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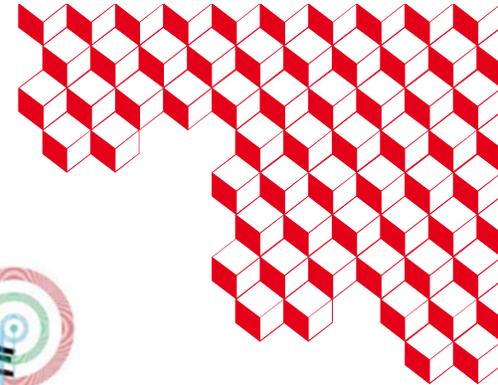
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X ray methods applied to corium material

E. Brackx¹, M. Jizzini^{1,2}, D. Menut³, P. Piluso⁴, R. Guinebretière²

¹ CEA, DES, ISEC, DMRC, Univ. Montpellier, Marcoule, France

² IRCER, Univ. Limoges, Limoges, France

³ Synchrotron SOLEIL, Ligne de lumière MARS, 91192 Gif-sur-Yvette, France

⁴ CEA, DES, IRESNE, DTN, Saint Paul lez Durance, France

EXRS, 24-28 June 2024



Corium formation with the severe nuclear accidents



Corium steam/water interaction:
specific solidification paths
(TMI-2, Chernobyl, Fukushima)

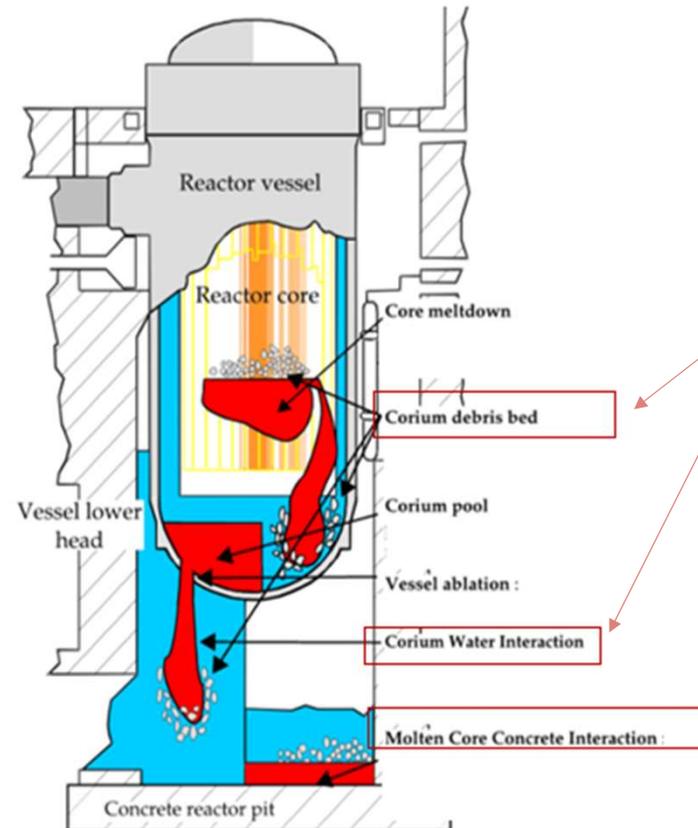
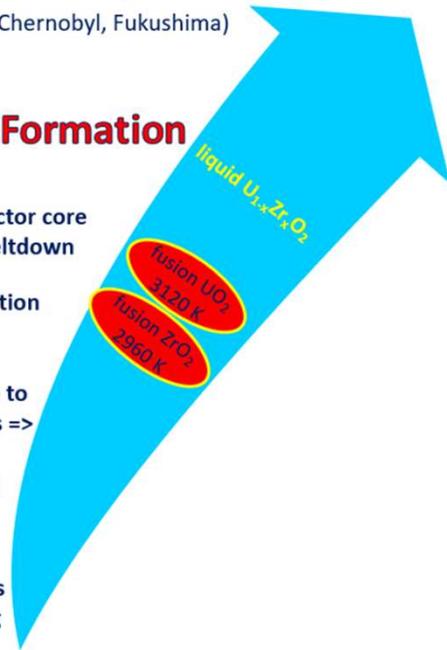
Corium Formation

Reactor core
meltdown

Steam formation

Decay heat due to
Fission Products =>
Increase of
temperature

Severe accidents
: Lost of Cooling



3 study parts

Corium-Water Interaction (ICE): formation of solid solutions $U_{1-x}Zr_xO_{2\pm y}$

Fuel Coolant Interaction : Severe Accident phenomenon including water corium interaction

1) Premixing

The melt is fragmented by hydrodynamic forces in coarse droplets.

2) Triggering

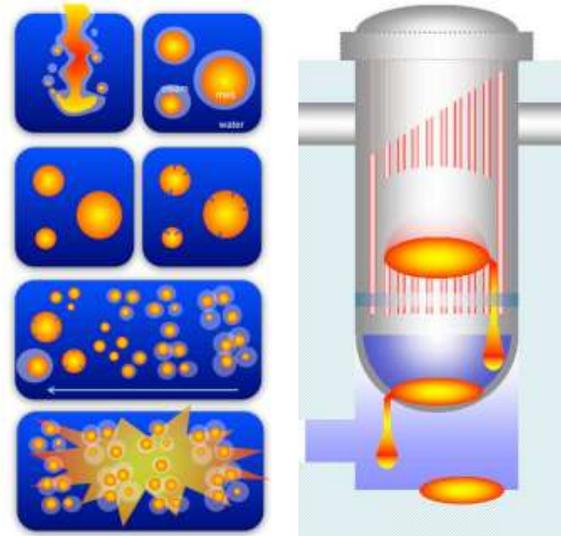
The melt is broken into fine droplets by thermal fragmentation.

3) Propagation

Thermal fragmentation process escalates through the premixed volume.

4) Explosion

the melt is finally transferred to the work of steam in a short time scale (few microseconds).

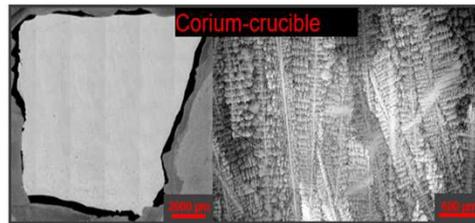
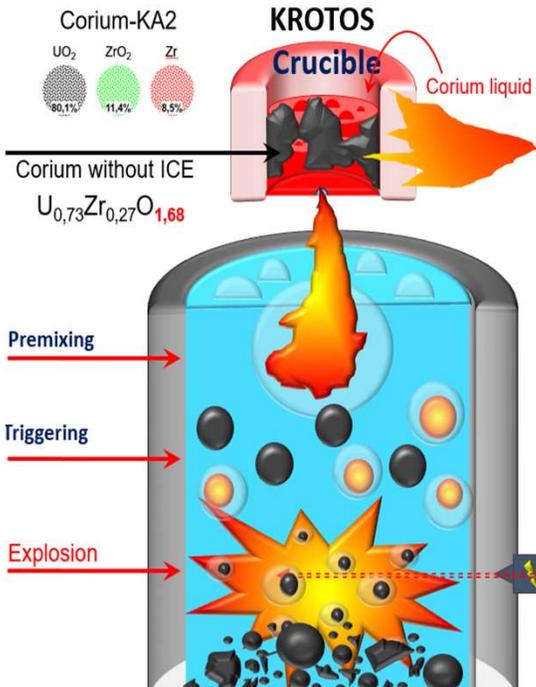


Corium-water (ICE) interaction/vapour explosion and prototypical corium formation $U_{1-x}Zr_xO_{2\pm y}$

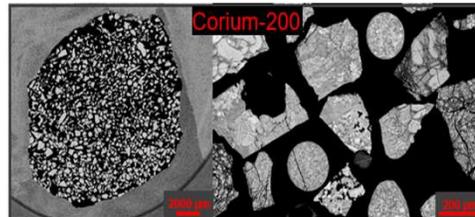


PLINIUS:

