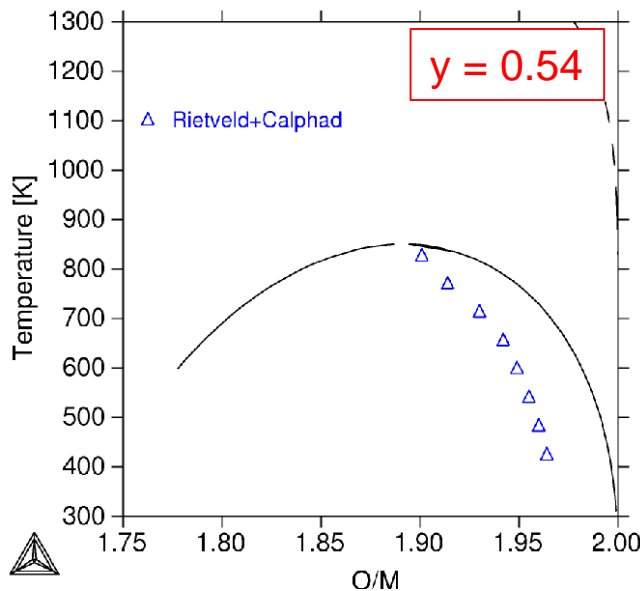
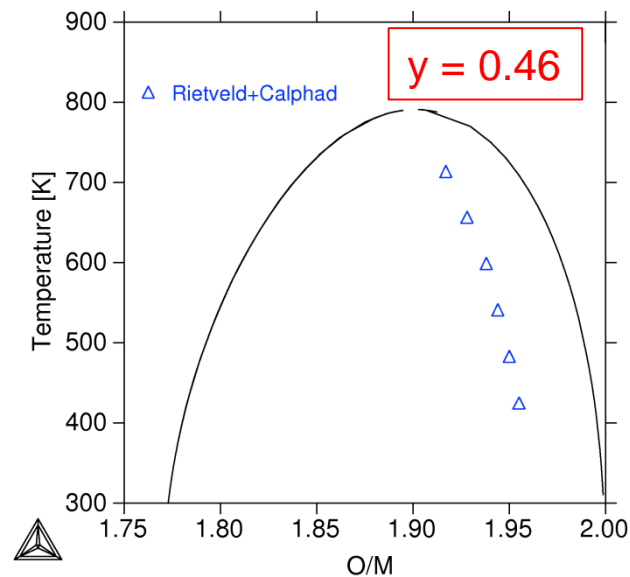
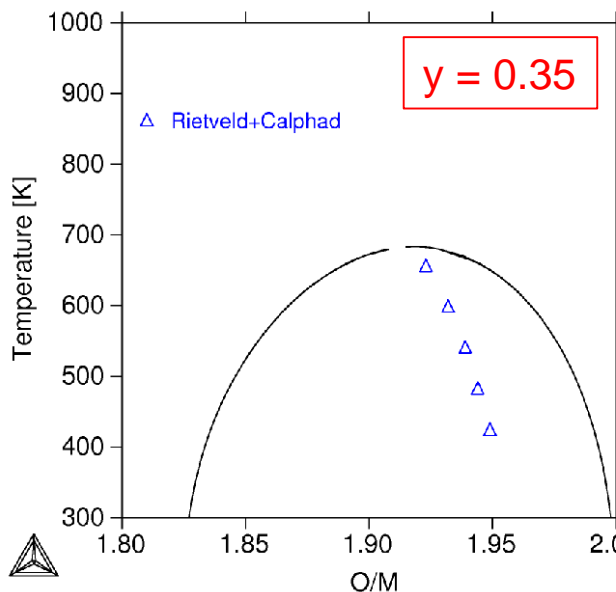
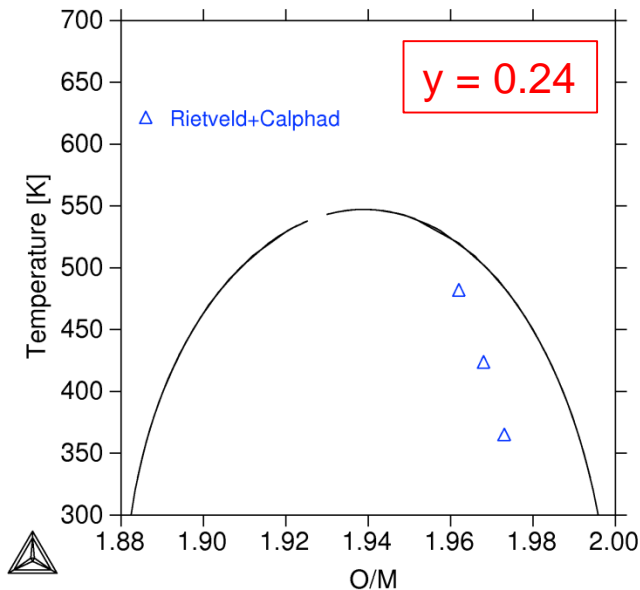


Phase fractions are positioned on  
the calculated miscibility gap



O/M value at each T

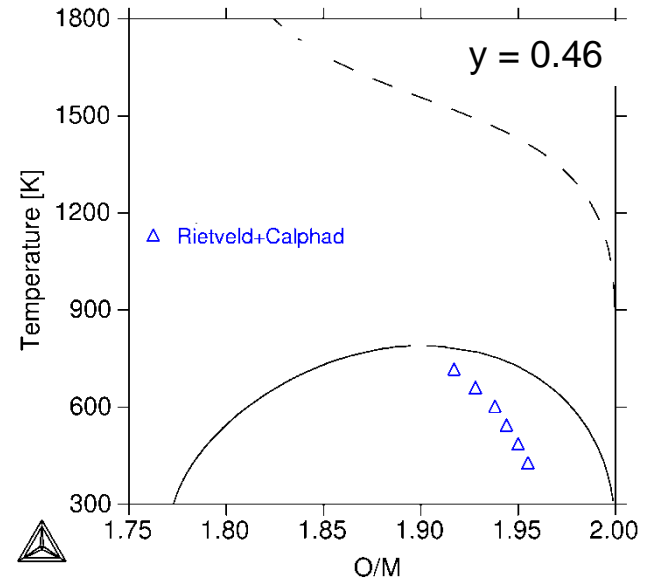
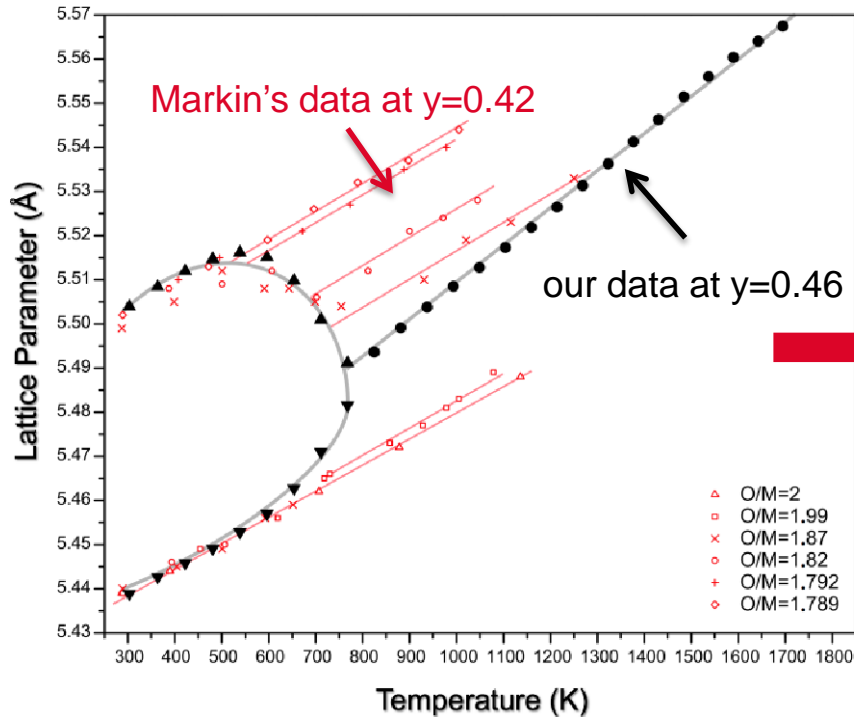
# Calculations + Rietveld



