Diamond and Active Materials

Fred Mosselmans

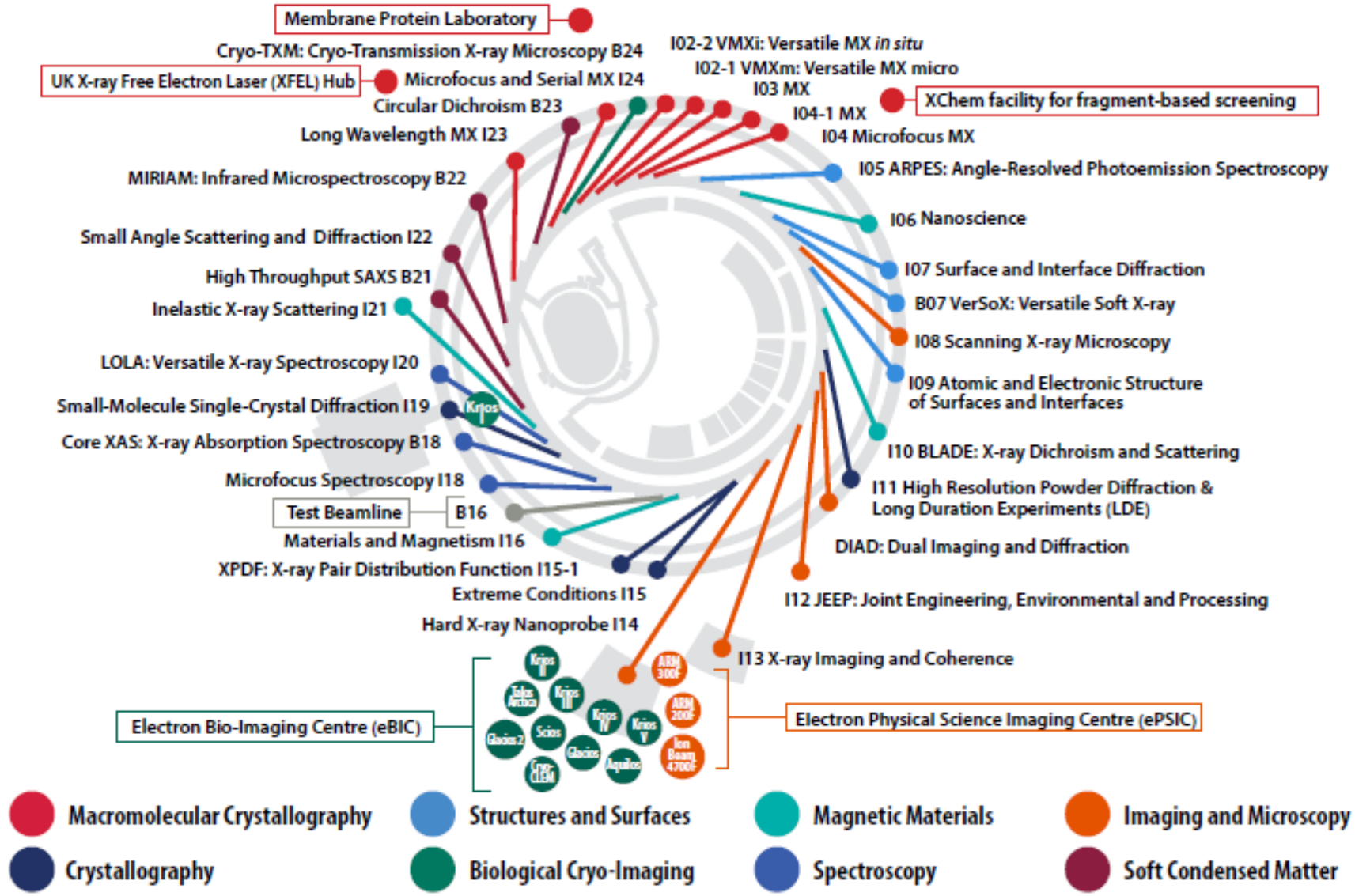
Outline

- Diamond Light Source
- The Active Materials Laboratory
- The Cell/Furnace for tensile testing on I12
- Active Experiments at Diamond
  - Spectroscopy
  - Diffraction
  - Imaging
  - Small angle scattering

Diamond Light Source

- UK National Synchrotron Source
- Harwell Campus
- Open since 2007
- Active experiments since 2009
- 2019-20 over 6000 and user visits and 6000 remote access use visits

Diamond Light Source



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Active Materials Laboratory

Project timeline

- Funding started November 2019
- Foundation work April 2020
- Building handover July 2021
- Lab complete July 2022

AML Lobby, storage room

- Lobby with requisite lab wear, lockers , hand foot monitor for use on exit
- Secure storage room for sample storage overnight with lead lined safes, lockable fridges and freezer.

AML Wet Lab

- Recirculating fume hood
- Anaerobic Coy Chamber
- Centrifuge
- Balances
- Fridge
- General Lab equipment
- Sluice sink for liquid waste disposal

AML Dry Lab

- 1200 C controlled gas furnace
- Anaerobic Dry glove box with microscope
- Anaerobic solvent tolerant glove box
- Pellet presses , one suitable for glove box use.
- Optical microscope
- Balances

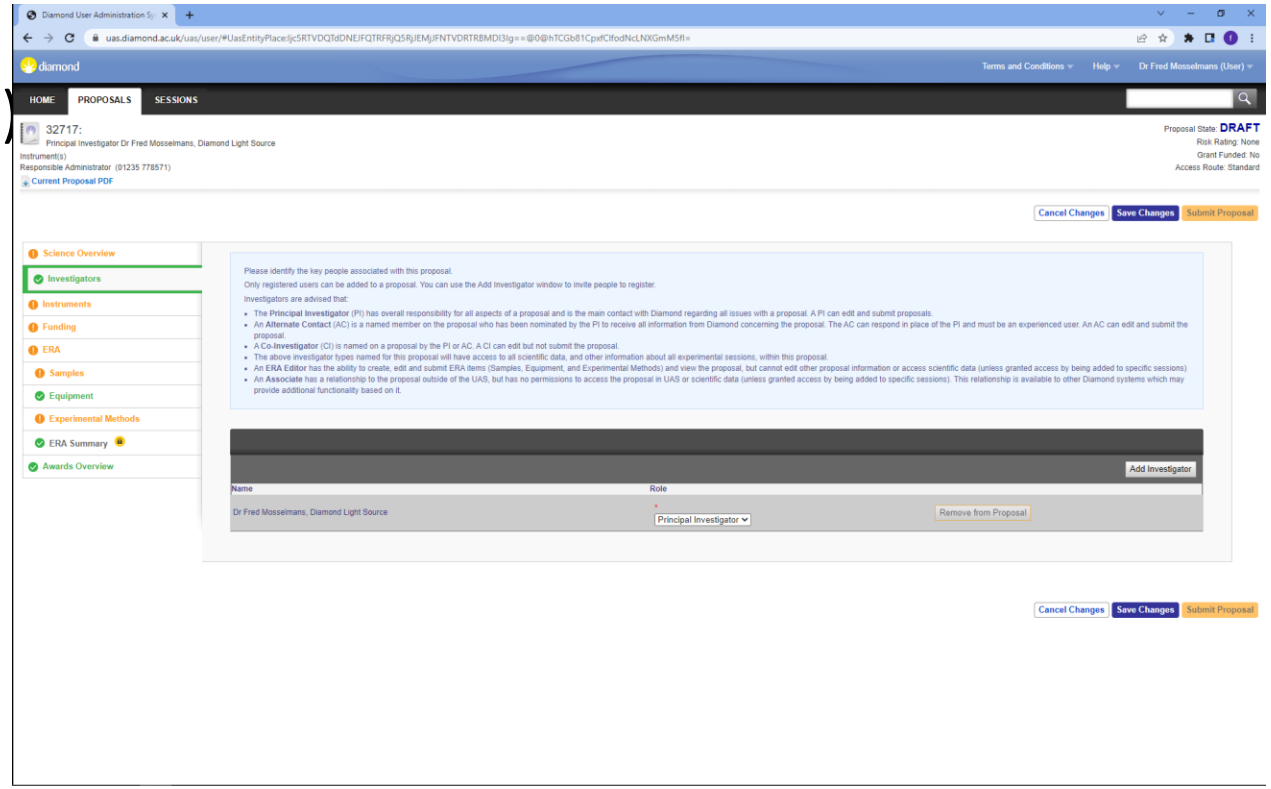
AML Counting room

- Gamma spectrometer
- Liquid Scintillation Counter

AML Lab access

- Access for use with beamtime via standard Diamond proposal route (next deadline **28/9/22**) (Proposal round every six months)
- Offline access also available through NNUF scheme.

