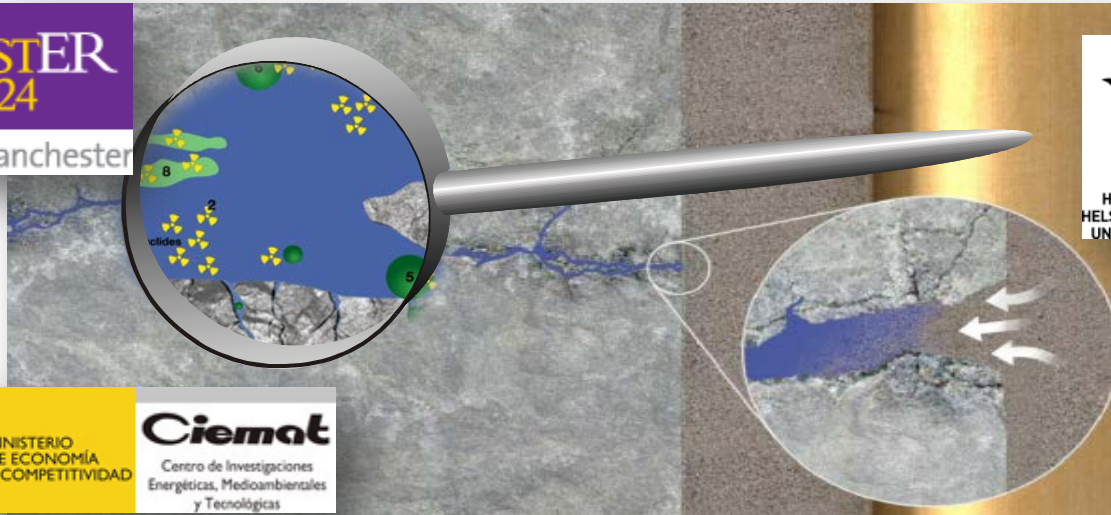


# Colloid mobility & radionuclide interaction

WP 3 Thorsten Schäfer (KIT-INE)

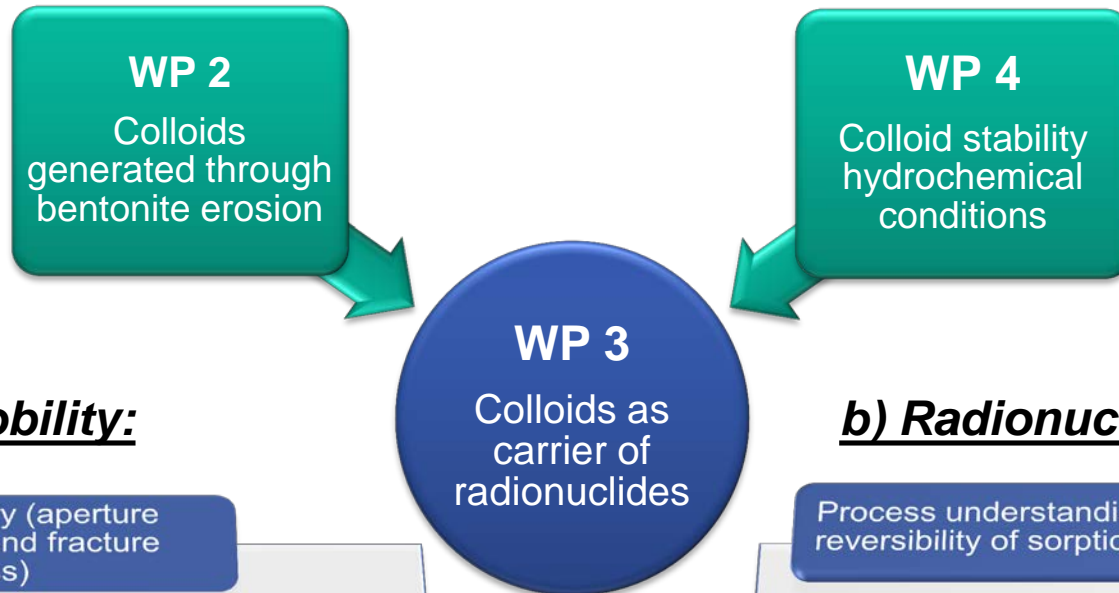
Institute für Nukleare Entsorgung (INE)



## In detail presentation concerning WP3

- *“Sorption behavior of Np(V) onto clays from Russian and Indian deposits” - Anna Yu Romanchuck (MSU)*
- *“Study of radionuclides migration through crushed granite in presence of bentonite colloids” - Kateřina Kolomá (UJV)*
- *“Effect of clay nanoparticle mobility, desorption and redox kinetics on radionuclide mobility investigated in an underground research laboratory (Grimsel Test Site, Switzerland)” - Thorsten Schäfer (originally foreseen Ingo Blechschmidt)*
- *“Radionuclide transport in granite fractures in the presence of bentonite colloids: Summary of the studies carried out at Ciemat” - Tiziana Missana (CIEMAT)*

## ■ Work package 3: Objectives



### a) Colloid mobility:

Fracture geometry (aperture size distribution and fracture surface roughness)

Chemical heterogeneity induced by the different mineral phases

Chemistry of the matrix porewater

### b) Radionuclide interaction:

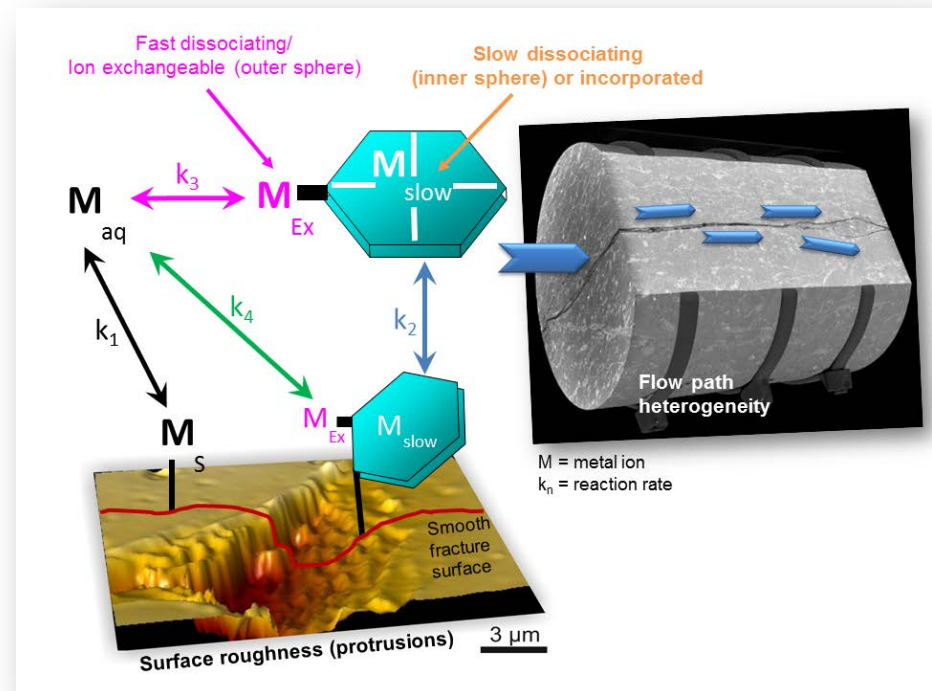
Process understanding of reversibility of sorption

Implementation in thermodynamic models

Identifying additional retention processes => matrix diffusion

# Key questions

1. What are the colloid mobility controlling processes and can we describe them appropriate?
2. Is the sorption of strongly sorbing radionuclides fully reversible, why do we observe kinetics?
3. Have we indications for additional retention processes occurring?





- **Macroscale investigations** on colloid mobility in near-natural systems,
- **Microscale investigations** on colloid mobility controlling processes,
- Process understanding of **radionuclide** colloid interaction with special emphasis on **sorption reversibility**
- **Kinetic model approach**
- **Mechanistical model** of RN colloid interaction.



**Retardation of colloid transport in the far field, will delay the arrival of radionuclides in the biosphere.**

**=> The extent of this isn't currently taken into account.**



Table 2.1

Selected composition of the Forsmark reference, saline, ice-melting and buffer-equilibrated waters. Concentrations are in mol/dm<sup>3</sup> (Duro et al. 2006a, TR-06-32, Table 3-1).

	Forsmark reference water <sup>1)</sup>	Saline water <sup>2)</sup>	Ice melting water <sup>3)</sup>	Buffer-equilibrated water <sup>4)</sup>
pH (downhole in situ for reference water)	7	7.9	9.6	7.1
Eh (downhole in situ for reference water) (mV)	-143	-314	-200	-130
[Na <sup>+</sup> ]tot	8.88E-02	3.49E-01	6.90E-04	0.145
[K <sup>+</sup> ]tot	8.75E-04	7.41E-04	5.00E-06	0.153
[Ca <sup>2+</sup> ]tot	2.33E-02	4.63E-01	1.40E-04	0.0130
[Mg <sup>2+</sup> ]tot	9.30E-03	1.11E-04	6.20E-07	5.46E-03
[HCO <sub>3</sub> <sup>-</sup> ]	1.77E-03	1.47E-04	4.50E-04	2.19E-03
[Cl <sup>-</sup> ]tot	1.53E-01	1.28E+00	1.60E-04	0.153
[S]tot	6.80E-03	3.56E-02	6.10E-05	2.09E-02
[Br <sup>-</sup> ]tot	2.98E-04	3.90E-03	3.80E-07	
[F <sup>-</sup> ]tot	4.42E-05	8.42E-05	3.60E-04	
[Si]tot	1.85E-04	4.99E-05	2.50E-04	6.64E-05
[Fe]tot	3.31E-05	7.66E-06	3.00E-09	3.31E-05
[Mn]tot	3.93E-05		5.00E-09	
[Li <sup>+</sup> ]tot	7.35E-06	7.74E-04		
[Sr <sup>2+</sup> ]tot	9.18E-05		2.00E-06	
[P]tot		3.23E-05		
Ionic strength	0.19	1.86	0.0012	0.21

<sup>1)</sup> SKB. Pers. Comm.

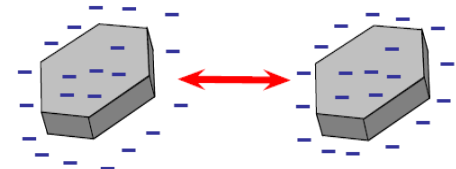
<sup>2)</sup> KLX02 in the interval 1,420–1,705 m with date of sampling 94/01/17. /Laaksoharju et al. 1995/.

<sup>3)</sup> Grimsel groundwater composition [discharging groundwater from the Migration shear zone (AU 96)].  
(Data compiled from /Bajo et al. 1989/, /Aksoyoglu et al. 1990/ and /Eikenberg et al. 1991/.)

<sup>4)</sup> Forsmark groundwater interacted with the bentonite buffer /Arcos et al. 2006/.

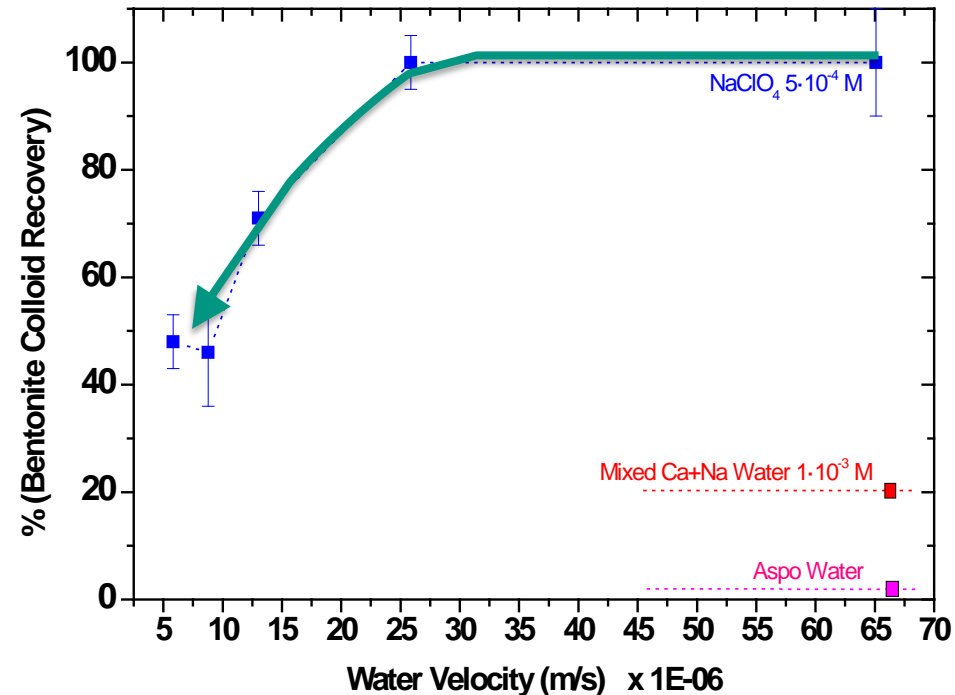
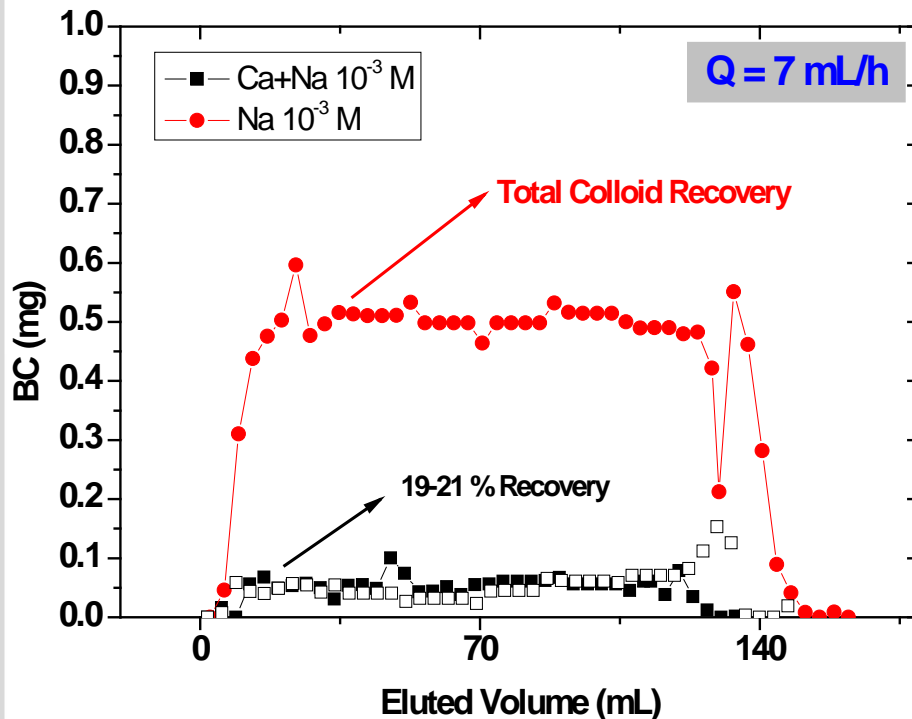


