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Thermodynamics applied to severe accidents - Present activities and perspectives

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DE LA RECHERCHE À L'INDUSTRIE

cea den

Thermodynamics applied to severe accidents – Present activities and perspectives

A. Quaini

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Context

Calphad

Experimental Results

TAF-ID database

Development of ATTILHA

Conclusions and perspectives

UO₂-PuO₂-ZrO₂: liquidus/solidus

U-Zr-O: miscibility gap in the liquid phase

Out of nominal functioning may lead to a nuclear accident



Severe accident (SA): the normal functioning of the nuclear power plant is not re-established



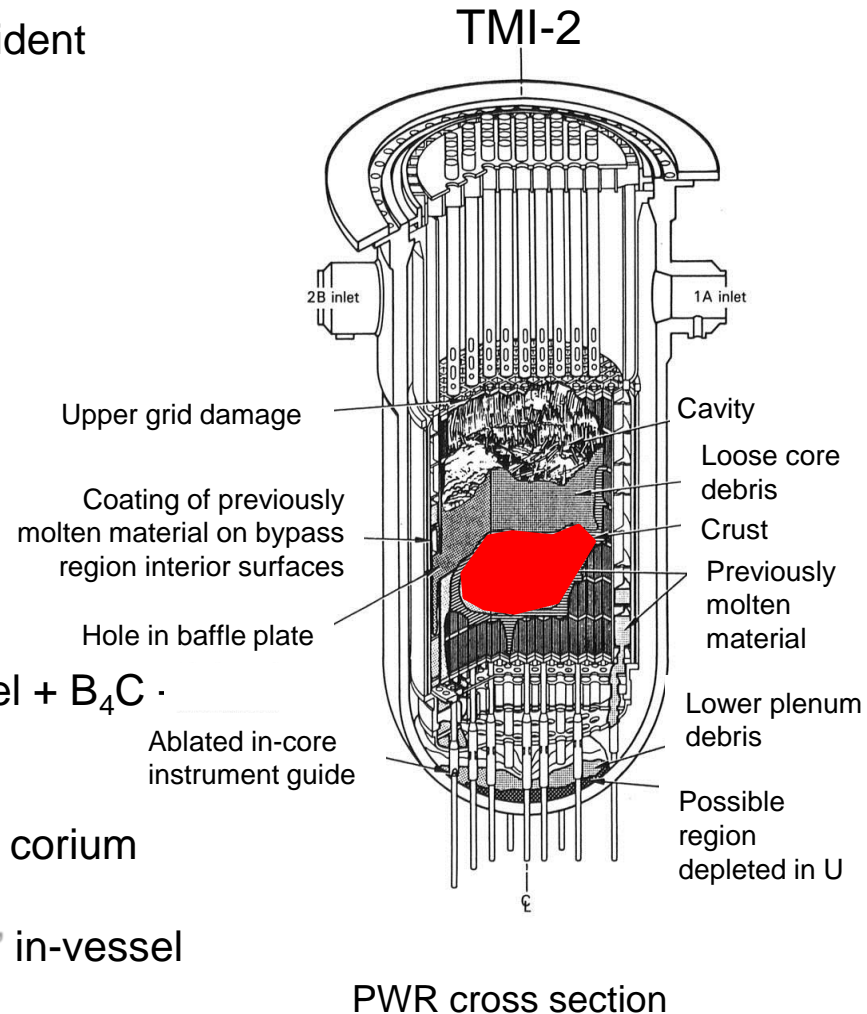
Fusion of the core and internal structure

→ Interaction $\text{MOx} + \text{Zircaloy} + \text{stainless steel} + \text{Inconel} + \text{B}_4\text{C}$ ·
FPs

$\text{U(Pu)-Zr-O-Fe-Cr-Ni-Ag-Cd-In-B-C-FPs}$ → In vessel corium

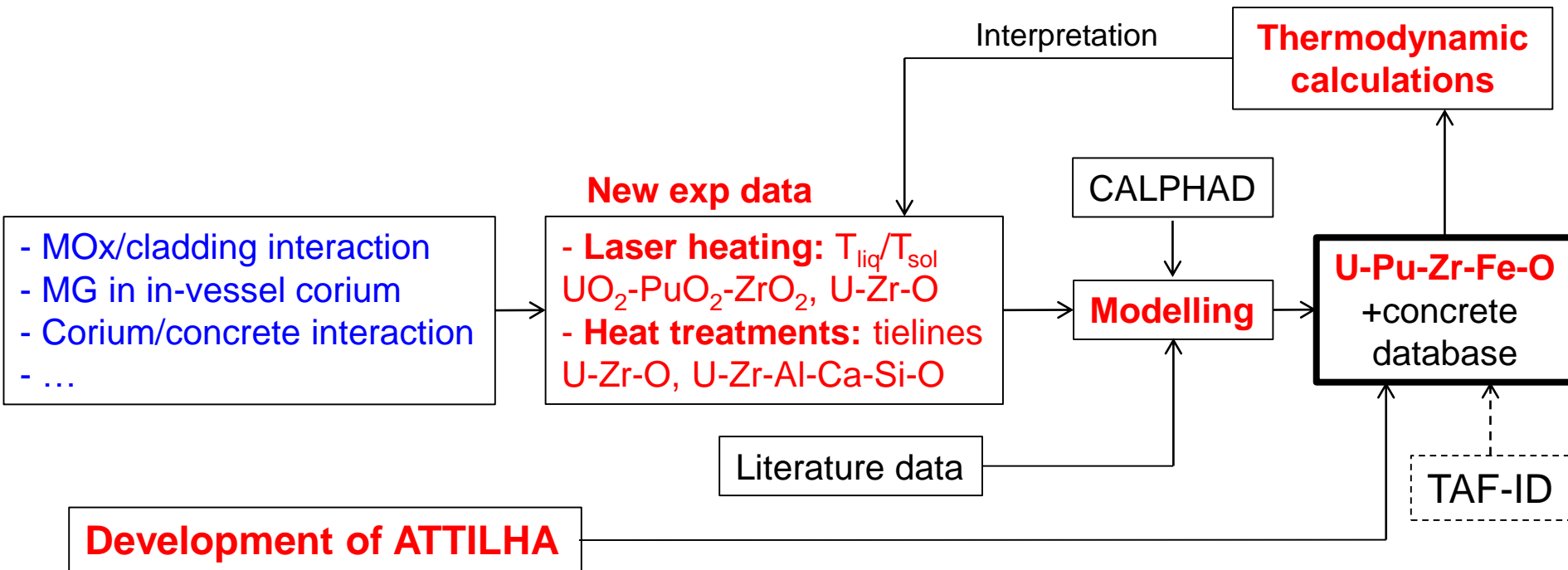
→ **U-Pu-Zr-Fe-O** system is selected as the “prototypic” in-vessel corium

→ **Thermodynamic database for corium**



OBJECTIVE

Improve the thermodynamic models of the in-vessel and ex-vessel corium systems

OBJECTIVE of the development of ATILHA

New experimental setup for the investigation of complex mixtures at very high temperature ($T > 2300$ K)

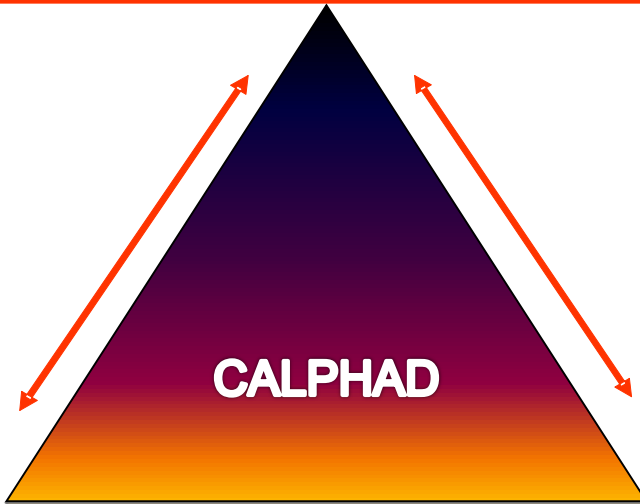
Minimisation of the Gibbs energy of the system

$$\min(G) = \min\left(\sum_{\alpha} n^{\alpha} G_m^{\alpha}(T, p, x_i^{\alpha} \text{ or } y_k^{(l,\alpha)})\right)$$

n=number of mole of phase α
 x=molar fraction of i in α
 y=site fraction

Critical analysis of experimental data

Prediction of higher order systems behaviour by extrapolation from lower order systems



Synergic approach
 Experiments \longleftrightarrow Calculations

Experimental data acquisition
 Thermodynamic data \Rightarrow Calorimetry, D.S.C.
 Phase diagrams \Rightarrow Heat treatments, D.T.A.

Thermodynamic modelling

Optimization
 (Code Thermo-Calc)

Thermodynamic database
 $G(\text{phases}) = f(T, x) @ P=1 \text{ atm}$

Minimization of G(system)
 (Code Thermo-Calc)