- All access is free for non-proprietary work



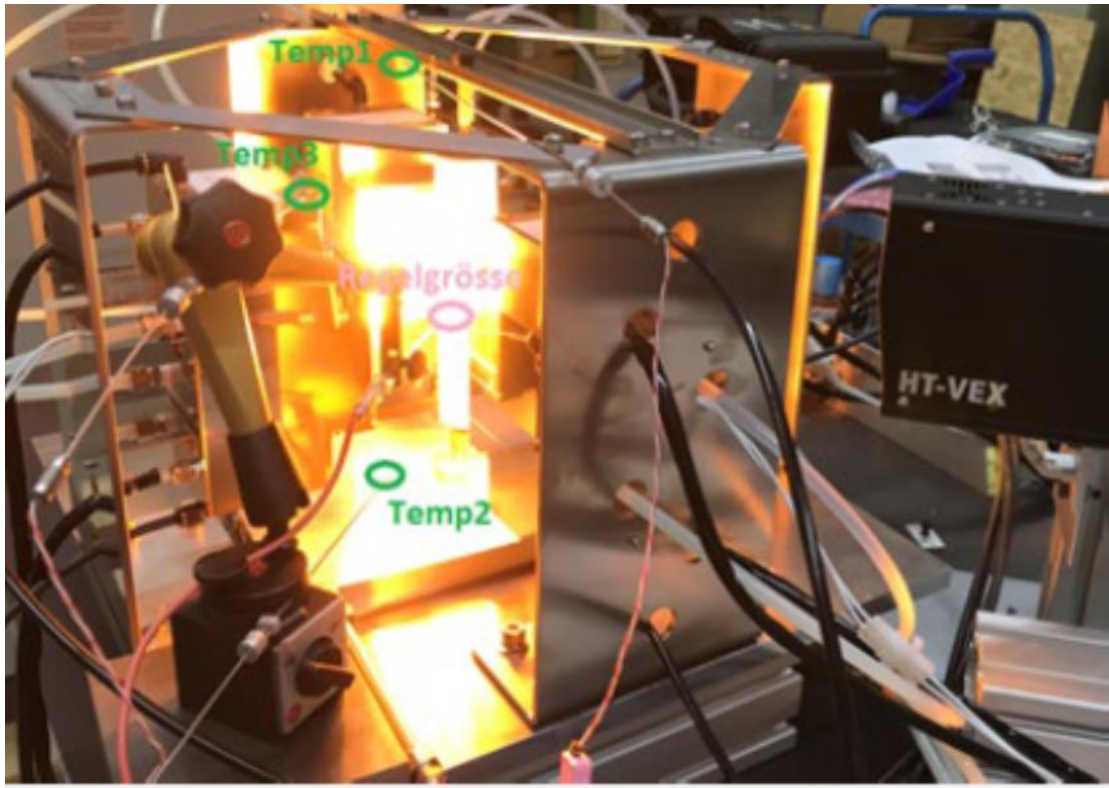
TR6 Furnace and cells

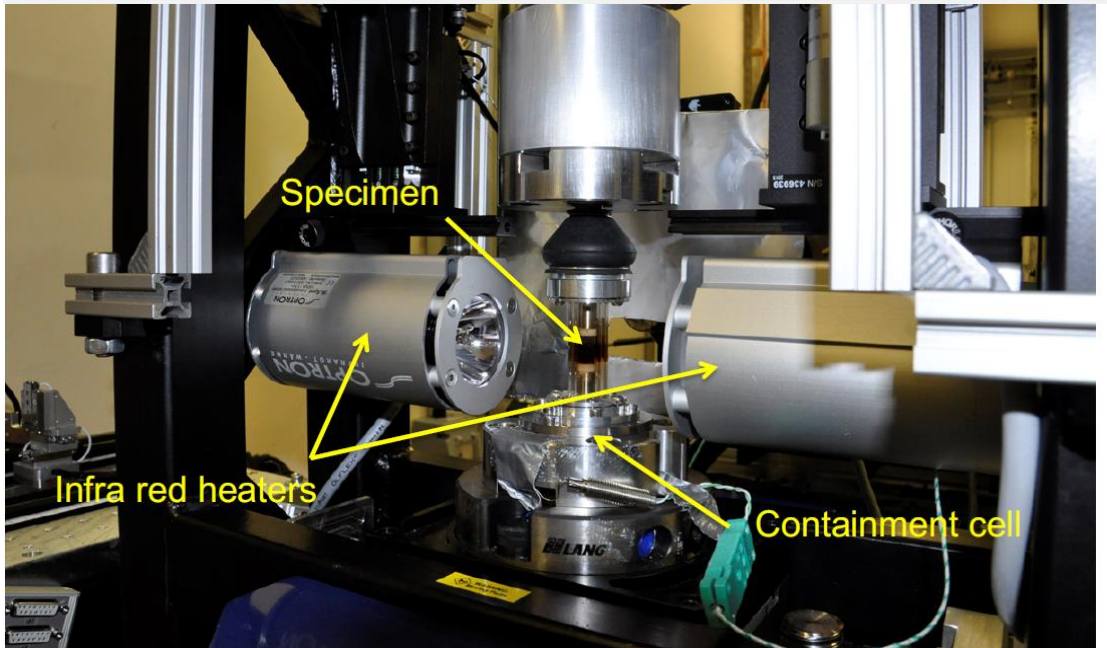
- To enable high temperature experiment of the 10 kN tensile rig (TR6) being procured for the High Energy diffraction/imaging beamline I12
- Quartz cells supplied by ICON led by David Dye
- 1000 C infra-red furnace supplied by Walther and Bai (TR6) supplier

TR6 Furnace and cells

- Delivery of both was much delayed by Covid-19
- Both now on site and SAT done or in progress.
- Enabling research similar to that by Paul Mummery on I13 looking at Graphite [Wade et al. Carbon 168, 230-244 (2020)]

- Sadly TR6 which was due for delivery early 2021, now not expected at DLS until January 2023 (Covid-19 and technical issues)
- Commissioning for active work expected to take best part of 12 months.

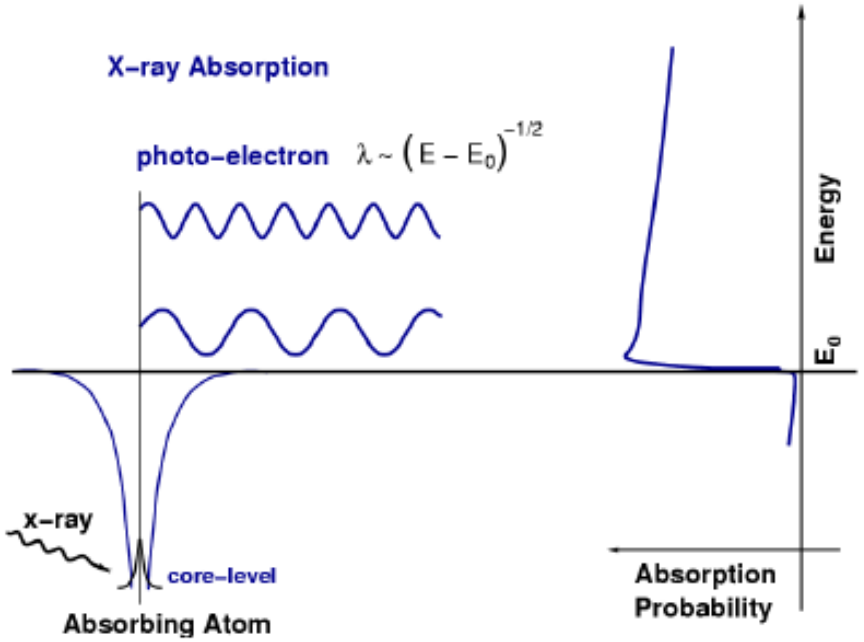




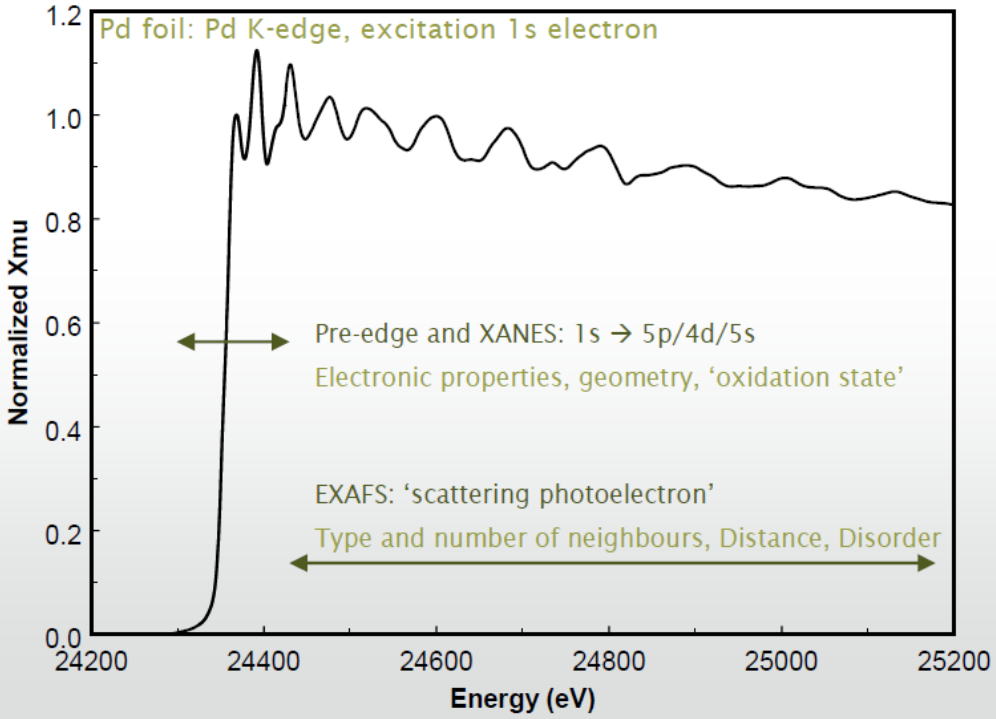
X-ray Absorption

X-ray absorbed by all matter through the so called **photo-electric effect**

- Core level electron absorbs energy x-ray: electron ejected from atom
- Atom left in excited state with an empty electronic level, i.e. *core hole*
- Any excess energy given to the ejected *photo-electron*



