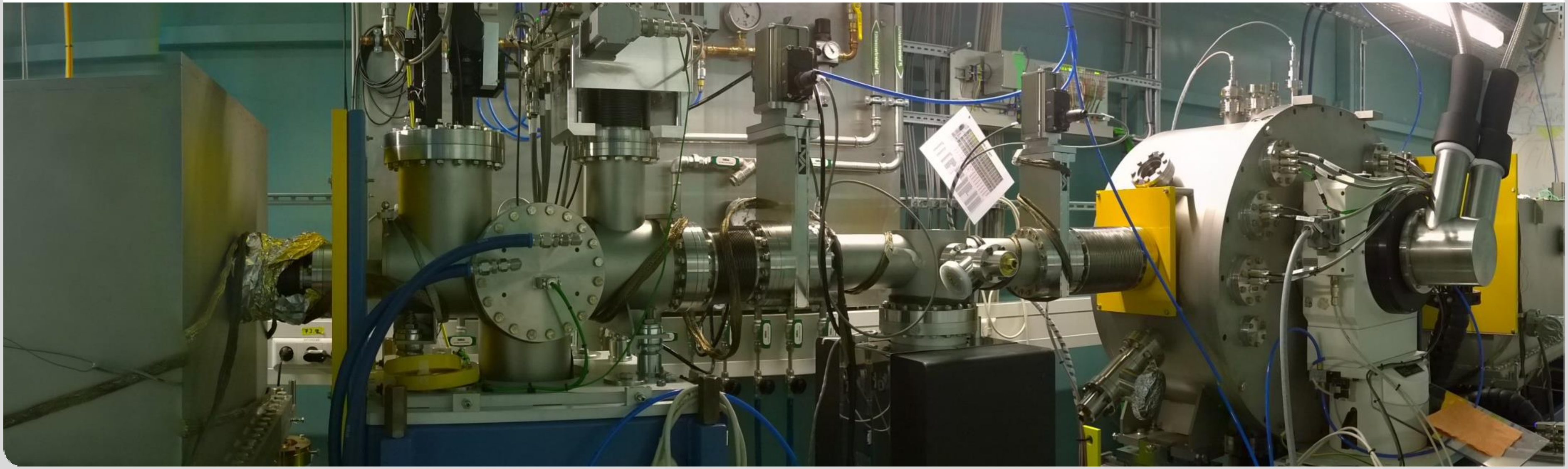
Hard X-ray XAS investigations of high level nuclear waste forms (HLW) at the KIT Light Source

European Summer School (Strasbourg - Karlsruhe) – 3. July 2024

JÖRG ROTHE – KARLSRUHE INSTITUTE OF TECHNOLOGY, INSTITUTE FOR NUCLEAR WASTE DISPOSAL



Nuclear energy phase-out - the German case

- Nuclear energy phase-out decision in Germany after the Fukushima incident taken in **2011**
- Site Selection Act (StandAG) passed the federal parliament in **2017** – 'white map', suitable site / host rock formation for geological disposal to be determined until **20??**…

HAW Interim Storage Facility Gorleben
Photo: GNS

- As a result of nuclear energy use over decades, a final volume of ~**29.000 m^3** high level, heat generating waste (HLW: spent nuclear fuel (SNF), vitrified residues from reprocessing) has been generated **until 2022**.
- The proposed strategy is to design a deep geological repository (DGR) in the most appropriate host rock providing for the highest possible level of safety. The DGR shall be operational earliest by **2050**. It is suspected, though, that planning, licensing and construction will take significantly longer!

→ **HLW interim storage capabilities required until the end of the 21st century!**

Background and motivation

Determination of the physical and chemical state of actinides and long-lived fission / activation products in **real** – **not simulated** – HLW matrices derived from nuclear processes (vitrification of reprocessing residues (HAWC) / irradiated reactor fuel pins) – in order to…

- Assess long term behavior / radionuclide release upon possible corrosive waste matrix degradation in a future DGR → **‘source term’**
- Understand and predict ageing of HLW in transport and interim storage casks (‘CASTOR’) upon prolonged dry storage (very likely to exceed 40 years) → **fuel cladding degradation / failure?**
- Develop and adapt suitable, highly versatile speciation methods for radionuclide materials with contact dose rates up to several mSv/h

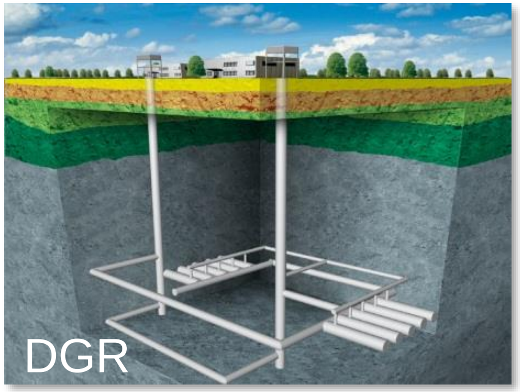
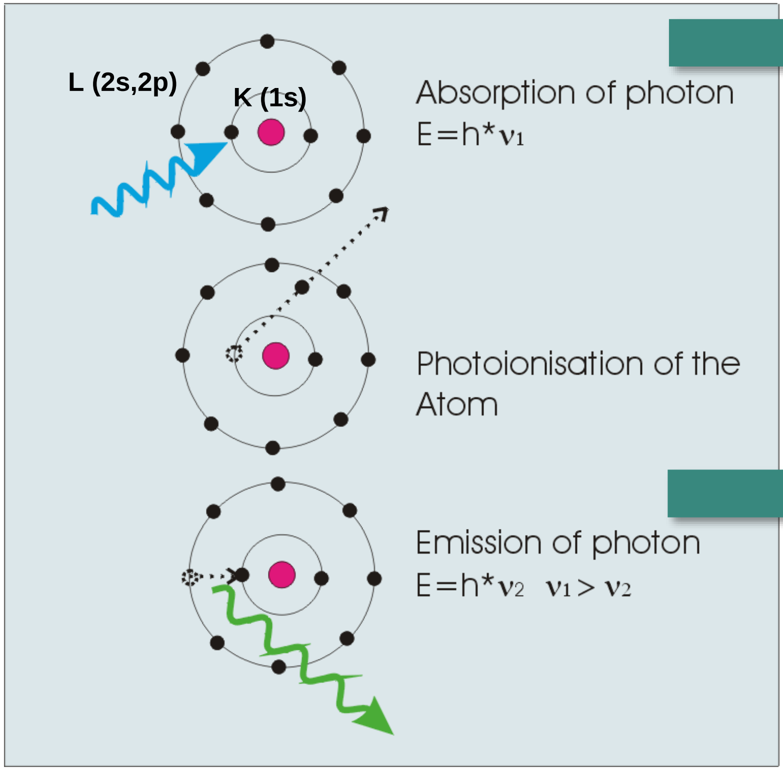



