Spatially resolved XRF, XAFS and XRD investigations with micrometer-scale resolution pertaining to nuclear waste disposal

KIT
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1. **Motivation for spatially resolved imaging/spectroscopy studies**
2. **Examples:**
   - **µ-XRF, µ-XAFS and STXM study of U speciation in a U-rich clay**
   - **µ-XRF/µ-XAFS results from a granite radionuclide tracer (Np) study**
   - **µ-XRF, µ-XAFS and µ-XRD of a U-rich sediment**
3. **Concluding remarks**

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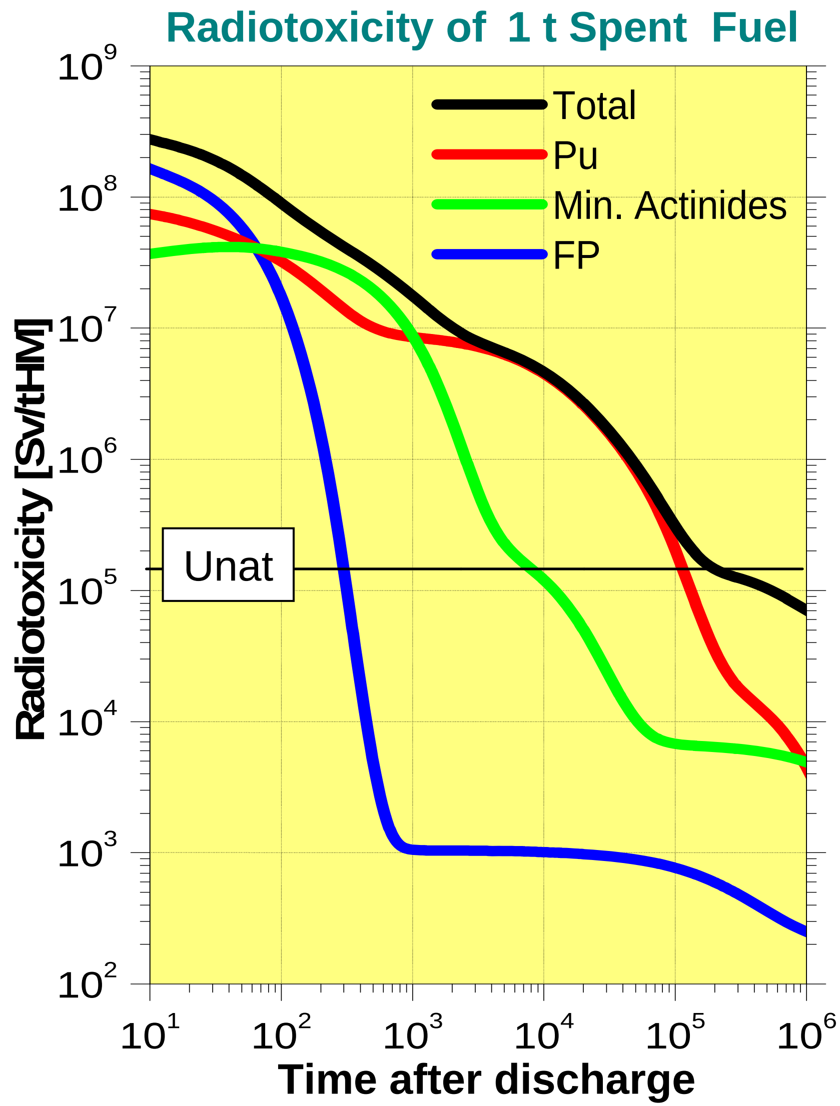
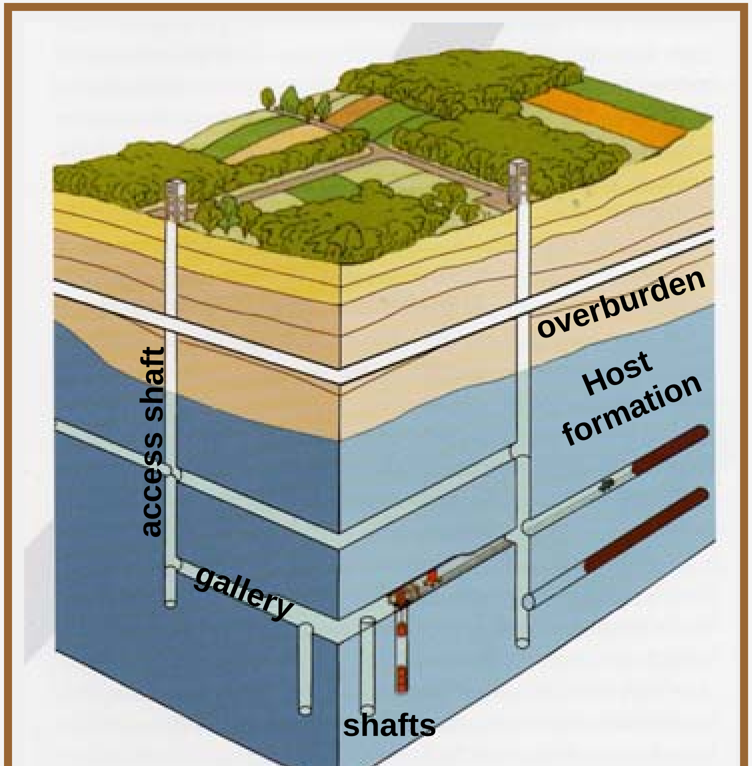
High level nuclear waste disposal safety assessment goal

Predict radioactive dose rates to man and environment and to ensure dose rates smaller than allowable levels over a near-geological time scale.

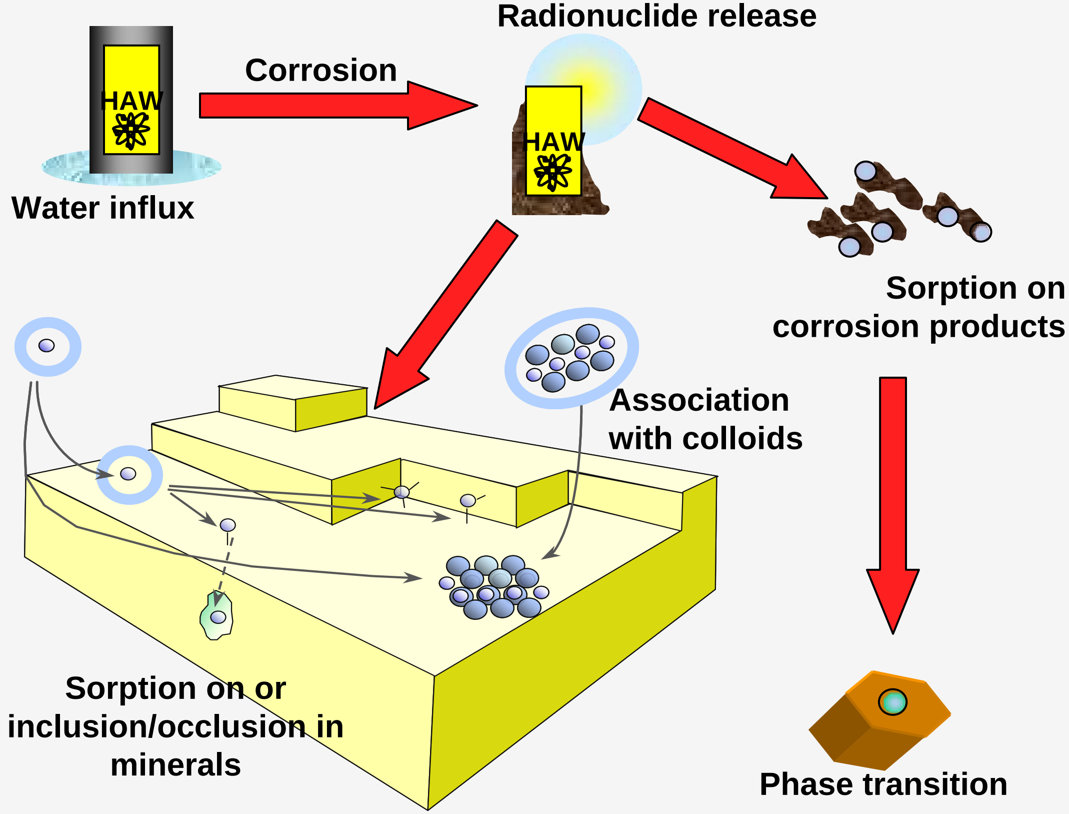


Radionuclide release in a nuclear repository

Repository water influx ➔ Container corrosion ➔ Radionuclide-Mobilization/Immobilization



Schematic representation of a repository (Informationskreis KernEnergie)



Size scale

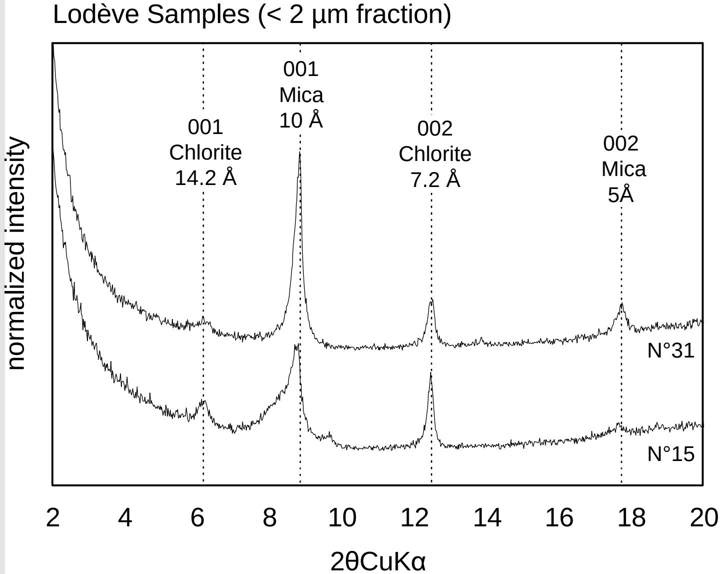
Geology (1000 m) — **Geochemistry (0.0000000001 m)**

Time scale

Reactions (0.0000000001 years) — **Half lives (1000000 years)**

U speciation in a U-rich clay

XRD <2µm fraction



Clay mineral fraction of the Lodève samples = Illite and Chlorite

Photographs and autoradiograms

Samples from from Autunian shales in the Permian Lodève Basin (France) embedded in acrylic.

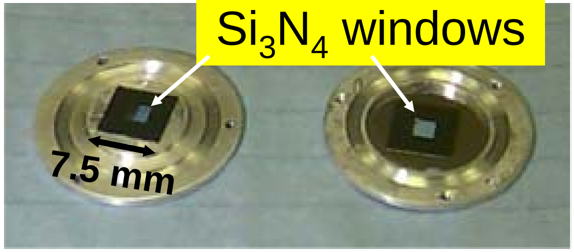
~25 mg 238-U/g sample (P15) | ~2 mg 238-U/g sample (P31)

Goal: identify mechanism of U immobilization. Adsorption/co-precipitation with iron hydroxides and/or clay minerals?

- **What is the U oxidation state?**
- **Is there any correlation between the U distribution and that of other elements?**

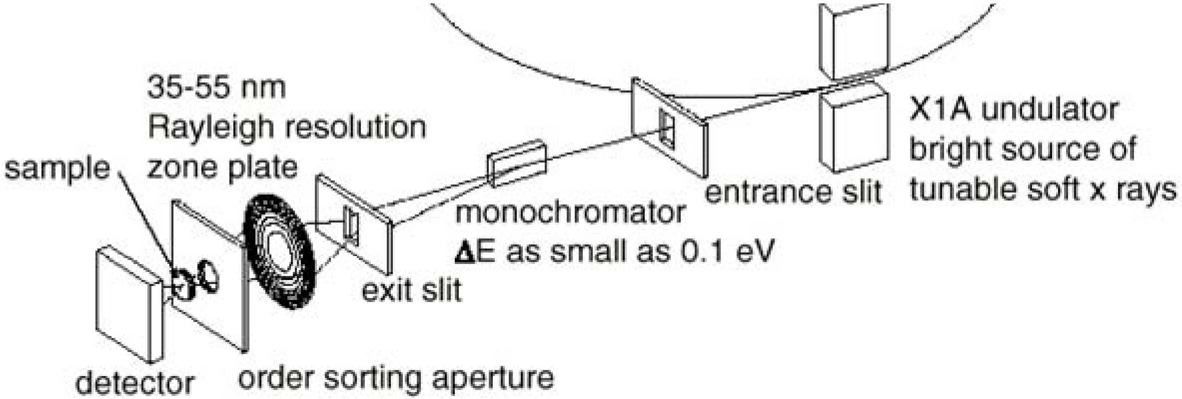
Scanning transmission X-ray microscopy (STXM)

- Energy range: 284 eV (C 1s) - 543 (O 1s) eV
- in-situ technique. 10-15% transmission for 1-2 µm H_2O, 200 nm Si_3N_4
- Sub-µm spatial resolution probing femto-L volumes



STXM X1A beamline layout at the National Synchrotron Light Source, Brookhaven, NY

Spectroscope: ***varying radiation wavelength***



Microscope: ***x,y scanning sample stage; contrast by imaging at different wavelengths***

Spectro-Microscopy – C 1s-NEXAFS from image stacks

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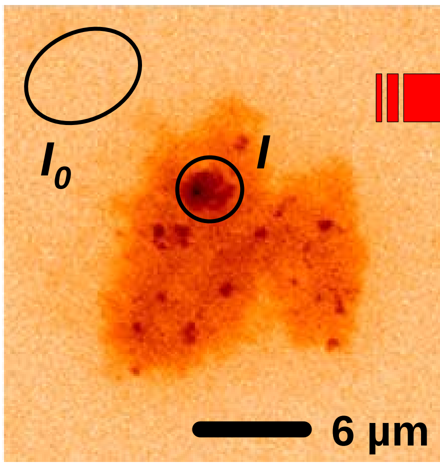
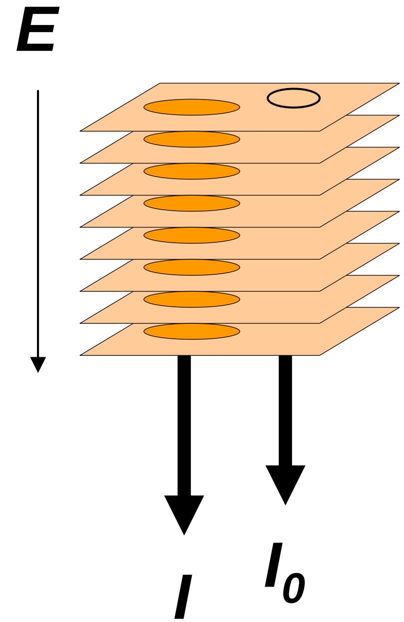
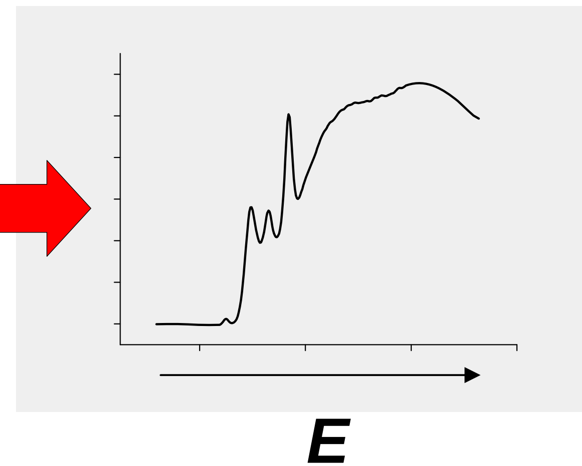
template image at a given E	alignment of image stacks	NEXAFS spectrum from intensity ratios



STXM image of a Eu(III)-loaded humic acid agglogerate, pH 5



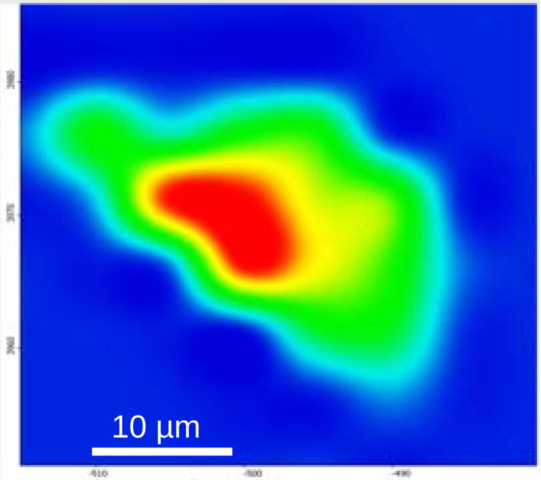
$$\mu * d = ln(I_0 / I)$$



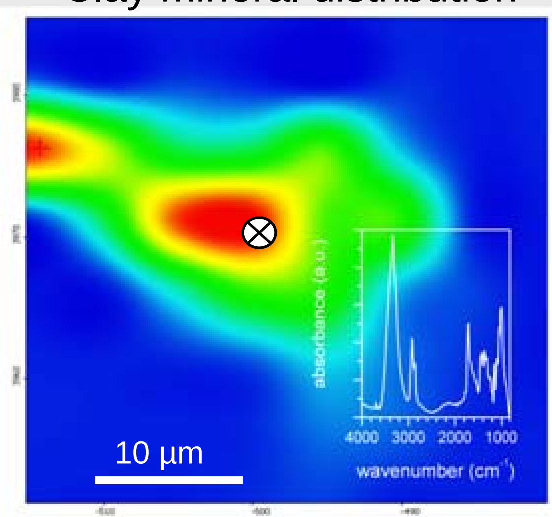
U-rich clay Bitumen - Clay Interaction

μ-FT-IR images

Aliphatic distribution



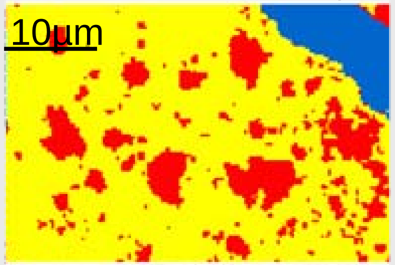
Clay mineral distribution

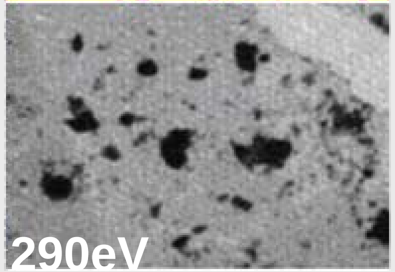


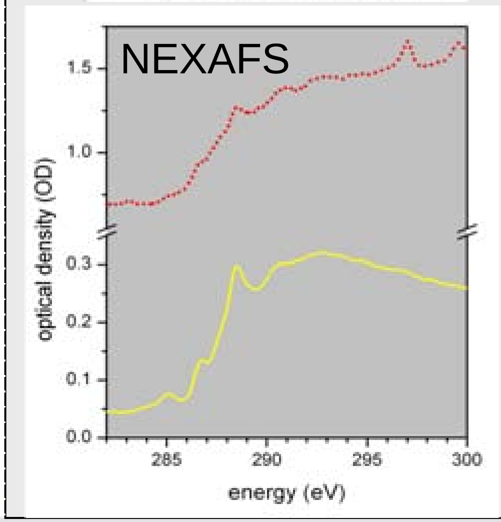
Distribution of organic matter and clay are correlated

STXM images& NEXAFS

PCA & cluster analysis

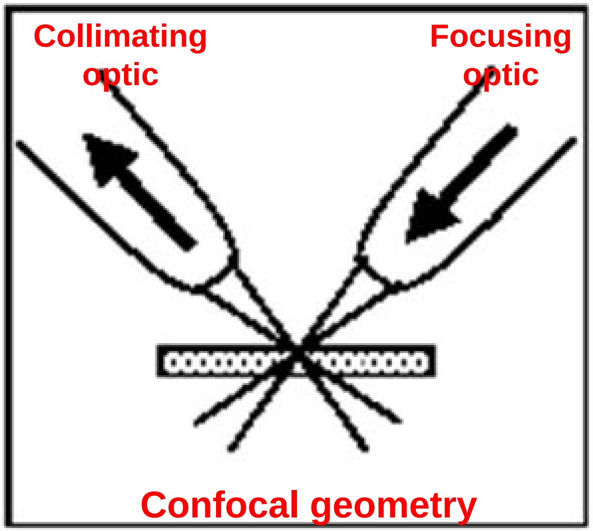


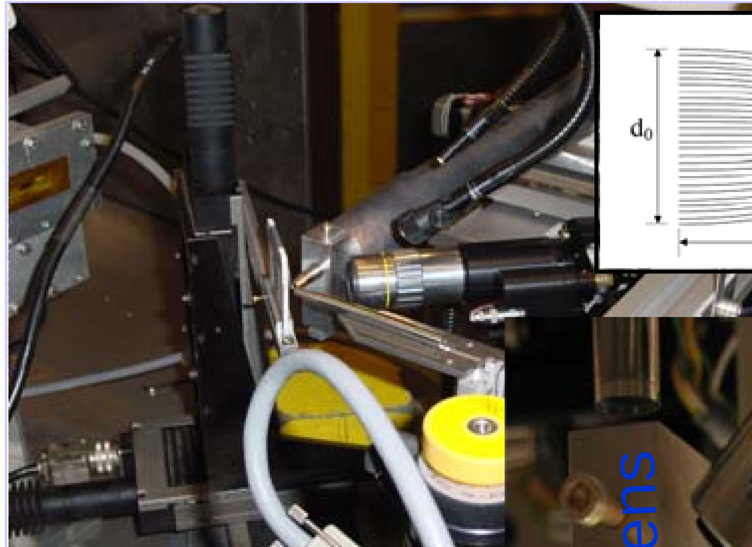


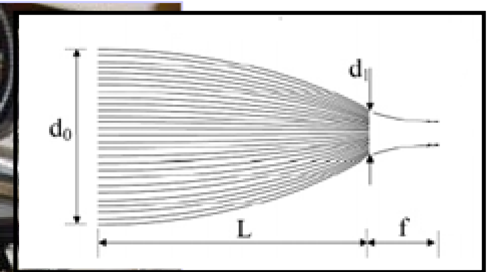


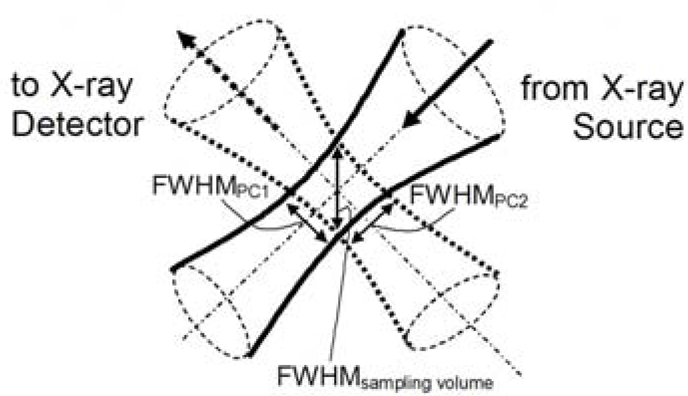
K L2,3-edges (297 & 299.6 eV) indicative of illite-type mineral. Positive correlation between organic matter and clay fraction.

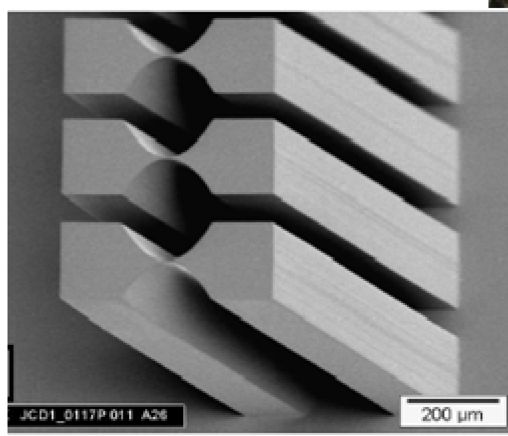
Confocal set-up for spatial and depth resolution

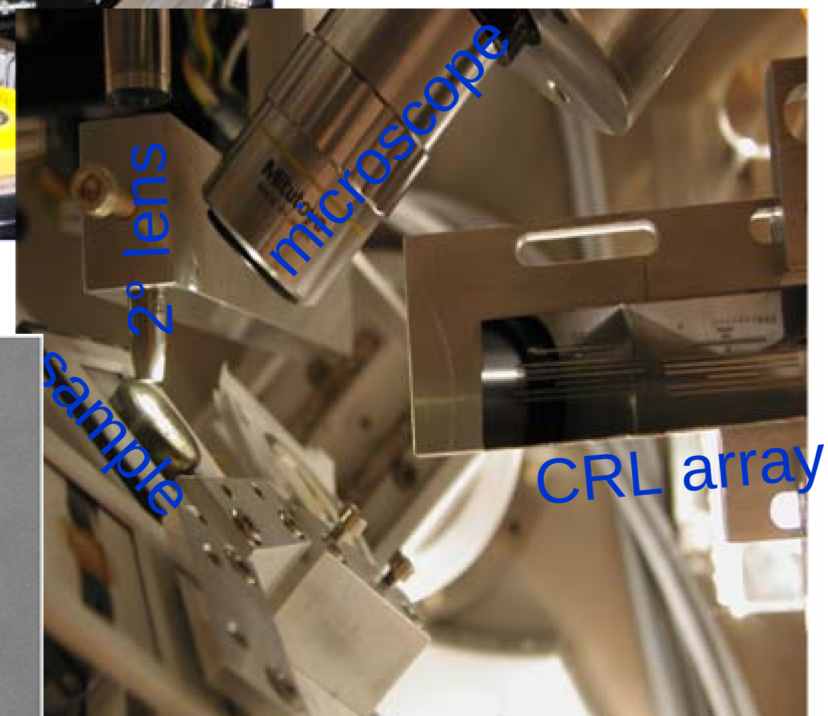












μ-XRF & μ-XANES

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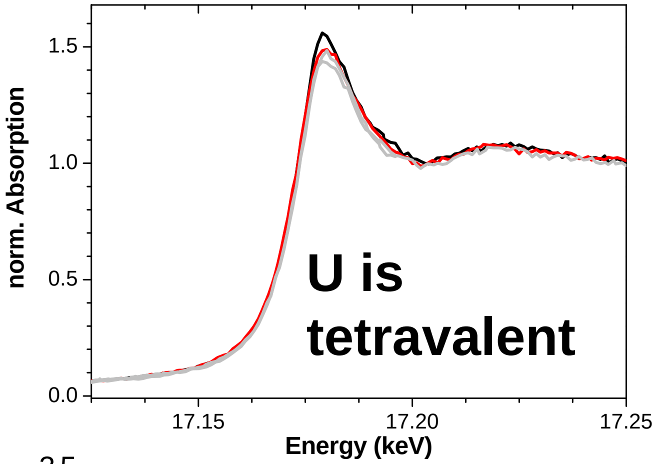
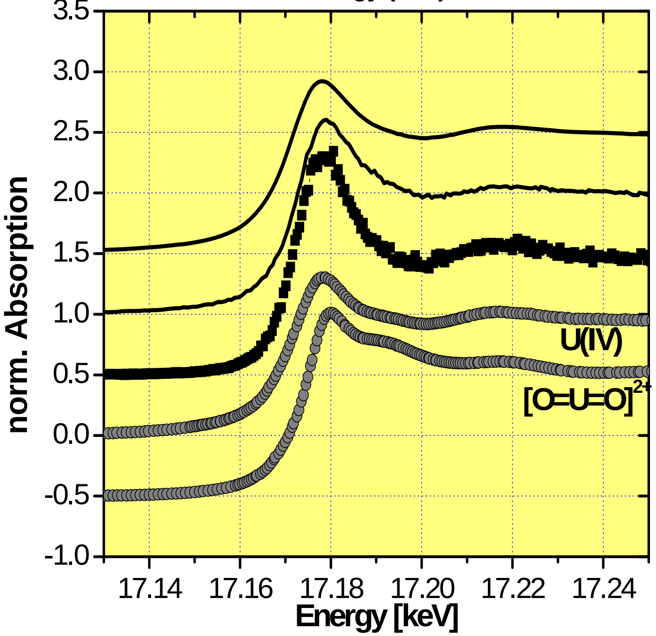
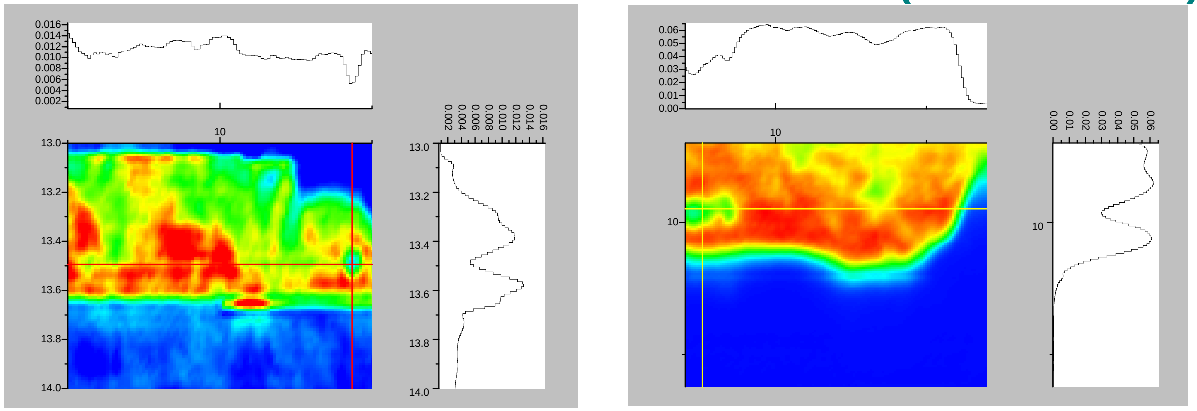
U L3 μ-XANES



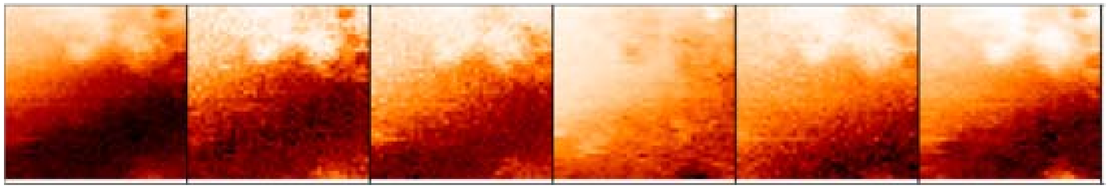


U distributions in P15 at two different areas (INE-Beamline)



U distribution maps (30 × 30 μm² step size)

Comparison to HASYLAB Beamline-L data



Distribution maps for a 800 x 760 μm² area (20 × 20 μm² step size)

U is correlated to light Z element distributions, not with Fe

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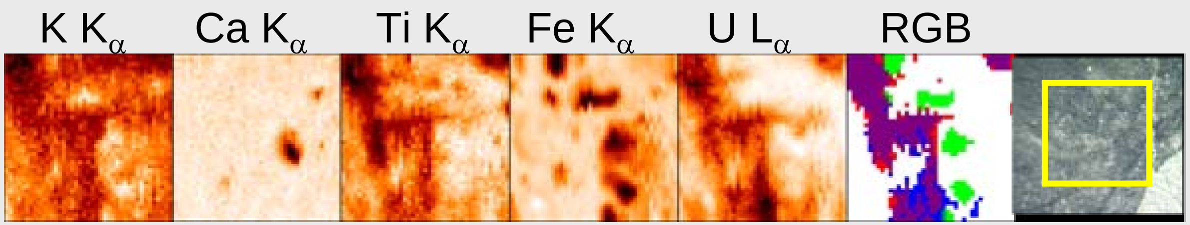
μ-XRF & μ-EXAFS

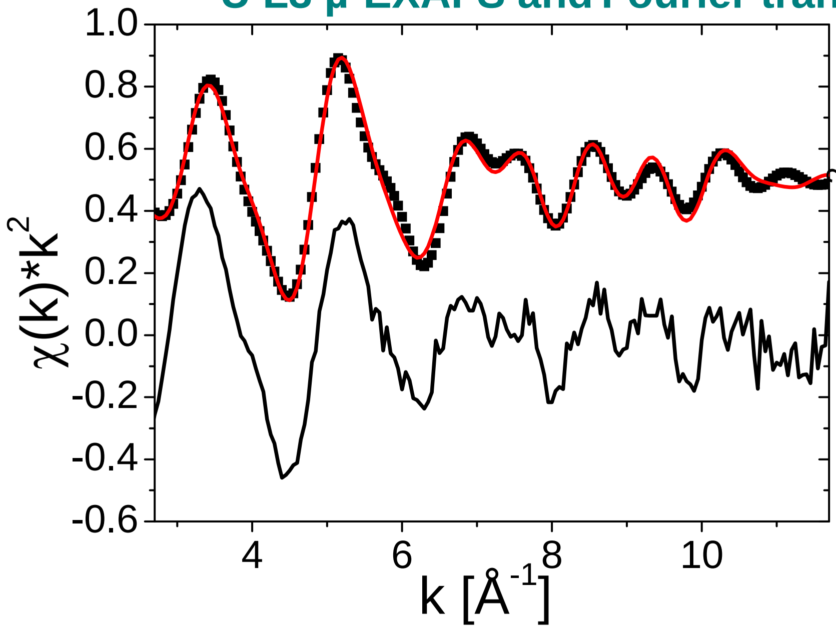
Distribution maps, red-green-blue (RGB=Ti, Fe, U) overlay and microscope image (P31)

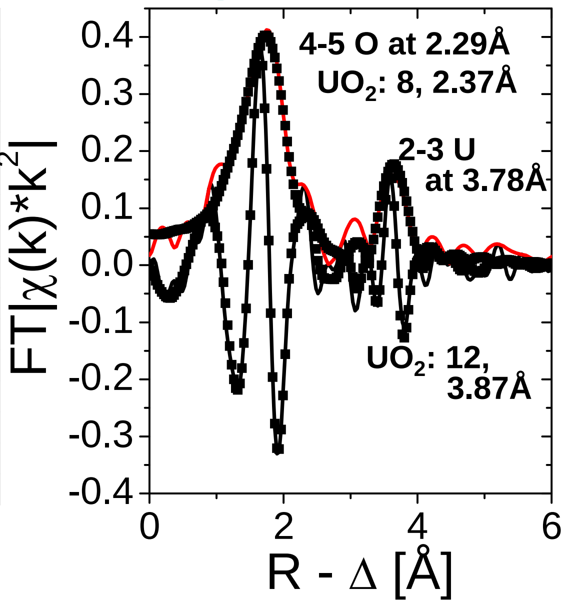


400 x 400 μm² section (10 × 10 μm² step size, 1s counting time), recorded under the surface

U is correlated to light Z element distributions, not with Fe

U L3 μ-EXAFS and Fourier transformed spectrum





U(IV) isUO_2-like
but with shorter inter-atomic distances & decreased intensities
→ nanocrystalline

U speciation in a U-rich clay - CONCLUSIONS

- **Uranium is U(IV)**
- **Organic matter is associated with clay minerals**
- **No correlation between U and Fe distributions**
- **Positive correlation between U and both K and Ca**

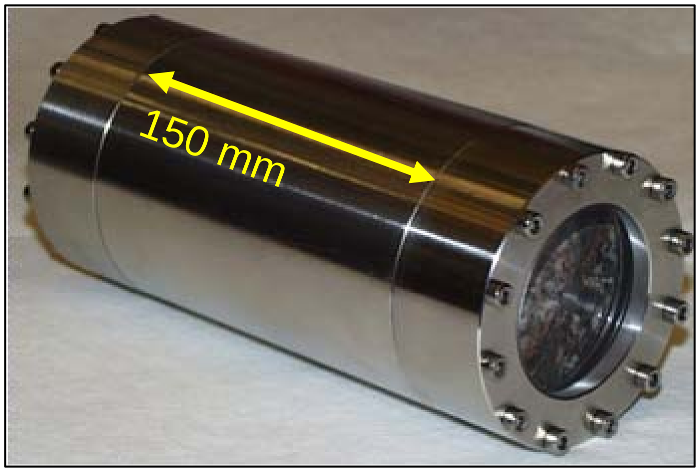
↳ **U is associated with organic matter/clay mineral aggregates**

↳ **Organic matter was redox partner for U reduction during immobilization**

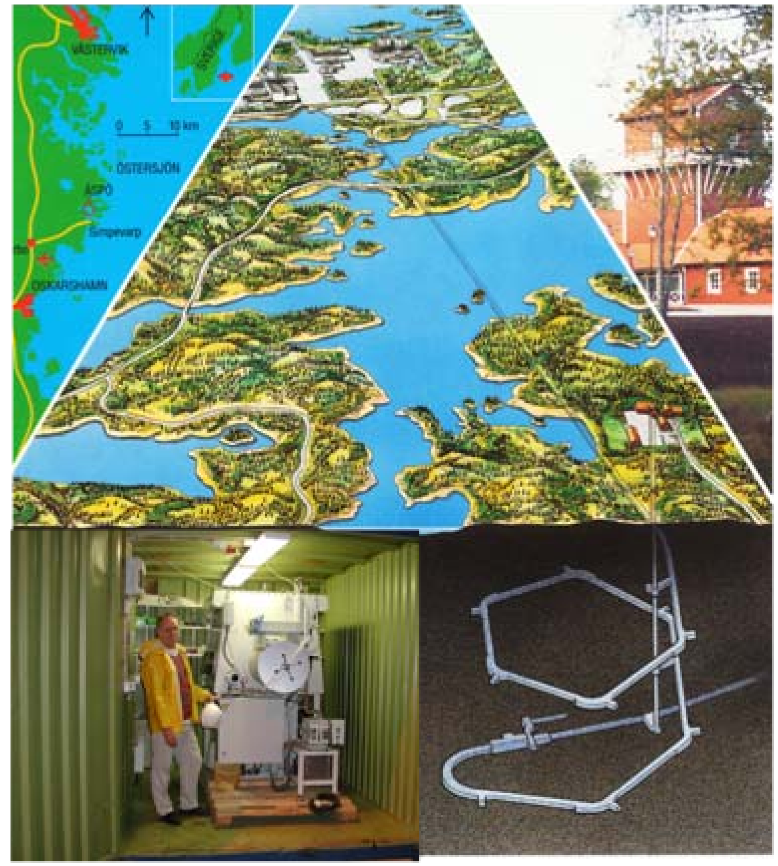
Fractured granite bore core sections after a tracer experiment in the Swedish Äspö Hard Rock Laboratory

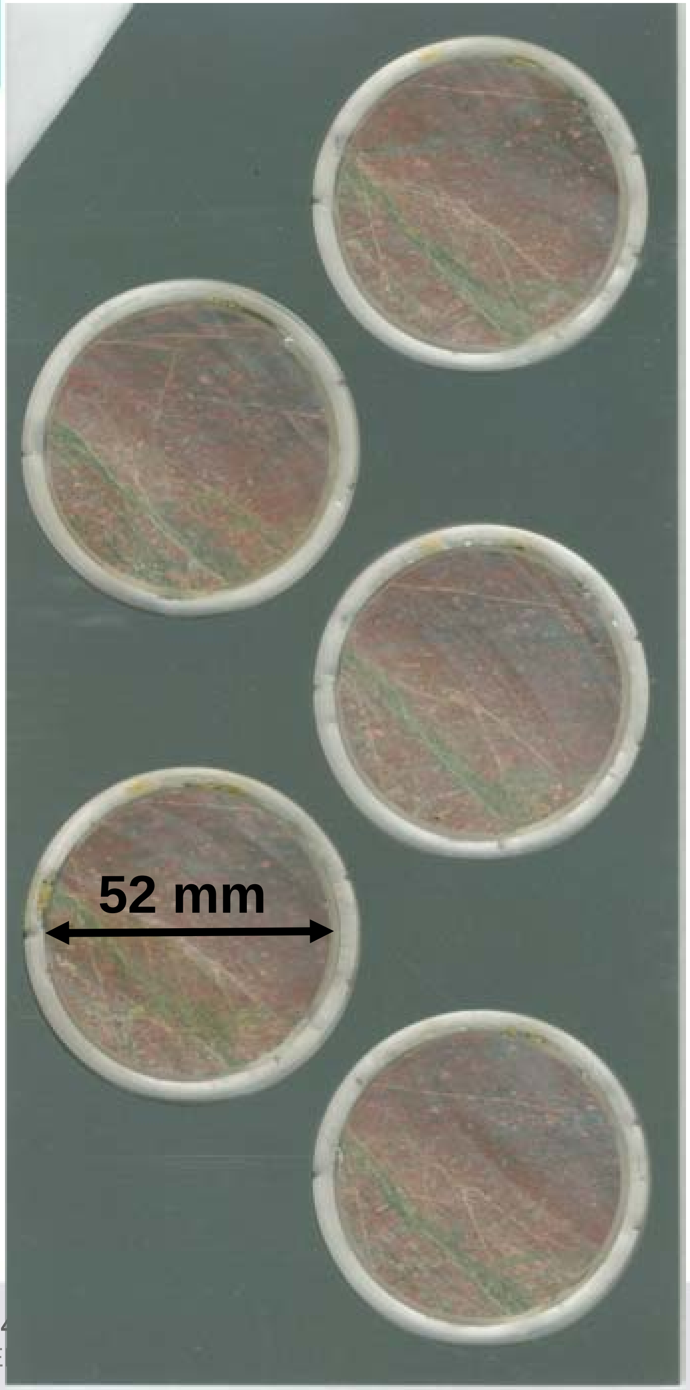
Fractured drill core (KOV 01 774.7-775.2) (core #8)

Drill cores provided by SKB (Svensk Kärnbränslehantering)



Steel sleeve with lid





Fractured granite bore core sections after a tracer experiment* in the Swedish Äspö Hard Rock Laboratory

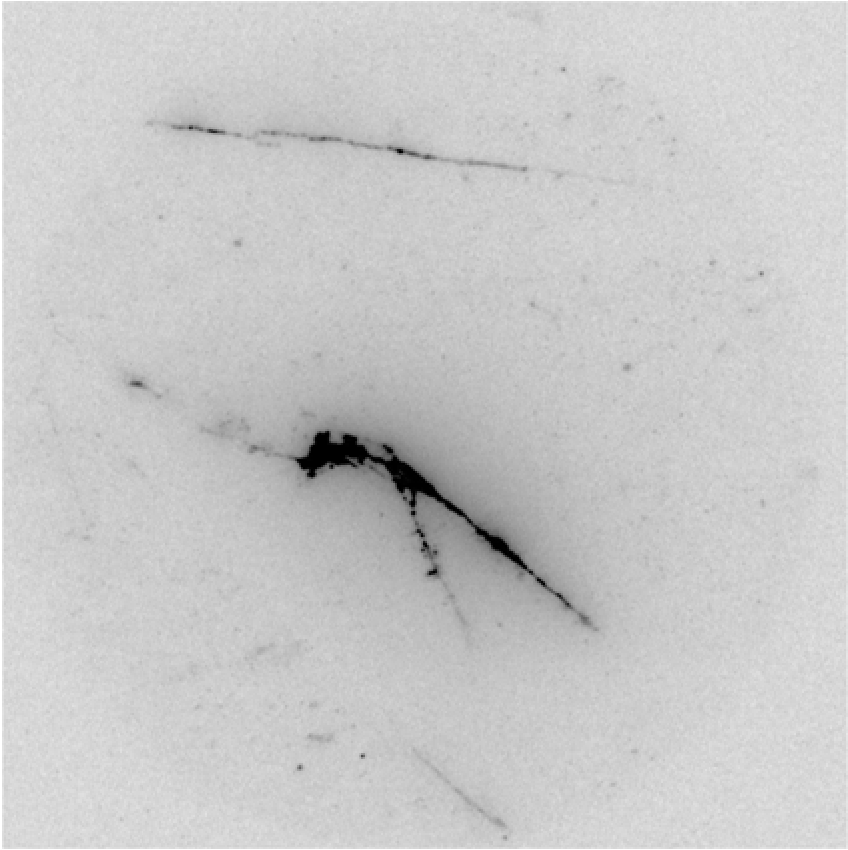
- 150 mm long bore core subjected to tracer cocktail with 14 mL 1E-5 mol/dm^3 pentavalent 237-Np.
- Elution under pressure with 80 mL Äspö groundwater → 26% Np-recovery
- ICP-MS analysis of abraded material from cutting sections and γ-counting (233-Pa daughter) of sections shows the highest [Np] 30 mm from column top to be < 3 nmol/g (<1 ppm)

What is the Np speciation?

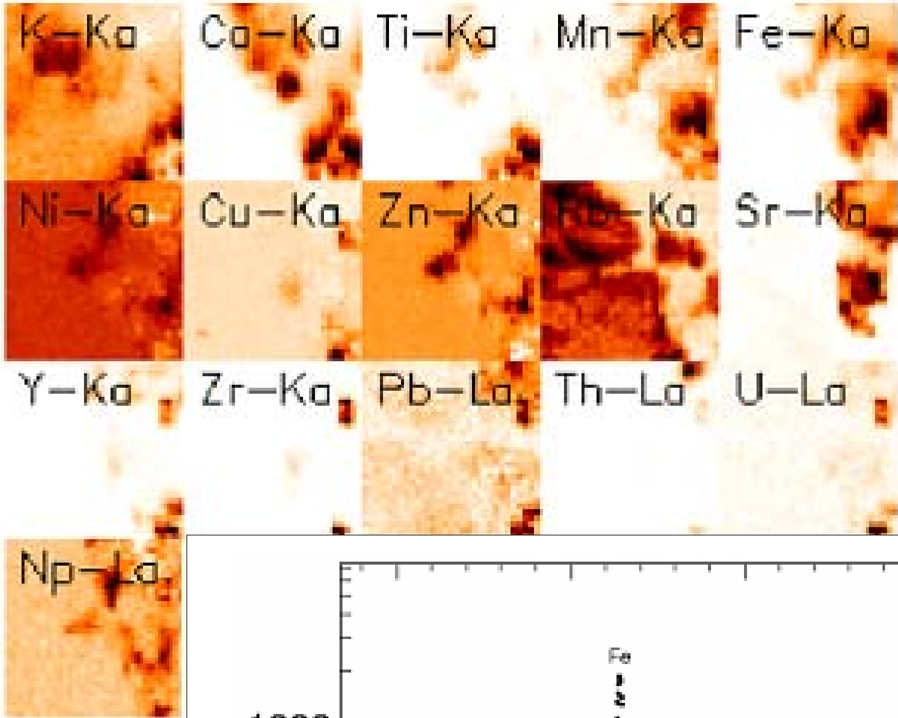
Is Np associated with any identifiable elements?

*Römer et al., FZK-Wissenschaftliche Berichte FZKA6770 (Oktober 2002).

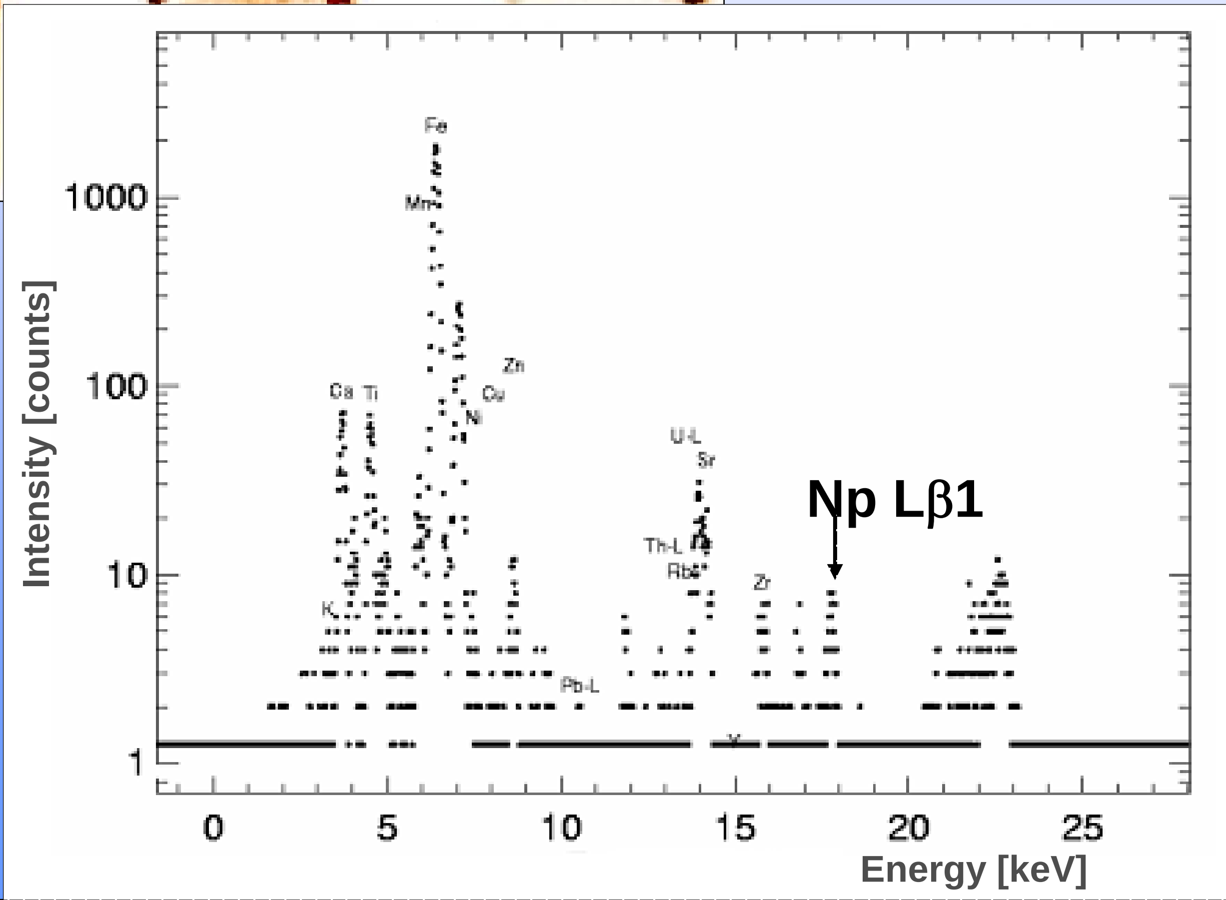
Granite bore core section and its autoradiogram after a tracer experiment in the Äspö Hard Rock Laboratory



Confocal µ-XRF results from ANKA Fluoro-Topo BL



Elemental distributions for a 300µm x 300µm area, 10µm stepsize; -58 µm below the surface



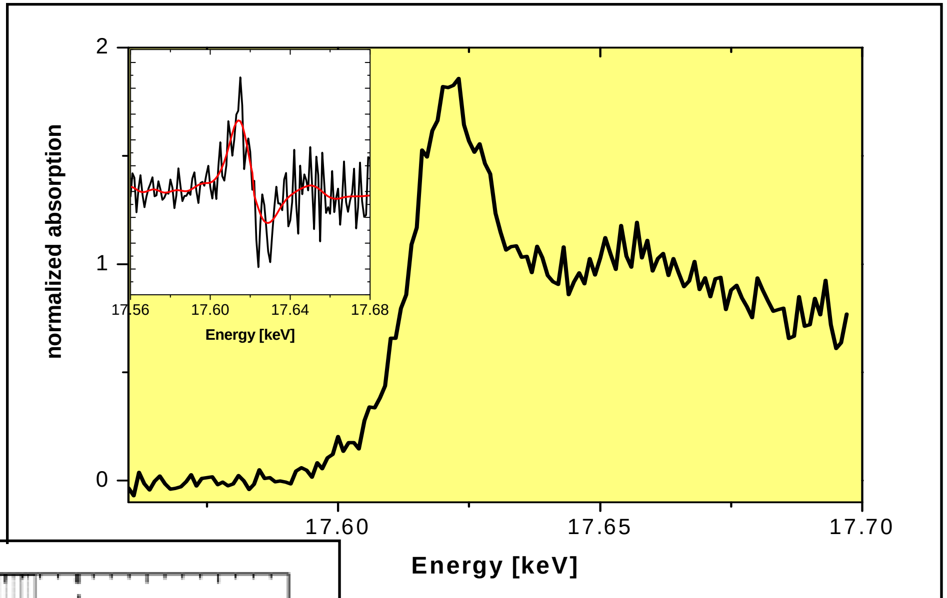
Pixel 235 has significant Np counts; to avoid spectral interference an E_{excite}~ 22.5 keV (Np L2 edge~21.6 keV)

$L\alpha_1$(Np) = 13.94 keV

$K\alpha_1$(Sr) = 14.17 keV

$L\alpha 1 = L3 \rightarrow M5$; $L\beta 1 = L2 \rightarrow M4$

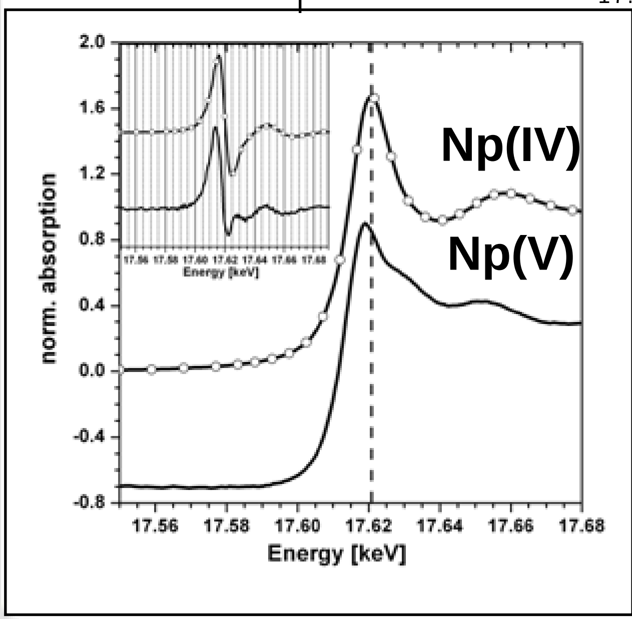
Np L3 XANES of Np hot spot



Np L3 µ-XANES collected from hot spot at a -50 µm depth

XANES lacks characteristic Np(V) multiple scattering resonance. White line at 17.621 keV

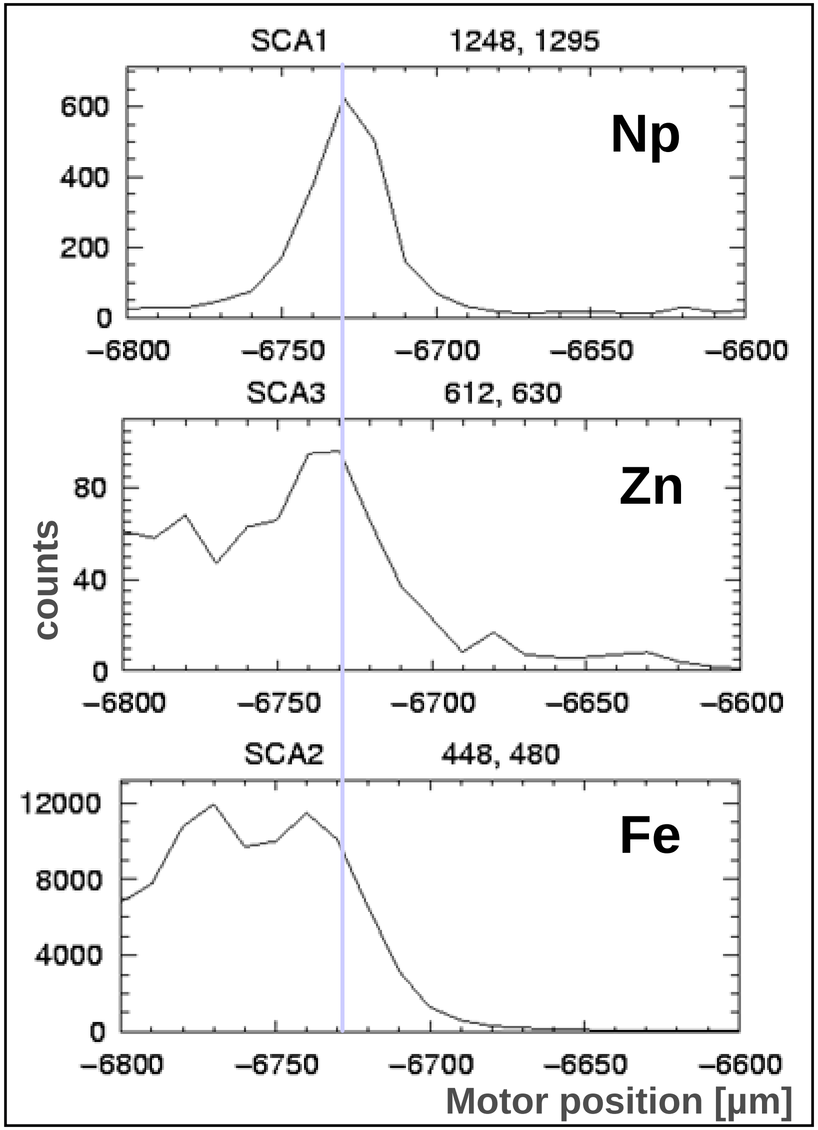
➩**Neptunium is Np(IV)**

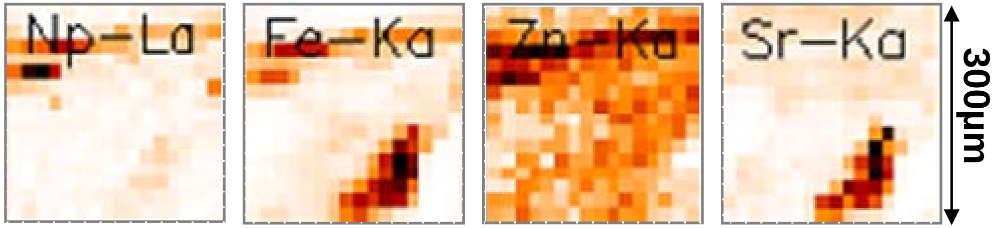


Np L3 XANES for Np(IV) and Np(V) solutions*

*from M.A. Denecke et al., Talanta 65, 1008 (2005).

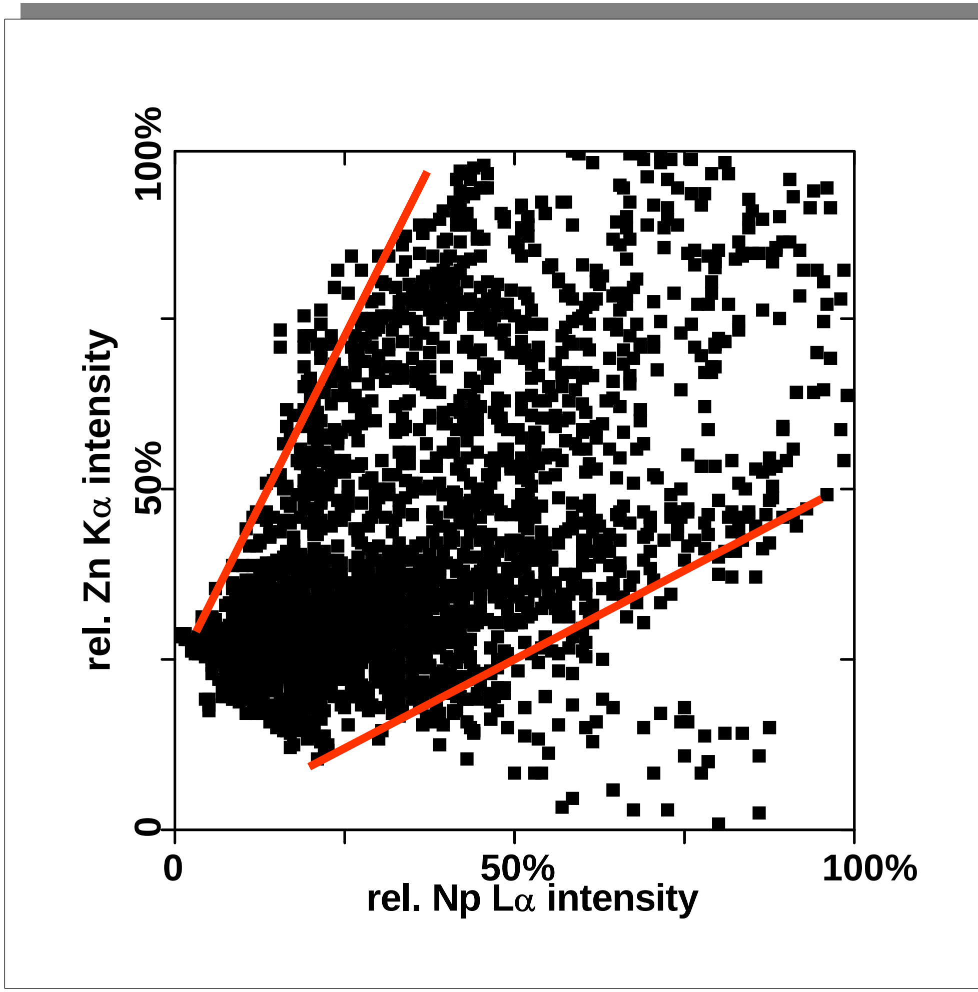
Np hot spots are often near Zn





Depth line scan recording windowed Np Lα_1, Zn Kα_1, and Fe Kα_1 counts from near the surface to -200 µm below.

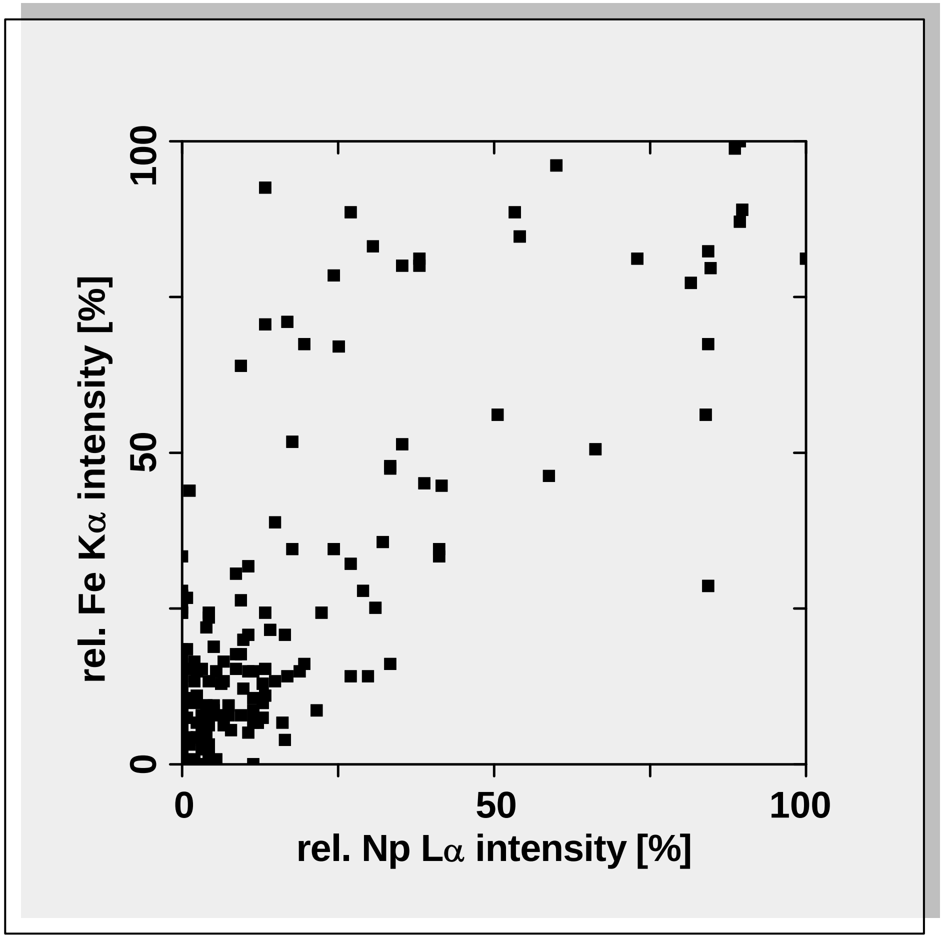
Np hot spots are often near Zn

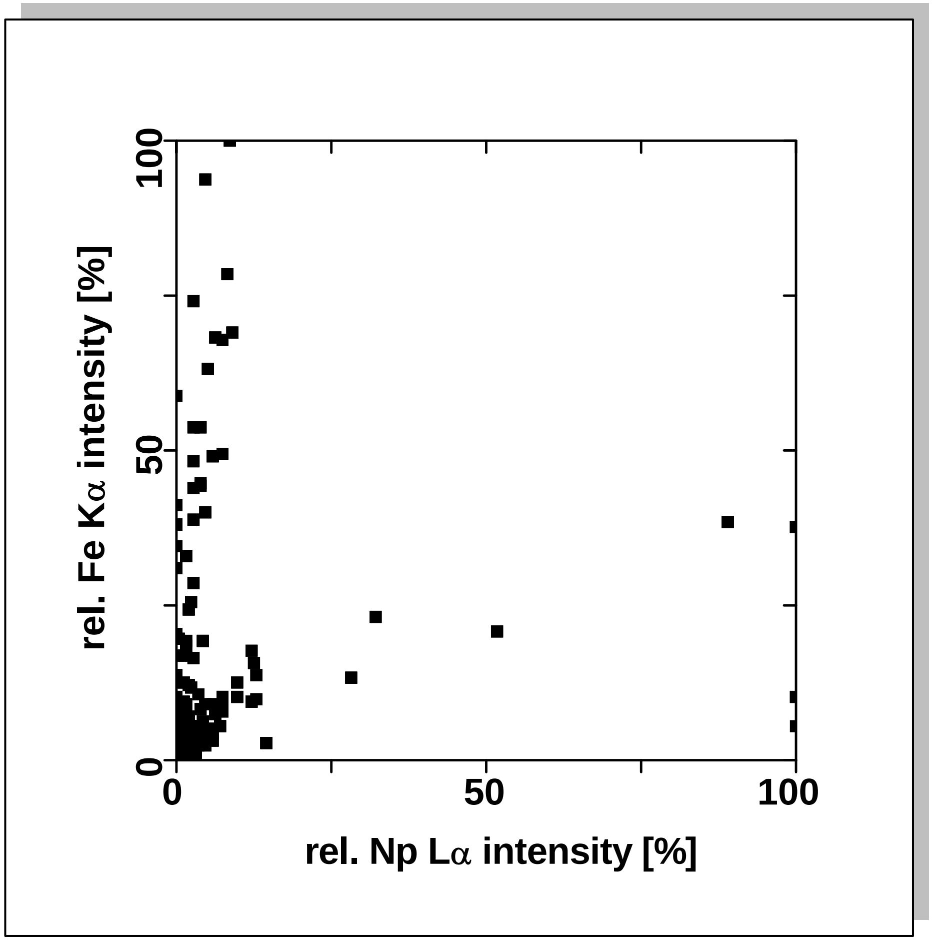


Np/Zn-correlation (normalized Np Lα versus Zn Kα signals) lies mainly within a fan defined by slopes ½ and 2.

➩ Np is associated with a Zn phase. Zn sulfide?

Np vs. Fe correlation from two different areas





Normalized Np Lα versus Fe Kα signals vary. Some areas with zero correlation, others with linear dependency.

Granite bore core tracer „post mortum“ study - CONCLUSIONS

Np is near or on small granite fissures (<100µm)

Np appears as small-sized particles

µ-XAFS reveal Np (introduced as Np(V)) is reduced to Np(IV).

Without spatial resolution, XAFS measurements are not possible.

Np(IV) found associated with Zn and Fe in fissures

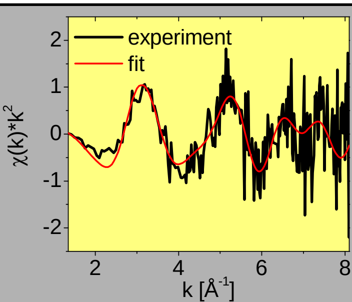
Speciation study of uranium-rich sediment from the natural analog site Ruprechtov

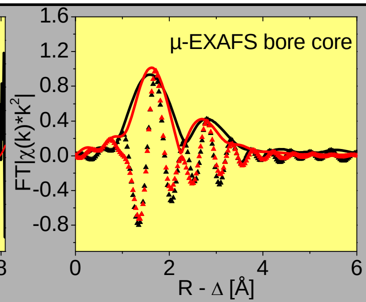
- What is the U-speciation in U-rich hot spots?
- Is a stable mineral form of the U identifiable?
- Are the U hot spots preferentially located near particular minerals or elements?

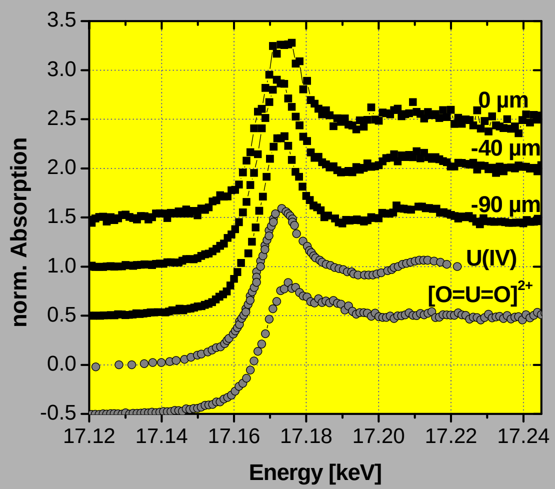
Confocal µ-XRF/µ-XAFS with lateral and depth spatial resolution

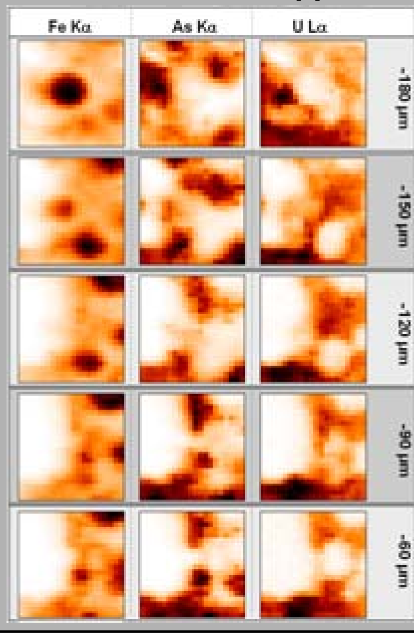
- Uranium is U(IV) and present as a phosphate (sulfate)
- U is correlated with As(V), not with Fe

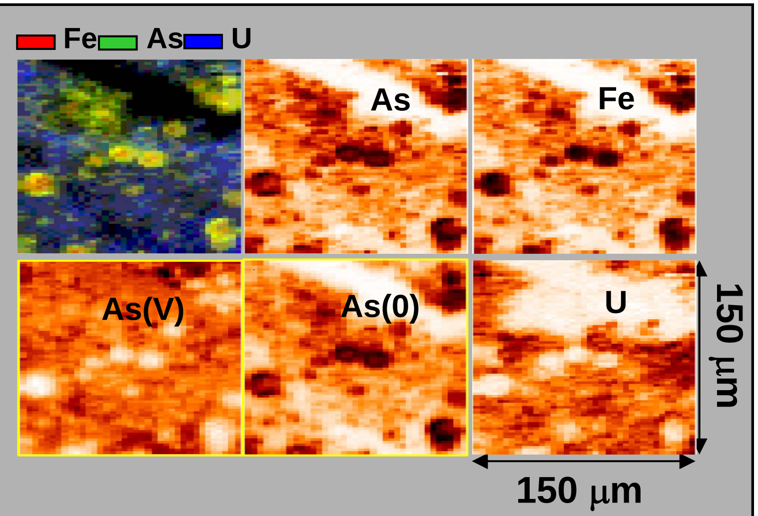
U L3 XAFS and elemental distributions at varying sample depth

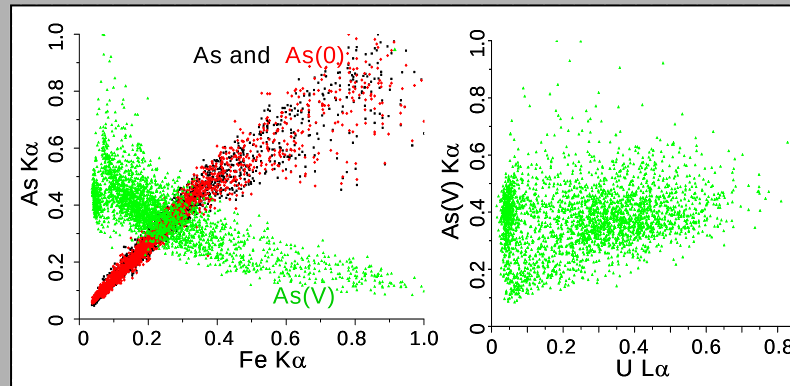








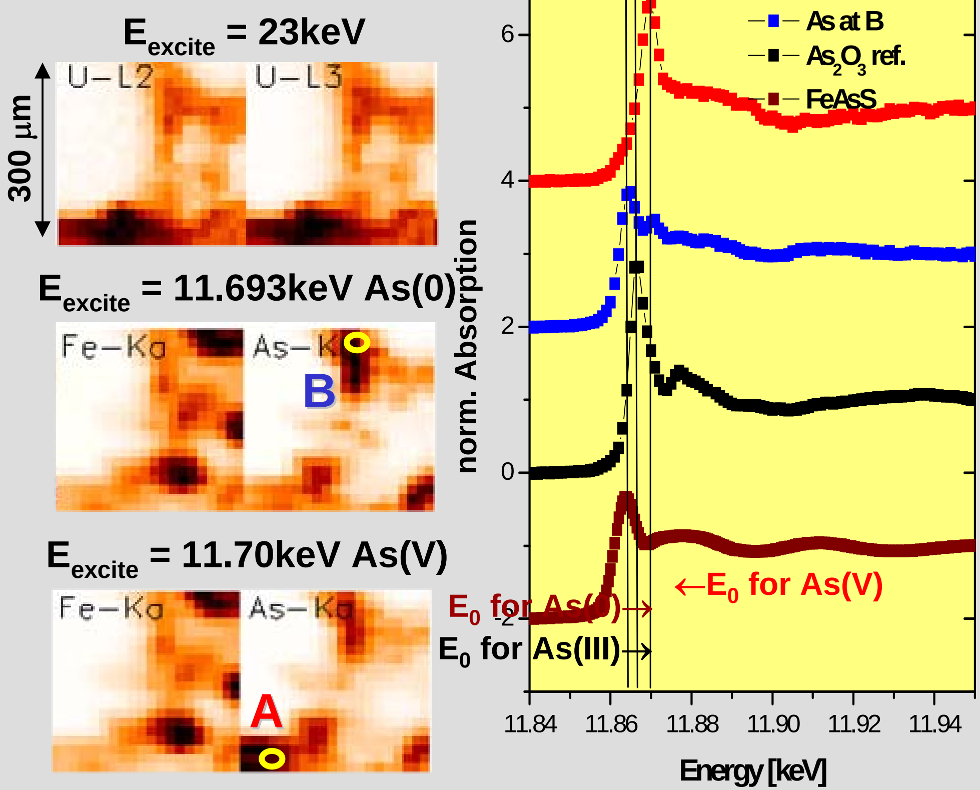


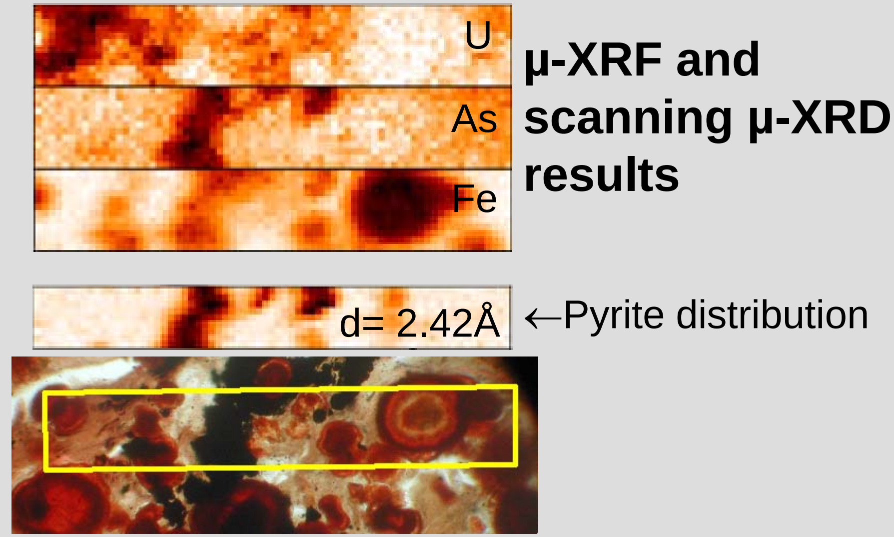


Combined µ-XRF/µ-XRD investigations

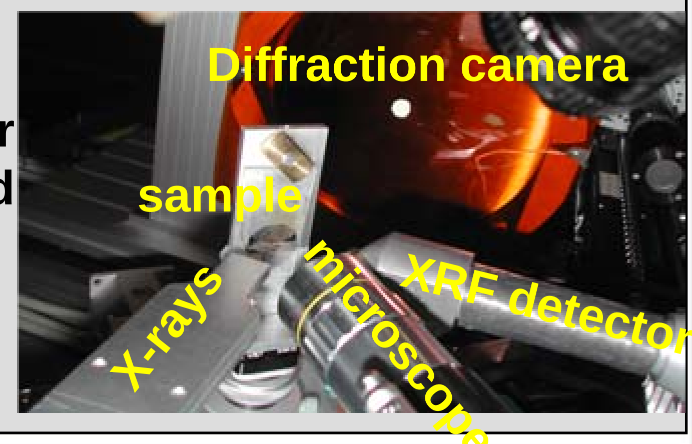
- *Arsenic is mixed valent (0 and V)*
- *As(0) likely present as nanoparticulate FeAsS or thin film coating on pyrite framboids*

As oxidation state maps & XANES





Set-up for combined µ-XRF/ µ-XRD



μ-XRF, μ-XAFS and μ-XRD study of U-rich sediment CONCLUSIONS

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- What is the speciation of the U in the U-rich hot spots?

  U(IV)

- Is there a stable mineral form of the U identifiable?

  A phosphate or sulfate phase (also a UO_2)

- Are the U hot spots preferentially located near other minerals or elements?

  Near As, likely As(V)

- Based on these results we can hypothesize a mechanism of U immobilization:

Dissolved As sorbed onto FeS_2, forming FeAsS. U(VI) reduction occurred on FeAsS sites, affecting U(IV) precipitation and formation of As(V).

$$\mathbf{FeAsS + 8H_2O \leftrightarrows HAsO_4^{2-} + SO_4^{2-} + Fe^{2+} + 15H^+ + 13e^-}$$

$$\mathbf{UO_2^{2+} + 2e^- \leftrightarrows UO_2\downarrow}$$

$$\mathbf{2FeAsS + 16H_2O + 13UO_2^{2+} \leftrightarrows 2HAsO_4^{2-} + 2SO_4^{2-} + 13UO_2(\mathit{am})\downarrow + 2Fe^{2+} + 30H^+}$$

$$\mathbf{\Delta_f G^0 \sim -43\ kJ/mol}$$

Concluding remarks concerning spatially resolved investigations for nuclear disposal safety

Long-lived actinide radionuclides make largest contribution to of nuclear waste radiotoxicity.

Mechanistic understanding of determinate processes in actinide-mineral interaction is requisite to predicting long-time actinide migration behavior.

Distribution of elements (µ-XRF), their speciation (µ-XAFS) and correlation to mineral phases (µ-XRD) help meet the challenge of characterizing/understanding these heterogeneous systems.