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

# Calculations + literature

- Single phase domain → comparison with literature

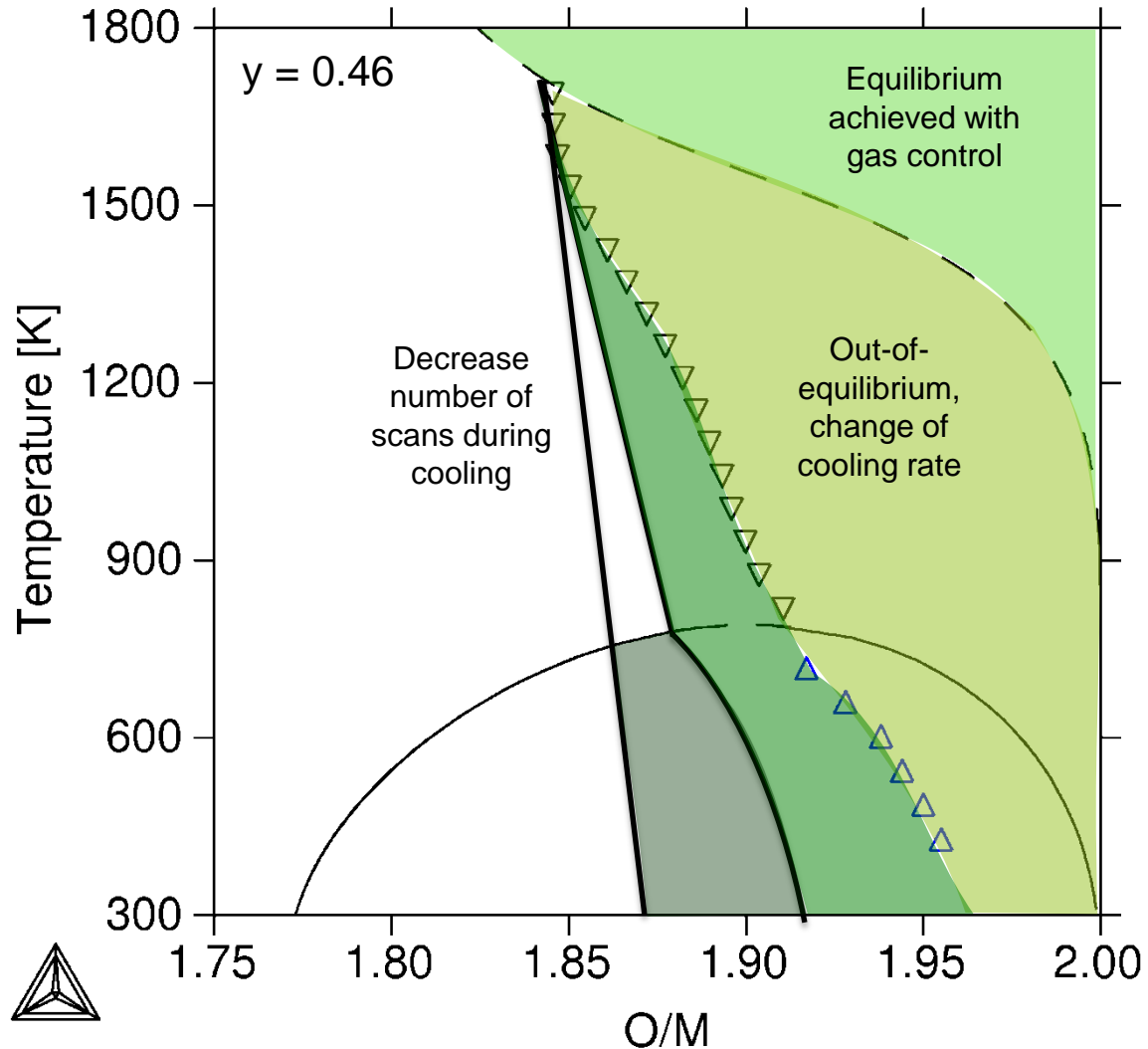


$$\frac{O}{M} = 21,3075 + 22,78 * 10^{-5} * T - 3,565 * a$$

At HT → equilibrium between sample and gas = reduced sample

At LT → equilibrium between sample and gas = stoichiometric sample

# To be or not to be at equilibrium ?

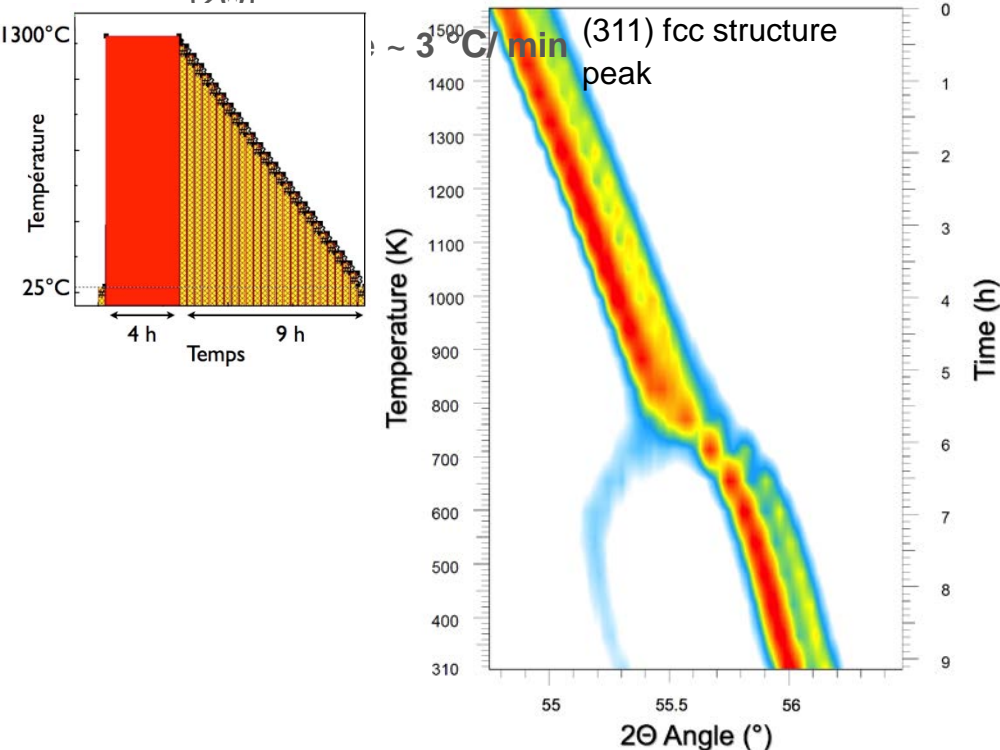


# Fast cooling experiment under He/5%H<sub>2</sub> + ~ 15 vpm (y = 0.46)

## Measurements in isothermal conditions

25 min per scan between 22 and 145°

(20)