Photo: GNS

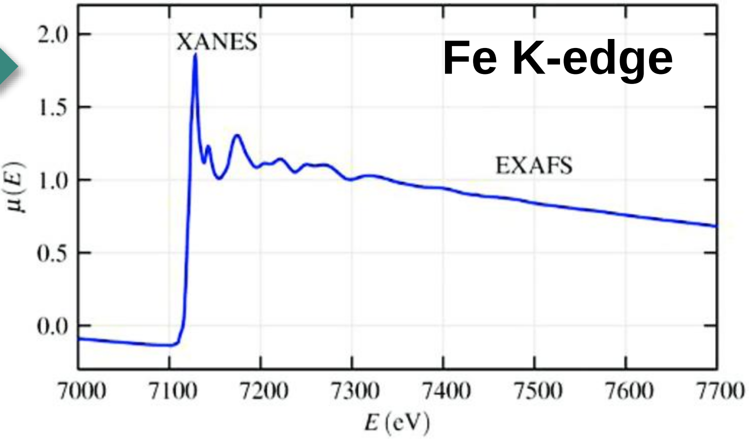
X-ray Absorption Spectroscopy (XAS)



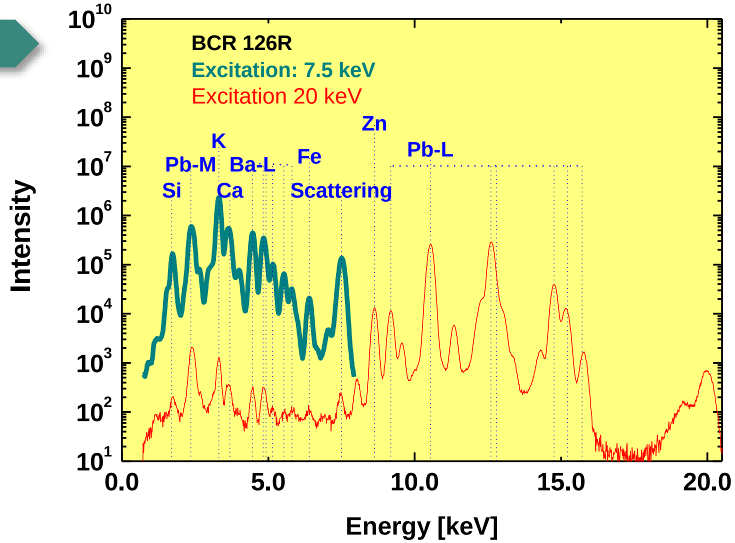
Absorption of photon
$E=h*\nu_1$

Photoionisation of the Atom

Emission of photon
$E=h*\nu_2 \quad \nu_1 > \nu_2$



XAS



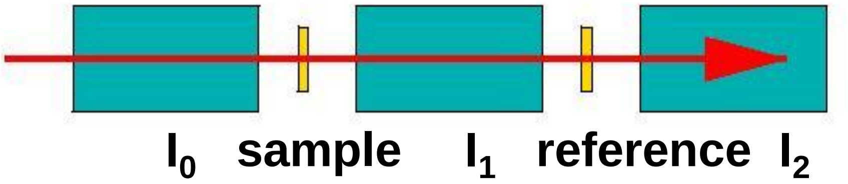
XRF

photo-absorption and following relaxation

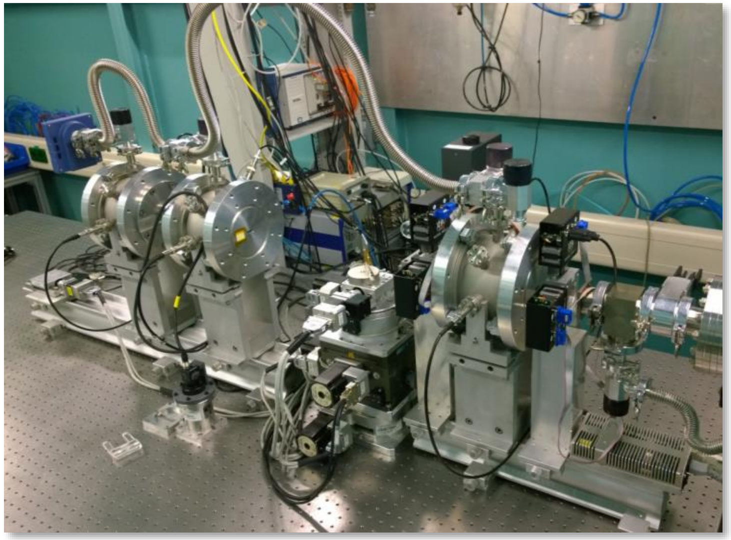
X-ray Absorption Spectroscopy (XAS)

XAS experiment: $\ln(I_0/I_1) = \mu(E)\cdot d$

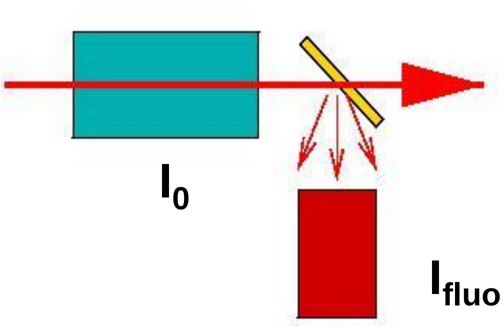
1. standard transmission geometry:



absorp. coefficient: $\mu(E)\cdot d = \ln[I_{0(1)}(E)/I_{1(2)}(E)]$

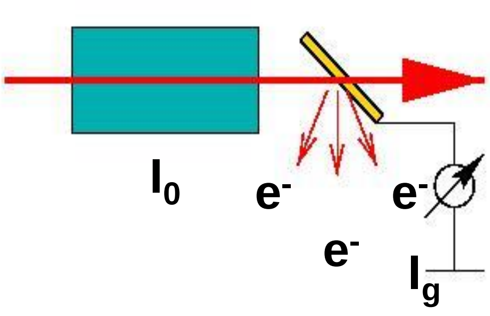


2. fluorescence detection mode:



absorption coefficient: $\mu(E) \sim I_{fluo}/I_0$

3. (total) electron yield detection mode:



(„ground current“)

absorption coefficient: $\mu(E) \sim I_g/I_0$

X-ray Absorption Spectroscopy (XAS)