X-ray Absorption Spectroscopy



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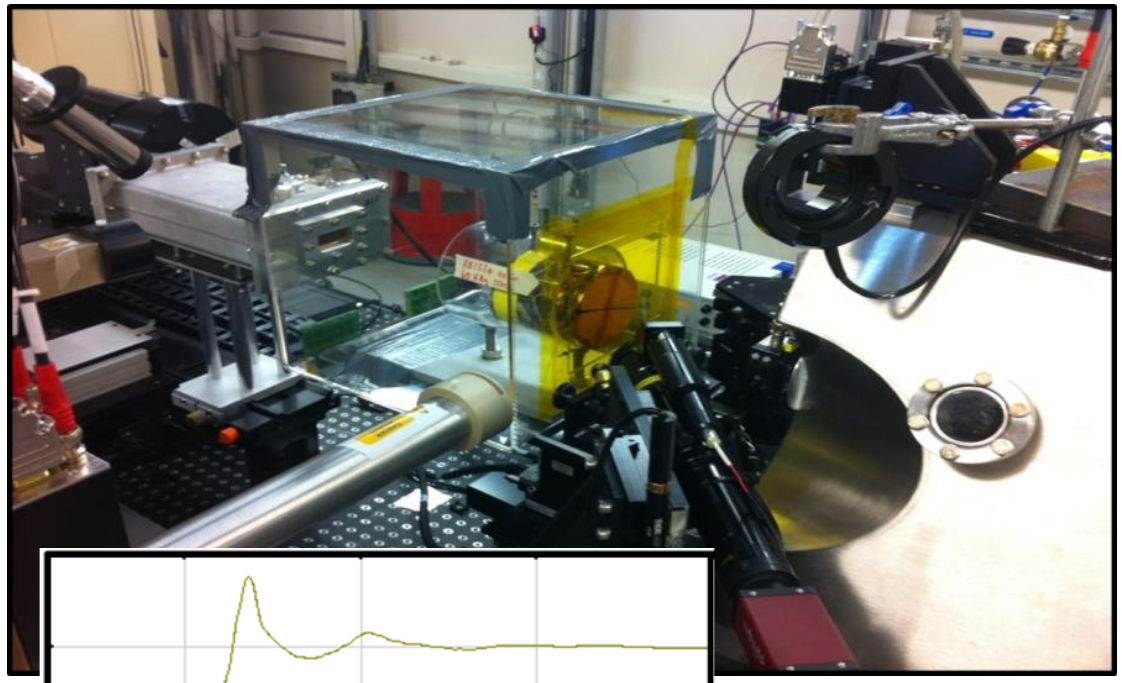
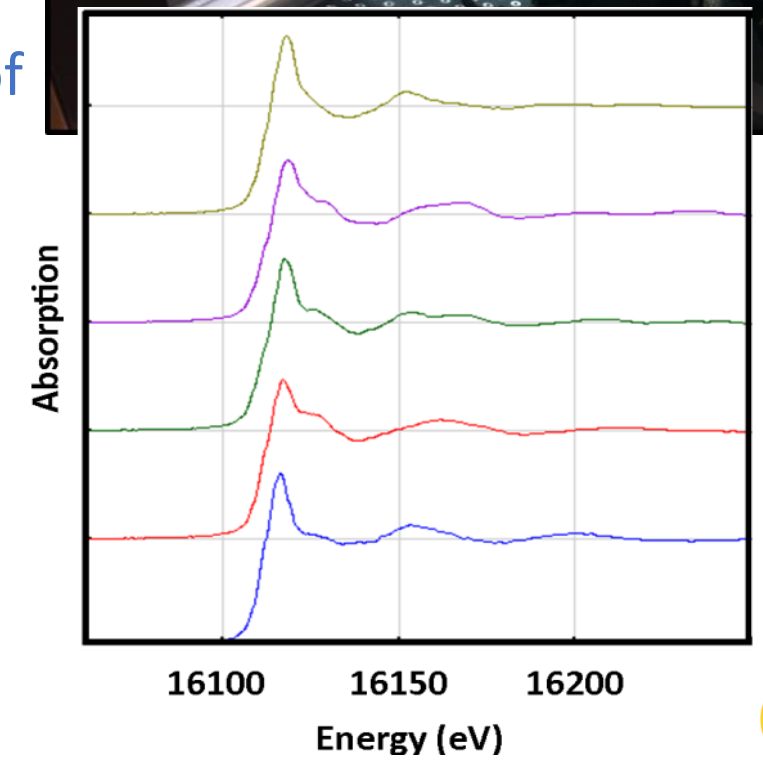
Hunterston Cooling Pond Core

- Hunterston A, Nuclear Power station in Ayrshire A small piece of core, 10 cm diameter, 30 cm long, was drilled from the 50 year old pond wall at the original water surface level.

- Autoradiographic analysis shows the presence of patches of active Cs and Sr on the painted, exposed surface of the core.

- In the coatings, a clear association of Sr with TiO2 has been observed, which suggests that radio-strontium may be scavenged to paint layers within the coatings.





Bower et al. Journal of Hazardous Materials, Vol. 317, 2016, 97-107.

Reflection EXAFS

Understanding absorbate mineral surfaces interaction

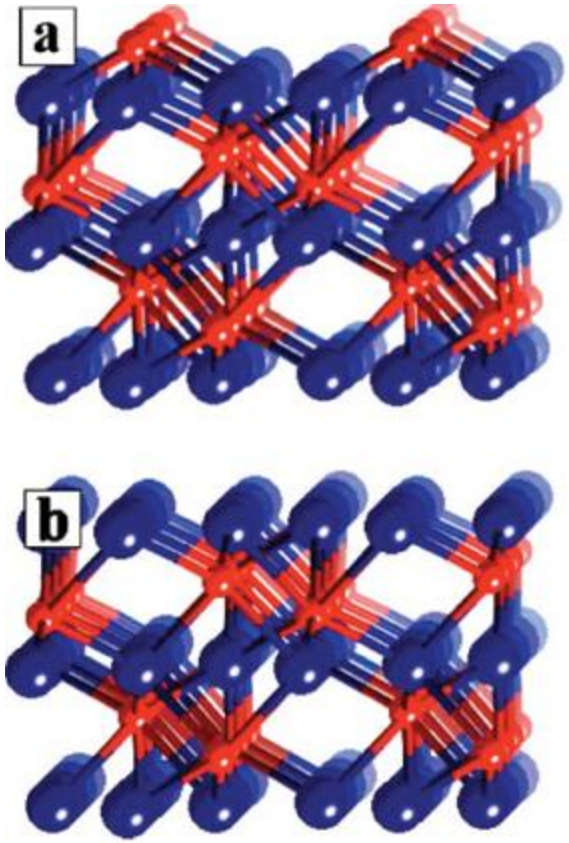
Reduce the complexity

Single surface - few or one site(s)