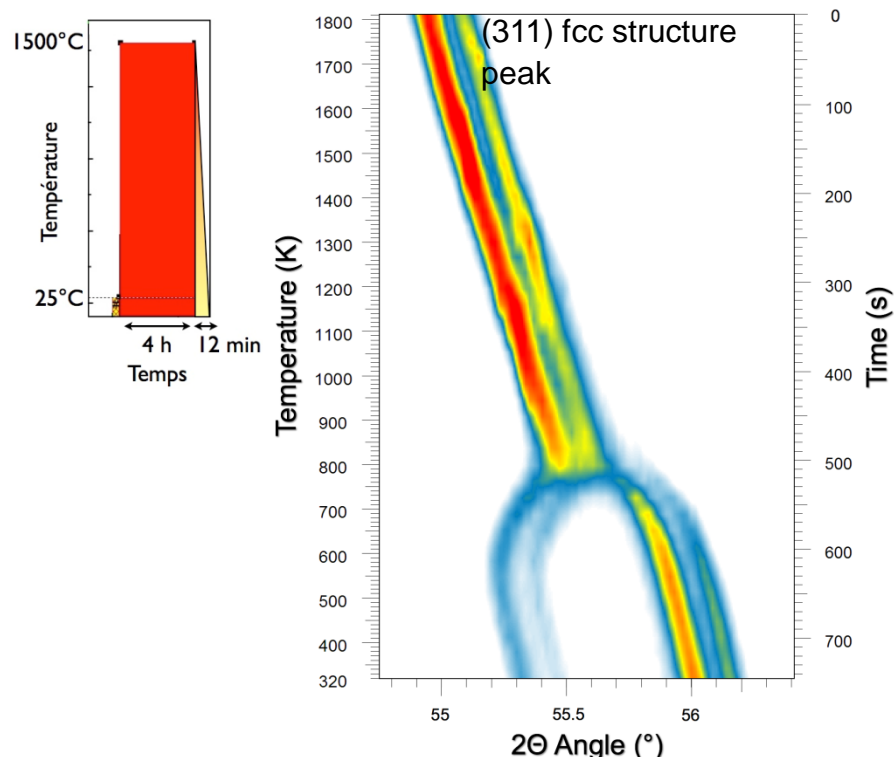


Phase separation at ~ 775 K and 2 fcc a = 5.439(1)Å and 5.504(5)Å

## Measurements in fixed-scan (non-isothermal)

14 s per scan on a restricted 3° (2θ) angular range

Cooling rate ~ 2 °C/ sec



Phase separation at ~ 775 K and 2 fcc a = 5.439(1)Å and 5.495(5)Å

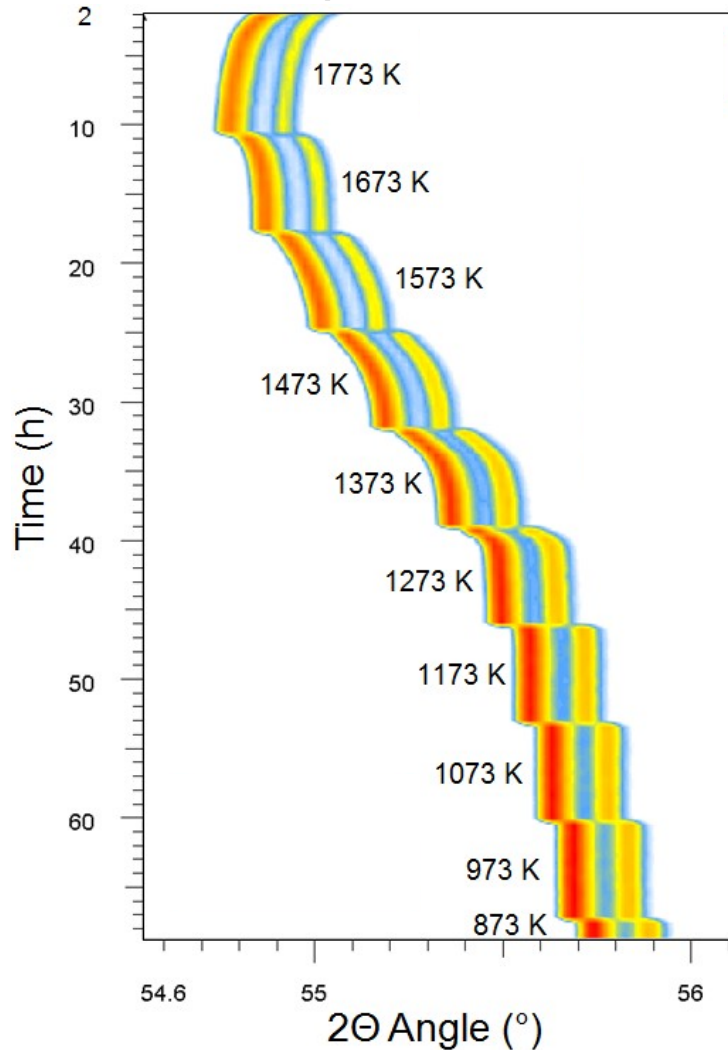
**Almost identical XRD results**

**Suggests that the phase separation is mostly governed by oxygen diffusion under both conditions**

# Slow cooling experiment under He/5%H<sub>2</sub> + ~ 15 vpm ( $y = 0.46$ )

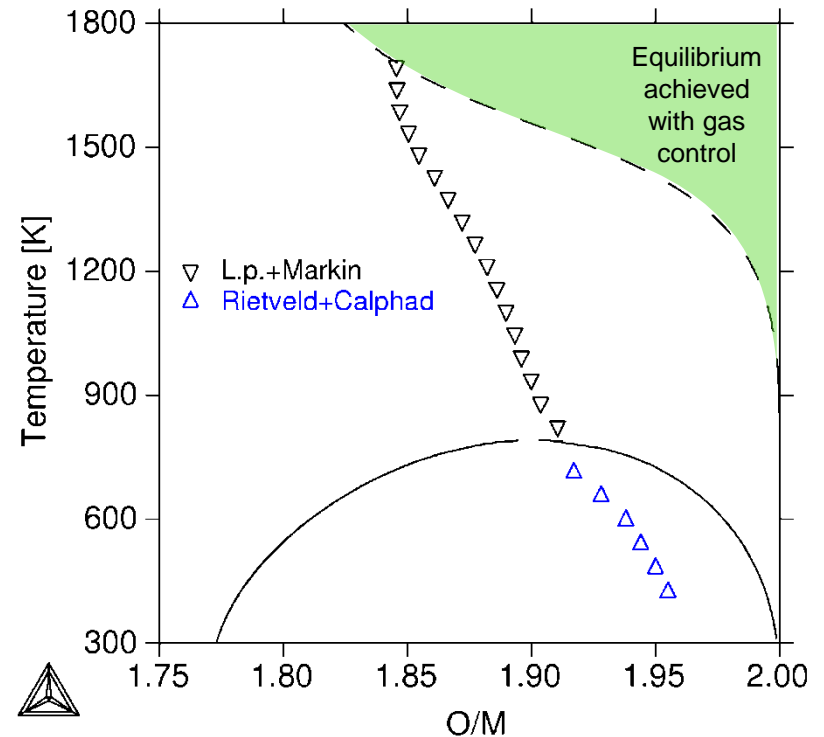
## Measurements in isothermal conditions

~ 7 hours at each temperature



No phase separation is observed

Oxygen stoichiometry (O/M=2) reached at 873K

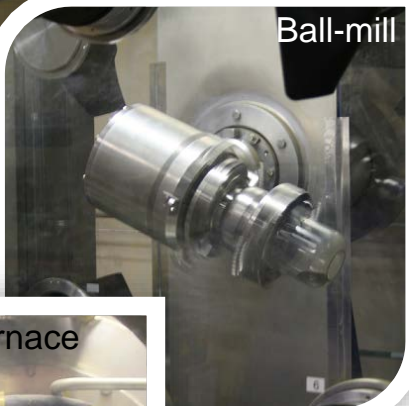


- We have developed a high temperature XRD with the capability of performing precise measurements : phases identification, I.p., fractions vs. T and  $pO_2$
- However, we are aware of the constraints of the experimental technique and try to deal with them
- Calculations with the CALPHAD method are useful to overcome experimental limitations (determination of the O/M as a function of T)
- With this HT-XRD, we have provided new experimental data, both in the hyper- and hypo-stoichiometric domains of the U-Pu-O system
- They will contribute to the available knowledge on this phase diagram, possibly ameliorating the currently available thermodynamic database
- The methodology used in the current work might be useful to investigate other oxides systems exhibiting a miscibility gap