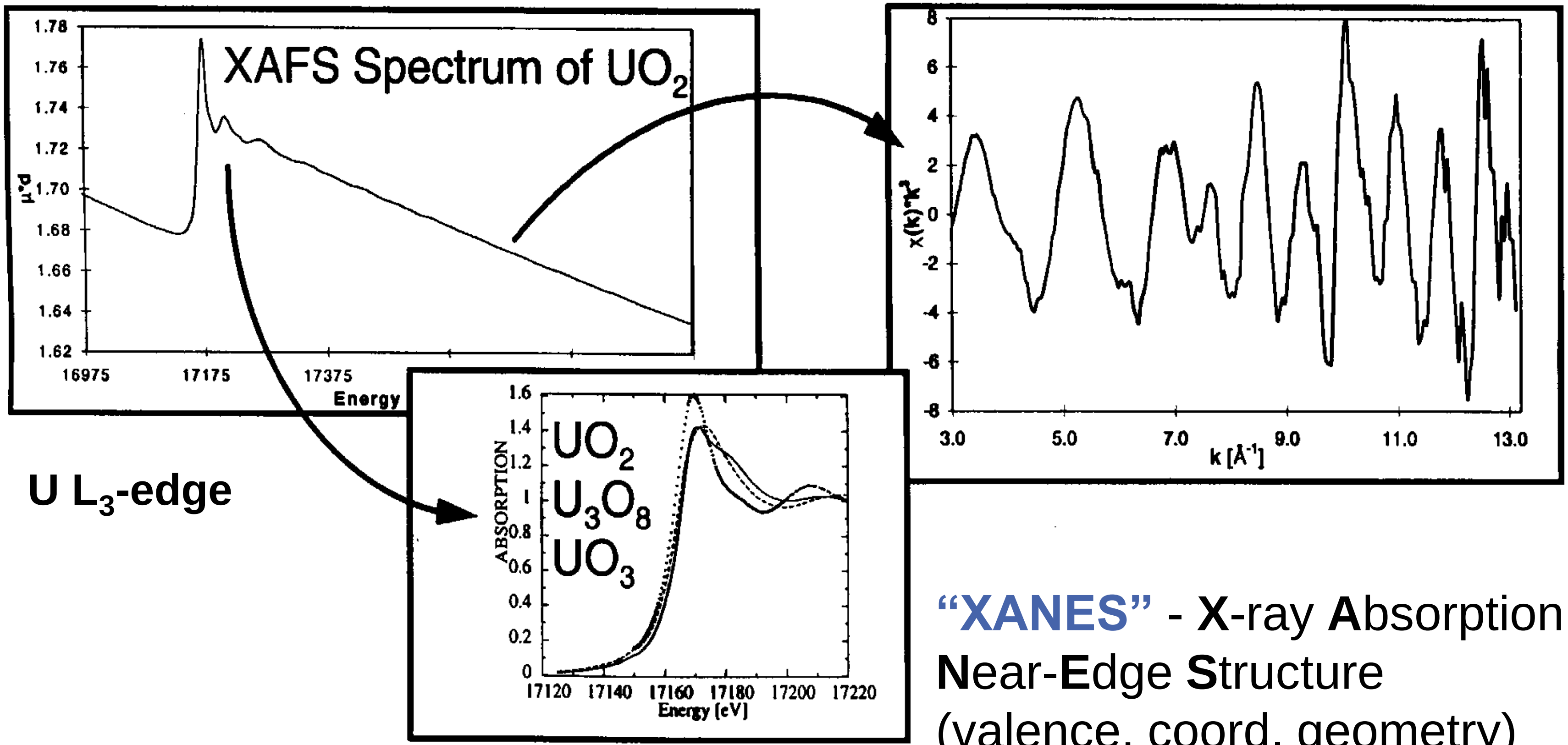
X-ray Absorption Fine Structure (XAFS)

Characteristics	**Advantages**
Element specific - drying and evacuation of samples is not necessary	In-situ studies are possible; mixtures can be investigated without separation
Measures short-range order	Non-ordered systems (amorphous solids, solutions, etc.) can be studied
N, R and neighbor types are determined	Allows direct element speciation, e.g., sorbed species: inner(outer)-sphere, mono(bi)-dentate, mono(poly)-nuclear, complexation
Source is polarized	Investigation of anisotropic samples (dichroism)

X-ray Absorption Spectroscopy (XAS)

XAS – absorption edges

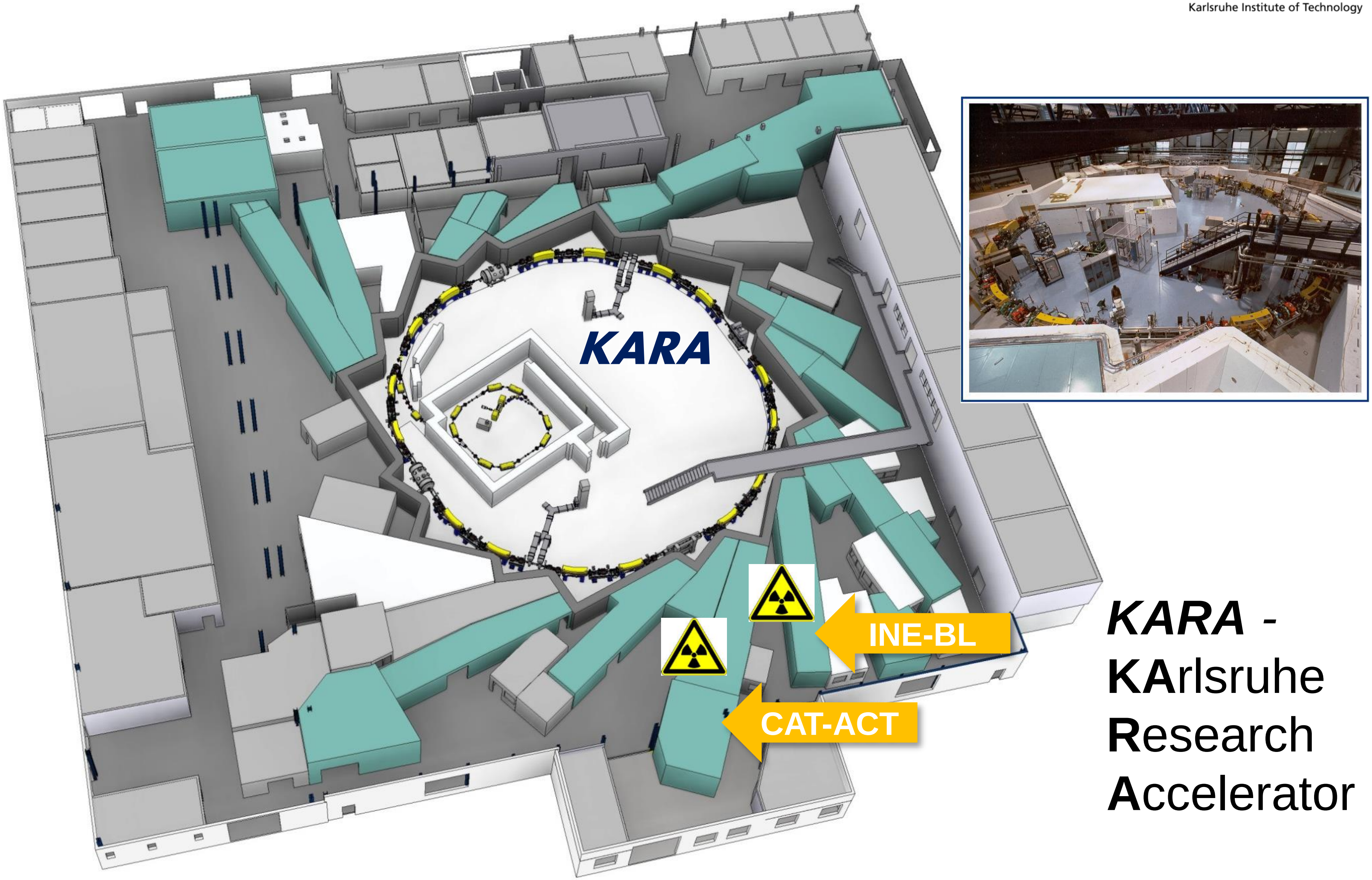
“EXAFS” - **E**xtended **X**-ray **A**bsorption **F**ine **S**tructure (coordination numbers, bond lengths, neighbor atom type)



U L_3-edge

“XANES” - **X**-ray **A**bsorption **N**ear-**E**dge **S**tructure (valence, coord. geometry)