Looking at just the top few layers

Depth profiling

Hematite 001 surface



Eggleston *et al. Geochemical Transactions* 2004 **5**:33

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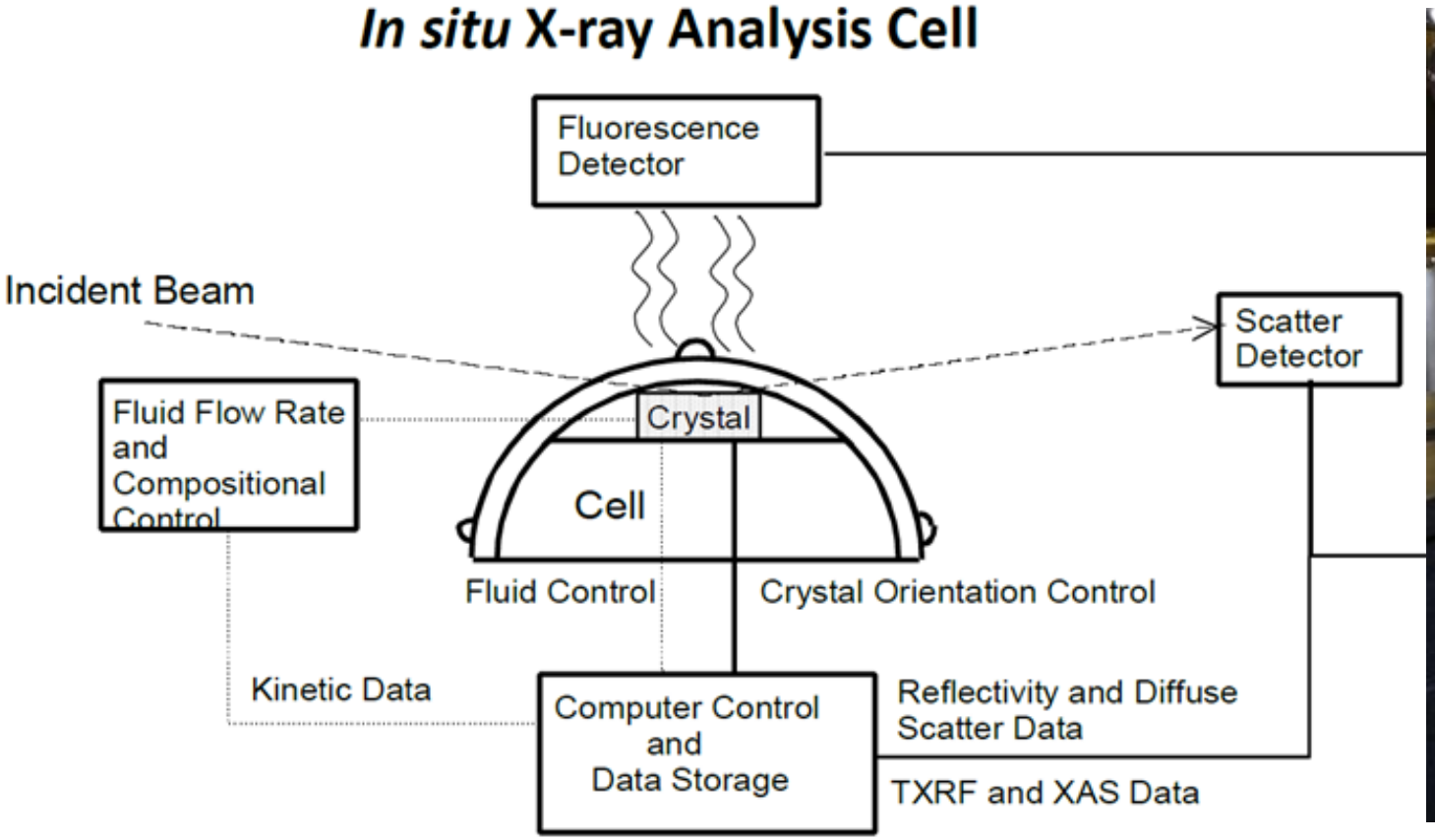
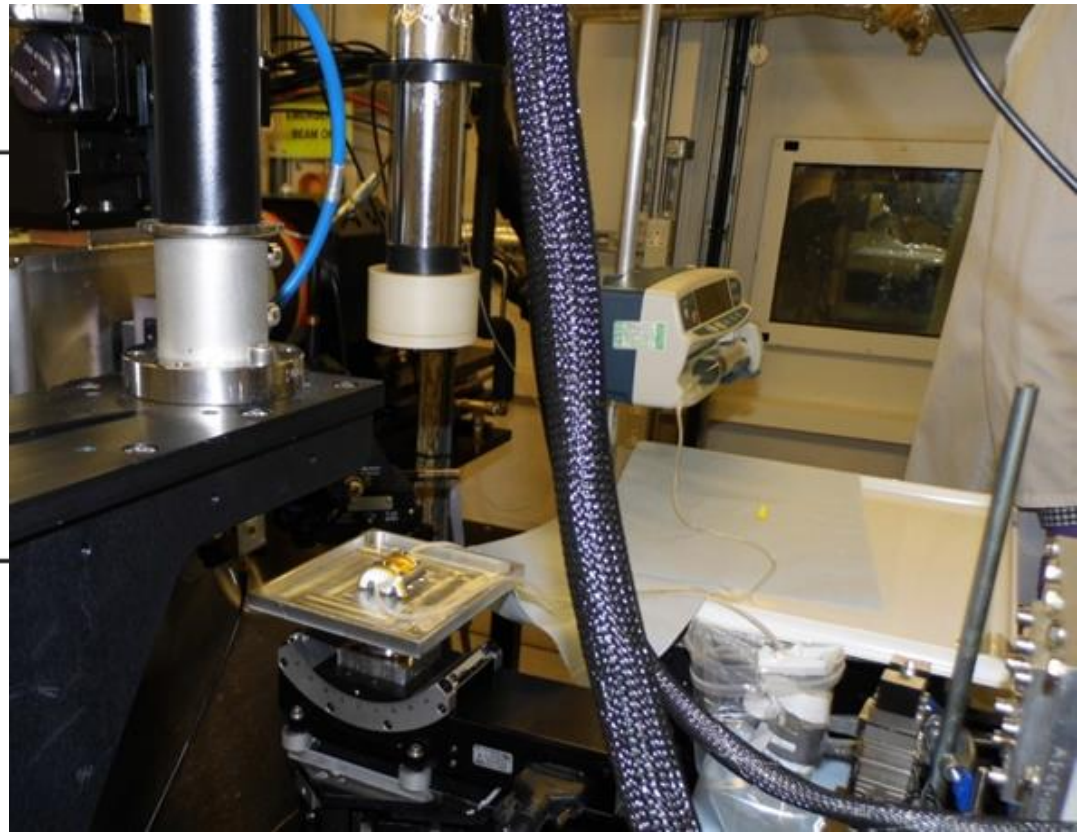
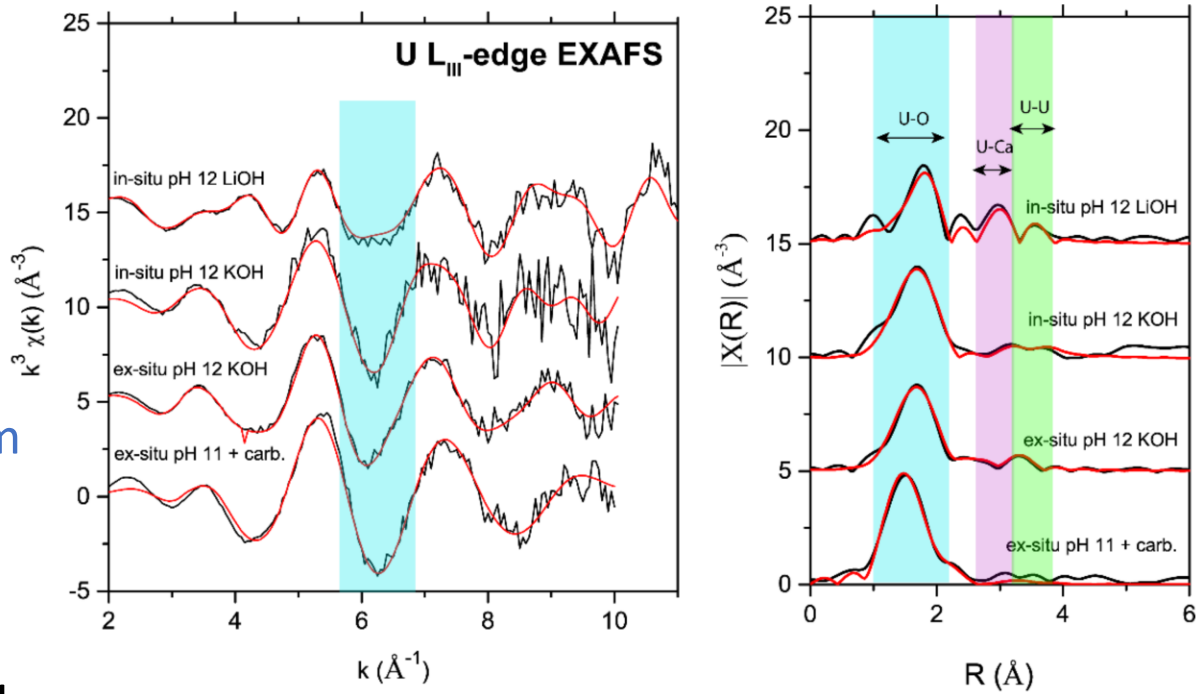
In situ flow analysis





Uranium (VI) Adsorbate Structures on Portlandite [Ca(OH)2] Type Surfaces

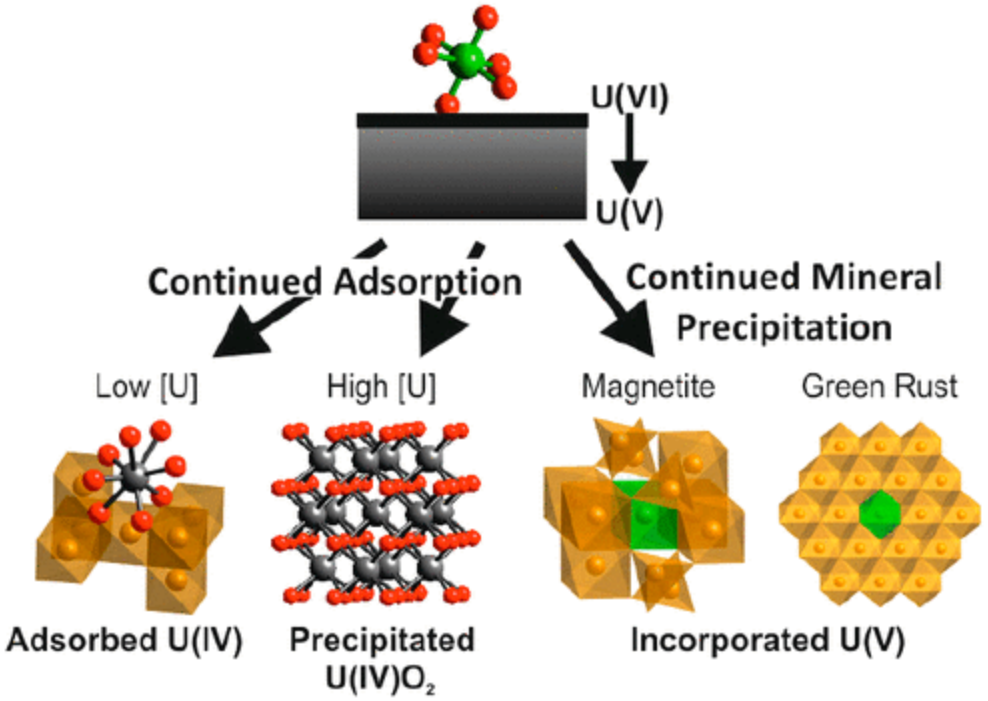
- Experimental EXAFS data looking at the CaO (111) analogue of the portlandite (001) surface are largely consistent with a six-coordinate structural layer or a deposit similar to calcium uranate,
- There is also strong evidence for uranyl-type coordination, as would be expected, to originate from the adsorbates predicted by the computational models.
- The X-ray absorption experiments show that the short preparation timescales of the in situ and ex situ experiments, of 2 to 48 h, respectively, indicate that the uptake of uranyl by portlandite is extremely rapid, particularly in the context of GDF timescales.