Raw powder



Ball-mill



Sintering furnace



$U_{1-y}Pu_yO_2$  pellet



Thank you for your  
attention

**Recent publications :**

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

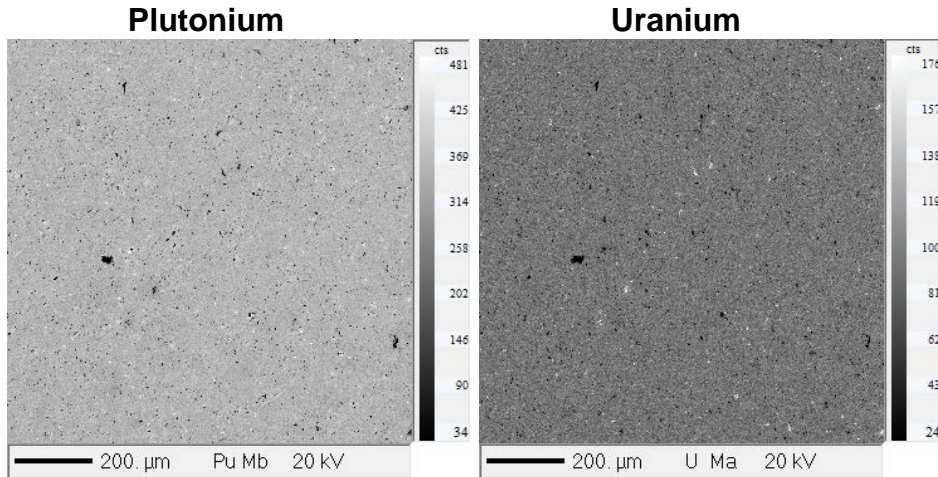
R. Vauchy *et al.* *Inorg. Chem.* 55(5), 2016, 2123-2132

R. Vauchy *et al.* *Appl. Mater. Today* 3, 2016, 87-95

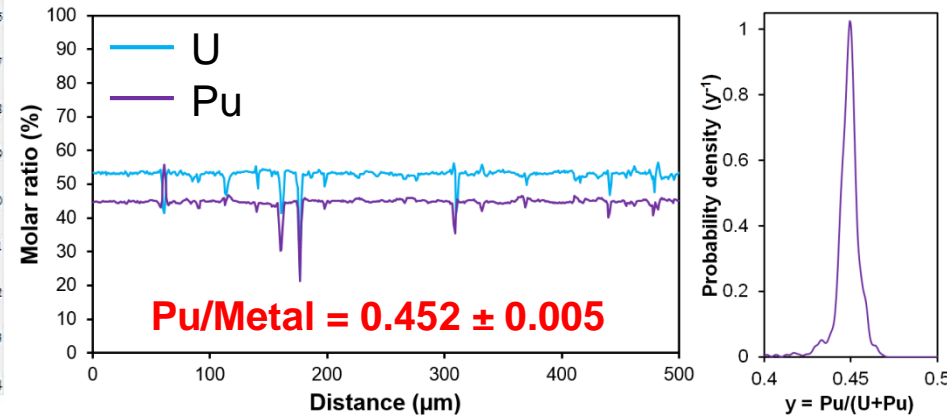


● Manufacturing of  $U_{0.55}Pu_{0.45}O_2$  pellets by powder metallurgy [1]

➔ Objective #1 : homogeneous U-Pu distribution

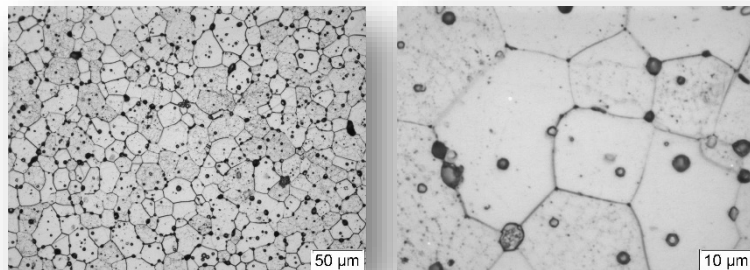


EPMA X-ray mapping in gray levels of Pu and U in  $U_{0.55}Pu_{0.45}O_2$  [2]



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

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



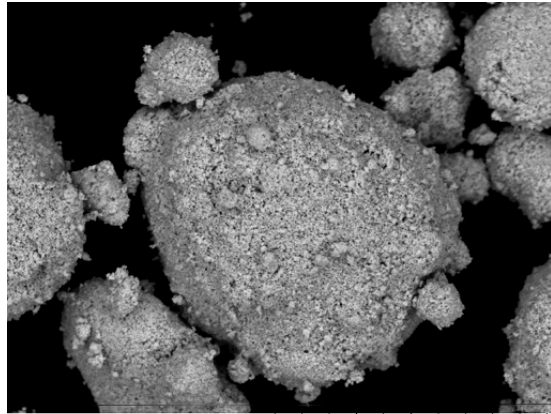
$\rho_{\text{apparent}}$ ( $\% \rho_{\text{theo}}$ )	Grain size ( $\mu\text{m}$ )
95.6(3)	30-40

[1] R. Vauchy et al. *Ceram. Int.*, 40(7B), 2014, 10991-10999

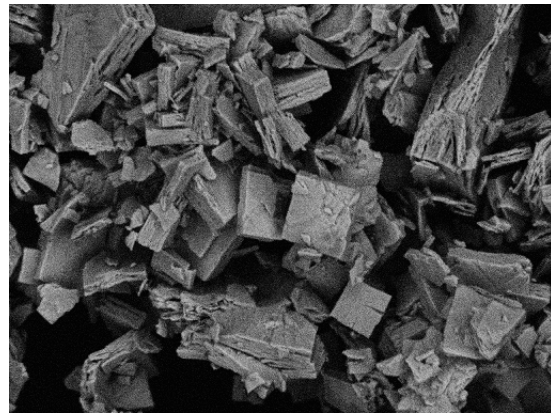
[2] R. Vauchy et al. *JNM*, 456, 2015, 115-119

# Optimized ceramic processing

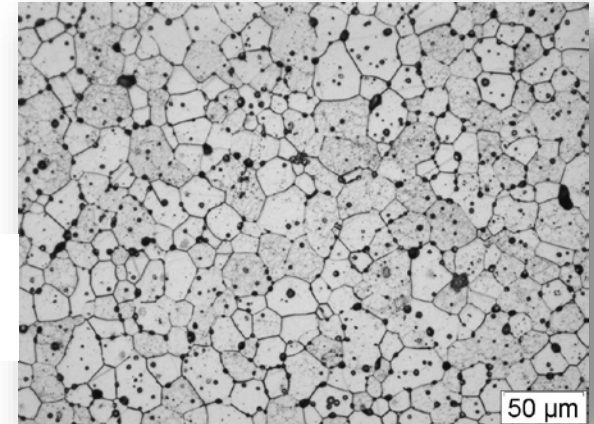
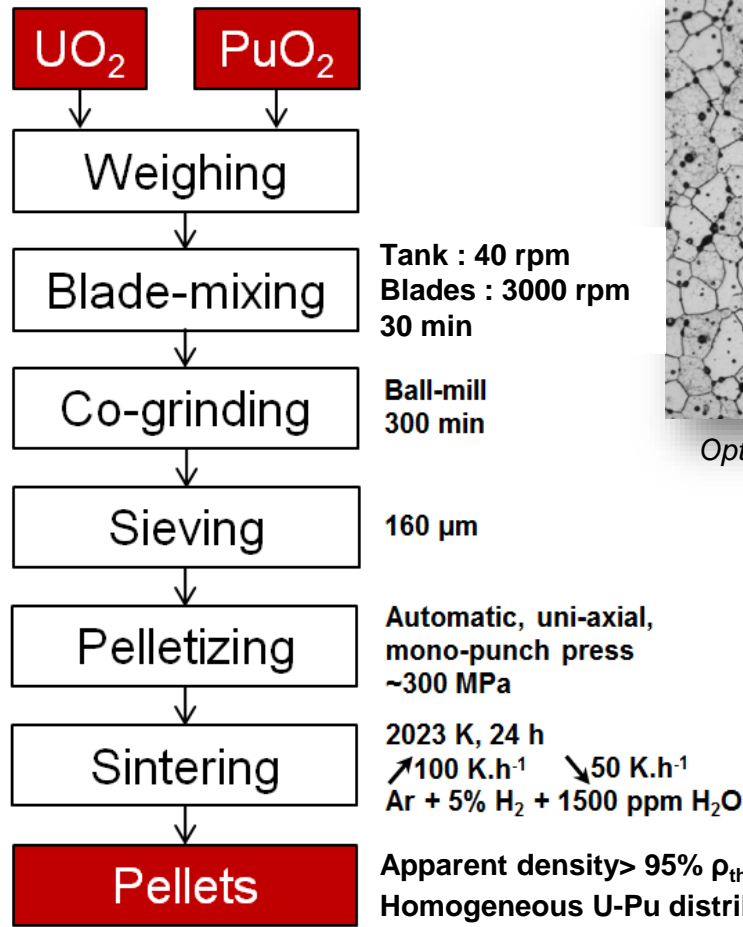
- Optimization of a powder metallurgy process [1]



