Synthesis, Characterization and Corrosion of Simulant Nuclear Fuel Debris

Dr. Claire Corkhill

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@clairecorkhill
@ISL_Sheffield

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Viktor Krasnov

Sergey Sayenko

CRP on Management of Severely Damaged Spent Fuel

Decommissioning a nuclear "meltdown"

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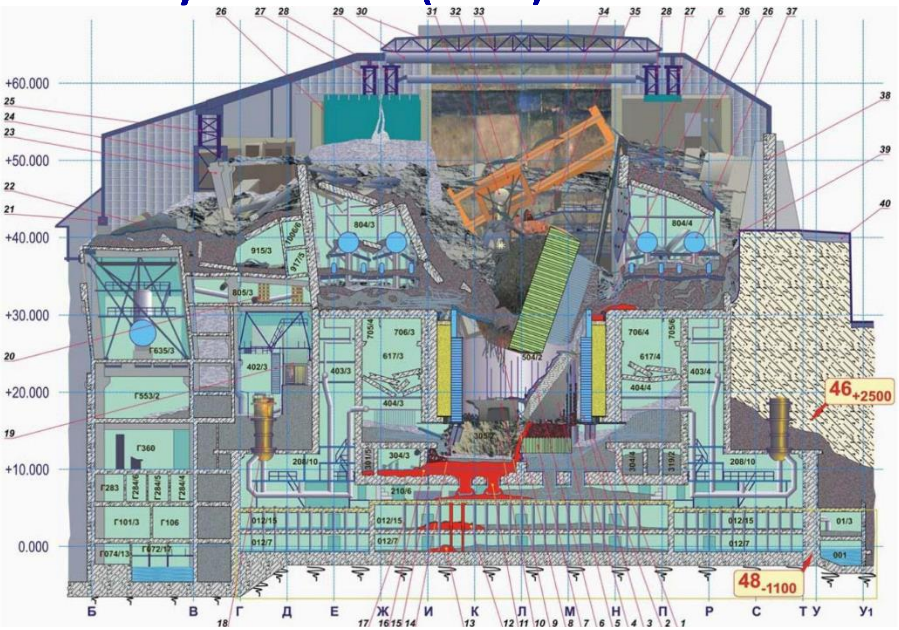
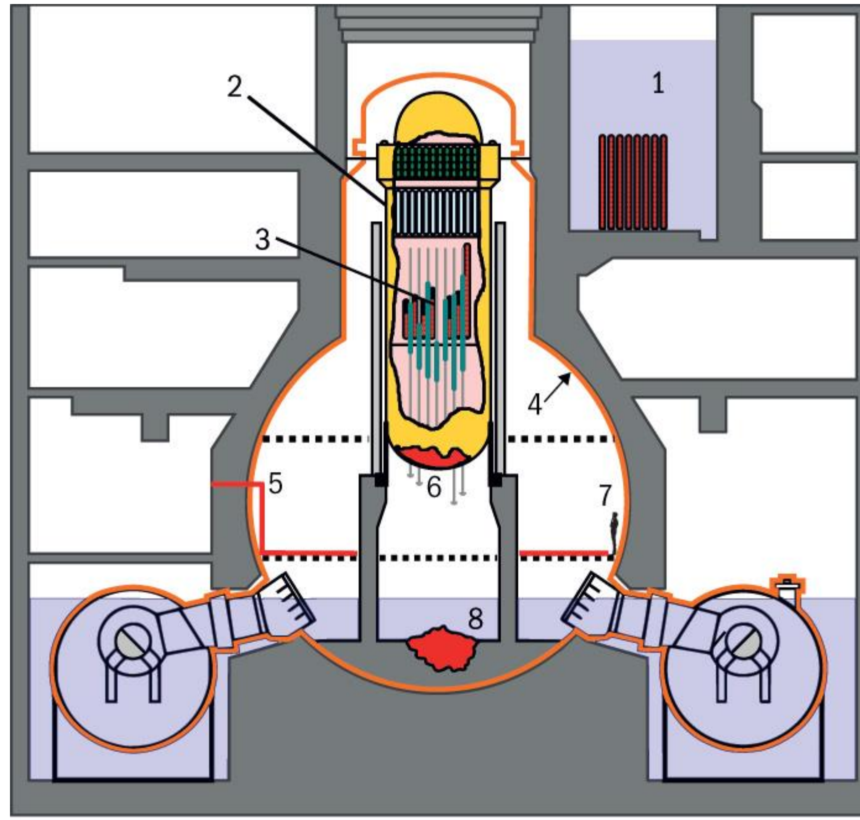
Chernobyl Reactor 4 (1986)



1. **How to remove fuel?** (mechanical properties, hardness etc.)
2. **Radioactive dust generation?** (respirable hazard)

Real materials are scarce (or not available) and difficult to handle.

Fukushima (2011)



1: Spent fuel pool
2: Reactor pressure vessel (RPV)
3: Damaged core assembly
4: Primary containment vessel (PCV)
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7: Person for scale
8: Fuel debris/corium on basement floor

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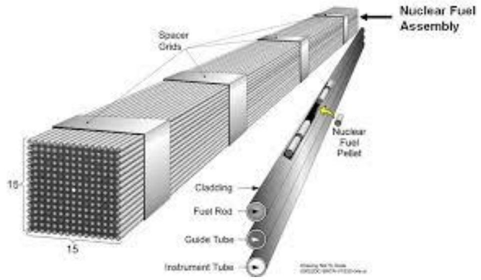
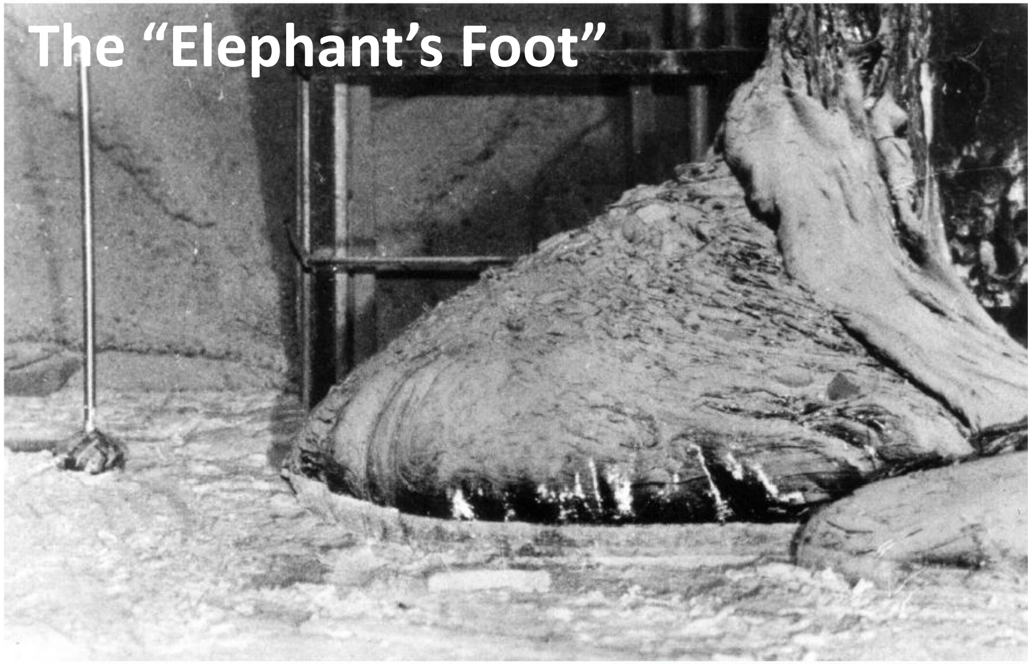
Nuclear Fuel Debris



$U_{1-x}Zr_xO_2$
solid solution

$U_{1-x}Zr_xO_2$ +
Concrete
+ Stainless steel

LFCM (Lava-like Fuel Containing Material)
MCCI (Molten Core-Concrete Interaction)



Brown Lava

Black Lava

Pictures courtesy of Boris Burakov.

