# Oxide phase characterization in simulated high burn-up $UO_2$ fuels in the early stages of a nuclear severe accident

C. Le Gall, E. Geiger, O. Proux, M. Rovezzi, P.L. Solari, M. Hunault, V. Klosek, C. Riglet Martial, J. Léchelle, F. Audubert, et al.

DE LA RECHERCHE À L'INDUSTRIE

# Oxide phase characterization in simulated high burn-up $UO_2$ fuels in the early stages of a nuclear severe accident

**MRS Spring Meeting 2018 | Claire Le Gall**

CEA Cadarache | DEN | DEC | SA3E | LAMIR

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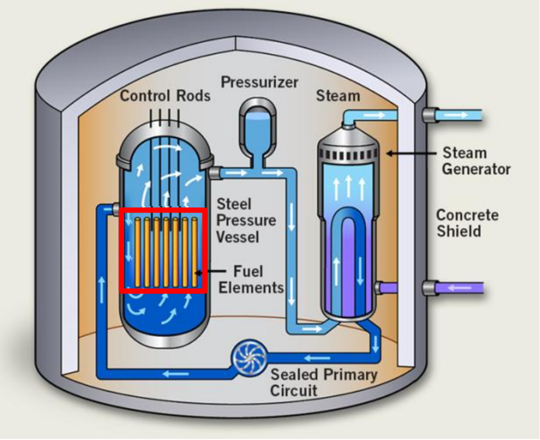
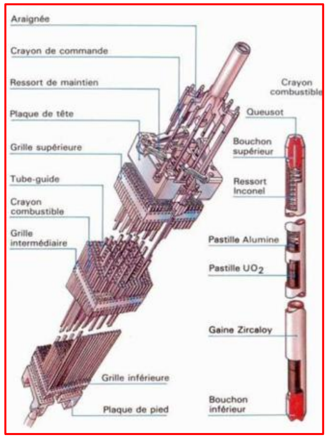
# NUCLEAR FUEL FISSION
## Fission products