Radionuclide research at the KIT Light Source



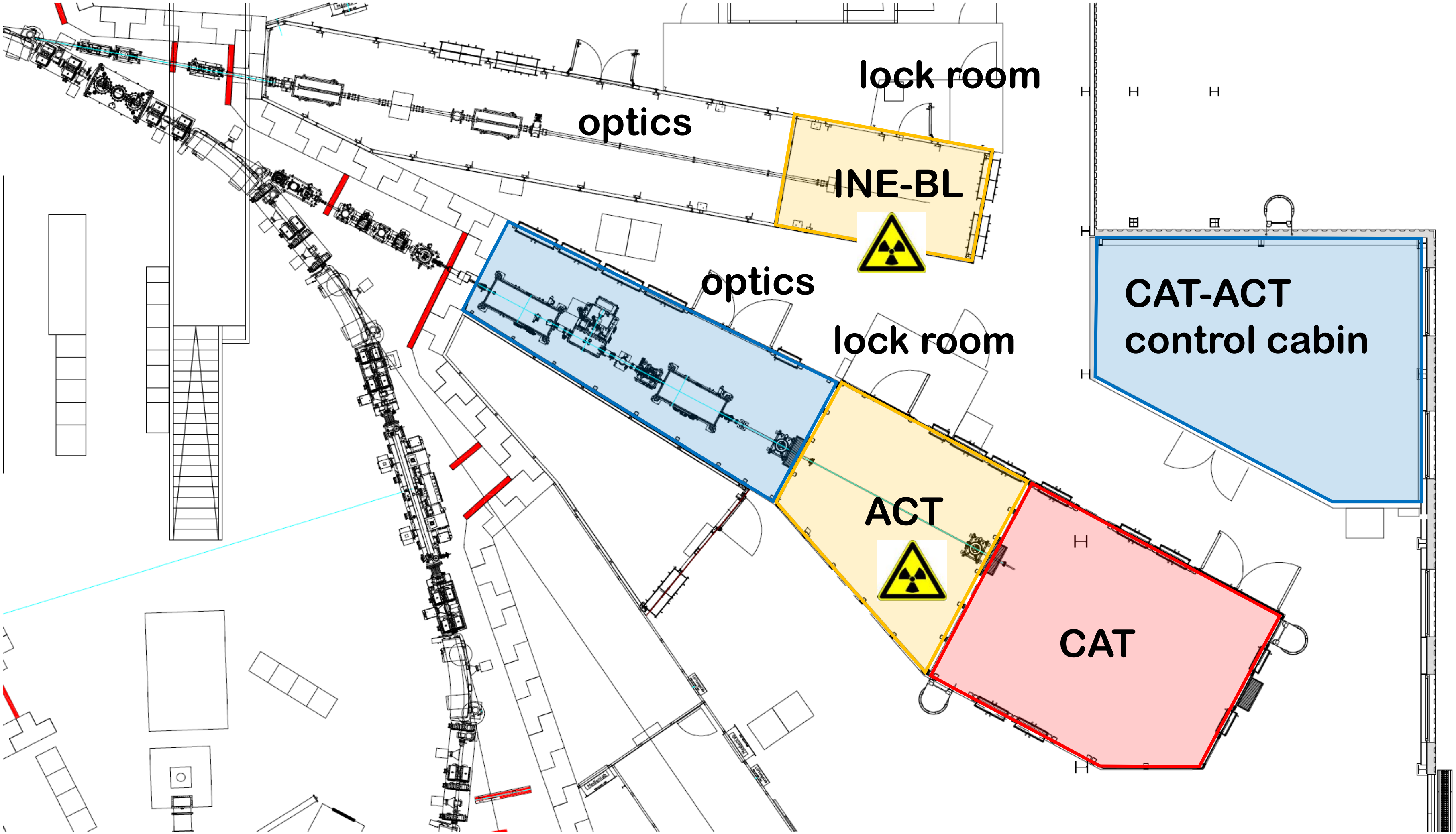
KARA **-**

KArlsruhe

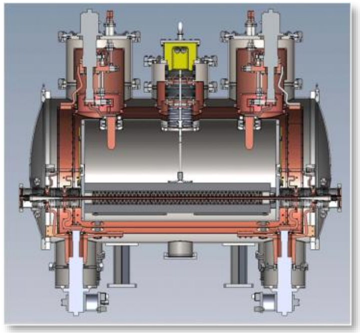
Research

Accelerator

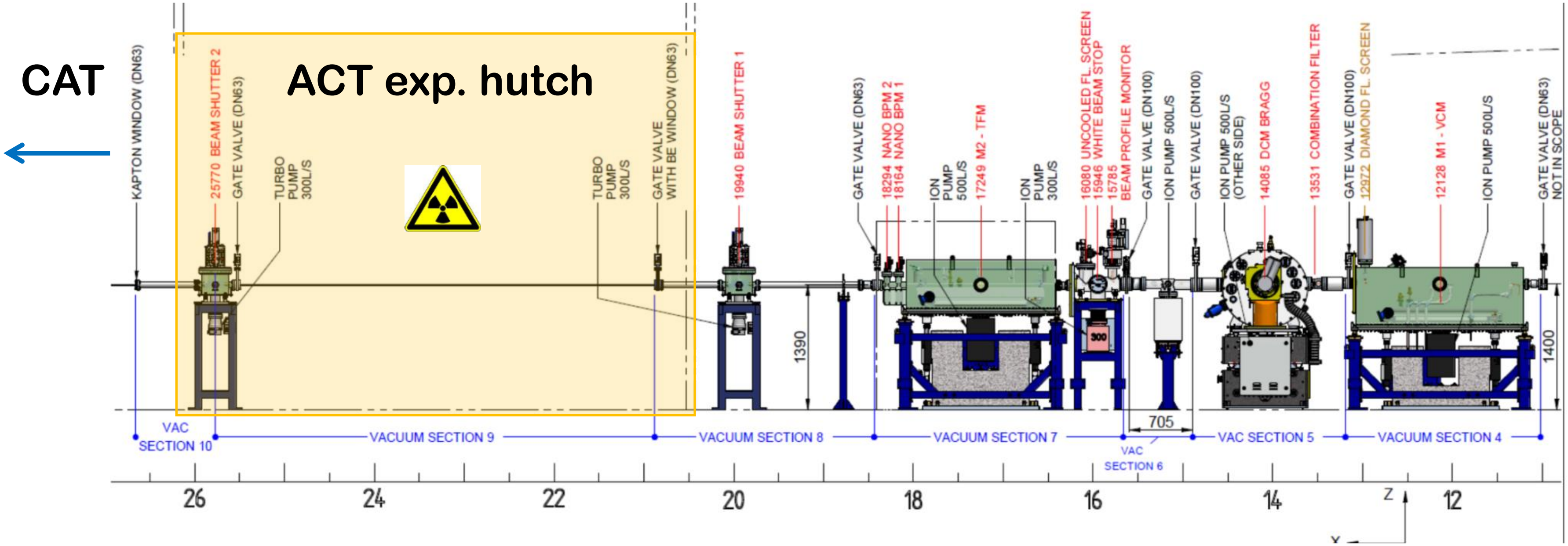
Radionuclide research at the KIT Light Source



CAT-ACT Beamline – layout



- 1 m, 2.5 T multipole supercond. wiggler source (E_C = 10.2 keV)
- cryo-cooled DCM (Si<111>/<311>, collimating 1st / focuss. 2nd mirror (FMB Oxford, GB)
- operation with mirrors: 3.4 – 35 keV, mirror-less above (~55 keV)
- two in-line experimental stations, 23 optic configurations