Thermodynamic properties
 Phase diagrams
 Application calculations

UO₂-PuO₂-ZrO₂ system

→ Experimental results

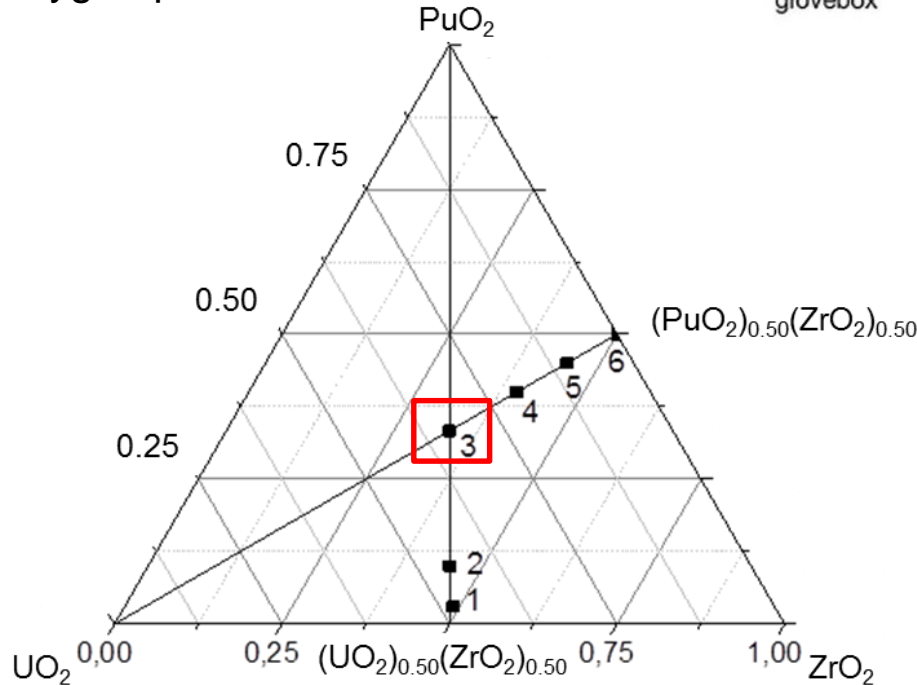
→ Calculations

→ Summary

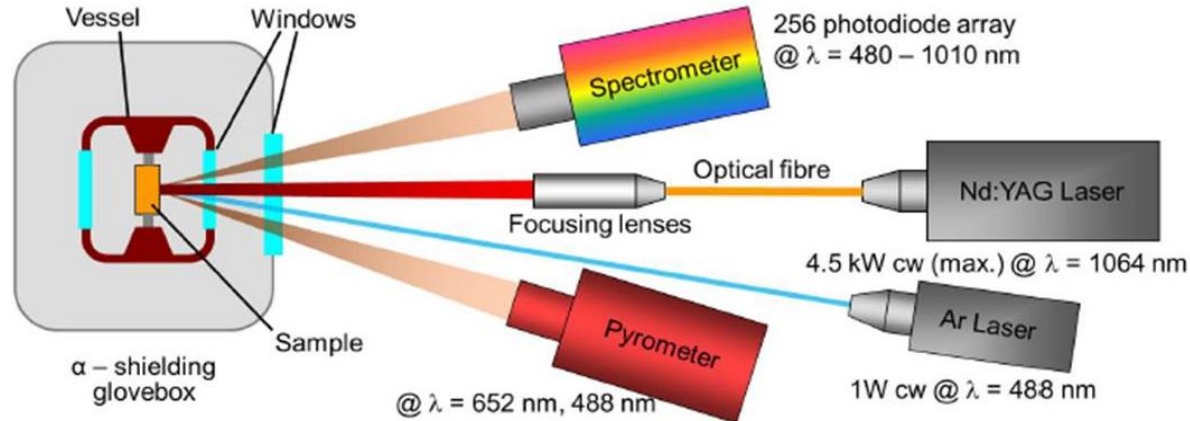
LASER HEATING SETUP

- Rapid measurements
- High power → High temperature
- Containerless
- Reducing/oxidising atmosphere
- T_{solidus} (Böhler et al.)

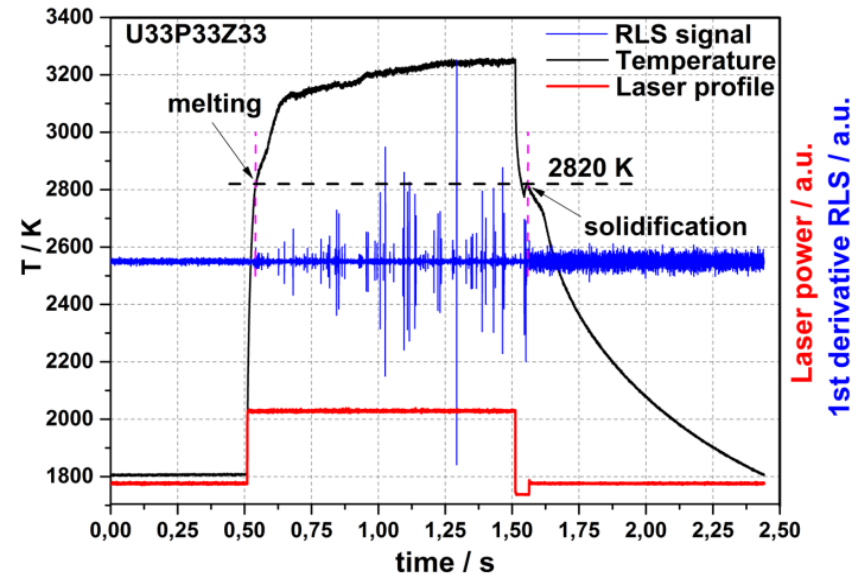
→ Oxygen potential is not controllable



ITU's Laser heating setup

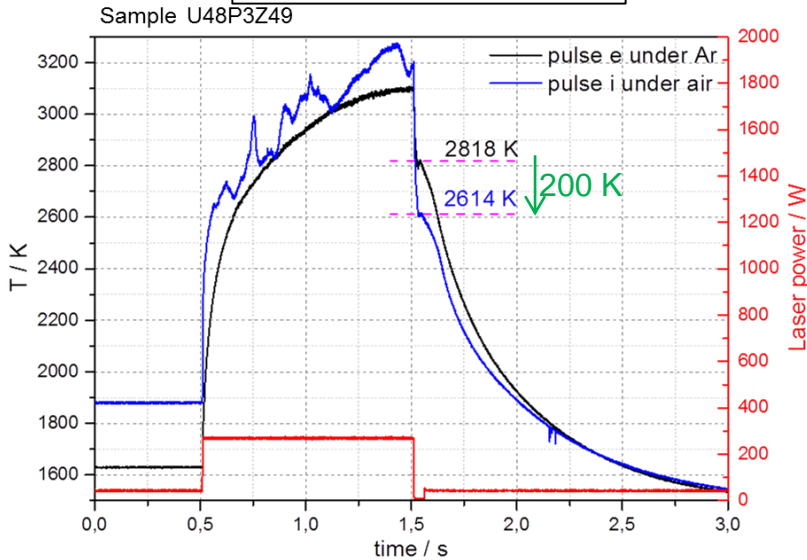


Manara et al., Rev. Sci. Instrum. 2008

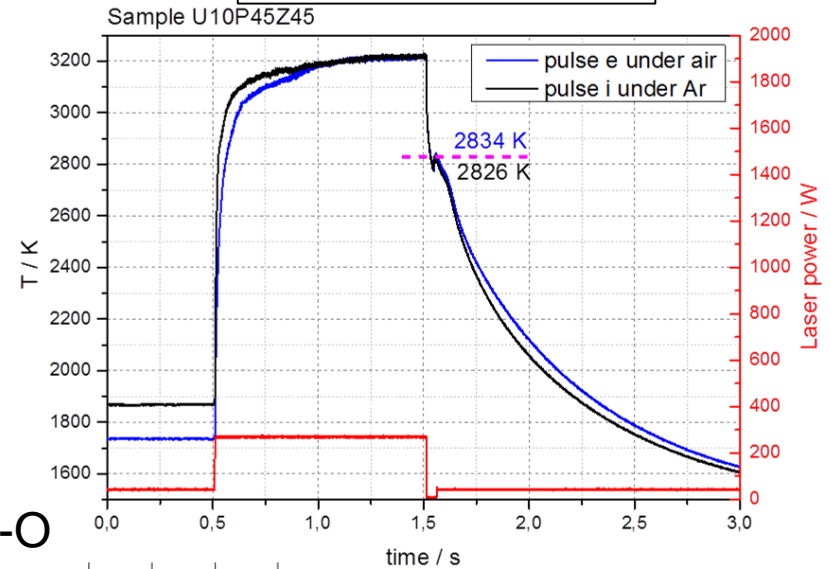


UO₂-PuO₂-ZrO₂ – EXPERIMENTAL RESULTS

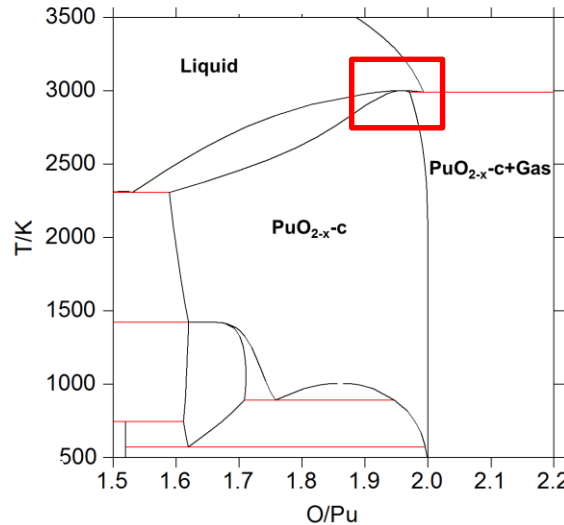
UO₂-rich sample



PuO₂-rich sample



Pu-O



$T_{air} < T_{Ar}$
large spread under air



Composition of the molten pool
moved towards O/M > 2

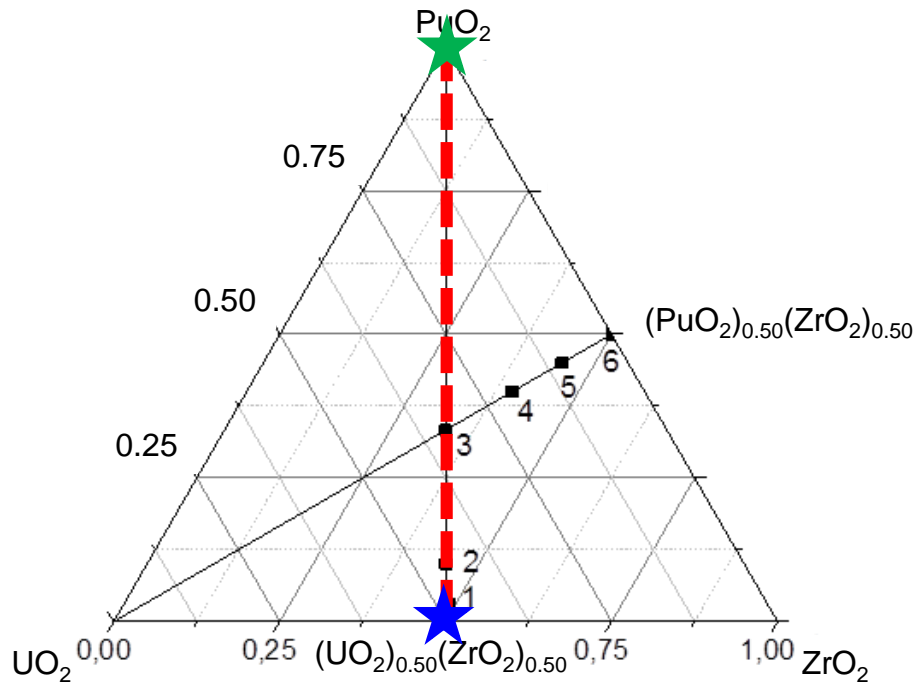
Experimental atmosphere
has a significant influence