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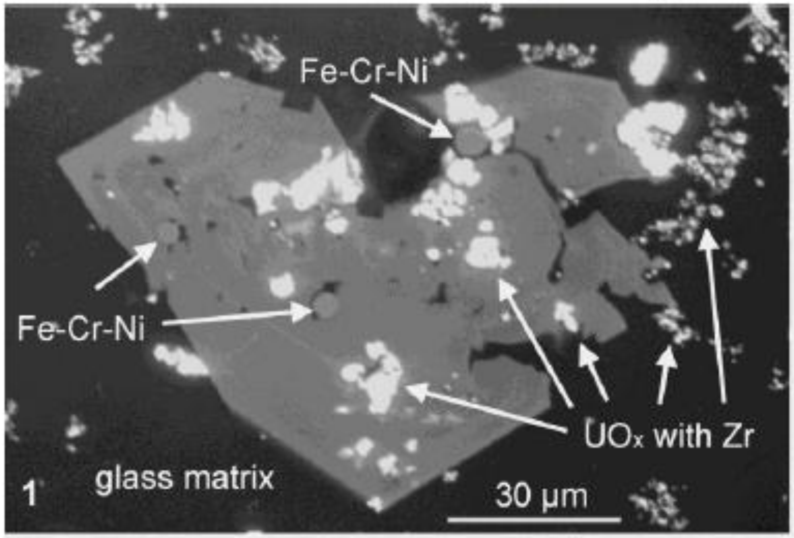
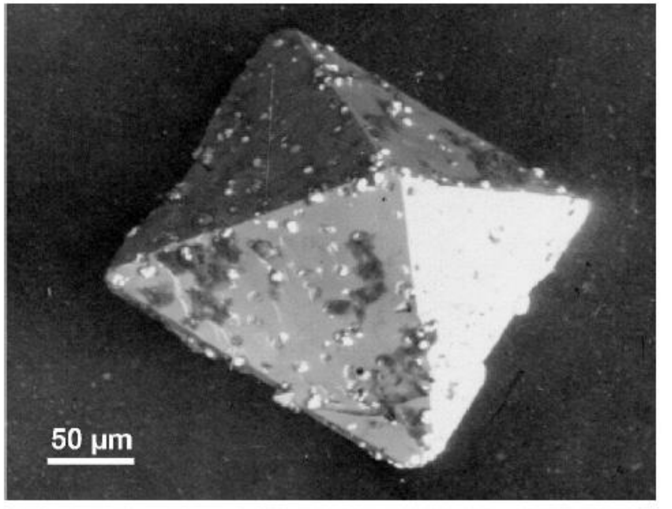
Lava-like fuel containing material

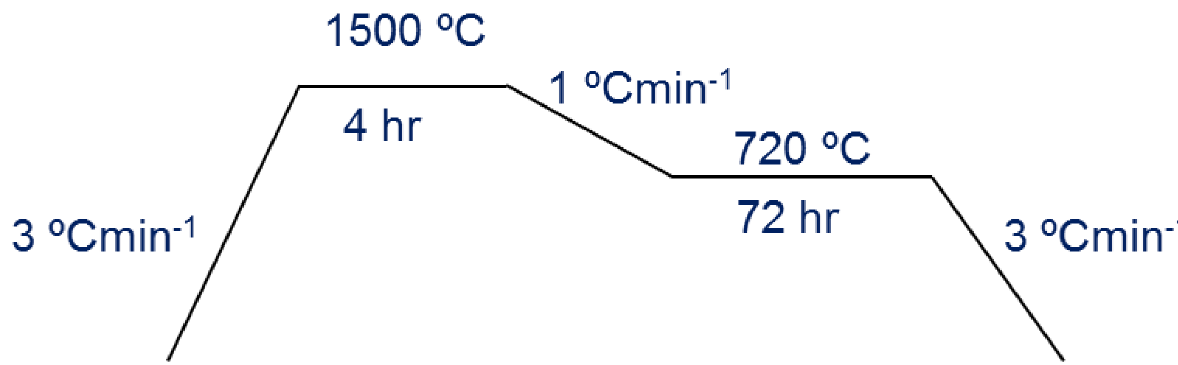


- **Cubic UO_x:** similar to stoichiometric UO_2 (a = 5.462-5.473 Å)
- **Cubic UO_x with Zr:** $(U_{0.985}Zr_{0.015})O_2$ to $(U_{0.895}Zr_{0.105})O_2$ (a decreases from 5.468 to 5.318 Å)
- **Tetragonal phase Zr-U-O** with varied chemical composition from $(Zr_{0.86}U_{0.14})O_2$ to $(Zr_{0.89}U_{0.11})O_2$
- **Monoclinic zirconia** with U (up to 6 wt.% U) with varied chemical composition from $(Zr_{0.995}U_{0.005})O_2$ to $(Zr_{0.967}U_{0.033})O_2$
- **High-uranium zircon (chernobylite)** $(Zr_{0.95}U_{0.05})SiO_4$ to $(Zr_{0.90}U_{0.10})SiO_4$ (a = 6.617; c = 5.990 Å).
- Little known about the glass matrix



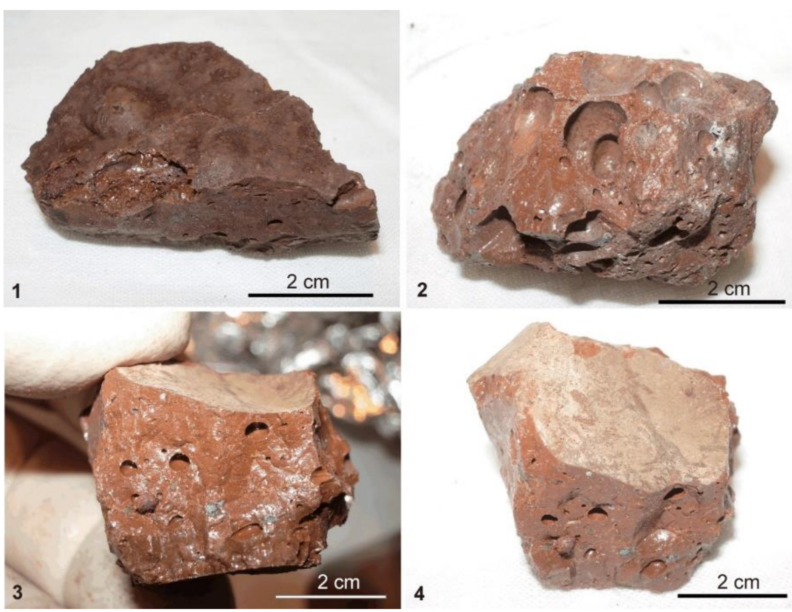
Anderson et al. Radiochimica Acta, 60, 149 (1993)

Chernobyl LFCM synthesis



- Material batched according to compositions reported in literature
- Batches melted in alumina crucibles under H_2/N_2 atmosphere- prevent oxidation of U
- Dual-purpose annealing step- reduce fragility of samples & increase crystallinity
- Initial batches did not form $ZrSiO_4$
- Batches reformulated with increased Zr content → $ZrSiO_4$ formed

Chernobyl LFCM synthesis



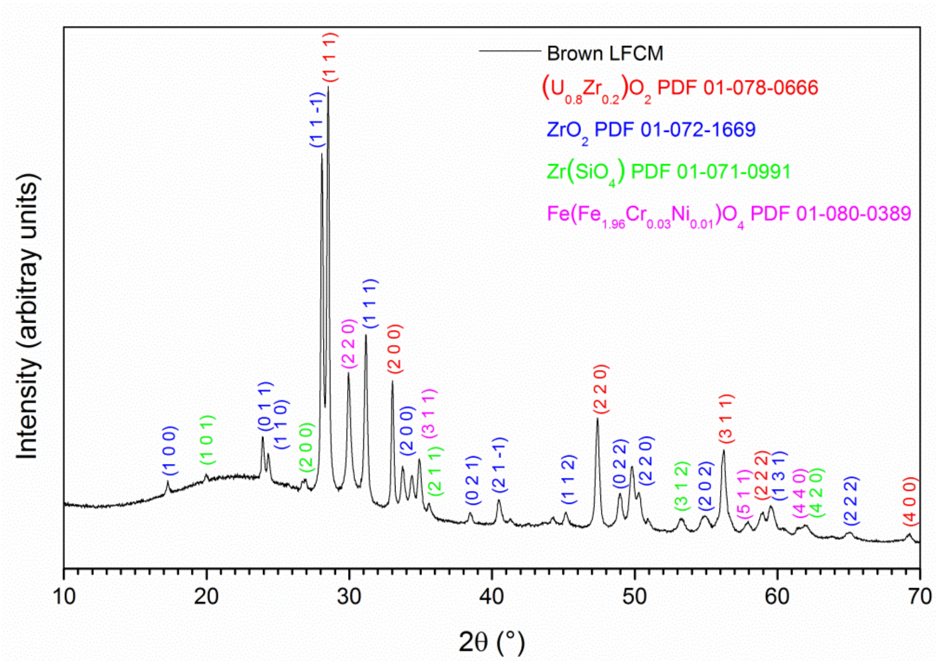
Pictures courtesy of Boris Burakov.