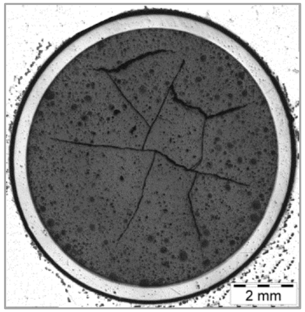


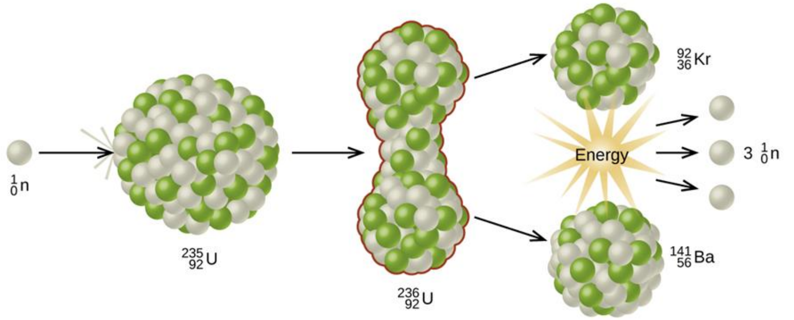

**Pressurized Water Reactor (PWR)**




**Fuel assembly**

**$UO_2$ or $(U,Pu)O_2$ fuel in its Zr alloyed cladding**

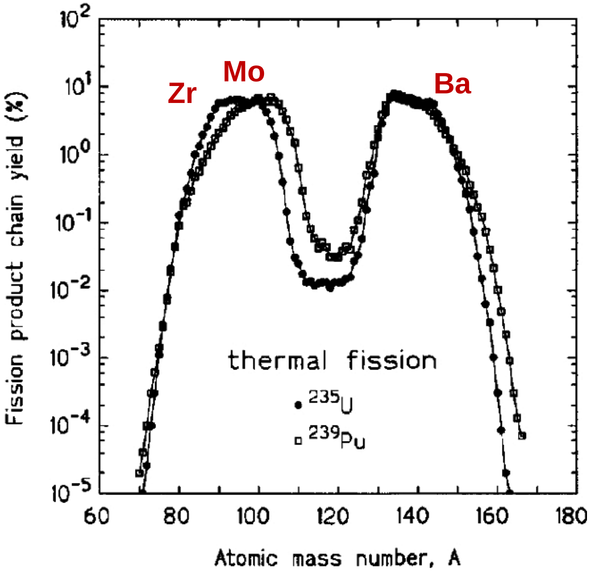



**Unstable nucleus**

**Fission Products (FP)**

**Fission yield: FP most probably producted**




**Fission occurs in nuclear fuel pellets**

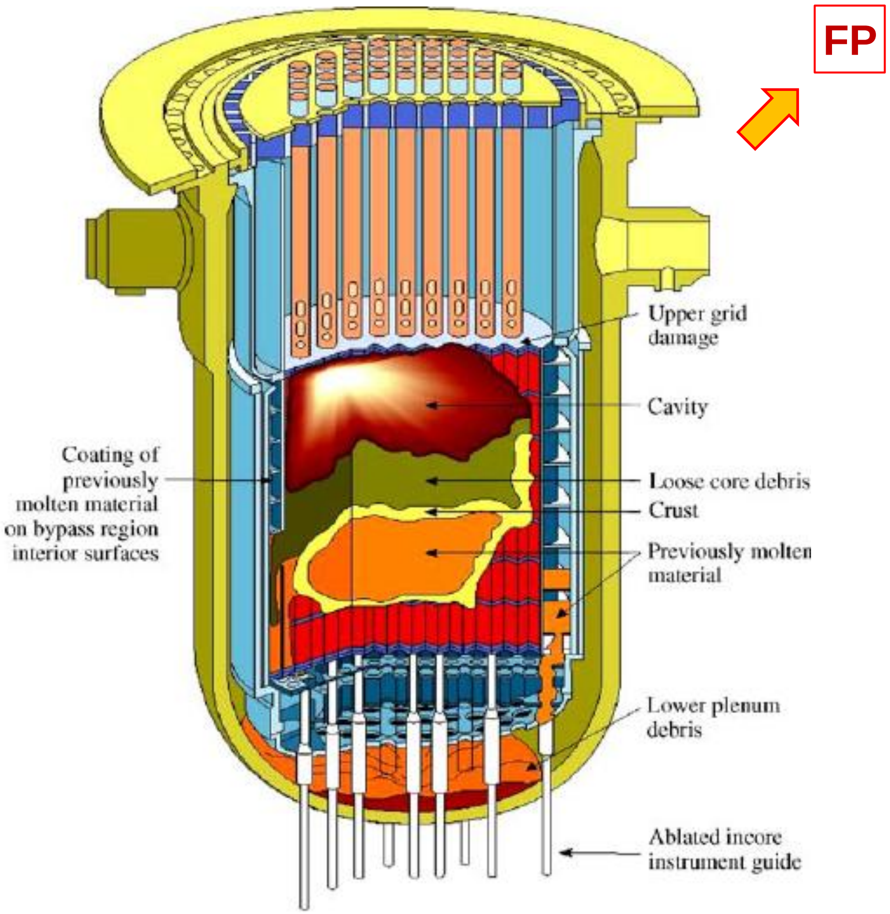


D. Heinze *Ph.D thesis* **(2010)**