$T_{air} \approx T_{Ar}$

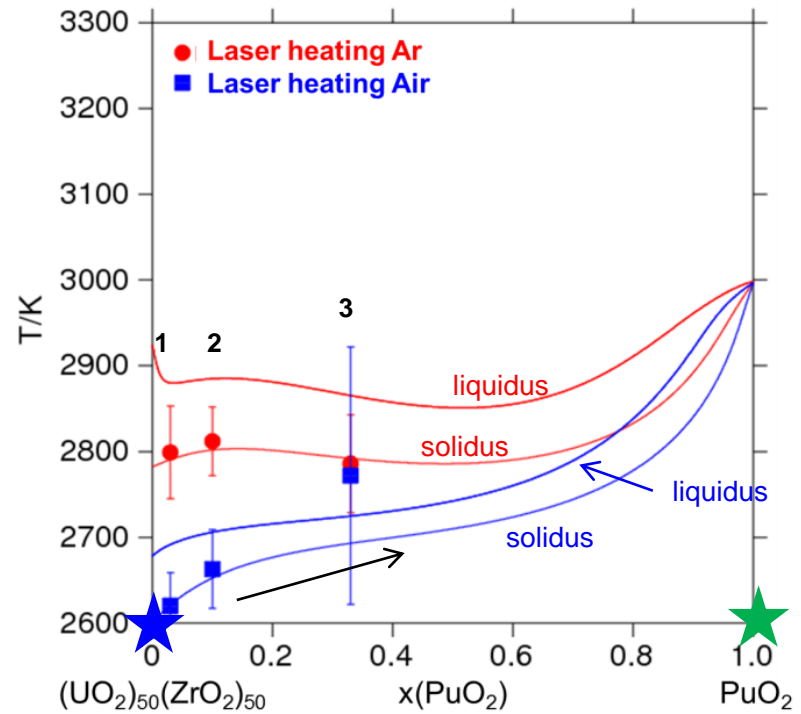


Experimental atmosphere
has a weaker effect

Calculations by extrapolation from the quaternary U-Pu-Zr-O system

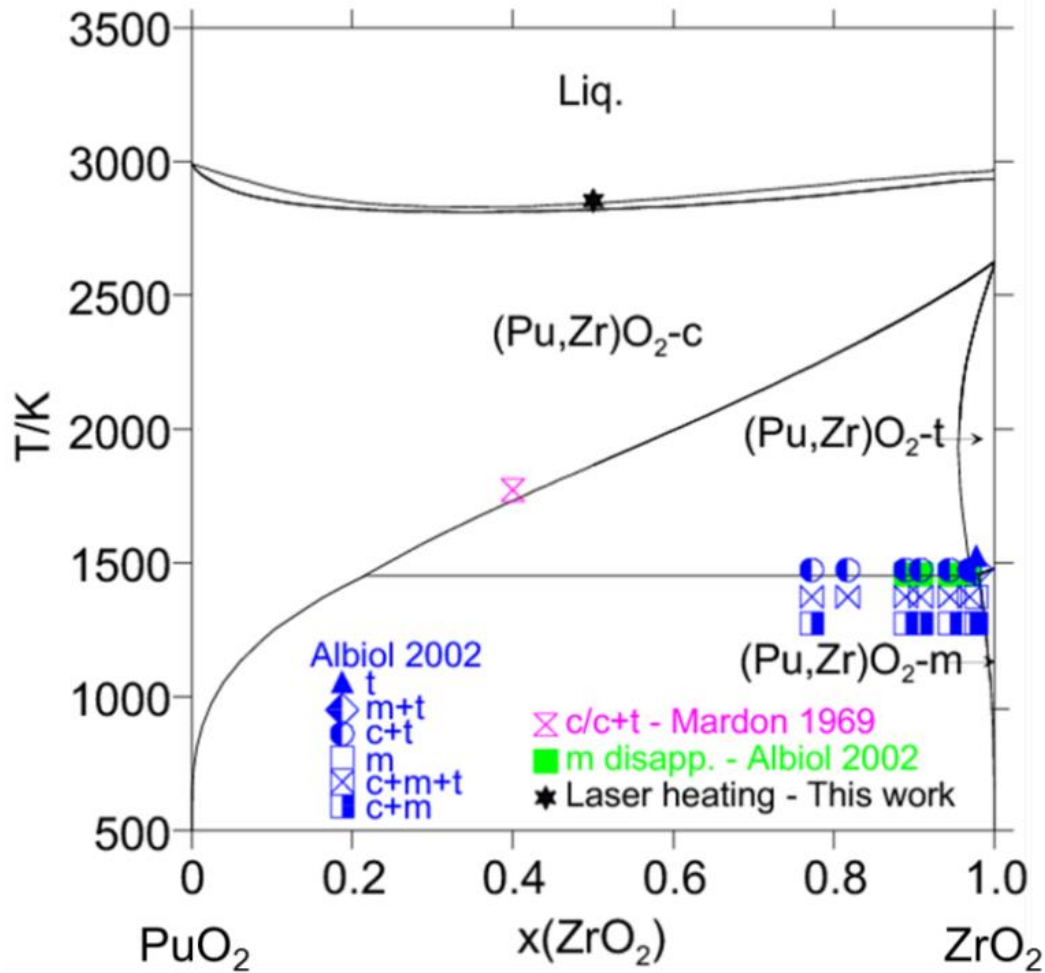


Solidus and liquidus temperatures



Oxidising and Reducing conditions → Excellent agreement with samples 1 and 2

Oxidising conditions → $T_{\text{solidus}} \uparrow$ adding PuO₂



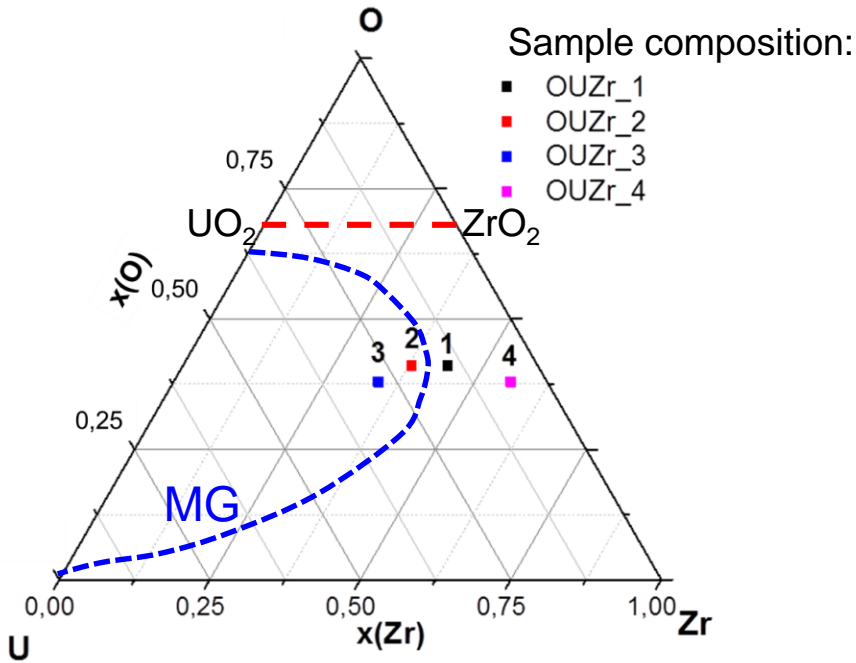
Contribution to the understanding of the high temperature thermodynamics of the U-Pu-Zr-O system