2013/07/22 H D5,9 x3,0k 30 um  
SEM on raw  $UO_2$  powder [2]



2013/07/24 HL D3,5 x3,0k 30 um  
SEM on raw  $PuO_2$  powder [2]



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

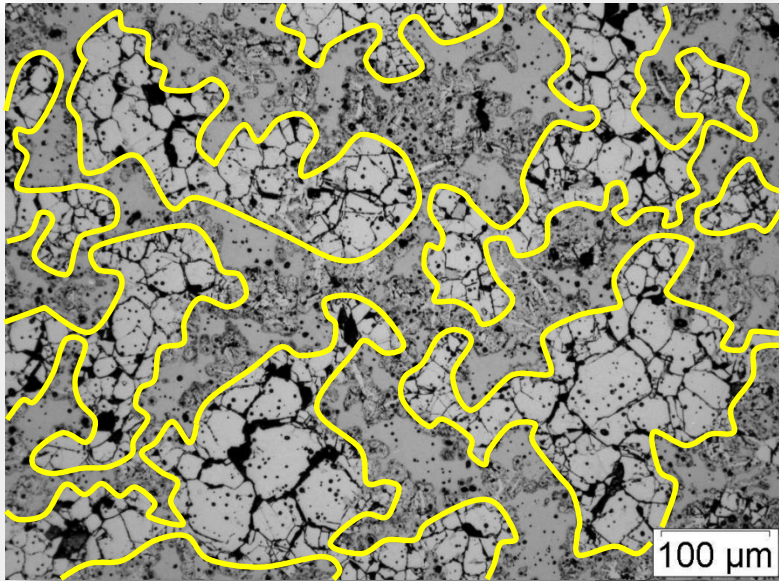
$\rho_{\text{apparent}}$ (% $\rho_{\text{theo}}$ )	Grain size ( $\mu\text{m}$ )
95.6(3)	30-40

$\longrightarrow$  Diffusion  
 $\longrightarrow$  U-Pu-O

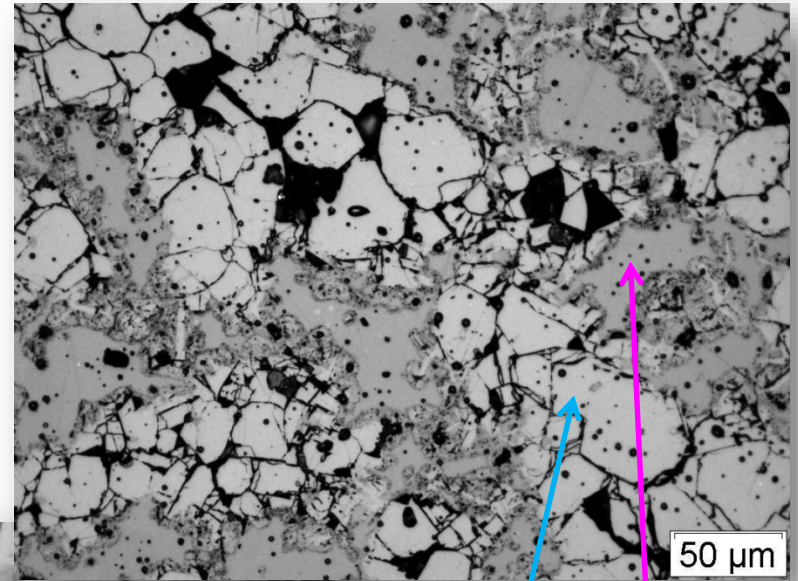
[1] R. Vauchy et al., *Ceram. Int.* 40, 2014, 10991-10999

[2] S. Berzati, *Thèse*, 2013

# Microstructural effects of phase separation



~0.05 K.s<sup>-1</sup>

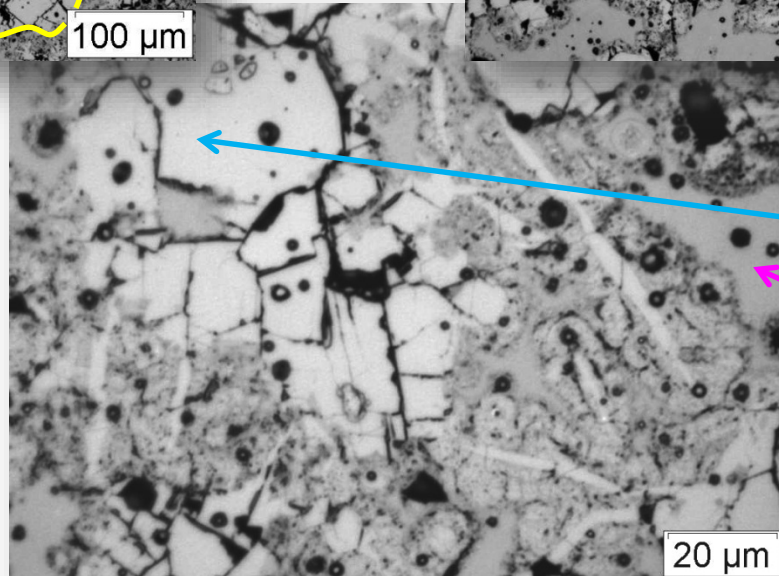


Two **distinct** zones **even before** chemical etching



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

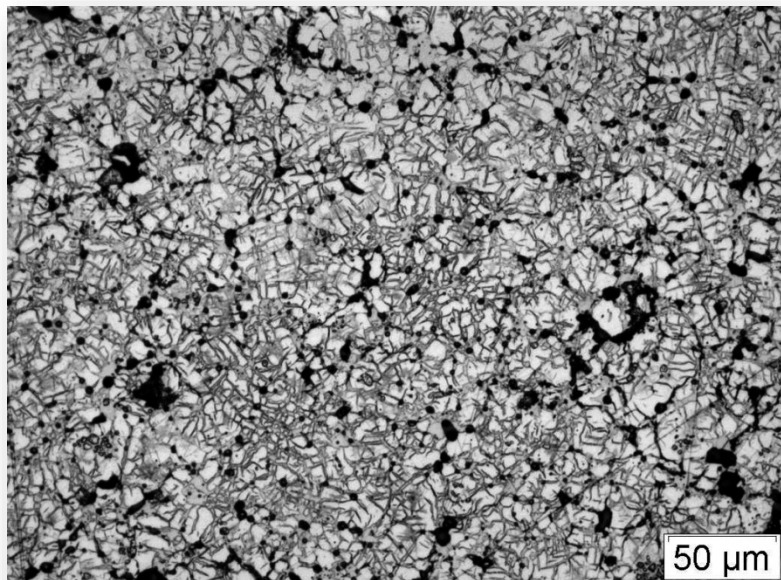
**Damaged** microstructure (cracks) owing to mechanical strains induced by the phase separation



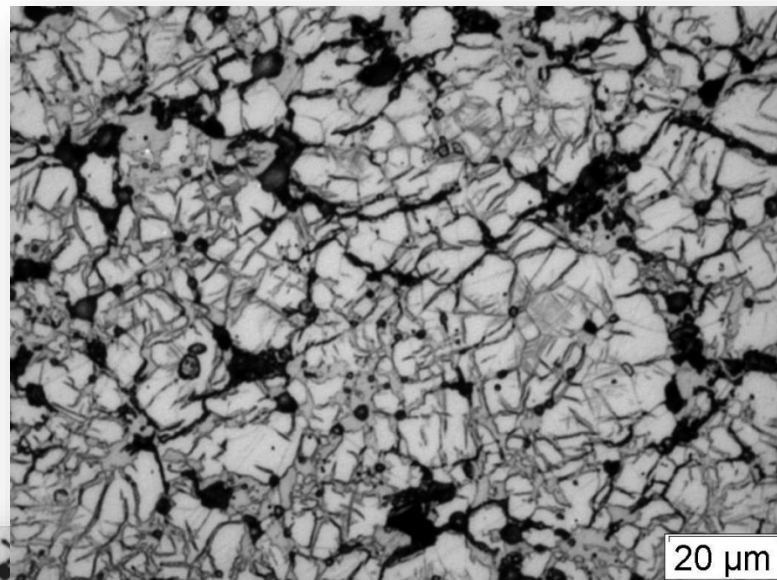
High-oxygen phase (O/M ≈ 2.0)