# SEVERE ACCIDENT PHENOMENA

## Source term

**Source Term** = **Nature and quantity of released radioactive materials** → **FP release from the fuel**




**Loss of coolant**

⇩

**Cladding oxidation**

⇩

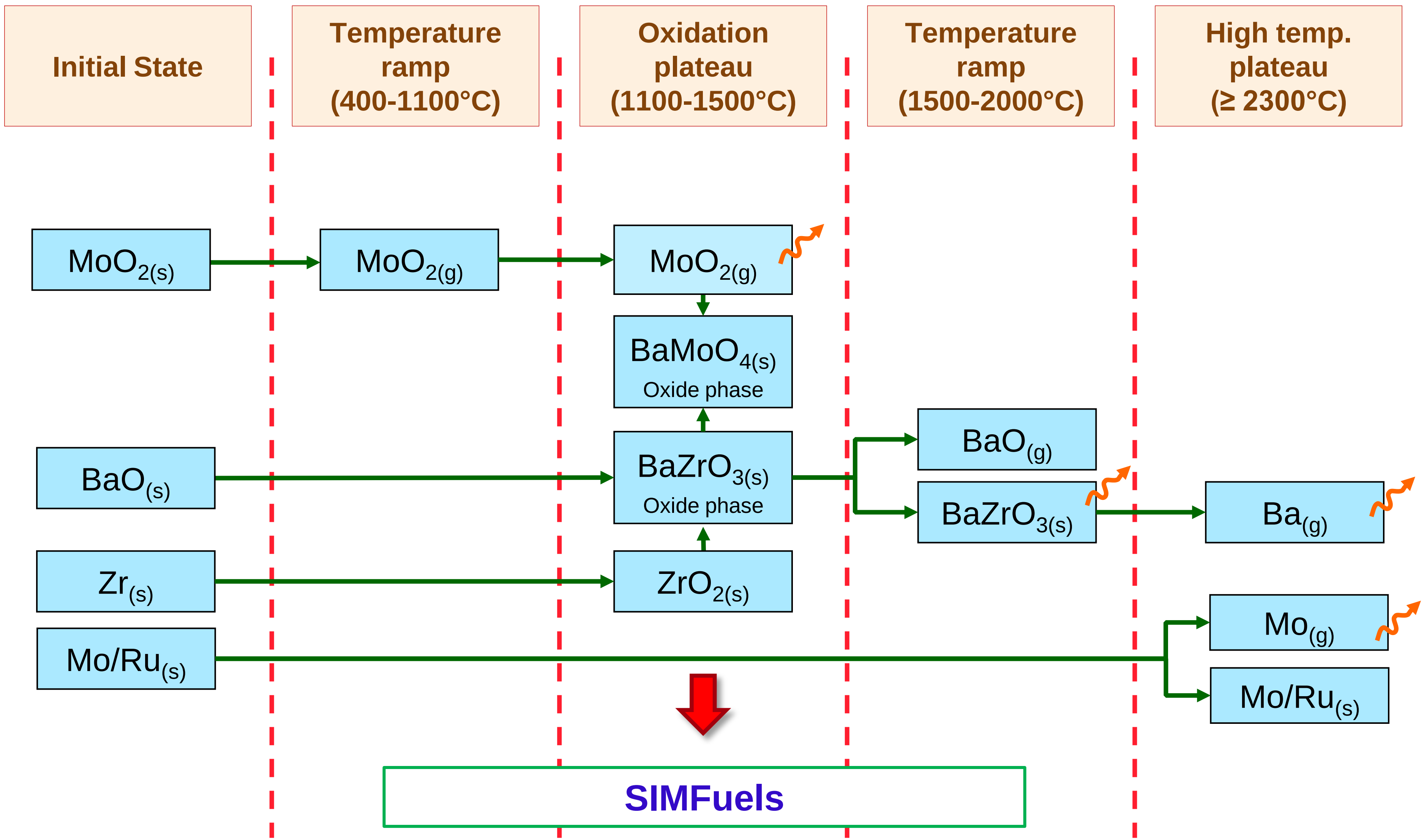
**Corium formation**



J. P. Van Dorsselaere et al., *NED 236* **(2006)**
B. R. Sehgal, *Nuclear safety in LWR* **(2012)**

# STUDY OF FPs BEHAVIOR

## Mechanism suggested in the literature





G. Nicaise, *8th International Conference on Candu Fuel* **(2003)**
G. Nicaise, *NT DPAM/SEMIC 2004/37* **(2004)**