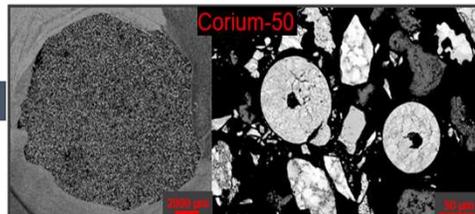
Experimental platform, located at the CEA Cadarache site



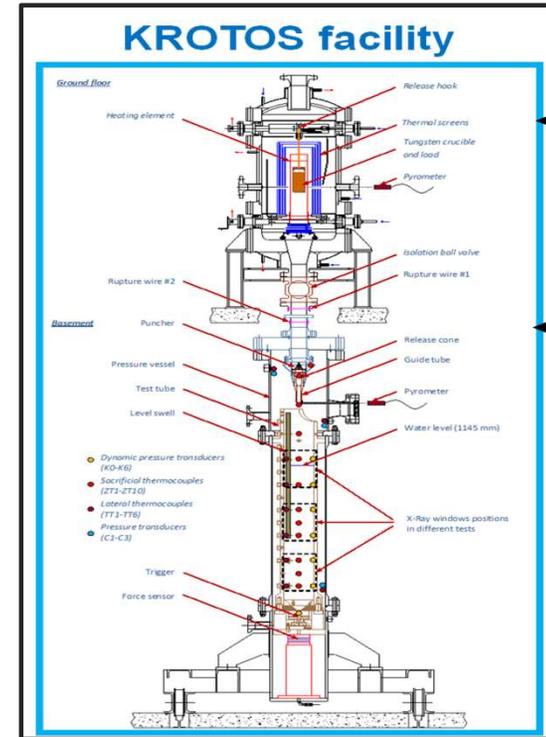
Residual material located into the crucible after the samples elaboration (a few minutes)



Corium powder formed after interaction with water: Pre-mixing, triggering, propagation without explosion (a few seconds)



Corium powder formed after interaction with water: Premixing, triggering, propagation then explosion (a few milliseconds).



Corium material analysis by EPMA and diffractions methods



X rays diffraction (HR-XRD),
(beam line MARS at
synchrotron SOLEIL)

Neutrons diffraction
(Line D2B at ILL)

Laue microdiffraction
(Beam line BM32 at l'ESRF)

Electron diffraction (SEM-EBSD)

Microanalysis (EPMA, CAMECA SX 100)



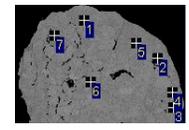
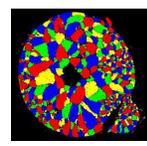
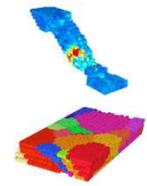
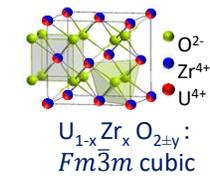
Cationic fluctuation
composition

Oxygen stoichiometry

Local deformation

Microstructure : size,
distribution and orientation of
crystals

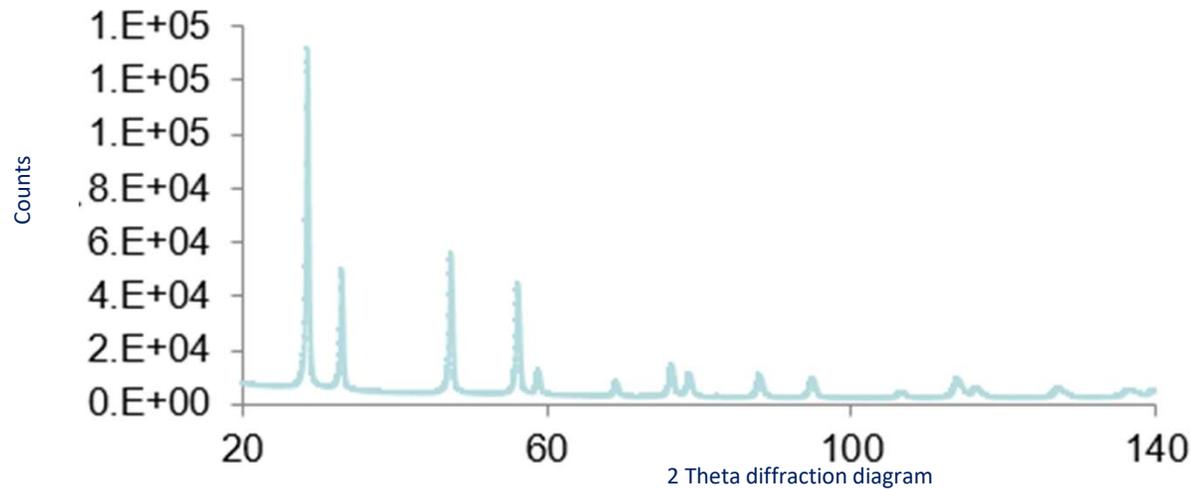
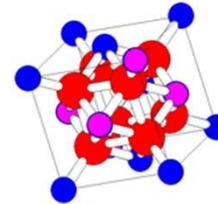
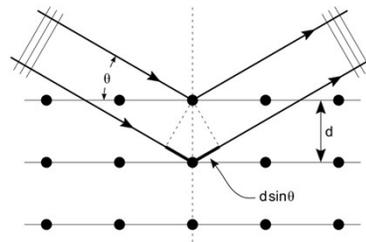
U Zr O local analysis



Structural material investigation

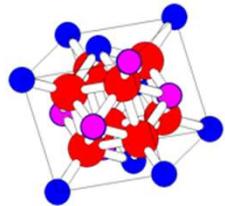
- X ray and neutron diffraction spectrometry: Technique for structural and microstructural investigation and cationic/ anionic composition.

$$n\lambda = 2d_{hkl} \sin \theta_{hkl}$$



Structural material investigation

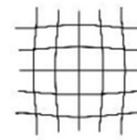
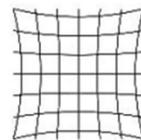
- X ray and neutron diffraction spectrometry : Technique for structural and microstructural investigation



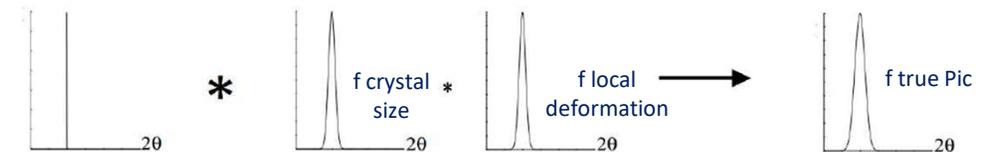
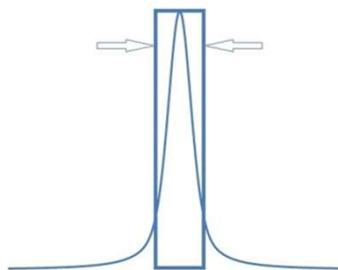
Chemical composition