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

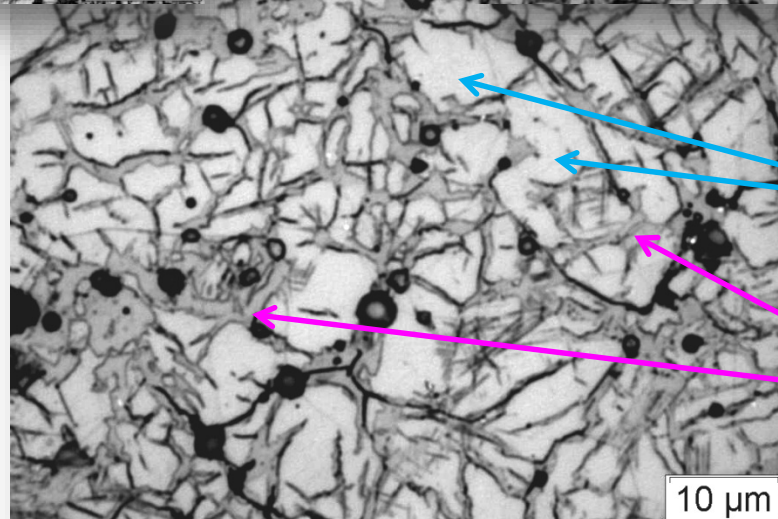
# Microstructural effects of phase separation



~300 K.s<sup>-1</sup>



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



High-oxygen phase (O/M≈2.0)

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

Damaged microstructure by cracks (not visible here)

DE LA RECHERCHE À L'INDUSTRIE

cea



# Samples fabrication and characterization

# Samples fabrication and characterization

Starting samples



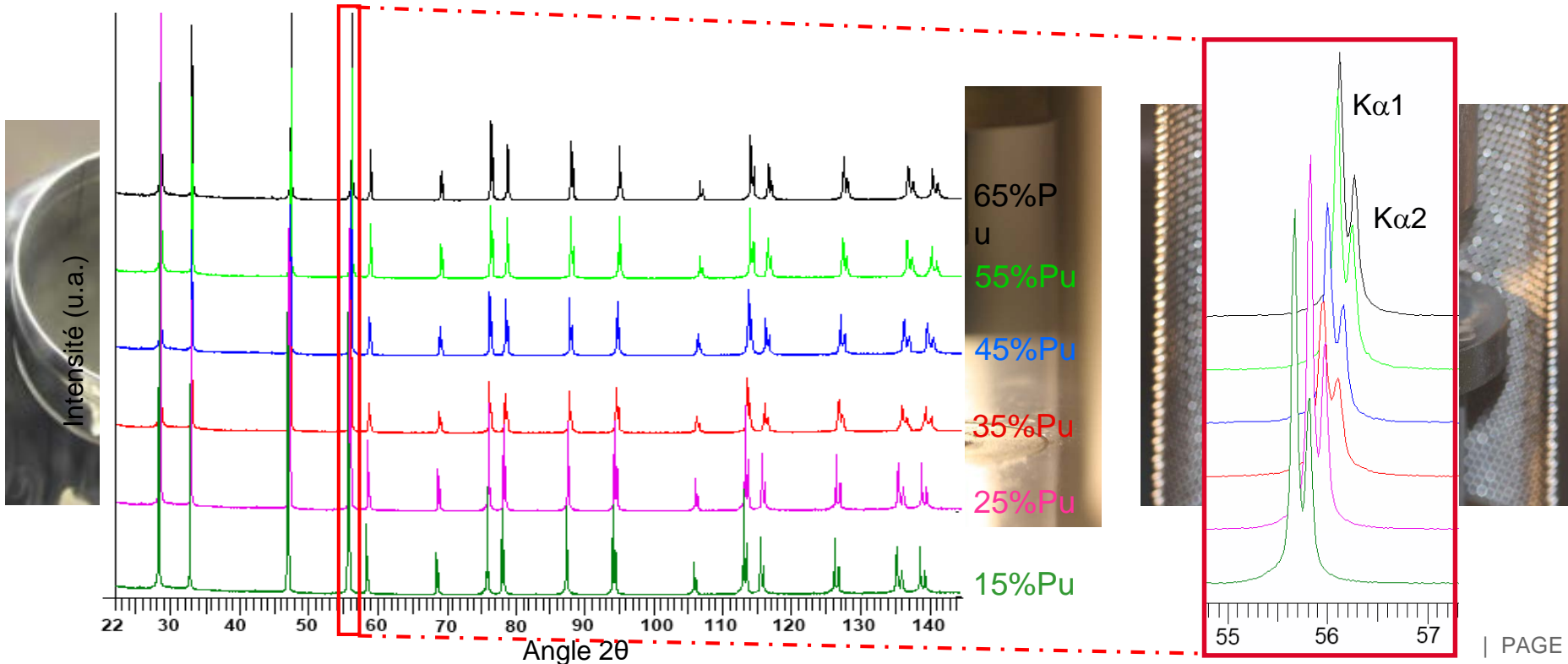
HT- XRD  
characterization

Co-grinding process



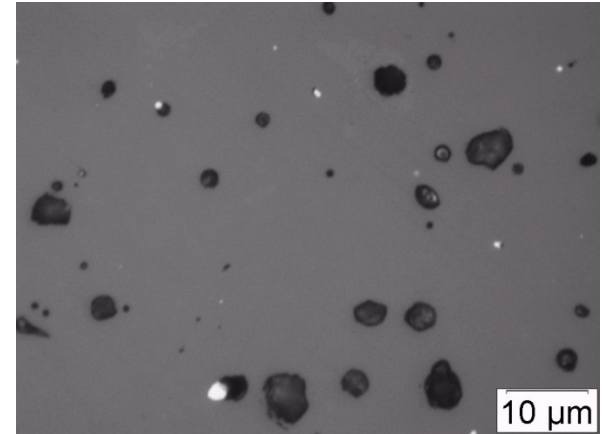
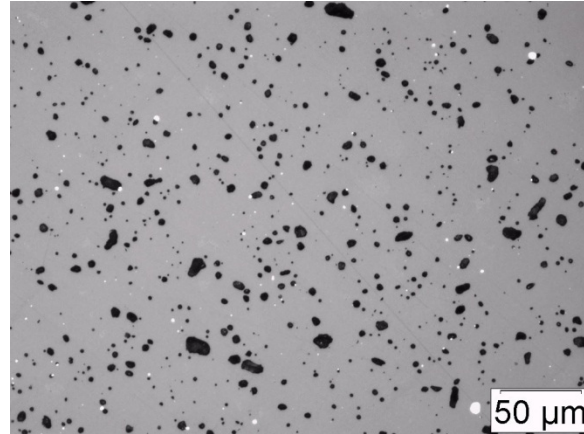
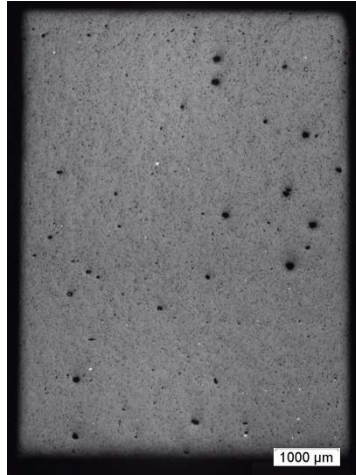
Air