E. Geiger, *PhD thesis* **(2016)**
H. Kleykamp, *J. Nucl. Mater.* **(1985)**

# SIMFuels SAMPLES

## Fabrication data

**Depleted $UO_2$ + 11 oxides (FPs surrogates)**

**Sintering at 1650°C during 2h under pure $H_2$**

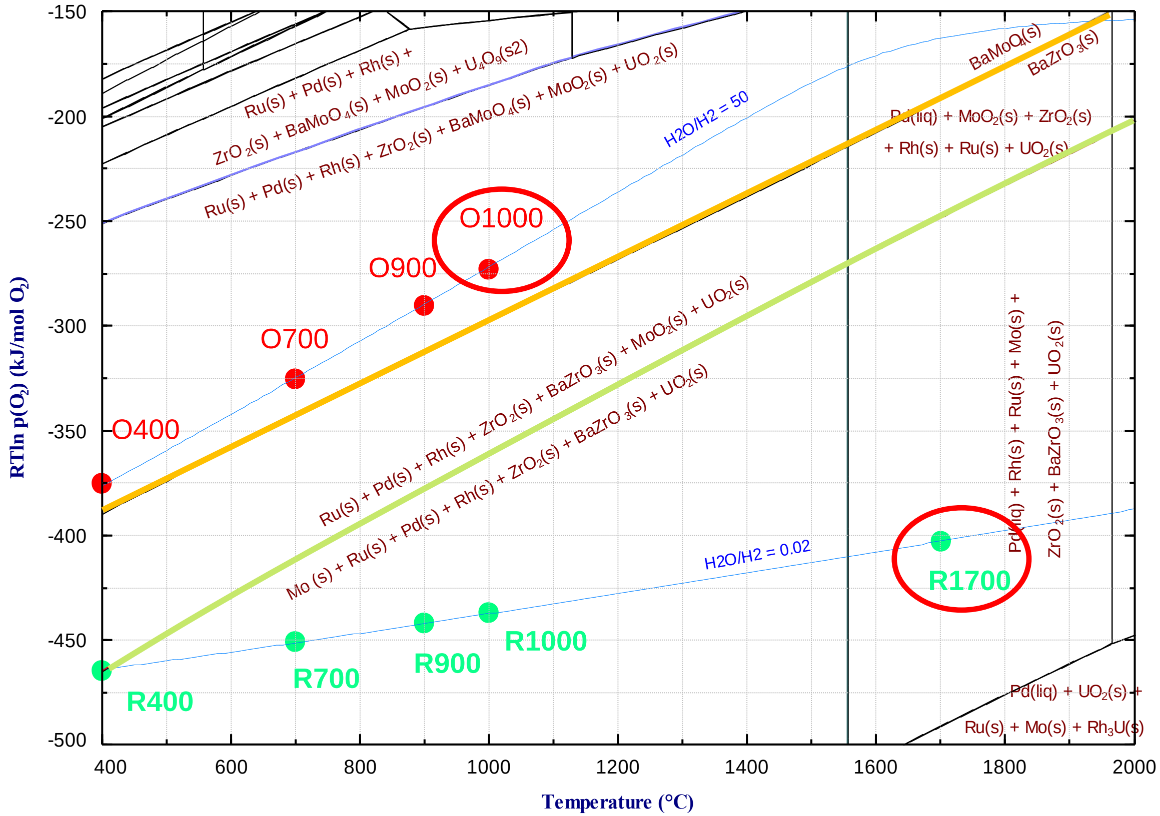
| Elements | Ba | Ce | La | Mo | Sr | Y | Zr | Rh | Pd | Ru | Nd |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Concentration (at%) | 0,26 | 0,61 | 0,20 | 0,51 | 0,13 | 0,06 | 0,60 | 0,03 | 0,42 | 0,64 | 0,91 |