Crystal size



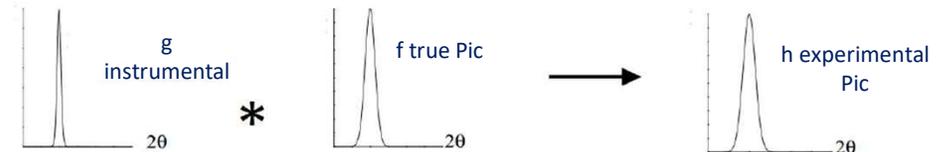
Local deformation



X ray Dirac Pic

Material effect

$$h(2\theta) = g(2\theta) * f(2\theta)$$



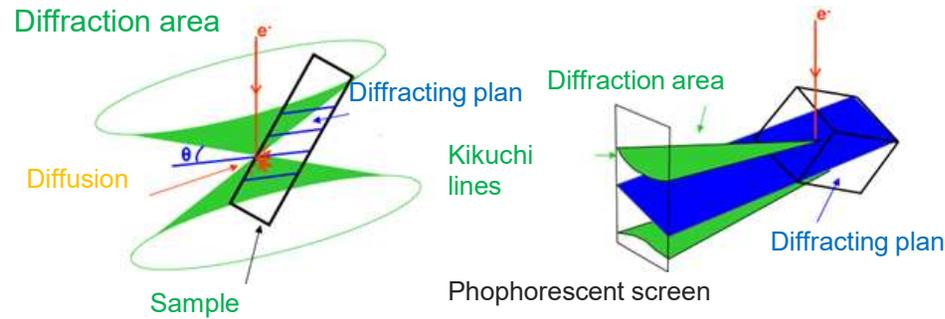
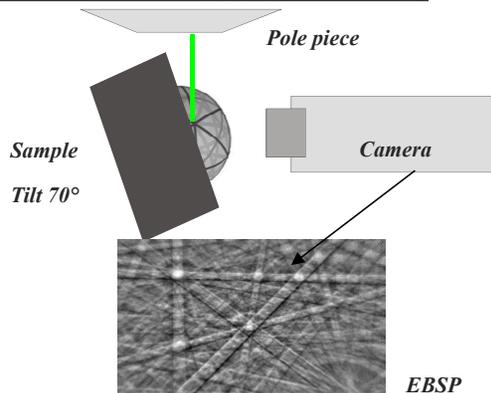
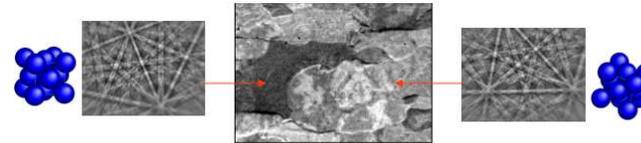
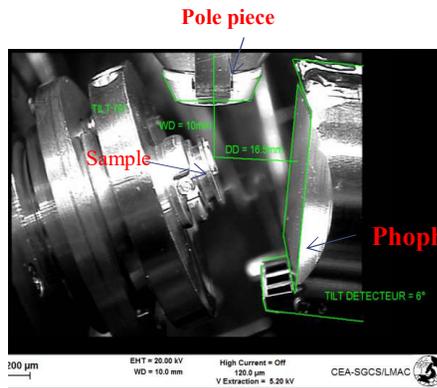
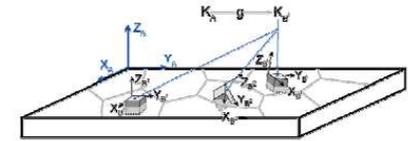
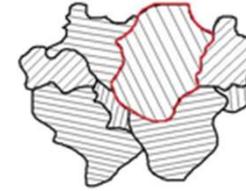
Instrumental effect



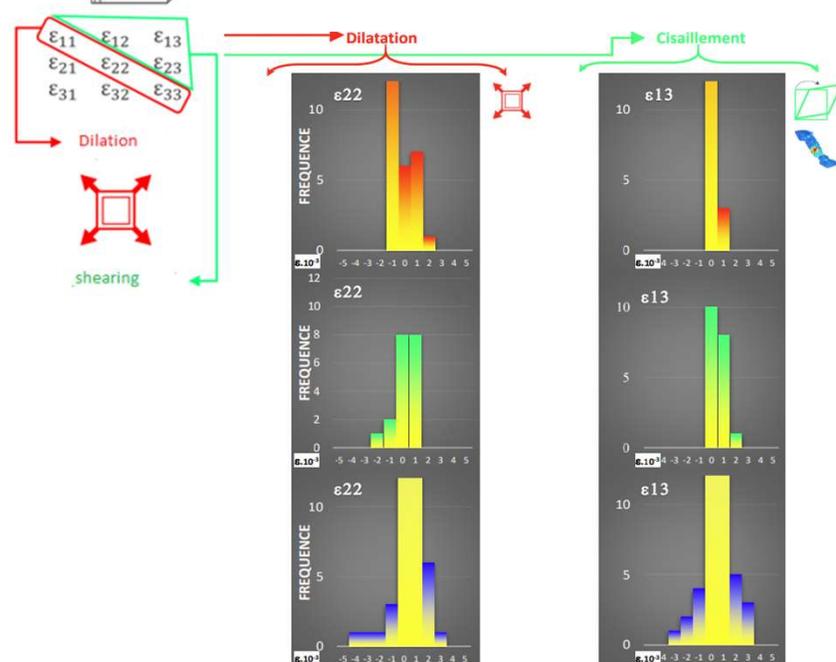
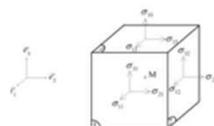
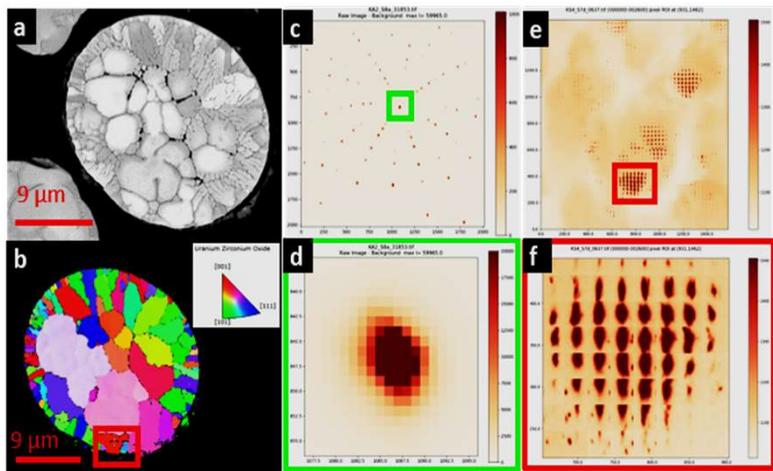
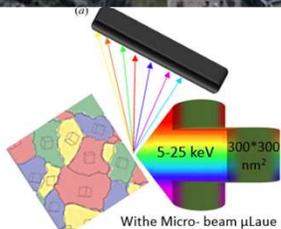
Micro texture material investigation

SEM/ EBSD

- Phase identification by kikuchi lines in the scale of μm
- Local area orientation of the grain and size



Micro texture material investigation



Microanalysis material composition by EPMA

Quantitative material composition results by EPMA

CAMECA SX100

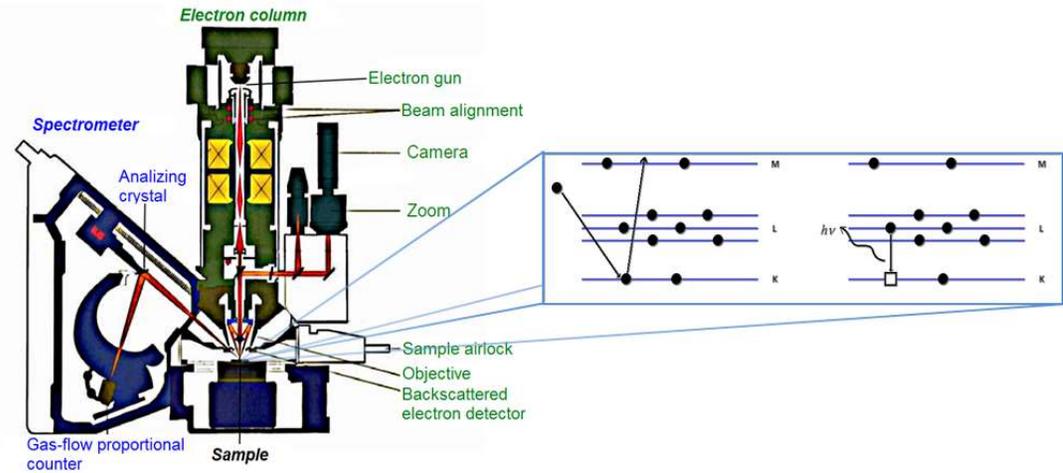
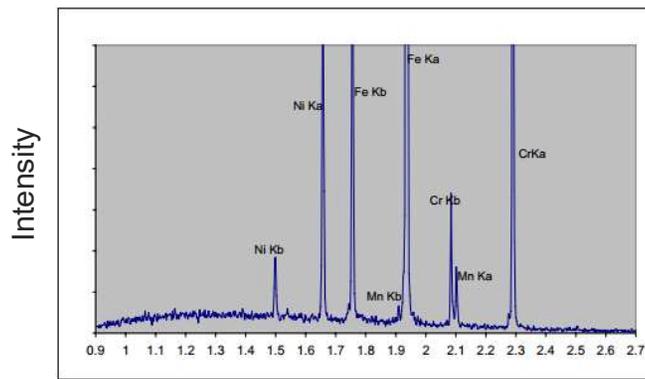