He + 5% $H_2$   
+ 10 ppm residual  $H_2O$

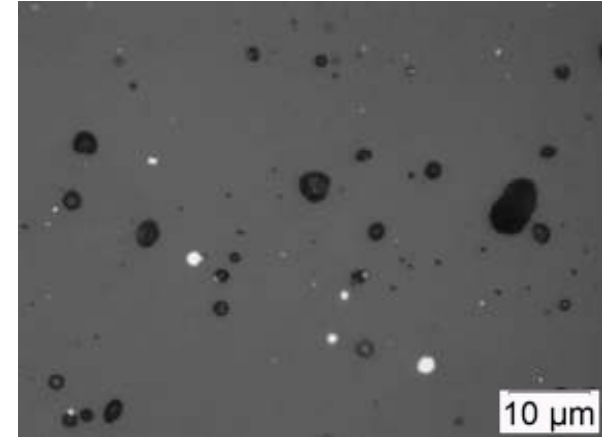
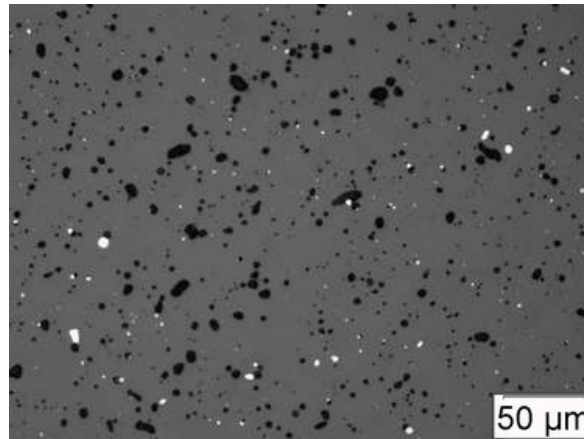
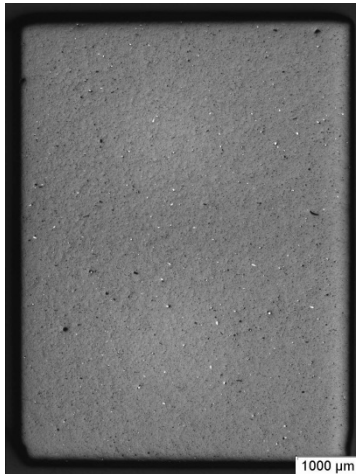


# Microstructure of starting samples

15% Pu



65% Pu



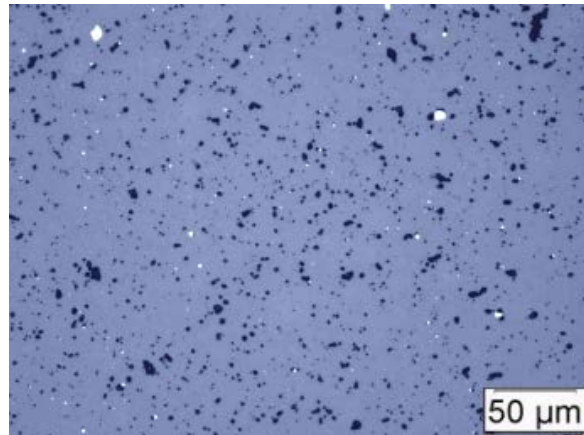
- Dense samples
- Homogeneous microstructure for all Pu content

# Effect of the phase separation on the microstructure

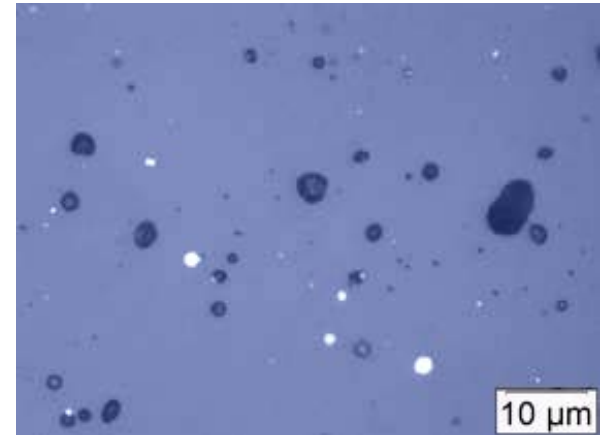
Monophasic sample



*macrography*

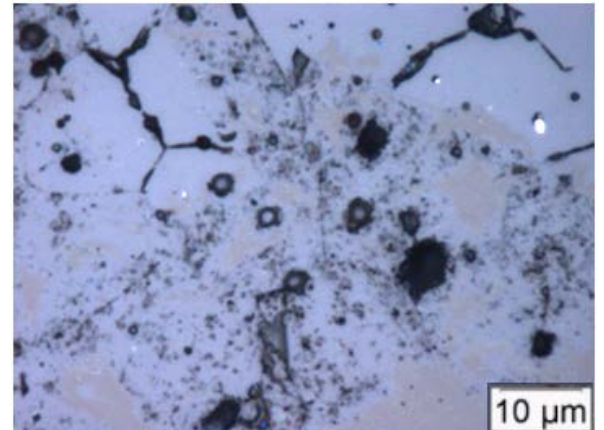
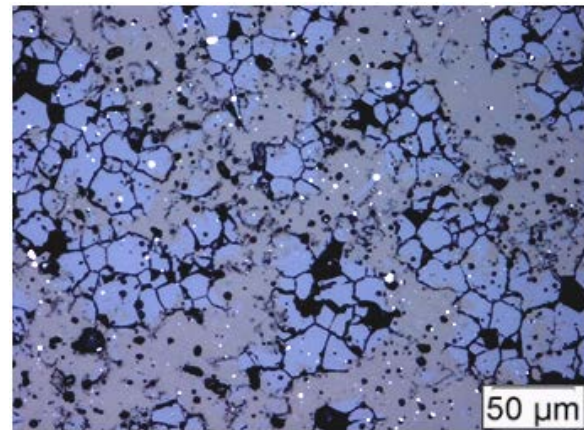
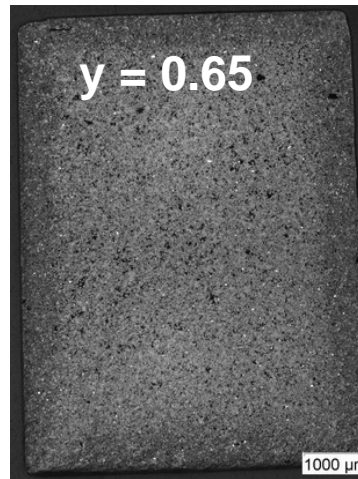


*X20 zoom*



*X100 zoom*

Biphasic sample

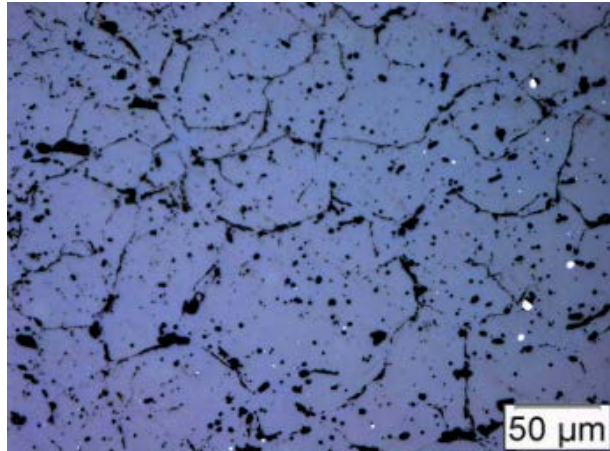


- ❖ Cracked material after phase separation
- ❖ Appearance of a new type of microstructure