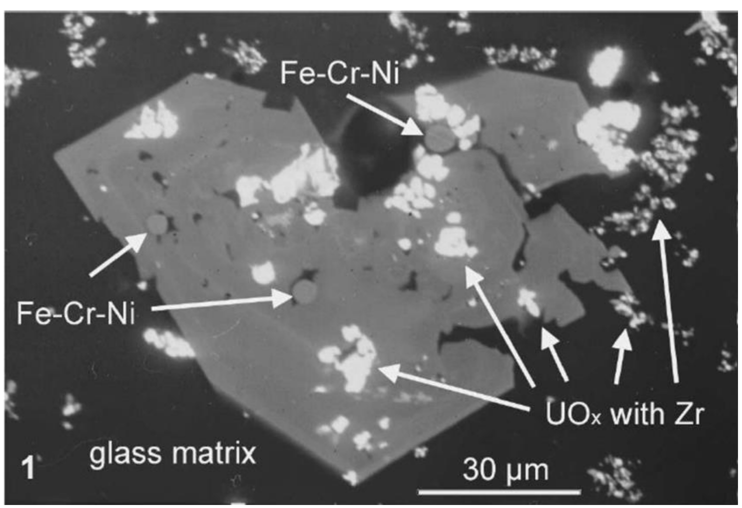
Brown lava: Iron contamination and high uranium content (~10 wt%)

Component	Mol%	Wt%
SiO_2	65.2	58.0
CaO	7.3	6.3
ZrO_2	**7.6**	**14.6**
Na_2O	7.9	7.6
Al_2O_3	1.9	3.0
Fe_2O_3 (Stainless Steel)	0.6	1.4
MgO	10.1	6.4
UO_2	2.4	10.0

Brown LFCM

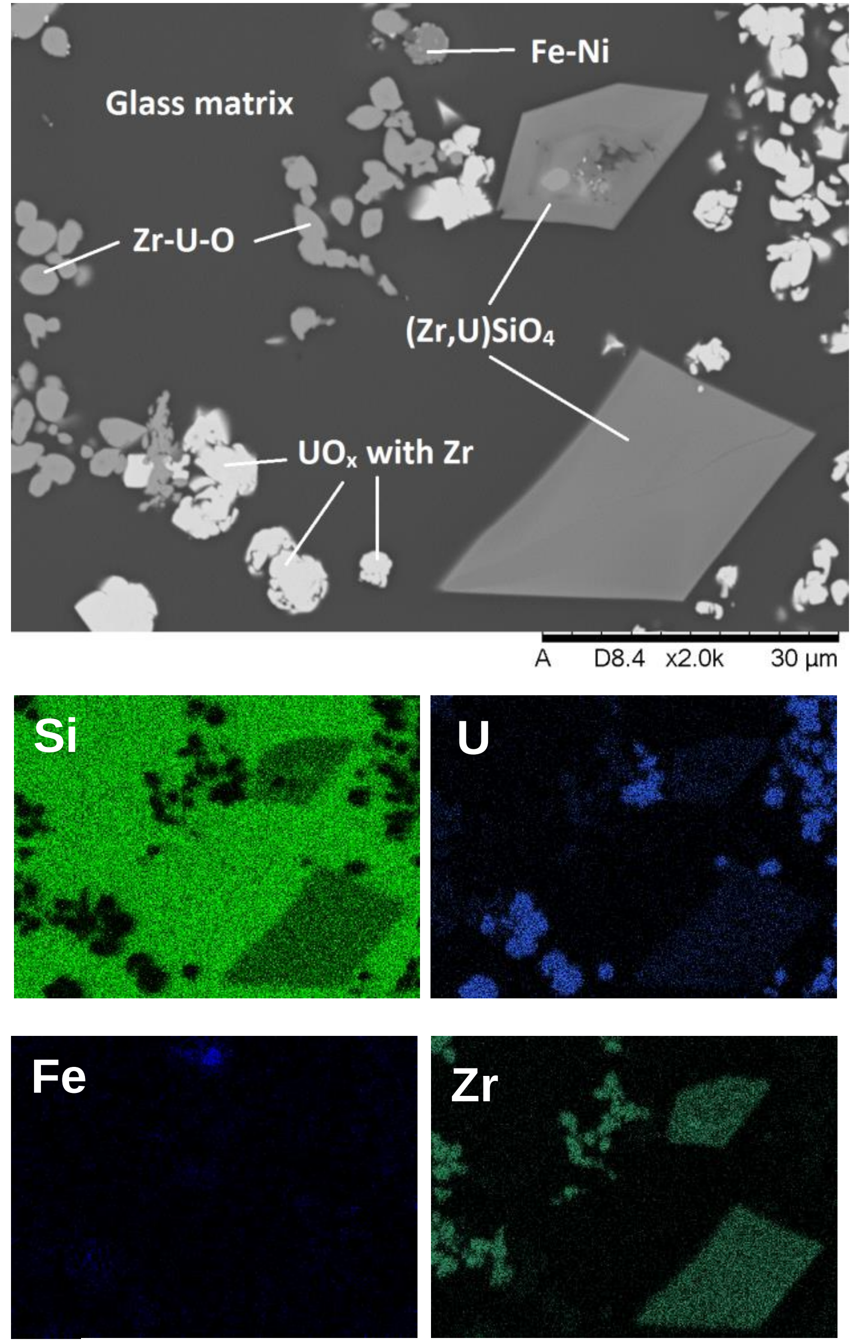
Simulant **Brown** LFCM





"Real" LFCM by Boris Burakov

Anderson et al. Radiochimica Acta, 60, 149 (1993)



Barlow et al. Nature Materials Degradation (2019)

Simulant **Brown** LFCM

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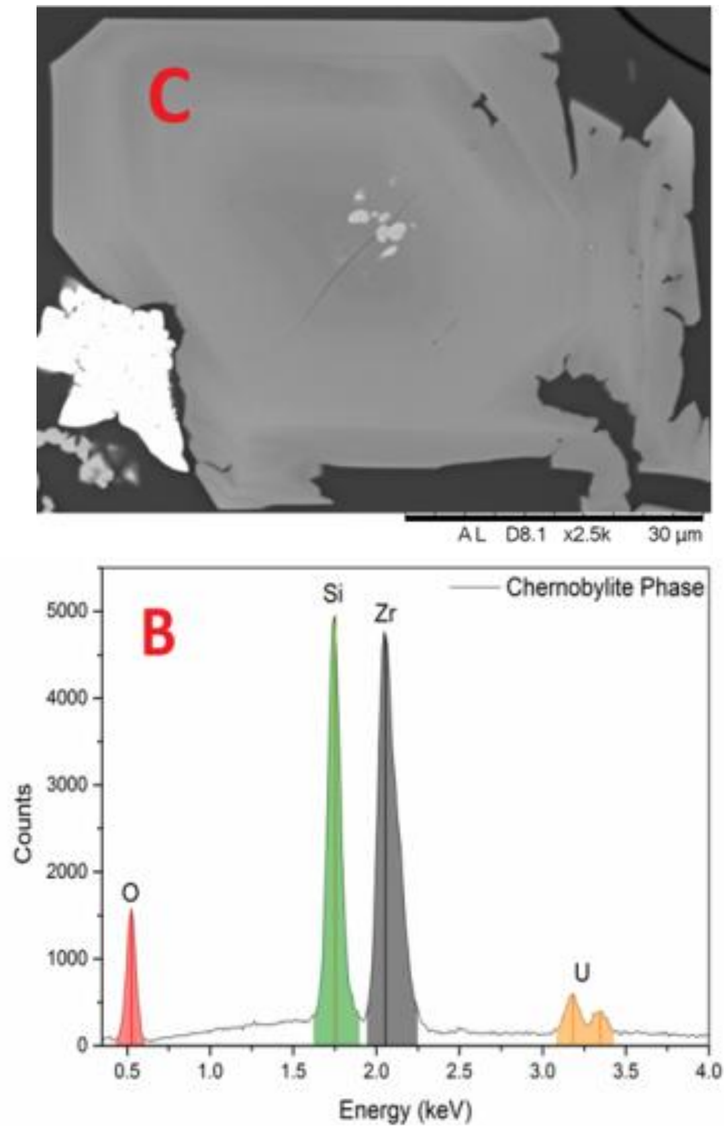
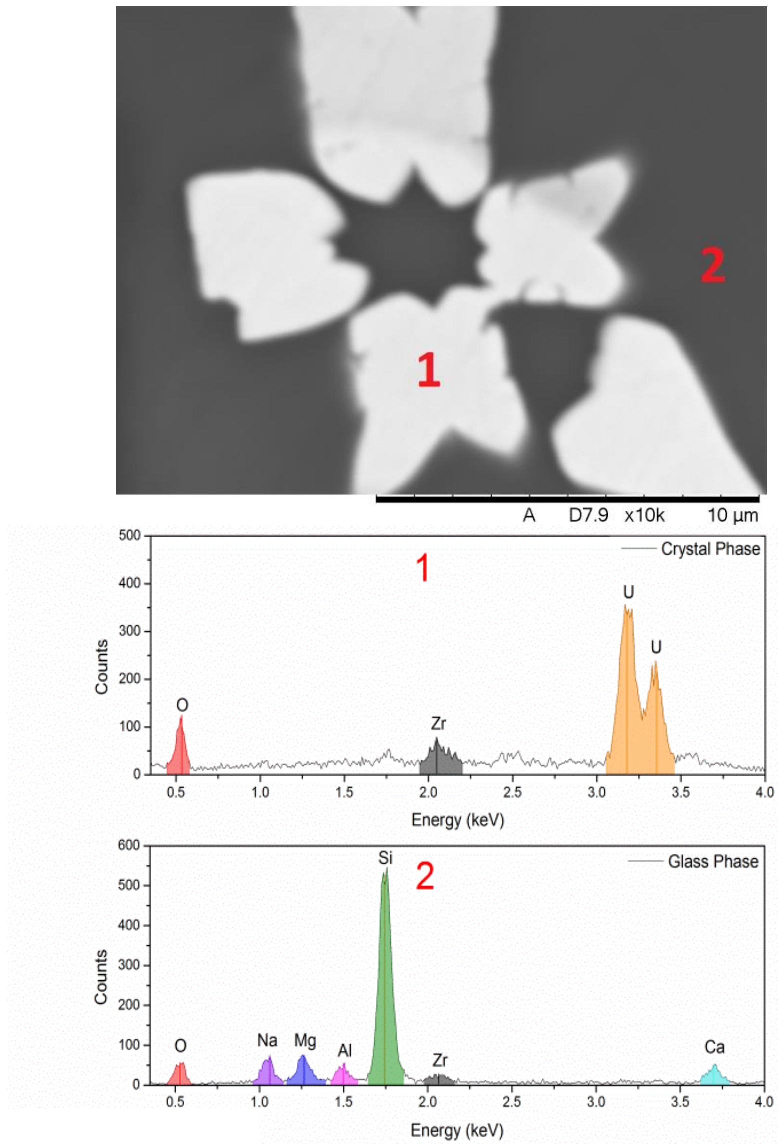
$(Zr_{0.90}U_{0.10})SiO_4$



