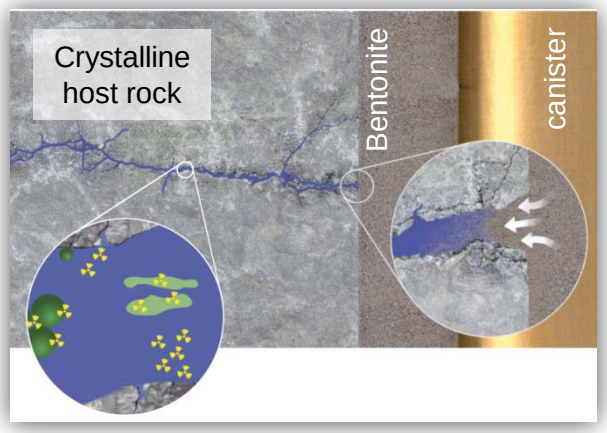
T. Schäfer, F. Huber, M. Lagos, F. Quinto, S. Büchner, Rinderknecht, F.,
S. Heck (KIT-INE)
A. Martin & I. Blechschmidt
U. Noseck & T. Reiche

INSTITUT FÜR NUKLEARE ENTSORGUNG (INE)
INSTITUTE FOR NUCLEAR WASTE DISPOSAL (INE)

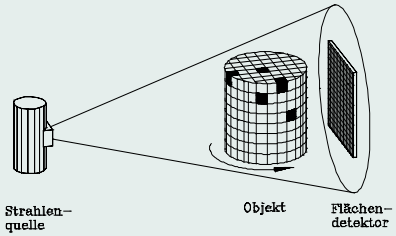
Effect of clay nanoparticle mobility, desorption and redox kinetics on radionuclide mobility investigated in an underground research laboratory (Grimsel Test Site, CH)

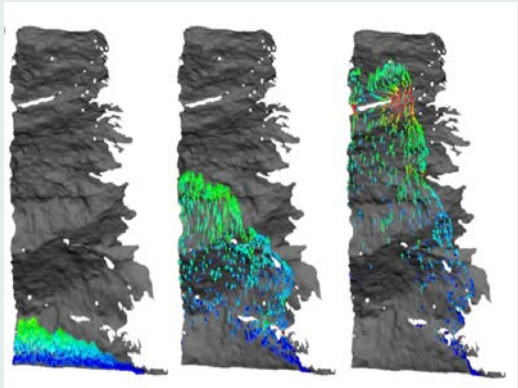
Research within URL projects (e.g. CFM)

- **Integrity of the geo-engineered barrier**
- **Upscaling from laboratory to field**
- **Colloid migration (filtration)**
- **Colloid associated RN transport**

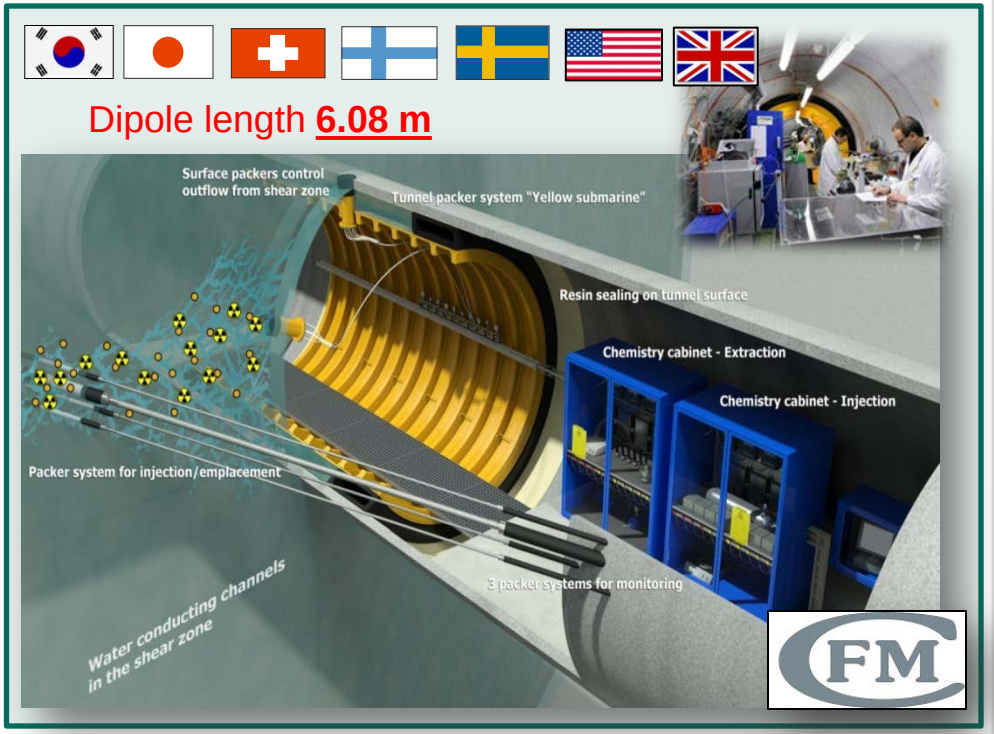


Laboratory → Underground Research Lab (URL)





Particle trace snapshots showing the heterogeneous spreading due to flow velocity variability.

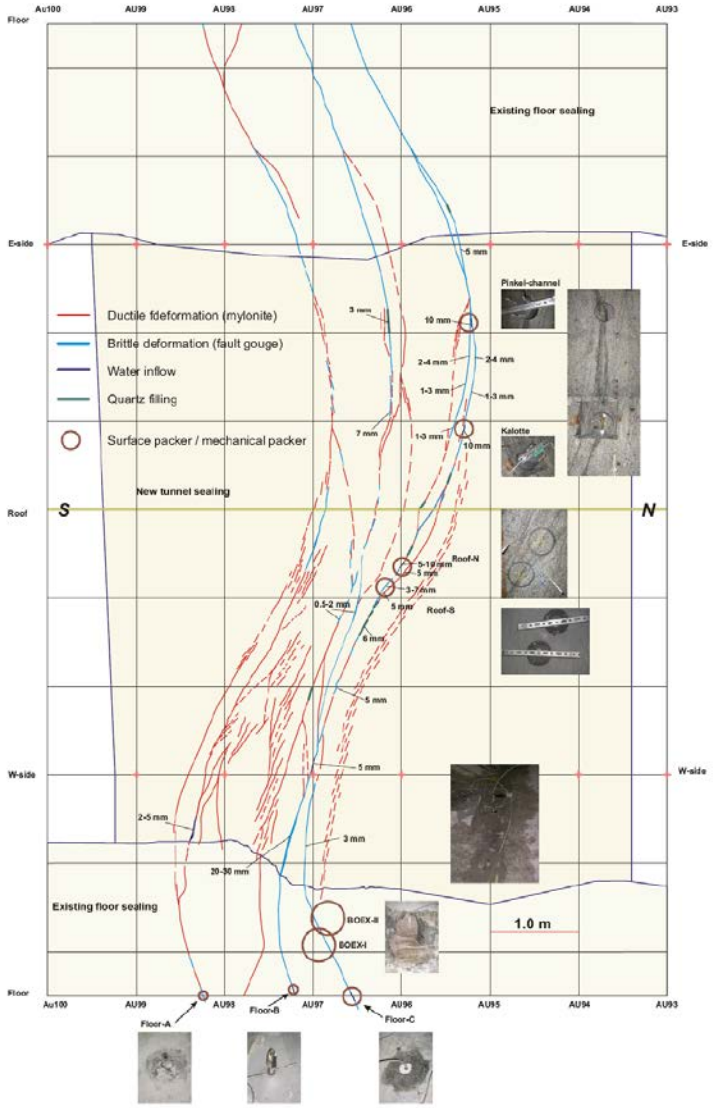


Migration (MI) shear zone (GTS, Switzerland)

(1730 m a.s.l., depth 450 m)

(1) Grimsel Test Site, (2) Rätherichsbodensee,
(3) Grimselsee and (4) Juchlistock.

- ✓ A zone with many discontinuities
- ✓ Signs of **ductile** and **brittle** deformation
- ✓ Some water inflow into the tunnel
- ✓ Core sample for lab experiments



CFM project: Tracer Test Runs

- With different combinations of **homologues** or **RN's**, colloids and conservative tracers
- Injection into the MI shear zone in borehole CFM 06.002-i2 and extraction at the Pinkel surface packer

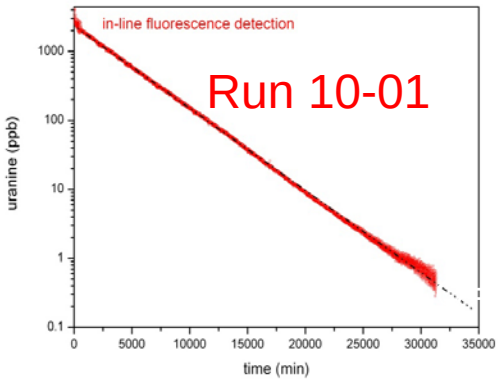
Run 08-01: direct tracer injection with 10 mL·min^{-1}; extraction flowrate 160 mL·min^{-1} (CRR configuration)

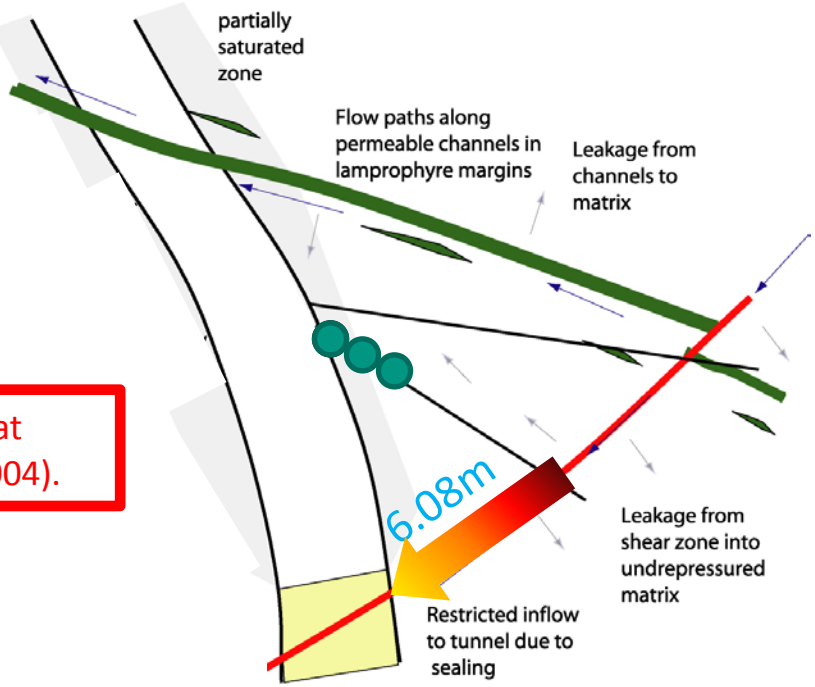
Run 10-01: tracer recirculation and 50 mL·min^{-1} extraction flowrate.

Run 10-03: tracer recirculation and 10 mL·min^{-1} extraction flowrate.

Run 12-02: tracer recirculation and 25 mL·min^{-1} extraction flowrate, slight injection with 0.33 mL·min^{-1}

Run 13-05: tracer recirculation in CRR 99.002-i2 and 5 mL·min^{-1} at BOMI 87.010-i2 (dipole within MI shearzone (see Geckeis et al. 2004).



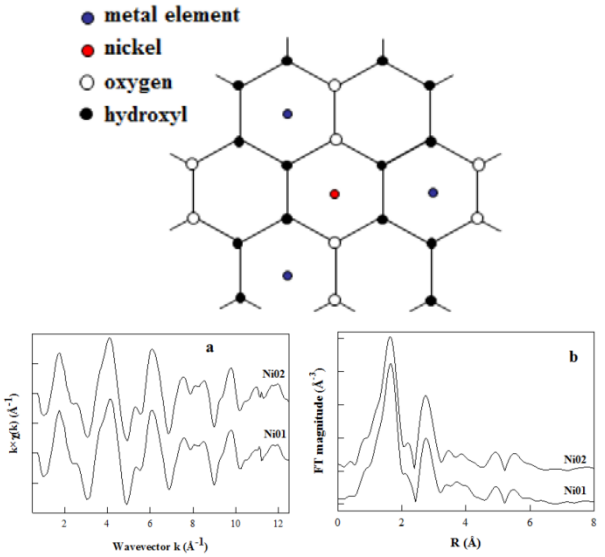


Injection Radionuclide cocktail: Run 12-02

- **Bentonite concentration:** raw material equilibrated with GGW
  - Total: 101.4 ± 2.5 mg/L
  - **8.9 ± 0.4 mg/L Ni-montmorillonite**, rest **Febex** derived colloids
- **Conservative tracer Amino-G:**
  - 1646± 8 ppb
- **ICP-MS & gamma- spectrometry data**

Tracer	concentration (mol/L)/ Total activity	Colloid association (min-max values)
^{22}Na	1.0-1.1·10^{-10} (1.17 MBq)	**0 - 3.5 %**
^{133}Ba	6.8-7.0·10^{-10} (1.97 MBq)	**24 – 34 %**
^{137}Cs	7.9-8.0·10^{-10} (785 kBq)	**97 – 98 %**
^{232}Th	5.3-5.6·10^{-9} (8 mBq)	**94 – 97 %**
^{237}Np	9.3-9.4·10^{-9} (119 Bq)	**0 - 1 %**
^{243}Am	7.0-7.4·10^{-11} (290 Bq)	**99 – 100%**
^{242}Pu	3.0-3.2·10^{-9} (190 Bq)	**99 – 100%**

Ni- montmorillonite



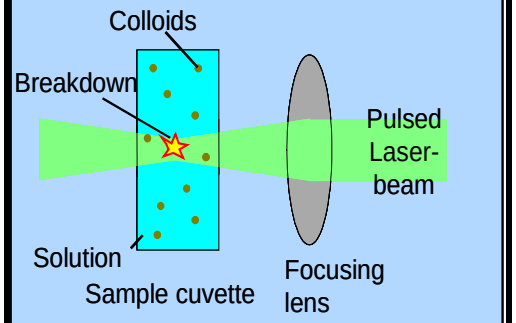
Reinholdt, et al. (2013)
Nanomaterials 3(1), 48.

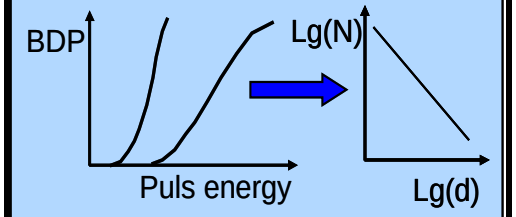
Laser induced breakdown detection (LIBD): On-site

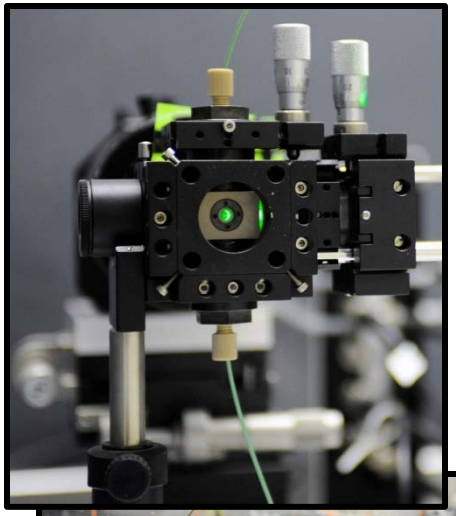
- The INE mobile LIBD system (MOB2)

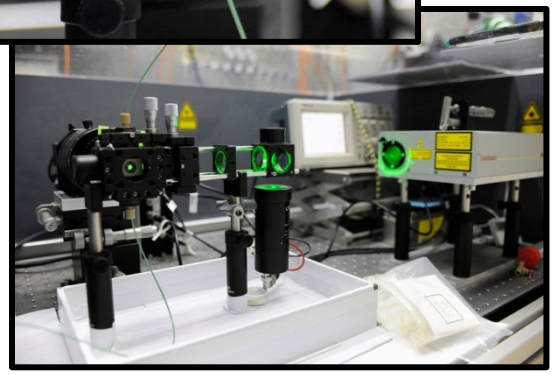
Laser-induced
Breakdown Detection (LIBD)

Single solid particles are ionized
in the focus of a laser beam;
Breakdown plasma formation;
Breakdown probability ~ f(N, d)
Laser energy dependency ~ f(d)

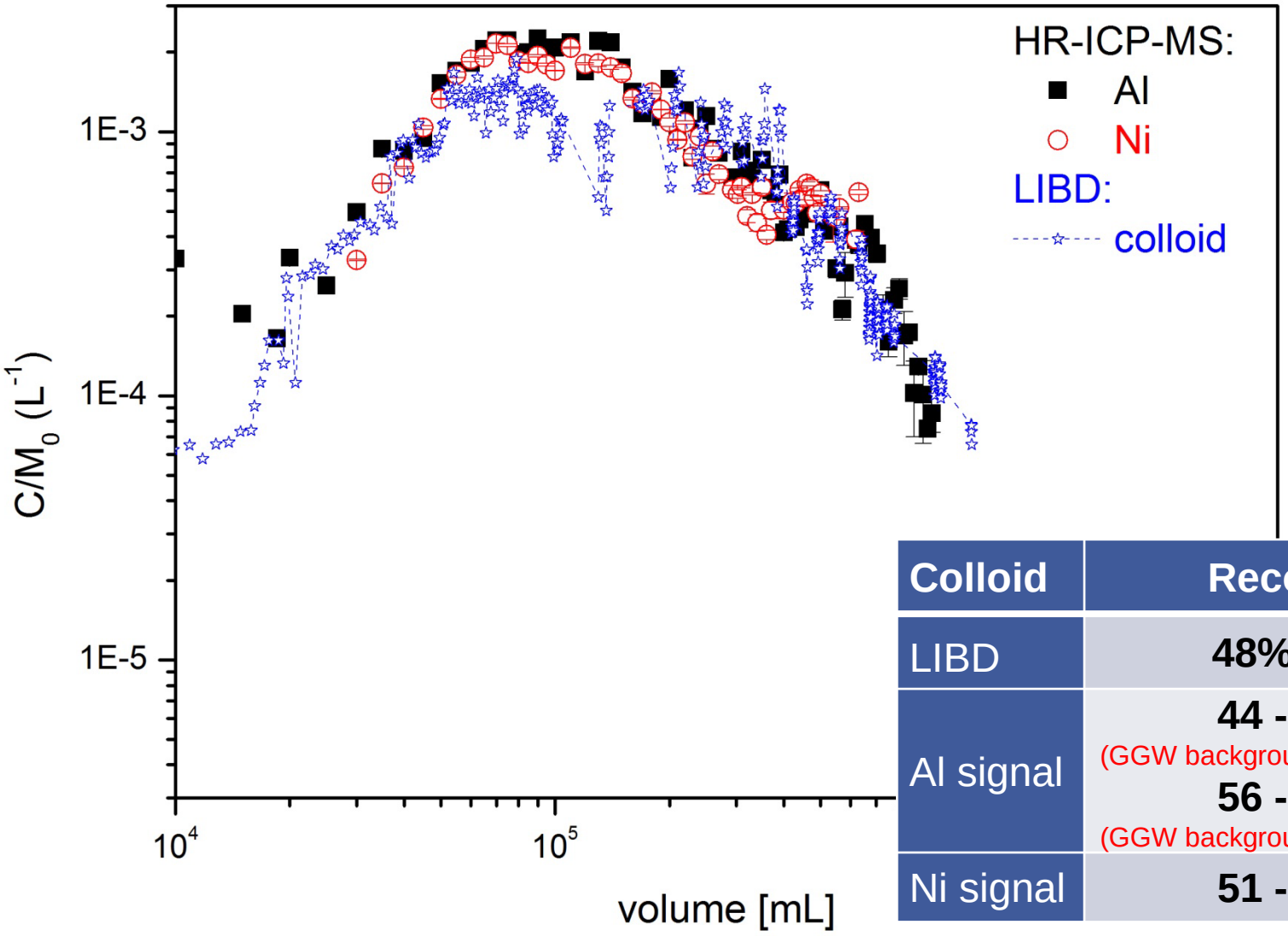






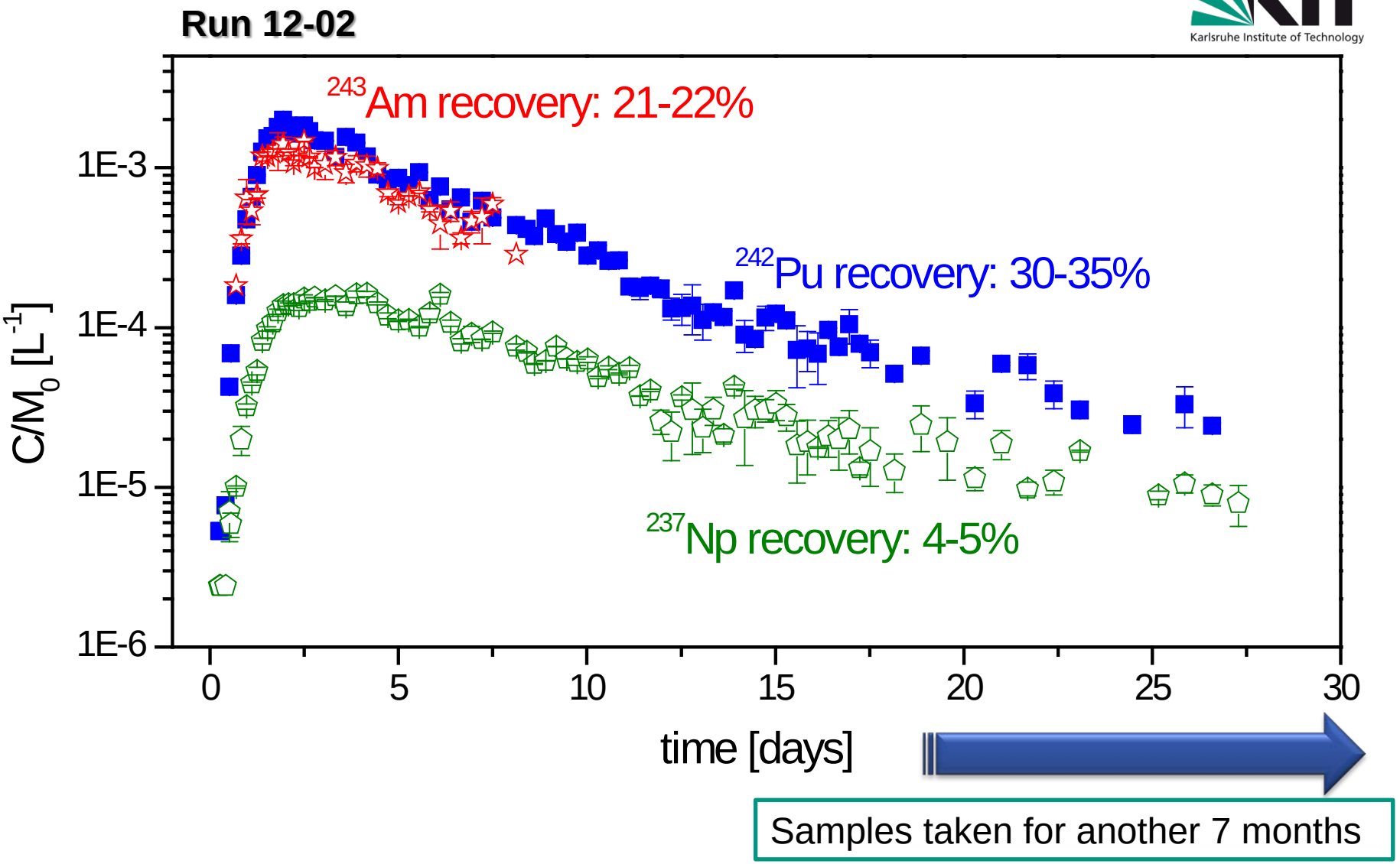


Comparison of colloid BTC's: Run 12-02



Colloid	Recovery
LIBD	**48% ± 5%**
Al signal	**44 - 49%** (GGW background signal 28ppb) **56 - 61%** (GGW background signal 25ppb)
Ni signal	**51 - 52%**

LIBD/SF-ICP-MS results: Am, Pu & Np recovery



Samples taken for another 7 months

Technique: Accelerator Mass Spectrometry (AMS)

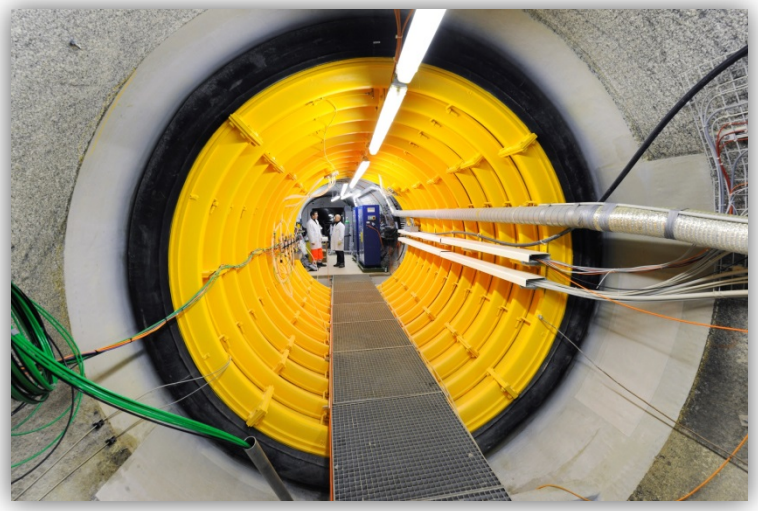
AMS of Actinides in Ground- and Seawater: *An Innovative Method Allowing for the Simultaneous Analysis of U, Np, Pu, Am, and Cm Isotopes below ppq Levels*.

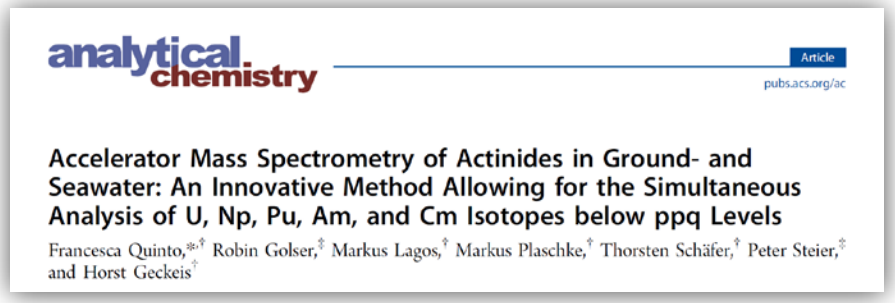
Quinto, Golser, Plaschke, Schäfer, Steier, Geckeis **(2015)** *Anal. Chem.* 87, 5766-5773.

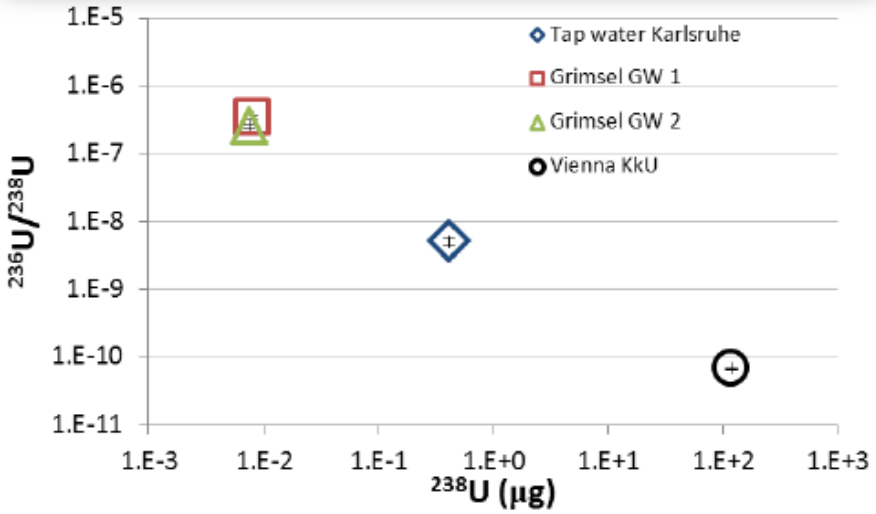
ppm	parts per million (10^{-6})
ppb	parts per billion (10^{-9})
ppt	parts per trillion (10^{-12})
ppq	**parts per quadrillion (10^{-15})**

1) Nuclear weapons test fallout

2) Mobility in fracture systems



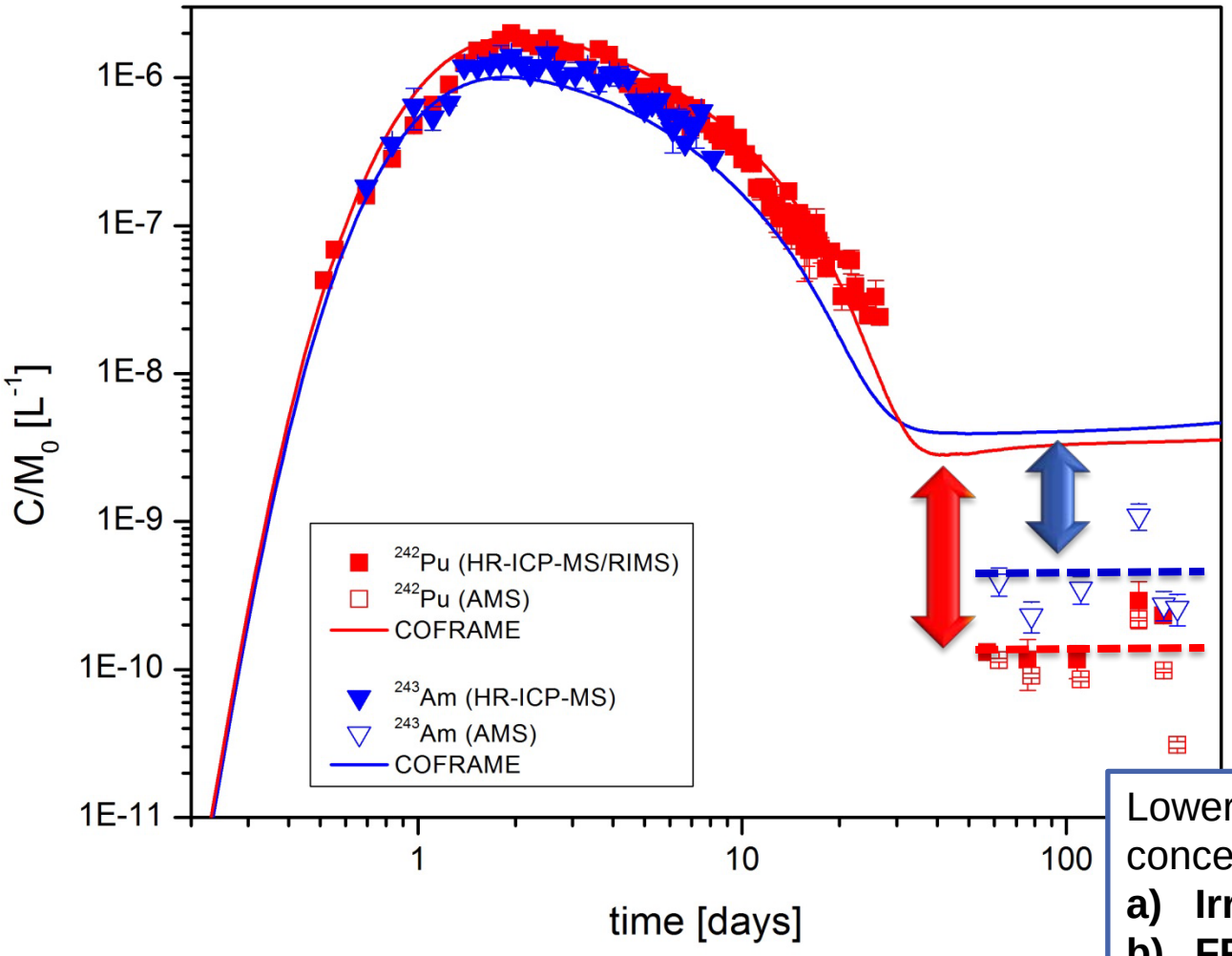




VERA (Vienna Environmental Research Accelerator)

- The $^{236}U/^{238}U$ isotopic ratios measured in the groundwater samples from the GTS (2.5 ± 0.1) x 10^{-7} and (3.4 ± 0.3) x 10^{-7}, as well as the ratio detected in the tap water samples from Karlsruhe (5.0 ± 0.6) x 10^{-9} are consistent with the global fallout origin.
- These findings indicate the mobility of global fallout ^{236}U which apparently is able to migrate together with meteoric water from the surface to depths down to the level of the GTS groundwater at 450 m.
- Interestingly, fallout Pu could not be detected indicating a much lower mobility under given conditions.

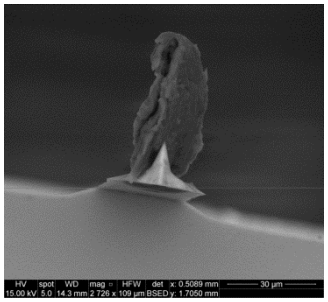
COFRAME Run 12-02:
Long-term $^{243}Am/^{242}Pu$ breakthrough

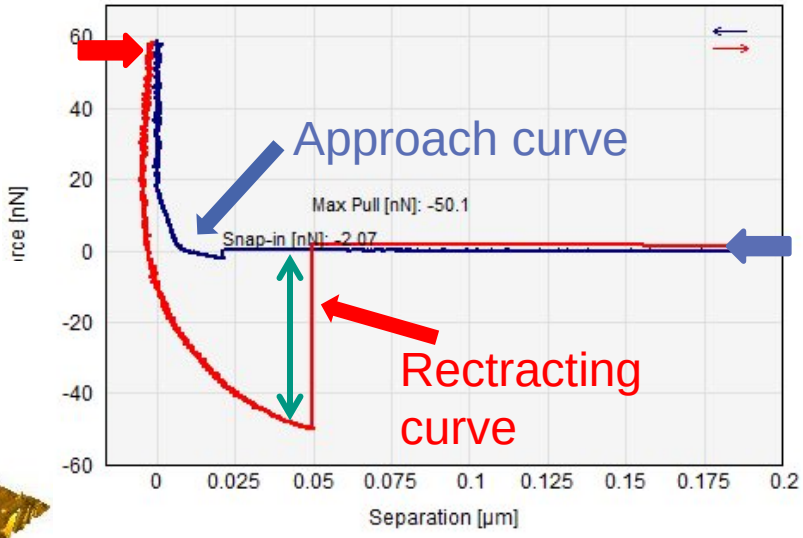


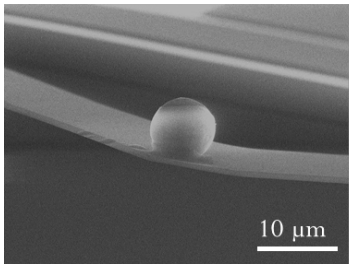
Lower dissolved Am/Pu concentration than expected:

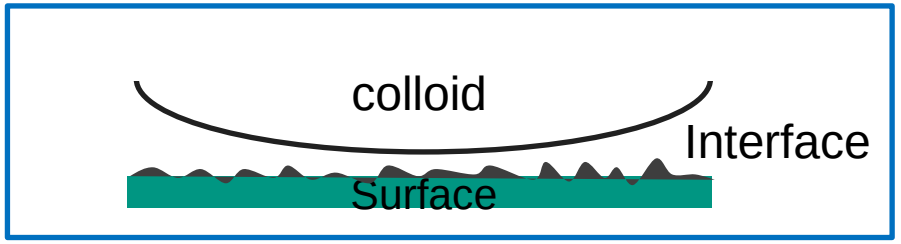
a) **Irreversible colloid sorption**
b) **FFM desorption kinetics**

2) Forces between colloid and granite/acrylic glass substrate (Colloid probe technique)

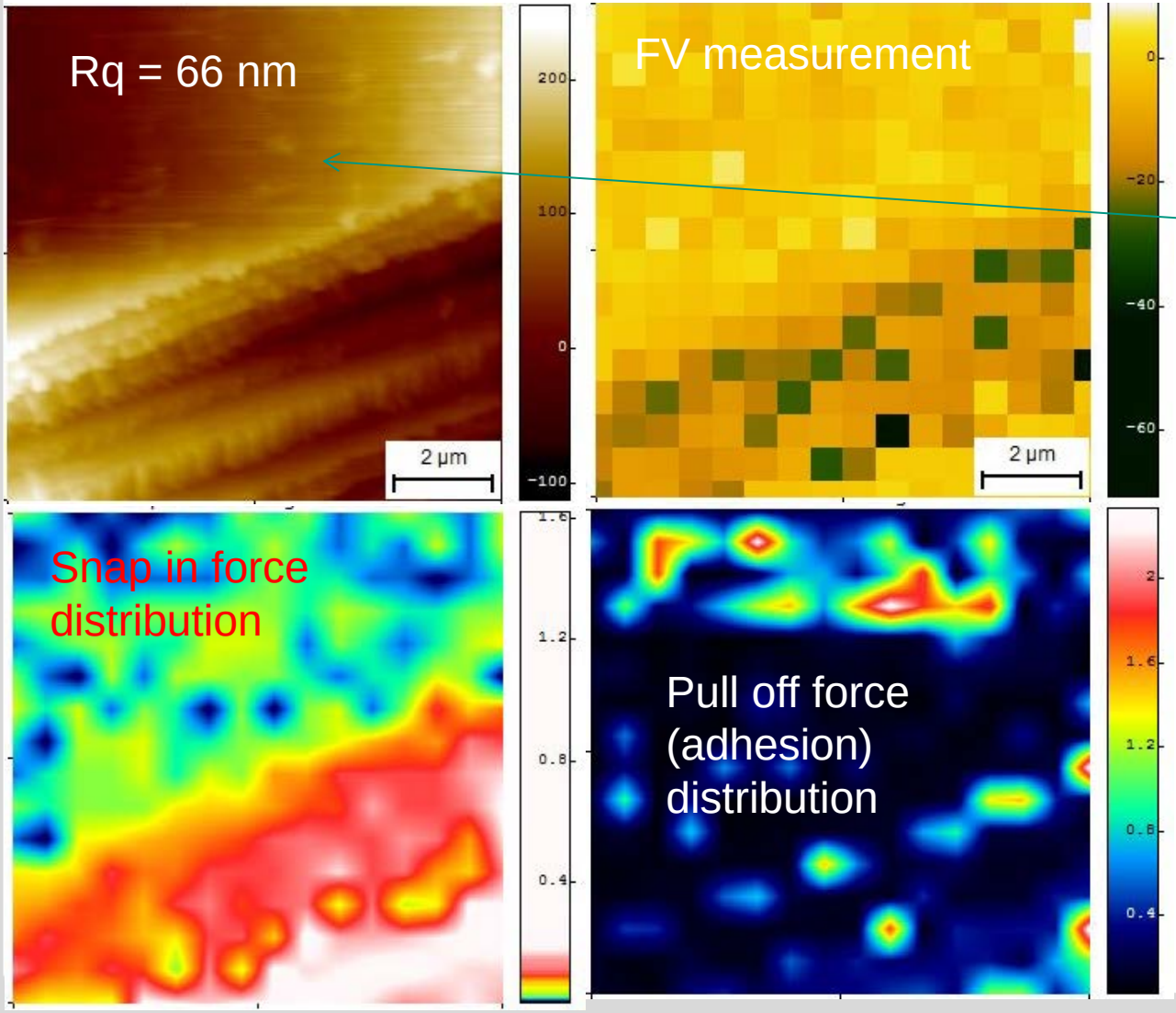


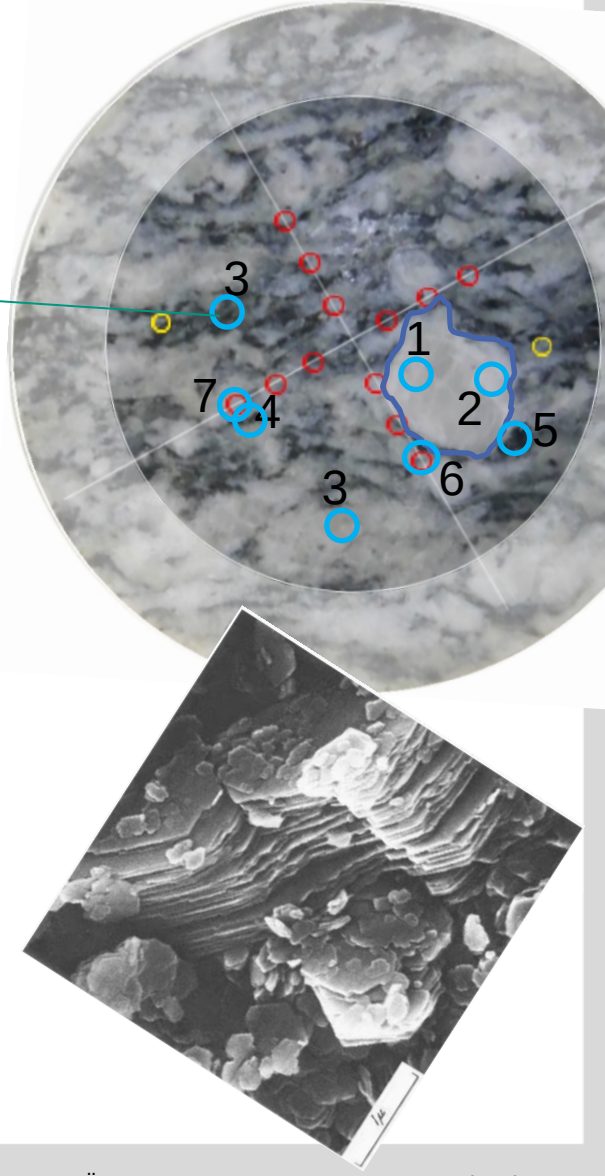






Biotite/Dark minerals (mica): 1µm colloid probe





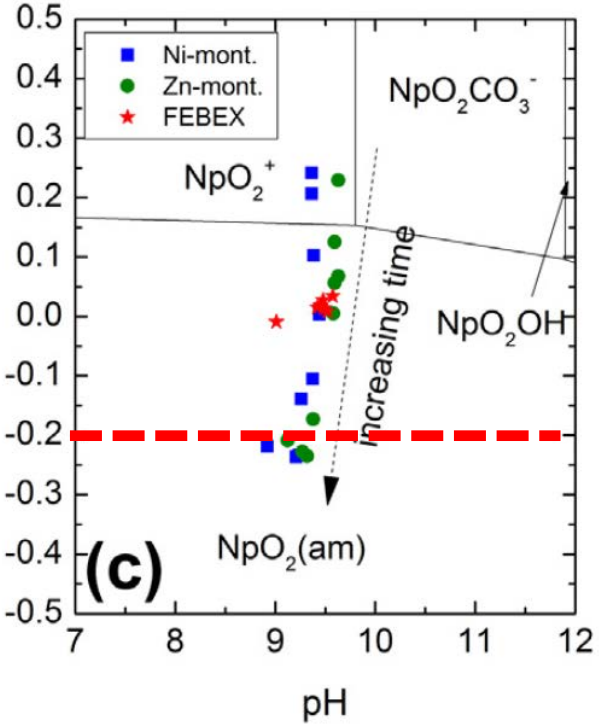
LIBD/HR-ICP-MS results: Am, Pu, U & Np recovery

	CRR Run 32	CFM Run 13-05
Peak arrival	80 min	2640 min
cons. tracer	92%	92.6%
U-233	103± 5%	15%
Np-237	82 ± 4%	4%
Am	70 %	25 %
Pu	86 ± 9 %	28%
Colloids	85-100 %	35-38%

Redox kinetics: Np(V) reduction

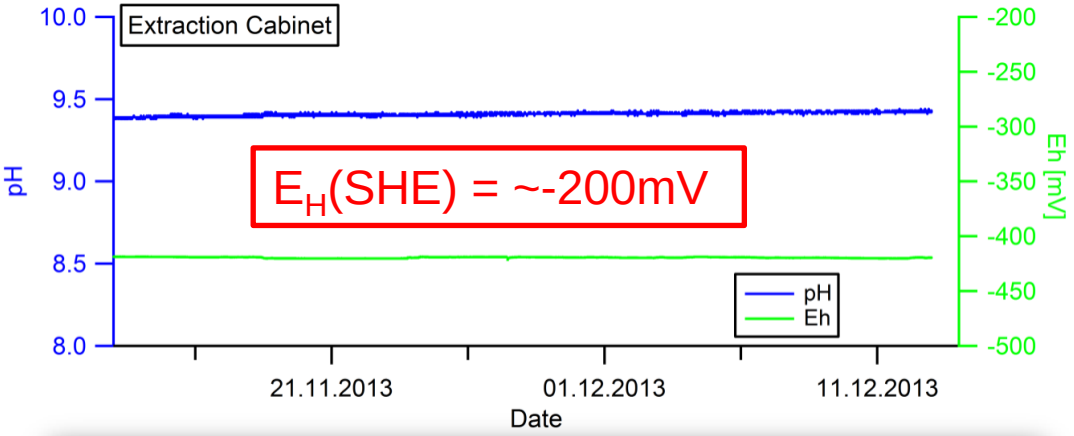
Karlsruhe Institute of Technology

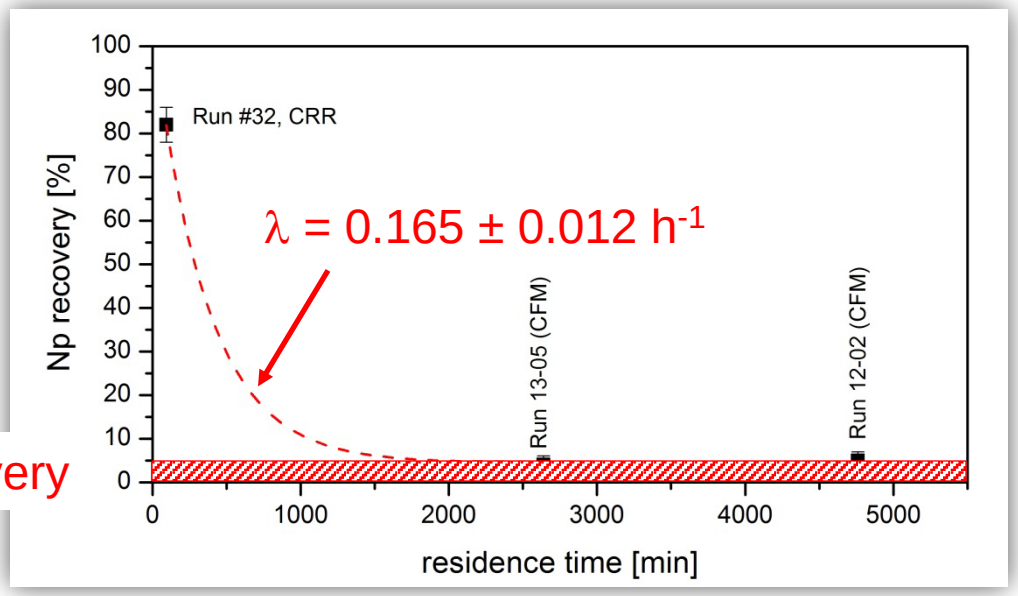
Laboratory investigations



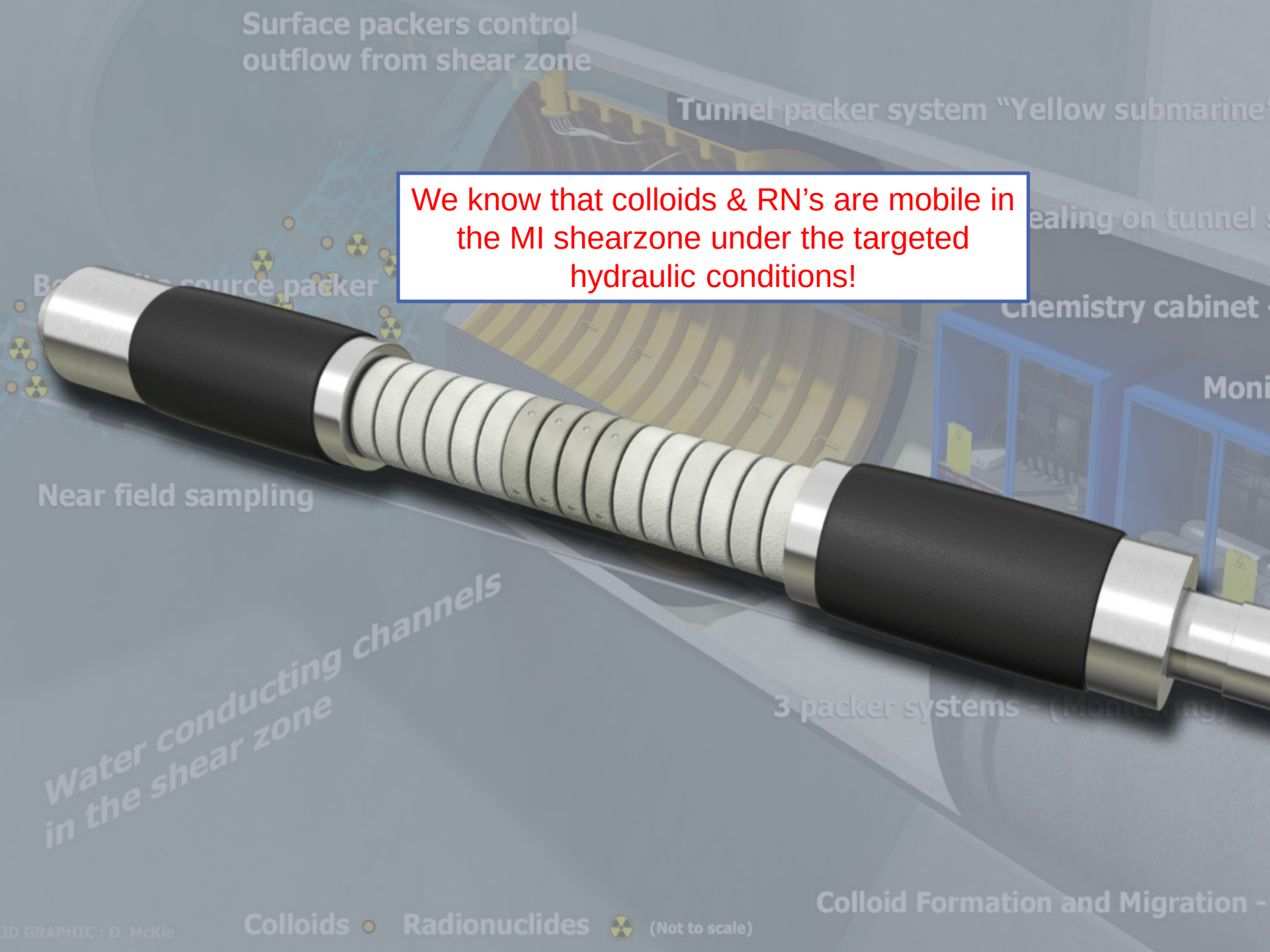
Huber et al. (2015) *GCA* 148, 426

On site measurement all year long



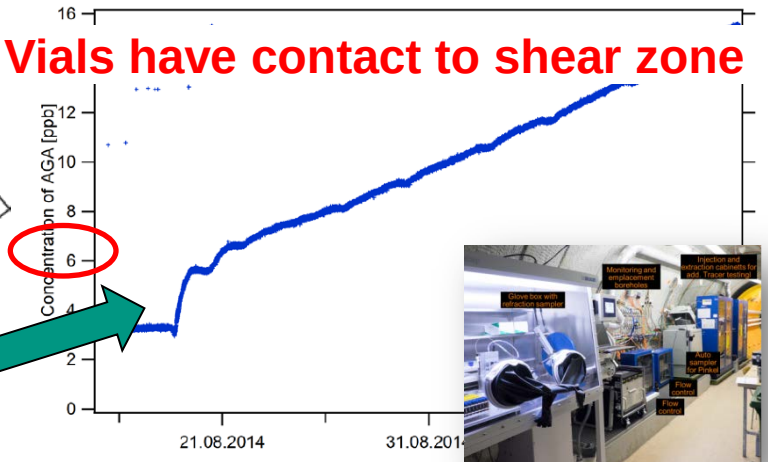


~ 5% recovery


Surface packers control outflow from shear zone
Tunnel packer system "Yellow submarine"
We know that colloids & RN's are mobile in the MI shearzone under the targeted hydraulic conditions!
Chemistry cabinet
Near field sampling
Water conducting channels in the shear zone
3 packer systems - (Monitoring)
Colloid Formation and Migration -
Colloids
Radionuclides
(Not to scale)
3D GRAPHIC : D. McKie

CFM Long-Term In situ Test (LIT)

start-up May 2014 (at GTS)



Near-field water chemistry:

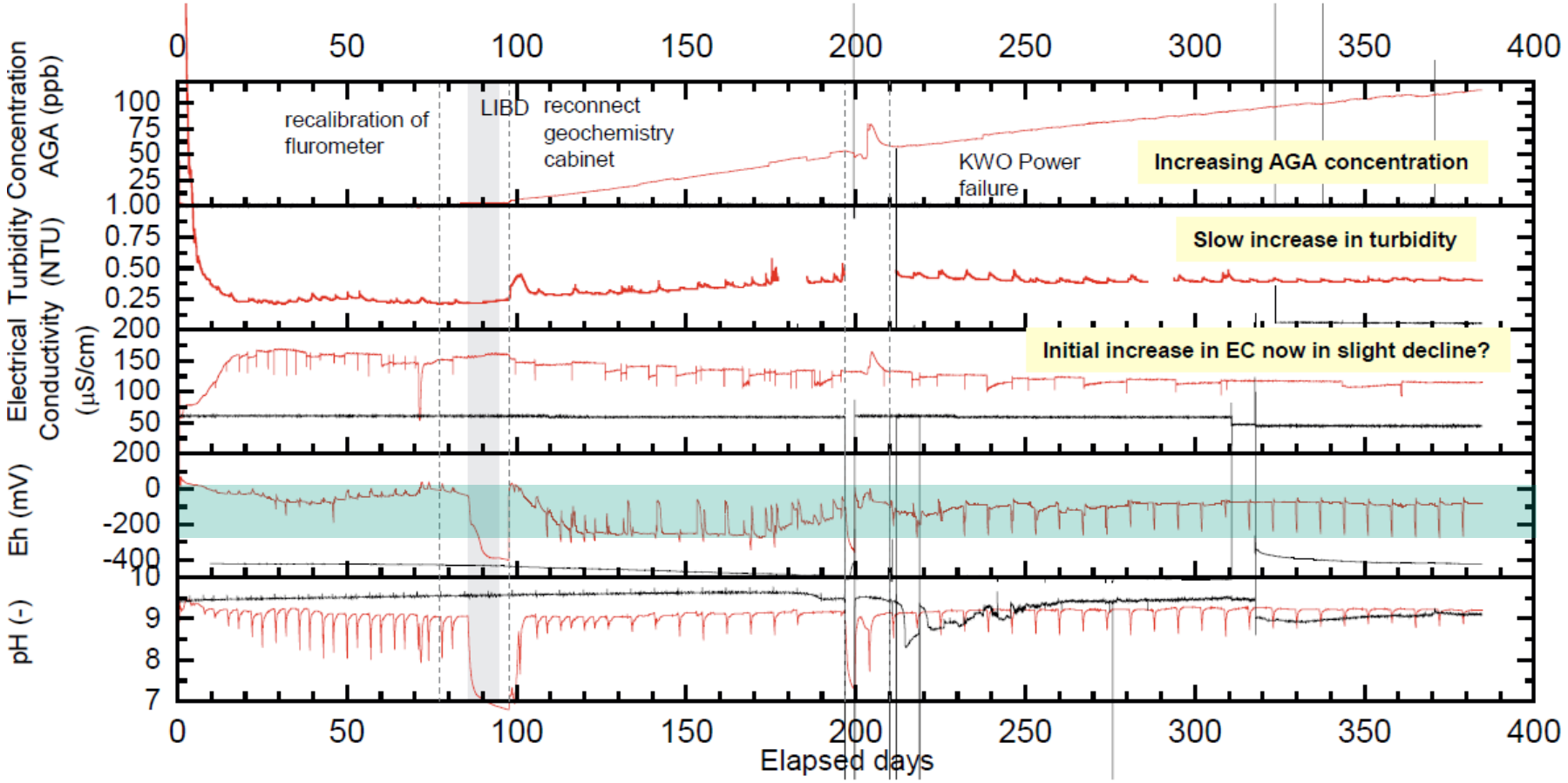
pH: 9.6 => 9.0

spec. cond.: 60 => 170µS/cm

$Eh_{(SHE)}$: -220mV => +170mV

16 glass vials filled with **^{45}Ca, ^{75}Se, ^{99}Tc, ^{137}Cs, ^{233}U, ^{241}Am, ^{242}Pu, ^{237}Np**, **Amino-G** and **synthetic Ni- montmorillonite** slurry emplaced.

Monitoring LIT

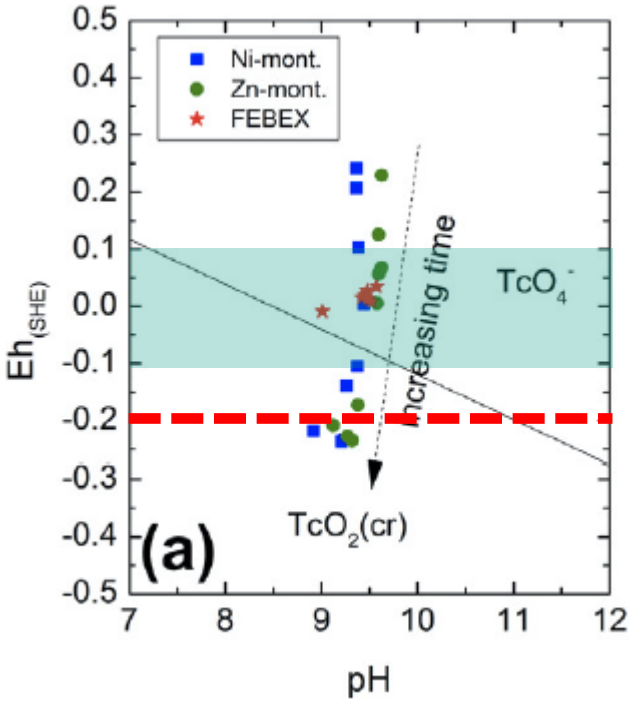


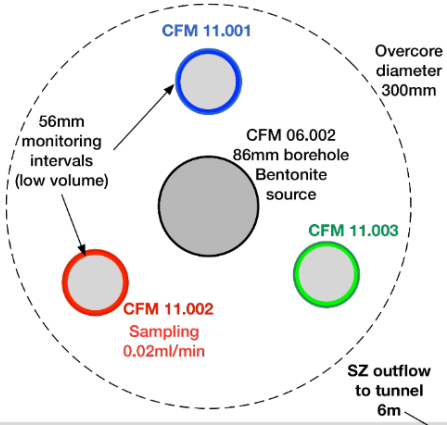
Vicinity of bentonite block extraction: „buffer equilibrated water“

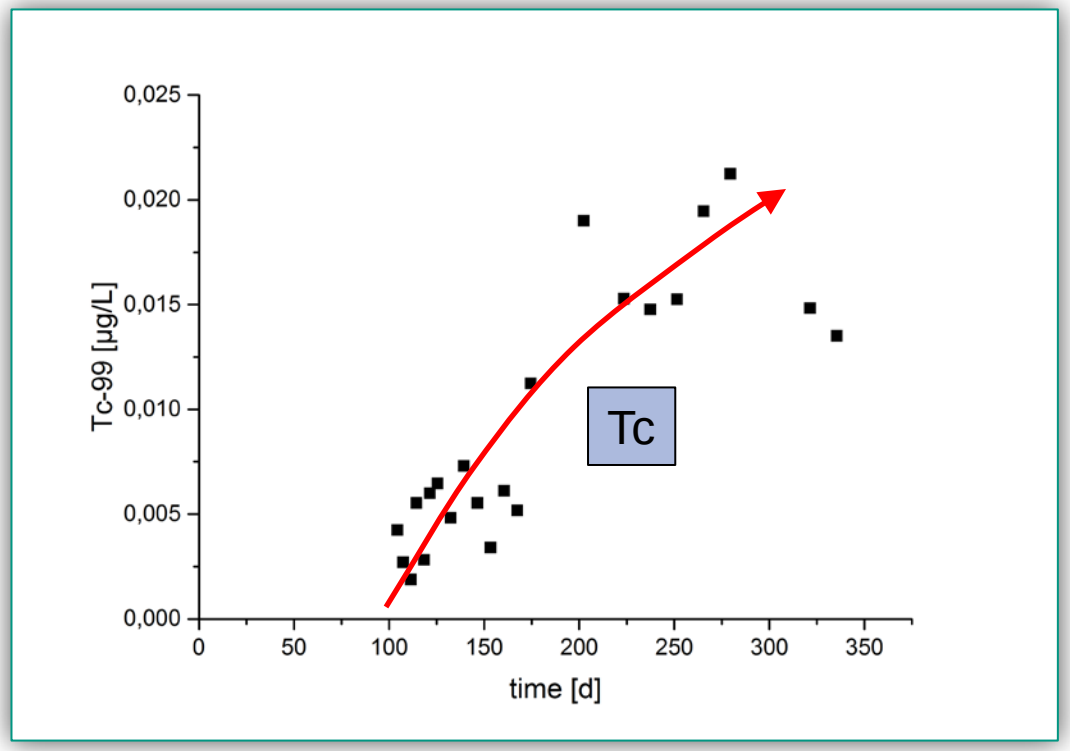
E_H(SHE) = ~-100mV to ~ +100mV; pH ~9.0

Technetium speciation & LIT observation

Huber et al. (2015) *GCA* 148, 426

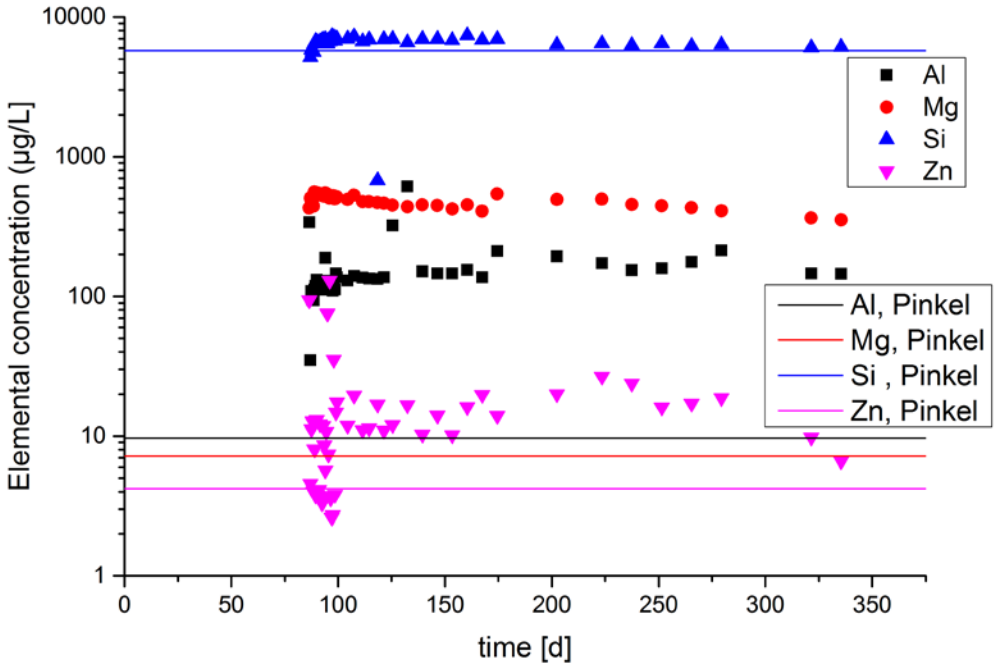






ICP-MS measurements

- Are there hints for increased colloidal release?
- Bentonite composition:
  - 90 % Febex bentonite
    - Al (10.1 %), Si (29.1 %), Mg (3.4 %), Fe (3.6 %)
  - 10 % Zn- montmorillonite
    - Zn (6.8 %), Al (11.8 %), Si (29.8 %)



[Al], [Mg], [Zn] increased

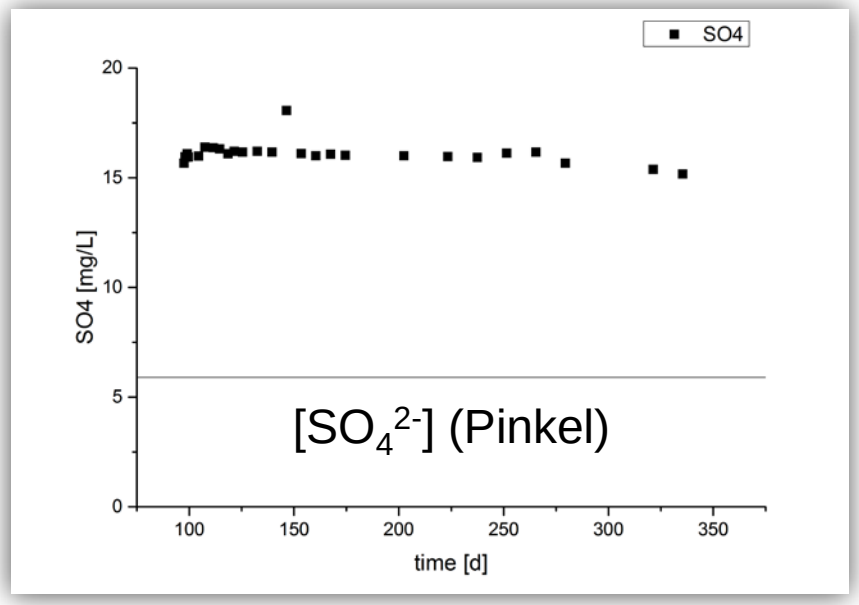
~ 1.5-3 mg/L colloids (Zn-values)

Assumption: all Al is from bentonite colloids

~ 1-2 mg/L colloids (Al-values)

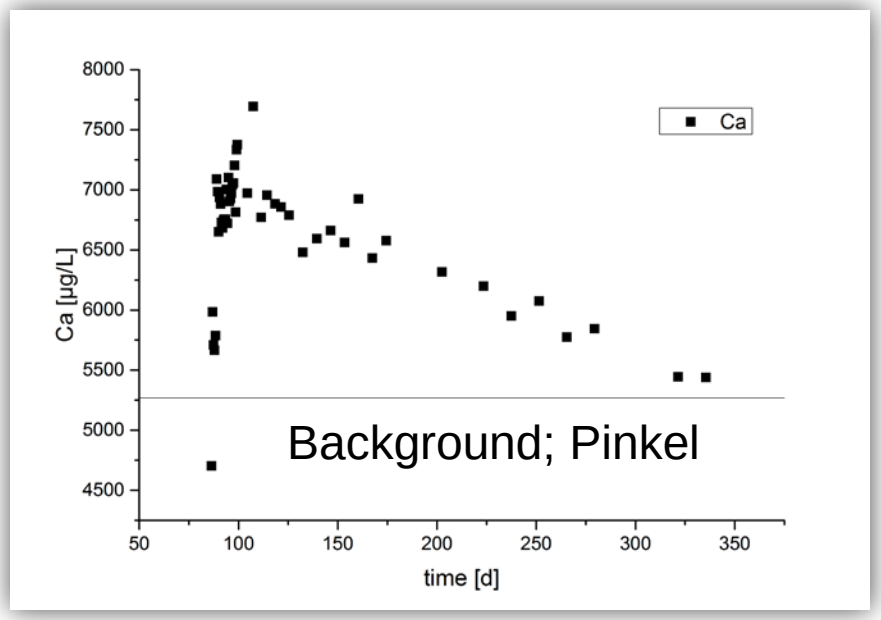
Additional Mg-source?

Contact water analysis – SO_4^{2-} & Ca^{2+}



[Ca^{2+}] evolution not in line with [SO_4^{2-}]

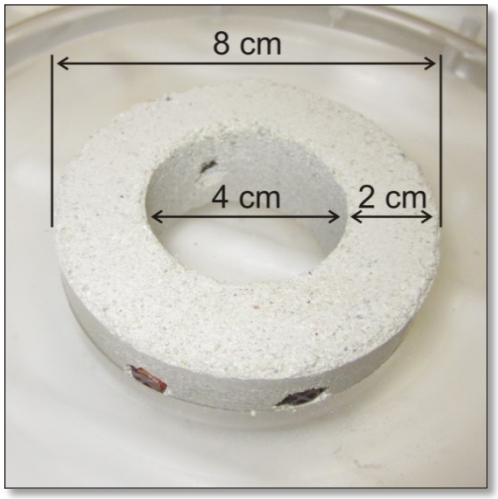
[Ca^{2+}] reduced due to cation exchange



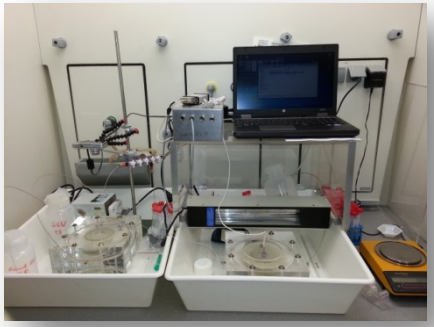
Artificial fracture cell - Bentonite sample

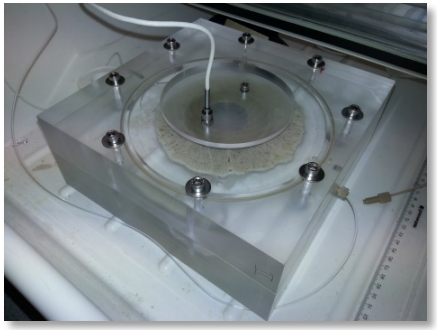
Erosion experiments at KIT-INE are focussed on natural groundwater systems

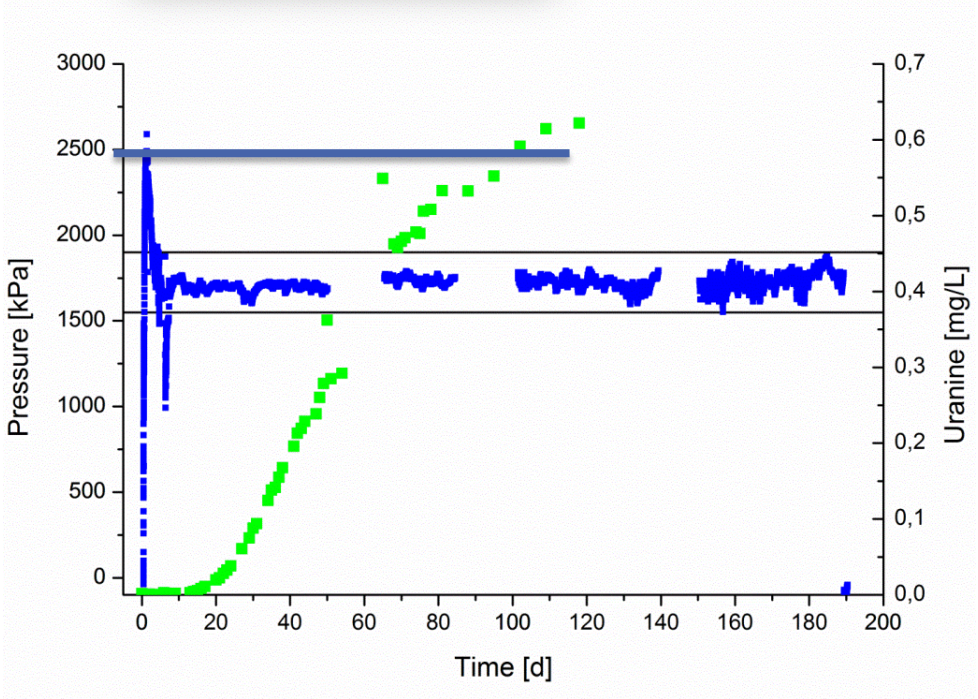
- Natural compacted Febex bentonite
  - 92% montmorillonite
  - 2% quartz
  - 2% plagioclase
- 1.65 Mg/m^3 dry density
- 98 mL sample volume
- Erosion takes place on a ring of 1mm height around the sample which is contacted with the water bearing fracture (initial contact area: 2.6 · 10^{-4} m^2)
- Experiments are performed without presaturation



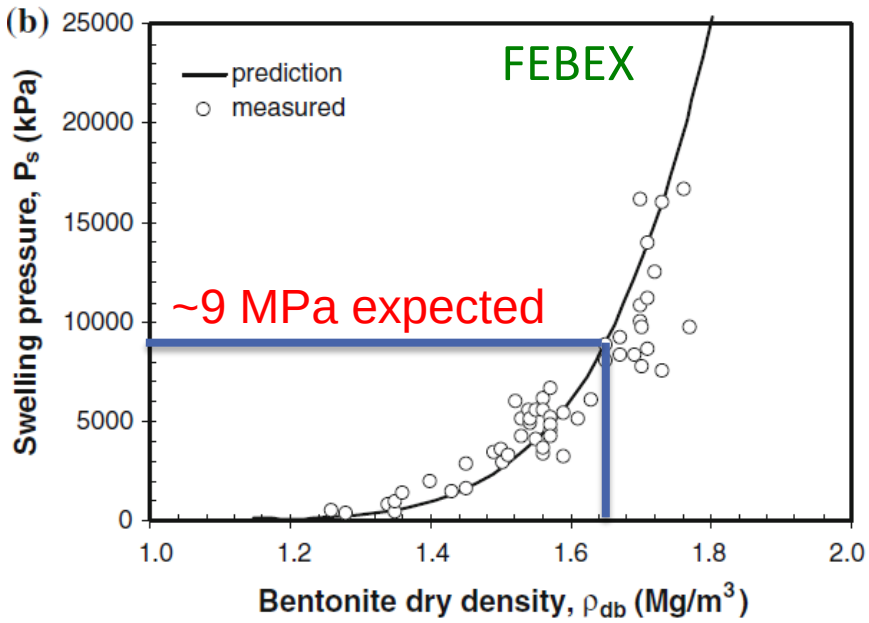
Artificial fracture set-up - Swelling pressure and fluorescence measurements



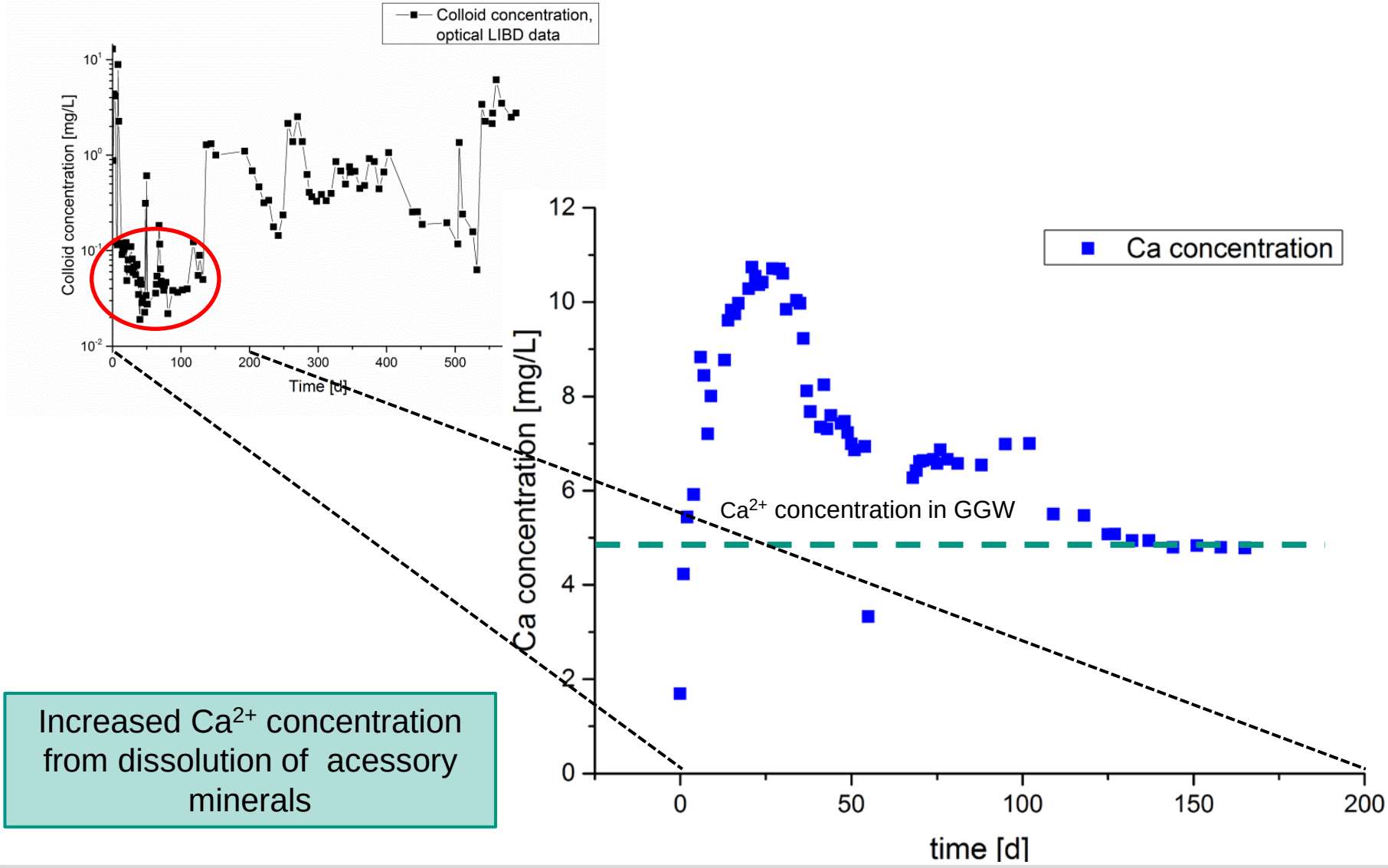




Agus & Schanz (2008) *Acta Geotechnica* 3:125–137

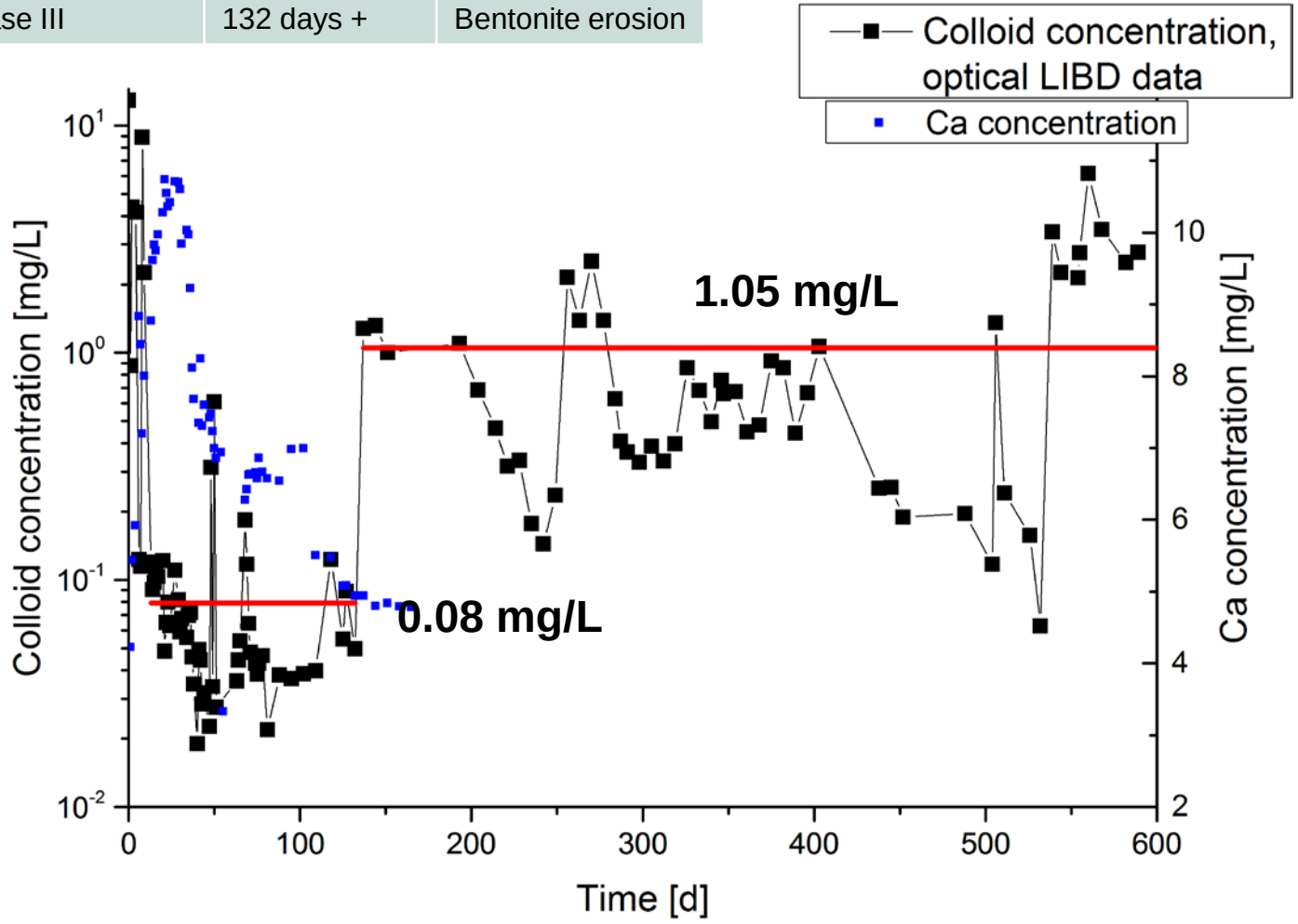


Artificial fracture set-up - Calcium concentration

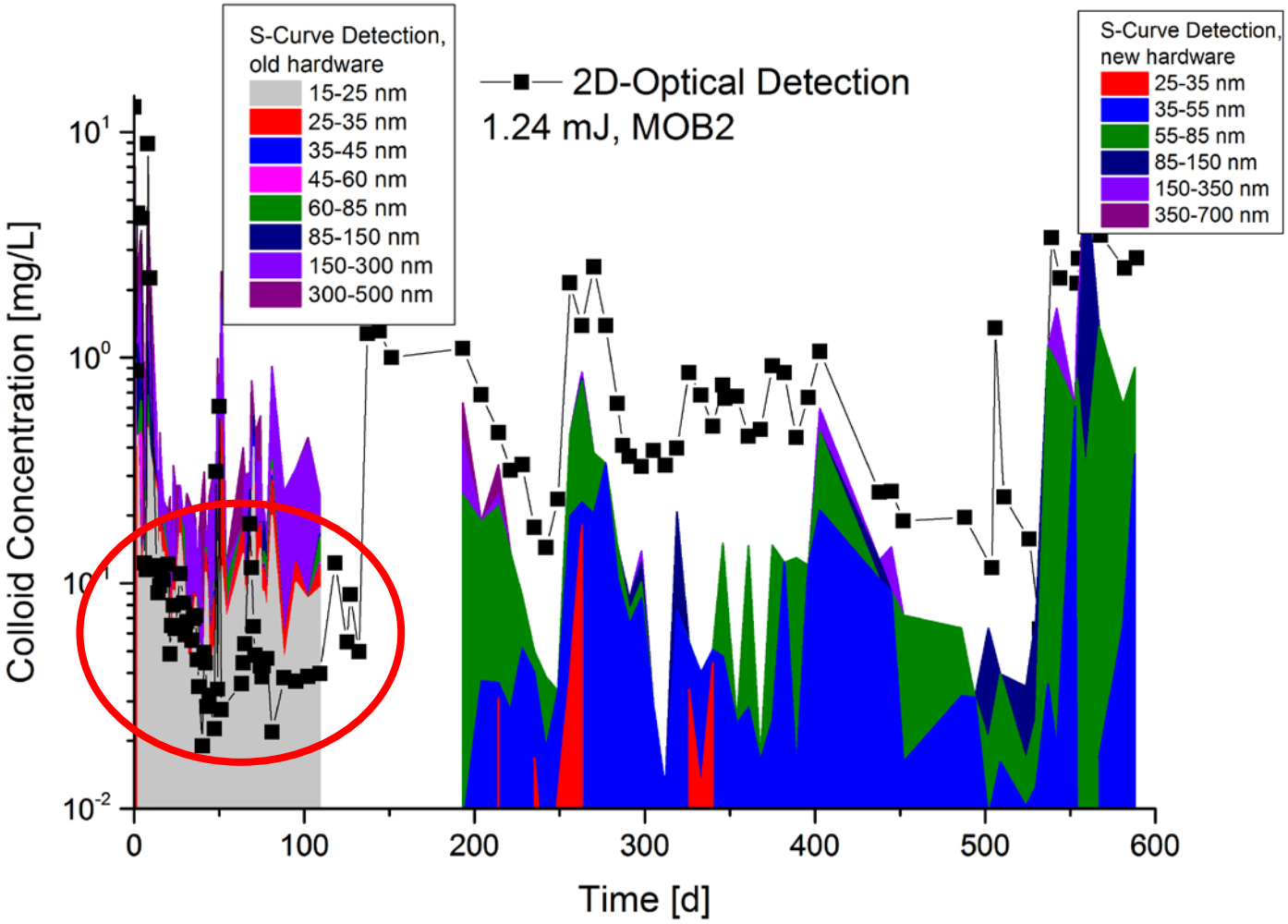


Increased Ca^{2+} concentration from dissolution of acessory minerals

Experiment phase	Timespan	Process
Phase I	0 – 12 days	Washing
Phase II	13 – 132 days	Dissolution
Phase III	132 days +	Bentonite erosion



Artificial fracture set-up - Colloid release

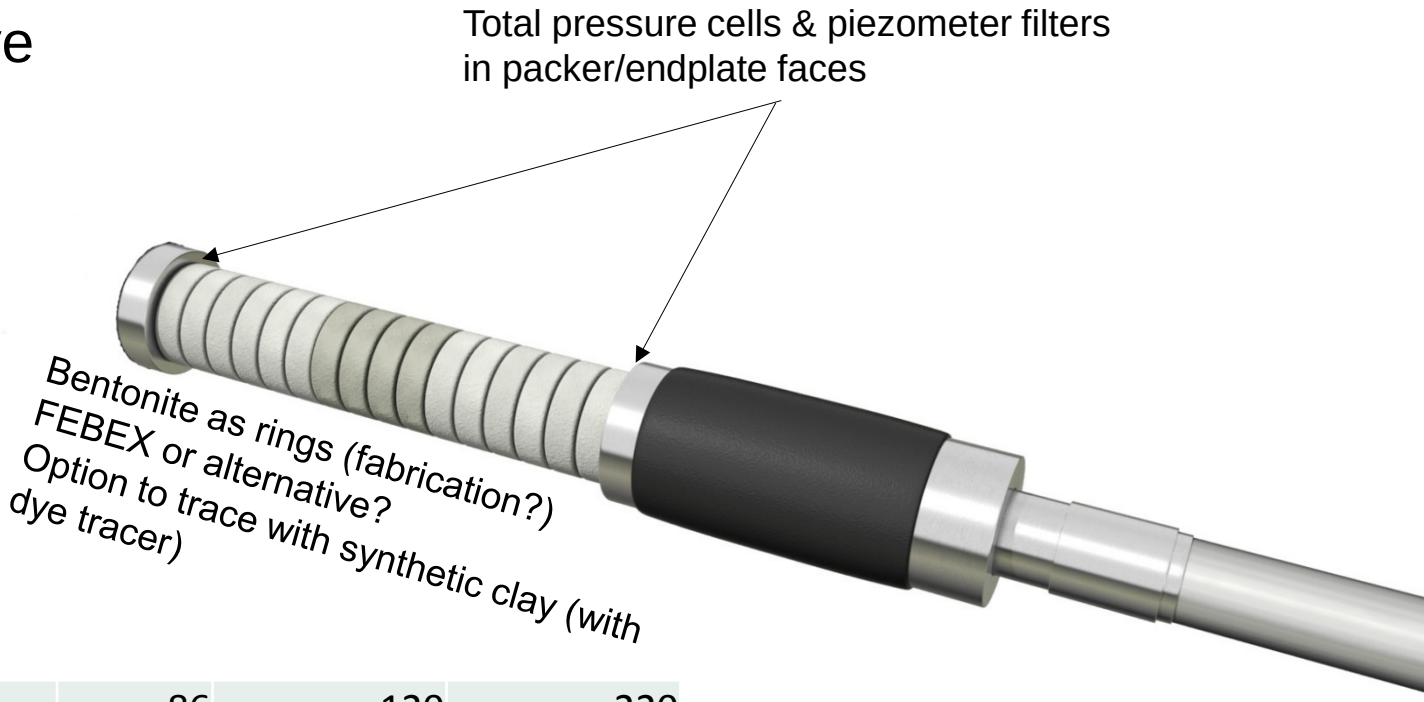


Artificial fracture set-up - Colloid release rates

- 36 mg bentonite colloids have been released from the artificial fracture set-up during 600 days
  - **0.7 mg** released in dissolution phase
  - **35.3 mg** released in erosion phase
- Colloid release rates are calculated as a function of the initial contact area between bentonite sample and groundwate
- Contact area
  - Sample diameter: 80 mm
  - Fracture height: 1 mm
  - **$2.6 \cdot 10^{-4}$ m^2**
  - Dissolution Phase: **$R_D = 8.3$ g/(a*m^2)**
  - Bentonite Erosion Phase: **$R_{BE} = 109.9$ g/(a*m^2)**

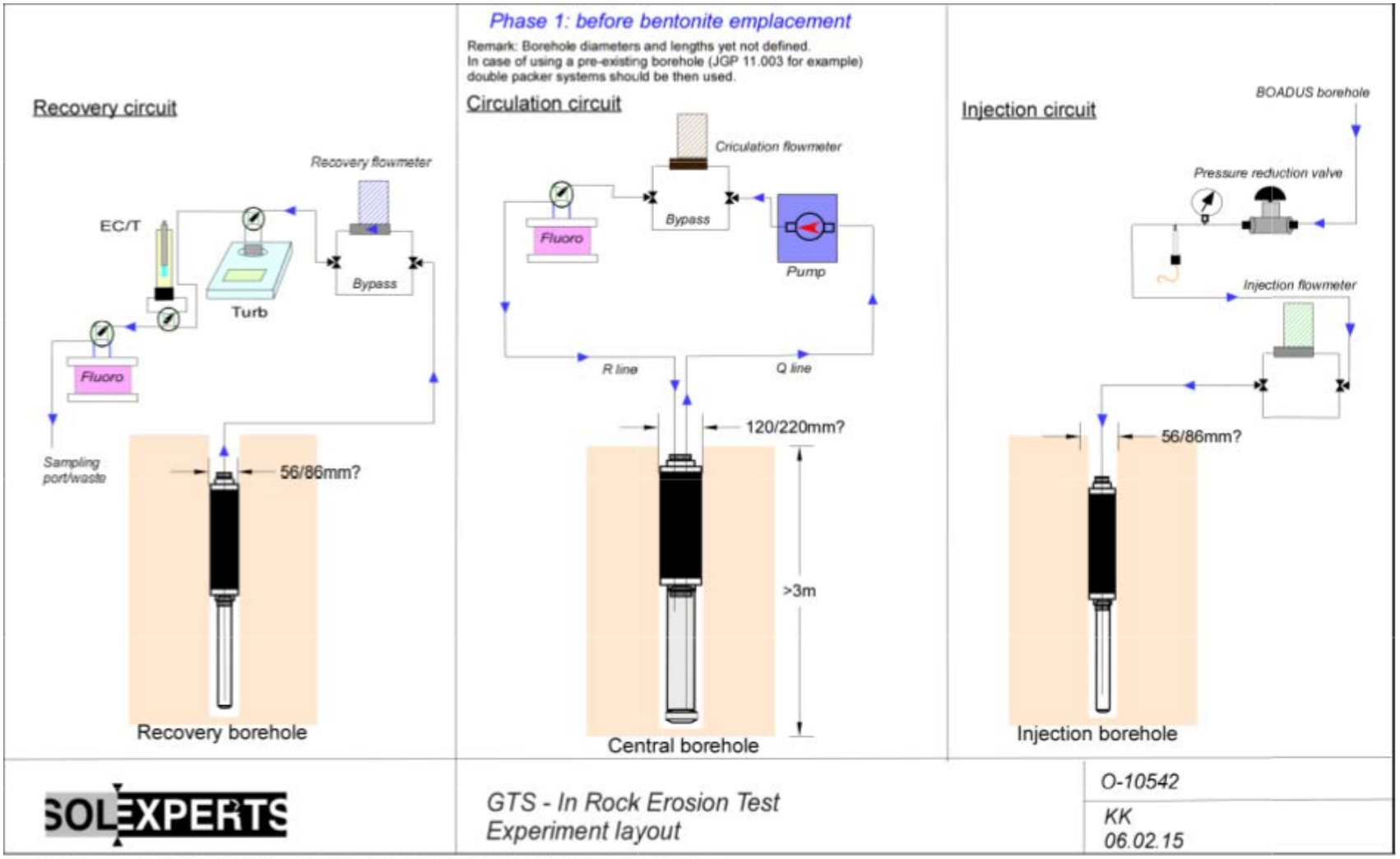
First concept: Bentonite source packer layout

- Similar to LIT but:
  - Single packer system
  - Larger diameter? 120, 220mm
  - No sleeve



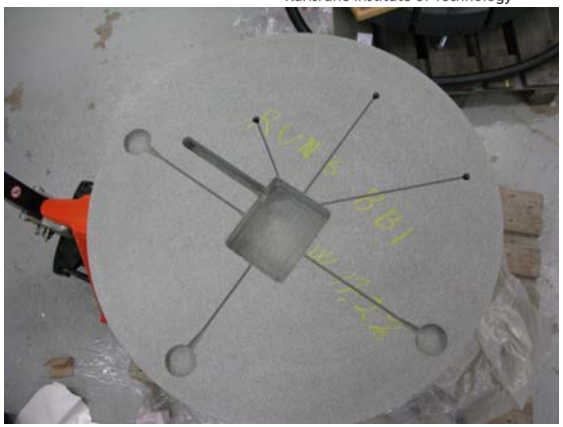
Borehole diameter (mm)	86	120	220
Effect density (g/cm^3)	1.50	1.56	1.60
Swelling Pressure (MPa)	2.94	4.34	5.96
Assumes 1.5mm gap and 43mm inner mandrel			

In-rock erosion test (i-BET): Phase 1

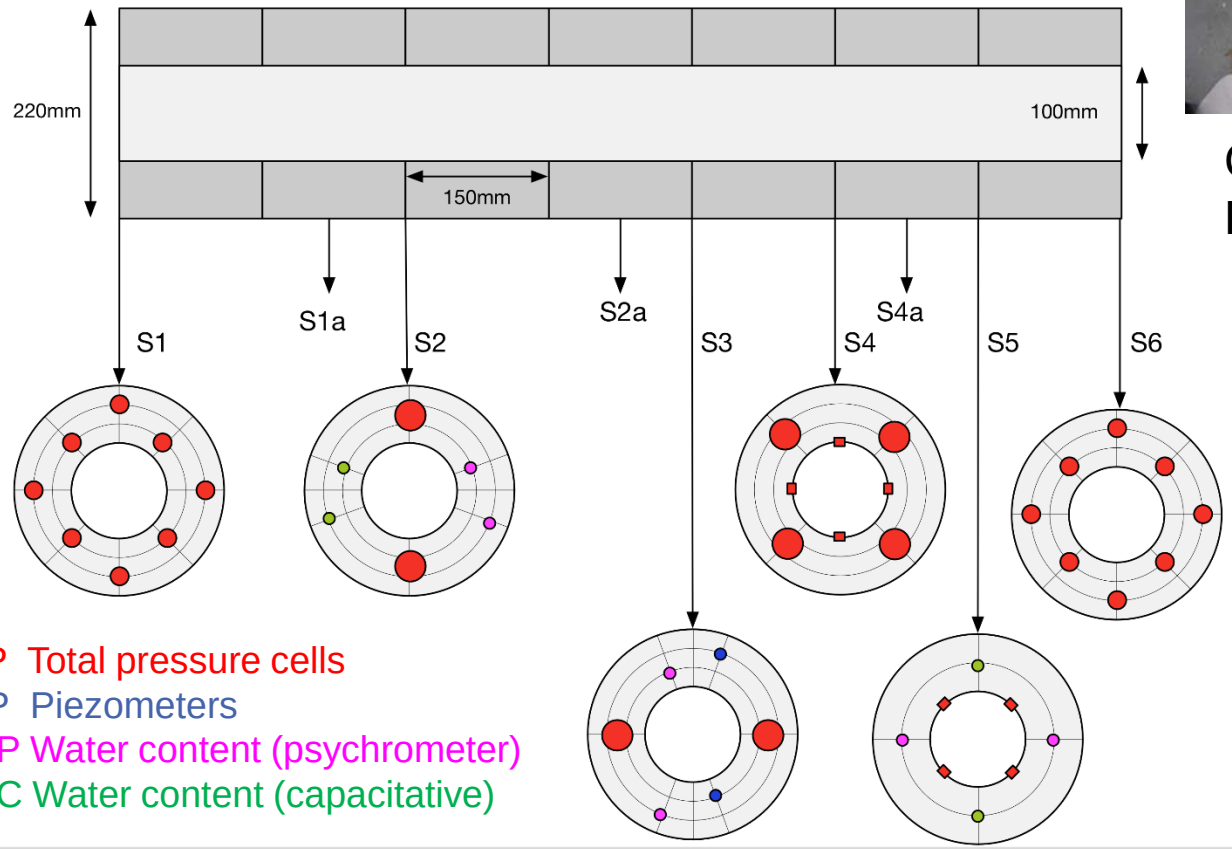


Revised concept: Fabrication/Instrumentation

Proposed instrumentation scheme Posiva/B+Tech
Alternative fibre optic and pressure-film total pressure measurements under investigation.
High density (ρ_{dry} = 1.81 g/cm$^{3)}$ MX-80. Cut from pre-compacted blocks and engineered with clots for instrumentation



CFM Instrumentation, Pintado (2015)



TP Total pressure cells
PP Piezometers
WP Water content (psychrometer)
WC Water content (capacitative)

Karlsruhe Institute of Technology

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- KIT-INE Grimsel Test Site entrance fee and CFM participation (**KOLLORADO-2, KOLLORADO-e** project) funded by BMWi/PtKA
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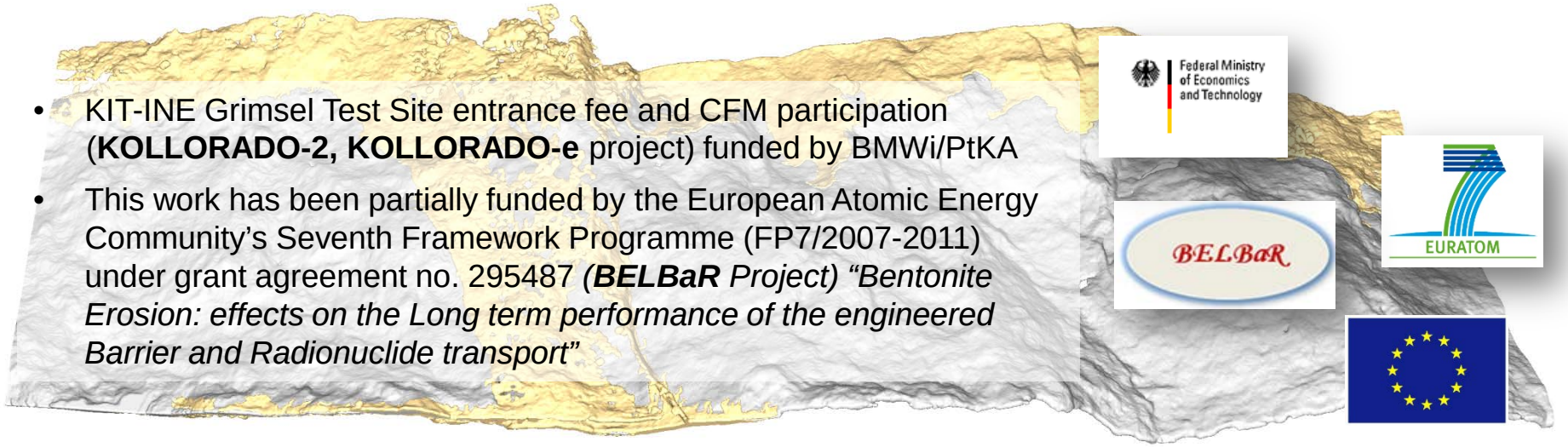


thank you for your attention