**Concentrations representative of an irradiated fuel with a burn-up of 76 $GWd.t_{HM}^{-1}$**

# SIMFuels SAMPLES

## Thermal treatments

**Ba - $O_2$ - Mo - Zr - Ru - Rh - Pd - U**




$$BaZrO_{3(s)} + MoO_{2(s)} + \frac{1}{2}O_{2(g)} \rightarrow BaMoO_{4(s)} + ZrO_{2(s)}$$

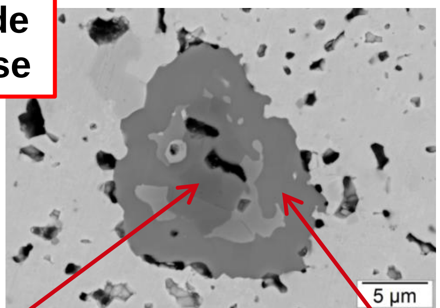
$$Mo_{(s)} + H_2O_{(l)} \rightarrow MoO_{2(s)} + H_{2(g)}$$

# CHARACTERIZATIONS

## SEM-EDX

**Sample as sintered**

**Oxide phase**




**O/Zr ≈ 2**

⇓

**$ZrO_2$**

**(Sr+Ba)/Zr ≈ 1**

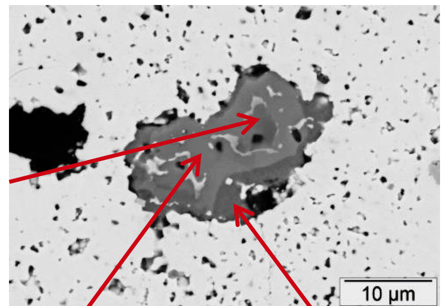
**O/Zr ≈ 2.5**

⇓

**$Ba_{0,8}Sr_{0,2}ZrO_3$**

**1000°C, -292 kJ.mol$^{-1}$**

**$ZrO_2$**




**$Ba_{0,8}Sr_{0,2}ZrO_3$**

**(Ba+Sr)/Mo ≈ 1**

**(Ba+Sr)/Zr ≈ 0.6**

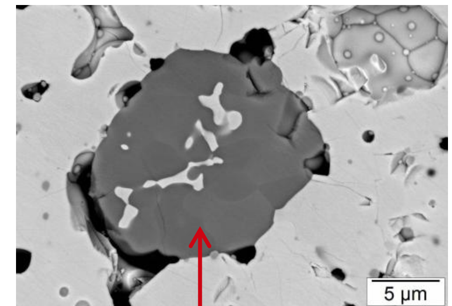
**O/Zr ≈ 4**

**O/Mo ≈ 5**

⇓

**(Ba, Sr)(Zr, Mo)$O_x$**

**1700°C, -426 kJ.mol$^{-1}$**




**$Ba_{0,9}Sr_{0,1}ZrO_3$**



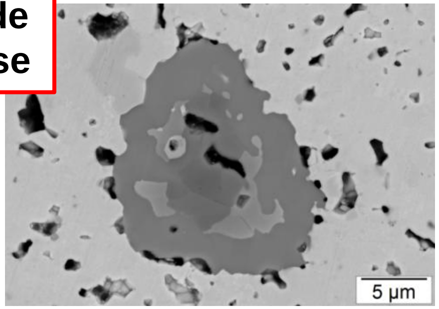
C. Thouzellier internship **(2017)**, H. Kleykamp, *J. Nucl. Mater.* **(1985);** E. Geiger et al. *ERMSAR proceedings* **(2015)**; E Geiger et al. *J. Nucl. Mater. (accepted)*