$(U_{0.8}Zr_{0.2})O_2$



Barlow et al. Nature Materials Degradation (2019)

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Simulant **Brown** LFCM: Advanced characterisation

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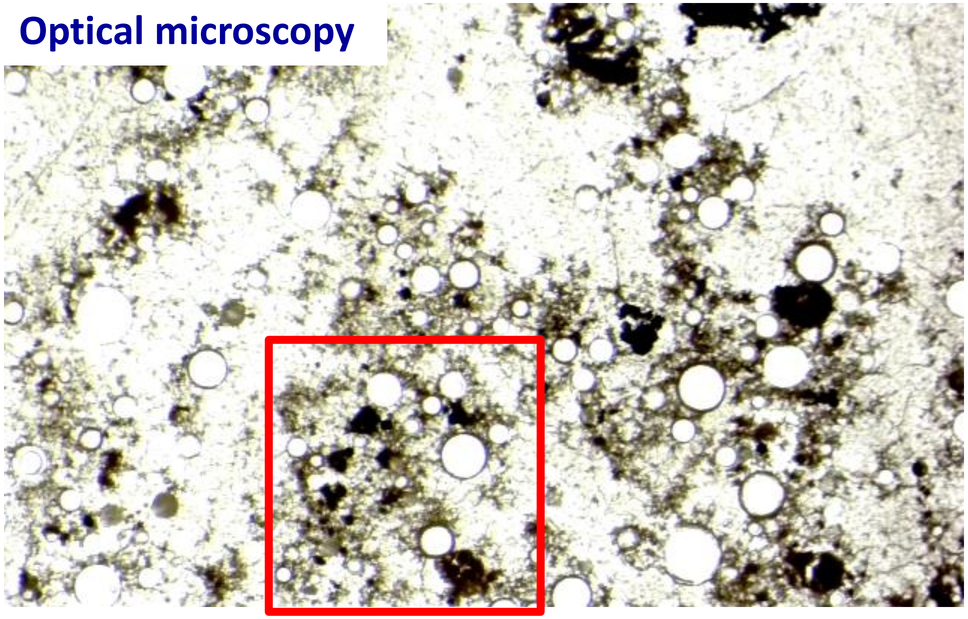
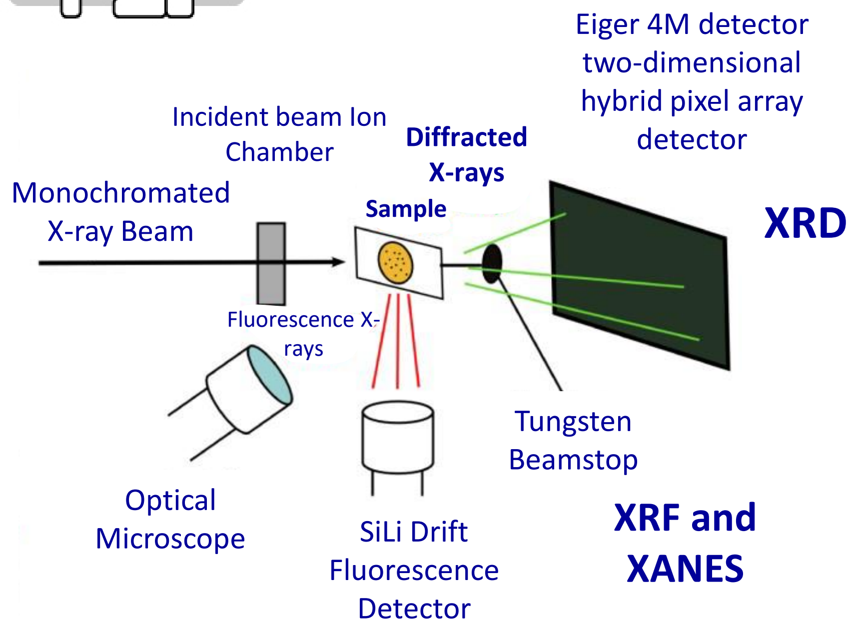
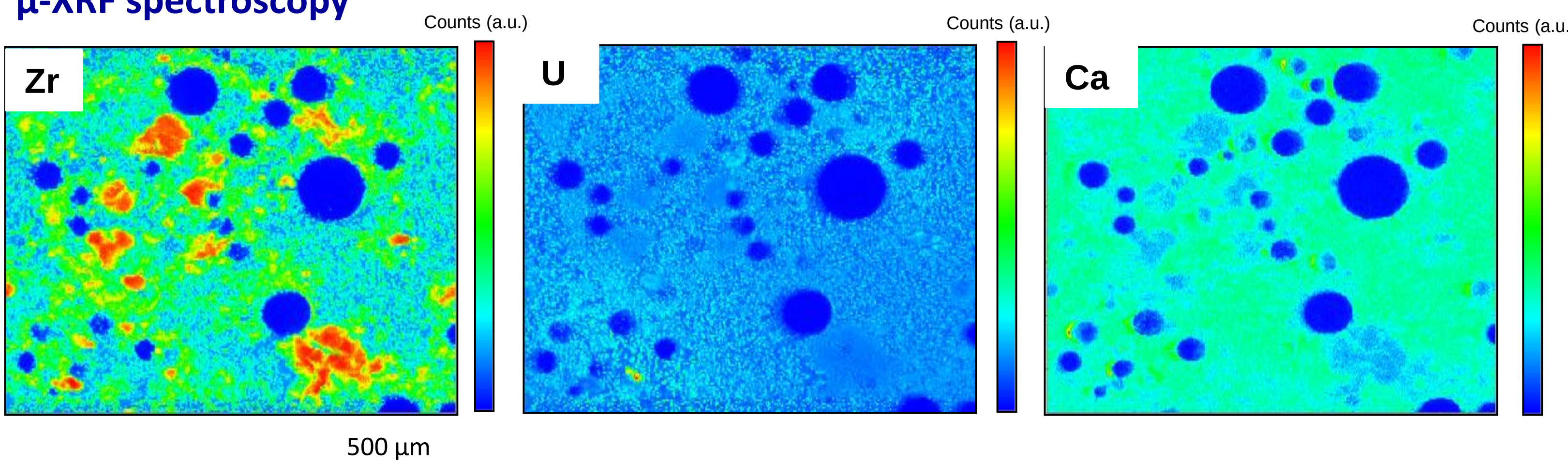
PSI