U-Zr-O and U-Zr-O-Fe systems

→ Experimental results: U-Zr-O

→ Calculations: U-Zr-O and U-Zr-Fe-O

→ Summary



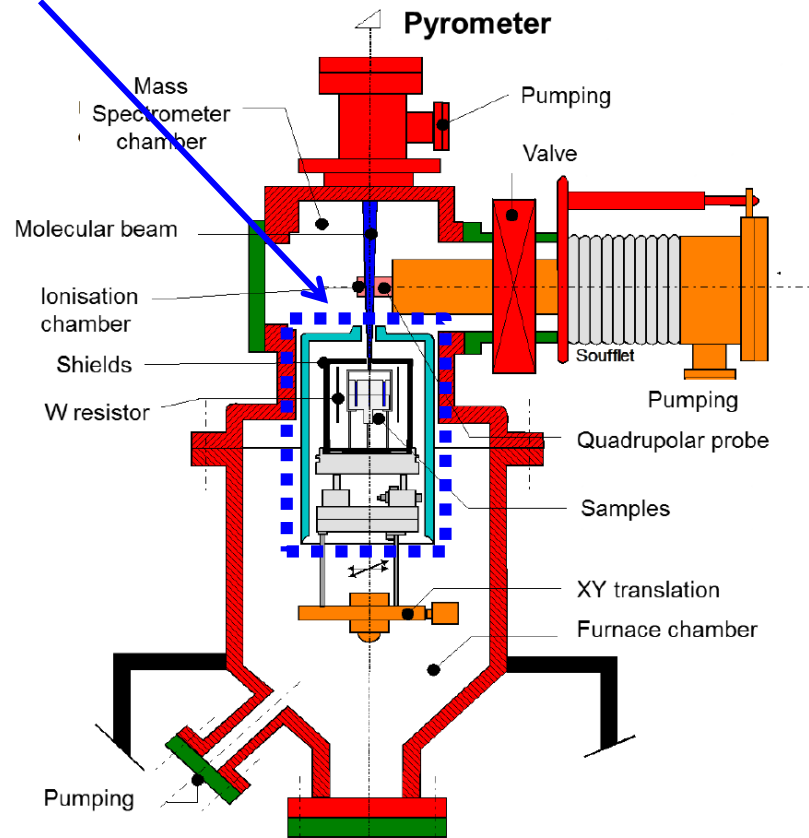
Heat treatment at 2567 K for 45 minutes

SEM-EDS/WDS analyses at CEA Marcoule

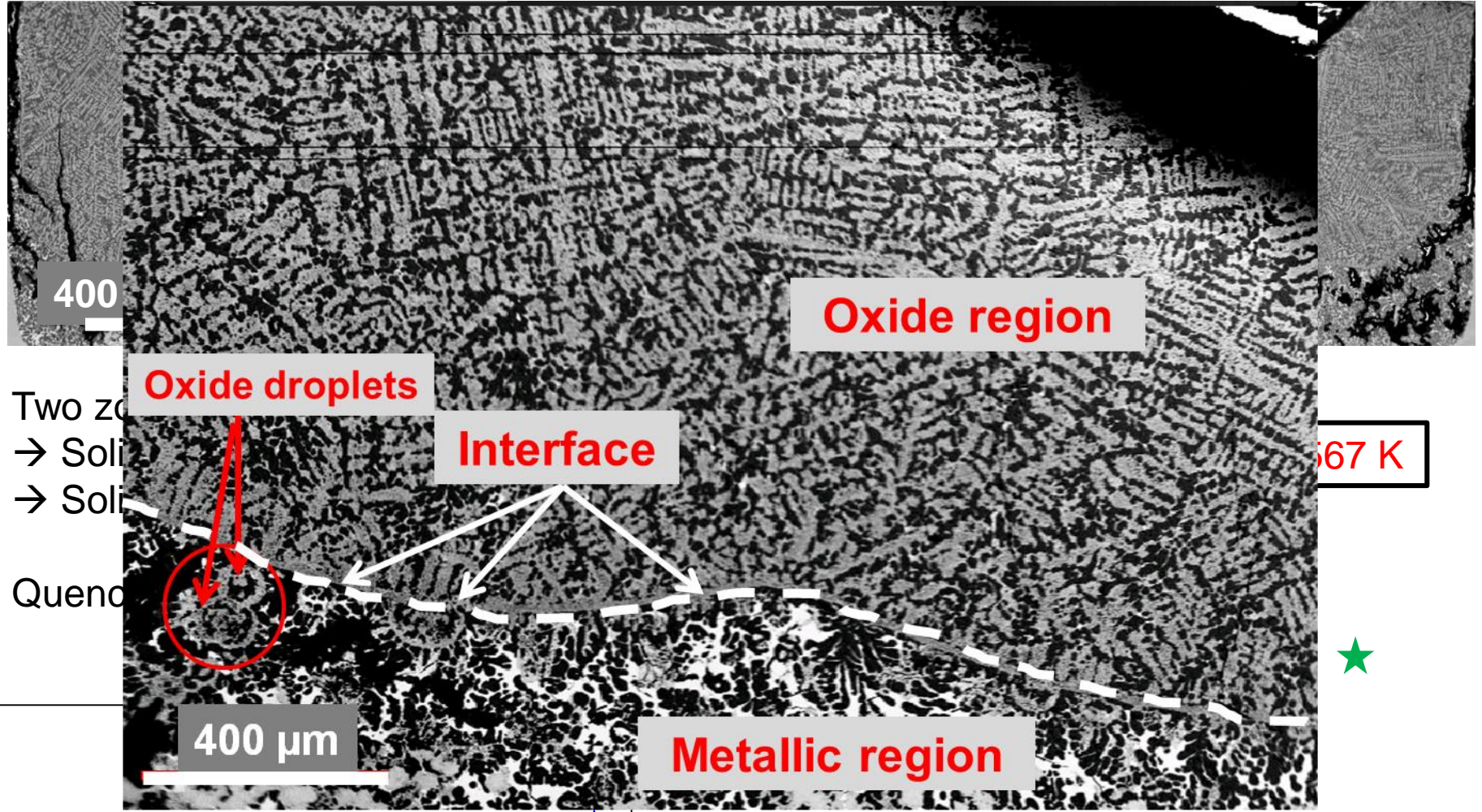
OUZr_2 and OUZr_3 → Miscibility gap

- Starting materials: U, Zr, ZrO_2 (in-situ fabrication)
- W crucible

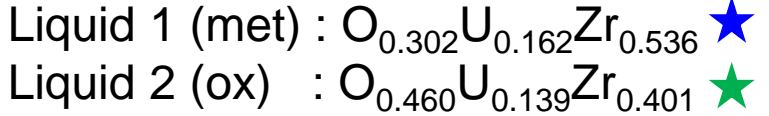
Joule effect furnace
Secondary vacuum



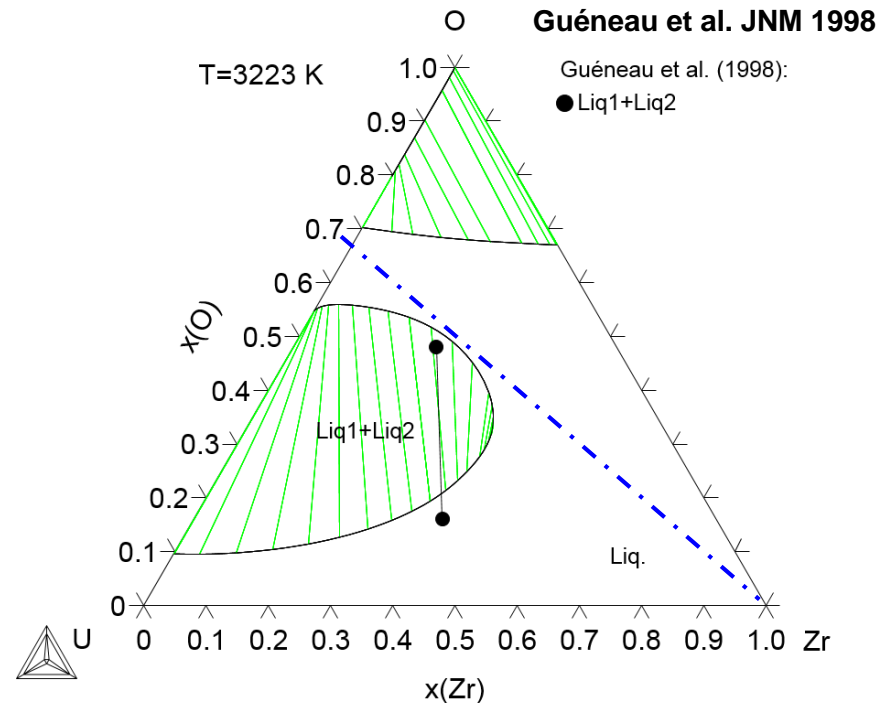
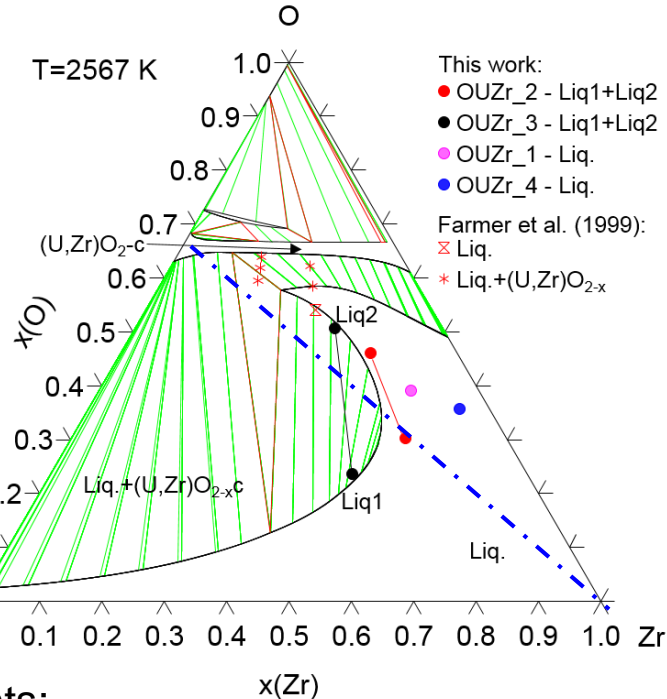
MISCIBILITY GAP IN THE U-Zr-O SYSTEM



Two zones
 → Solid
 → Solid
 Quenched

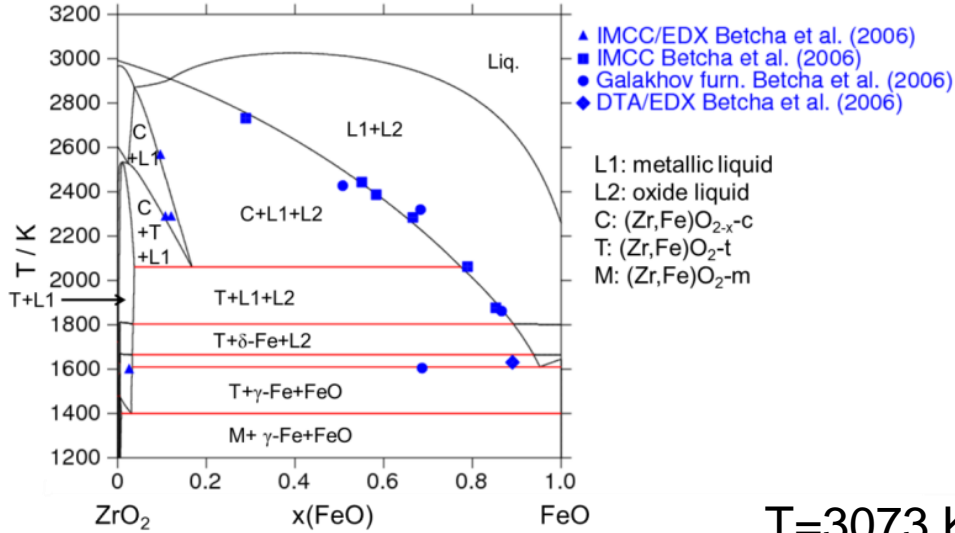


Calculated isothermal sections



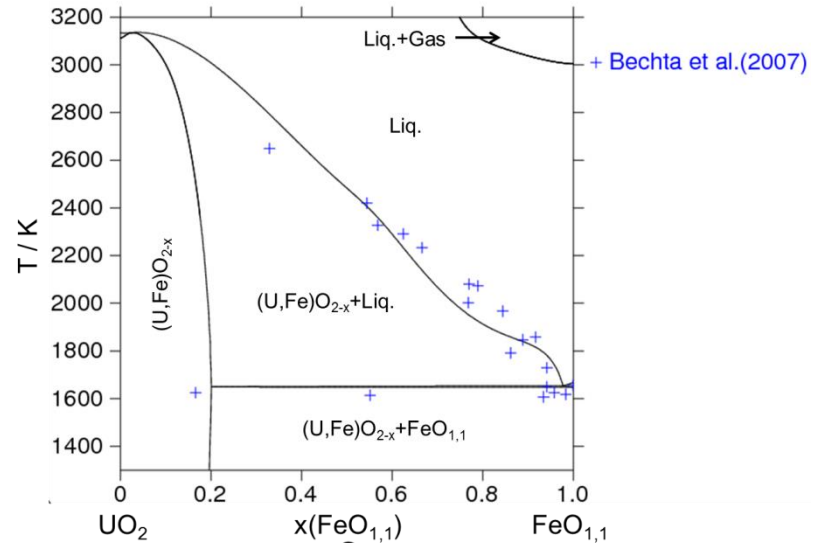
- Reassessment of the U-Zr-O system - *Quaini et al. JNM 501 (2018) 104-131*
- Tie-lines at 2567 K → **improvement of the description of the miscibility gap in the liquid phase**
- Good agreement between calculations and experimental results
- MG exists between ~2450 K and ~3100 K along the **UO₂-Zr** section