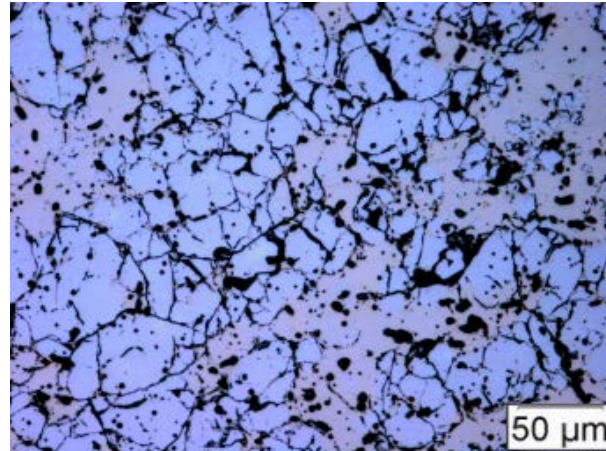


# Effect of the phase separation on the microstructure

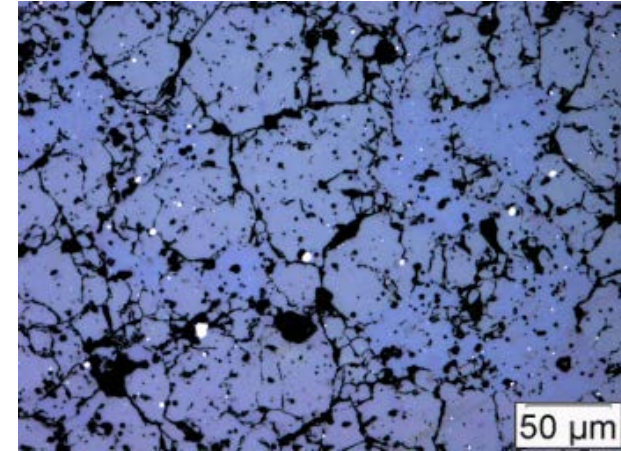
25%Pu



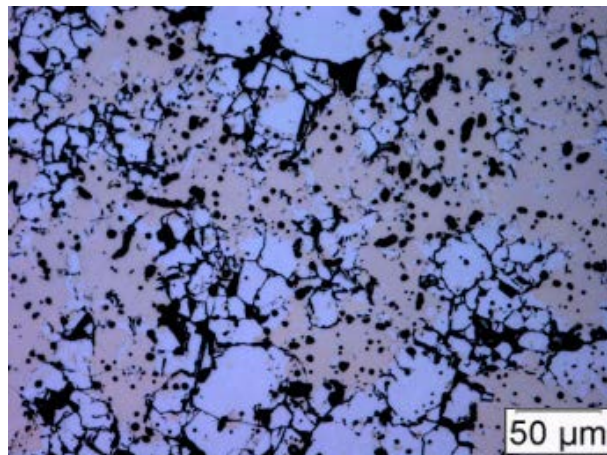
35%Pu



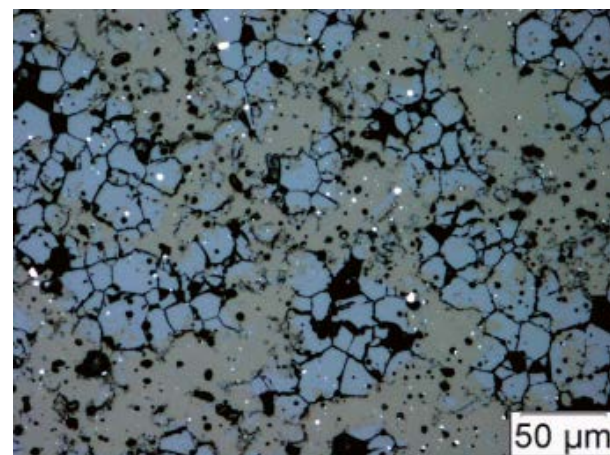
45%Pu



55%Pu

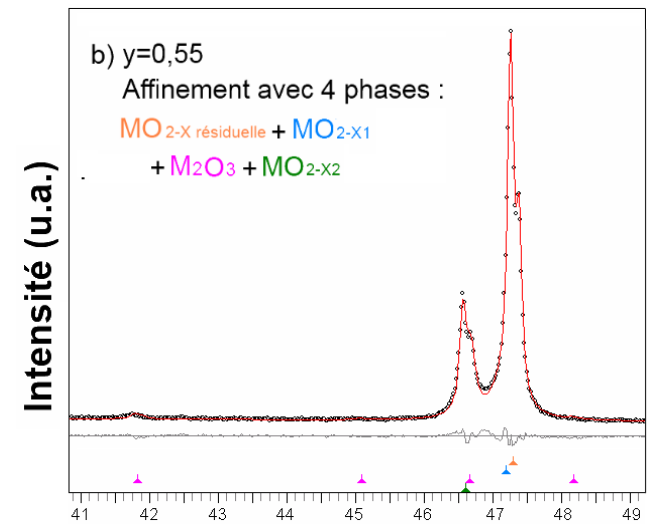
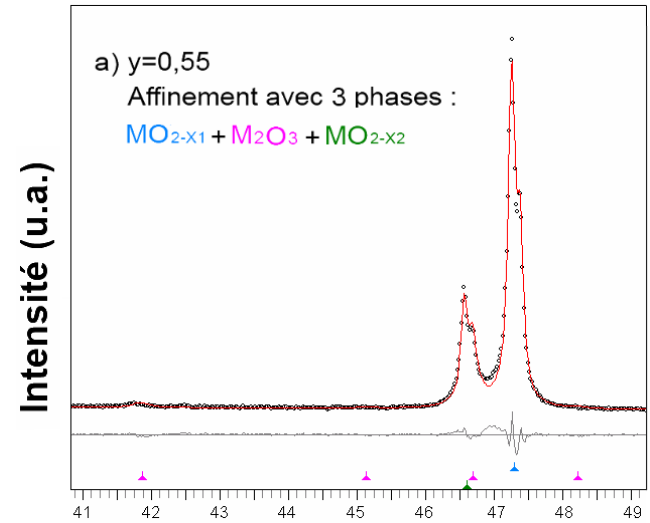
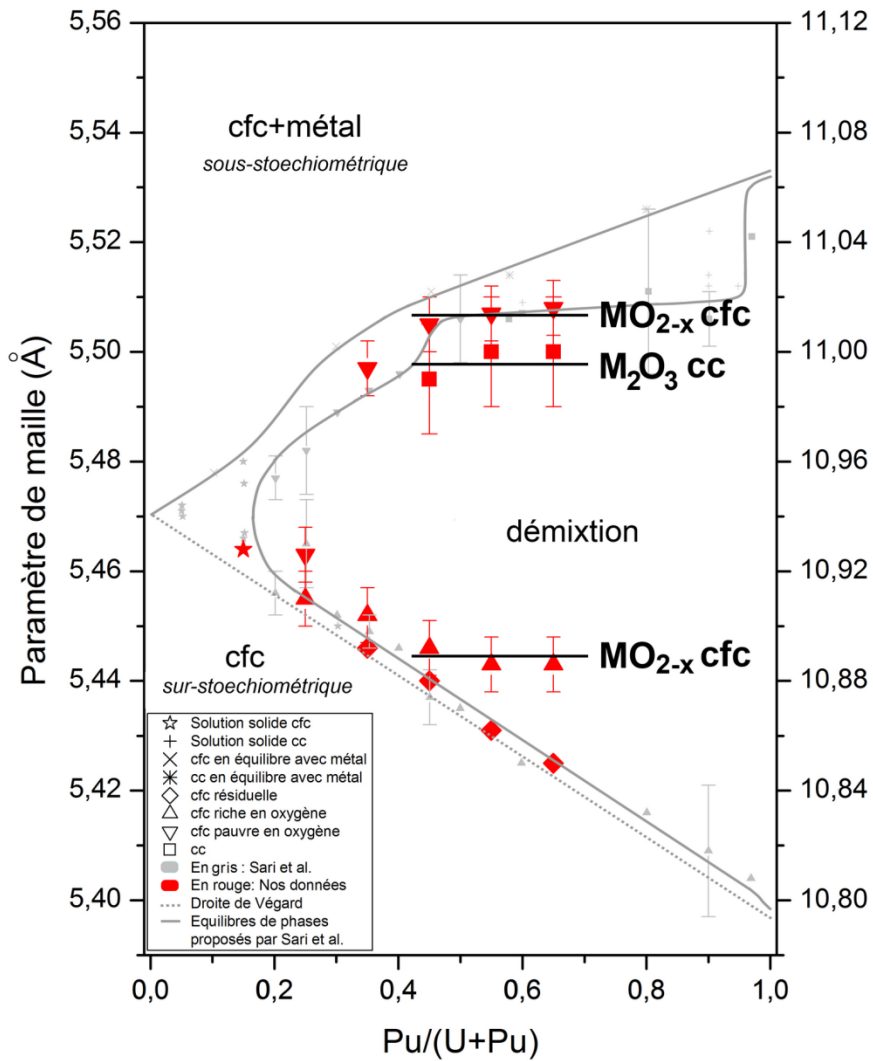


65%Pu



- ❖ Significant impact on the microstructure
- ❖ The higher the Pu content, the more cracks are observed

# Affinement Rietveld : triphasé + phase résiduelle



# Affinement Rietveld : triphasé + phase résiduelle