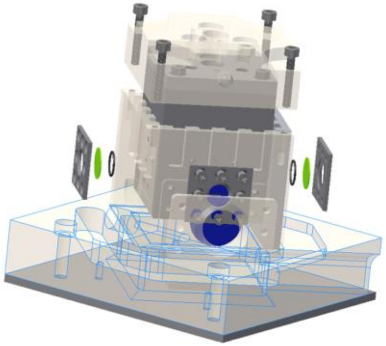
Radionuclide research at the KIT Light Source

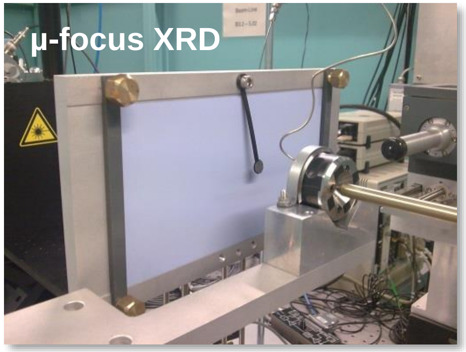
- INE-BL fully operational since October 2005 - 2nd dedicated SR beamline for radioactive materials in Europe (2019: INE-BL, ACT, ROBL, µXAS, MARS)
- CAT-**ACT** fully operational since fall 2016
- Energy range 2.1 – 55 keV, bending magnet (INE-BL) or superconducting wiggler source (CAT-ACT)
- XAS detection limits (*An*) ~ $1 \cdot 10^{-6}$ mol/l, < 5 ppm (!)

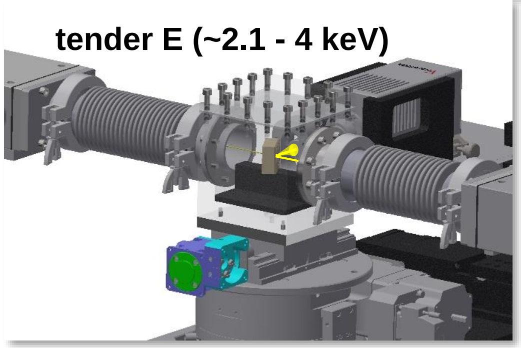
Both stations licensed for working with 10^6 times the exemption limit and up to 200 mg of fissile isotopes U-235 and Pu-239 within a double containment (sum rule applicable)

Radionuclide research at the KIT Light Source

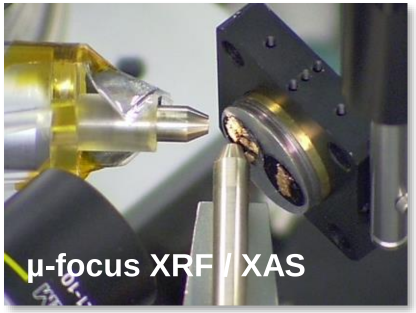

standard bulk inert gas


electrochemical cells

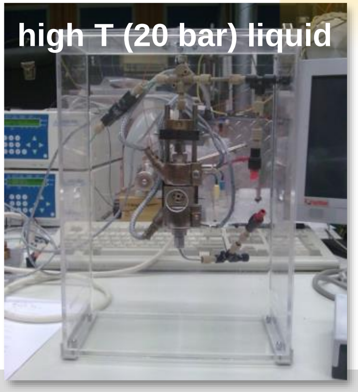

µ-focus XRD

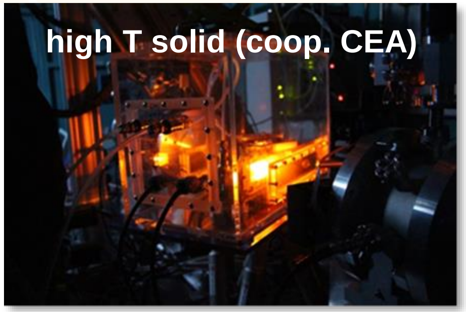

tender E (~2.1 - 4 keV)

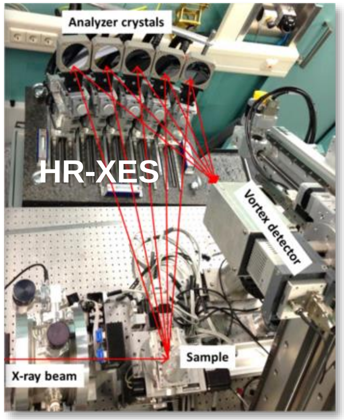
radionuclide speciation with synchrotron radiation


µ-focus XRF / XAS


low T (LN2)


high T (20 bar) liquid


high T solid (coop. CEA)


HR-XES

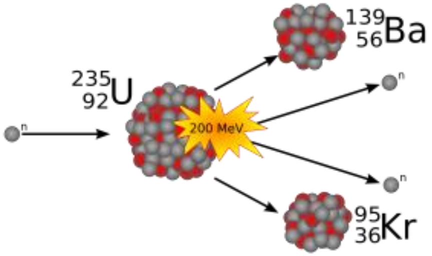
XAFS/XRF investigation of a spent nuclear fuel (SNF) segments

sampled from a test fuel rod irradiated at the Gösgen PWR, Switzerland
fuel type: 238-UO_2 with initial enrichment of 235-U: 3.8%
burn-up ~50.4 GWd / (t HM), 5% FIMA

3.45 mSv/h (~1 µSv/h in 1 m distance)

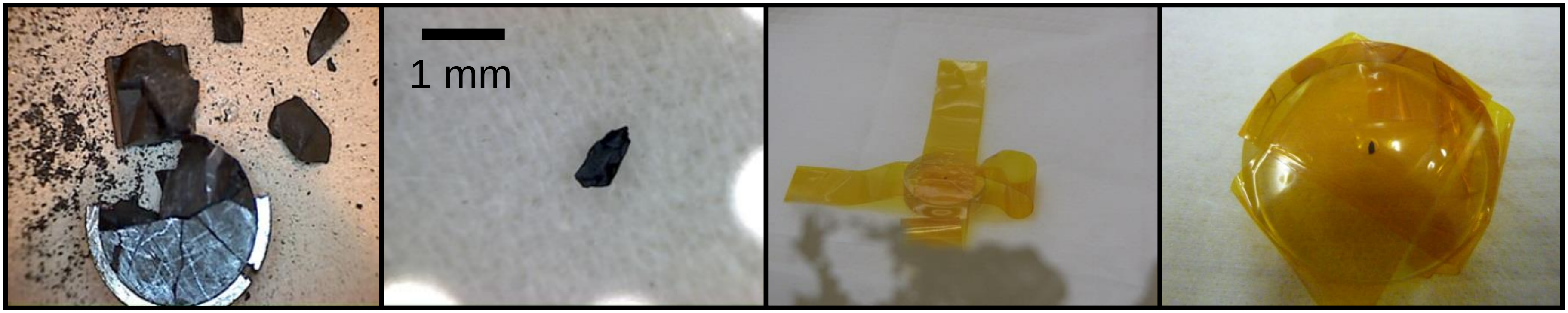
$$^{238}U_{0.962}\,^{235}U_{0.038}O_2$$

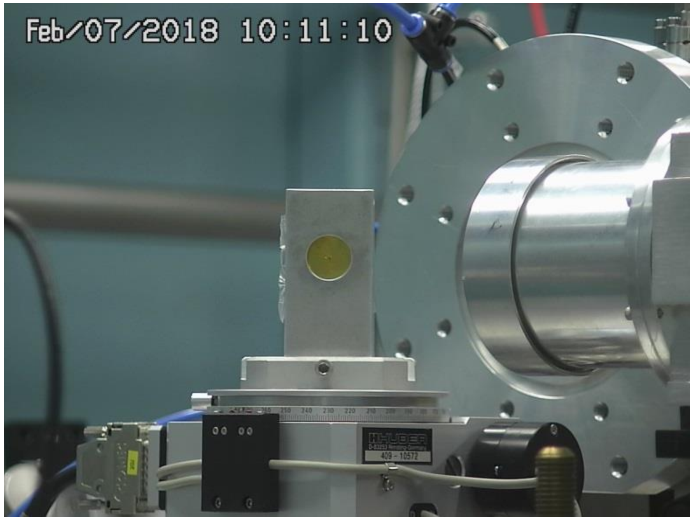
neutron capture fission



concentration of individual FPs does not reach 1 at%!