X-ray intensity measurement

X-ray emission was produced by interaction of the electron beam with the sample. The emitted photons were recorded with different wavelength-dispersive spectrometers.

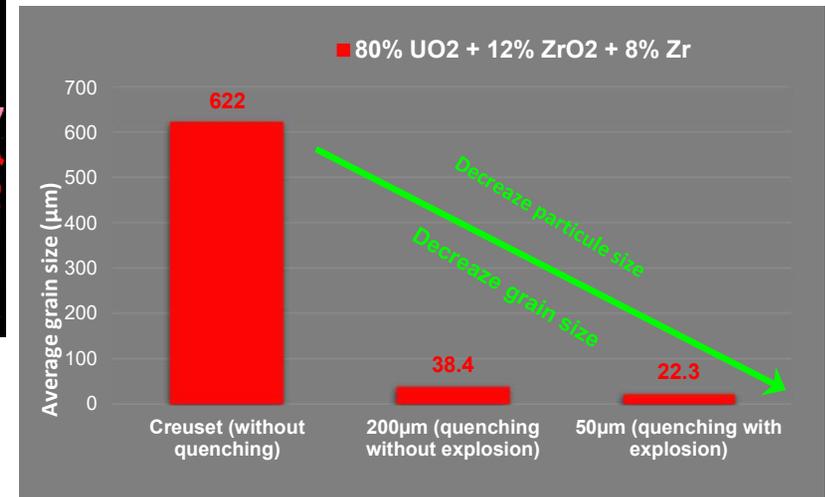
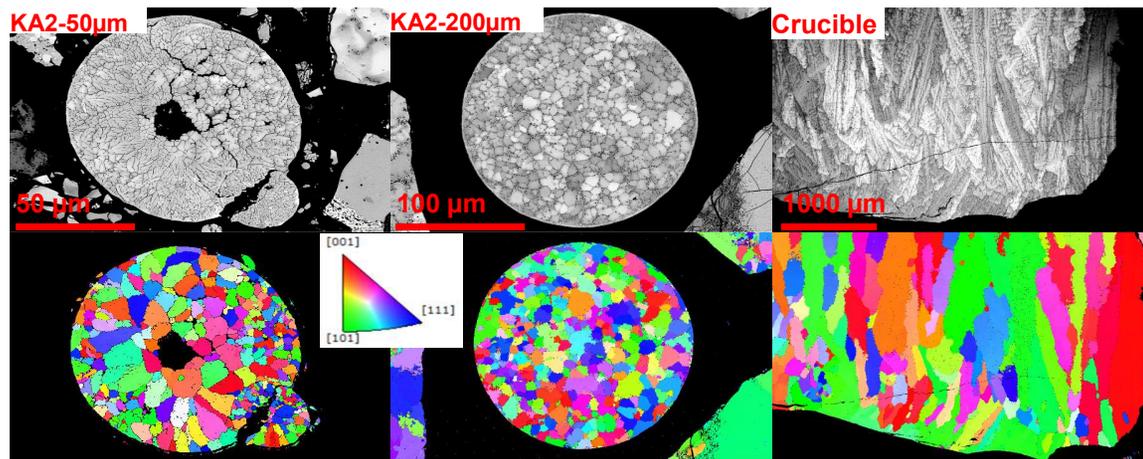


- Five spectrometer, optical camera
- Quantitative analysis from beryllium to uranium



Energy of X rays

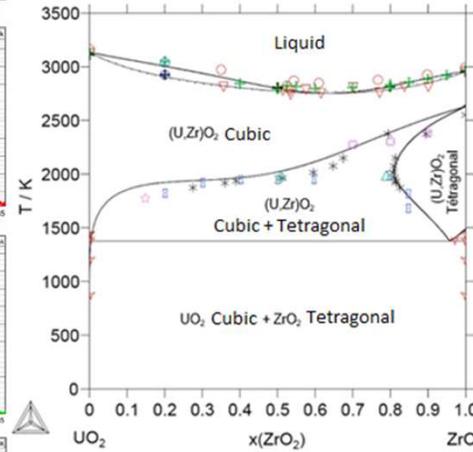
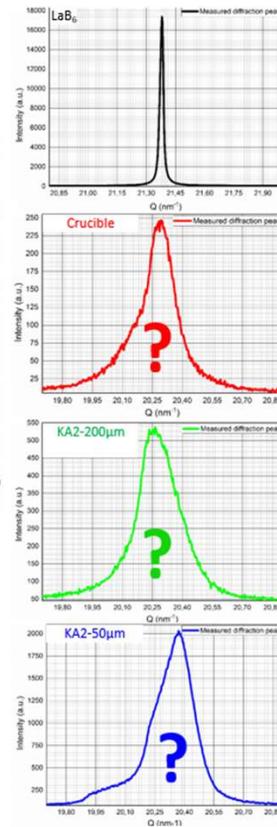
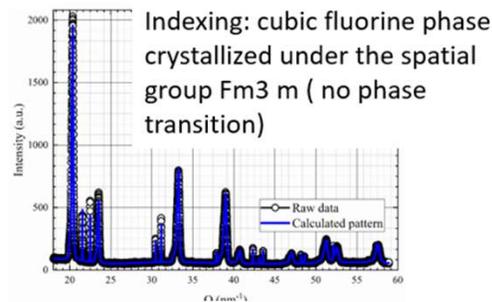
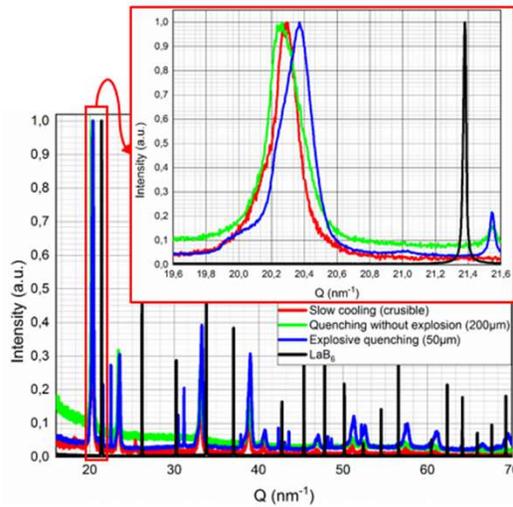
Microstructural study of corium by SEM EBSD



- Crystal size decreases with decreasing particle size and increasing cooling rate.
- Crystal size is much larger than micrometer.