Optical microscopy





µ-XRF spectroscopy



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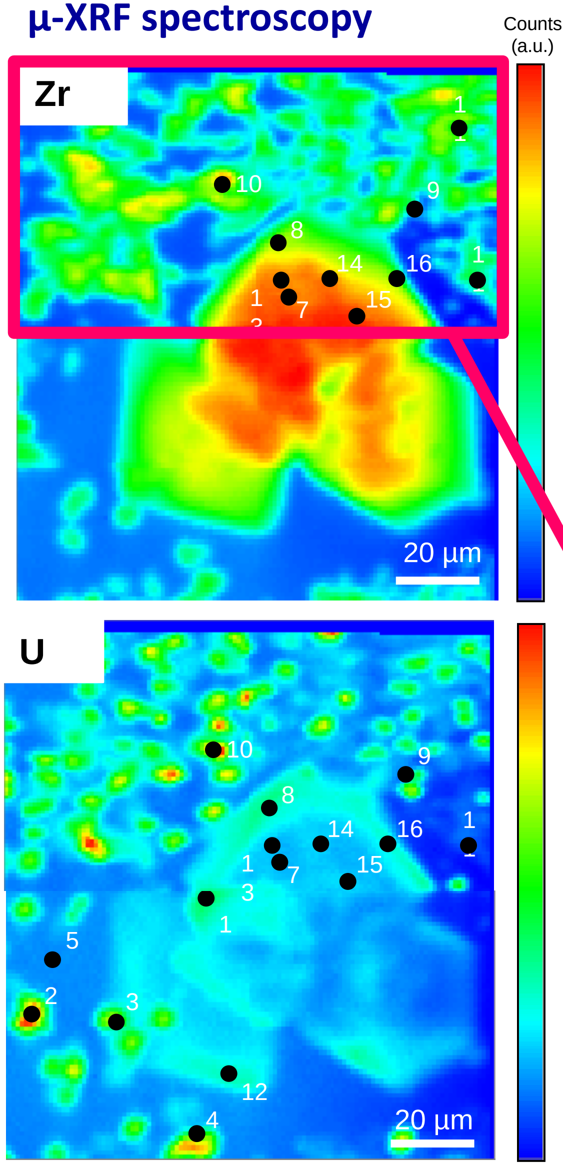
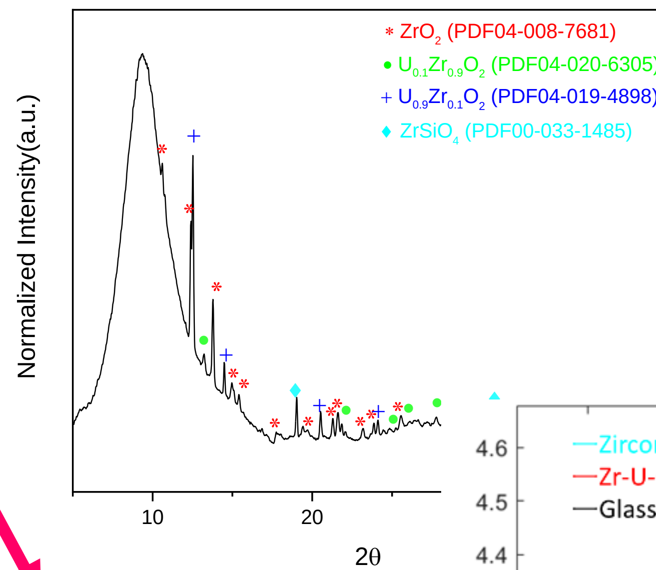
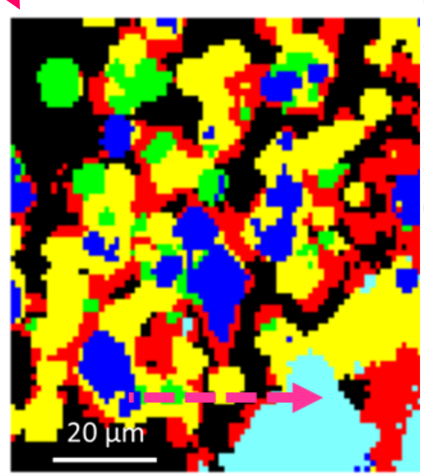
Simulant **Brown** LFCM: Advanced characterisation

μ-XRF spectroscopy

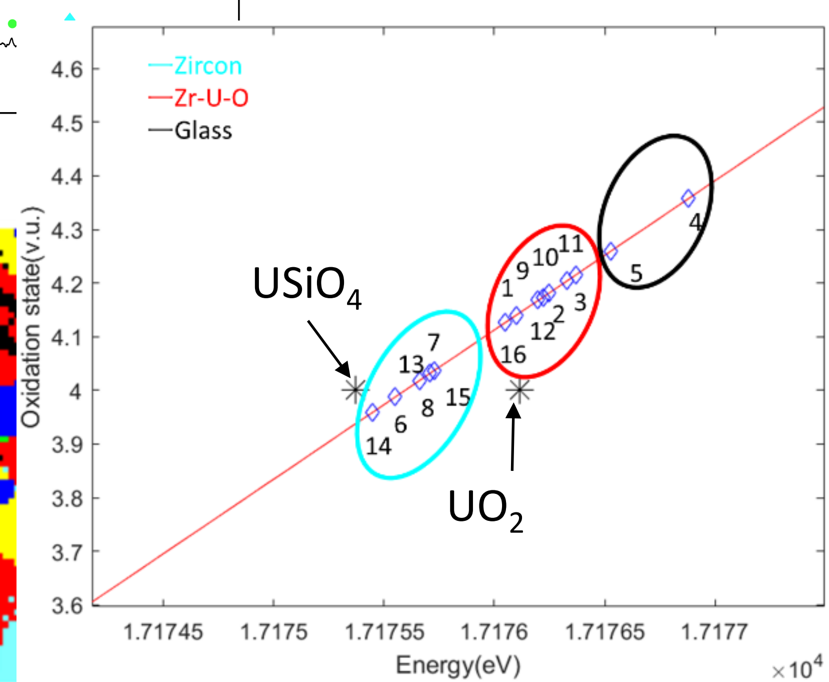


μ-XRD mapping: phase identification





U L_{III}-edge μ-XANES



Ding et al. in prep

Nuclear fuel debris corrosion

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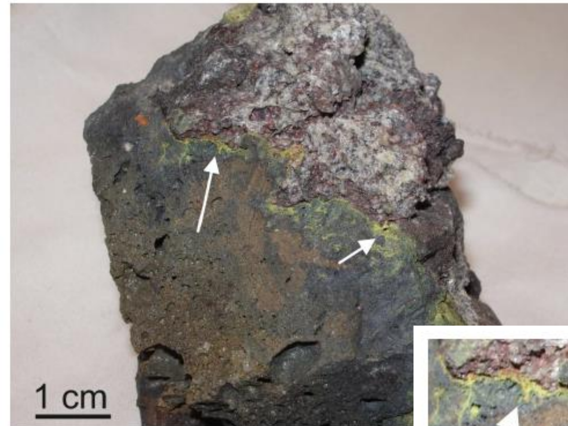

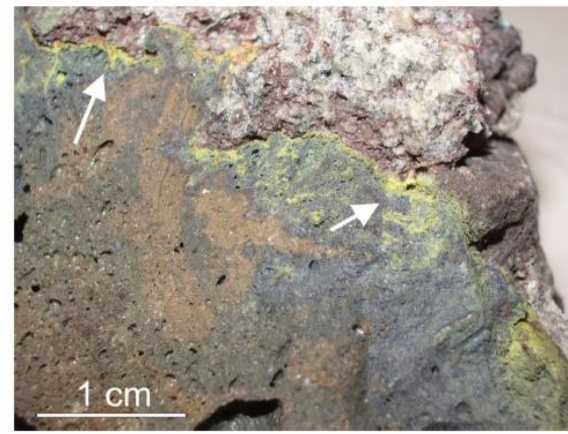

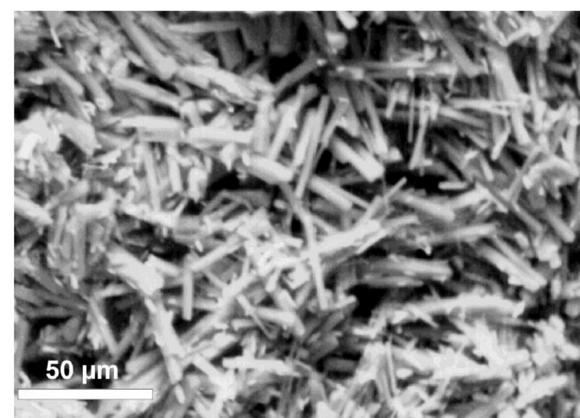

Evidence of secondary mineralisation in Chernobyl reactor, and samples removed to laboratory

- $Na_3H(CO_3)_2 \cdot 2H_2O$
- $UO_3 \cdot 2H_2O$
- UO_2CO_3
- $Na_4(UO_2)(CO_3)_3$
- $UO_4 \cdot 4H_2O$ (studtite)

Pictures courtesy of Boris Burakov.

Corrosion of Chernobyl LFCM

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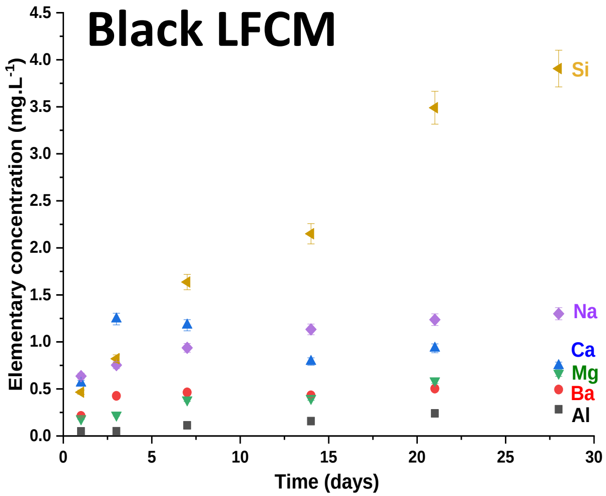
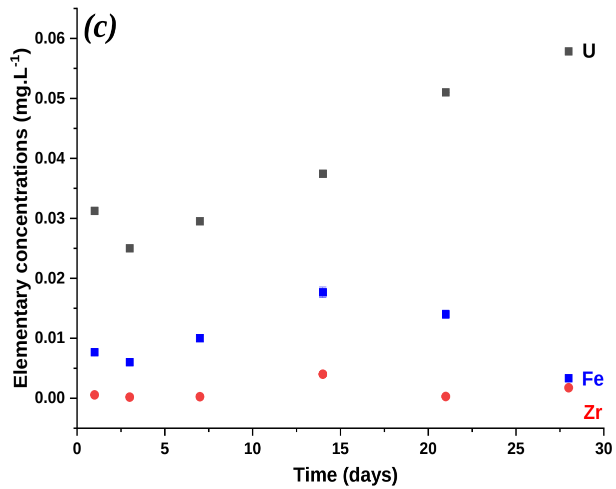
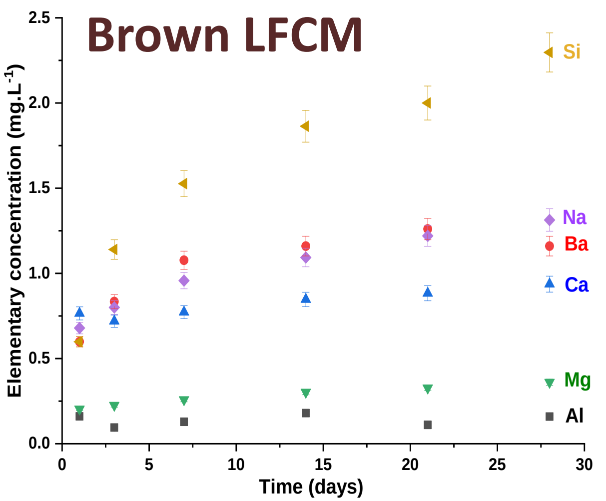
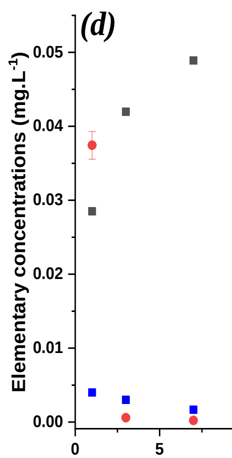