Fe-Zr-O



T=3073 K

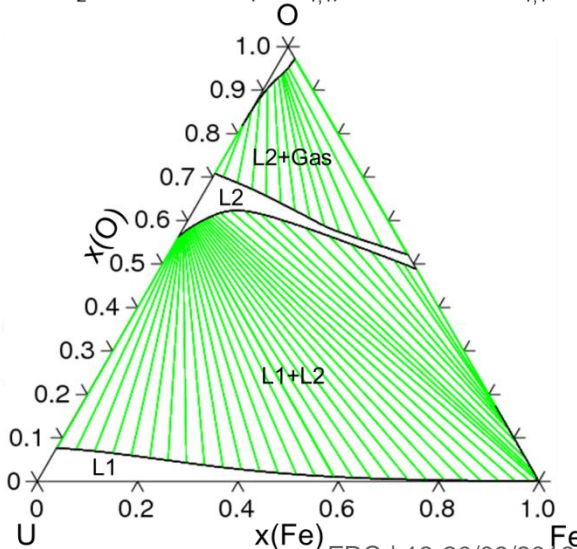
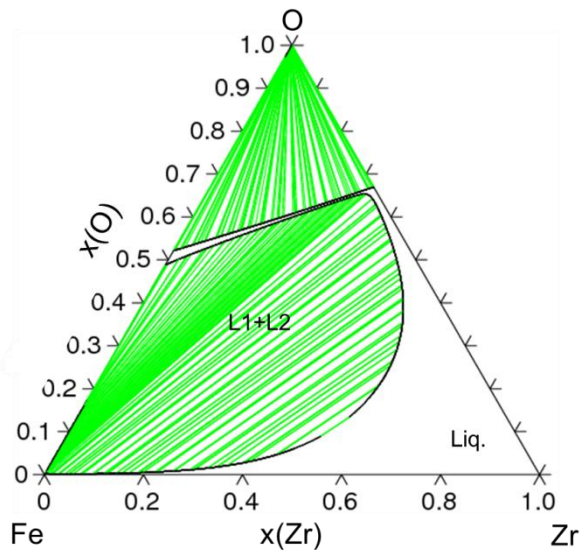
Fe-U-O



Existence of a MG

Fe-Zr-O, Fe-U-O

NO EXP DATA



TAF-ID database

Application calculations

Prototypic in-vessel corium system: U-Pu-Zr-Fe-O

10 binaries sub-systems → TAF-ID database

10 ternaries sub-systems

System		Existent ternary experimental data
Fe-Pu-U	Extrapolation from binaries	
Fe-Pu-Zr	Extrapolation from binaries	
Fe-U-Zr	N. Dupin (TAF-ID database)	
Pu-U-Zr	Extrapolation from binaries	
O-Fe-Pu	Extrapolation from binaries	
O-Fe-U	Quaini, PhD thesis (2015)	UO ₂ -FeO
O-Fe-Zr	Quaini, PhD thesis (2015)	ZrO ₂ -FeO; ZrO ₂ -Fe ₂ O ₃
O-Pu-U	Guéneau et al. JNM 419 (2011)	
O-Pu-Zr	Quaini, PhD thesis (2015)	PuO ₂ -ZrO ₂
O-U-Zr	Quaini et al. JNM 501 (2018) Quaini et al. JNM 509 (2018)	UO ₂ -Zr; UO ₂ -Zr(O); MG tie-lines

Application to a simplified in-vessel corium : $UO_2-ZrO_2+steel$

Miscibility gap in liquid in-vessel corium:

$$\rho_{metallic} < \rho_{oxide}$$

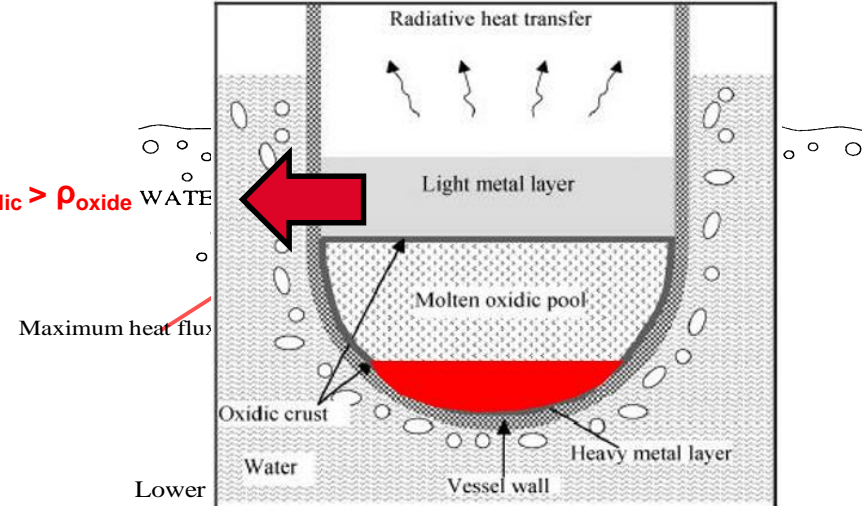


Degree of oxidation of zirconium
U/Zr ratio
Amount of molten steel



$$\rho_{heavy\ metallic} > \rho_{oxide}$$

Thickness of upper metallic layer ↓
→ Enhanced focusing effect
→ Failure of the reactor vessel



Application to a simplified in-vessel corium : UO_2 -Zry+steel

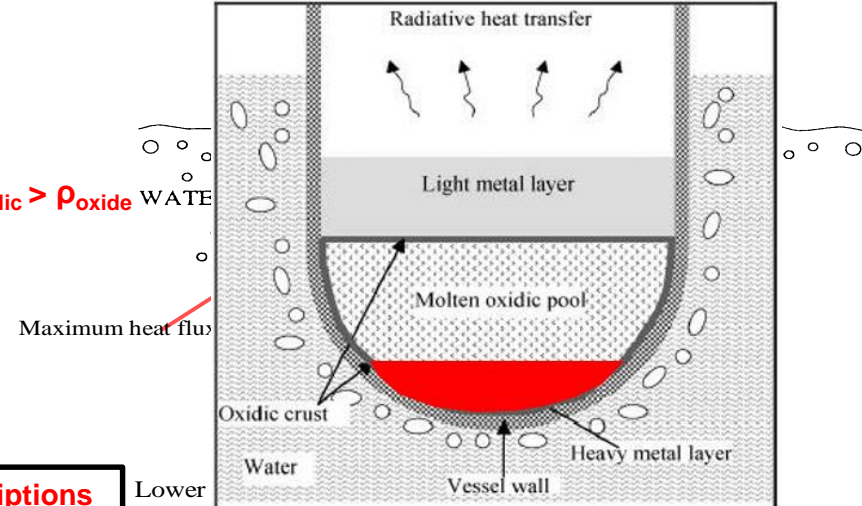
Miscibility gap in in-vessel corium:

$\rho_{\text{metallic}} < \rho_{\text{oxide}}$ → Degree of oxidation of zirconium
U/Zr ratio
Amount of molten steel

→ $\rho_{\text{heavy metallic}} > \rho_{\text{oxide}}$

Thickness of upper metallic layer ↓
→ Enhanced focusing effect
→ Failure of the reactor vessel

Calculations obtained by extrapolation (15) binary and (20) ternary descriptions



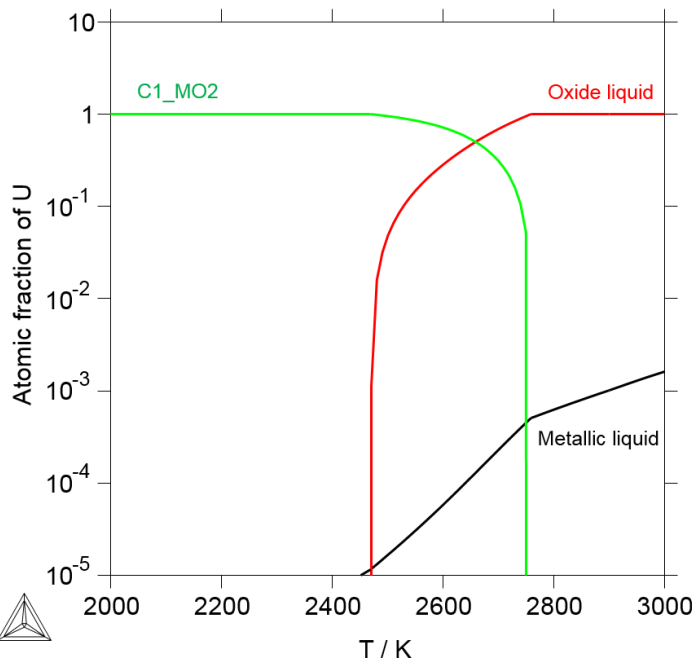
Corium E2	Oxide liquid		Metallic liquid		
	Overall	Exp.	TAF-ID	Exp.	TAF-ID
Weight %		50	49.4	50	50.6
U	30.0	61.0	60.7	<0.6	0.03
Zr	9.3	19.8	18.8	<0.4	0.005
Fe	37.9	1.2	2.8	70.0	72.2
Ni	5.4	<0.2	0.0006	12.0	10.7
Cr	9.3	2.2	1.6	16.2	16.8
O	8.1	15.1	16.1	0.5	0.3