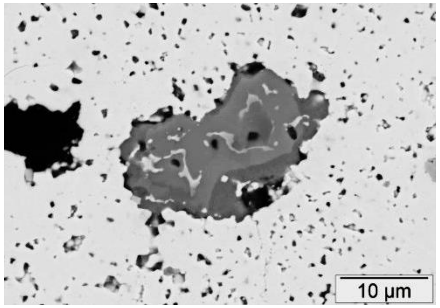
# CHARACTERIZATIONS

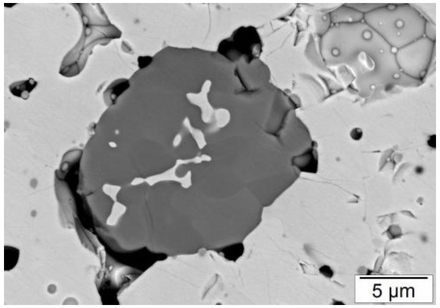
## SEM-EDX

**Sample as sintered** | **1000°C, -292 kJ.mol$^{-1}$** | **1700°C, -426 kJ.mol$^{-1}$**

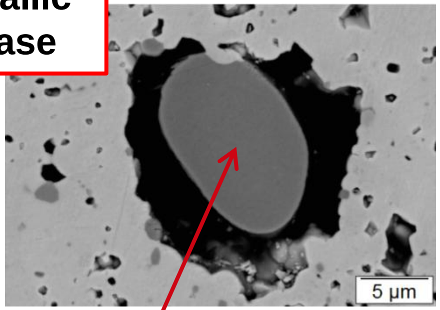
**Oxide phase**

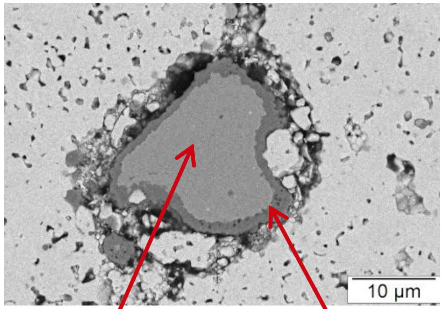


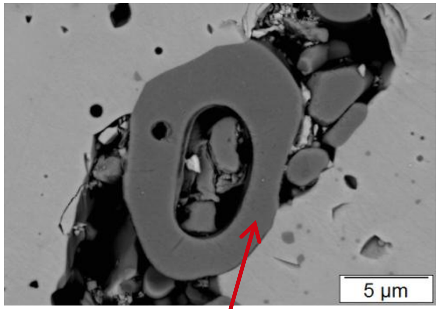




**Metallic phase**




**100% Mo**

**100% Mo** **O/Mo ≈ 2**

**$MoO_2$**

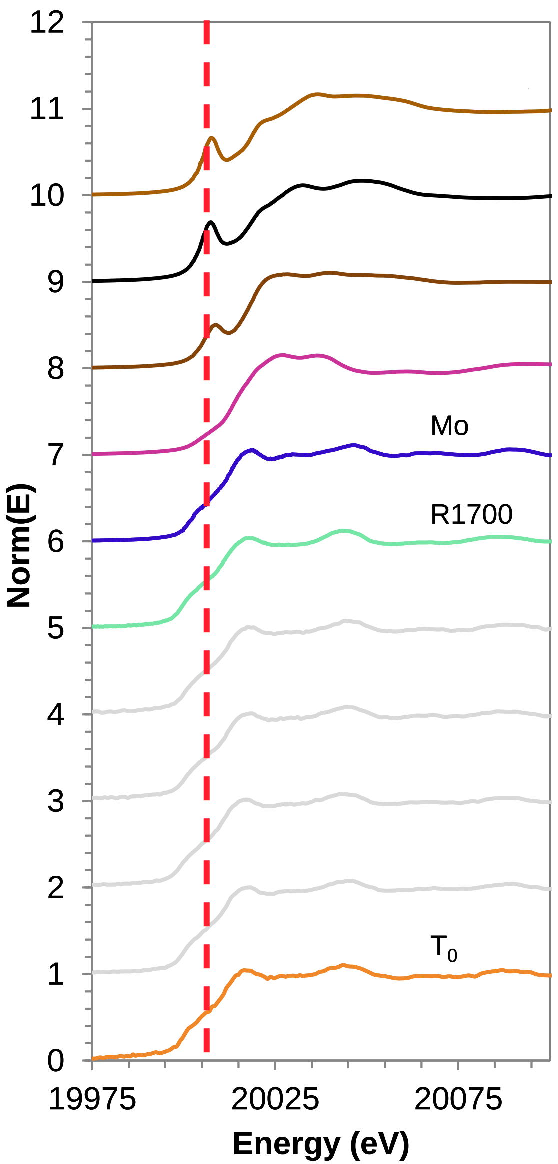
**100% Mo**

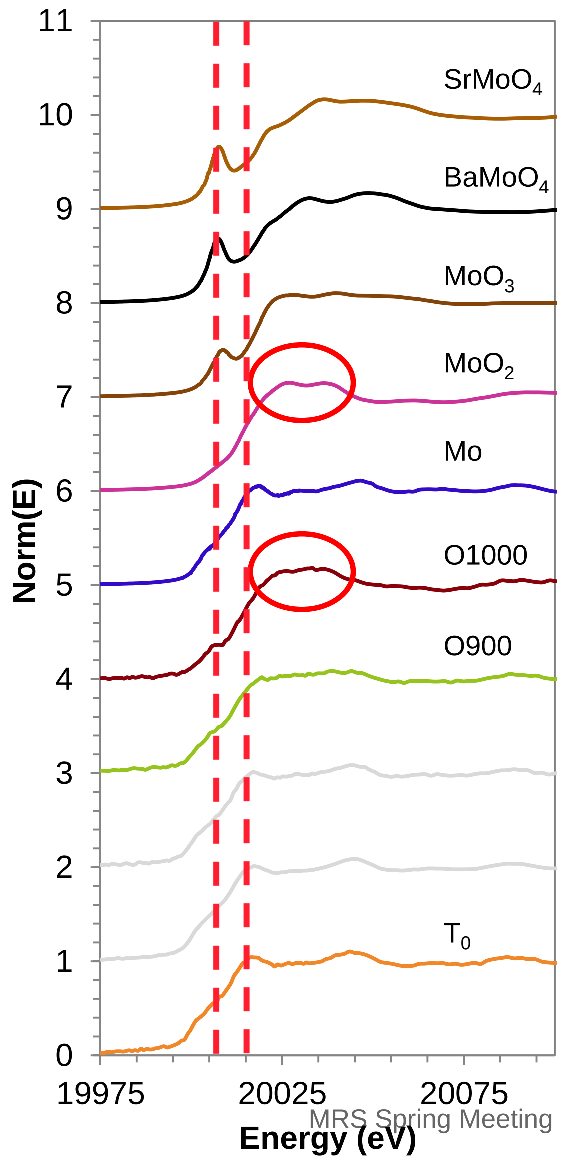


C. Thouzellier internship **(2017)**, H. Kleykamp, *J. Nucl. Mater.* **(1985);** E. Geiger et al. *ERMSAR proceedings* **(2015)**; E Geiger et al. *J. Nucl. Mater. (accepted)*