ASTM 1285 (PCT-B), 50°C, 35 days. Analysis by ICP-MS.





Black LFCM: $NR_U = (9.28 \pm 1.19) \times 10^{-5}$ g m^{-2} d^{-1}

Brown LFCM: $NR_U = (7.28 \pm 1.51) \times 10^{-5}$ g m^{-2} d^{-1}

Real Black LFCM: $NR_U = 1.8 \times 10^{-5}$ g m^{-2} d^{-1}

Rogozin et al. Radiochemistry, 4, 160 (1991)

Barlow et al. Nature Materials Degradation (2019)

Fukushima Daiichi fuel debris

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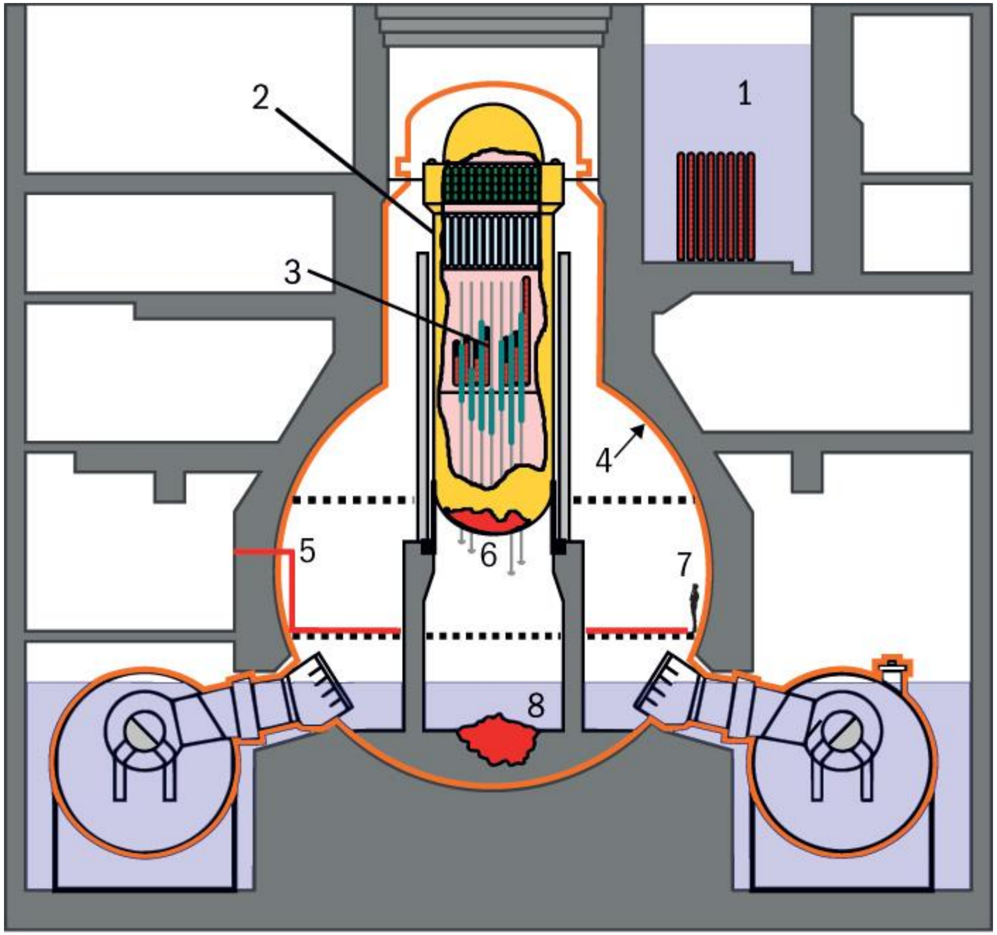

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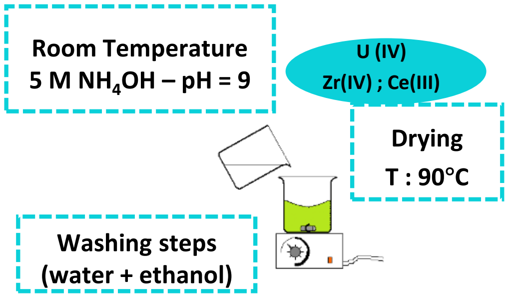
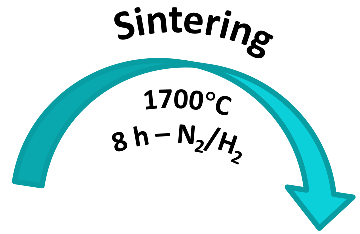
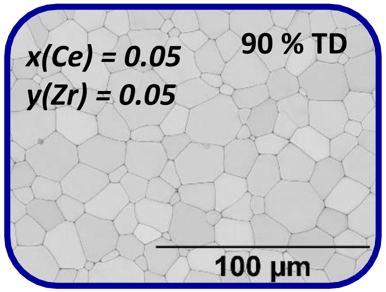
Fuel retrieval due to start in the next few years: Concerns over Pu inventory of fuel debris