Corium A1	Oxide liquid		Metallic liquid		
	Overall	Exp.	TAF-ID	Exp.	TAF-ID
Weight %		68	69.7	32	30.3
U	60.4	67.3	66.3	45.6	46.9
Zr	17.3	17.8	20.7	16.4	9.5
Fe	9.7	1.8	0.20	26.6	31.5
Ni	1.5	0.3	0.0001	4.1	4.9
Cr	2.2	0.5	0.09	5.9	7.1
O	8.9	12.3	12.8	1.4	0.05

Application to a simplified in-vessel corium : UO_2 -Zry+steel

Corium E2	Oxide liquid		Metallic liquid		
	Overall	Exp.	TAF-ID	Exp.	TAF-ID
Weight %		50	49.4	50	50.6
U	30.0	61.0	60.7	<0.6	0.03
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Fe	37.9	1.2	2.8	70.0	72.2
Ni	5.4	<0.2	0.0006	12.0	10.7
Cr	9.3	2.2	1.6	16.2	16.8
O	8.1	15.1	16.1	0.5	0.3

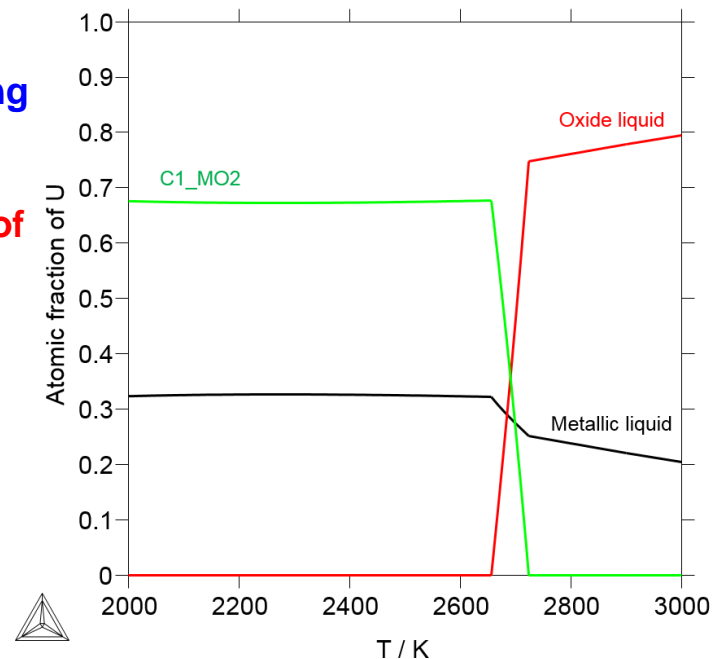
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O	8.9	12.3	12.8	1.4	0.05



Different behaviour during stratification

Concentration of U (and minor actinides) in liquid phases

Re-criticality



Advanced Temperature and Thermodynamics Investigation by a Laser Heating Approach



Development of a versatile experimental setup

ATTILHA

Aerodynamic levitation

Containerless measurements

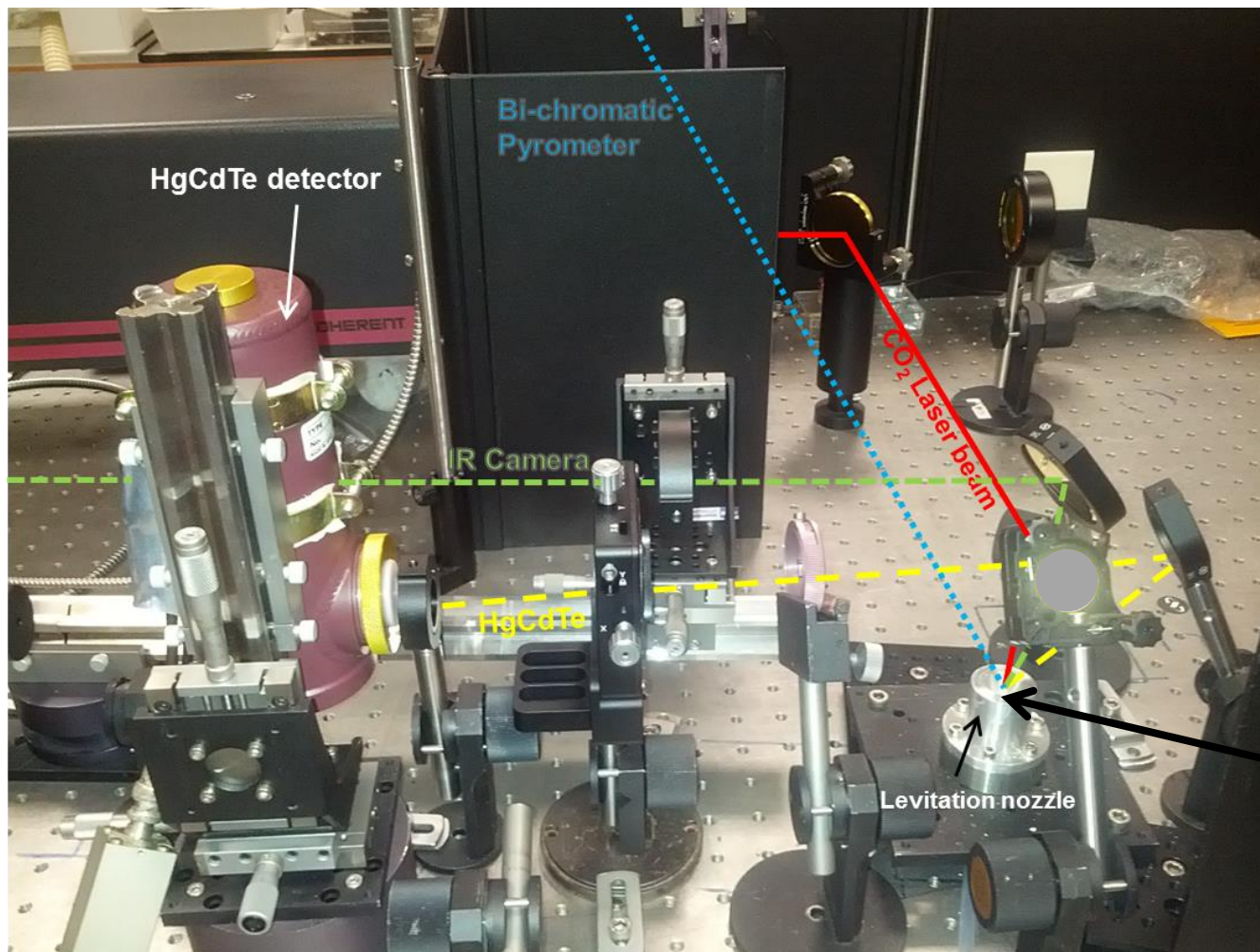


Experimental data at high temperature ($T > 2300$ K) on complex systems

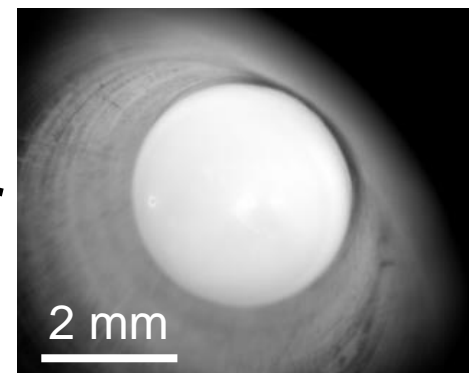


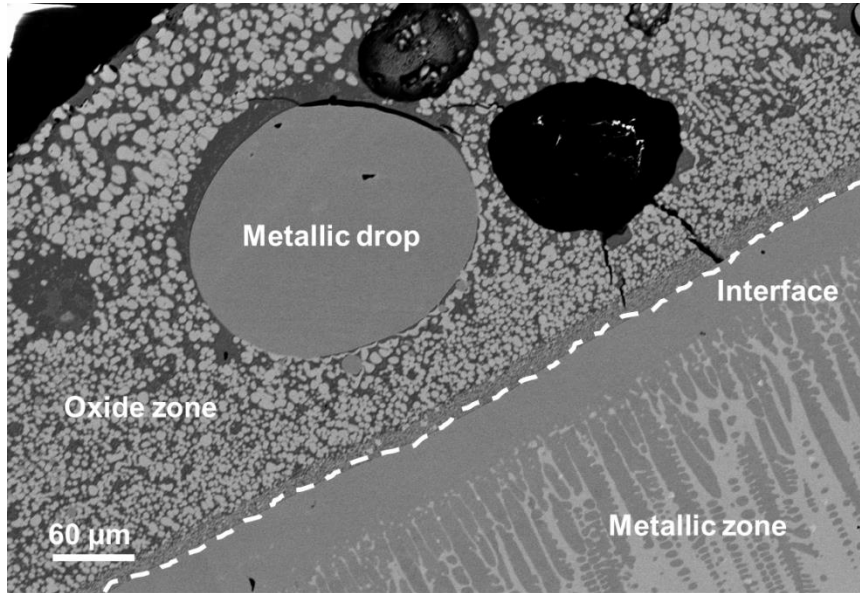
Phase diagram data (liquidus, solidus, eutectics)
Thermo-radiative properties (emissivity)
Thermo-physical data (surface tension, density)

ATTILHA setup



Levitating Al₂O₃ droplet in the Al-nozzle





New result

Starting composition: $\text{Fe}_{0.85}\text{Zr}_{0.15}$

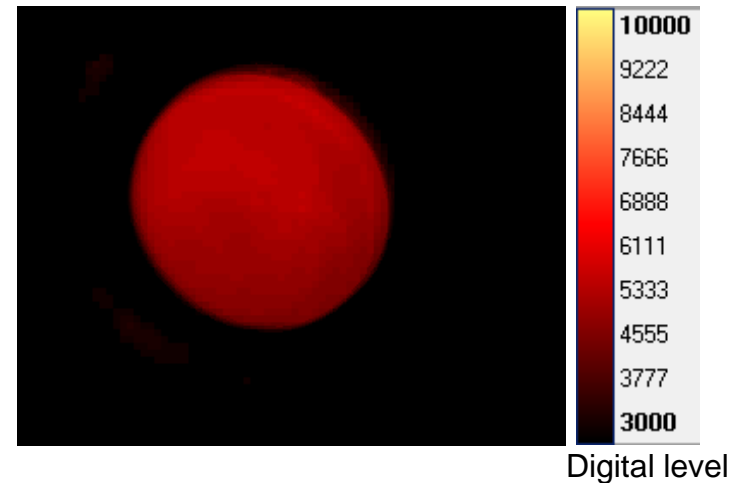


Levitation gas: He

Composition moved into the ternary Fe-Zr-O system

tie-line: $\text{Fe}_{0.97}\text{O}_{0.03} - \text{Fe}_{0.05}\text{Zr}_{0.32}\text{O}_{0.63}$