# CHARACTERIZATIONS

## X-ray Absorption Spectroscopy at Mo K-edge




**No strong evolution of Mo XANES reducing conditions**

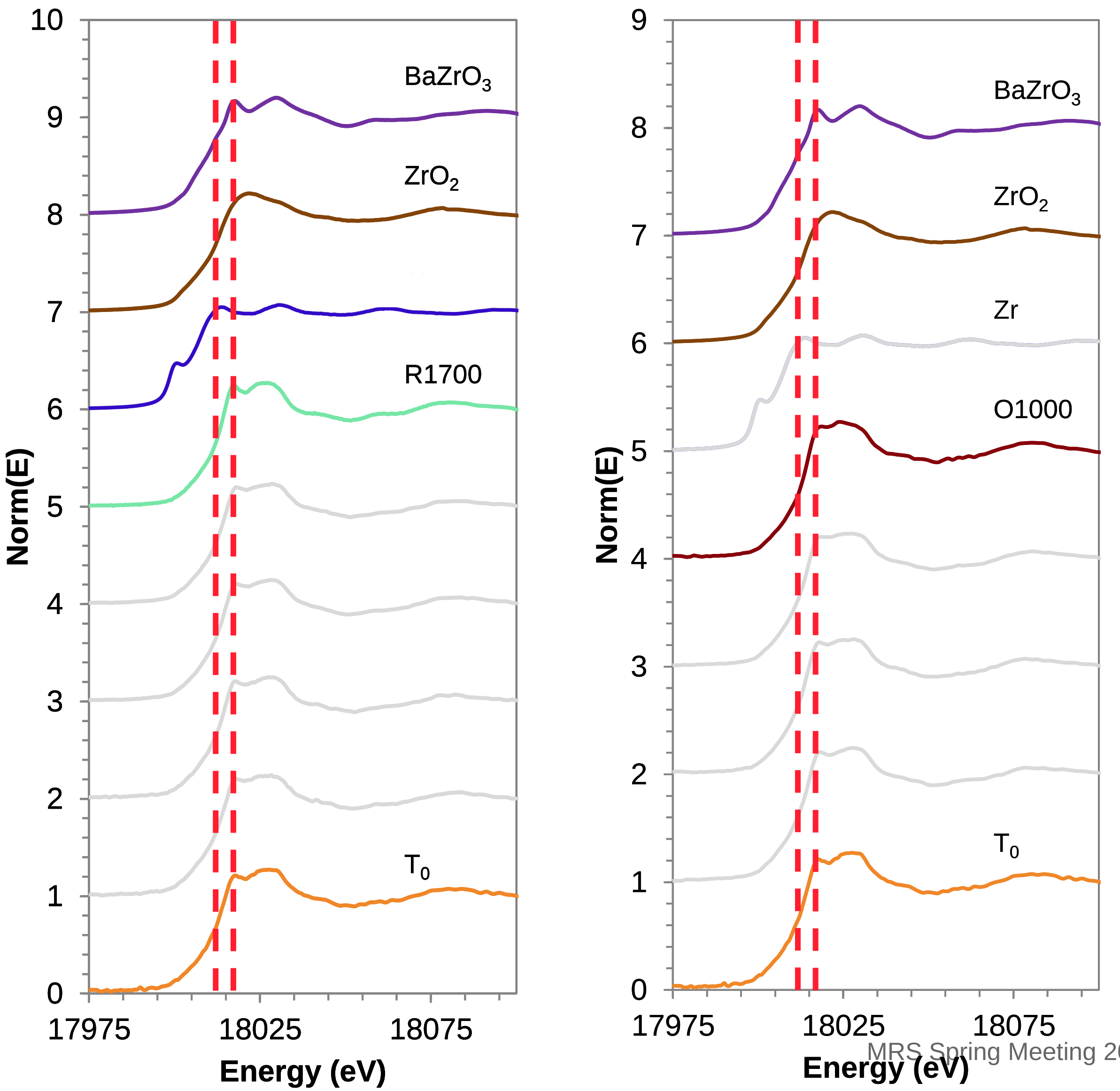
**Metallic Mo**

**Evolution of Mo local environment from 900°C in oxidizing conditions**

**Consistent with Mo oxidation, $MoO_2$ formation and the oxide phase evolution**

# CHARACTERIZATIONS

## X-ray Absorption Spectroscopy at Zr K-edge




**Zr XANES evolution at 1700°C in reducing conditions**

**Consistent with the continuous $BaZrO_3$ formation and stabilization**

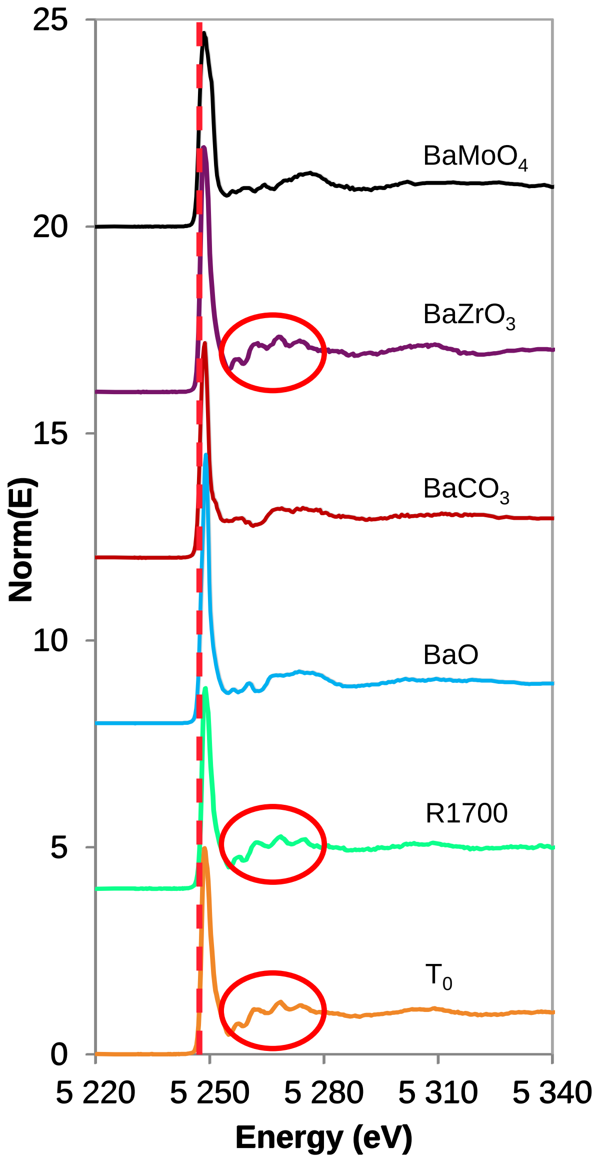
**Zr XANES evolution from 1000°C in oxidizing conditions**