Interpretation of asymmetric widening of diffraction lines

XRD in laboratory:



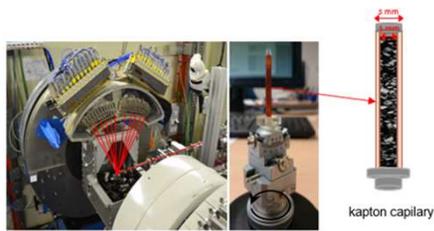
- ✓ Very large asymmetric enlargement in relation to instrumental function
- ✓ Only one cubic phase of the space group $Fm\bar{3}m$, whose cationic compositions vary (no phase transition)
- ✓ Cationic fluctuation in cubic solid solutions crystallised under the spatial group $Fm\bar{3}m$
- ✓ The simultaneous presence of several compositions whose mesh parameters vary with the difference in U/ Zr or/and oxygen content



Structural analysis by X-ray and neutron diffraction



X-ray diffraction on the MARS beam line at the SOLEIL synchrotron:
study of fluctuations in cationic composition

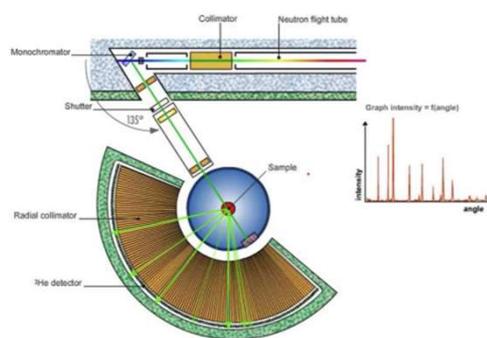
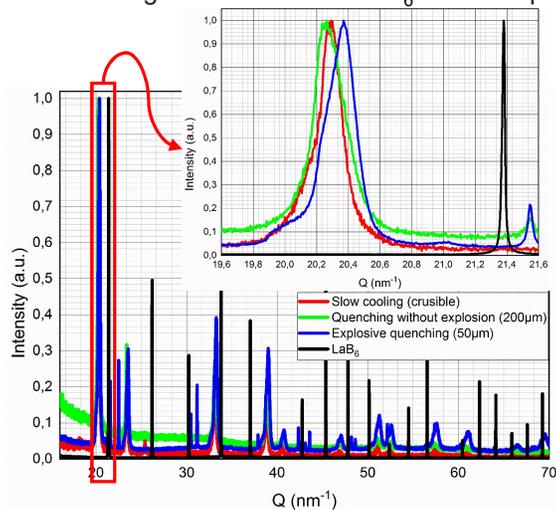


MARS beam line SOLEIL synchrotron CX2 station: HR-XRD station equipped with 24 crystal analyzers.

Neutron diffraction on line D2B to ILL:
study of anionic composition, oxygen stoichiometry

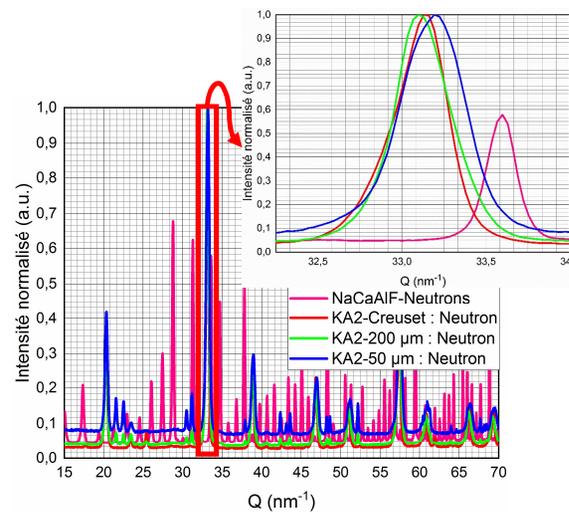


The instrumental resolution function: ($\lambda = 0,7276 \text{ \AA}$)
Diffraction diagram collected on LaB_6 standard powder



Line D2B to ILL station: high resolution neutron diffraction station, equipped with a 2D detector composed of 128 ^3He linear detectors.

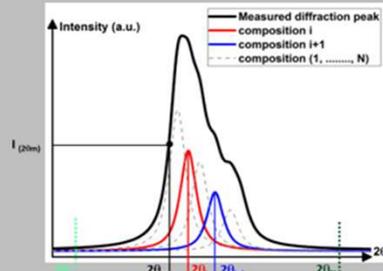
The instrumental resolution function: ($\lambda = 1,5941 \text{ \AA}$)
Diffraction diagram collected on $\text{Na}_2\text{Ca}_3\text{Al}_2\text{F}_{14}$ standard powder



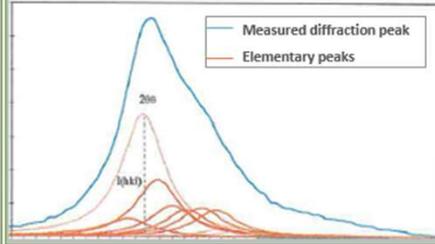
Diffraction diagram decomposition method



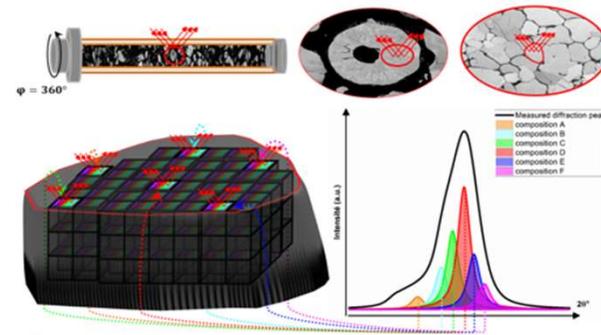
Houska^[1] : HOUSKA was interested in the modeling of diffraction peaks profiles from coherent domains of varying compositions (Cu- Ni, Pd and Au intermetallic systems)



P. Buisson^[2] : Applied and validated on typical solid solutions $U_{1-x}Pu_xO_2$



Decomposition method of diffraction diagrams collected on corium solid solutions $U_{1-x}Zr_xO_{2±y}$



Principles :

- Decomposition of a peak profile with a strong asymmetric broadening characteristic of a cationic composition distribution, into a series of N elementary peaks.
- The mathematical function and the shape parameters are obtained from a standard (LaB6).
- Each elemental peak represents a particular cationic composition.

[1] C. R. Houska, « X-Ray Diffraction from a Binary Diffusion Zone », *Journal of Applied Physics*, vol. 41, n° 1, p. 69-75, janv. 1970, doi: [10.1063/1.1658380](https://doi.org/10.1063/1.1658380).

[2] P. Buisson, P. Piluso, M. Pernet, et M. Anne, « Determination of the Cationic Composition Distributions in Mixed Uranium and Plutonium Oxides by Diffraction-Line Profile Analysis », *MSF*, vol. 378-381, p. 777-783, oct. 2001, doi: [10.4028/www.scientific.net/MSF.378-381.777](https://doi.org/10.4028/www.scientific.net/MSF.378-381.777).

Application of the decomposition method on prototypical corium

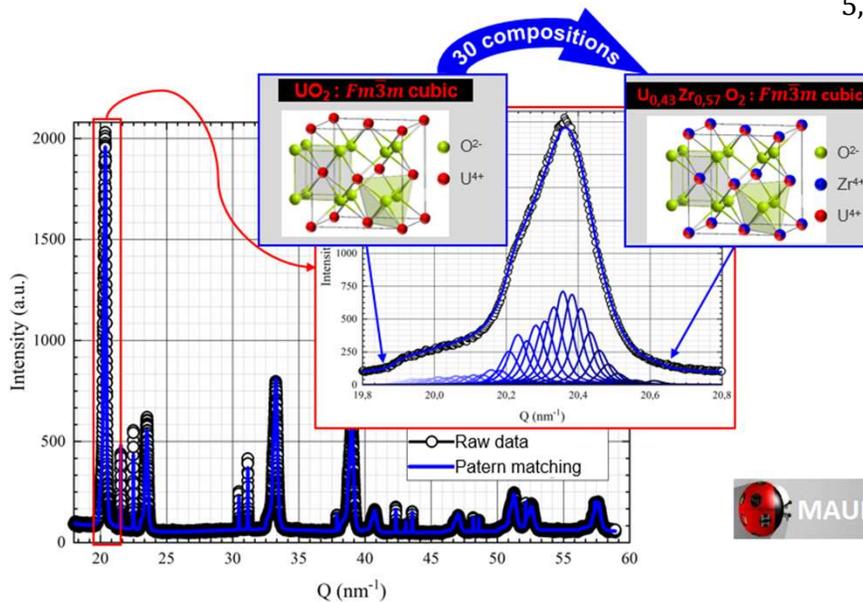


Choice of N elementary peaks:

$$N \approx \frac{\text{full width of } U_{1-x}Zr_xO_{2\pm y}}{\text{FWHM du LaB}_6} = 50 \text{ pics}$$