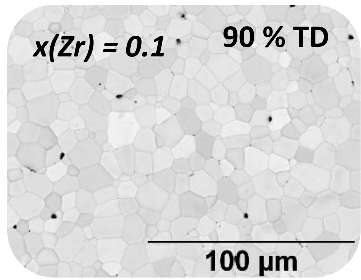
Synthesis of $U_{(1-x-y)}Zr_xCe_yO_2$



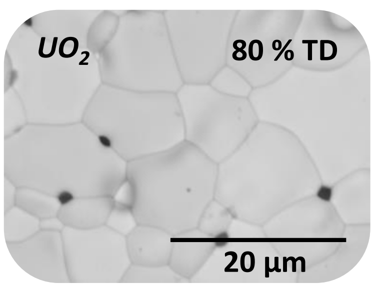




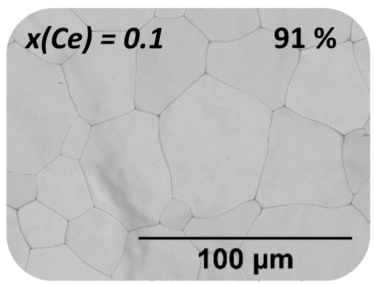
Grain size: 13.2 ± 0.5 µm



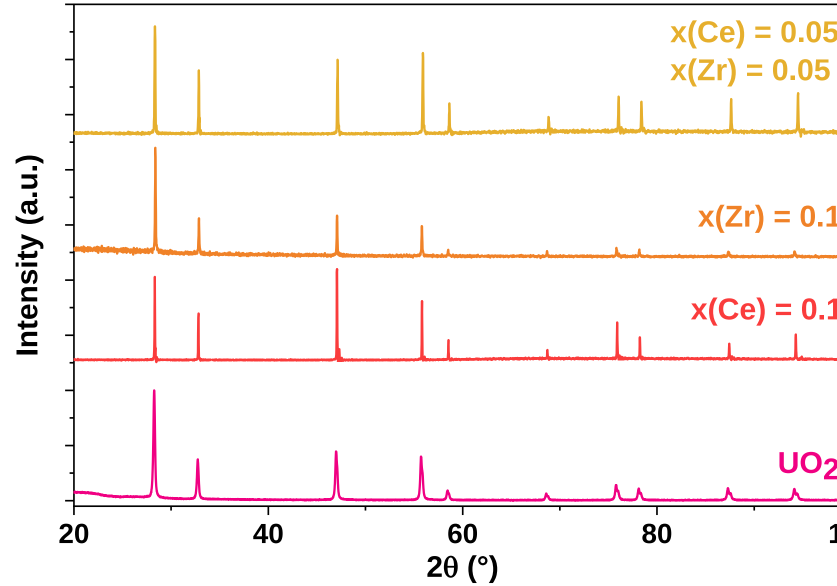
Grain size: 8.3 ± 0.4 µm



Grain size: 5.3 ± 0.4 µm



Grain size: 27.4 ± 0.5 µm



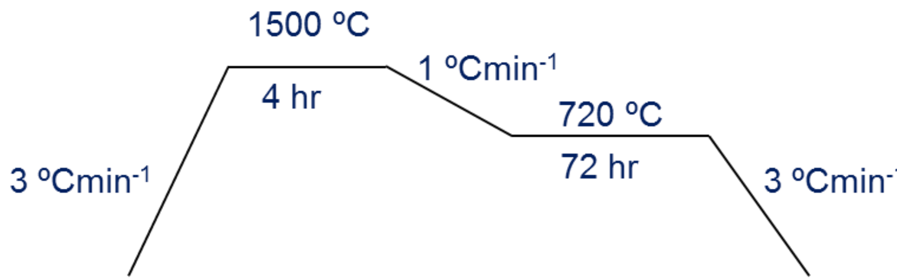
Composition	Lattice parameter (Å)	Literature
UO_2	5.467 ± 0.002	5.468 ± 0.001
$U_{0.90}Ce_{0.10}O_{2\pm y}$	5.462 ± 0.001	5.4647
$U_{0.90}Zr_{0.07}O_{2+y}$	5.437 ± 0.001	5.429 ± 0.002
$U_{0.90}Ce_{0.06}Zr_{0.03}O_{2\pm y}$	5.436 ± 0.001	–

- ✓ Incorporation of Ce & Zr into fluorite structure
  - ↠ Lattice contraction due to the incorporation of smaller size Zr^{4+} in UO_2

U^{4+}(VIII): 1 Å Zr^{4+}(VIII): 0.84 Å Ce^{3+} (VIII): 1.143 Å

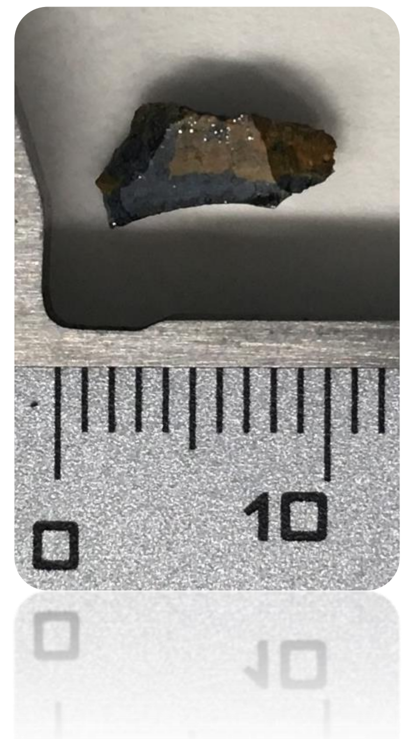
Desgranges, Inorg. Chem., 2009
Kulkarmi, J. Nucl. Mater., 2009
Norris, J. Nucl. Mater., 1983

Synthesis of MCCI



Component	Wt.%
SiO_2	43.6
CaO	8.85
Al_2O_3	10.78
ZrO_2	4.56
Stainless Steel	2
$U_{0.9}Ce_{0.05}Zr_{0.05}O_2$	10.87

Fukushima cement mortar



Gausse et al. in prep

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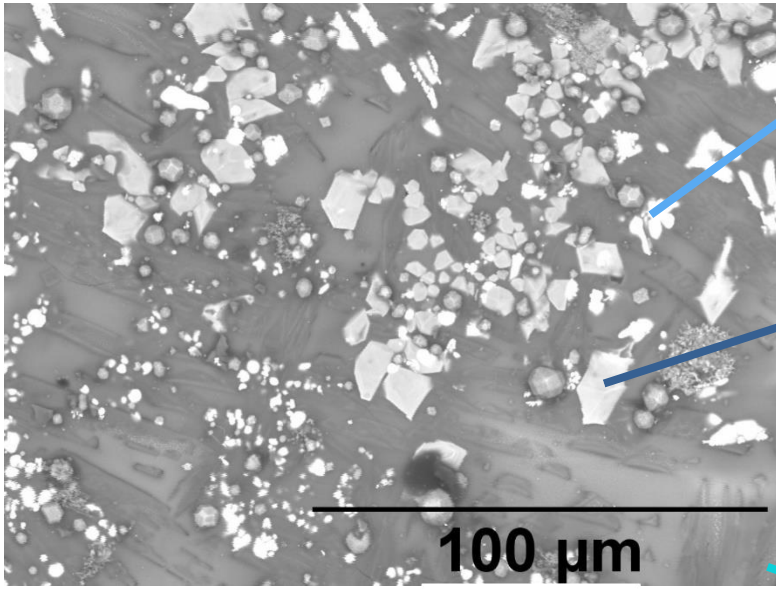
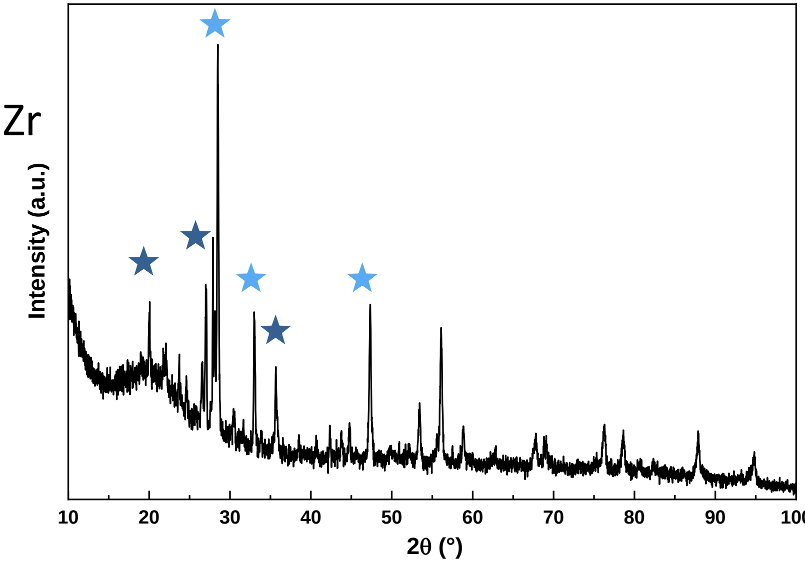
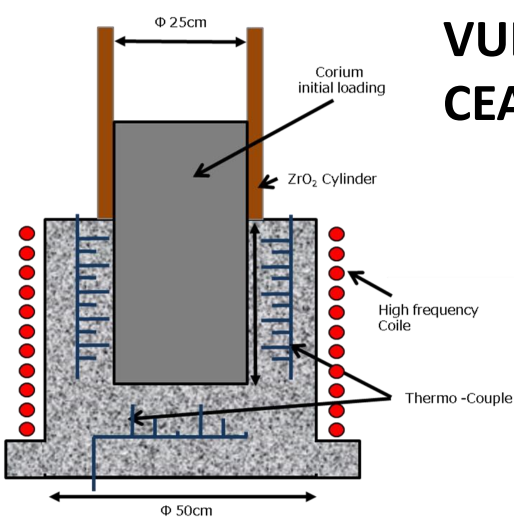
Characterisation of MCCI

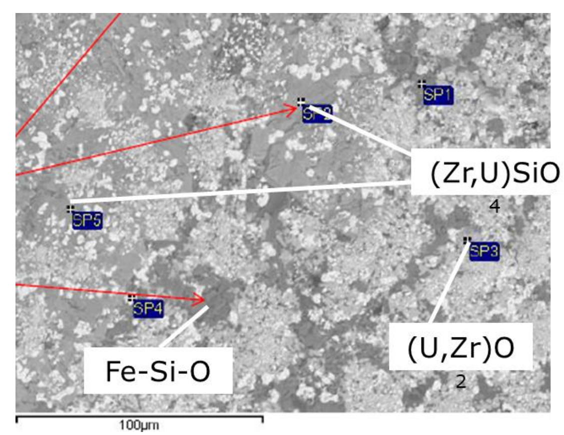




VULCANO test facility, CEA



Test section and Corium initial loading (VF-U1 Test)



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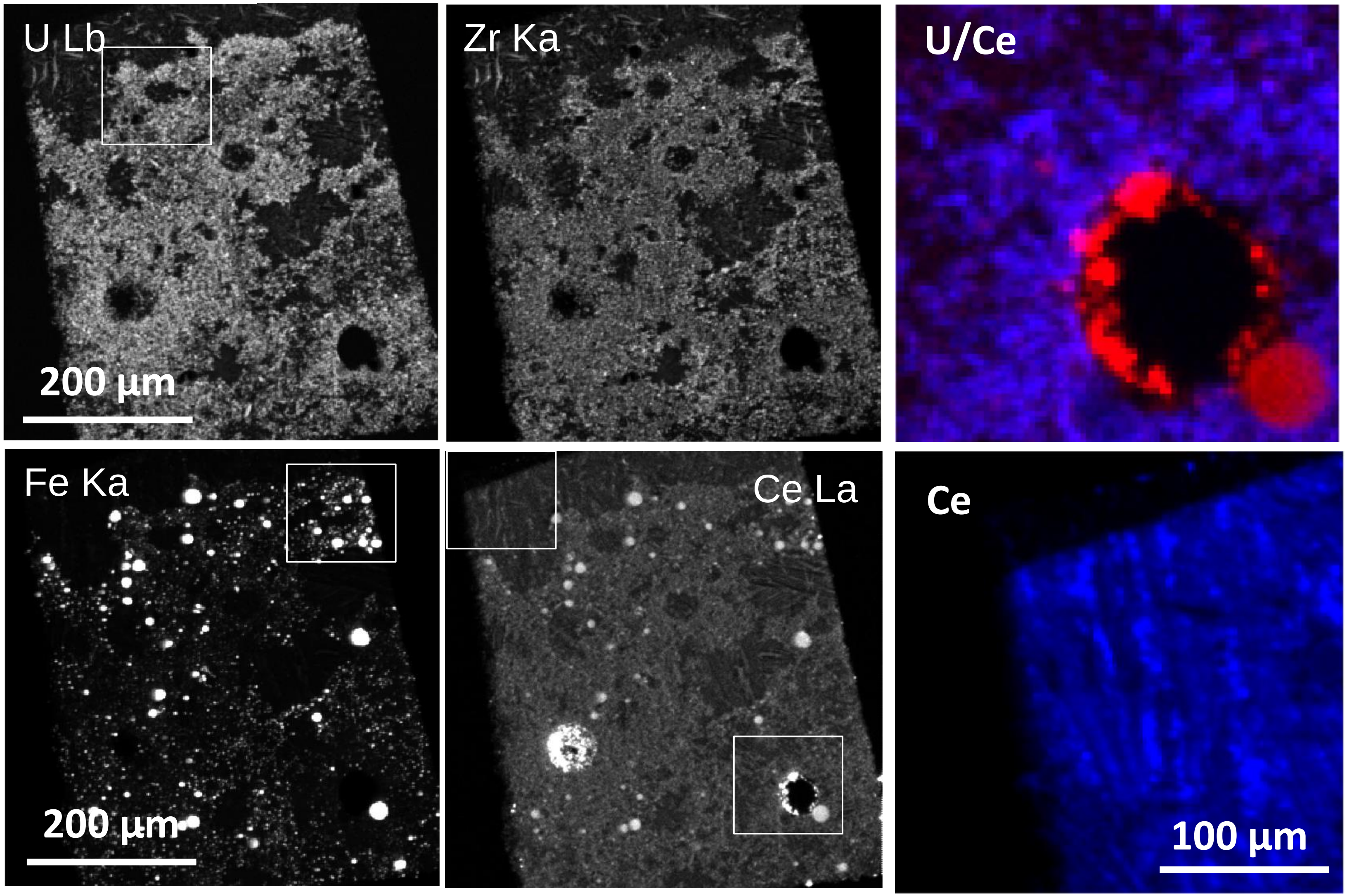
Characterisation of MCCI



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Corrosion behaviour of MCCI

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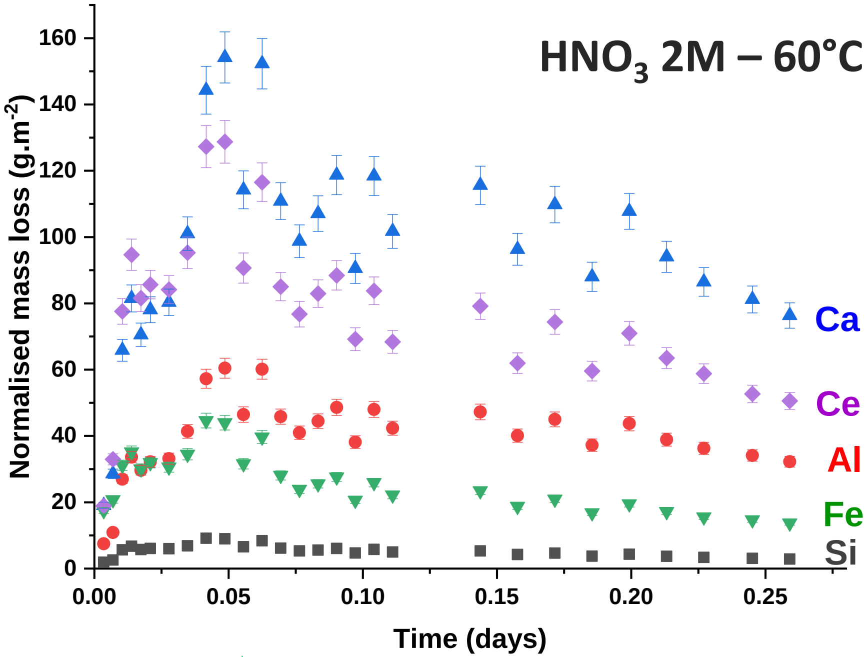

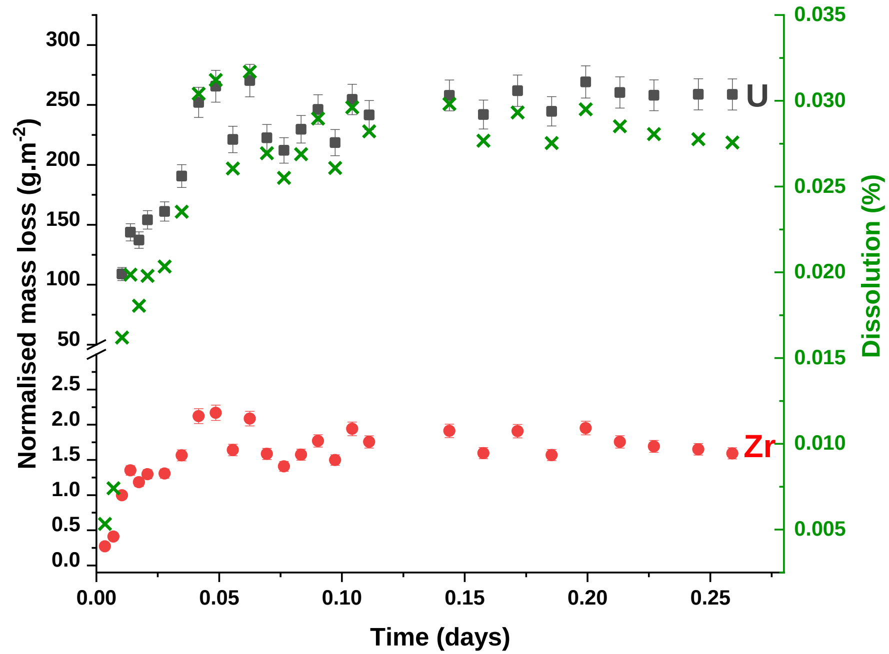

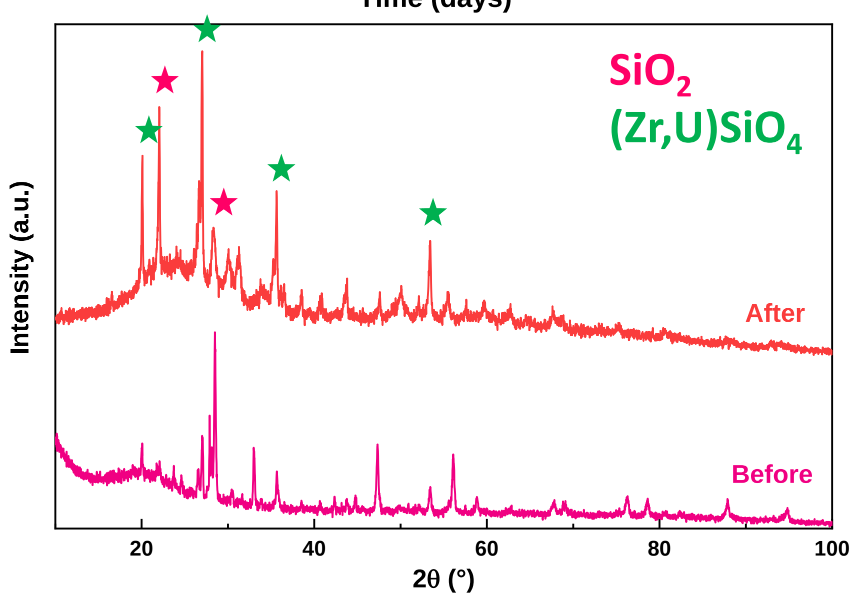

- UO_2 and ZrO_2-phases decreased
- Increased amorphous content
- U and Zr-phases reached steady state (passivating layer?)
- Ce follows behavior of glass elements

Conclusions

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Decommissioning nuclear accident reactors requires an understanding of the complex nature of the fuel debris

We have developed a suitable low-radioactivity surrogate for nuclear fuel that bears good resemblance to Chernobyl "lavas"

We have further developed these materials for application to Fukushima decommissioning, particularly to understand behaviour of cerium (plutonium)

Ongoing experiments are trying to understand the corrosion / dissolution behaviour of nuclear lavas and meltdown minerals

We are working with partners in Ukraine and Japan to help implement successful and timely decommissioning.

Thank you for your attention!

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