**Destruction of part of the $BaZrO_3$ phase and formation of $ZrO_2$ ?**

**Consistent with the oxide phase evolution (Mo reacts with Ba)**

# CHARACTERIZATIONS

## HERFD-XANES at Ba $L_3$-edge



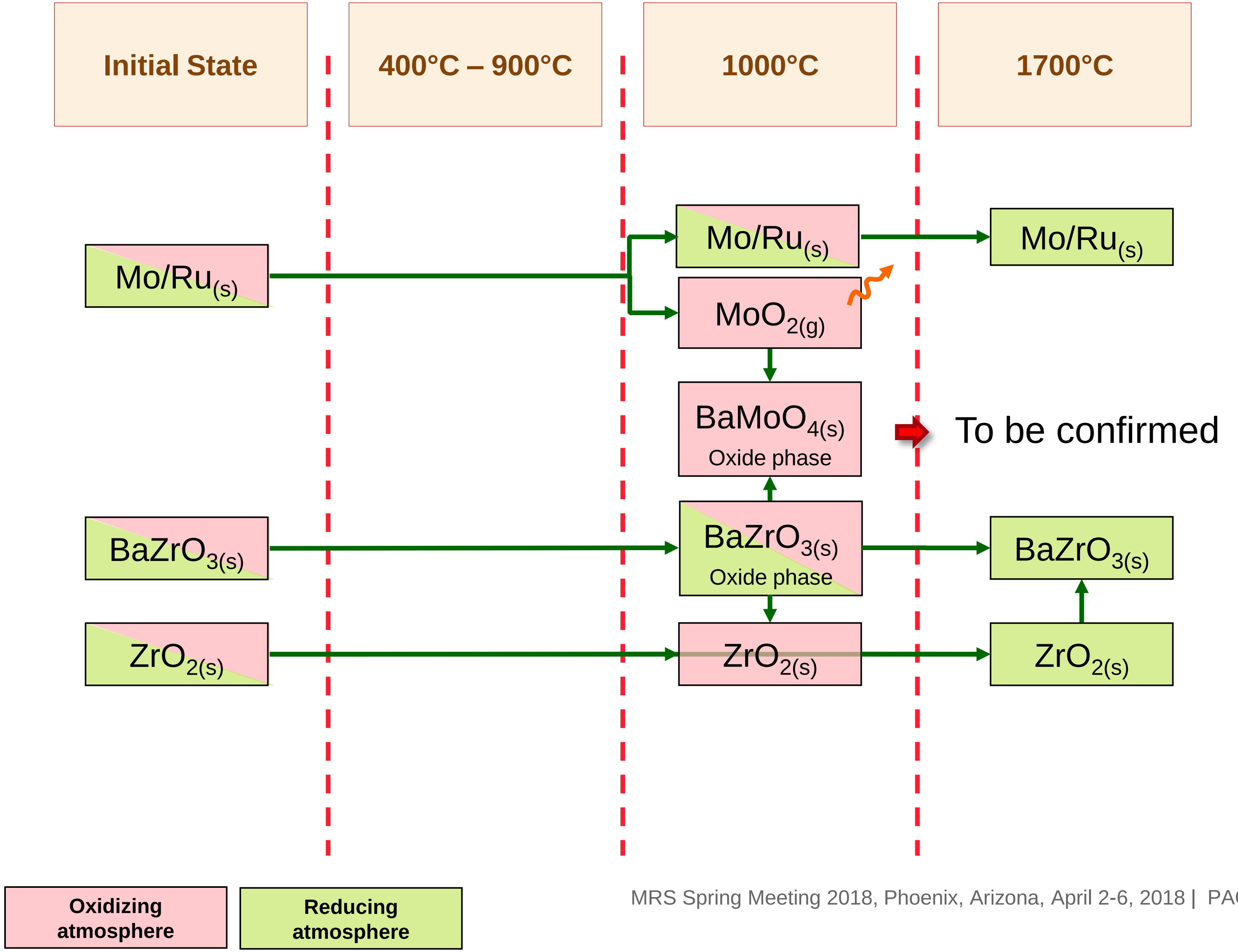

**No Ba XANES evolution at 1700°C in reducing conditions**

**$BaZrO_3$**

**XANES analyses of the O-samples scheduled in April 2018**

# CONCLUSIONS

## Evolution of the oxide phase



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# X-RAY ABSORPTION SPECTROSCOPY

## Principle