Choice of N elementary cationic compositions:

Vegard Low : $a = 5,468 - 0,3296 x$
 $0 < x < 0,57$; $\Delta x = 0,02$
 $5,46800 < a < 5,28013$; $\Delta a = 0,006592$

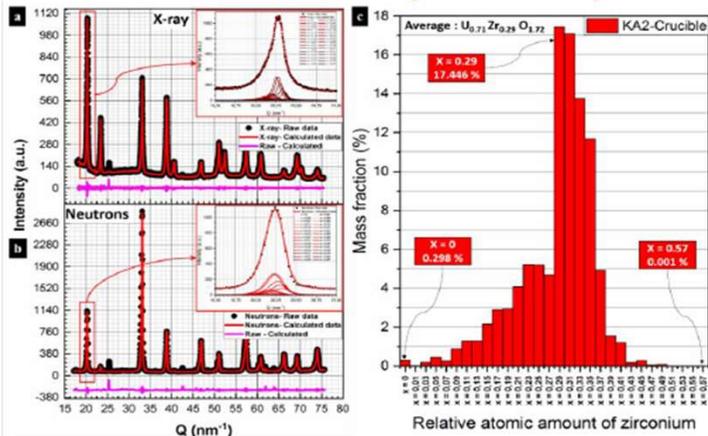


- Extraction of composition fluctuations by global simulation of diffraction diagrams.

- The calculated diagram is the sum of 30 contributions, each corresponding to a given composition.

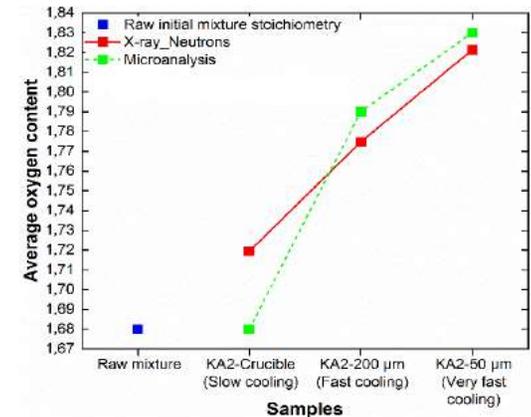
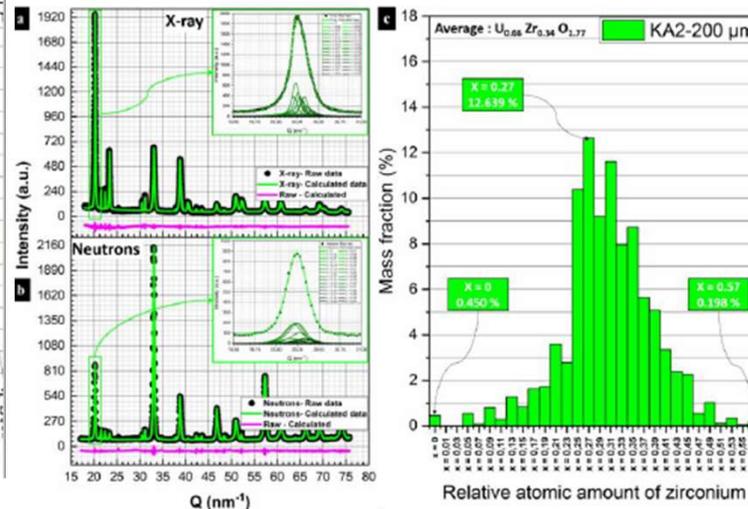
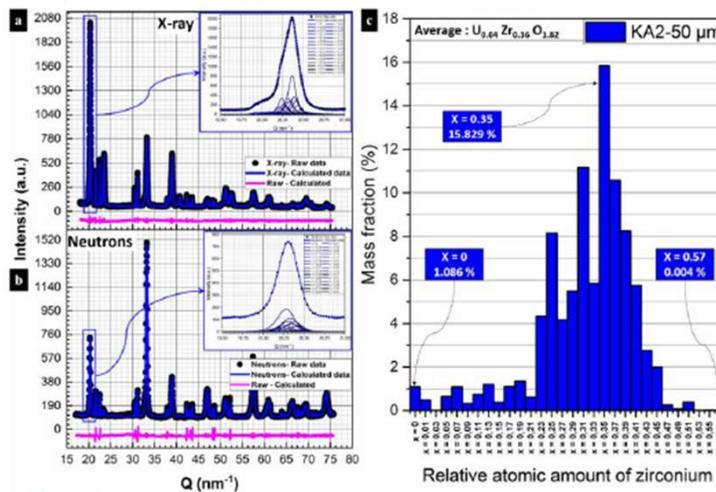


Quantification of the fluctuation of cation compositions and oxygen content by combined Rietveld X-ray and neutron diffraction analysis



Corium solid solution $U_{1-x}Zr_xO_{2.5y}$	KA2-Crucible			KA2-200			KA2-50		
Atome	U_{1-x}	Zr_x	$O_{2.5y}$	U_{1-x}	Zr_x	$O_{2.5y}$	U_{1-x}	Zr_x	$O_{2.5y}$
$B_{iso} (\text{Å}^2)$	0,324	0,636		0,319	0,915		0,363	1,598	
microstrain (%)	0,08			0,09			0,1		
Composition with combined diffraction (neutrons-X rays)	$U_{0,71}Zr_{0,29}O_{1,72}$			$U_{0,66}Zr_{0,34}O_{1,78}$			$U_{0,64}Zr_{0,36}O_{1,82}$		
Composition with EPMA microanalysis	$U_{0,58}Zr_{0,42}O_{1,88}$			$U_{0,6}Zr_{0,4}O_{1,79}$			$U_{0,63}Zr_{0,37}O_{1,83}$		
R_B	4,27			3,72			4,44		
R_{wp}	6,42			5,45			6,56		
R_{exp}	9,31			10,81			10,20		

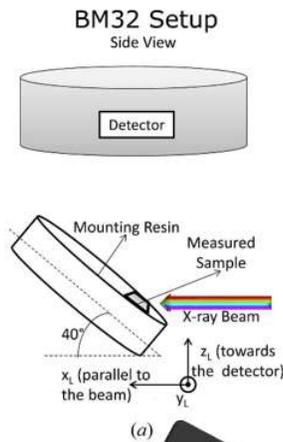
→ Combined Rietveld analysis with X ray and neutron diffraction accurate the determination of solid solution, this result are in good agreement with local EPMA microanalysis realized in the sample.