Lee at al. Minerals 2021, 11(11), 1241;

Uranium(V) Incorporation Mechanisms and Stability in Fe(II)/Fe(III) (oxyhydr)Oxides

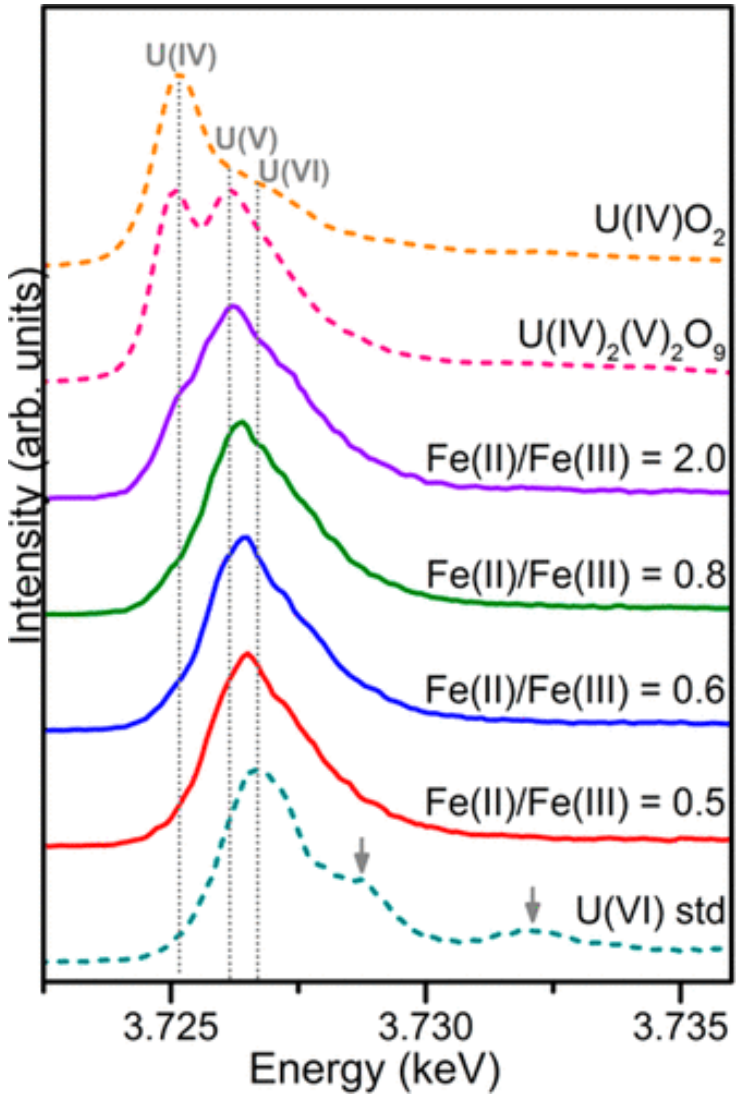
- Synthesize both magnetite and green rust with U(VI) via a co-precipitation process
- Examine the products with XAS and other techniques
- Magnetite was nanoparticulate, sizes ranging from 1 to 20 nm
- Green rust was present as pseudohexagonal plates of approximately 50–600 nm, and in chloride form



Roberts et al., Environ. Sci. Technol. Lett. 2017, 4, 10, 421–426

Oxidation state determination by M4 edge spectroscopy

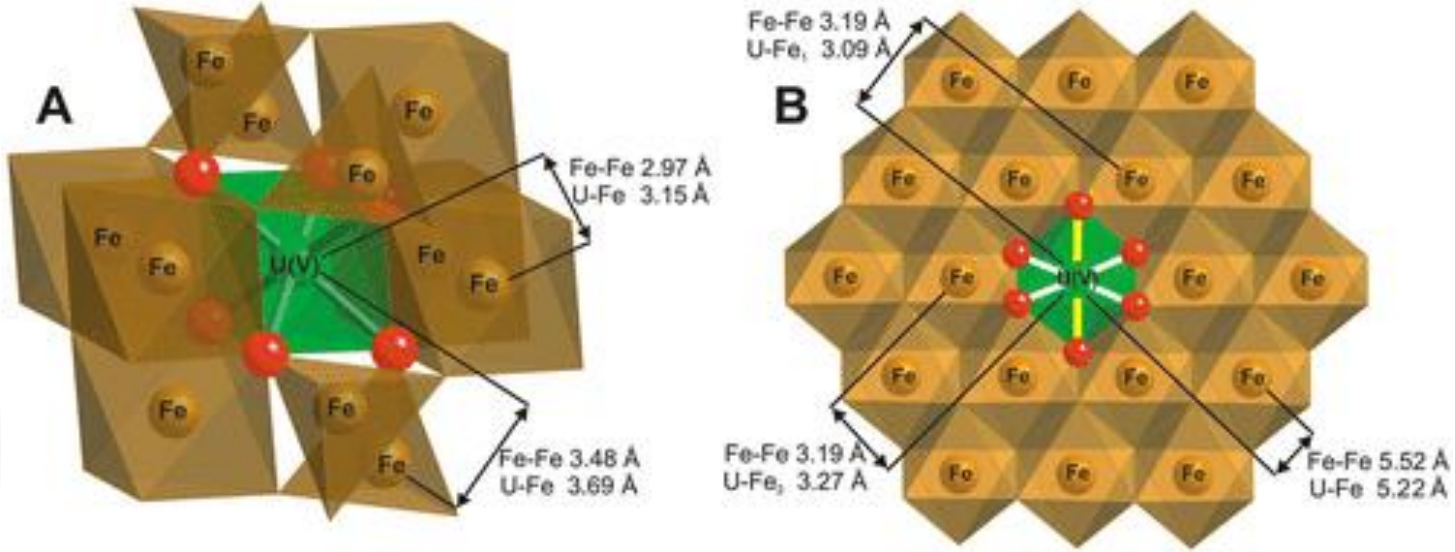
- Both magnetite and Green rust with varying Fe II/Fe III ratios show a substantial U (V) content stablised in the Iron oxide
- Over 80% in the lower Fe II/Fe III ratios, over 60% in the Fe II/Fe III 2.0 sample
- This data was collected at the ESRF but the technique will be routinely available at Diamond by the end of next year



Structural determination with EXAFS

- In both systems U(V) is incorporated into the mineral structures via direct substitution of U for octahedrally coordinated Fe. In magnetite, the average U(V)–O bond length is 2.17 Å [Fe(II)/Fe(III) = 0.5 and 0.6], consistent both with U(V) in uranate-like coordination.

- Dissolution data shows 35–40% of U is released with minimal Fe dissolution, suggesting this fraction is near-surface-associated U(V)/U(VI) and UO2, with the remaining U distributed evenly throughout the particles



- The incorporation of U(V) into green rust [Fe(II)/Fe(III) = 0.8 and 2.0] also occurs via direct substitution for octahedrally coordinated Fe within the sheet structure of the layered double hydroxide.

- Dissolution data indicate that 35–40% of U is present as a discrete phase or is near-surface-associated, which is consistent with the presence of UO2 in the XAS, formed via the process stated above, and some near-surface-associated U(V)

Roberts et al., Environ. Sci. Technol. Lett. 2017, 4, 10, 421–426

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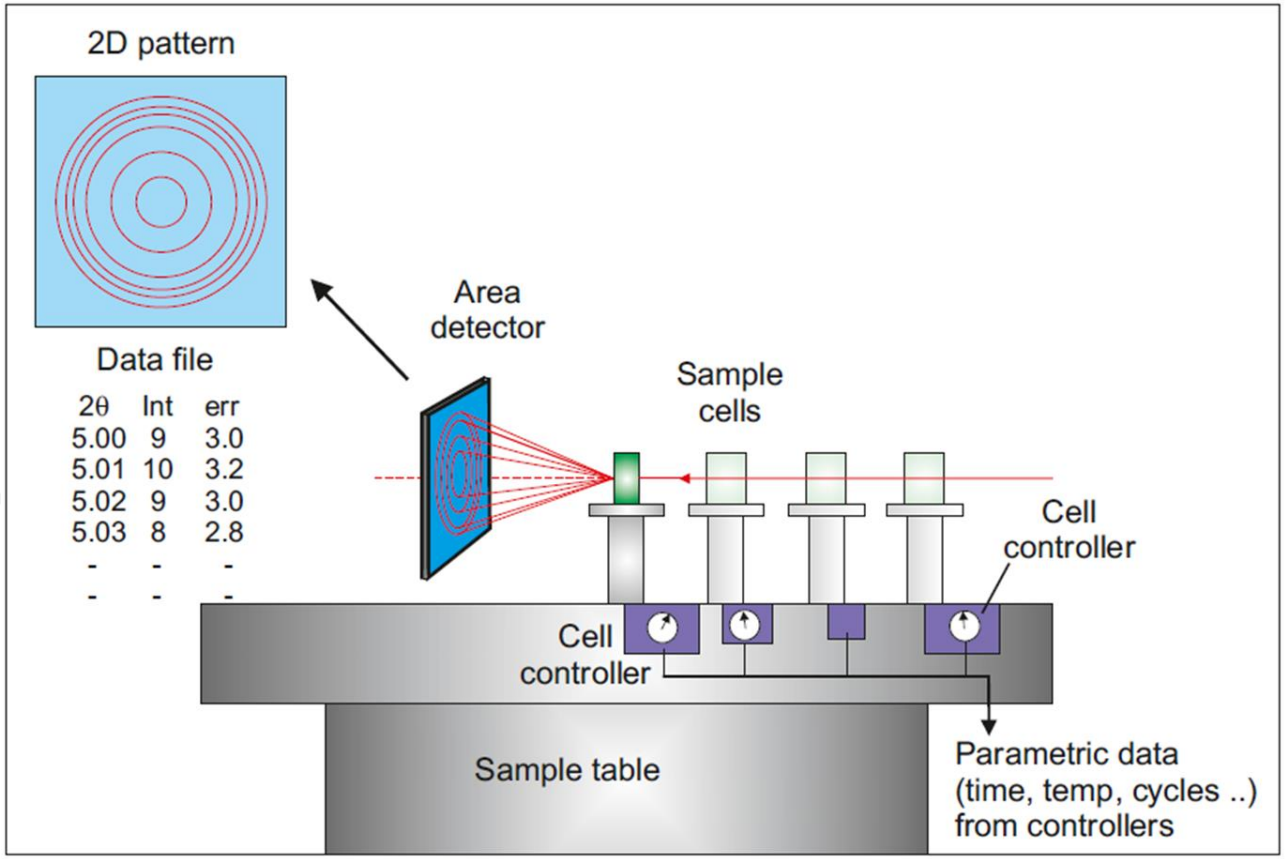
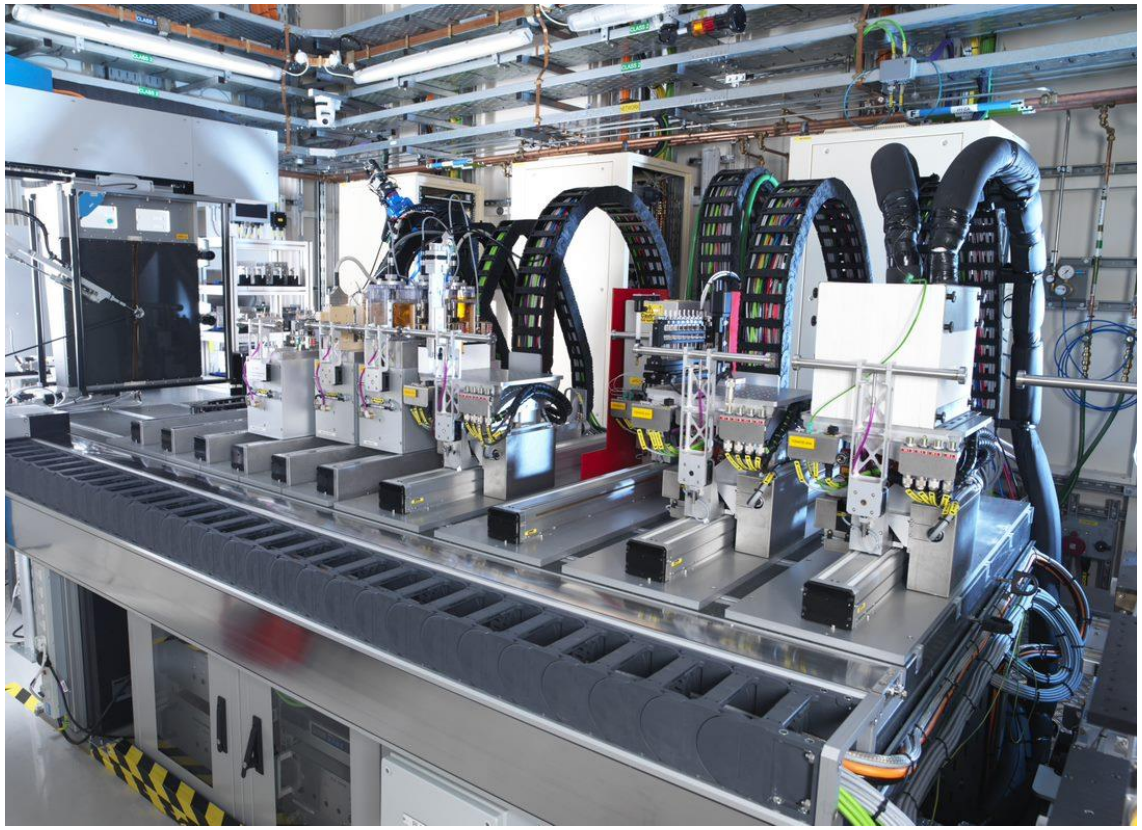
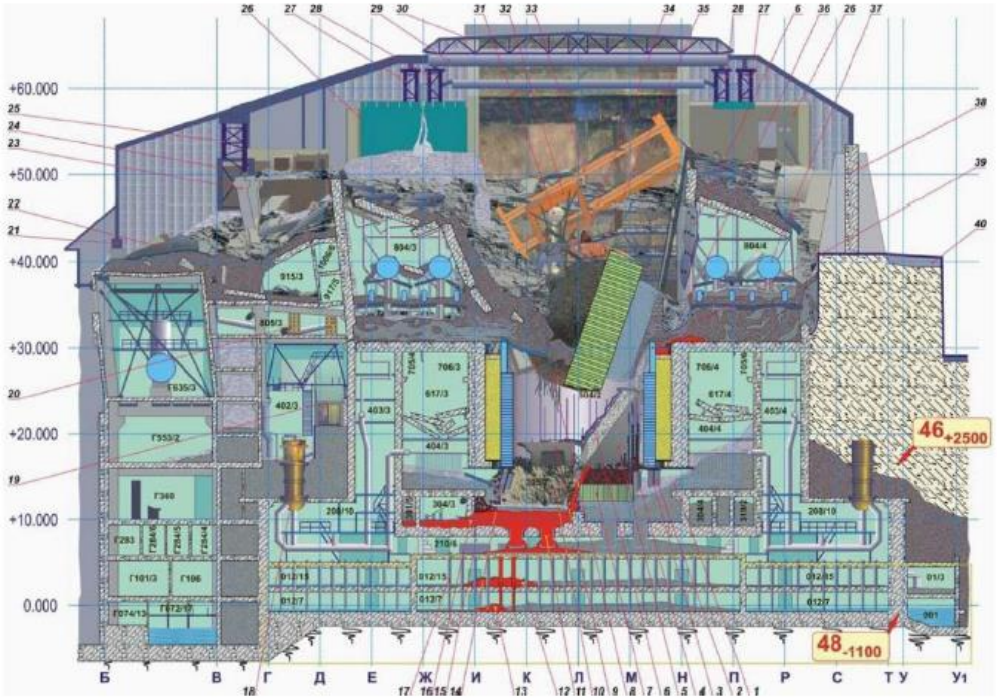
Long duration experiments monitored weekly I11 LDE





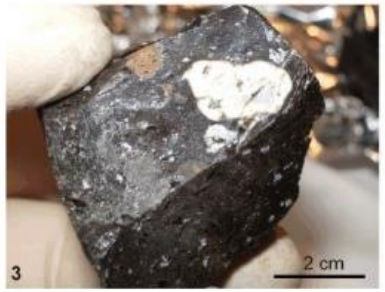
Understanding reactor fuel

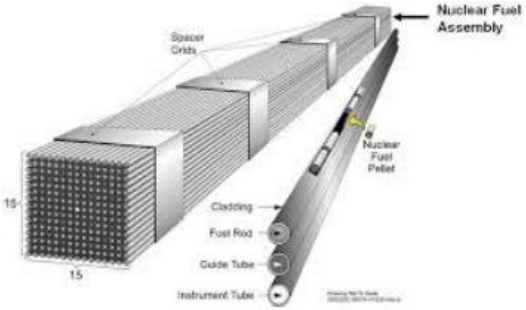
Chernobyl Reactor 4 (1986)



Brown Lava

Black Lava





$U_{1-x}Zr_xO_2$
solid solution

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

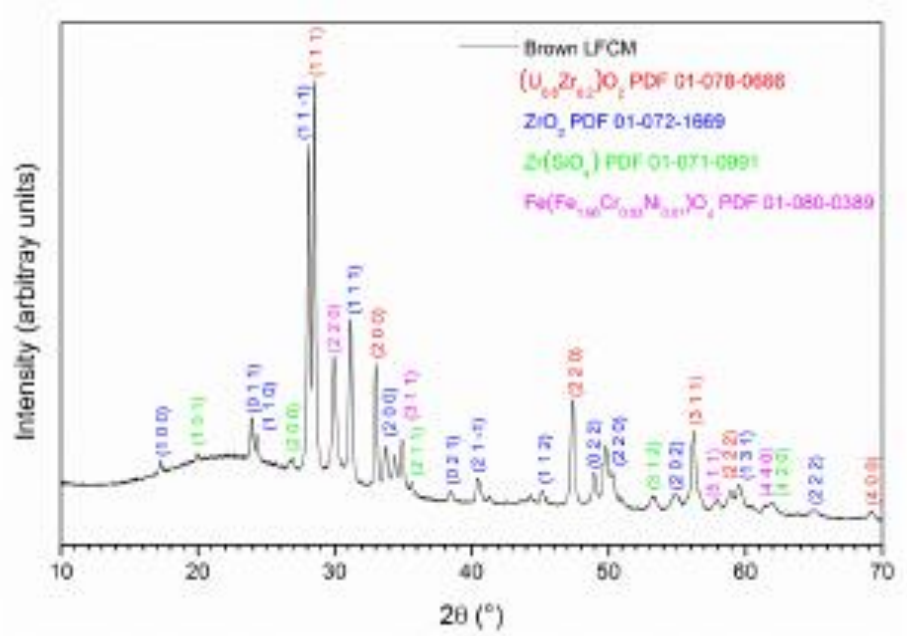
Decommissioning requires:

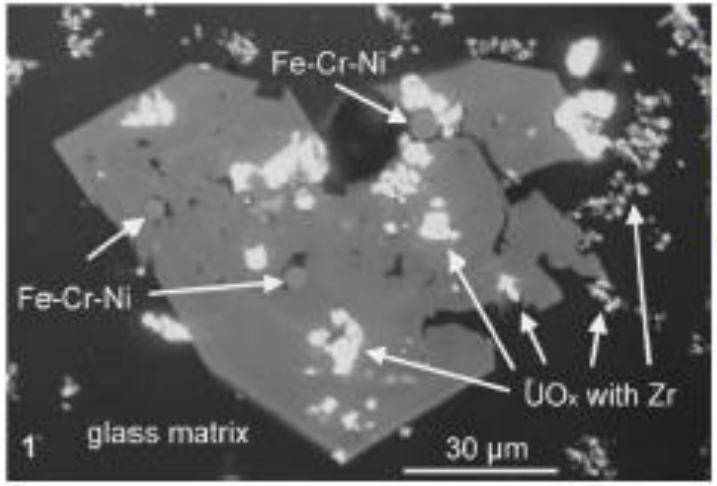
- Understanding of fuel chemistry
- Knowledge of mechanical properties
- Evaluation of corrosion mechanisms and generation of α-active dust

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

Slides from Claire Corkhill

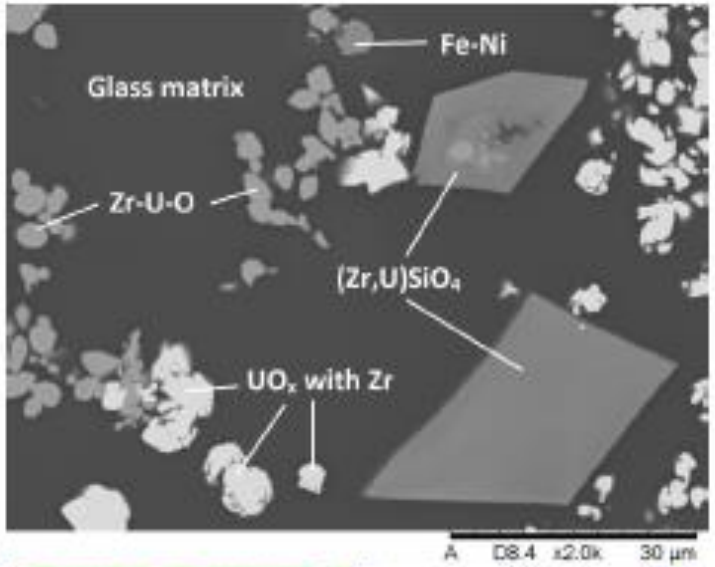
Simulant Chernobyl Fuel

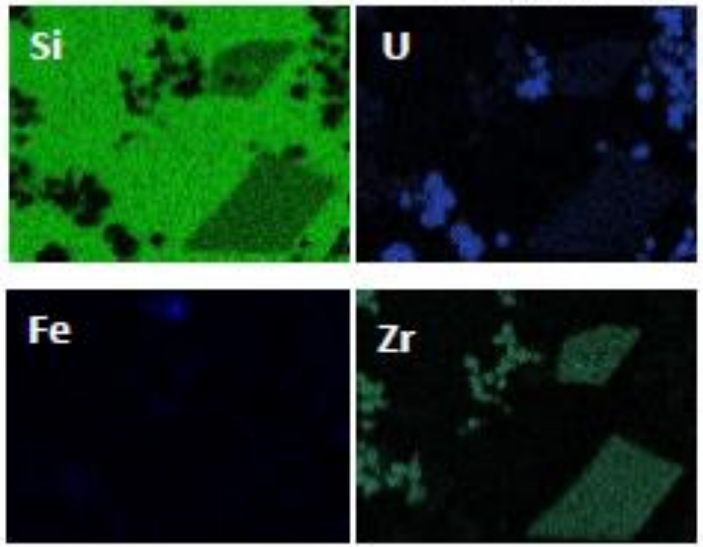




"Real" LFCM by Boris Burakov

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

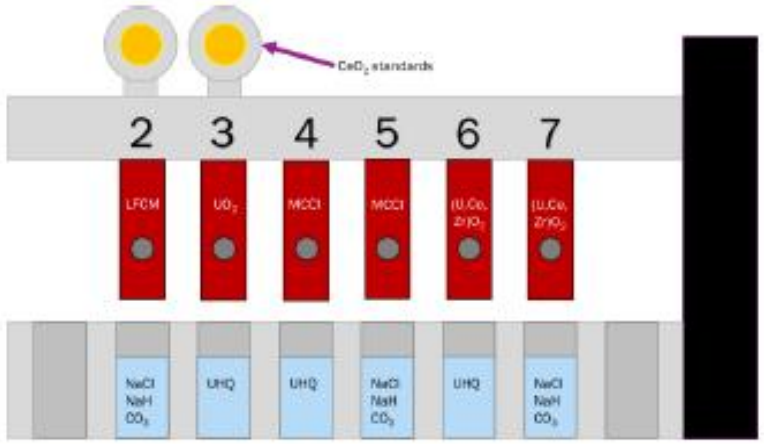




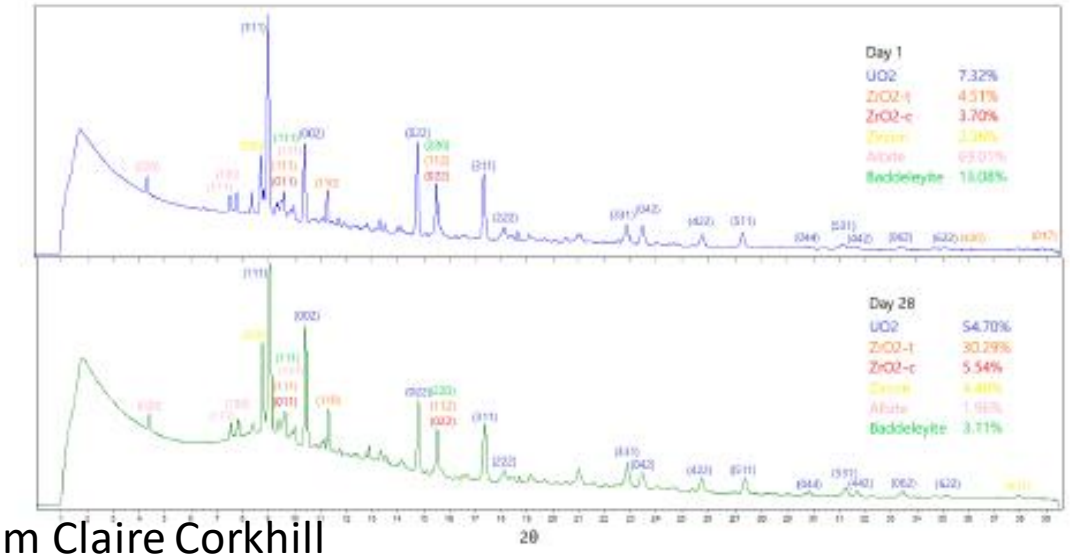
Chernobyl: Barlow et al. npj Mater. Degrad. (2019); Ding et al. JMCA (2021),
Fukushima: Ding et al. npj Materials Degradation (2022)

Slides from Claire Corkhill

Weekly diffraction patterns



Weekly diffraction patterns acquired from UO_2 SIMfuel and Chernobyl / Fukushima fuel debris, during *in-situ* corrosion



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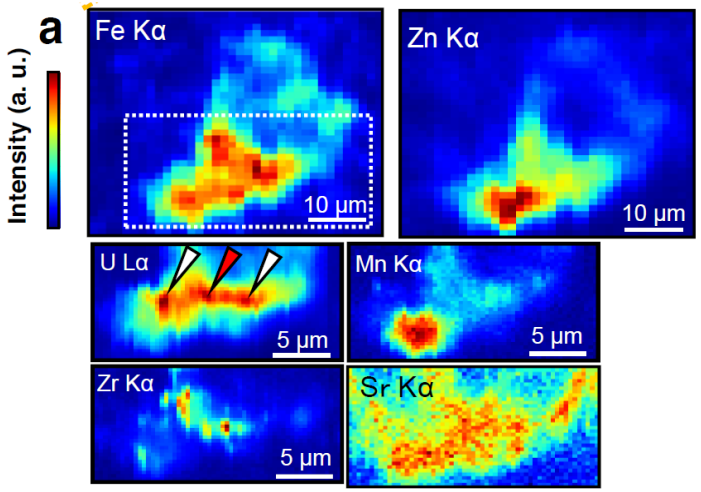
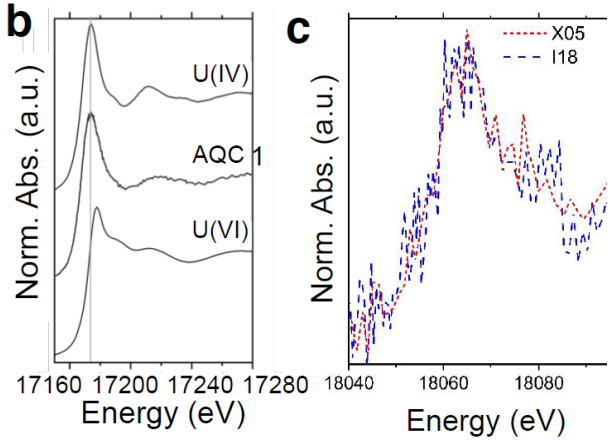
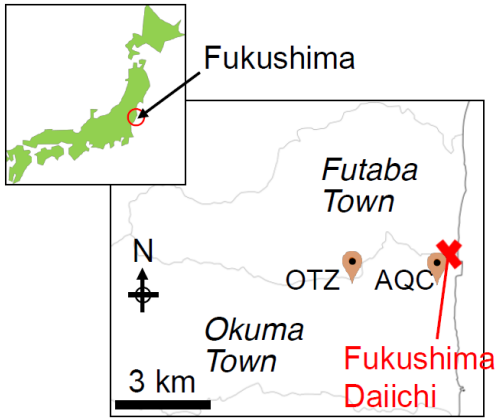
Beamline I11-LDE
X-ray Diffraction

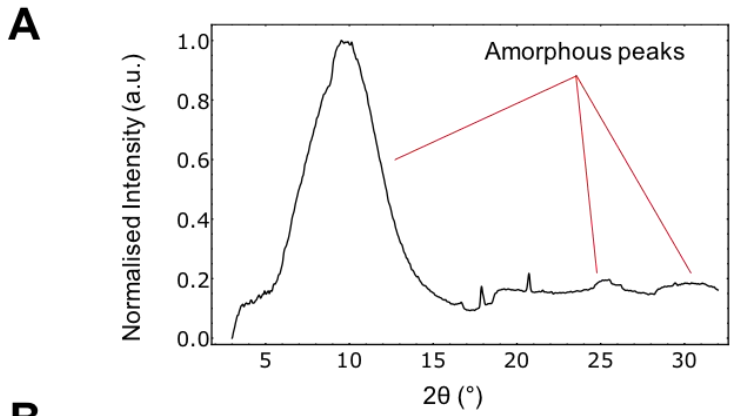
Slides from Claire Corkhill

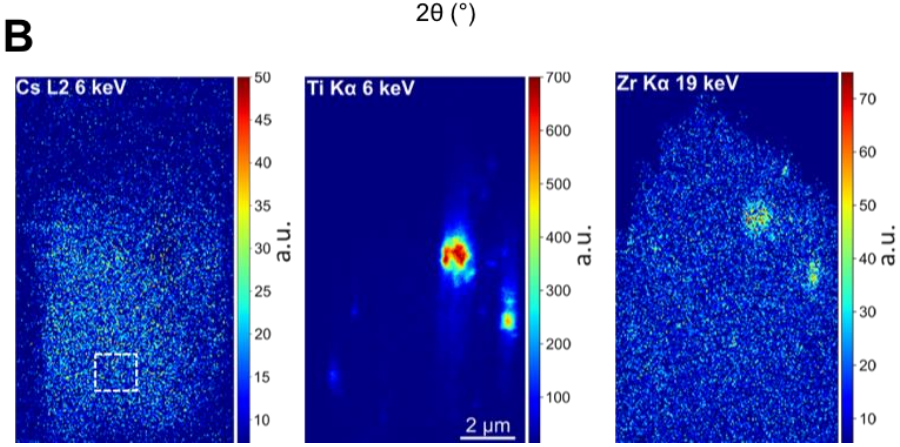
Imaging active materials in particles











Kurihara et al. (2020) Science of the Total Environment, 743, 140539
Morooka et al. (2021) Science of the Total Environment, 773, 145639

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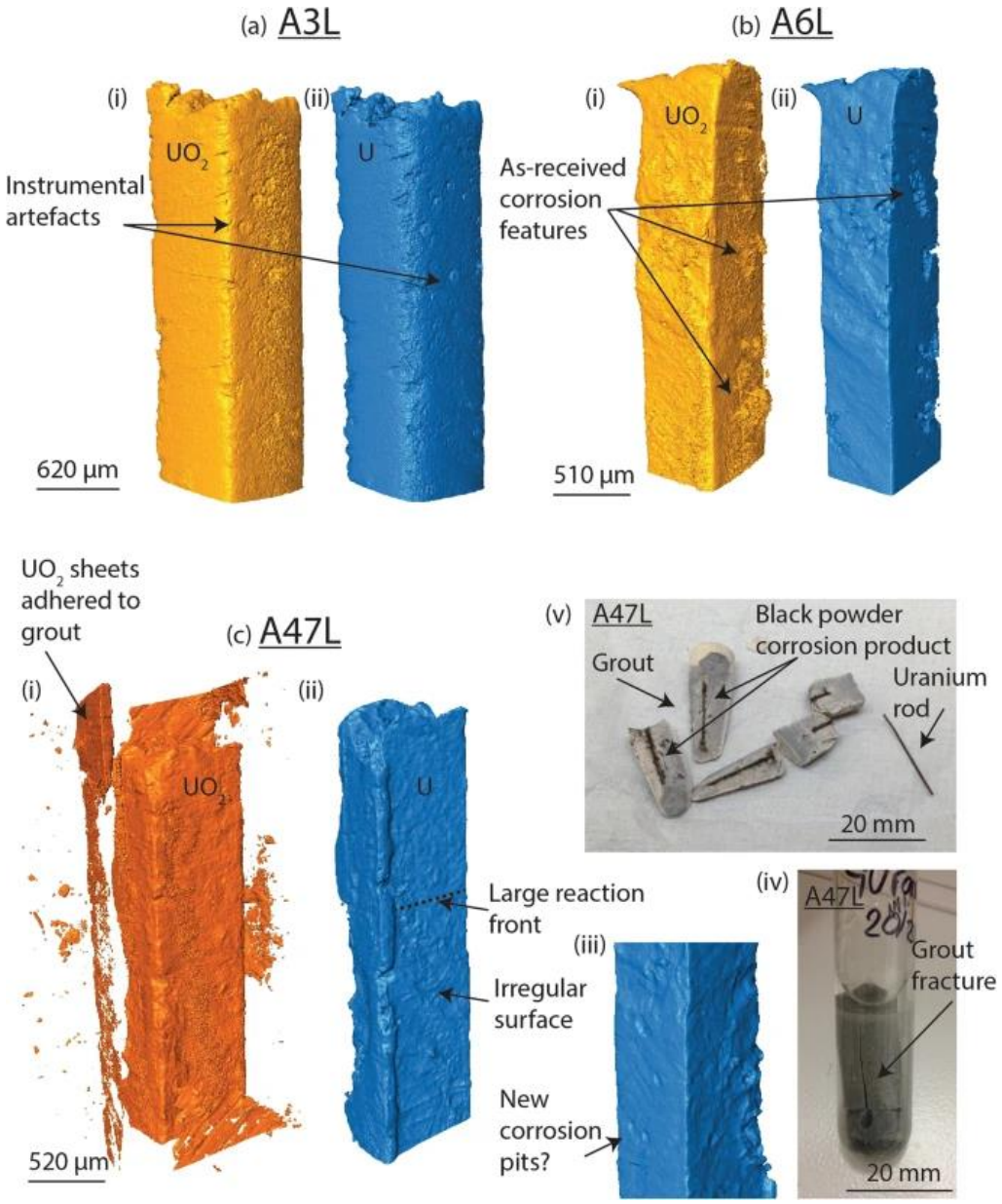
High Energy Imaging and Diffraction

Tomographic and XRD study on the corrosion of uranium rods in grout in deionised water

UO_2 was considered the dominant corrosion product forming on both the nitric acid etched and as-received uranium metal. It was evident that UO_2 growth increased over time, with some samples exhibiting accelerated corrosion in comparison to others.

Stitt et al. 2018 Scientific Reports 8: 9282



Small Angle X-ray Scattering to look at colloid formation

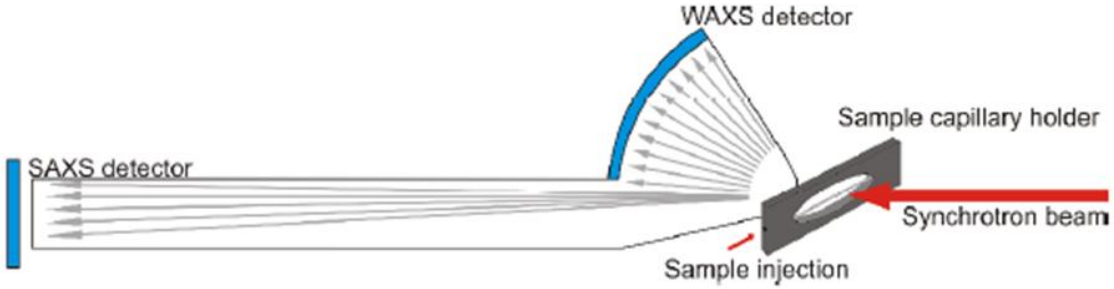
First radioactive experiments performed at the non-crystalline diffraction beamline (I22) at Diamond Light Source

Aged 42 µM U(VI) solution samples from filtration experiments

- 1 week
- 20 months
- 32 months

In-situ experiments

42 µM U(VI) experiments performed at the beamline for *in-situ* time resolved analyses



Bots et al. Langmuir 2014, 30, 14396–14405

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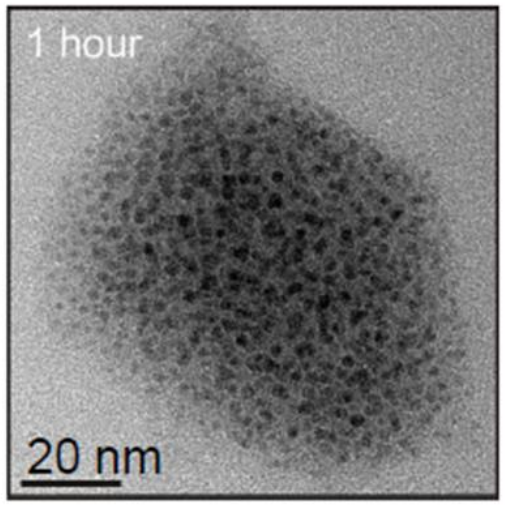
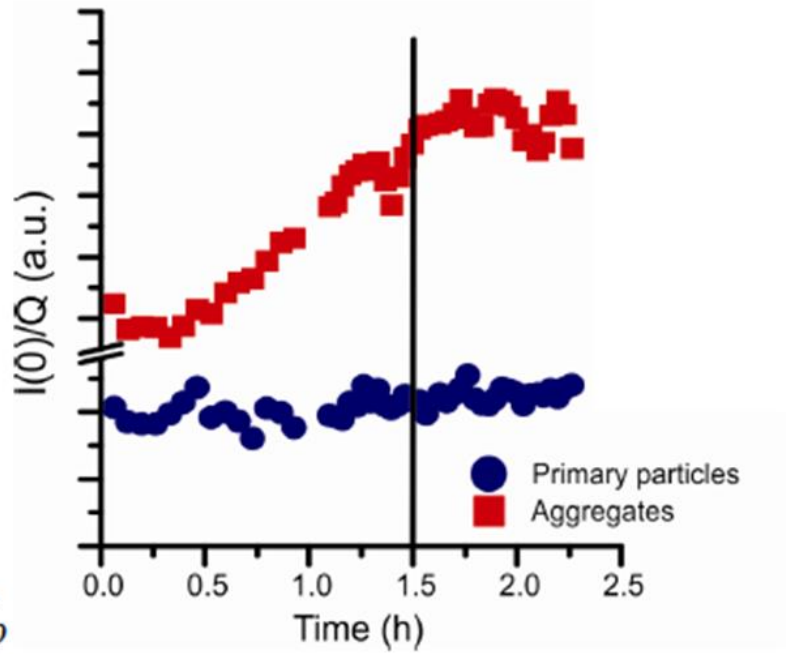
In situ results





Time-resolved experiments

$$\frac{I(0)}{Q} \approx V_p$$

Particle volume

- Primary particles -> nucleation dominated
  -> nucleated as amorphous particles
- Aggregates -> growth through aggregation and/or nucleation on aggregate surfaces

Bots et al. Langmuir 2014, 30, 14396–14405

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Acknowledgements

- NNUF II/ EPSRC for funding the AML project EP/T011246/1
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- Flow cell Roy Wogelius EPSRC : EP/I036389/1
- U in Fe Oxides Sam Shaw and STFC
- LDE Claire Corkhill
- Particle imaging Gareth Law and Satoshi Utsunomiya NERC NE/M014088/1
- U Hydride Tom Scott
- U colloids Sam Shaw