Experimental procedure: SNF bulk fragments





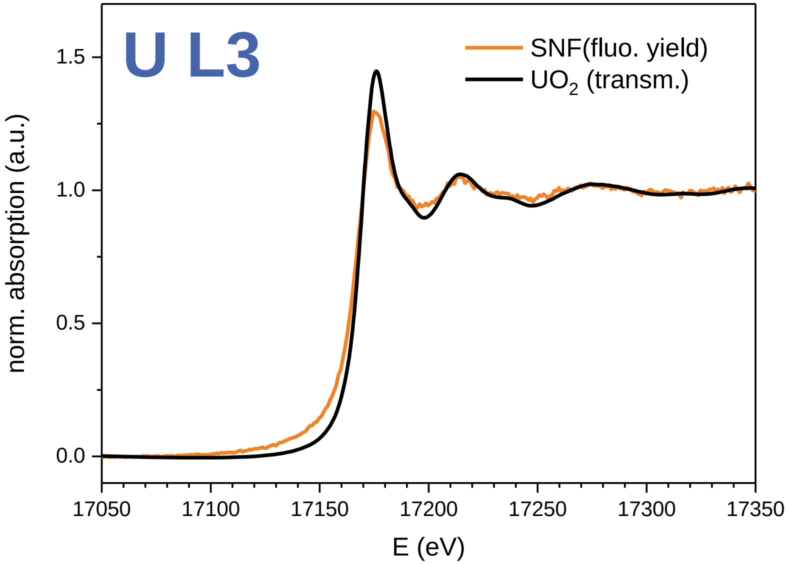
- Particle selected and isolated at INE shielded box line
- Transfer to doubly sealed plexiglass sample holder in ventilated fume hood
- Dose rate in contact: **up to 15 mSv/h** (~5 µSv/h in 1.5 m distance)
- Procedure developed for nuclear waste glass characterization by XAFS/XRF

(*K. Dardenne et al., J. Nuc. Mat. 2015*)

Actinides and immobile fission products

Measurements up to now: **U L3**, **Pu L3**, **Am L3** - **Cm L3** below detection limit*

Element	Th	U	Np	Pu	Am	Cm	Zr
total at.%	6.27E-7	3.09E+1	2.61E-2	3.70E-1	5.45E-2	1.62E-3	4.12E-1

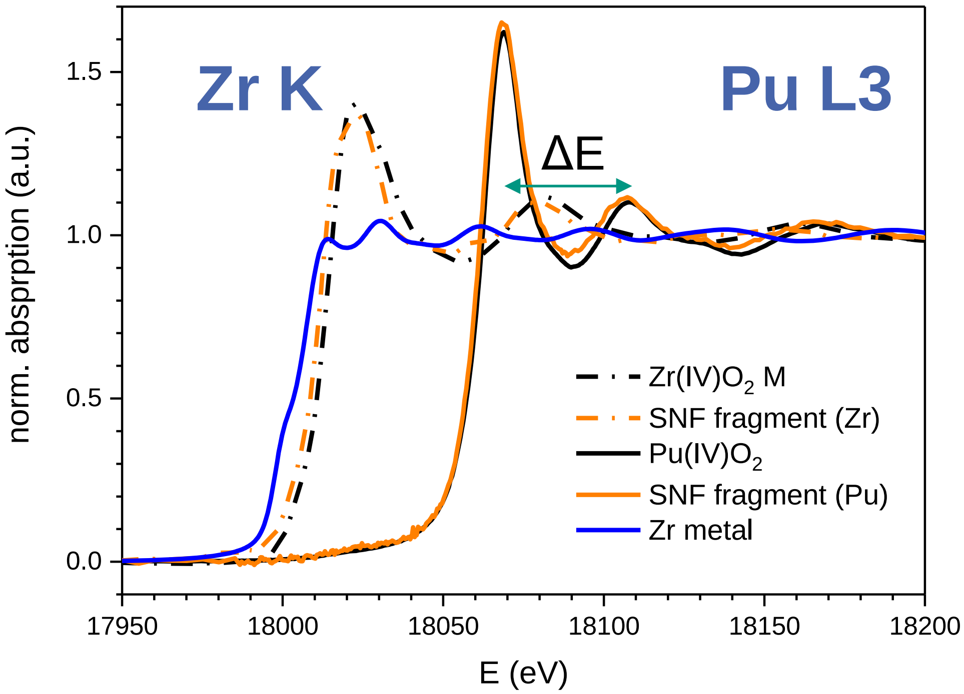


Uranium:

- U present as dioxide U(IV) – as in uraninite reference sample
- Strong non-linearity (“self absorption”) effects as expected when recording XAFS of a concentrated element in a bulk sample by total yield fluorescence detection

**J. Rothe et al., Geosciences 9 (2019) 91*

Actinides and immobile fission products



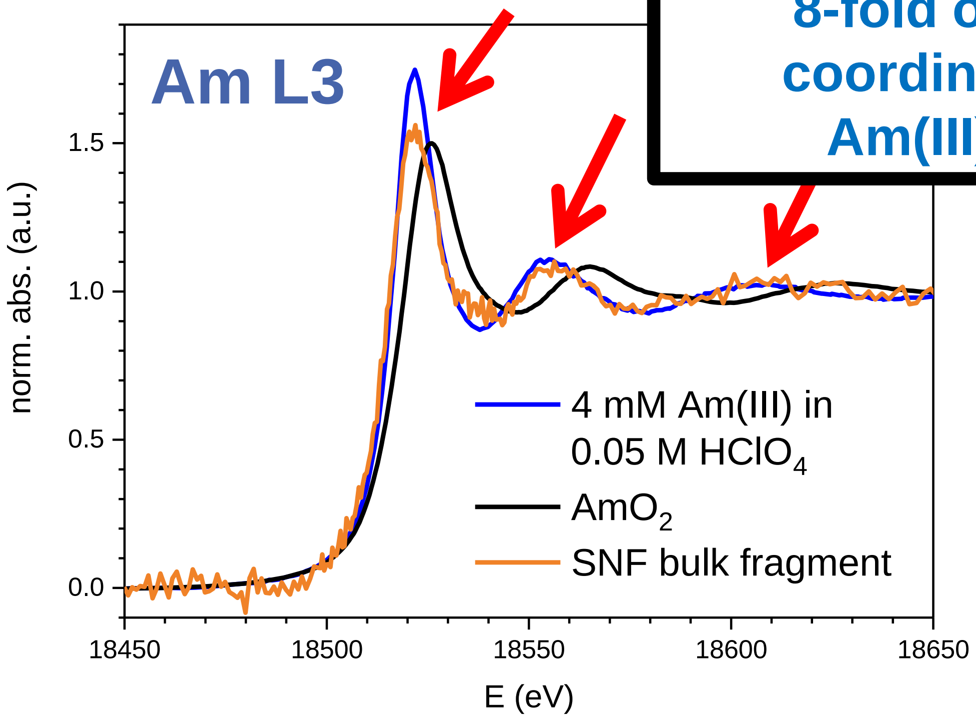
Zirconium:

- tetravalent as in monocl. Zr(IV)O_2
- WL shape and EXAFS data point to higher symmetry site compared to m-Zr(IV)O_2 (7 1st shell O distances)

Plutonium:

- Pu present as Pu(IV), fluorite structure as in Pu(IV)O_2
- ΔE: WL – "shape resonance" points to U(IV) lattice position

Actinides and immobile fission products



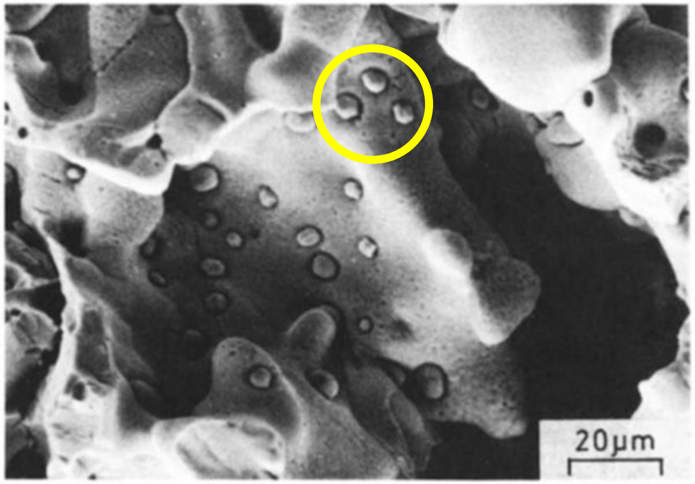
8-fold oxygen coordination – $Am(III)O_8^{13-}$

Americium:

- Am incorporated as trivalent cation
- Am isotopes formed through β^--decay of ^{241}Pu and consecutive n-capture
- no recoil / displacement in UO_2 matrix to be expected
- charge balance by formation of $Am(III)O_7^{11-}$ (oxygen vacancies)?
- **UO_2 may act as redox buffer: Am(IV) → Am(III) / UO_2 → UO_{2+x}***

**D. Prieur et al., Inorg. Chem. 2011*

Metallic alloy particles (ε-phases)



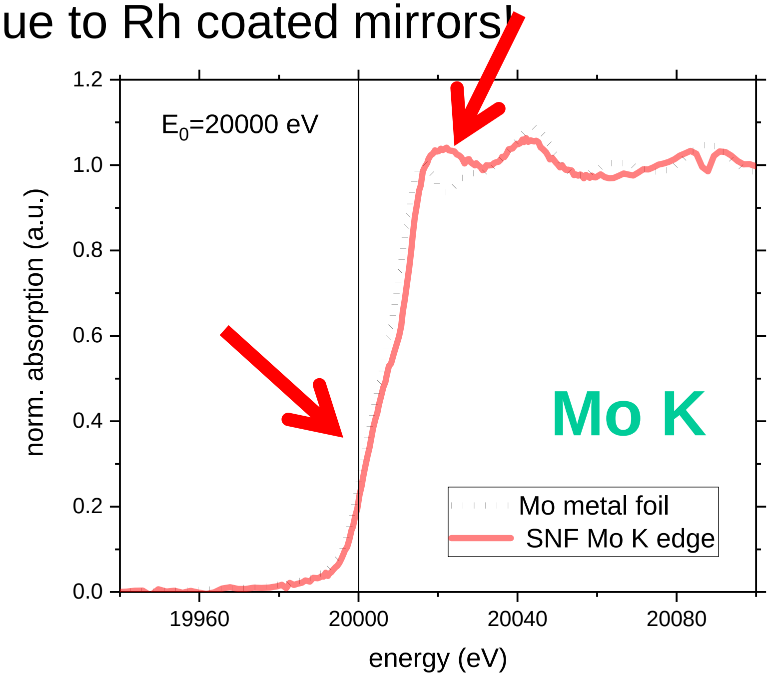
SEM image taken from *H. Kleykamp, J. Nuc. Mat. 131, 1985*

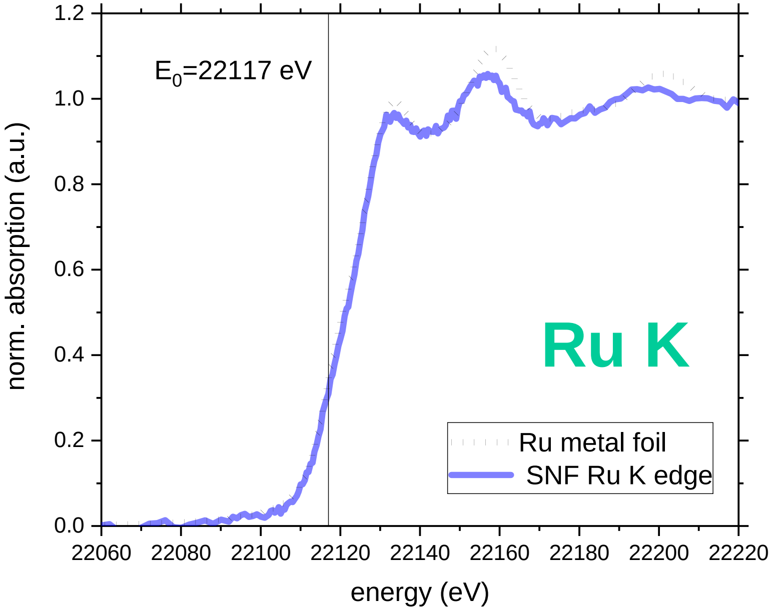
- µm-sized metallic alloy particles known from SEM/TEM-EDX studies* of SNF (”white inclusions”, “ε-phases”), larger and enriched towards the cooler rim (**miscibility determined by solid solution thermodynamics!**)
- 4d transition metals **Mo – ^{99}Tc – Ru – Rh – Pd – … (Te)**
- might act as catalyst for H_2 activation, counteracting SNF corrosion / FP & *An* oxidation!

**D. Cui et al., J. Nuc. Mat. 420, 2012*

Metallic alloy particles (ε-phases)

Measurements up to now: **Mo K**, **Ru K**, **Pd K**, **Tc K, Te K** – Rh hampered due to Rh coated mirrors!