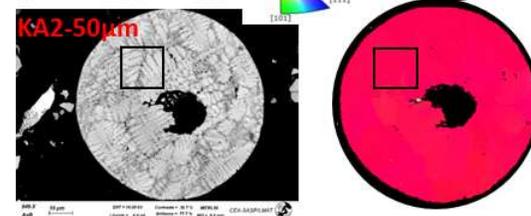
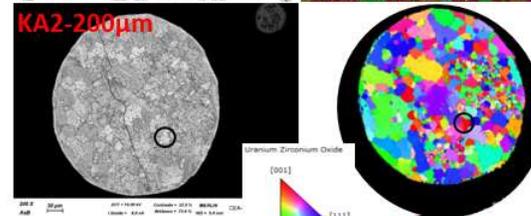
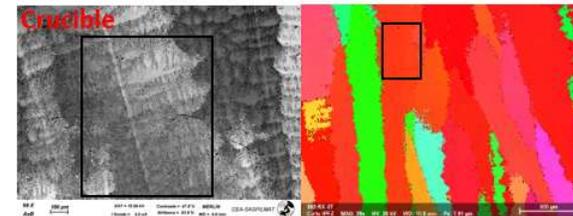
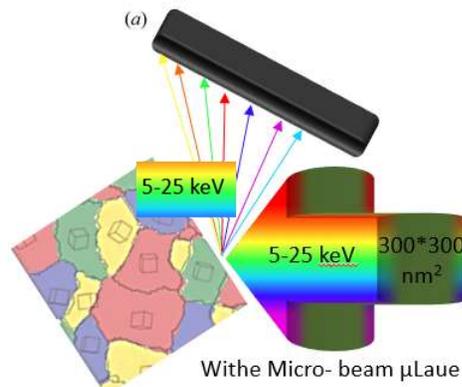
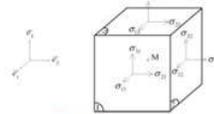
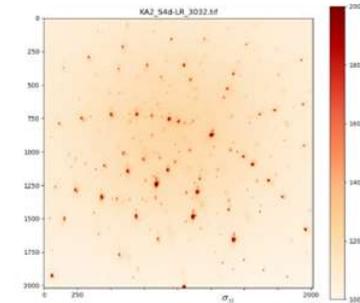


Local deformations analysis by μ Laue diffraction

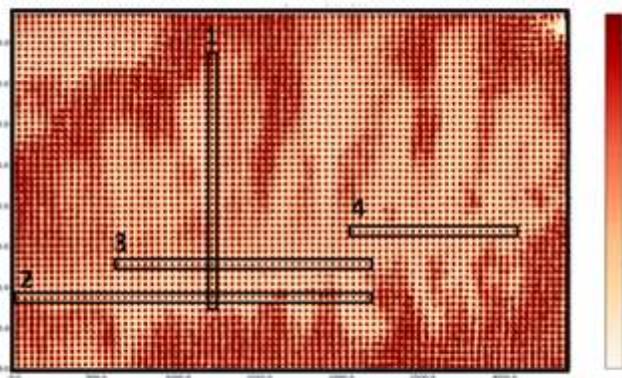
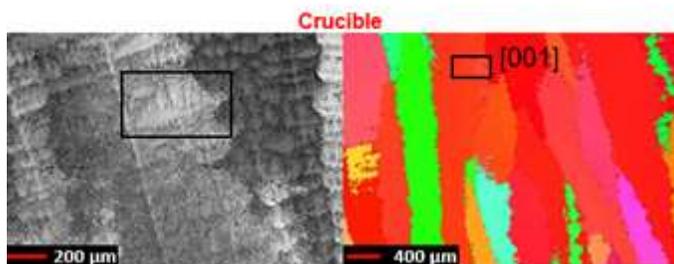
Local deformations analysis by μ Laue diffraction



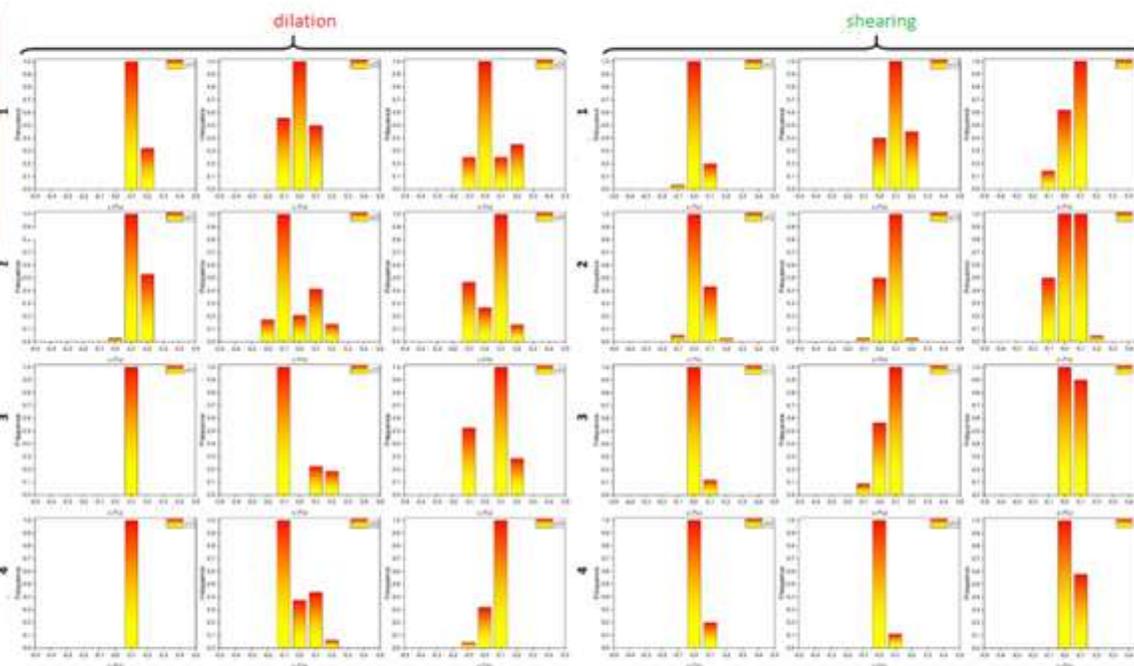
Are fluctuations in cationic compositions accompanied by local deformations?



Local deformations analysis by μ Laue diffraction

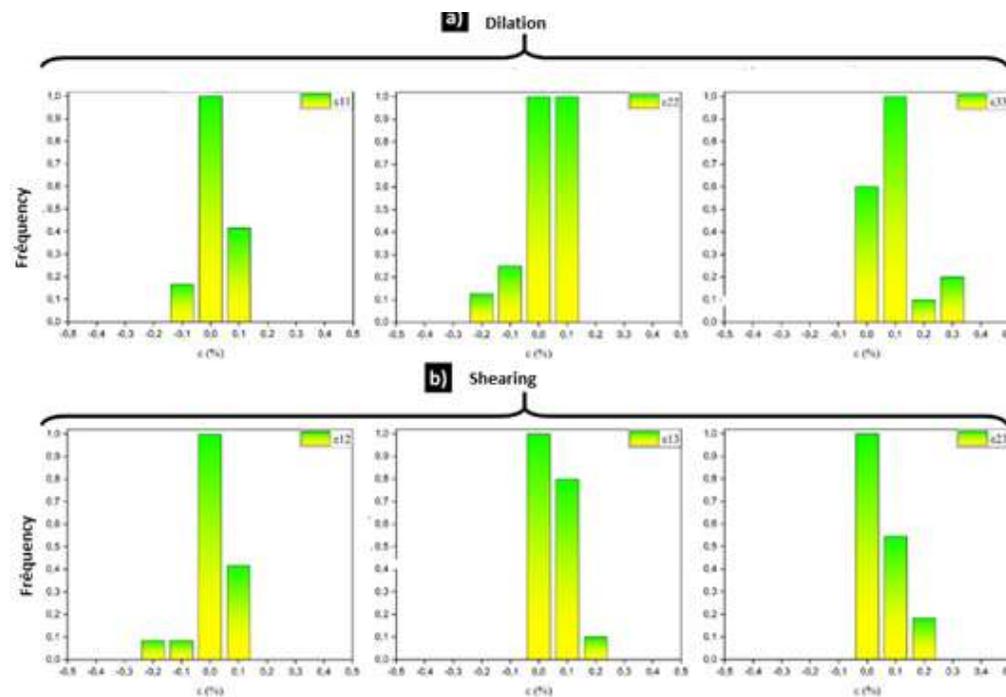
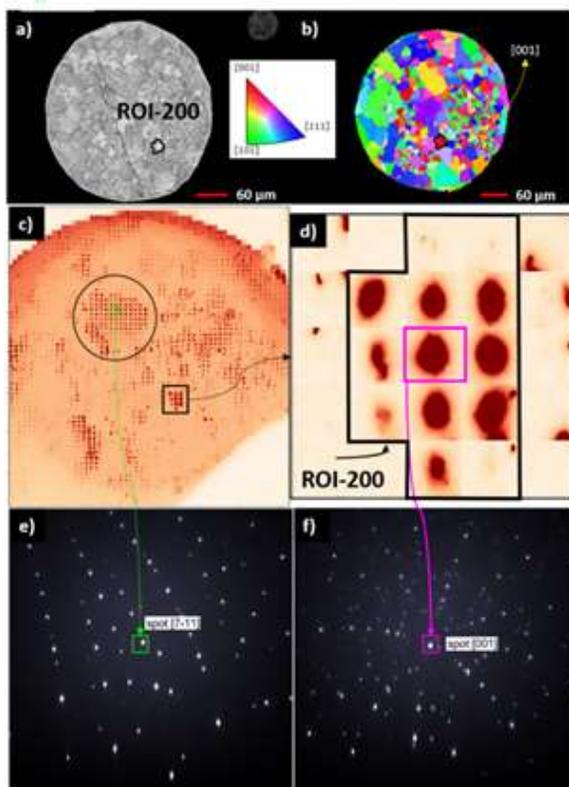


Local deformation rate 0.2%



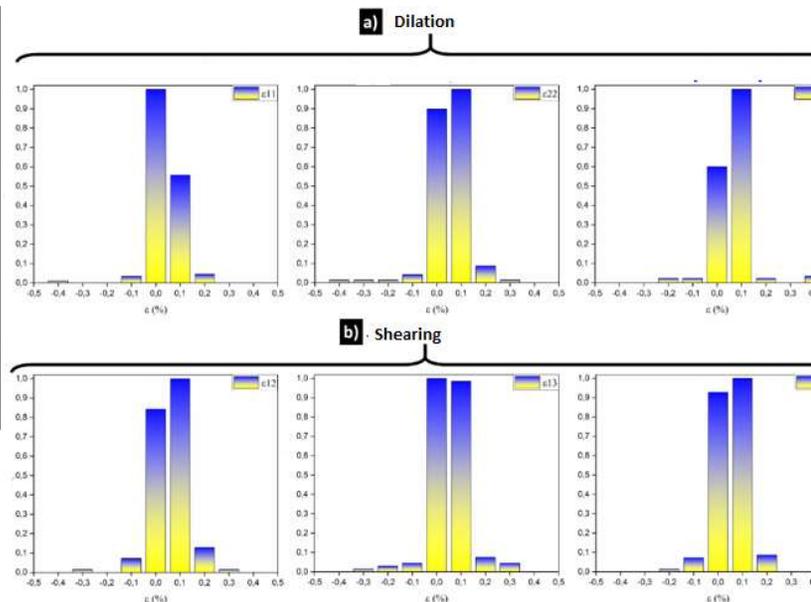
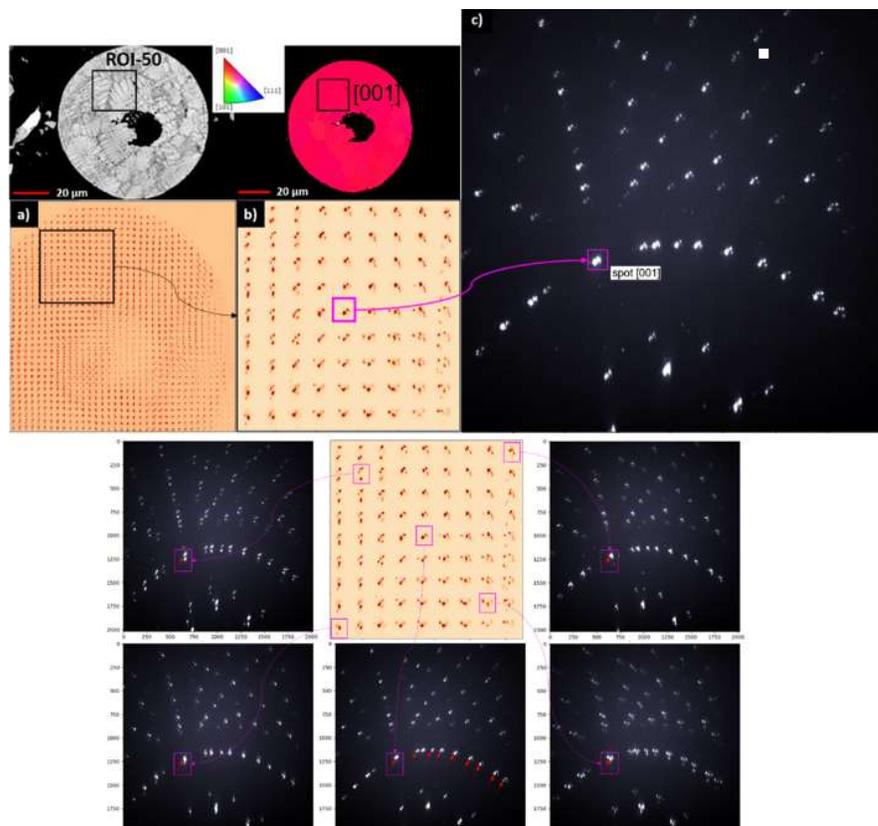
No significant difference between the distributions of strain tensor components according to transverse or longitudinal directions of dendrite

Local deformations analysis by μ Laue diffraction



Local deformation rate of 0,3%

Local deformations analysis by μ Laue diffraction



Local deformation rate 0.4 %

→ LAUE micro-diffraction : Interplay between composition fluctuations and stresses into crystals of uranium-zirconium and can show an increase of local deformation rate with the fast cooling.



Conclusion

- **Corium : heterogeneous and complex material (i.e geological material), Specific analytical procedure has to be developed through electron microscopy, diffraction method and X ray spectrometry**
- **Quantitative analysis is allowed by WDS EPMA and light element can be measured like O.**
- **Diffraction methods give structural information**
- **Combined Rietveld analysis with X ray and neutron diffraction accurate the determination of solid solution, this result are in good agreement with local EPMA microanalysis realized in the sample.**
- **LAUE micro-diffraction : Interplay between composition fluctuations and stresses into crystals of uranium-zirconium and can show an increase of local deformation rate with the fast cooling.**
- **EBSD can measured the formation of grain size during process**
- **The new methodology can do determination of the relationship between corium cooling process and the cationic-anionic composition variation into the uranium-zirconium solid solutions in radioactive corium materials.**
- **Analytical approach through electron microscopy and diffraction methods and condition parameters could be transferred (i.e, F.P, M.A, Pu) in hot cell condition**



Thank you for your attention!

Thanks to :

Emmanuelle Suard scientist of D2B at ILL

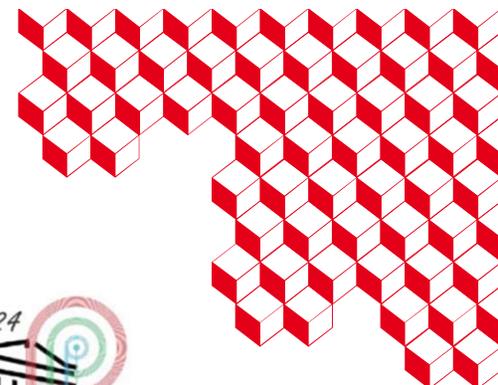
Jean Sébastien Micha scientist of BM32 at ESRF synchrotron

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Université
de Limoges



CEA MARCOULE

30200 Bagnols sur Cèze

France

emmanuelle.brackx@cea.fr