Infrared camera footage



Acquisition 200 Hz

Video player 12.5 Hz

Observation of dynamic phenomena:

→ **Formation of 2 liquids in-situ**

Estimation of the emissivity ratio between the two liquids

→ $\epsilon_{\text{oxide}} \sim 2\epsilon_{\text{metal}}$

Thermodynamic database for corium compositions

Calphad approach : experiments + calculation

Contribution to the U-Pu-Zr-Fe-O system thermodynamic description

→ Experimental results have been obtained

* $\text{UO}_2\text{-PuO}_2\text{-ZrO}_2$

* U-Zr-O

* Fe-Zr-O

→ Needs for further results to build a fully reliable database

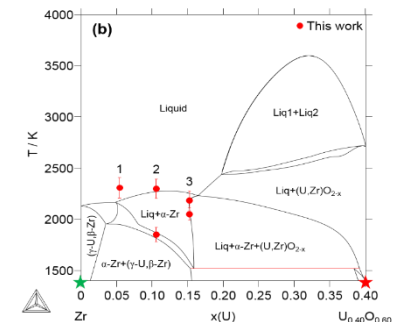
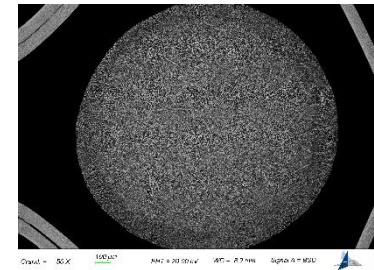
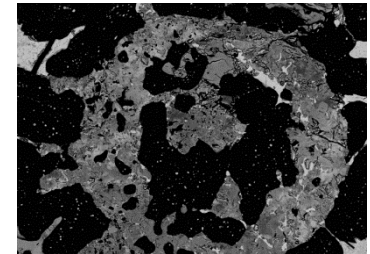
TAF-ID database

→ Thermodynamic calculations on complex systems

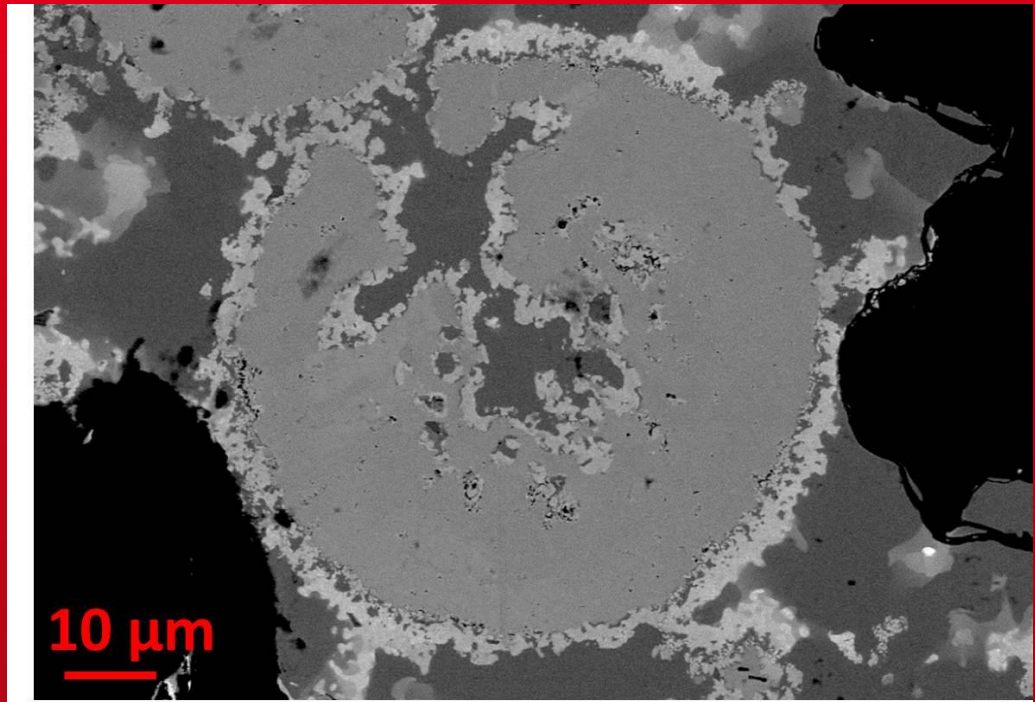
Development of a dedicated experimental setup: ATTILHA

→ Containerless

→ Contactless (i.e., aerodynamic levitation)



THANK YOU FOR YOUR ATTENTION



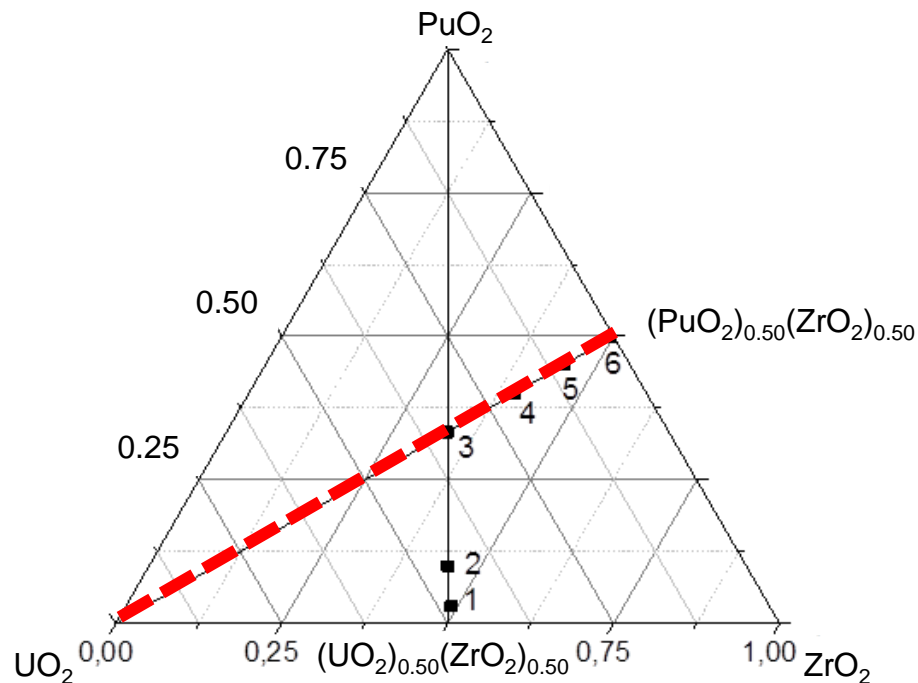
Commissariat à l'énergie atomique et aux énergies alternatives
Centre de Saclay | 91191 Gif-sur-Yvette Cedex
T. +33 (0)1 69 08 21 70 | F. +33 (0)1 69 08 92 21

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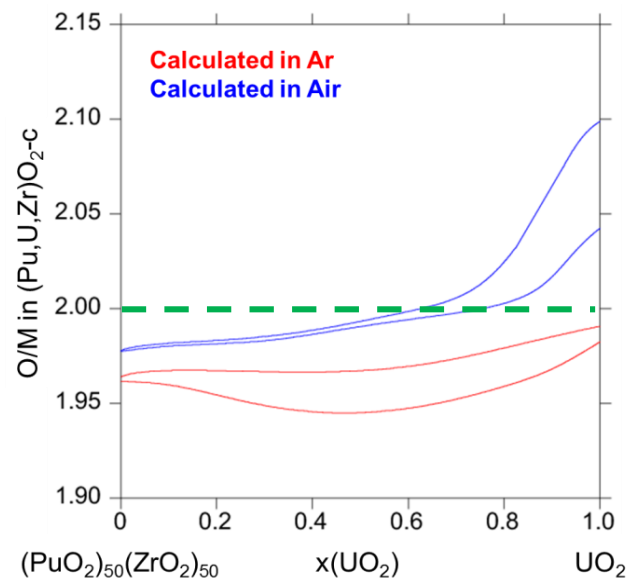
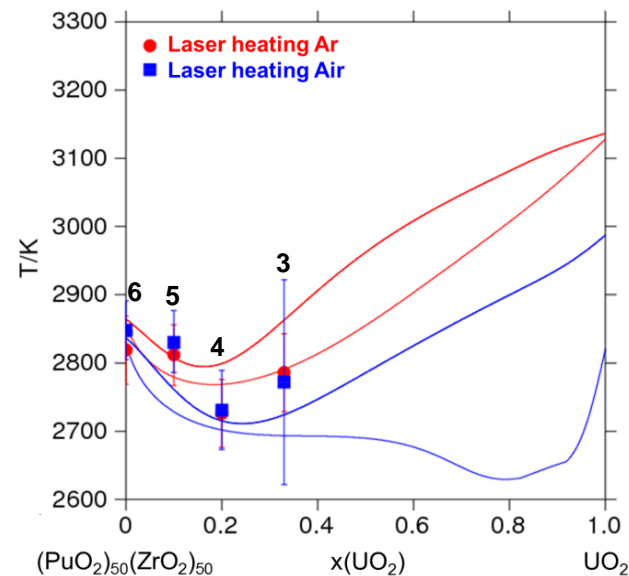
Direction de l'Énergie Nucléaire
Département de Physico-Chimie
SCCME
Laboratoire de Modélisation
Thermodynamique et Thermochimie
CEA de Saclay

cea den UO₂-PuO₂-ZrO₂ SYSTEM – CALCULATION RESULTS

Calculations by extrapolation from the quaternary U-Pu-Zr-O system



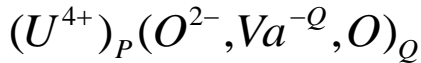
Oxidising conditions → solidus approaching UO₂ corner
 → O/M in (Pu,U,Zr)O_{2±x}