Molybdenum:

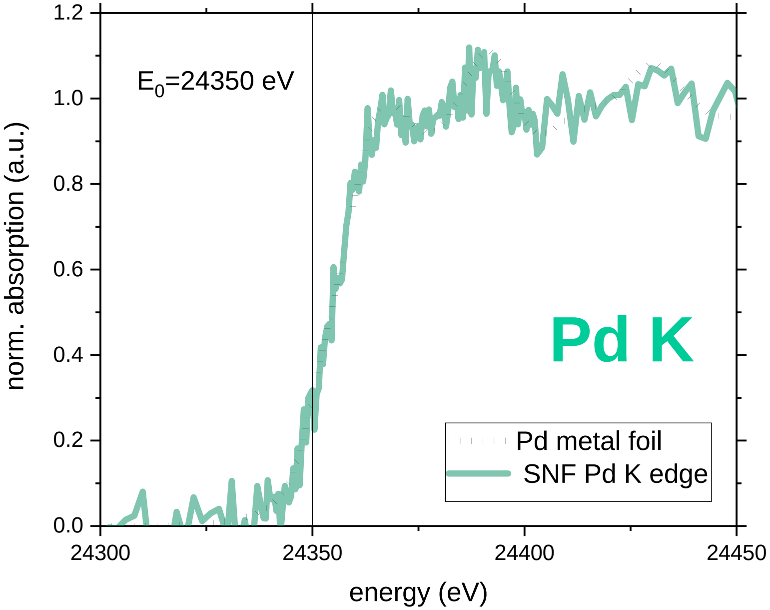
- metallic state – Mo(0)
- different fine structure compared to hcp 4d-metals
- Mo assumed to exist in other phases

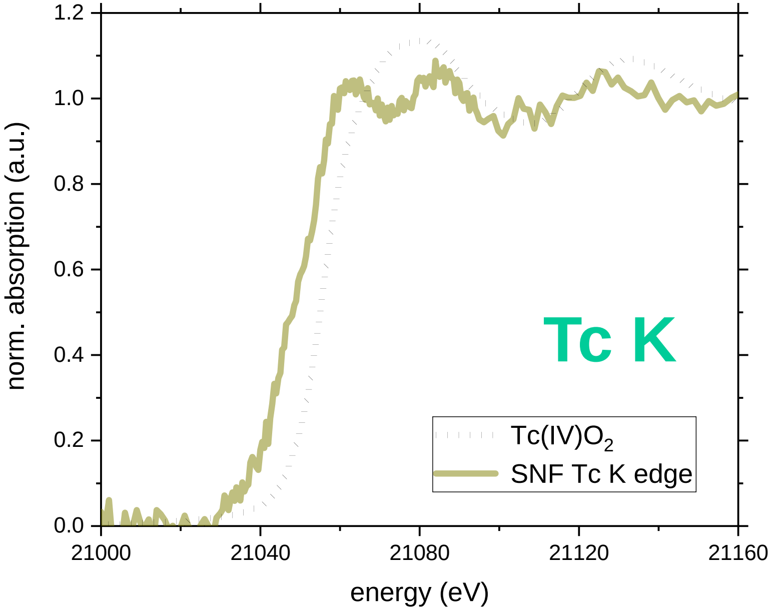
Ruthenium:

- metallic state – Ru(0)
- 4d metal hcp structure

Metallic alloy particles (ε-phases)

Measurements up to now: **Mo K**, **Ru K**, **Pd K**, **Tc K** – Rh hampered due to Rh coated mirrors!





Palladium:

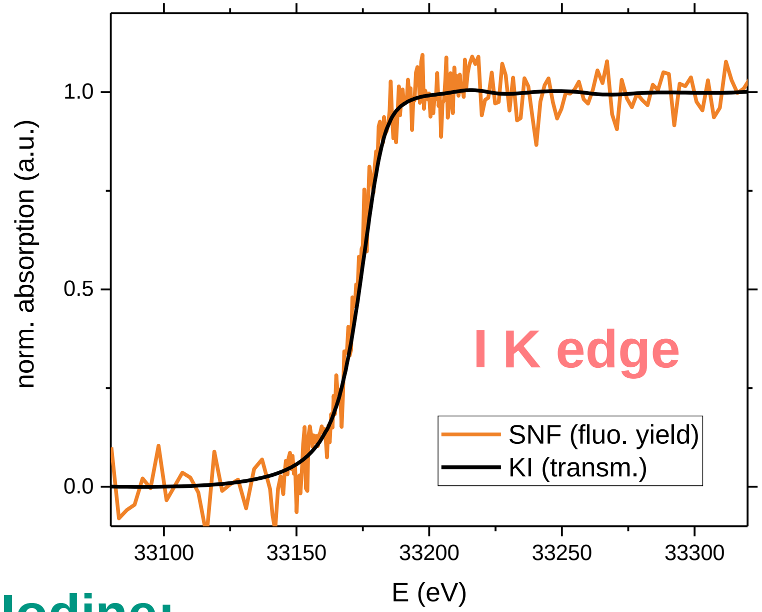
- metallic state – Pd(0)
- exact coincidence with hcp-Pd metal

Technecium:

- metallic state – Tc(0) deduced from edge shape coinciding with Pd / Ru and comparison to Tc(IV)O_2

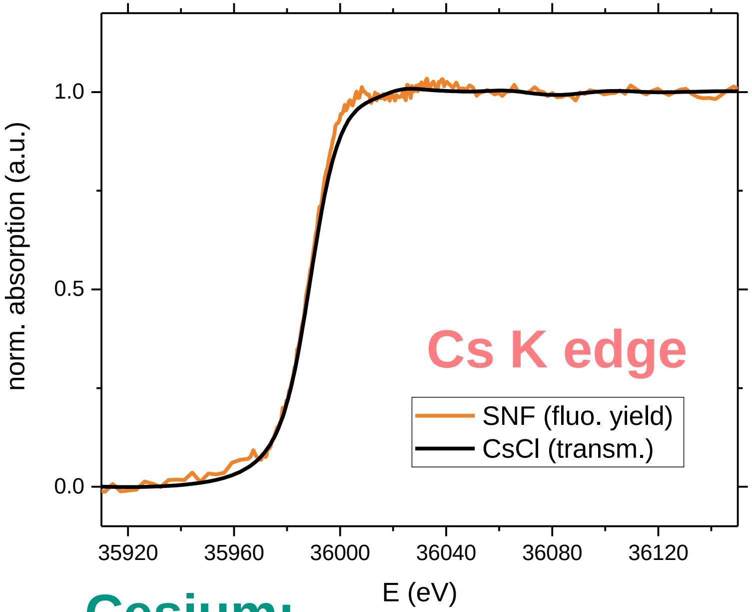
Mobile fission products

Highly mobile FPs, partly segregated from SNF matrix - primarily released upon initial water contact: **137-Cs**, **129-I**, **79-Se, …**



Iodine:

- most volatile FP
- $T_{1/2}$ (129-I) = 15.7 Ma
- I present as iodide (I^-)
- 1st time detected as FP!
- **conc. 0.0085 at% (calc. 0.017)**



Cesium:

- determines initial SNF radiotoxicity $T_{1/2}$ (137-Cs) = 30a
- present as Cs^+
- **conc. 0.069 at% (calc. 0.167)**

Take home messages:

- XAS as direct speciation method to analyze trace elements and matrix constituents alike without prior separation
- Applicable in solids, liquids and gases
- High penetration depth of (tender to hard) X-rays enables investigation of well contained / shielded (radio-)toxic samples as well as *in situ* experiments
- Analysis via fingerprinting, photoelectron-scattering calculations (EXAFS) or more sophisticated quantum chemical methods (XANES)
- A plethora of related methods (cf. next presentation by T. Vitova) available, strong development towards laboratory instrumentation

Vielen Dank
Thanks for your attention
Merci beaucoup
感谢您的关注

Tour of KIT Light Source / Beamlines: