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Supplement of

Diffusive transport of uranium and americium through clay rock down to ultra-trace levels

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Diffusion of U(VI) and Am(III) through Opalinus Clay studied down to ultra-trace levels

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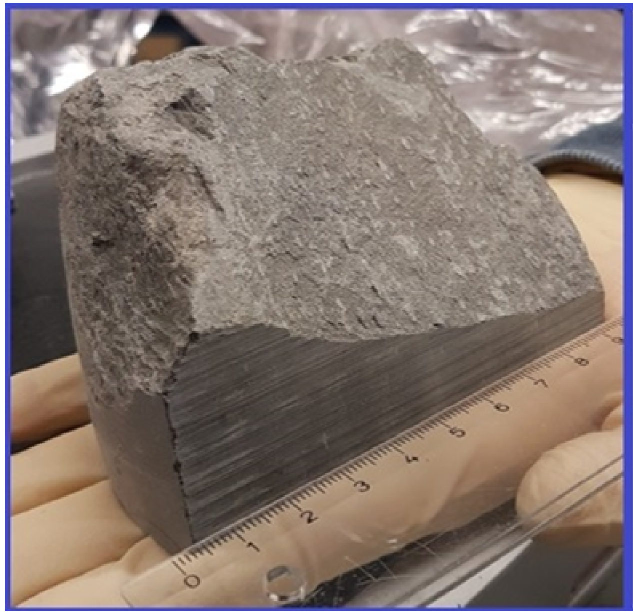
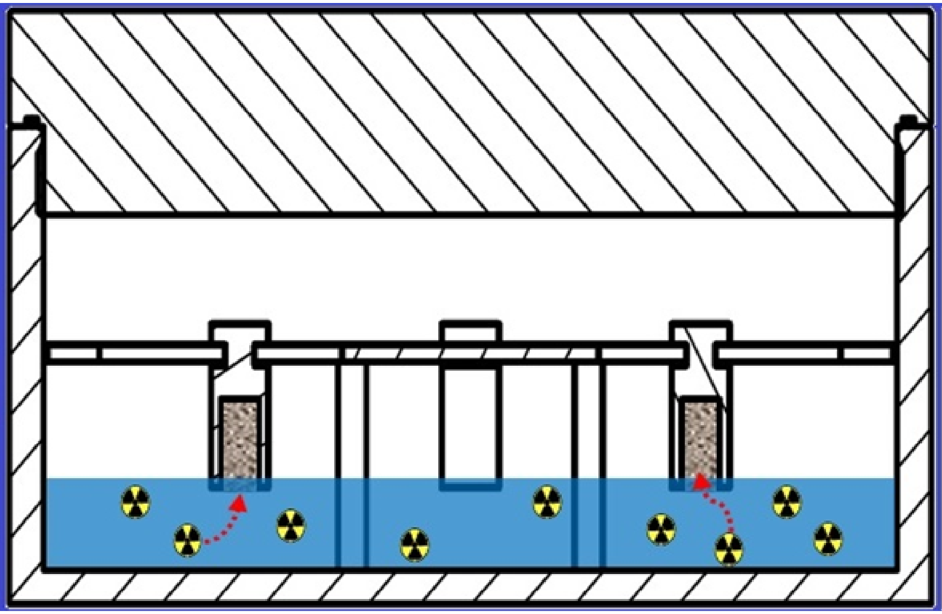
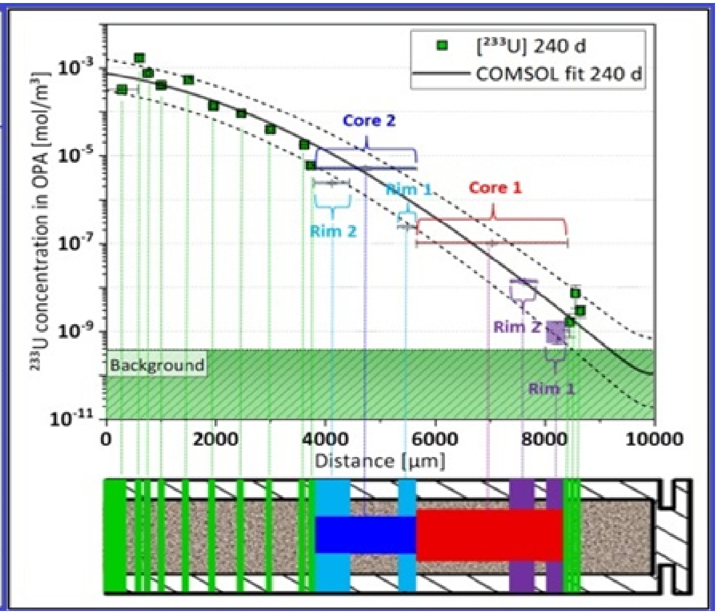




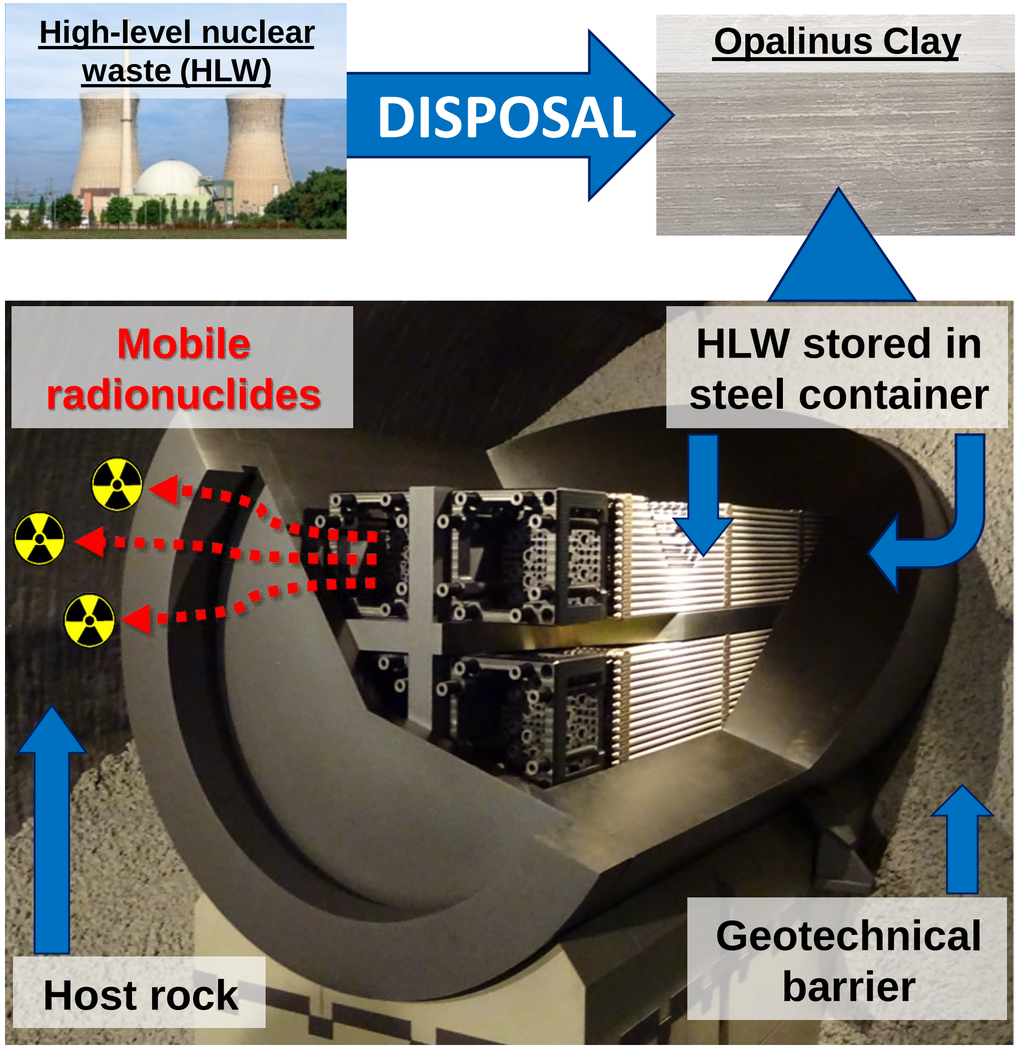


Motivation

Expected scenario

- Porewater interacts with HLW
- Radionuclides dissolve partly
- Main transport mechanism in clay rock: **Diffusion**
- **Assumption:** Actinides present mainly in low oxidation states (**+III**, **+IV**) due to reducing conditions
- **Consequence**: Low solubilities, strong sorption & slow diffusion of actinides through clay rock
- ➢ Ultra-trace actinide concentrations in the far-field are expected

➔ Aim: Study of actinide diffusion in clay rock down to ultra-trace levels



Data on actinide diffusion available in literature

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Reference	Conditions	Tracer(s)	Clay	Limit of detection (LOD) / (mol/m³)
Yamaguchi *et al.* (2007)	reducing	$^{237}Np(IV)$, $^{238}Pu(IV)$	Bentonite	**≈ 3 × 10^{-2}**
Wu *et al.* (2009)	aerobic	$^{237}Np(V)$	OPA	**≈ 7 × 10^{-2}**
Joseph *et al.* (2013)	anaerobic	$^{233}U(VI)$	OPA	**≈ 10^{-4}**

Gap in knowledge: Diffusive behavior of actinides << 10^{-4} mol/m³?

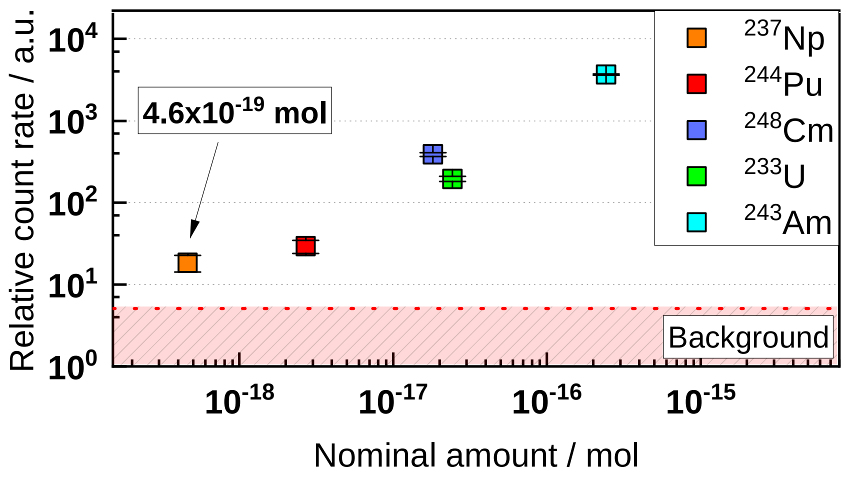
➔ **Aim: Explore potential differences in diffusive behavior of actinides at ultra-trace vs. higher concentrations**

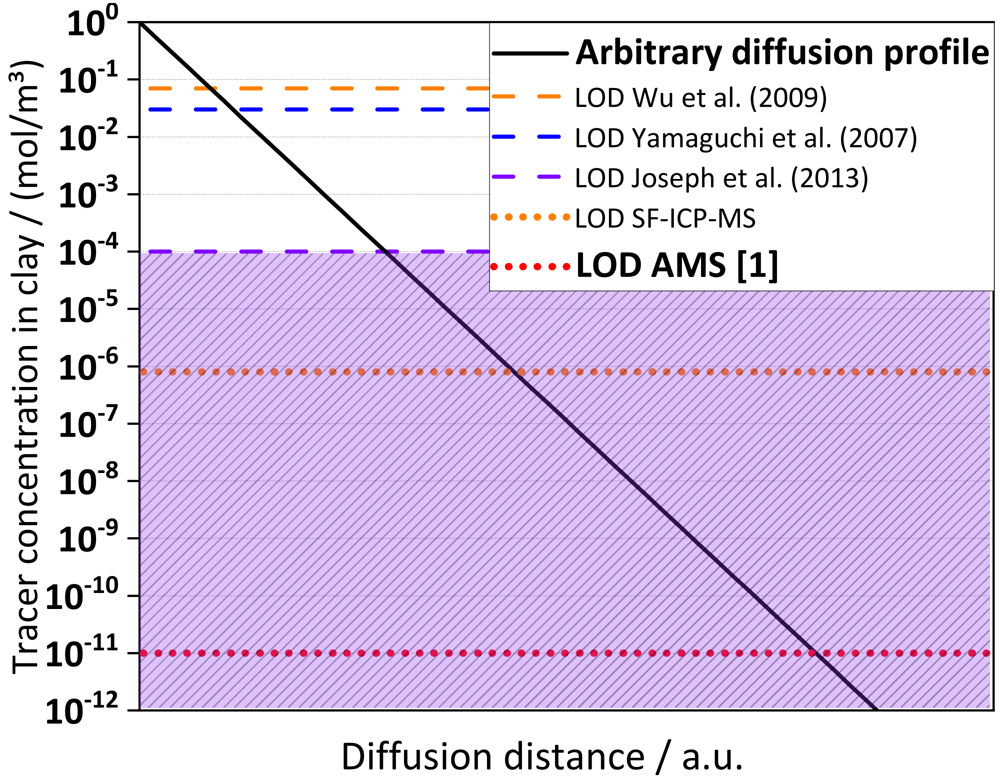
Method of choice

- **Requirement:** Extremely sensitive analytical technique
- <u>**A**</u>ccelerator <u>**M**</u>ass <u>**S**</u>pectrometry (**AMS**)

➢ <u>**Most sensitive**</u> analytical technique for ultra-trace determination of long-lived actinides in environmental samples

➔ $LOD_{Actinides}$ ≈ 5×10^{-19} mol/sample in clay matrices ≈ <u>10^{-11} mol/m³</u> (≈ 2 ng/m³)



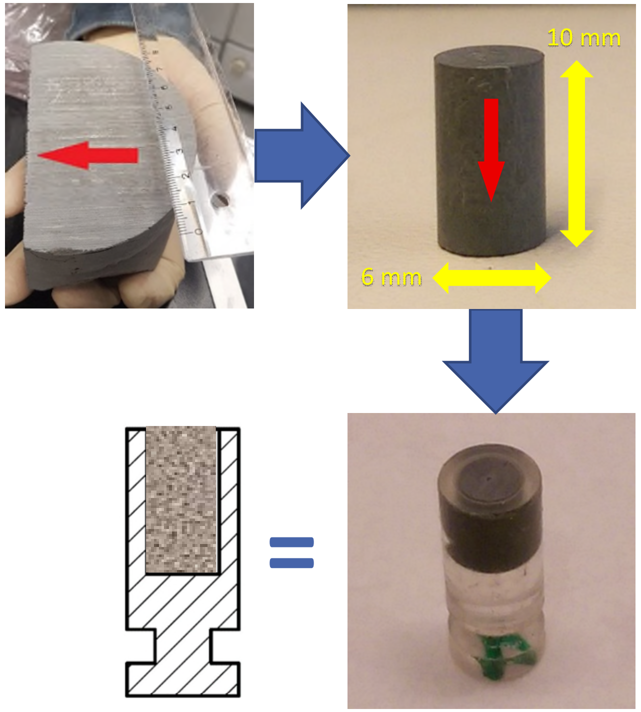


[1] Glückman, D., et al., Concurrent determination of U, Np, Pu, Am and Cm in clay systems at ultra-trace levels with AMS (under internal revision).

In-diffusion setup

Clay rock samples

- Opalinus Clay (OPA), shaly facies (Mont Terri, Switzerland)
- Drilled parallel to the bedding
- Preparation of cylindrical samples
- Embedded in PMMA („Plexiglas“) sample holder with epoxy resin



In-diffusion setup

Diffusion reservoir (PMMA)

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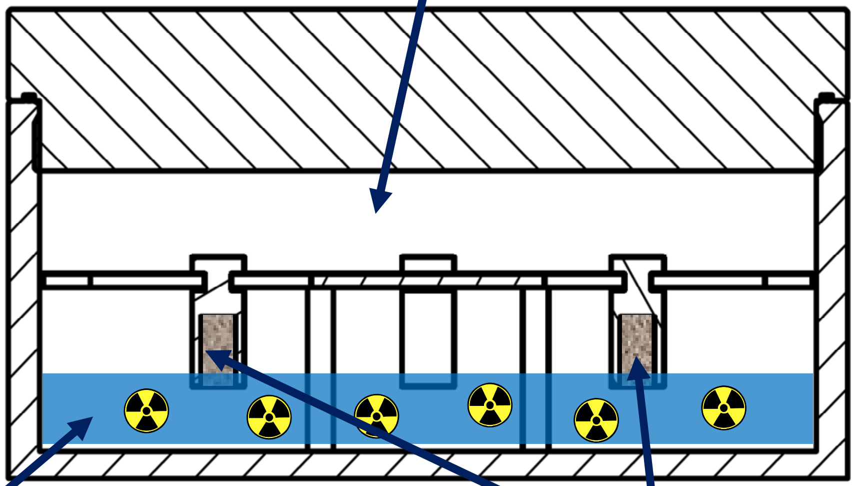
Ar atmosphere, <1 ppm O_2



Synthetic pore water composition [1]:

400 mL pore water

- $pH_0 = 8.0 \pm 0.1$
- ^{243}Am(III): $c_0 \approx 4 \times 10^{-9}$ mol/L
- ^{233}U(VI): $c_0 \approx 4.5 \times 10^{-9}$ mol/L

2 clay samples on carousel

Experimental time:

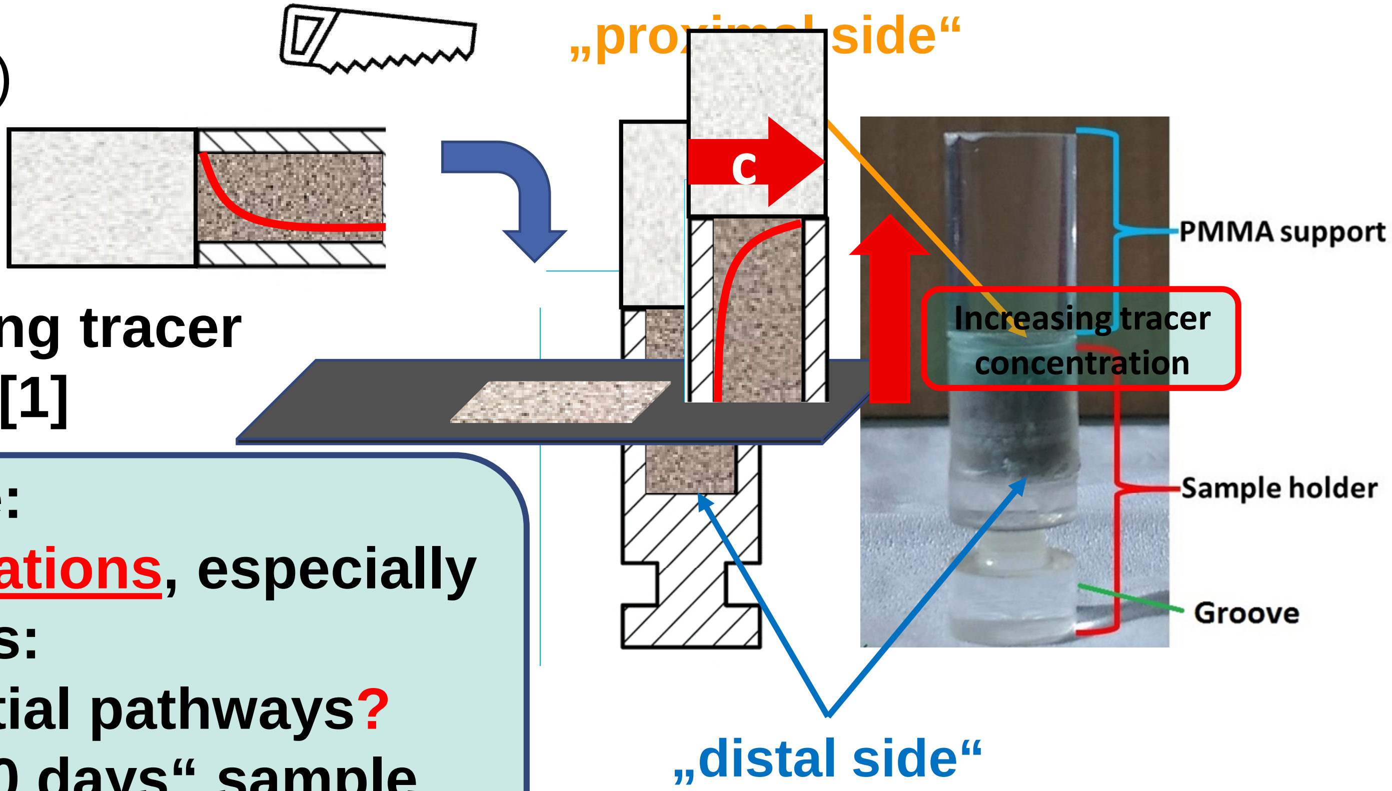
- 126 days
- 240 days

[1] Gimmi, et al., Geochim. Cosmochim. Acta, 2014, 125, 373–393.

Sample processing ("126 days" sample)

- Removal of clay sample from diffusion reservoir
- PMMA cylinder glued on top (support)
- Saw off groove
- Expose back part of clay sample

➢ **Processing in direction of increasing tracer concentration by abrasive peeling [1]**

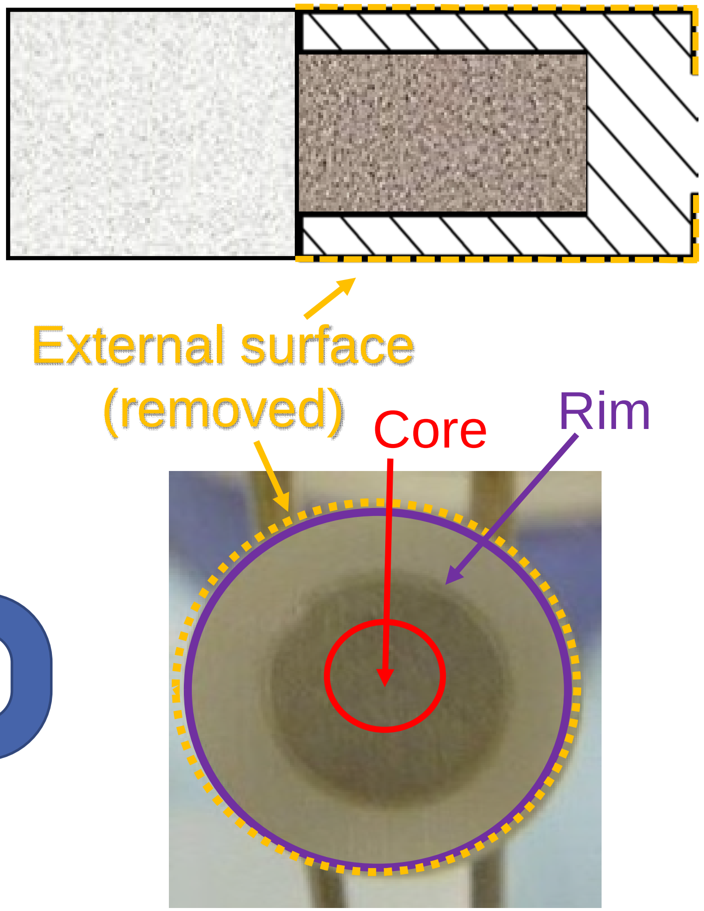


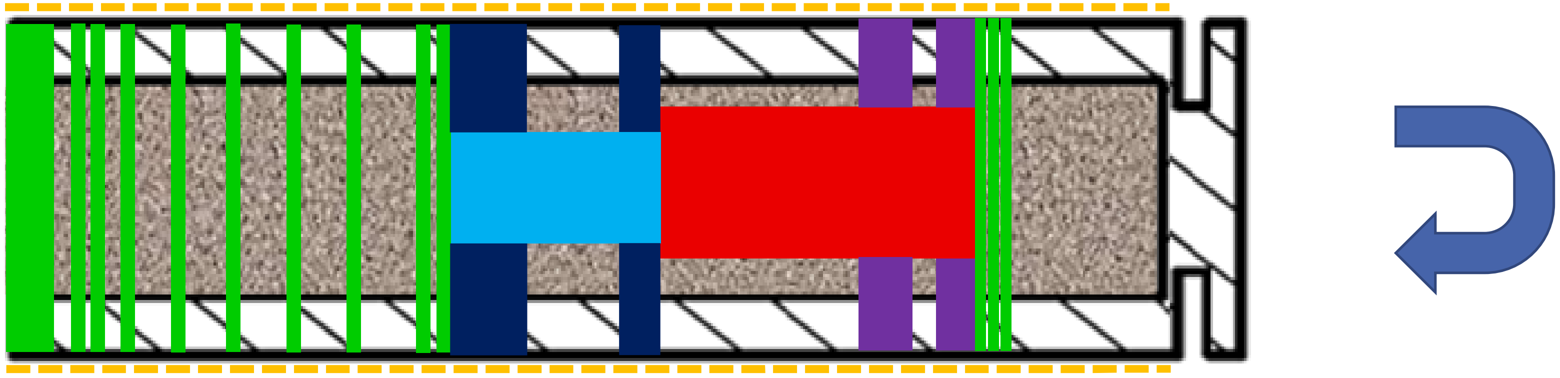
„126 days" sample:
Unexpectedly high tracer concentrations, especially for longer distances:
Cross-contamination? Preferential pathways?
➔ Processing procedure for „240 days" sample adjusted!

[1] L. R. Van Loon, W. Müller, A modified version of the combined in-diffusion/abrasive peeling technique for measuring diffusion of strongly sorbing radionuclides in argillaceous rocks: a test study on the diffusion of caesium in Opalinus Clay, Appl. Radiat. Isot., 2014, 90, 197–202.

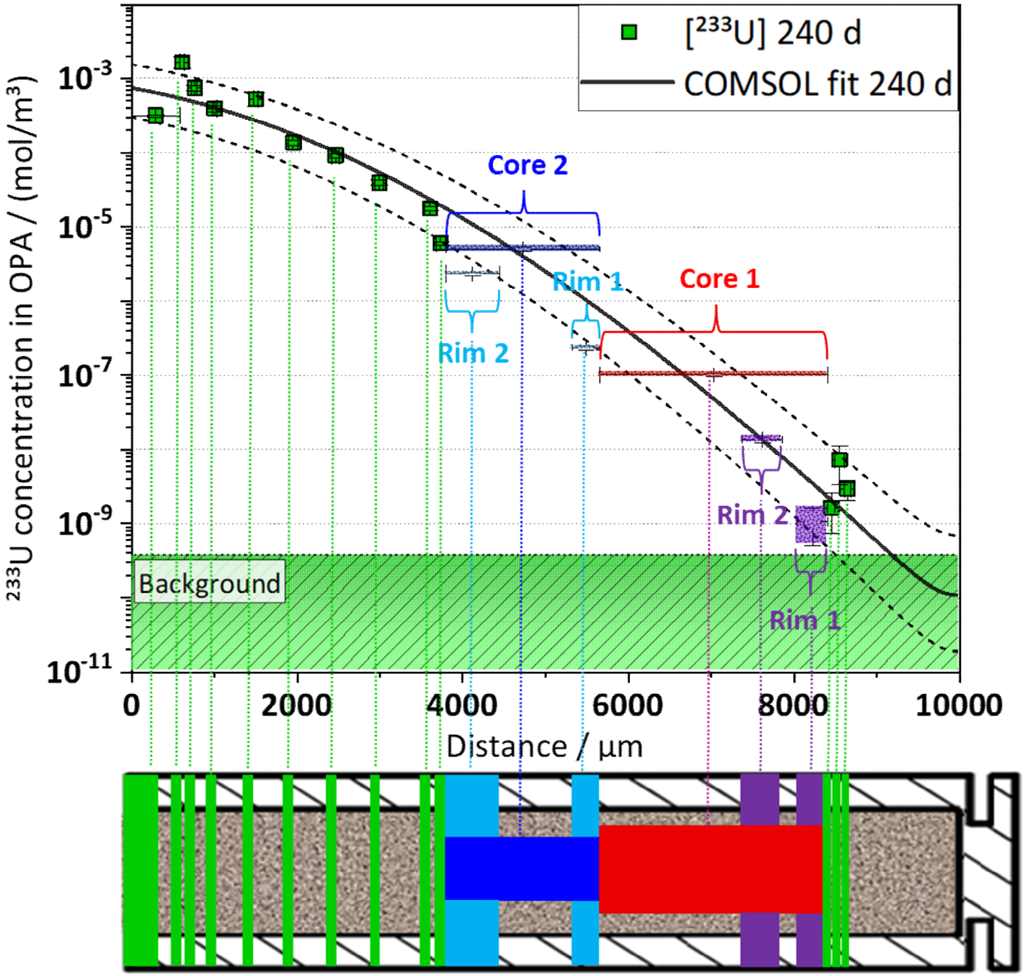
Sample processing (“240 days” sample)

- Removal of external surface (≈ 100 µm)
- ➢ **Elimination of sample holder contamination**
- Drilling of core segments (**red**, **light blue**) and abrasion of corresponding rim segments (**purple**, **dark blue**)
- ➢ **Investigation of preferential pathways across sample rim**
- Abrasion of full segments (**green**): **Abrasive peeling**





Diffusion of $^{233}U(VI)$ through OPA



- Determination of concentration profile down to **≈ 10^{-9} mol/m³**
- **Improvement by 5 orders of magnitude compared to previous studies**
- Core and rim segments follow general trend of decreasing ^{233}U concentration
- **No preferential pathway across sample rim**

Diffusion of $^{233}U(VI)$ through OPA

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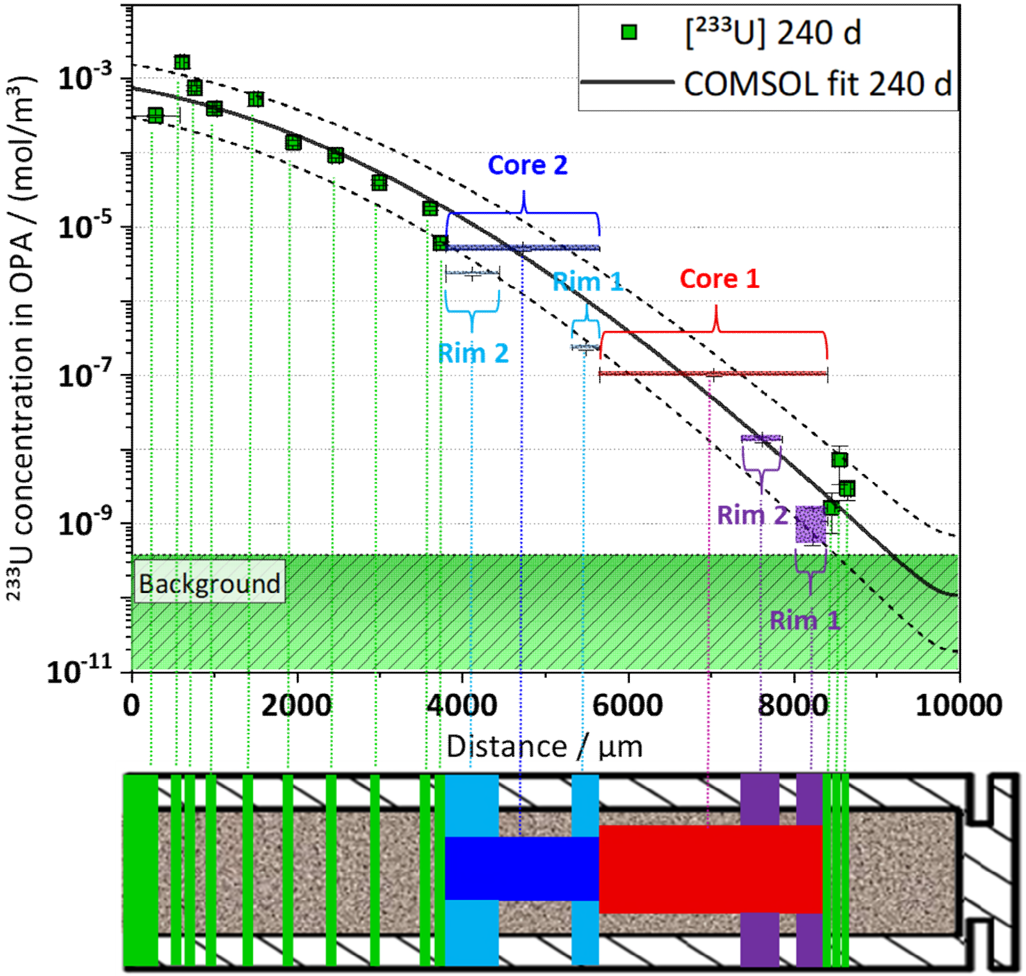
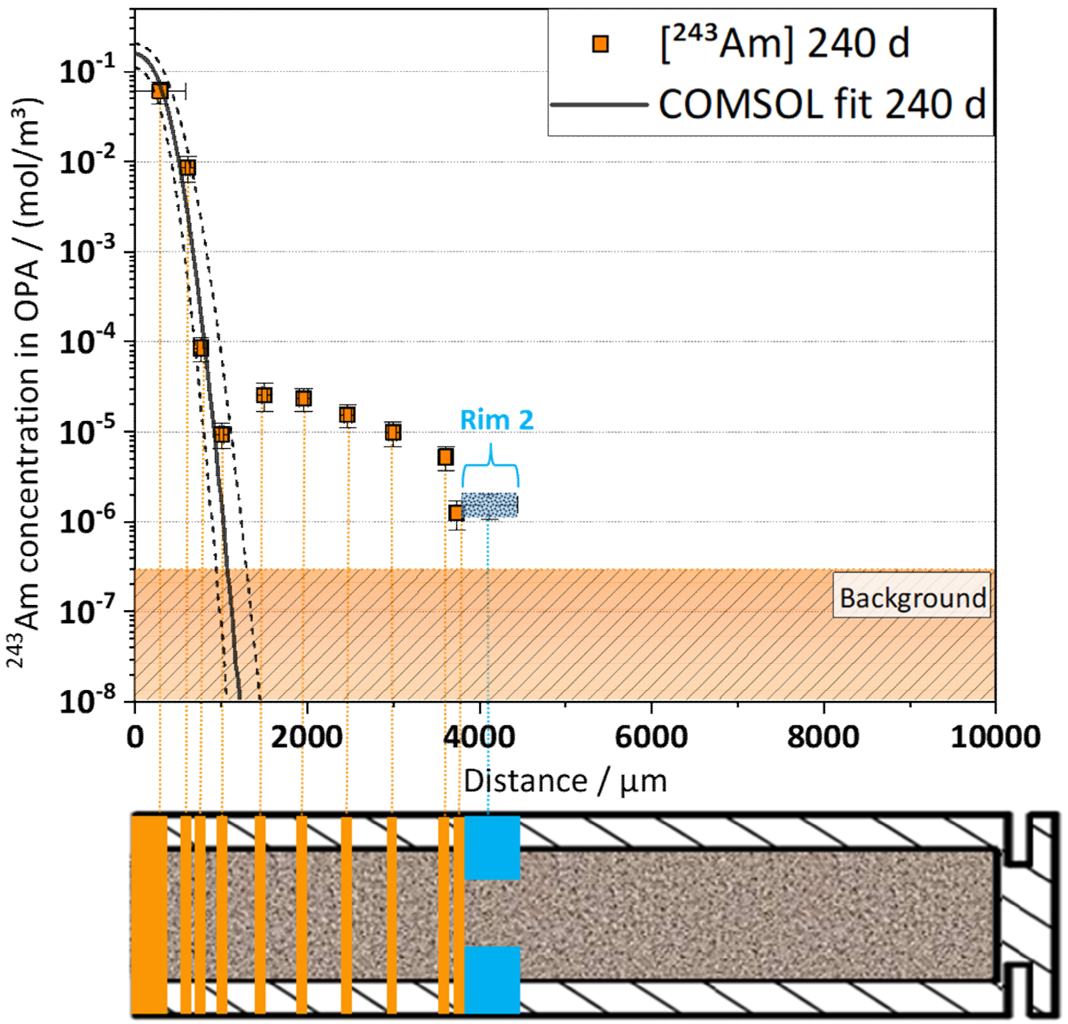


- Distribution coefficient K_d fairly in agreement with literature data
- Effective diffusion coefficient D_e **higher** due to different diffusion directions **[2]**

Parameter	This work	Literature
K_d / (m³/kg)	0.105 (+0.111/–0.065)	0.025±0.003 **[1]**
D_e / (× 10^{-11} m²/s)	1.6 (+2.0/–1.1)	0.19±0.04 **[1]**
Bedding	parallel	perpendicular
Confining pressure	none	5 MPa

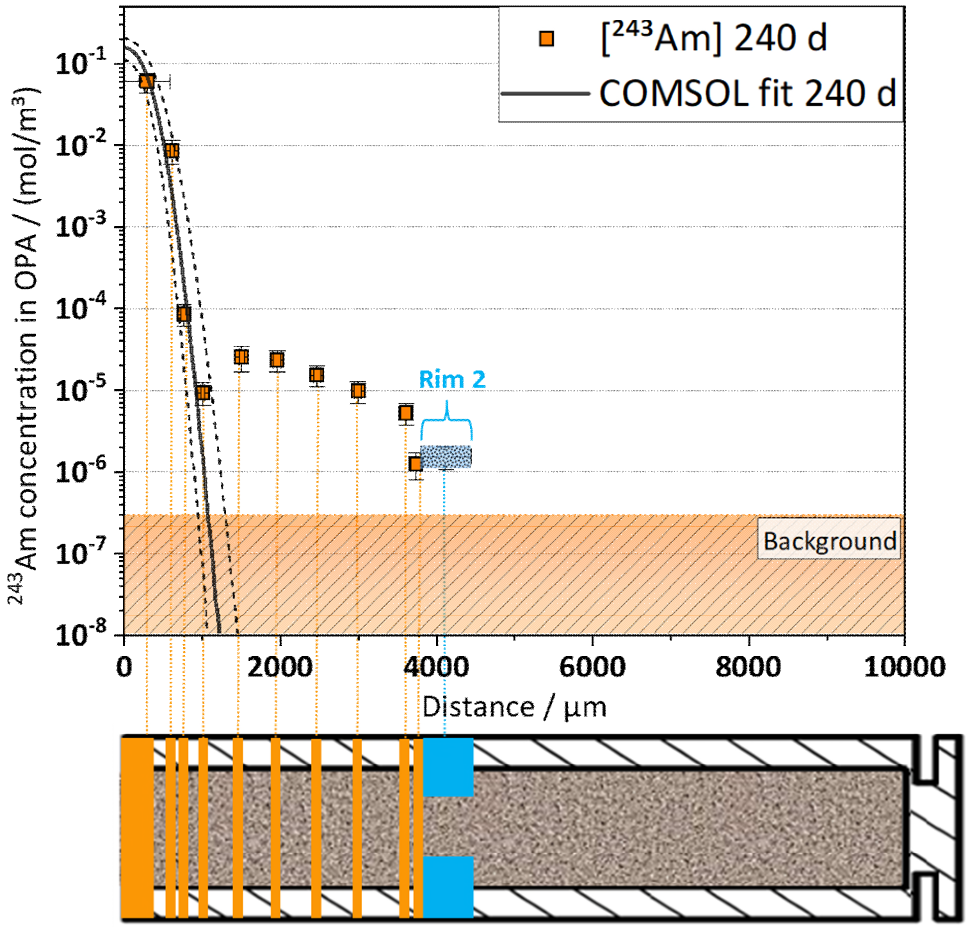
[1] C. Joseph et al., Diffusion of U(VI) in Opalinus Clay: Influence of temperature and humic acid, Geochim. Cosmochim. Acta, 2013, 109, 74–89.
[2] L. R. Van Loon. et al., Anisotropic Diffusion in Layered Argillaceous Rocks: A Case Study with Opalinus Clay, Environ. Sci. Technol., 2004, 38, 5721–5728.

Diffusion of ^{243}Am(III) through OPA



- Determination of concentration profile down to **≈ 10^{-6} mol/m³**
- Profile is featured by two different sections:
  - **0−1000 µm: Strong decrease in concentration**
  - **1500−4000 µm: Less distinct decrease**
  - **„fast runner" profile?**

Diffusion of ^{243}Am(III) through OPA



- K_d of first profile section in fair agreement with literature data
- D_a significantly **lower** compared with literature data

➔ **Different experimental conditions**

Parameter	This work	Literature
K_d / (m³/kg)	100±30	63 **[1]**
D_e / (× 10^{-10} m²/s)	2.4(+2.1/–1.1)	
Apparent diffusion coefficient **D_a / (× 10^{-15} m²/s)**	1.0(+0.9/–0.5)	17 **[2]**
Density / (kg/m³)	2400	1600 **[2]** (sand-bentonite)
Main diffusing species	$[Am(CO_3)]^+$	$[Am(CO_3)_3]^{3-}$ **[2]**

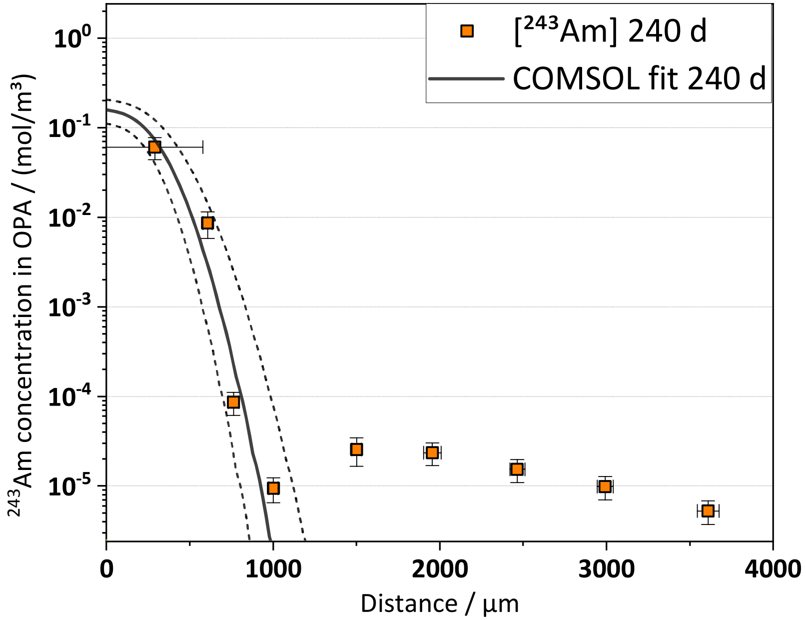
[1] M. H. Bradbury, B. Baeyens, Far field sorption data bases for performance assessment of a high-level radioactive waste repository in an undisturbed Opalinus Clay host rock. PSI Technical Report 03-08, 2003, Paul Scherrer Institut, Villigen, Switzerland.

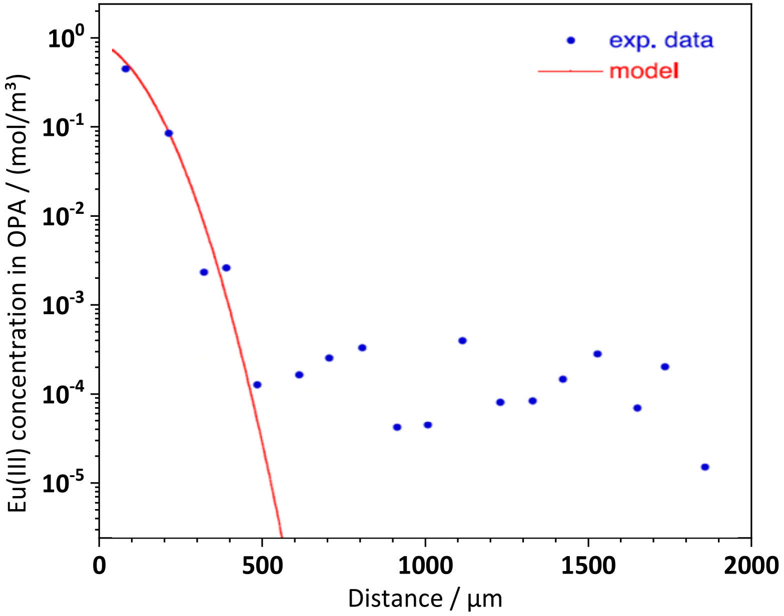
[2] T. Sawaguchi, et al., Diffusion of Cs, Np, Am and Co in compacted sand-bentonite mixtures: evidence for surface diffusion of Cs cations, Clay Miner., 2013, 48, 411–422.

Comparison of Am(III) and Eu(III) diffusion

Parameter	This work	Literature [1]
Tracer	Am(III)	Eu(III)
Initial tracer concentration / (mol/L)	4×10^{-9}	1×10^{-8}
Diffusion time / d	240	200
K_d / (m³/kg)	100±30	60
D_a / (× 10^{-15} m²/s)	1.0(+0.9/–0.5)	0.35

[1] PSI Progress Report 2019; Laboratory for Waste Management (LES), Paul Scherrer Institut, Villigen, Switzerland, 2020.



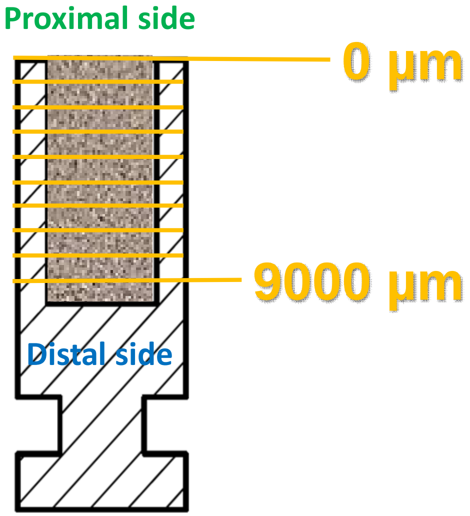


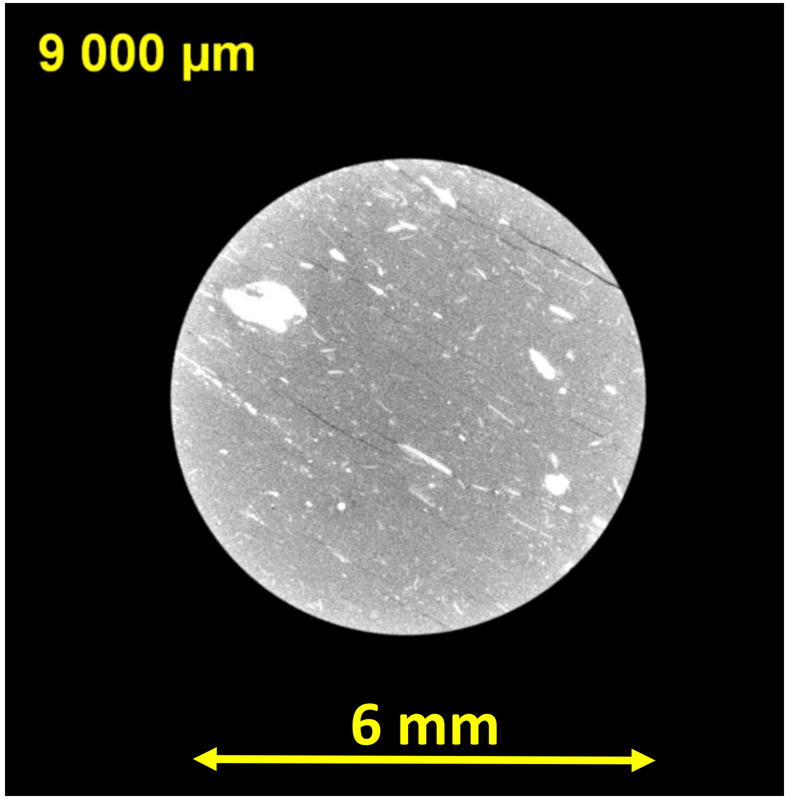
µCT investigation of clay rock sample

KIT IAM-ET: Adrian Lindner, Dr. Wolfgang Menesklou, Dr. Jochen Joos

Is the „fast runner“ profile caused by micro cracks?

- Abundance of cracks increases in direction of the proximal sample side
- Crack diameter up to **50 µm**





Hypothesis:

Tracers were transported by a combination of:

- **Pore diffusion** ➔ through porous clay matrix
- **Water diffusion** ➔ along cracks (faster process!)

Outlook

- Ongoing short-term diffusion experiments with $^{233}U(VI)$ and $^{243}Am(III)$ for **20, 40 & 60 d**
- Setup of COMSOL Multiphysics model **including crack geometry**

➔ **<u>Goal:</u> Investigation of „fast-runner“ profiles**

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Thank you for your attention!