Liquid phase

Two ionic sublattice model

Adapted to describe both metallic and oxide liquids



$$G_m^{Liq} = {}^{ref}G_m^{Liq} + {}^{ideal}G_m^{Liq} + {}^{excess}G_m^{Liq}$$

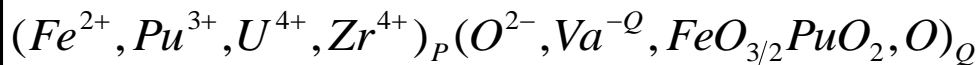
$${}^{ref}G_m^{Liq} = y_{U^{4+}} y_{Va} G_{(U^{4+})_1(Va)_4}^0 + y_{U^{4+}} y_{O^{2-}} G_{(U^{4+})_2(O^{2-})_4}^0 + y_{U^{4+}} y_O G_O^0$$

$${}^{ideal}G_m^{Liq} = QRT(y_{O^{2-}} \ln y_{O^{2-}} + y_{Va} \ln y_{Va} + y_O \ln y_O)$$

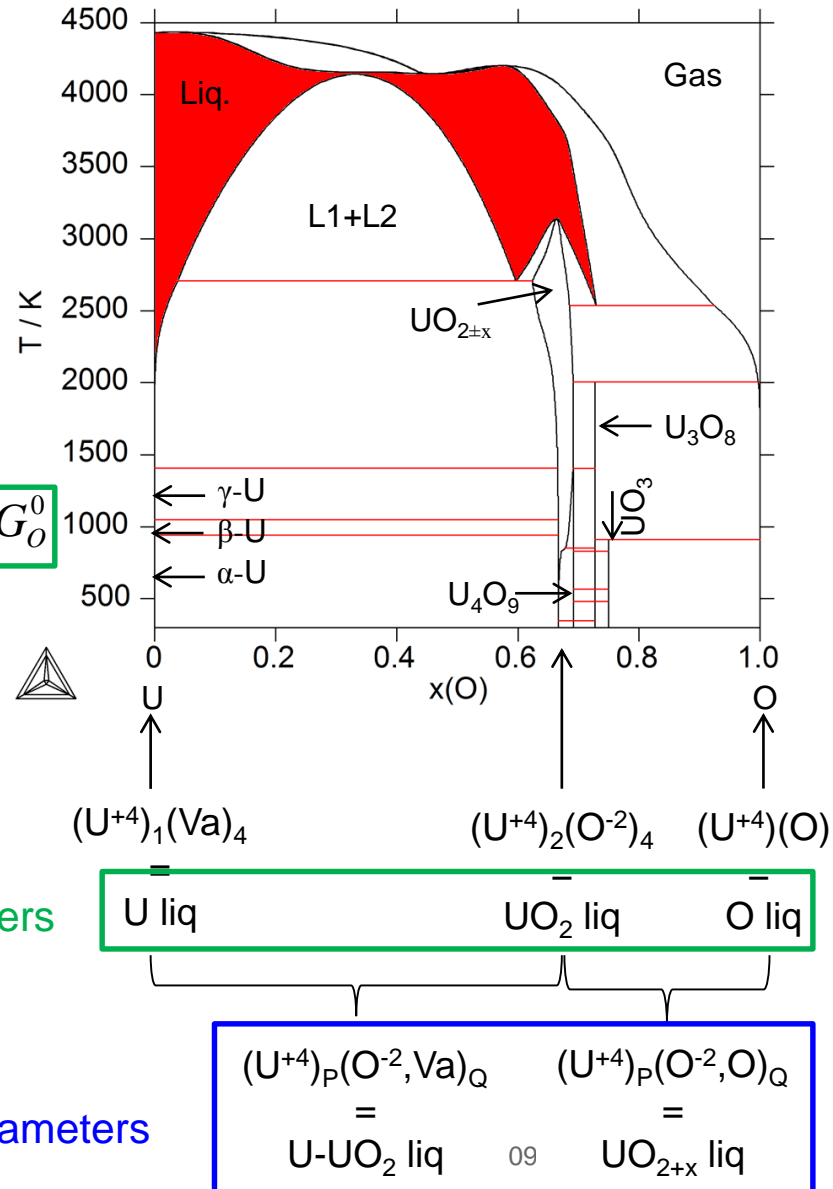
$${}^{excess}G_m^{Liq}$$

In-vessel corium liquid

Endmembers



Interaction parameters

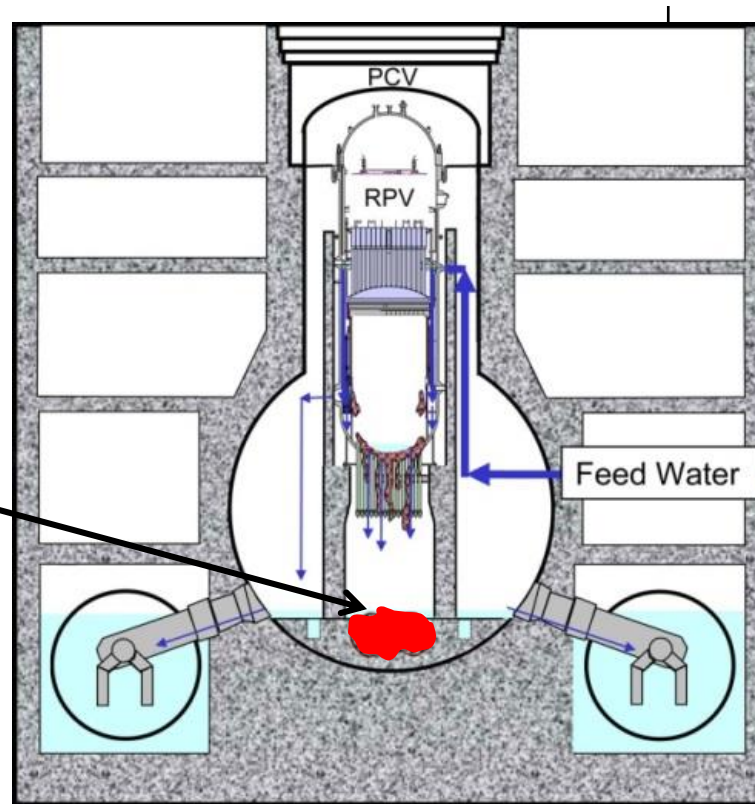


Ex-vessel scenario: Application to the interaction in-vessel corium/concrete

→ Reactor steel vessel failure

Fukushima Unit 1

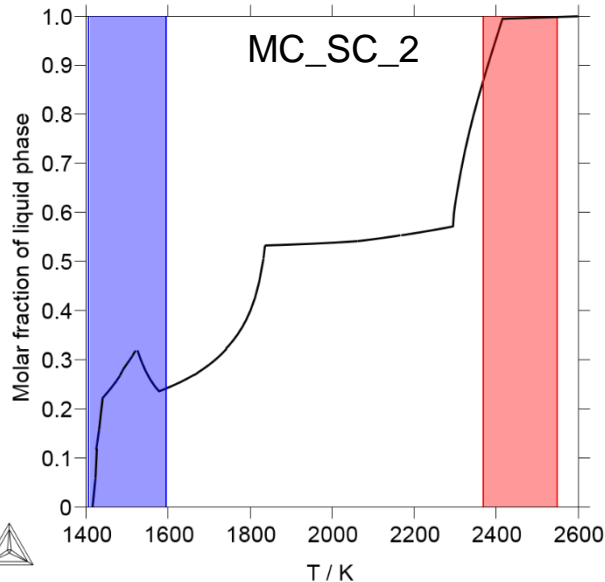
Corium/concrete interaction



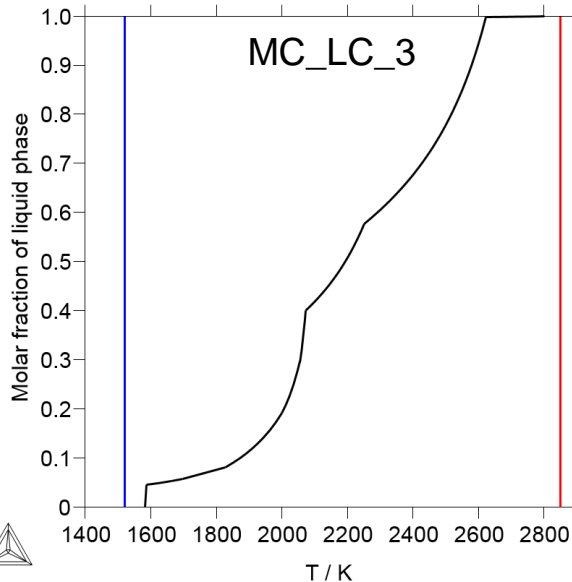
Ex-vessel scenario: Application to the interaction in-vessel corium/concrete

Calculations obtained by extrapolation from (28) binary, (56) ternary, 7 quaternary and 1 quinary descriptions

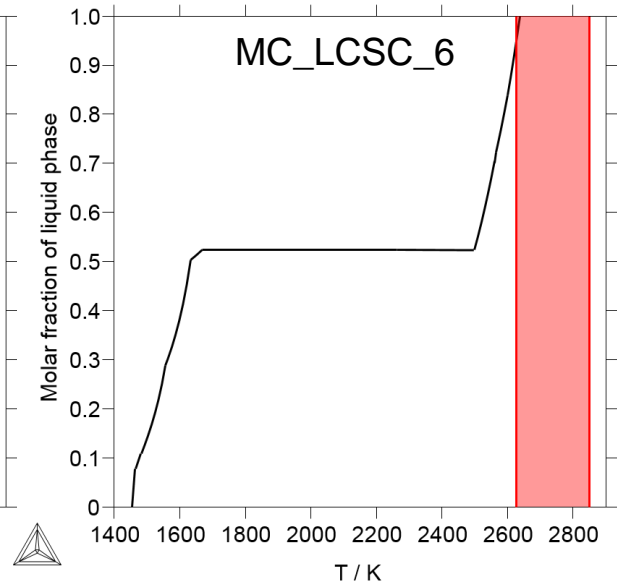
	Concrete type	Weight %							Solidus / K		Liquidus / K	
		UO ₂	ZrO ₂	CaO	SiO ₂	Al ₂ O ₃	MgO	Fe ₂ O ₃	Exp.	TAF-ID	Exp.	TAF-ID
MC_SC_2	Siliceous	56.5	16	4.1	21.5	1.4	0.275	0.275	1407-1595	1422	2369-2549	2418
MC_LC_3	Limestone	56.6	15.9	19.5	3.3	0.8	3.6	0.3	1520	1584	>2850	2801
MC_LCSC_6	Mix	56.6	16	10.4	11.3	1.4	3.9	0.5	1360	1456	2628-2850	2642



Last melting phase: C1_MO2



Last melting phase: CaUO₄



Last melting phase: C1_MO2