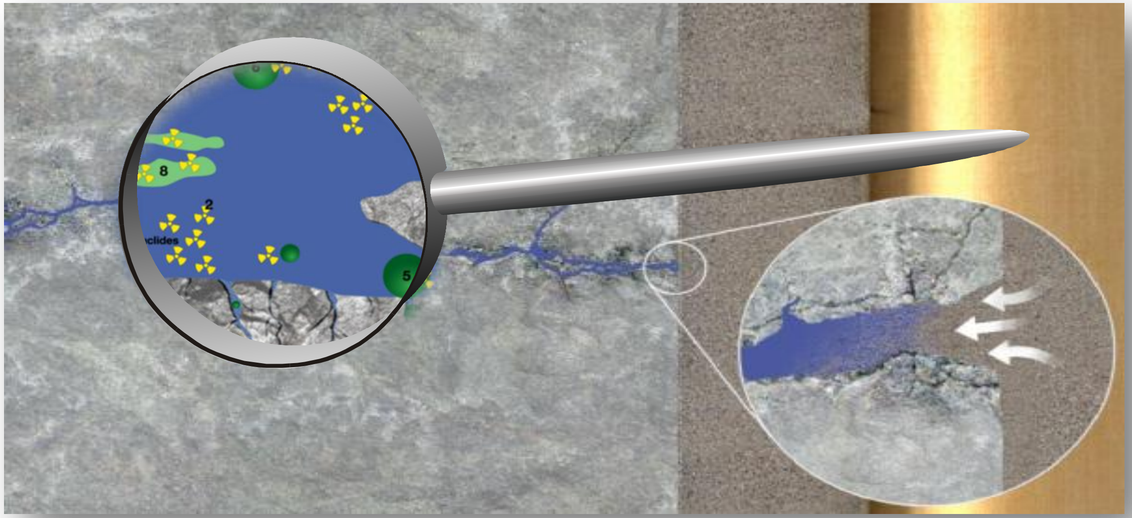
INE contribution to CP BELBaR

Thorsten Schäfer

Institute für Nukleare Entsorgung (INE)



Person months: WP distribution

		Work Effort (Person months)						
		Sum						
No.	Partner	1	2	3	4	5	6	
4	KIT-INE	**1**	**6**	**14**	**7**	**8**	**0**	
	SUM:	1	6	14	7	8	0	36.0

Personell involved:

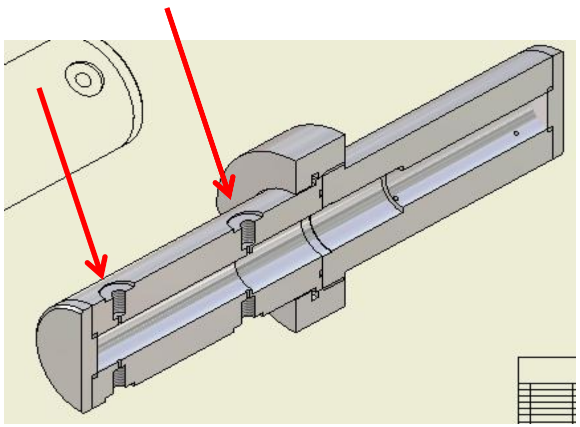
WP 1: <u>Thorsten Schäfer</u>
WP 2: <u>Muriel Bouby</u>, Patrick Höss (Postdoc), Wolfgang Hauser
WP 3: <u>Gopala Darbha (Postdoc)</u>, Eike Stage (PhD), Muriel Bouby, Florian Huber (Postdoc)
WP 4: <u>Muriel Bouby,</u> Eike Stage (PhD), Karin Knapp Norrfors (PhD, KTH)
WP 5: <u>Florian Huber</u> (Postdoc)

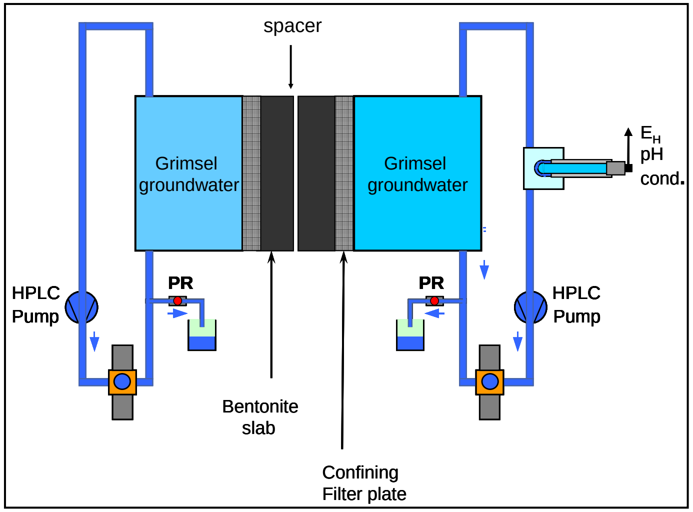
WP2: Erosion (6 PM's)

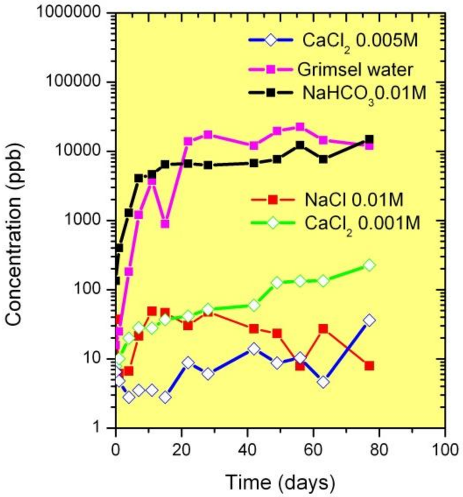
- **Objectives: …mechanisms of erosion ….quantify the (maximum) extent ….erosion under different physico-chemical conditions.**

KIT-INE contribution twofold:

1. Colloid generation experiments with **compacted bentonite (FEBEX or MX80) having different Na-/Ca-ratios through cation exchange**, contacted or not with radionuclides of different valence states under various chemical conditions (pH, IS, cation composition, presence of organic matter) and static and/or dynamic conditions. The **effect of sand admixture on bentonite erosion is also foreseen** to be studied.
   I. Colloid formation followed by e.g. ICP-MS, PCS, LIBD, SEM/EDX or STEM/HAADF and AsFlFFF/ICP-MS.
   II. Addition of **structural labelled montmorillonite** is foreseen to reduce analytical uncertainty on erosion analysis.







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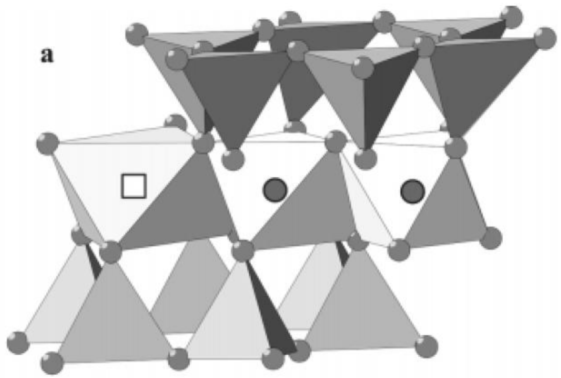
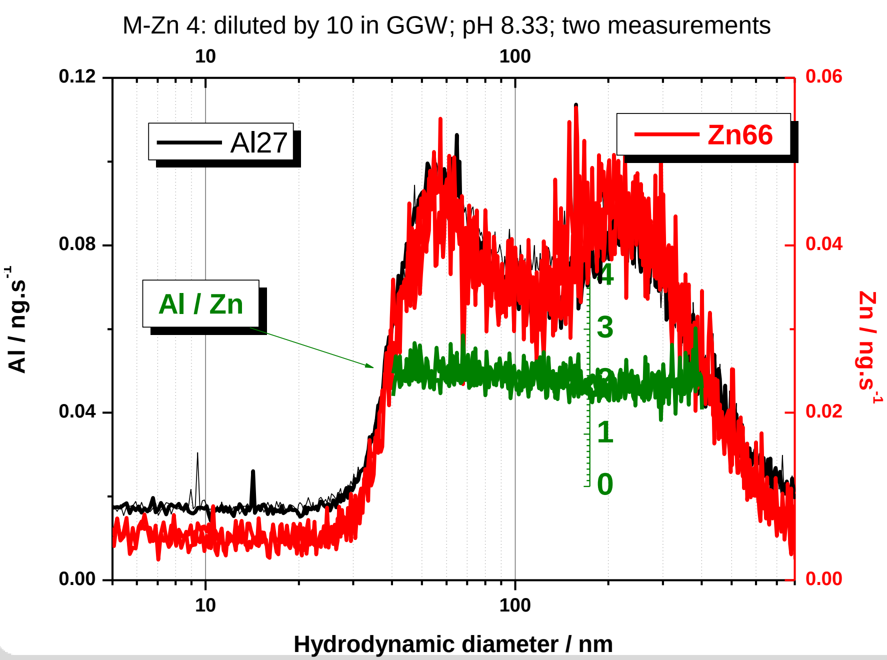
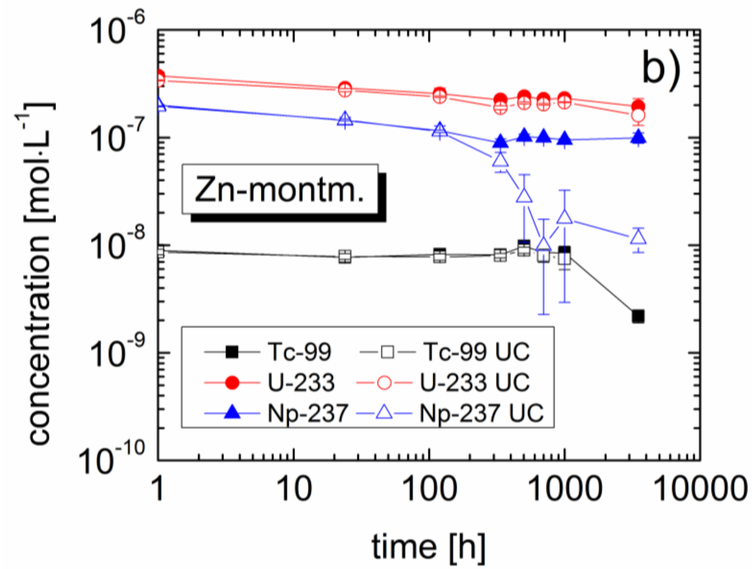
Zn- labelled montmorillonite

(collab. J. Brendlé, Univ. Mulhouse)



6.9 mass-% Zn structural bond

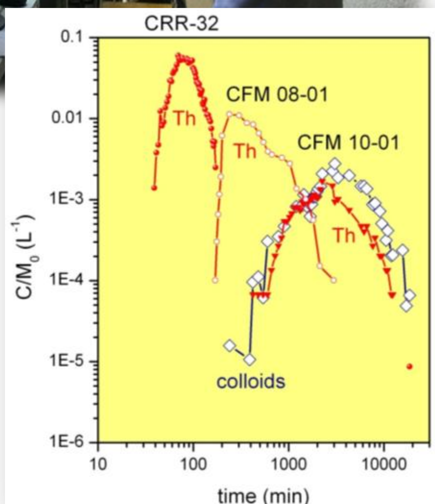


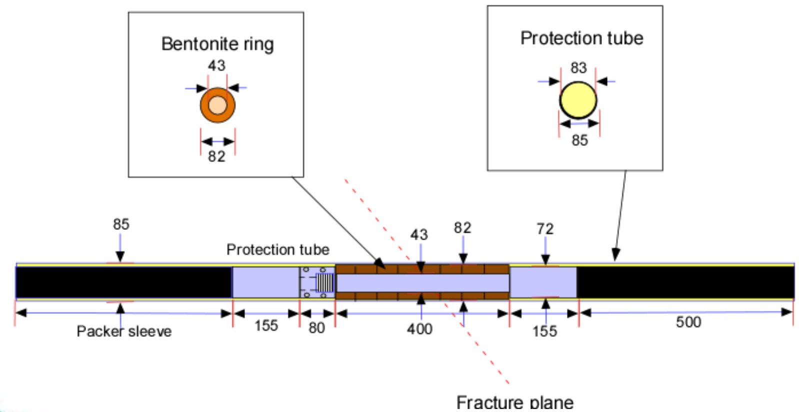


- The Al/Zn mass ratio is constant over the entire peak range at a value of ~2.
- Ca- CCC is ~ 1mM
- Very similar RN desorption kinetics to Febex bentonite

(see Huber et al. (2011) Appl. Geochem. *26*, 2226.)

Bentonite erosion under near-natural conditions (CFM)





Courtesies: SolExperts/NAGRA

- Succeeded to achieve near-natural flow velocities in MI shearzone (GTS site): ~$1.3 \cdot 10^{-5}$ m/s
- Colloids and homologues (Hf, Th, Eu, Tb) are still mobile, RN colloid migration test currently running.
- Compacted, RN- labeled bentonite emplacement early summer.

Full partners: SKB/KTH, POSIVA/HU, KIT-INE, DOE/LANL

Associated group: CIEMAT

WP2: Erosion (6 PM‘s)

2. **Post-Mortem analysis (gel layer and bentonite plug characterization) of bentonite erosion experiments** partly running over durations of approx. four years will be performed. In an initial stage the contact water will be **exchanged in consecutive steps to methanol and successively exchanged to an epoxy resin and hardened**. After cutting of the bentonite plug/gel layer using focused ion beam (FIB) or microtome characterization via laser ablation LA-ICP-MS (exchangeable cation composition), XRD (mineralogy, accessory mineral distribution) and STEM/HAADF (morphology, pore structure and mineralogy) will follow. This data will be linked to the observed bentonite erosion behaviour.

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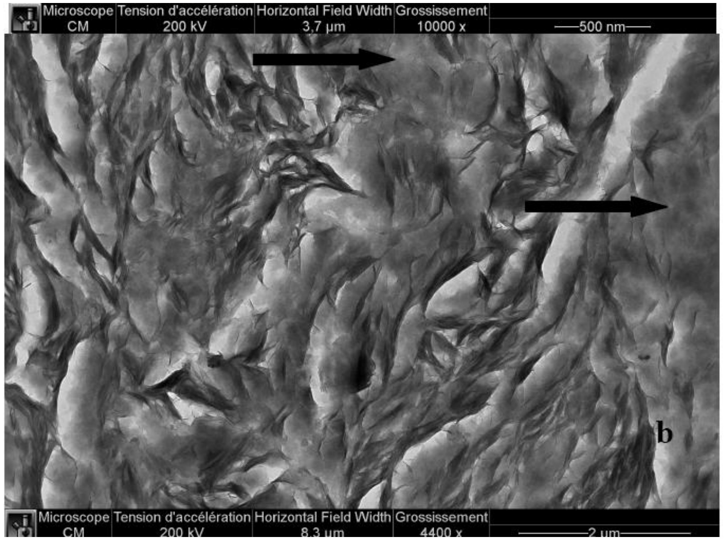
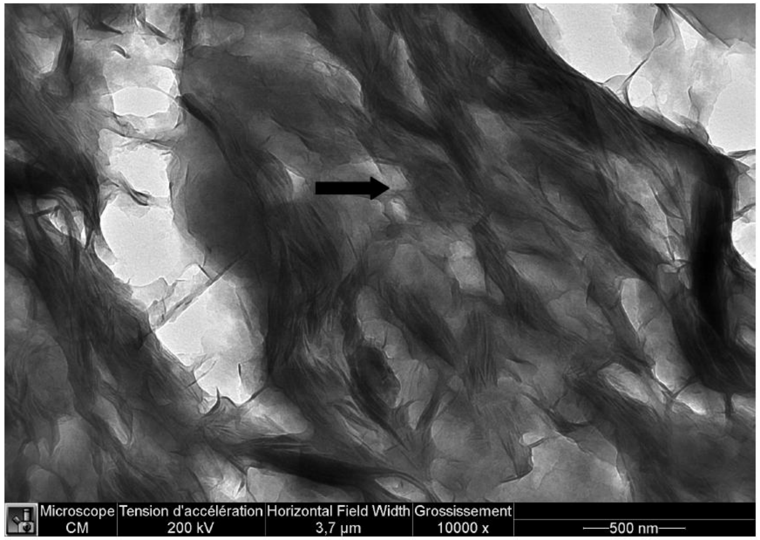
Bentonite gel layer characterization





- Erosion experiments partly running over durations of approx. four years
- Resin impregnation technique used developed by BRGM
  - Optimization of exchange processes, addition of a fluorescent dye (e.g. uranine) to resin.
- Hardened bentonite plug/gel layer will be cut using focused ion beam (FIB) or microtoming

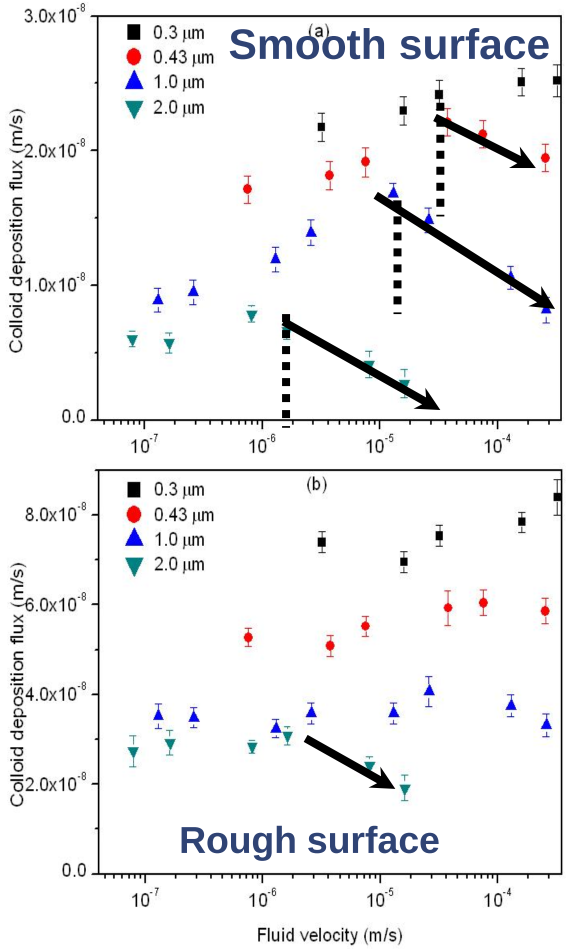
WP3: Colloid radionuclide & host rock interaction (13 PM‘s)

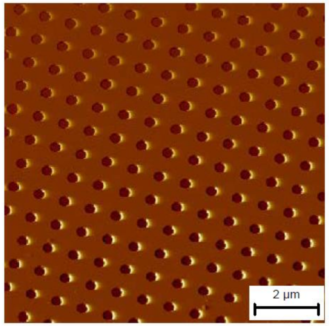
- **Objectives: Clay colloids…. could be a carrier of radionuclides…mobility f(aperture, roughness) and chemical heterogeneity.**

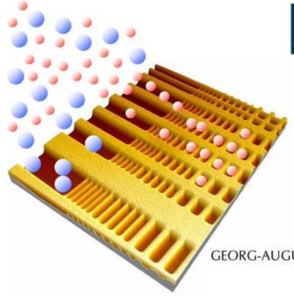
1. **KIT-INE** will focus on the **colloid attachment probability α** and especially the effect of **divalent cation (Ca) concentration** and **natural organic matter (fulvic acids)** will be systematically investigated starting from nanoscale methods using atomic **force microscopy (AFM) force distance maps (AFM)** on granite components (mineral phases) and synthetic material (Si- wafer) over batch type studies on fracture filling material to colloid migration studies in **natural over-cored fractures from e.g. the Äspö system.** Structural labeled montmorillonite colloids will be used to reduce the uncertainty in attachment factor quantification and test the attachment reversibility (K_D approach).
2. In addition, **via CT data a replica in PE of a natural core fracture** might be available within the project duration to allow directly the differentiation between charge heterogeneity and surface roughness effects contributing to colloid retention.

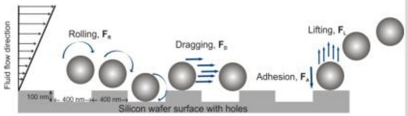
Roughness/ topography effects on Si wafer

Darbha et al. *Langmuir* (in review)

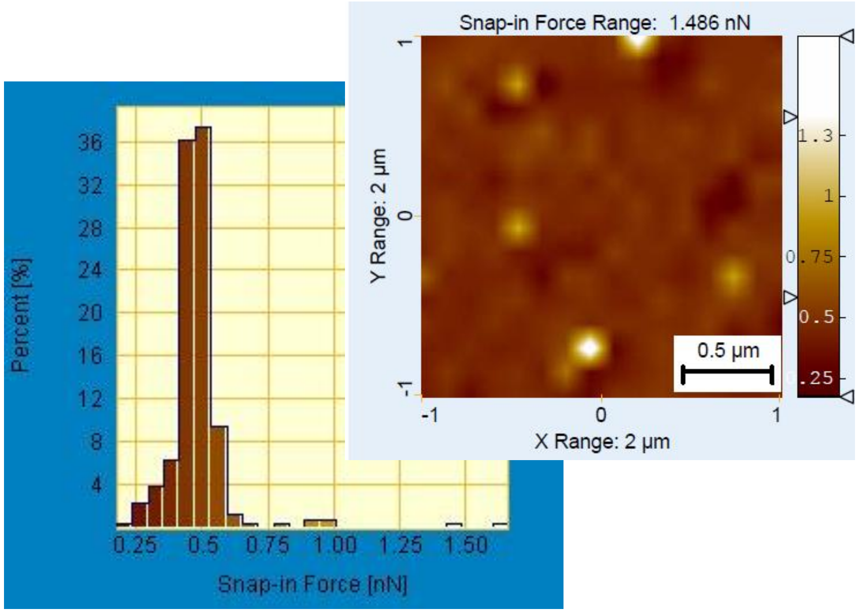






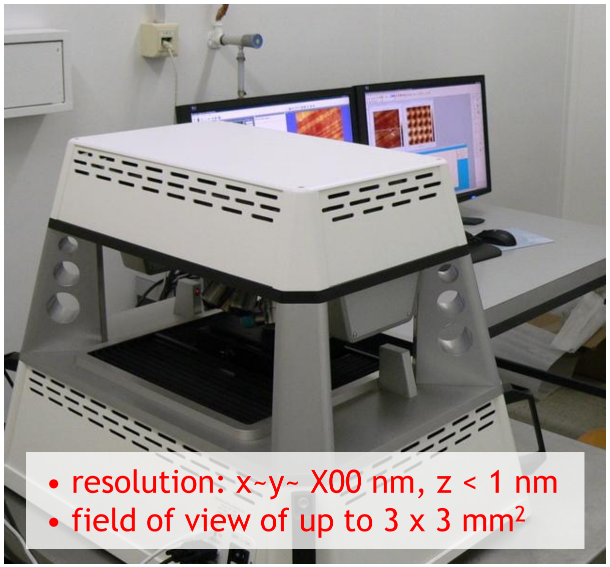


Highest snap-in force found in pits, average snap-in force on flat surface around ~0.5 nN

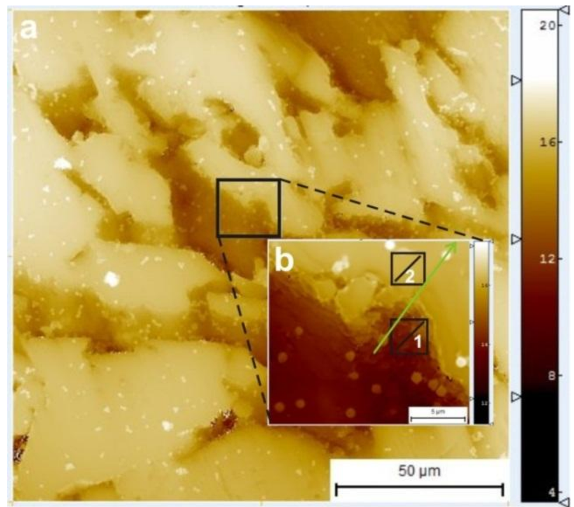


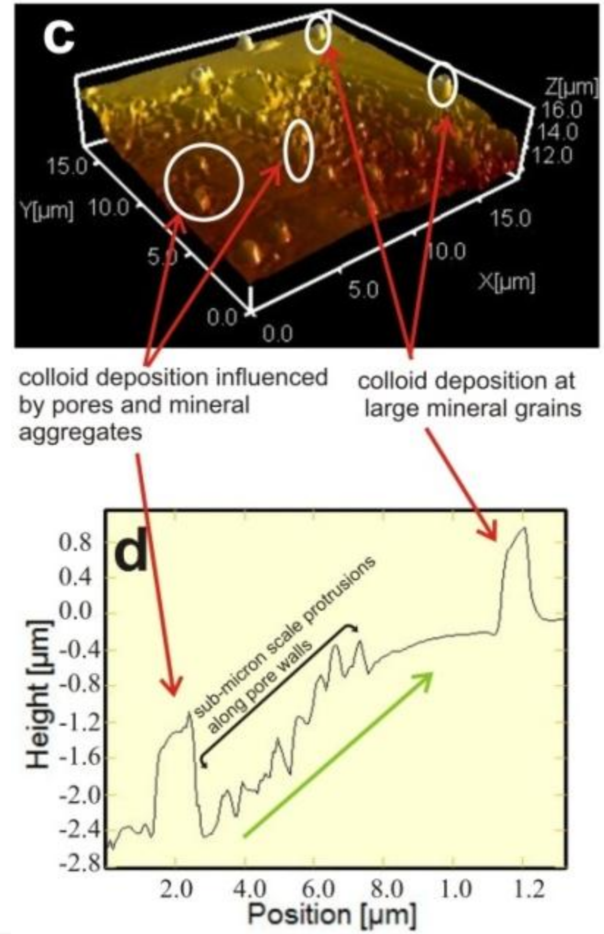
Impact of mineral aggregate surface topography

Vertical scanning interferometry (VSI)



- resolution: x~y~ X00 nm, z < 1 nm
- field of view of up to 3 x 3 mm²





Colloid sorption lies in asperities with smaller dimensions (density = 2.6 ± 0.55 µm^{-1}, size = 0.55 ± 0.18 µm, height = 0.41 ± 0.06 µm) rather than asperities with large dimensions (density = 1.2 ± 0.62 µm^{-1}, size = 1.41 ± 0.35 µm, height = 0.63 ± 0.22 µm). The absence of such protrusions on large feldspar and quartz grains leads to an enhanced applied torque (drag force) over adhesion force. This explains less colloidal retention onto their surfaces.

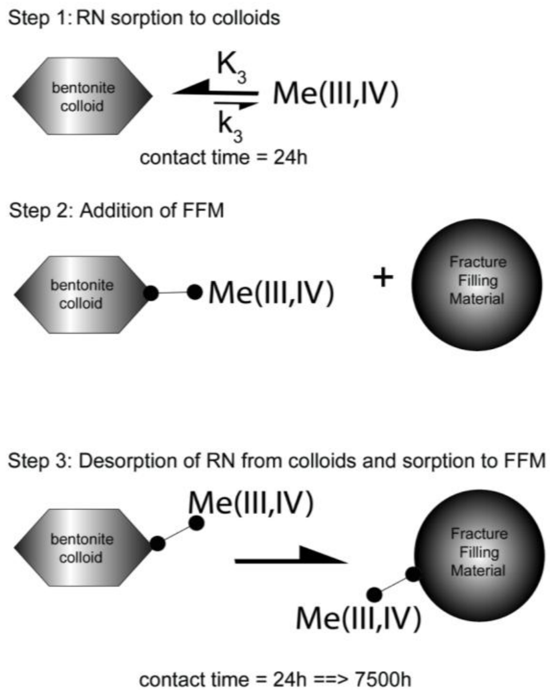
WP3: Colloid radionuclide & host rock interaction (13 PM's)

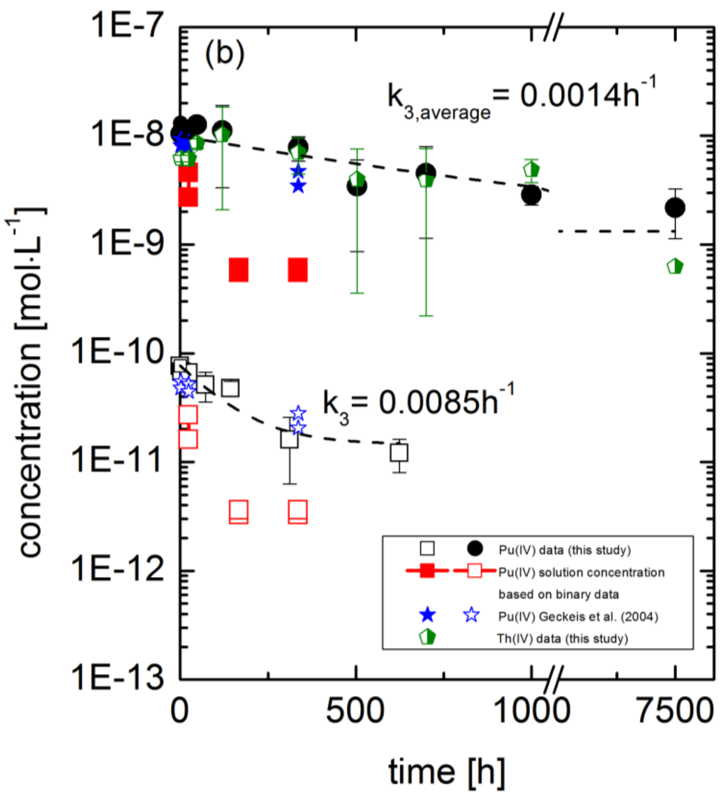
- **Objectives: Clay colloids…. could be a carrier of radionuclides…mobility f(aperture, roughness) and chemical heterogeneity.**

2. **The second activity will focus on the radionuclide bentonite sorption reversibility/ irreversibility.** The mechanistical understanding for An(IV) clay colloid interaction is still pending **(eigencolloid formation or surface precipitation on clay surface?).** In order to understand this partial "irreversible" character of the An(IV) sorption onto bentonite colloids compared to An(III) sorption a detailed investigation of the An(IV) species characterization on the bentonite clay colloids surface is needed. Characterization will include state of the art methods like **AsFlFFF/ICP-MS, STEM-HAADF and CE/ICP-MS.** In addition, **isotope exchange studies**, e.g. $^{228}Th/^{232}Th$ to retrieve information on reversibility are foreseen. The experiments will also focus on the potential **effect of bentonite colloid size on sorption capacity** and reversibility verifying the applicability of BET surface area scaling.

Pu(IV) bentonite colloid sorption reversibility in contact with FFM

Huber, Kunze, Geckeis, Schäfer (2011) *Appl. Geochem.* 26, (12), 2226-2237.

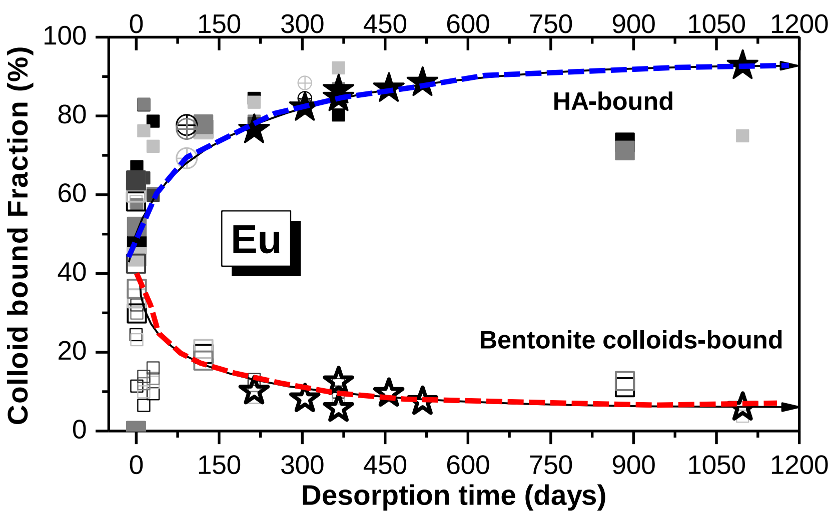


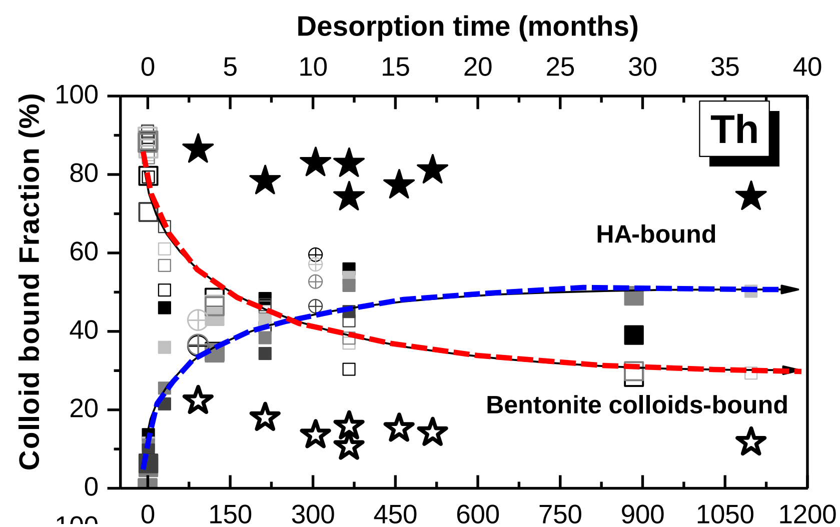


Eu(III)- versus Th(IV) bentonite colloid sorption reversibility in contact with humic substances

Bouby, Geckeis, Lützenkirchen, Mihai, Schäfer (2011) *Geochim. Cosmochim. Acta 75(13), 3866.*

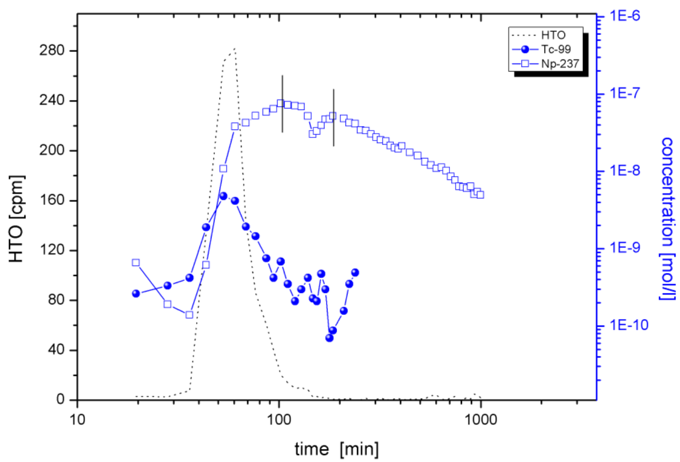
Th(IV): $4.3 \cdot 10^{-8}$ mol/L; 20 mg/L Febex bentonite colloids; 10 mg/L HA





Process understanding pending in the tetravalent actinide case!

Migration experiments: Glacial melt water



	Äspö GW	Orig. GGW	Equ. GGW core#8	Equ. GGW core#8
	09.-11.07	12.02.08	4.3.08	1.4.08
pH	7.5 ± 0.1	9.67	9.89	9.8
$E_{h(SHE)}$	~ +62mV	n.d.	~ +50mV	~ 0mV
I [$mol \cdot L^{-1}$]	0.153	0.0026	0.0041	0.0049
[Mg^{2+}]	76.4 $mg \cdot L^{-1}$	12.6 $\mu g \cdot L^{-1}$	36.3 $\mu g \cdot L^{-1}$	46.7 $\mu g \cdot L^{-1}$
[Ca^{2+}]	0.87 $g \cdot L^{-1}$	5.3 $mg \cdot L^{-1}$	9.0 $mg \cdot L^{-1}$	9.4 $mg \cdot L^{-1}$
[Na^{+}]	1.2 $g \cdot L^{-1}$	14.7 $mg \cdot L^{-1}$	50.3 $mg \cdot L^{-1}$	53.7 $mg \cdot L^{-1}$

- Quantum dots (QD) have shown to be mobile under given geochemical conditions
- For clay colloid associated tri- and tetravalent RN (Th, Pu and Am), no breakthrough observed within the experimental duration. **=> retention**
- Stop flow experiments show within three weeks an [Ca] increase to ~1mM in the porewater (matrix diffusion)
- AFM studies: Rapid colloid adsorption in the alkaline Grimsel regime only on apatite and/or in the presence of Ca(II).

WP4: Colloid stability (7 PM's)

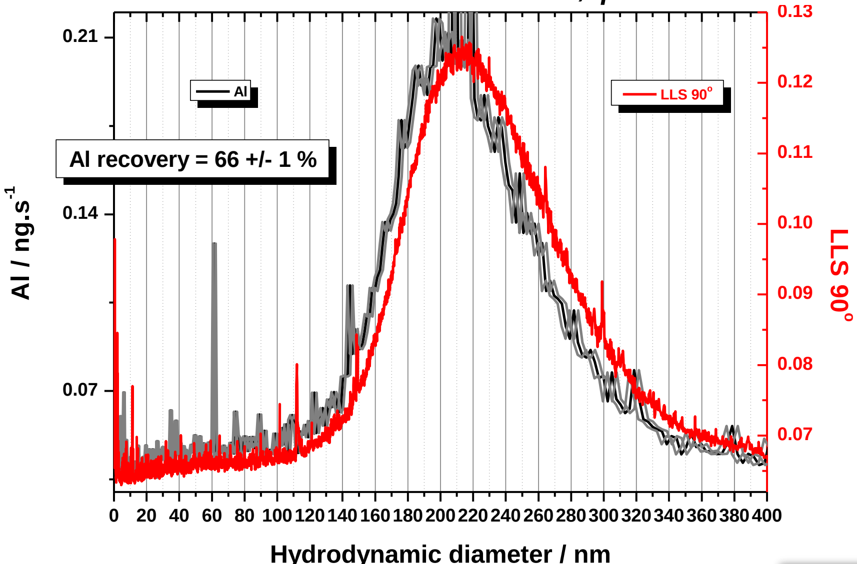
- **Objectives: Clay colloid stability…. f(I,pH)….strongly site-specific….influence of complexing agents (DOM) to reduce uncertainty.**

- **KIT-INE:** Systematic **colloid stability studies** will be performed by **KIT-INE** to investigate the **pH, ionic strength** and especially the organic matter effects on bentonite clay colloids **(MX-80 and FEBEX) stability over long time period (4 years) under glacial melt water conditions.** Measurements on the influence of DOC (Fulvic acids) on clay colloid stability (Ca- and Na-CCC) are needed to reduce the uncertainty in potential additional stabilizing effects naturally occurring. Experimental methods will include time resolved dynamic light- scattering for fast coagulation studies **(stability ratio W and critical coagulation concentration CCC) and AsFlFFF/ICP-MS for the slow coagulation rates** expected under stabilizing conditions (glacial melt water) together with laser-induced breakdown detection **(LIBD).**

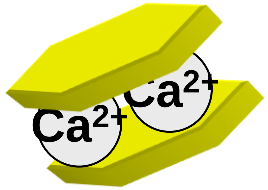
Clay colloid stability: Glacial melt water (Grimsel)

Bouby, Geckeis, Lützenkirchen, Mihai, Schäfer (2011) *Geochim. Cosmochim. Acta 75(13), 3866.*

***10 years** old FEBEX bentonite colloid solution stored in a brown PET bottle; pH now 8.0*



Ca^{2+} ion induced agglomeration



Ca-CCC = 10^{-3} M (Seher et al. 2010)

At 3.3 10^{-4} M [Ca], pH 9-10, W~ 100

➜**Slow clay colloid agglomeration expected**

- Monomodal size distribution
- Peak maximum at 210 nm
- Al recovery decreased to 66 %

- The low IS and high pH conditions of the Grimsel GW are not sufficient to fully stabilize clay colloids
- Long-term agglomeration could occur
- Influence of DOC?

WP5: Conceptual and mathematical models (8 PM's)

- **Objectives: ….validate and advance the conceptual and mathematical models …predict mass loss of clay in dilute waters and clay colloids…clay colloids facilitated radionuclide transport.**
- **KIT-INE** contribution to WP 5 will be threefold:

1. Currently a real 3D flow-field model is set-up on a natural over-cored fracture from Äspö (core#8). It is planned to simulate a virtual clay plug using a constant or **flow rate dependent erosion rate and compare these results with 2D/cubic law simplifications for uncertainty analysis**. Strong interaction with partner **VTT and KTH** is foreseen to discuss on the implementation of the real 3D flow-field in their erosion model.
2. In order to address colloid transport in natural fractures we plan to use a Discrete Phase Modeling (DPM) / Multiphase modeling (solid+liquid) approach with the Fluent particle tracking (colloid simulation) option under variation of attachment factor and repulsion.
3. It is furthermore foreseen to use a **surface complexation model** implementing cation exchange processes to link surface charge effects on attachment probability and model with this approach the chemical effects on colloidal facilitated transport.

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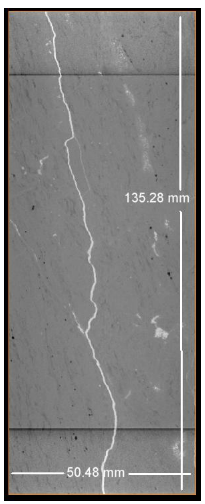
Micro-scale CFD modeling in a µXCT scanned single fracture

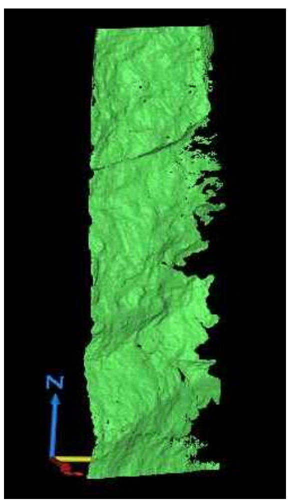
Huber, Enzmann, Wenka, Dentz & Schäfer *J. Contam. Hydrol.* (in review)

Modeling workflow

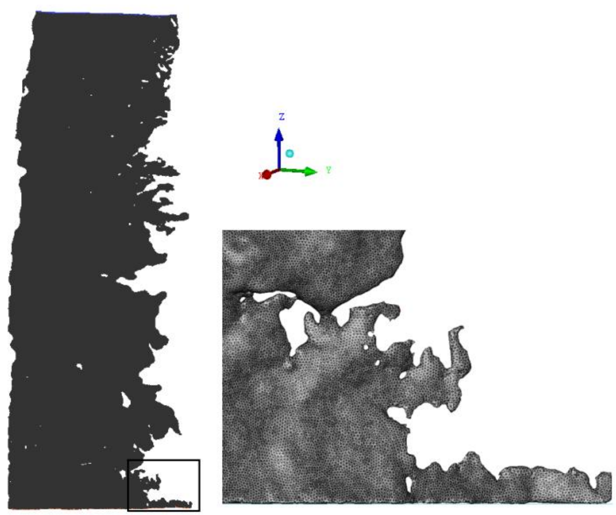
µXCT



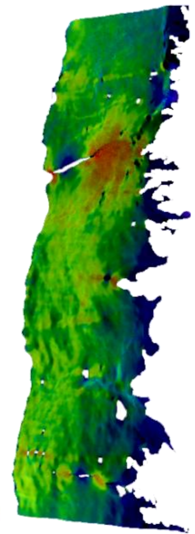
Geometry reconstruction



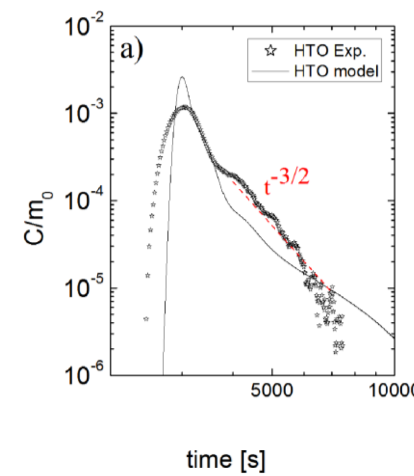
Preprocessing



Postprocessing



Comparison with „reality“



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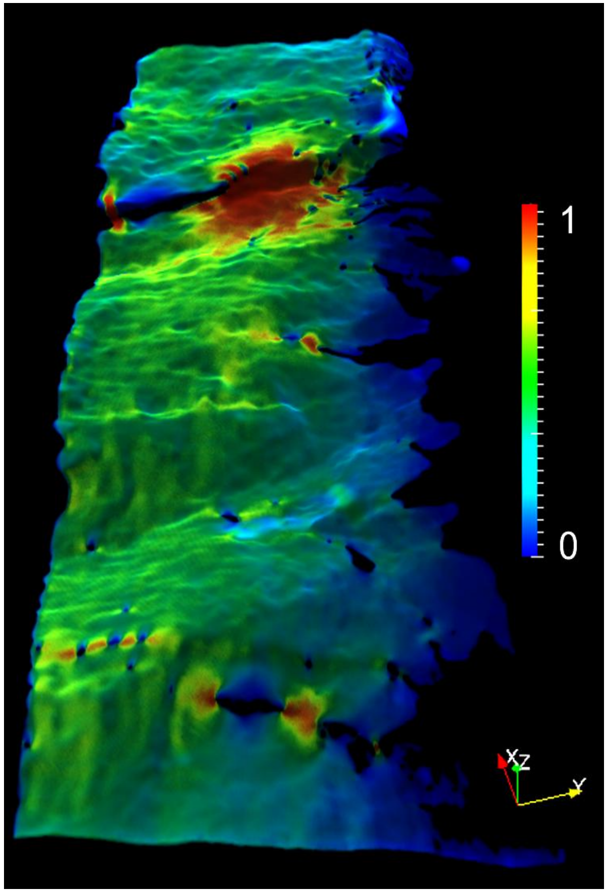
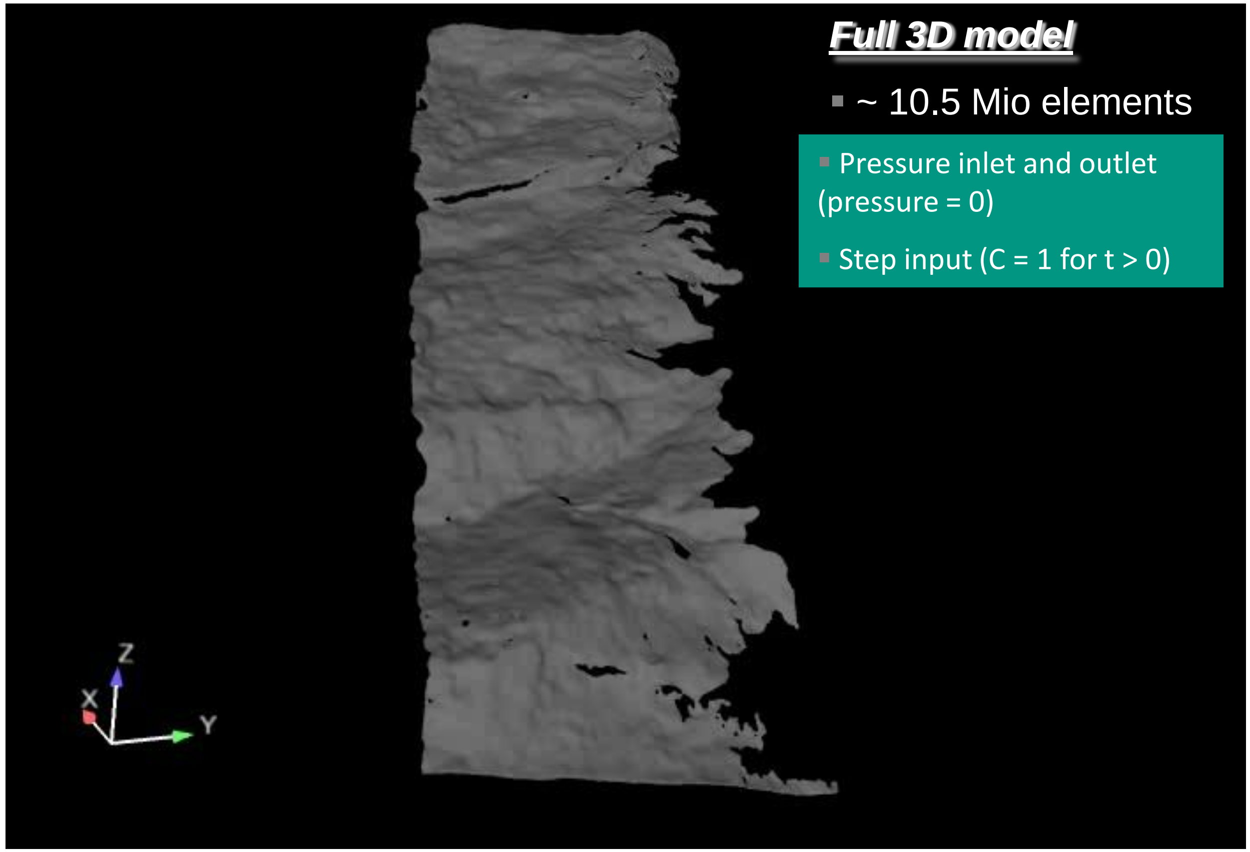
Velocity distribution



Particle tracing



Next activities:

Topic: **Core scale modeling**

1) A real 3D flow-field model is set-up
   - *Simulation of a virtual clay plug with constant erosion rate*
   - **VTT has received the fracture surface STL file to implement in COMSOL.**
   - *Comparison with 2D/cubic/quadratic law simplifications for uncertainty analysis (planned stay of F. Huber @ KTH V. Cvetkovic)*
   - *Fluent particle tracking (colloid simulation) under variation of attachment factor, repulsion etc.*
   - *Reactive transport/colloid transport alone streamlines coupling PHREEQC as surface complexation model (stay F. Huber @ AMPHOS21/CSIC J. Molinero/M.Dentz late spring 2012).*

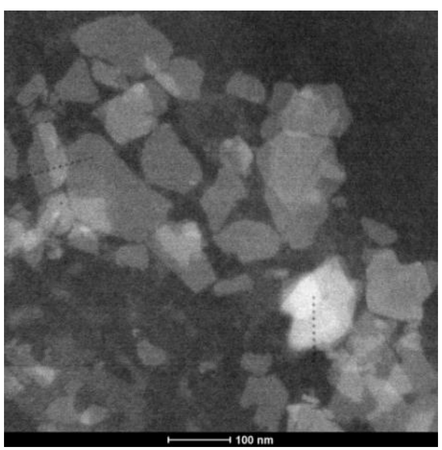
2) Apply the methology (µCT, 3D flow field) to a core from the Grimsel Test Site

Thank you for your attention!

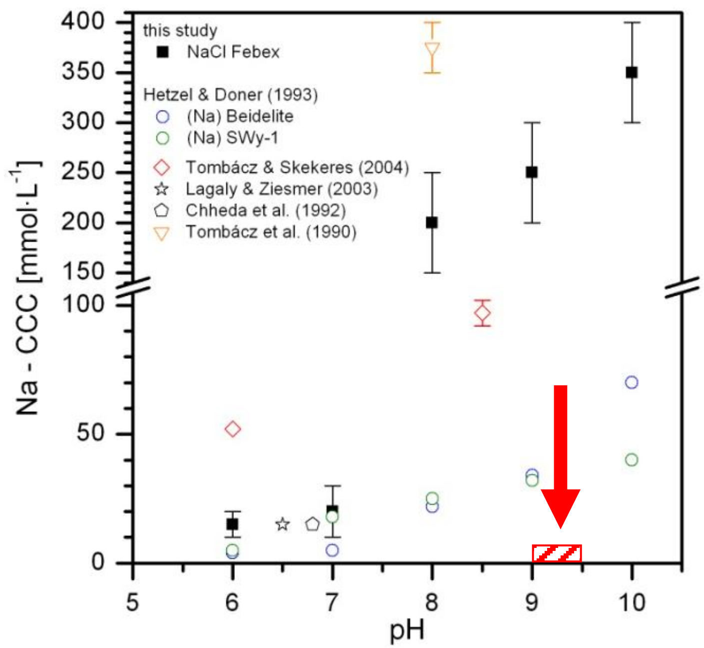
Clay colloid stability:

Influence of pH & cation

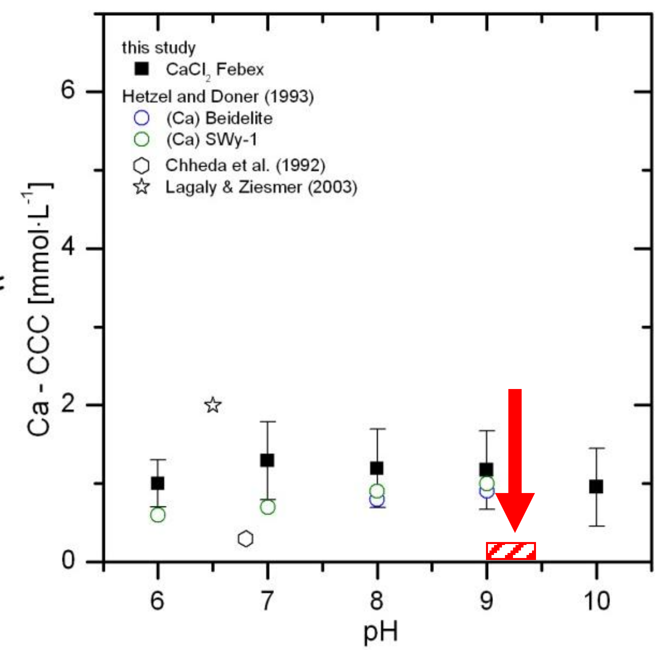
Schäfer, Huber, Seher, Missana, Alonso, Kumke, Eidner, Claret, Enzmann (2012) *Appl. Geochem. 27(2), 390.*



$\Sigma(Na^+, K^+, Rb^+, Cs^+)$: 0.7mmol/L



$\Sigma(Ca^{2+},Mg^{2+},Sr^{2+})$: 0.14 mmol/L



- Na-CCC pH dependent, Ca-CCC 1-2 mmol/L
- TEM-EDX analysis revealed different Al:Si ratios; also variation in stability?
- Work has also shown that geological origin has influence on bentonite stability (presence of amorphous Si phases)