Dilute Glacial melt water



# Colloid retardation/retention

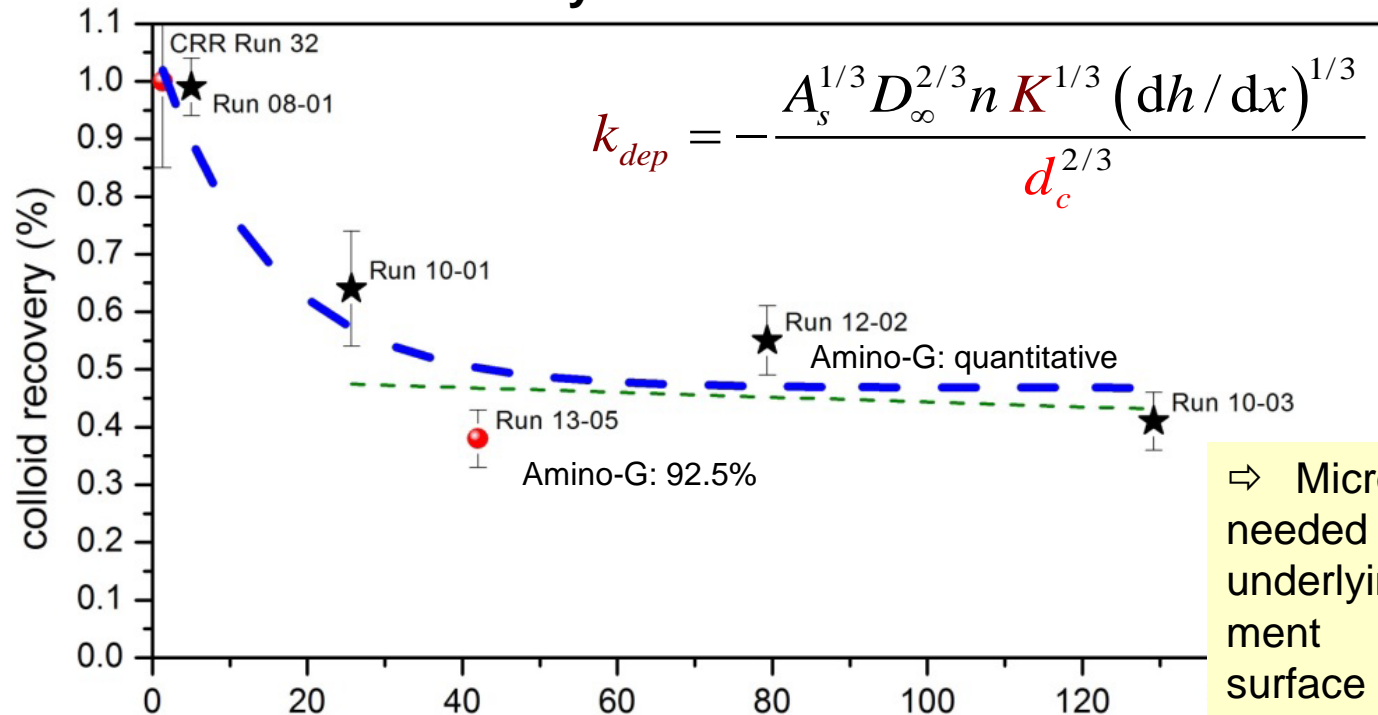
## Recovery $f(v, I)$ column migration experiments





# Colloid Formation & Migration Experiment [www.grimsel.com](http://www.grimsel.com)

Colloid recovery: *function of residence time*

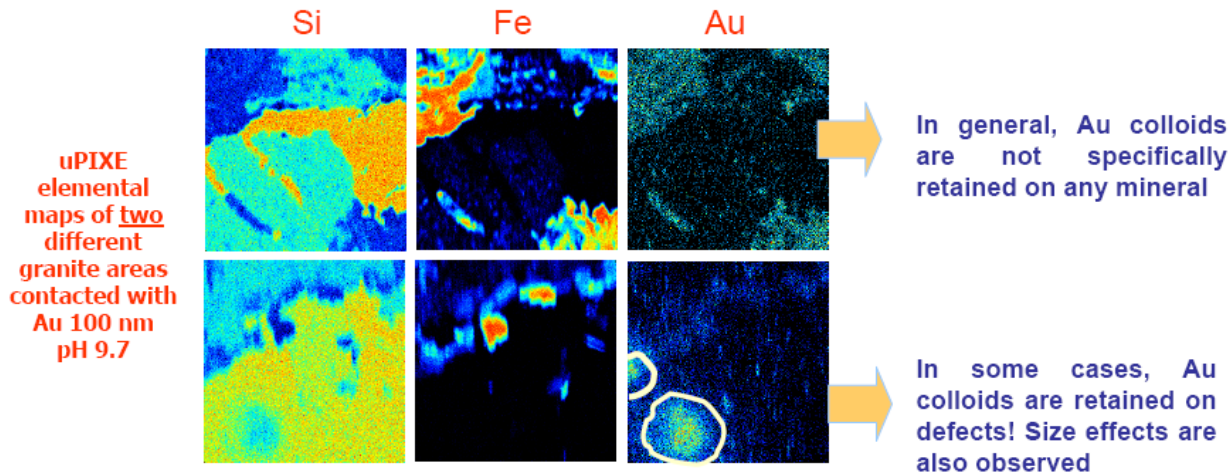


smaller grains (FFM),  
lower velocity,  
greater surface area  
⇒ **higher  
deposition rate**

⇒ Microscopic information  
needed to clearly identify  
underlying colloid attach-  
ment process (charge,  
surface roughness)

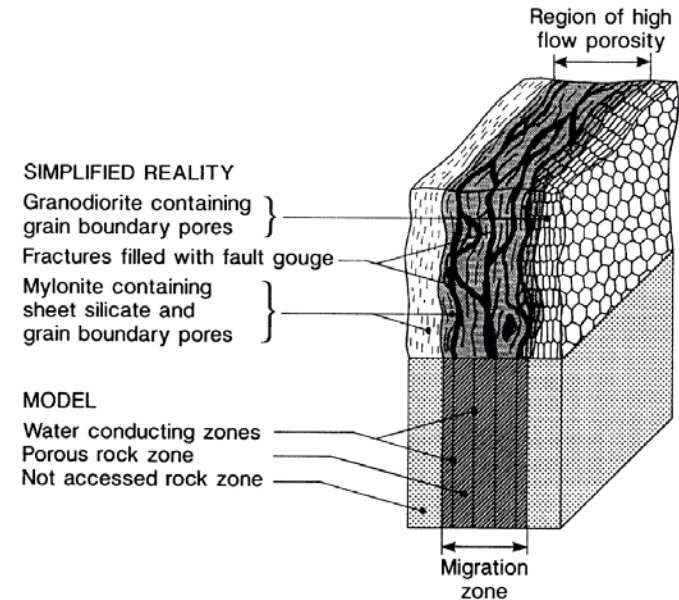
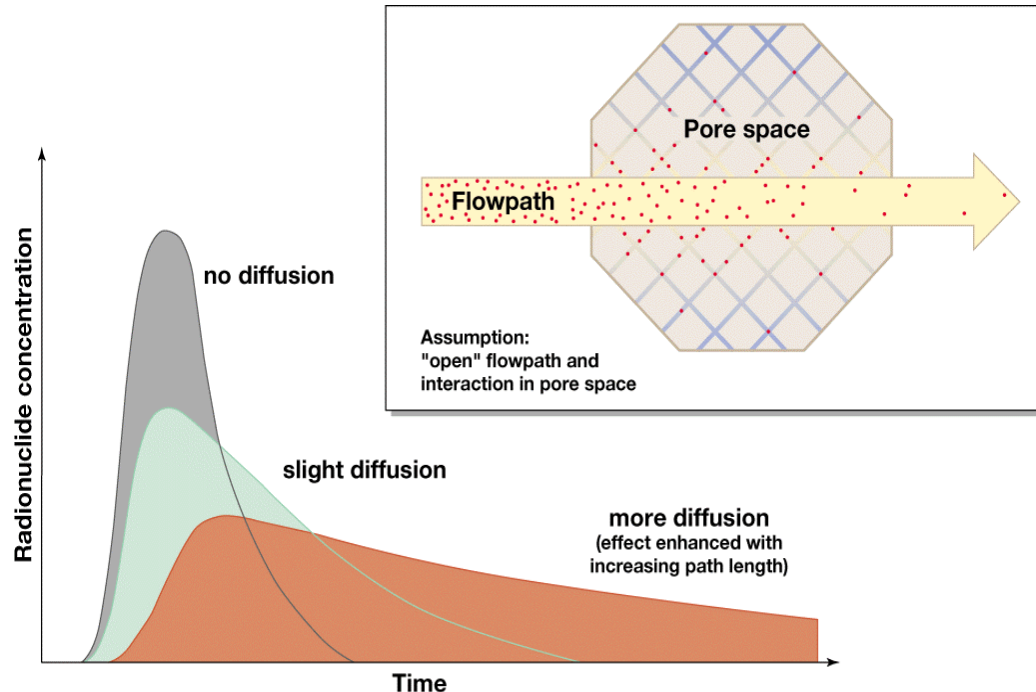
- Colloid retention has been observed even at conditions where high retention was not expected, i.e. under unfavorable electrostatic conditions (Missana et al., 2008a; Schäfer et al., 2004). The mechanisms that contribute to colloid retention are not yet fully understood. (Geckeis et al, 2008; Missana et al, 2008b; Albarran et al, 2011; Missana et al, 2011; Schäfer et al, 2012).

## Colloid mobility in fractured rocks (PIXE investigations)



- Colloid diffusion in rock matrix can eliminate colloids from the flow paths despite being considered a minor mechanism. **All diffusion coefficients measured were in the range of  $D_a = 10^{-18} \text{ m}^2/\text{s}$ .** No significant differences in  $D_a$  were measured amongst colloid of different charge but the main changes were attributed to size variations. Maximum surface distribution coefficients measured were  $K_a = 3 \cdot 10^{-3} \text{ m}$ .

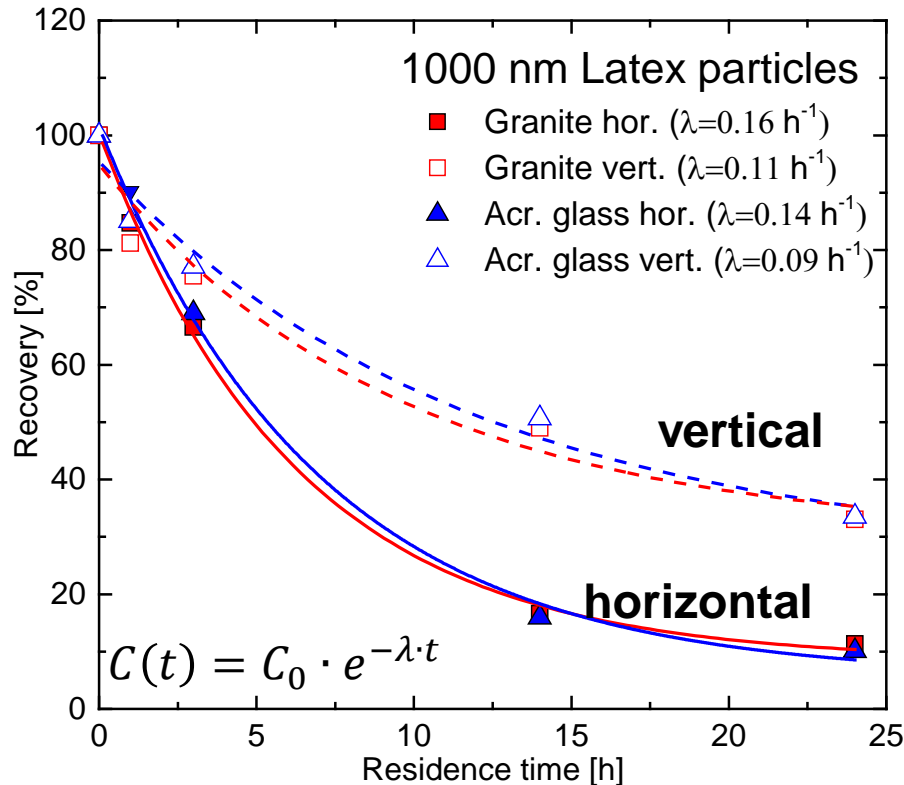
# Process of colloid retention/retardation



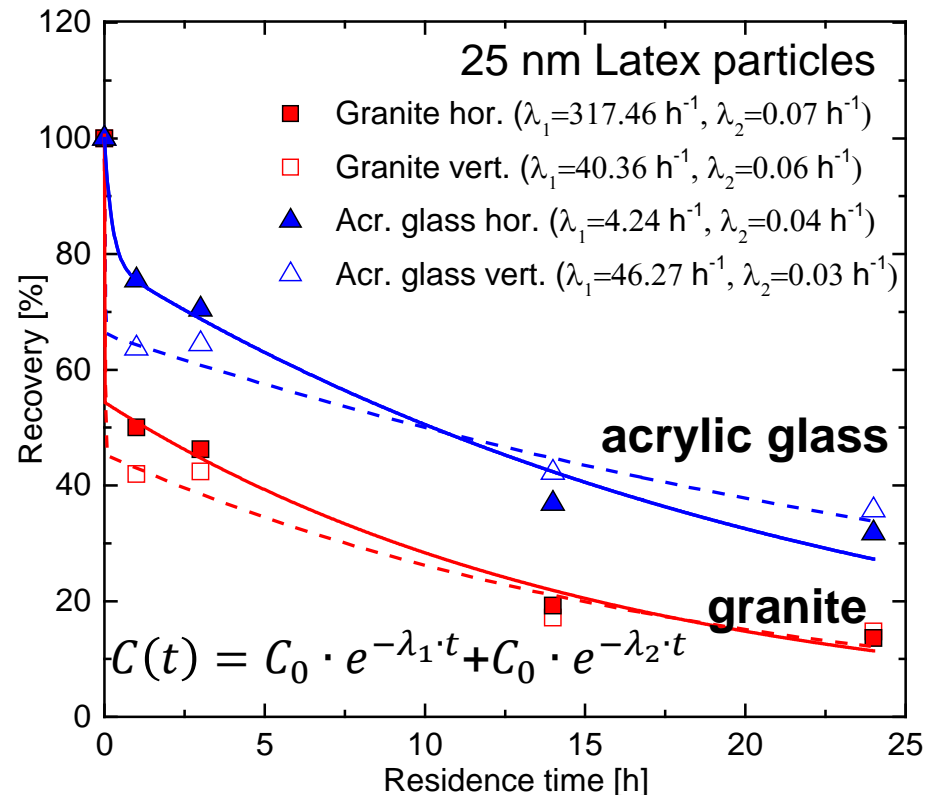
- Tailing slope has frequently been interpreted by matrix diffusion, tailing of the colloids is mainly caused by the structure of the flow field and that for the colloid transport matrix diffusion is of minor importance. (Kosakowski, 2004; Möri et al., 2003; Huber et al., 2012).

# Colloid recoveries $f$ (fracture orientation, surface roughness)

Madeleine Stoll et al. (to be submitted)



**Particle retention influenced by fracture orientation**



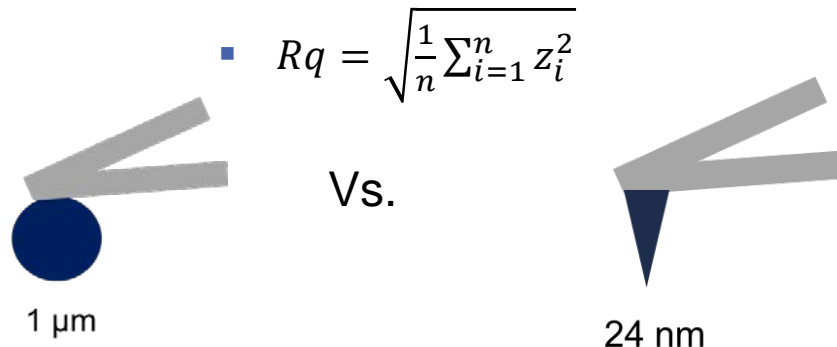
**Particle retention influenced by fracture surface material**

# Atomic Force Microscopy

AFM measurements on granite and acrylic glass disc

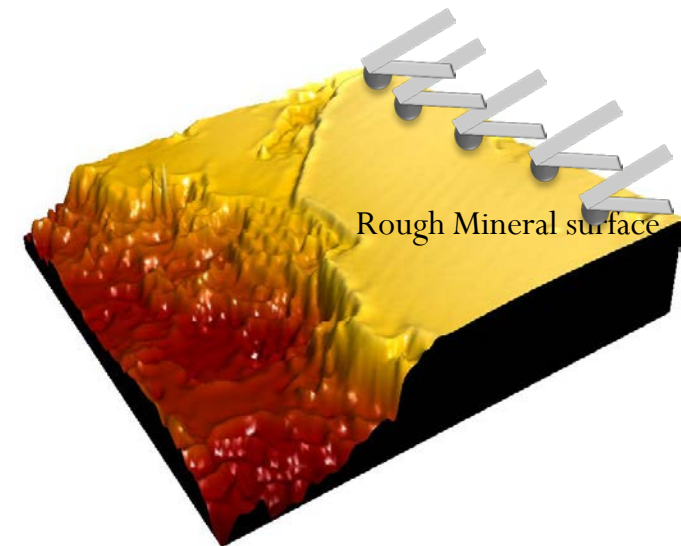
## 1) Topography

- Both granite and acrylic glass disc are scanned by **1  $\mu\text{m}$  colloid probe** and  **$\sim 24$  nm sharp tip** to obtain the topography of the substrates and further to quantify the roughness ( $Rq$ ):



$$Rq = \sqrt{\frac{1}{n} \sum_{i=1}^n z_i^2}$$

Colloid probe technique



Parameters measured:

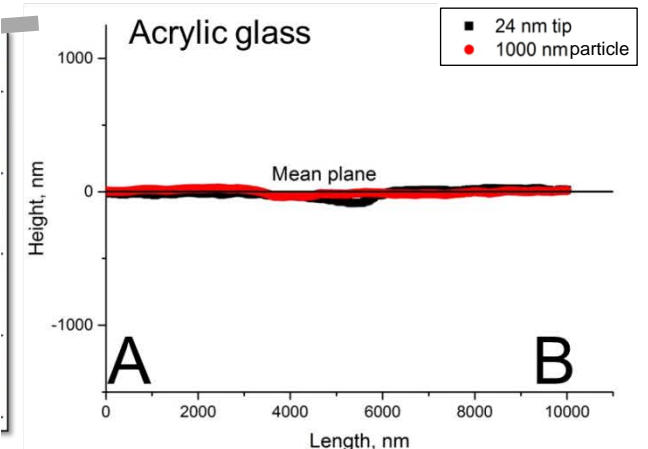
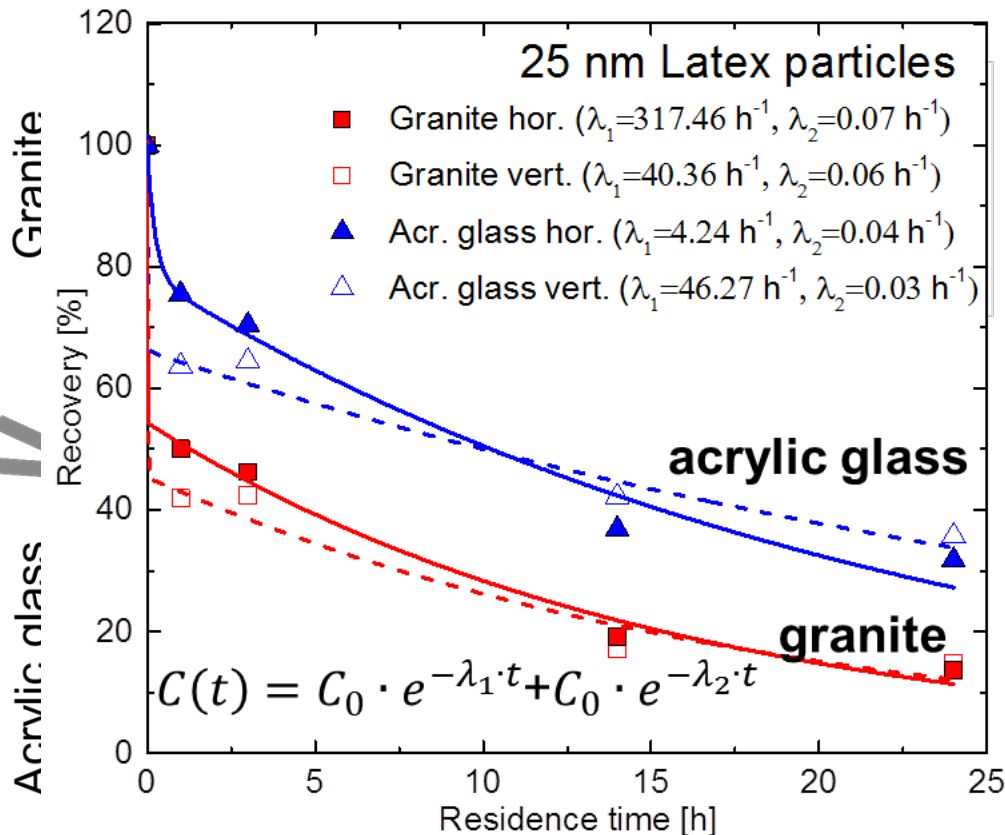
1. **Surface topography**
2.  $F_{\text{Adhesion}}$
3. Snap-in force
4. Force-volume measurements



# 1) Topographic images and surface profiles

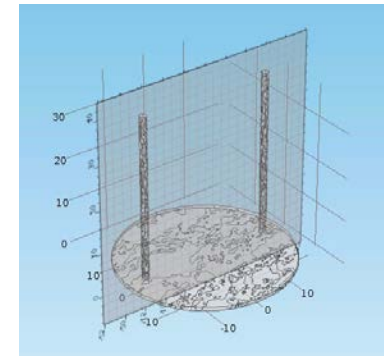
Image obtained with  
1000 nm colloid probe

Image obtained with  
24 nm sharp tip

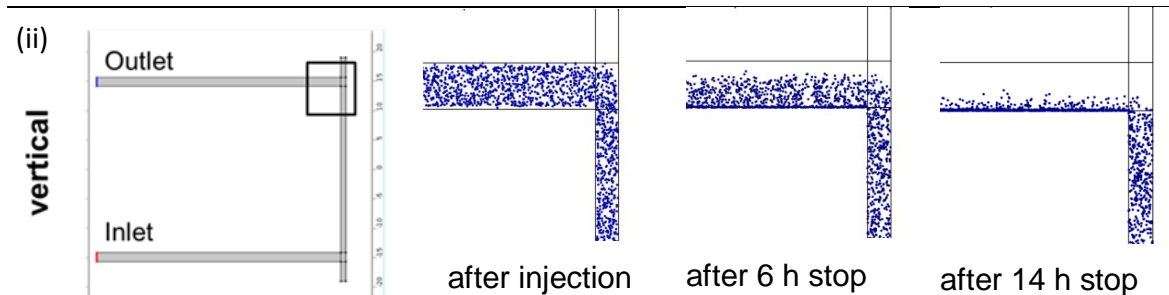
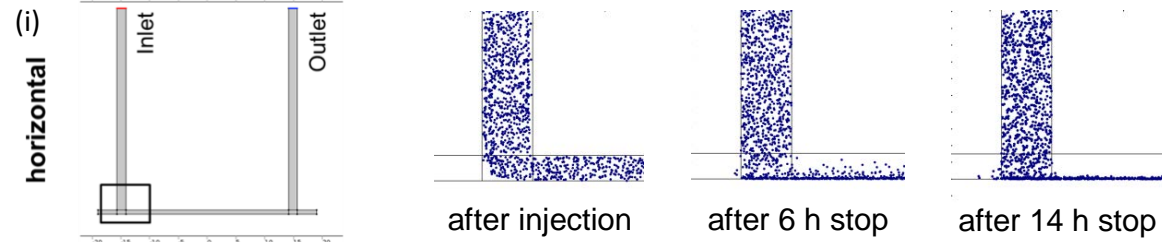
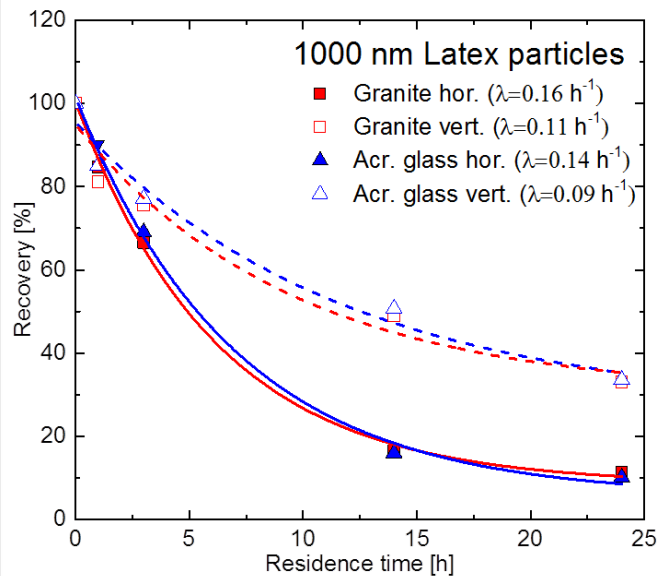
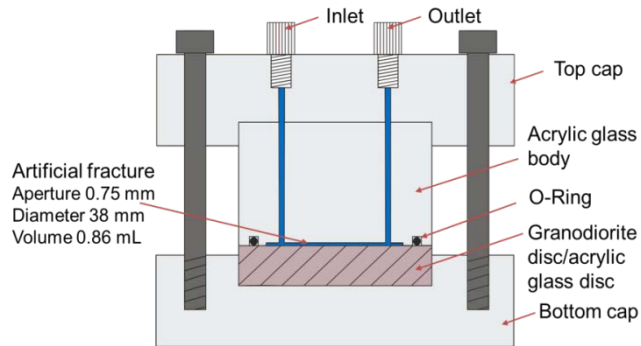


Increased roughness directly enhances diffusivity of the 25 nm particles into scratches and cracks on the substrate in contrast to the 1000 nm particles





# Colloid recoveries $f_{\text{(fracture orientation)}}$



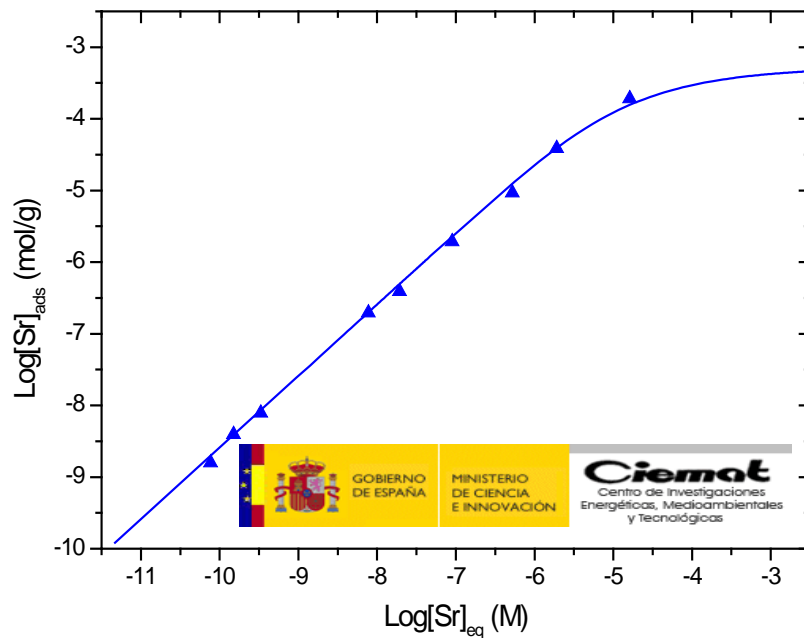
Pure sedimentation independent of the surface used => **fracture orientation is the key**



Is the assumption of reversible linear sorption of radionuclides on colloids justified?

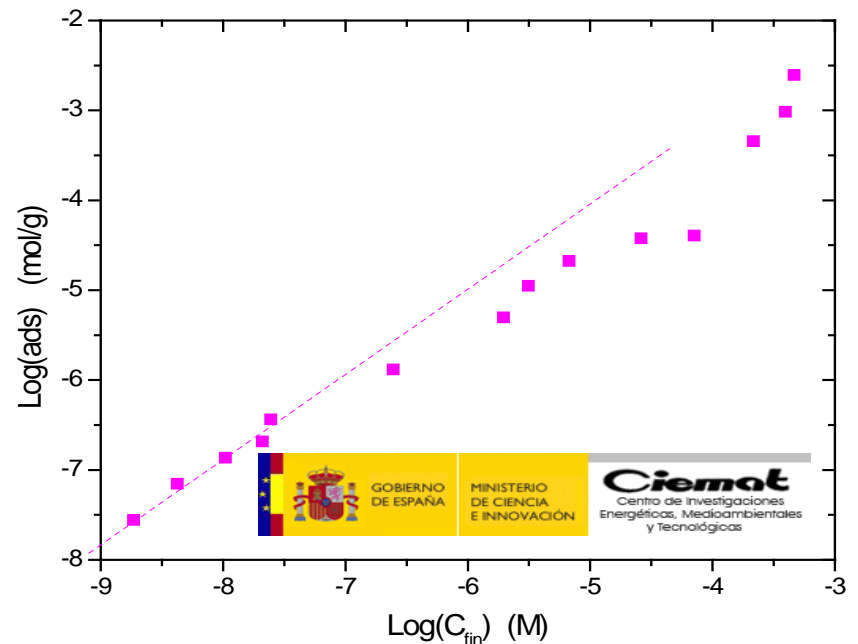
# Linear sorption assumed

## Strontium



Cation exchange & inner sphere surface complexation; **Linear**.

## Cadmium

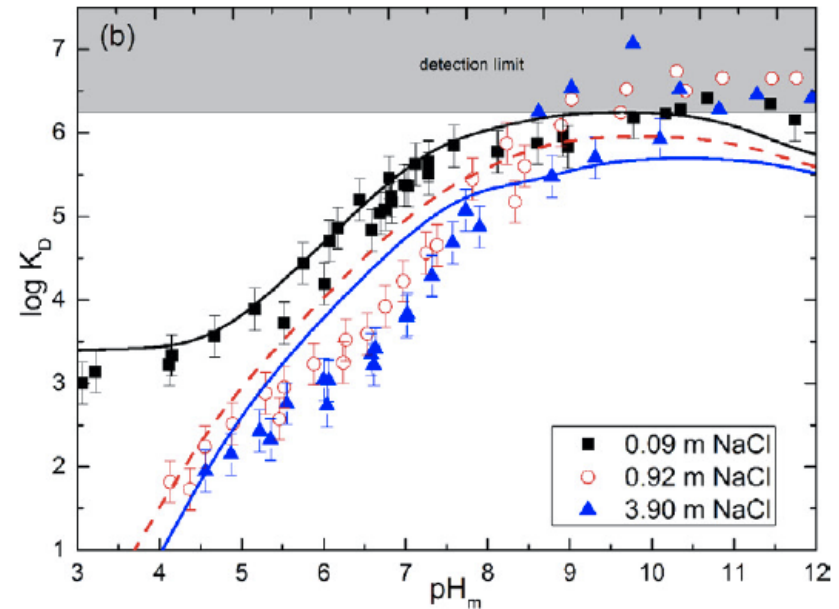
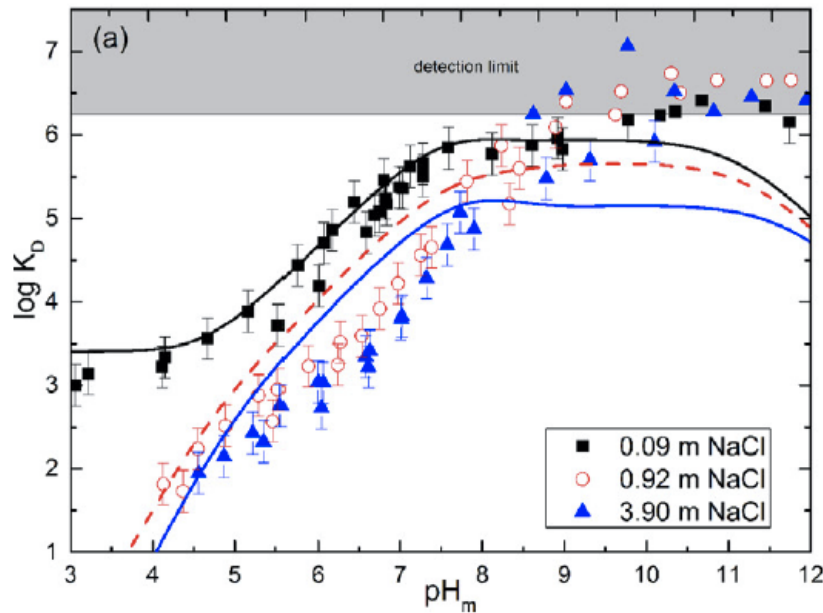


Cation exchange & inner and outer sphere surface complexation; **Linear**.

# Linear sorption assumed

Schnurr, A.; Marsac, R.; Rabung, T.; Lützenkirchen, J.; Geckeis, H., Sorption of Cm(III) and Eu(III) onto clay minerals under saline conditions: Batch adsorption, laser-fluorescence spectroscopy and modeling. *GCA* **2015**, *151*, 192-202.

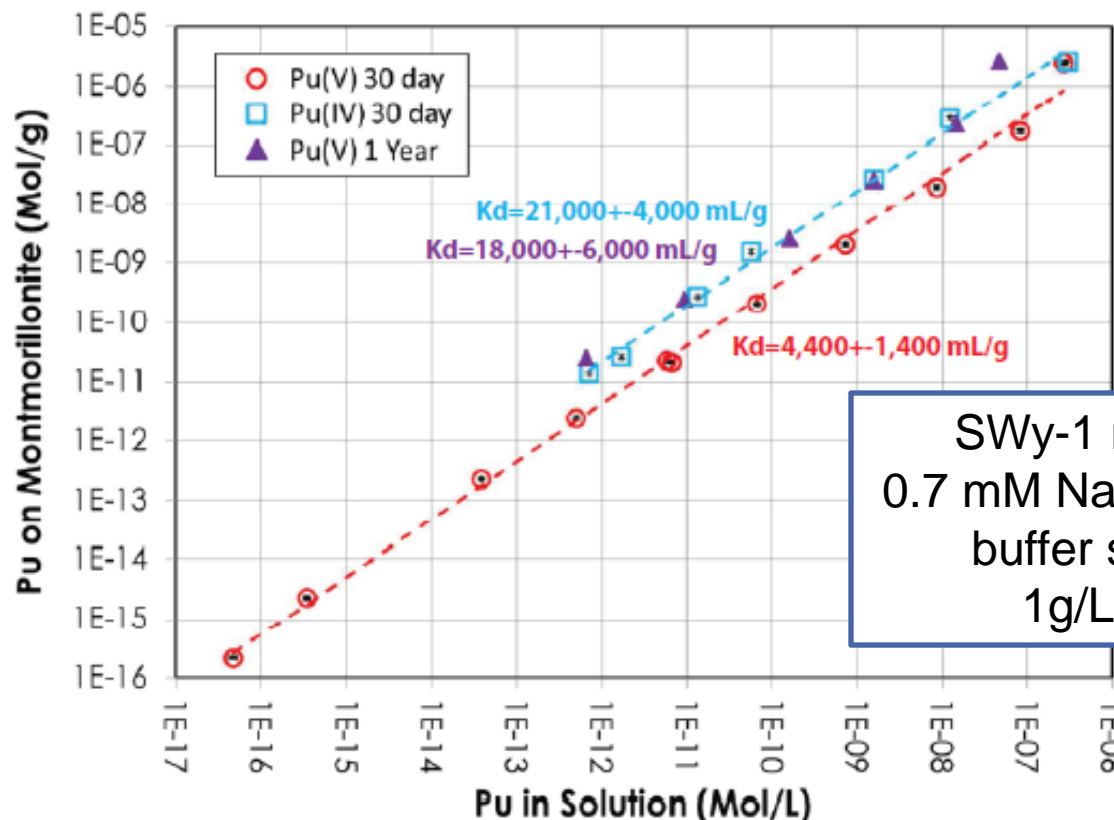
## Sorption of Cm(III) and Eu(III) onto clay minerals



Sorption edges for Eu ( $m_{\text{Eu, total}} = 2.0 \cdot 10^{-7} \text{ m}$ ), S:L 2 g/L, on Na-SWy-2 montmorillonite as a function of  $\text{pH}_m$  and at different NaCl concentrations.

# Pu(V) & Pu(IV) sorption to montmorillonite

Begg, J. D.; Zavarin, M.; Zhao, P. H.; Tumey, S. J.; Powell, B.; Kersting, A. B., Pu(V) and Pu(IV) Sorption to Montmorillonite. *Environ. Sci. Technol.* **2013**, *47*, (10), 5146-5153.

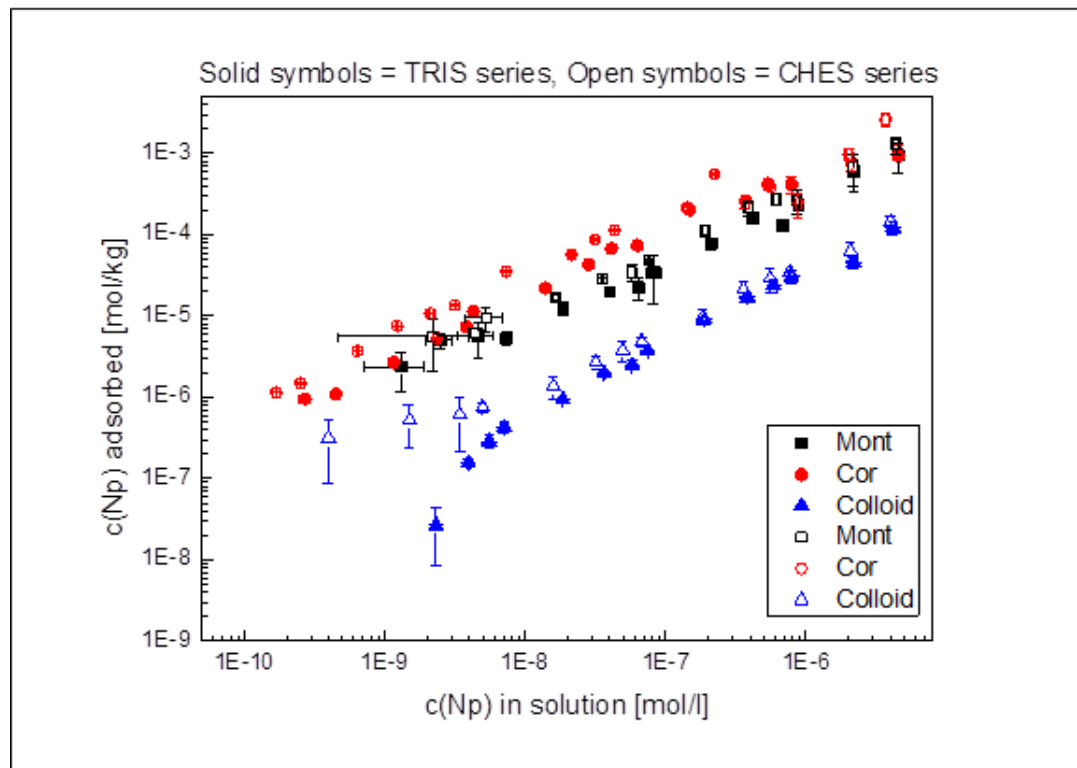


SWy-1 montmorillonite  
0.7 mM NaHCO<sub>3</sub>, 5 mM NaCl  
buffer solution (pH 8)  
1g/L suspension

# Sorption isotherms of Np(V) onto corundum, montmorillonite and bentonite colloids

## ■ TRIS and CHES buffer solution

- Na- montmorillonite and
- Bentonite colloid dispersion (MX-80 Volclay)
- N<sub>2</sub>-glove box (exclusion of Np-carbonato complexes)





## From WP1

Issue	Safety case position at start of BELBaR	Outcomes for final State-of-art report
Radionuclide sorption	<p>To assess the possible role of rapid reversible sorption/desorption onto colloids in facilitating transport, the following assumptions have been adopted:</p> <ol style="list-style-type: none"> <li>1. equilibrium sorption of radionuclides onto mobile and immobile colloids,</li> <li>2. equilibrium sorption of colloids onto fracture surfaces, and</li> <li>3. colloid-free matrix pore space (conservative assumption, but also realistic for the small pore sizes of granitic rock).</li> </ol> <p>Reversible, linear sorption of radionuclides onto colloids has been assumed.</p>	<p>Is the assumption of reversible, linear sorption of radionuclides onto colloids justified? (WP3)</p>

Colloid, radionuclide and host rock interactions (WP3) – the main thing here is to determine the sorption reversibility of radionuclides to the colloids and whether the current assumption of reversible sorption can be justified.

# Why does 'irreversible' binding matter

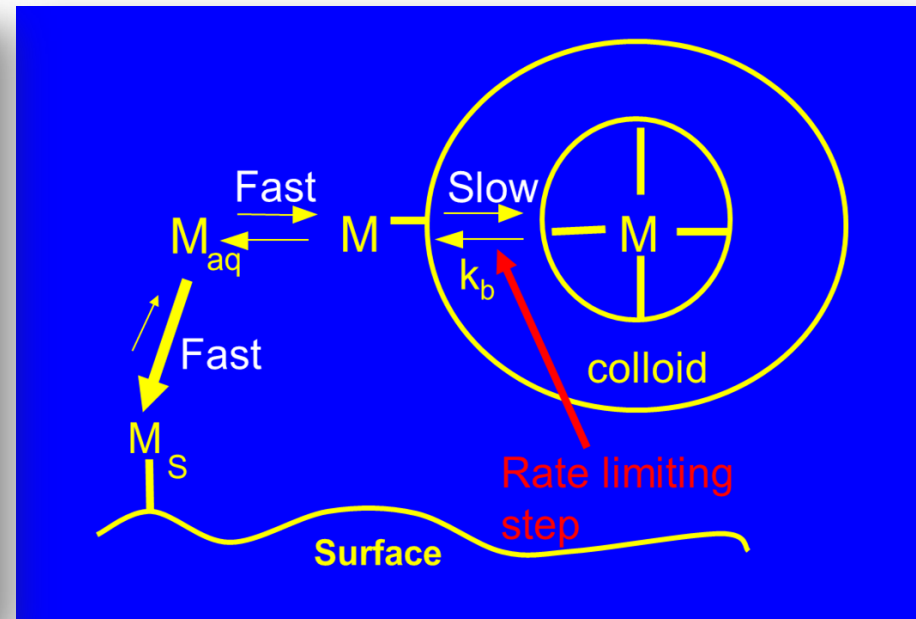
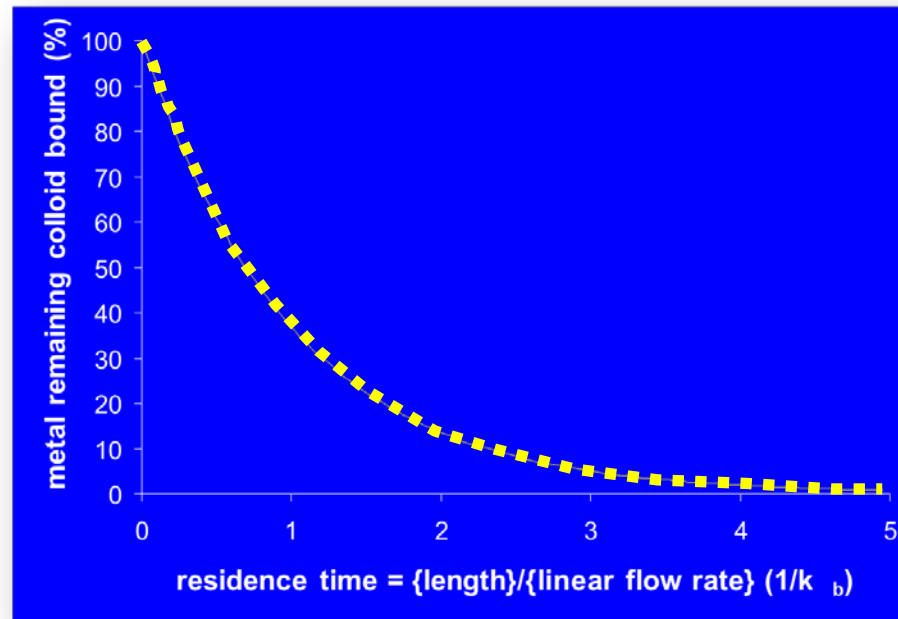
## Effect of dissociation rate constant on transport

For humics:

$$k_b = 10^{-7} - 10^{-6} \text{ s}^{-1}$$

$$k_b = 0.00036 - 0.0036 \text{ h}^{-1}$$

$$k_b = 3.15 - 31.54 \text{ a}^{-1}$$

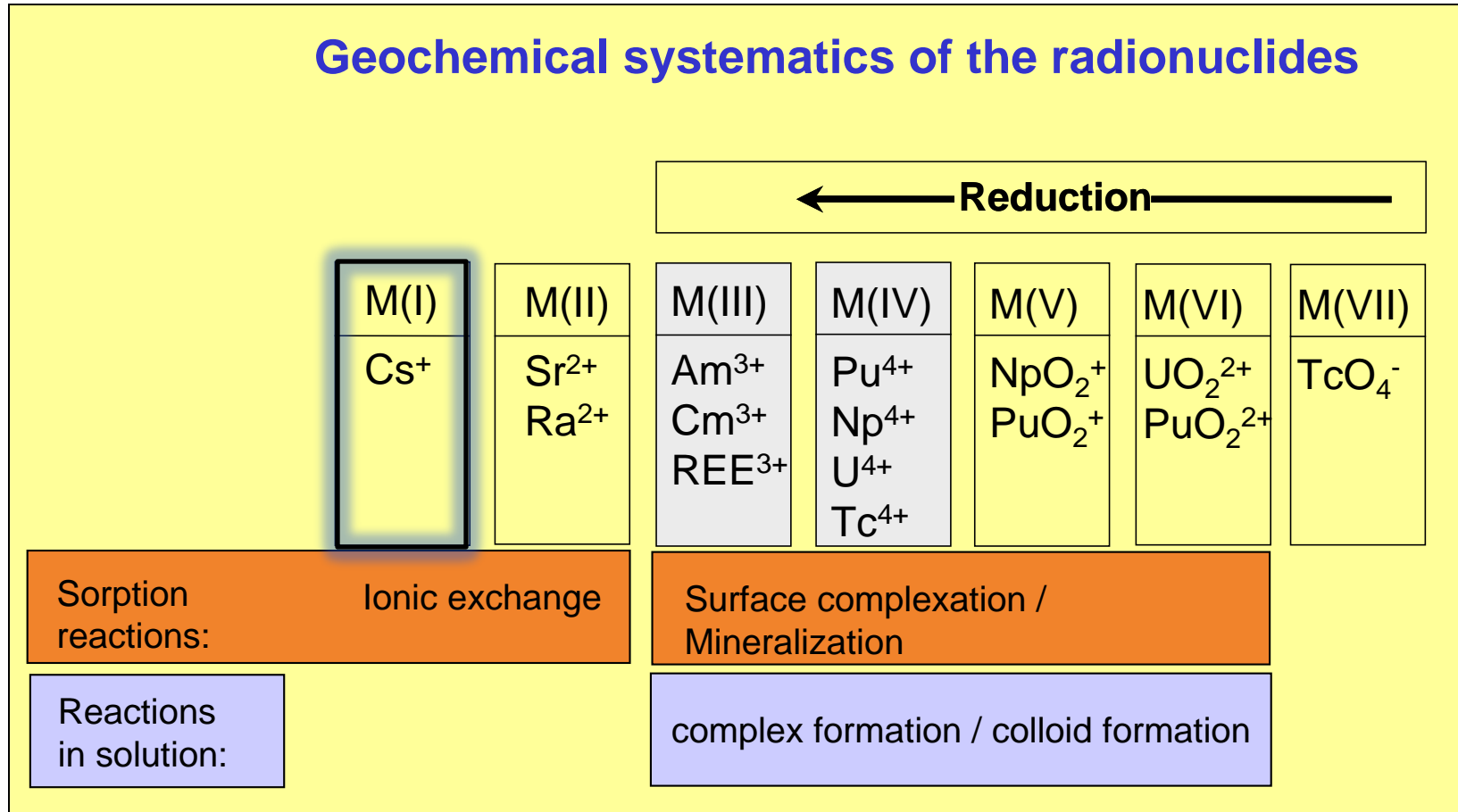


Reversibility tests via:

- pH decrease
- Ionic strength increase
- Addition of rock/fracture filling material
- Addition of organic ligands (FA / EDTA)

# Radionuclides to be discussed

## Geochemical systematics of the radionuclides



## Cs reversibility vs. irreversibility

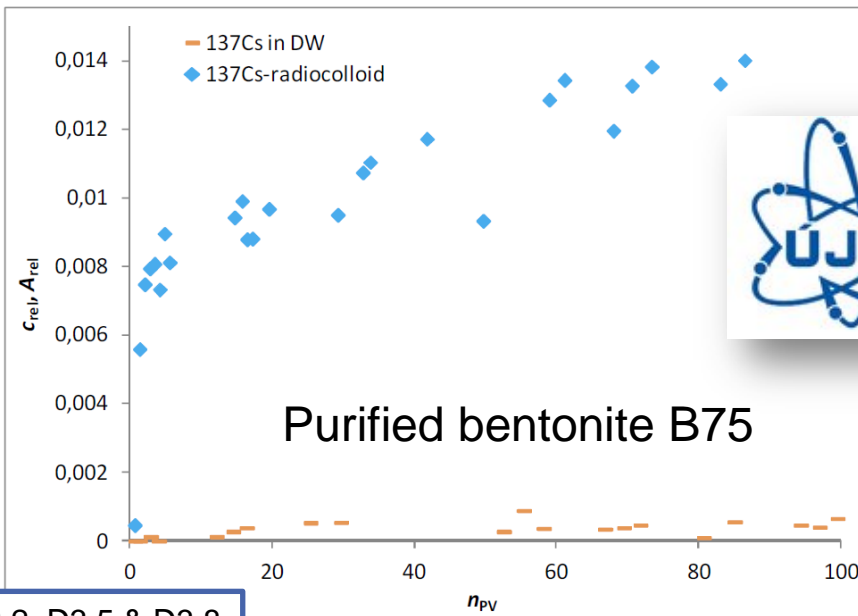
Zachara, J. M.; Smith, S. C.; Liu, C. X.; McKinley, J. P.; Serne, R. J.; Gassman, P. L., Sorption of Cs<sup>+</sup> to micaceous subsurface sediments from the Hanford site, USA. *Geochim. Cosmochim. Acta* **2002**, *66*, (2), 193-211.

- The amount of **poorly exchangeable Cs** on the planar sites represented approximately **3.5% of the total planar site concentration**.
- Collapse of vermiculite and smectite interlayers induced by sorbed Cs or the high KNO<sub>3</sub> desorption solution may explain this poorly reversible fraction.
- This apparent fixation occurred almost immediately after Cs addition,
  - Did not correlate with aging time of the sorption complex (0.5-120 d)
  - Reversibility was negligible even after 500 h of contact with excess K.

## Cs reversibility vs. irreversibility

- The reversibility has been verified for montmorillonite. In adsorption experiments at lower Cs<sup>+</sup> concentration  $<10^{-4}$  M, Cs<sup>+</sup> adsorption was full reversible. (Kunipia F®)

Iijima, K.; Tomura, T.; Shoji, Y., Reversibility and modeling of adsorption behavior of cesium ions on colloidal montmorillonite particles. *Appl. Clay Sci.* **2010**, *49*, (3), 262-268.

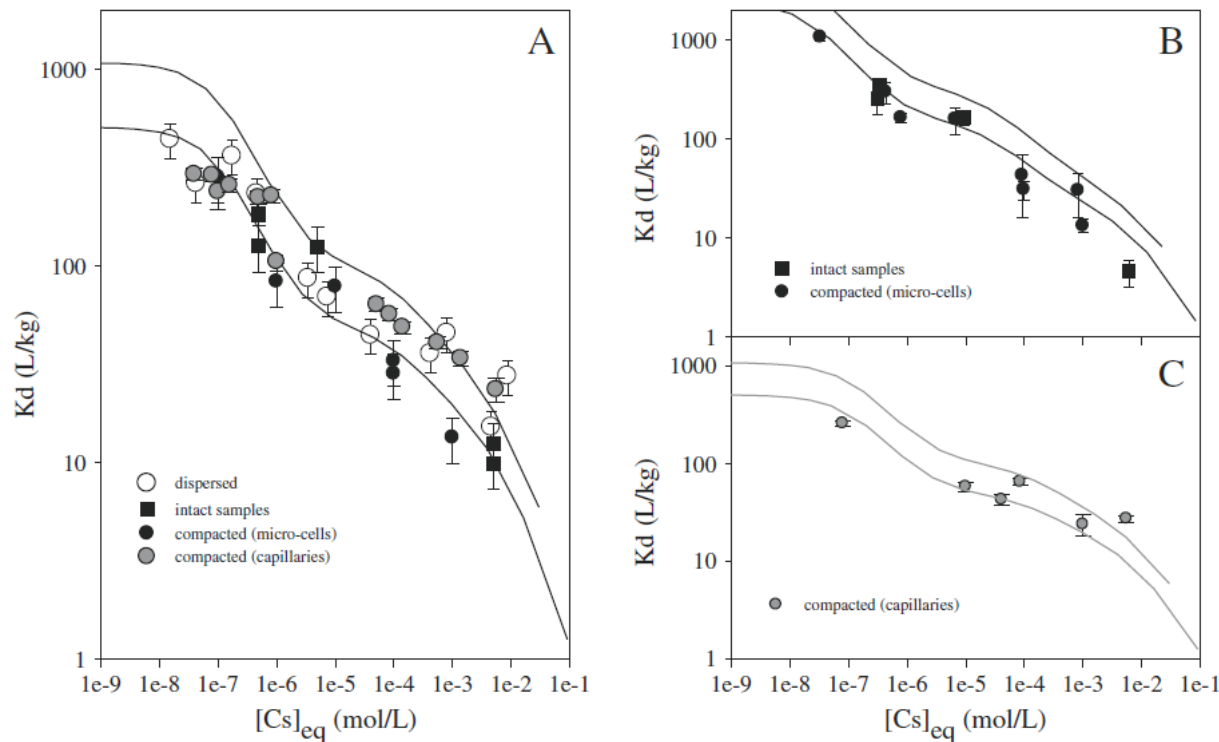


D3.2, D3.5 & D3.8

- 1% of cesium passed through crushed granite sorbed on bentonite colloids
- however the most of cesium was desorbed from bentonite colloids and retained in granitic rock.
- Thus, cesium sorption on bentonite is mostly reversible under the hydraulic conditions.

# Cs reversibility vs. irreversibility

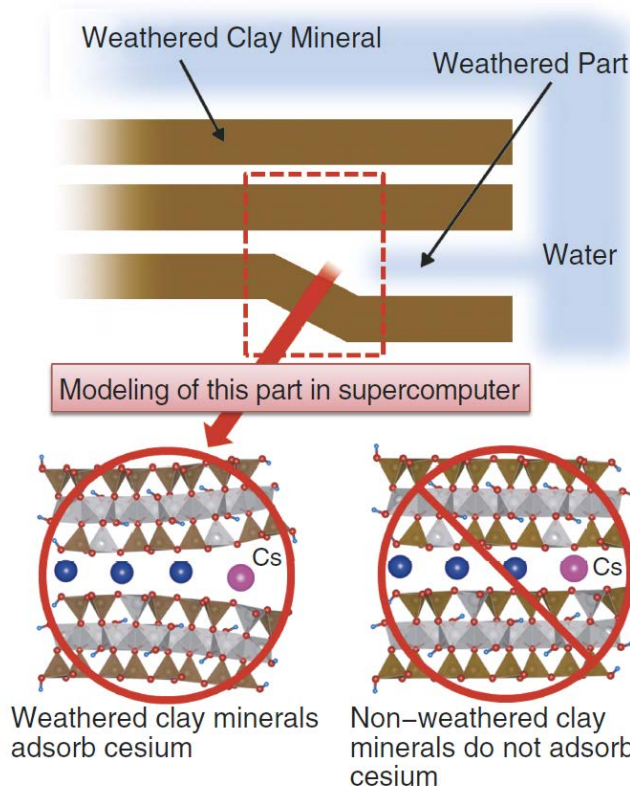
Chen, Z.; Montavon, G.; Ribet, S.; Guo, Z.; Robinet, J. C.; David, K.; Tournassat, C.; Grambow, B.; Landesman, C., Key factors to understand in-situ behavior of Cs in Callovo–Oxfordian clay-rock (France). *Chem. Geol.* **2014**, *387*, 47–58.



- **Callovo- Oxfordian Clay Rock** in all cases studied (reversibility tests performed after a sorption phase in the compacted state fixed between 5 months and 5 years), the sorption process was reversible in disagreement with results obtained on similar but different illite materials.
- Furthermore, no significant difference was found between dispersed and compacted systems, so no compaction effect on  $K_d$  values was observed.



# Cs reversibility vs. irreversibility



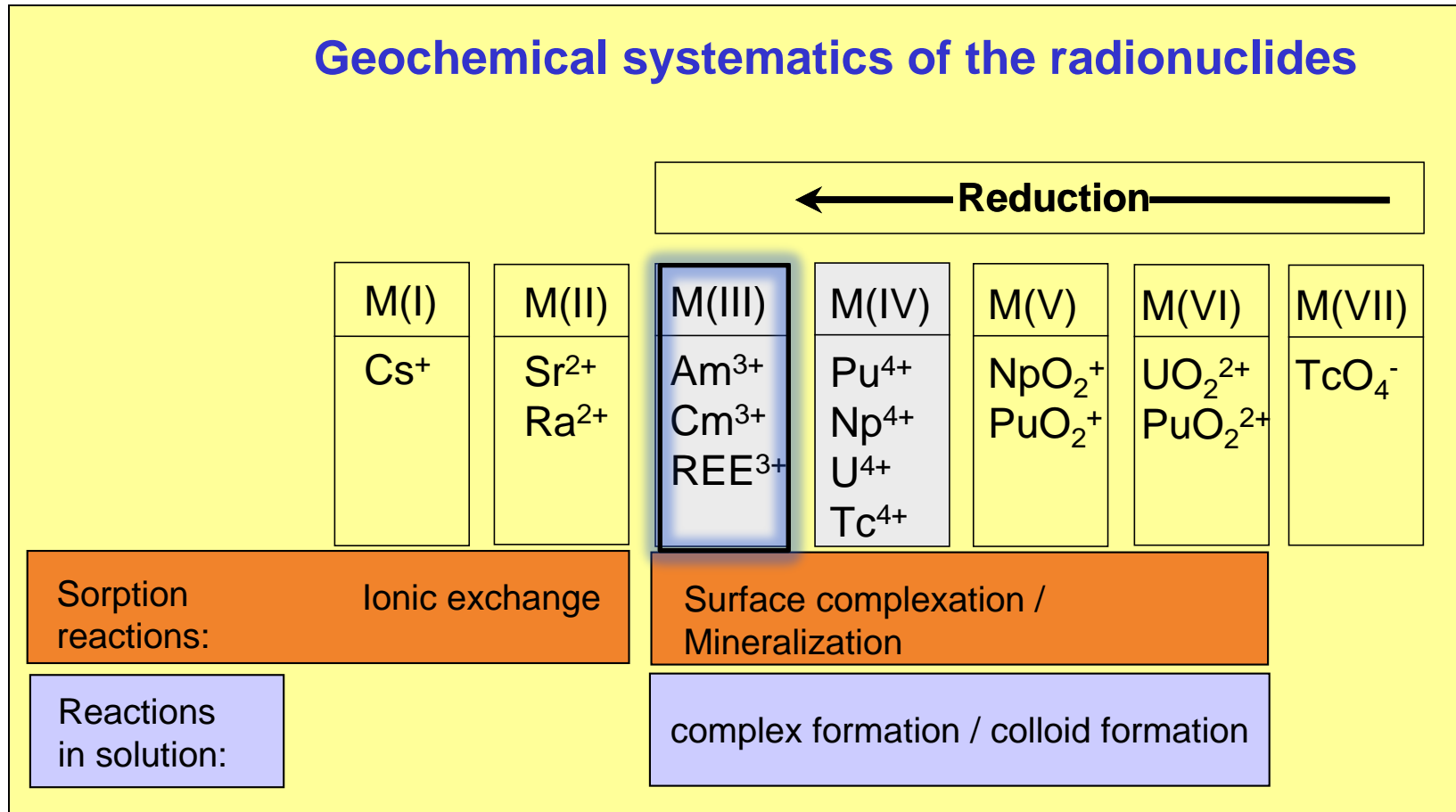
Okumura, M. et al., Mechanism of Strong Affinity of Clay Minerals to Radioactive Cesium: First-Principles Calculation Study for Adsorption of Cesium at Frayed Edge Sites in Muscovite, Journal of the Physical Society of Japan, vol.82, no.3, 2013, p.033802-1-033802-5.

- This difference in behavior may be related to the difference in the illite studied, i.e. a **soil-type illite** (Comans and Hockley, 1992; Smith and Comans, 1996; de Koning and Comans, 2004), which would be more altered with **more open “FES”** than a **sedimentary formation-type illite**.

- This stresses the need to study not only generic clay samples but also samples that are relevant to the sites/ buffer/ backfill material under consideration.
- Chemical purification might induce artefacts.

# Radionuclides to be discussed

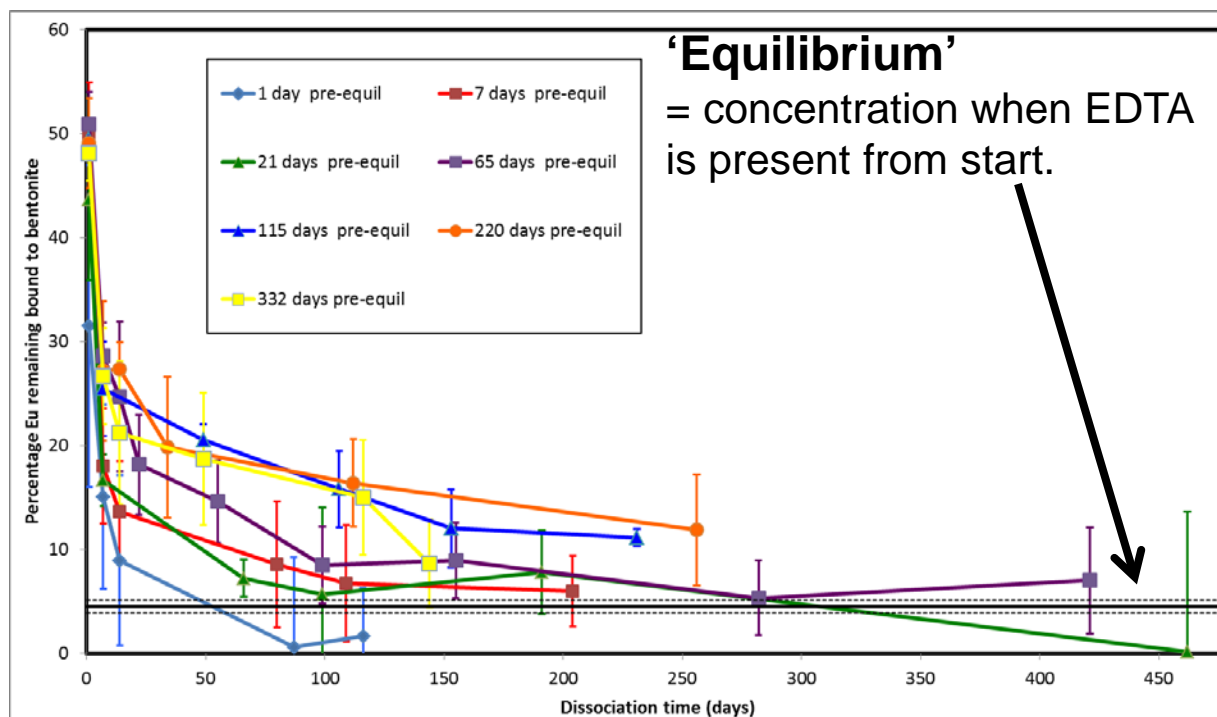
## Geochemical systematics of the radionuclides



# Eu(III) reversibility vs. irreversibility

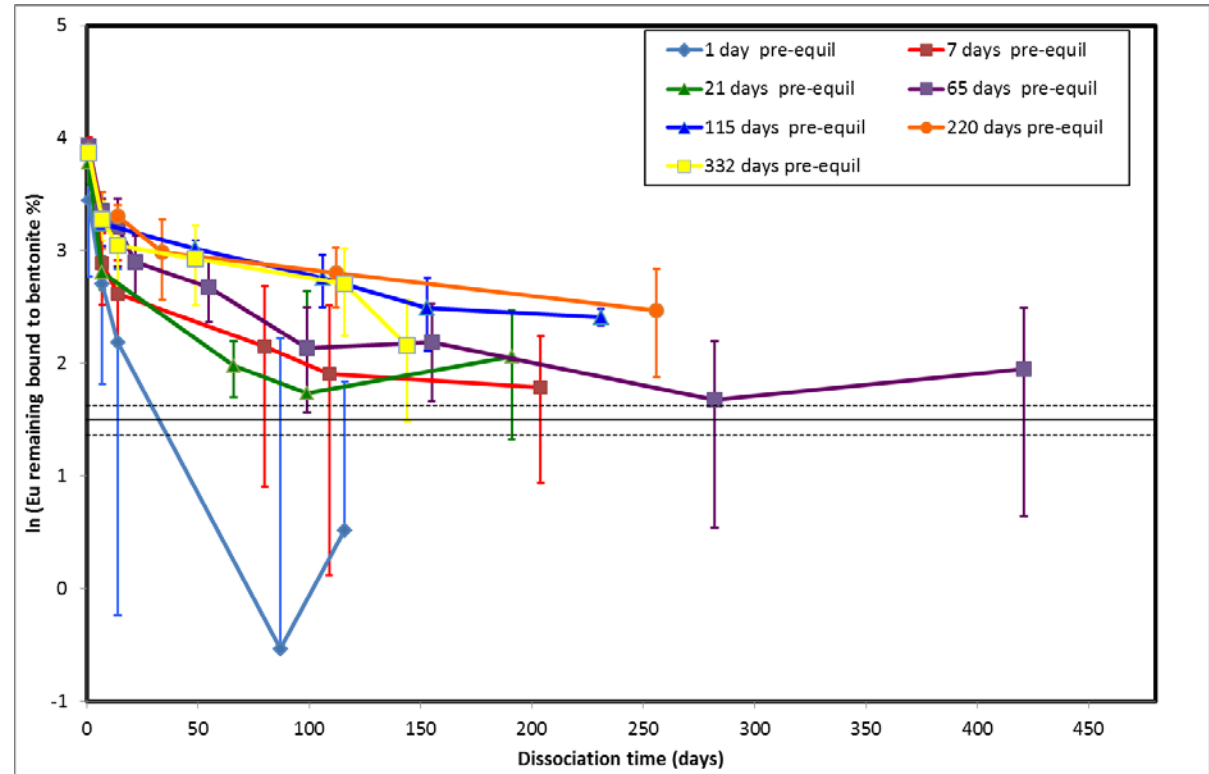
**Bulk Ligand competition experiments (EDTA)**

**Na-Montmorillonite (Wyoming) SWy-1**



- Evidence for slow release of Eu(III) from the bentonite;
- Amount of 'non-exchangeable' Eu(III) increases with pre-equilibration time;
- All systems still heading towards equilibrium.

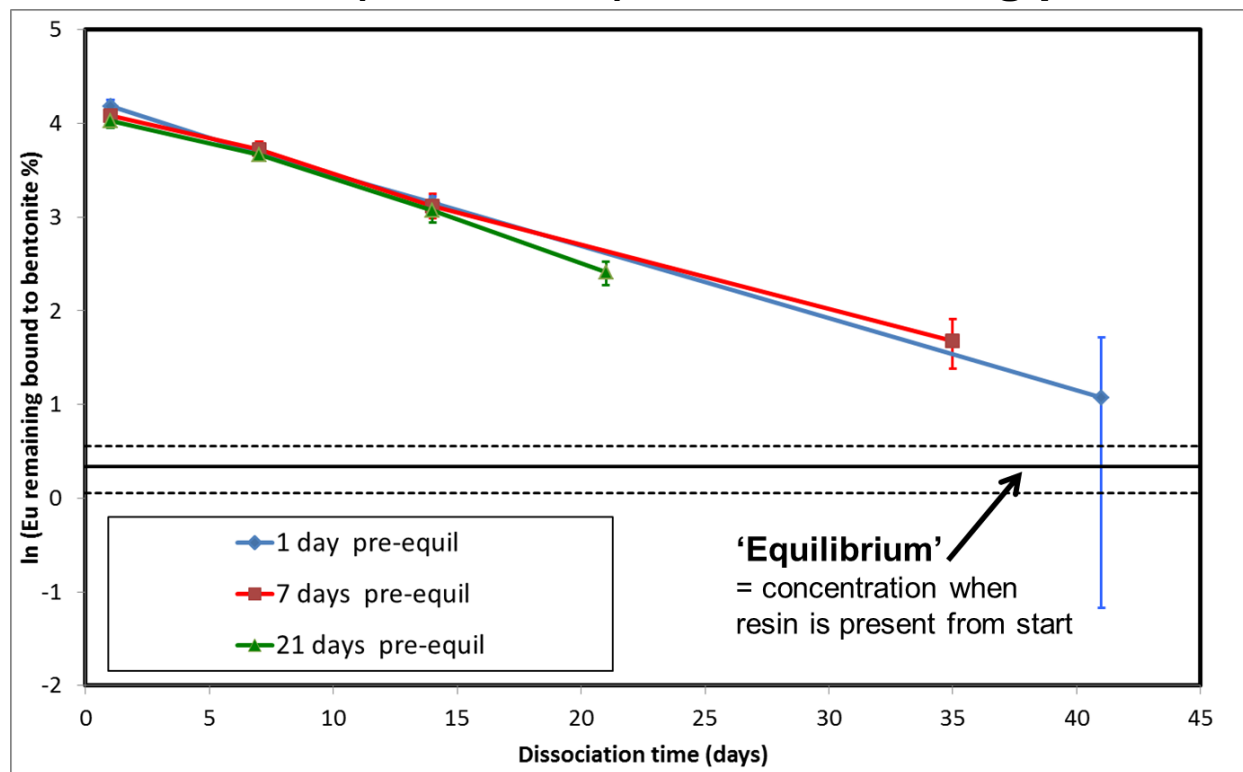
## Ligand competition experiments (EDTA): log plots



- Dissociation rate constant does not depend upon pre-equilibration time (beyond 1 week);
- Small increase in amount slowly dissociating with time.

## Colloid (200-500nm) dissociation: log plots

### Colloid Ligand competition experiments (EDTA)



- Kinetics are remarkably uniform between the different systems;
- Unlike the bulk experiments, a single dissociation rate can describe the dissociation kinetics from 1 day onwards.

## Dissociation Rate Constants Eu(III)

### BULK BENTONITE

Average rate constant:  $5.67 \times 10^{-8} \text{ s}^{-1}$   $(1.8 \text{ a}^{-1})$

Rate constant range:  $3.7 \times 10^{-8} - 1.0 \times 10^{-7} \text{ s}^{-1}$

Amount: approximately 25%, constant after 100 days

### COLLOIDAL BENTONITE

Average rate constant:  $8.9 \times 10^{-7} \text{ s}^{-1}$   $(28.1 \text{ a}^{-1})$

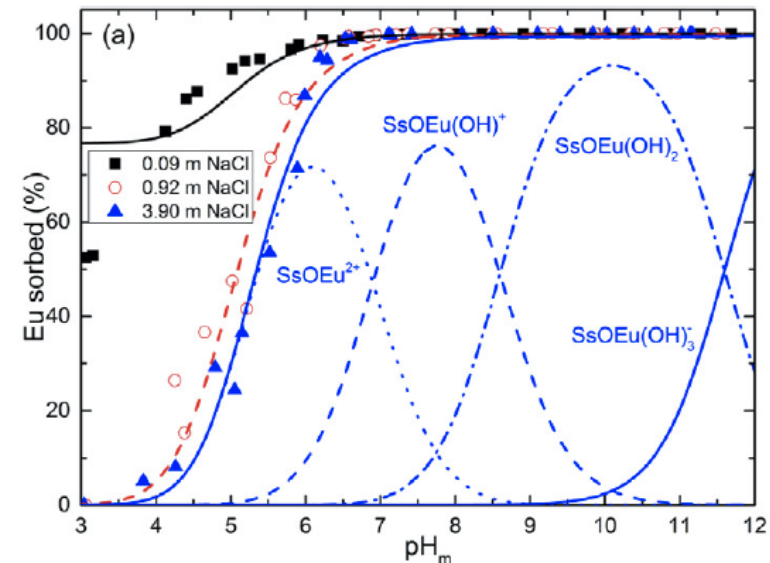
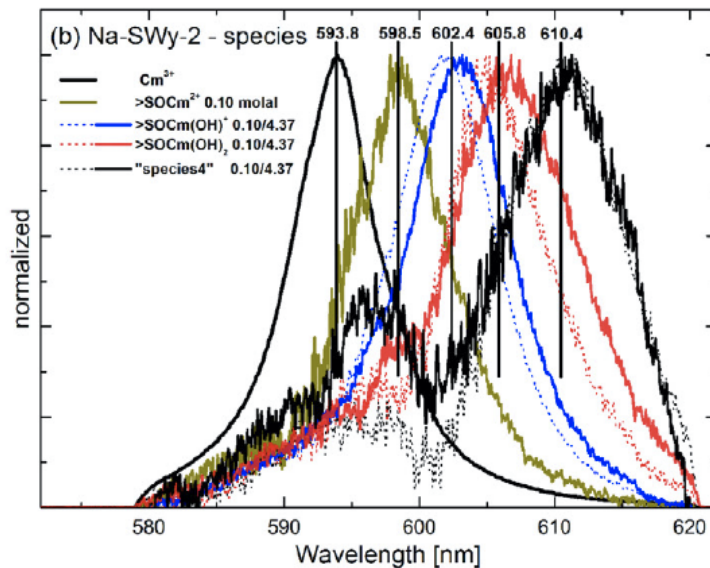
Rate constant range :  $8.3 \times 10^{-7} - 9.5 \times 10^{-7} \text{ s}^{-1}$

Amount: 64 – 70%, independent of pre-equil' time



# Spectroscopic evidence for full reversibility?

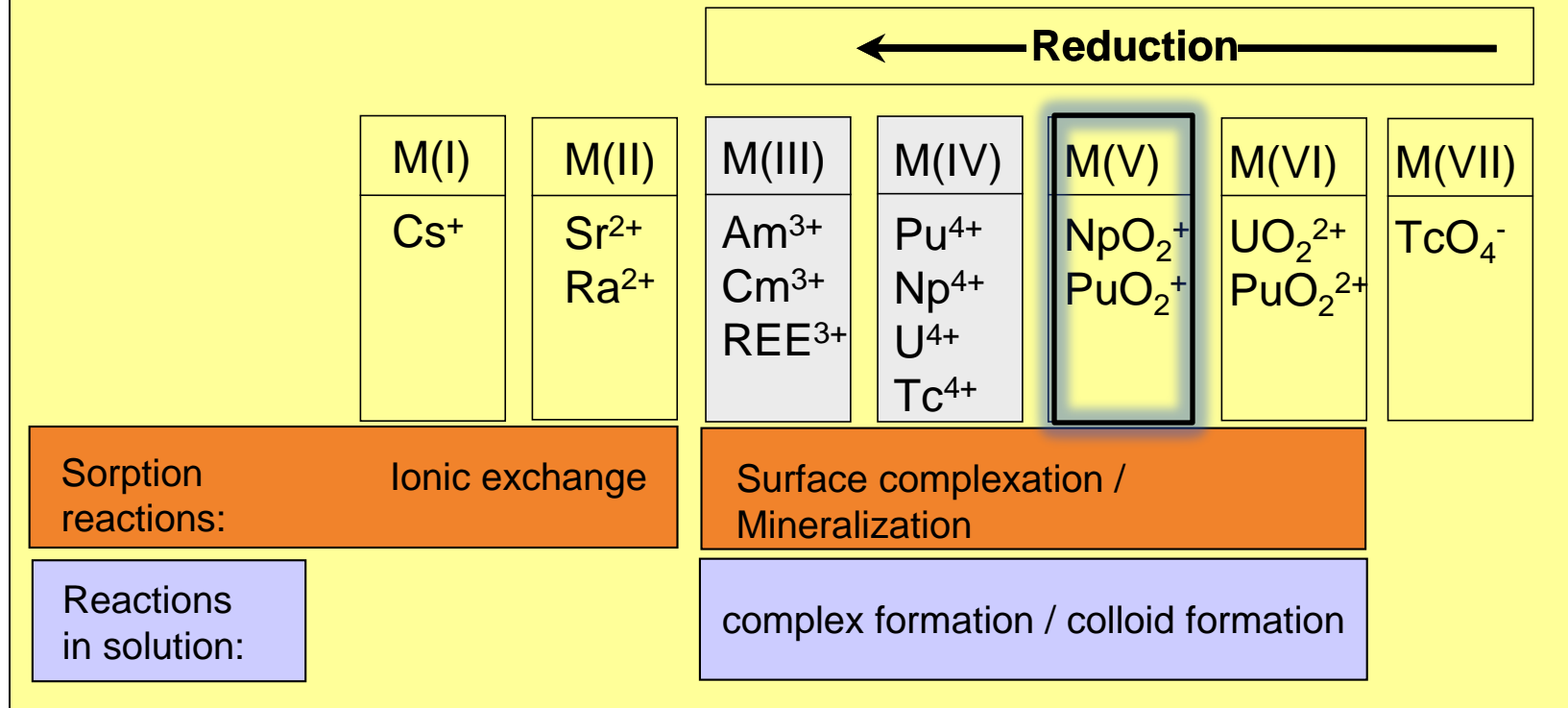
Schnurr, A.; Marsac, R.; Rabung, T.; Lützenkirchen, J.; Geckeis, H., Sorption of Cm(III) and Eu(III) onto clay minerals under saline conditions: Batch adsorption, laser-fluorescence spectroscopy and modeling. *GCA* **2015**, *151*, 192-202.



- Fluorescence lifetime ( $\tau$ ) measurements up to weakly alkaline pH conditions show in addition to the Cm3+ aquo ion with  $t = 68 \pm 2 \mu\text{s}$  a lifetime component of  $t = 120 \pm 15 \mu\text{s}$  for montmorillonite which can be attributed to inner-sphere surface species
- => No indication of structural incorporation / irreversible sorption**

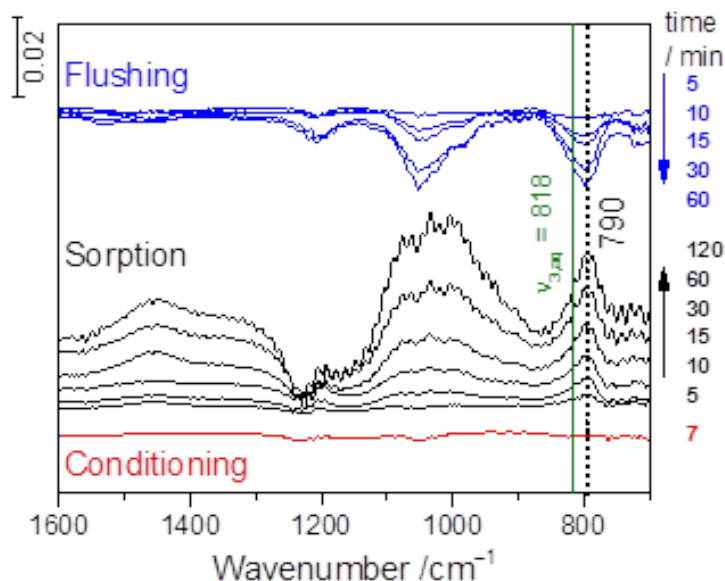
# Radionuclides to be discussed

## Geochemical systematics of the radionuclides

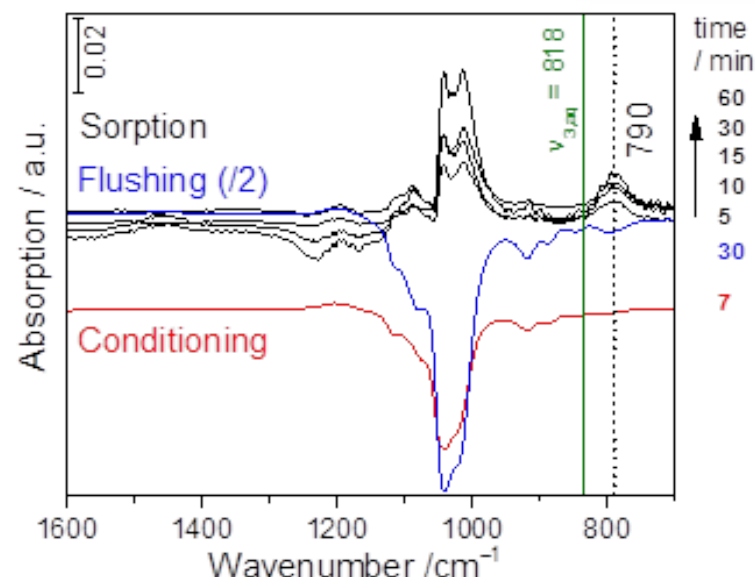


# ATR FT-IR measurements of Np(V) sorption

## corundum



## montmorillonite

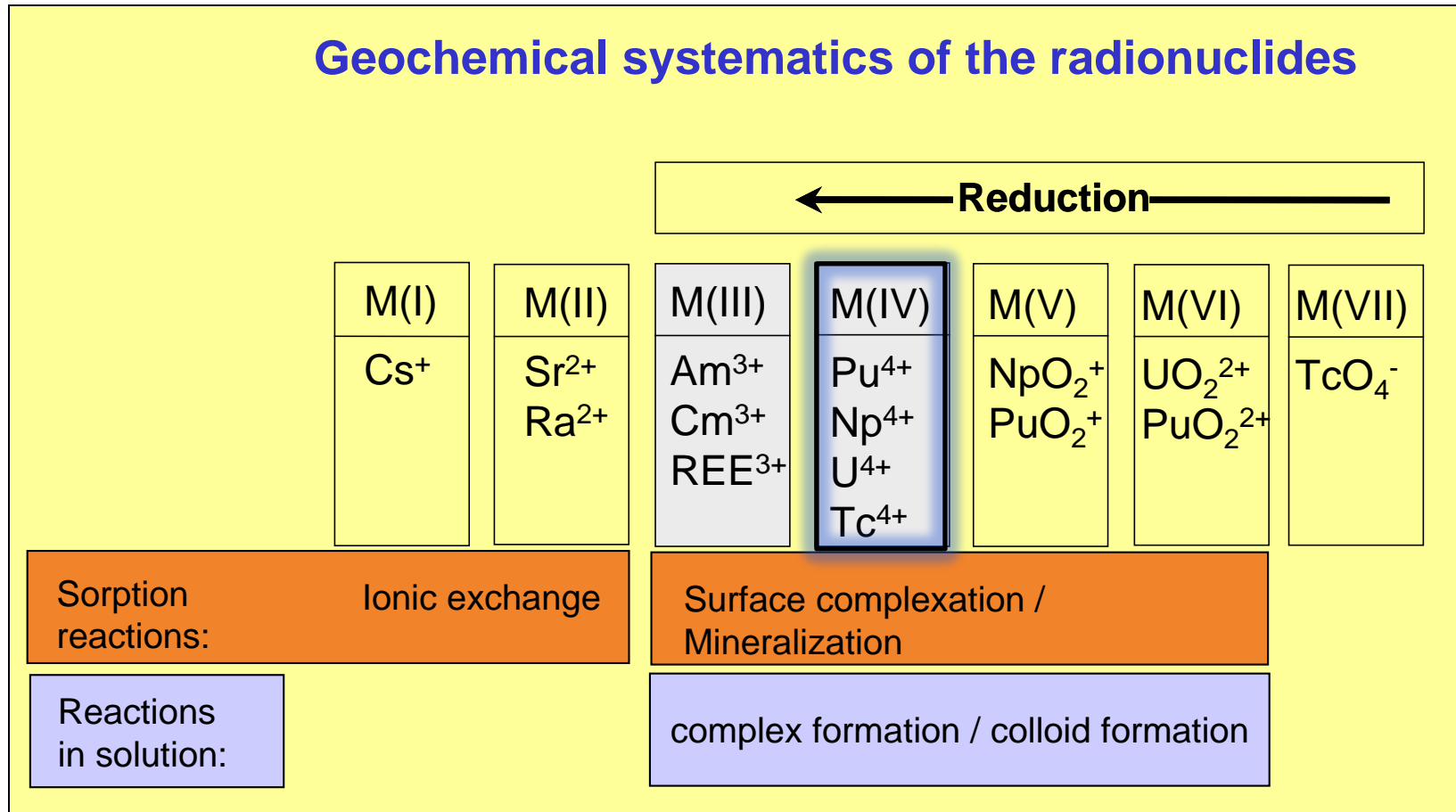


50  $\mu\text{M}$  Np(V); 0,01 M NaCl in  $\text{D}_2\text{O}$ ; pD 9.6; flow rate 0.1 mL/min.

- Fast desorption kinetics could be observed with ATR-FT IR, where a complete removal of the neptunium(V) sorption complex characterized by an adsorption band at 790  $\text{cm}^{-1}$  was observed.

# Radionuclides to be discussed

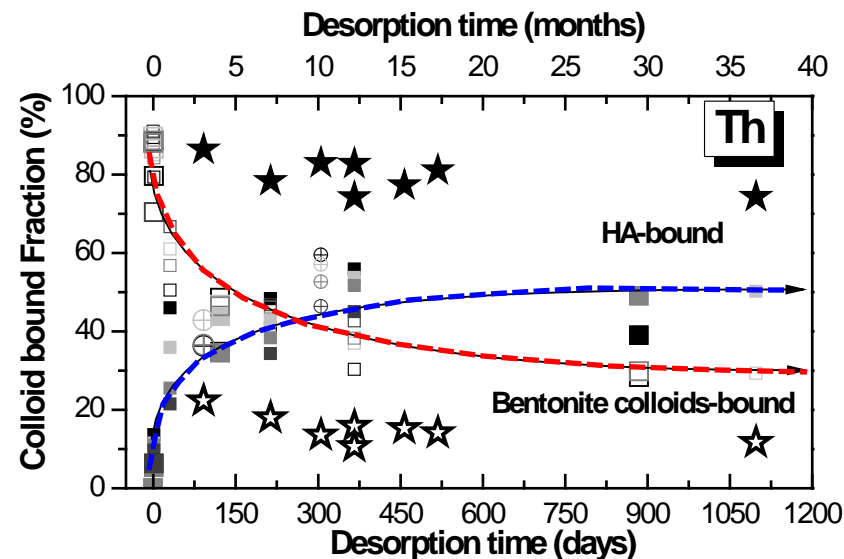
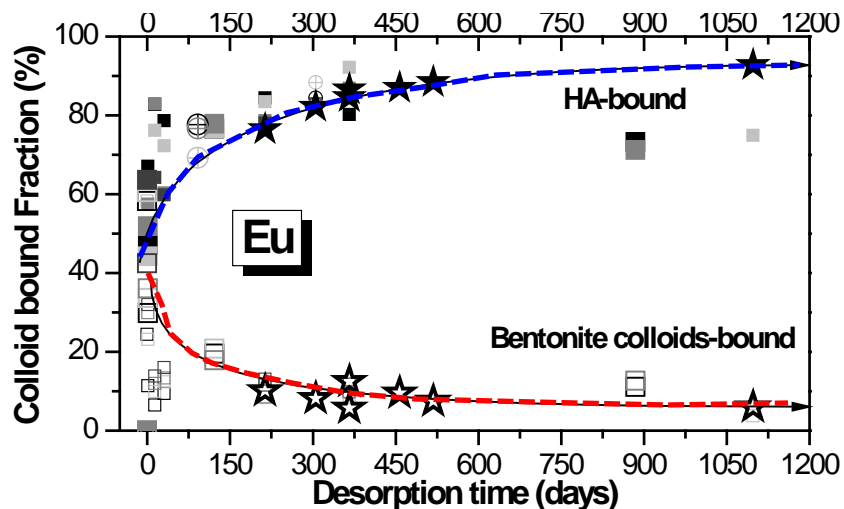
## Geochemical systematics of the radionuclides



# 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!**

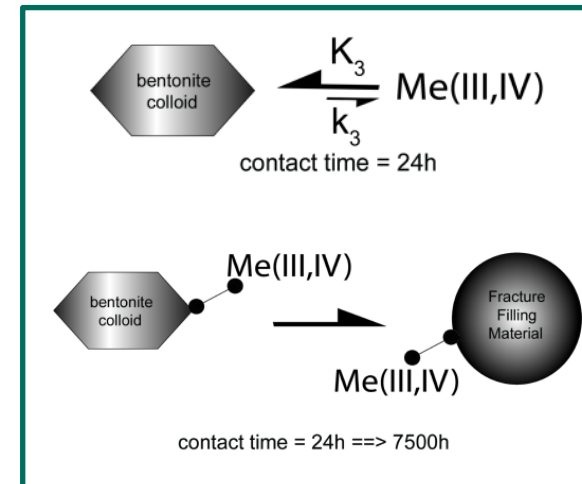
# Bentonite radionuclide **desorption kinetics**

Huber et al. (2011) *Appl. Geochem.* 26, 2226.; Huber et al. (2015) *GCA* 148, 426.

**From binary system data**  
(Note: No colloid – FFM interaction)

$$R_{d,tot} = \frac{K_{d,FFM}}{1 + C_C \cdot K_{d,coll}}$$

\*Binary data from NTB 03-02



	<sup>232</sup> Th(IV)	<sup>242</sup> Pu(IV)	<sup>243</sup> Am(III)
syn. Zn-Montm.	8.0 [a <sup>-1</sup> ]	2.0 [a <sup>-1</sup> ]	10.5 [a <sup>-1</sup> ]
syn. Ni-Montm.	0.03 [a <sup>-1</sup> ]	13.2 [a <sup>-1</sup> ]	10.5 [a <sup>-1</sup> ]
FEBEX bentonite colloids	not possible	7.8 [a <sup>-1</sup> ]	32.4 [a <sup>-1</sup> ]

**Pu(IV) desorption rate (M. Zavarin, LLNL): 1.5 [a<sup>-1</sup>]**

# Desorption experiments on MX-80, the Th(IV) case $[^{232}\text{Th}] = 10^{-8}\text{M}$

Norrfors et al, 2016, *Applied Clay Science* (in preparation).

## ■ pH decrease to 2.7

- Th: is initially sorbed ( $> 95\%$ ) to all clay colloidal fractions. After 1 year at pH 2.7, whatever the first sorption contact times,  $80 \pm 5\%$  of the Th are desorbed from the clay colloids.

## ■ Ionic strength increase: 0.5 M IS with $\text{CaCl}_2$ , pH 7.4

- Th and Pu: previously sorbed remain associated with the clay colloids which sediment.

## ■ Addition of crushed bedrock material (CBM): S/L 1:4

- After 1 year, drastic changes are observed as a function of contact time prior to the addition of the CBM and the clay colloidal size fractions. Longer  $t_{\text{sorp}}$  reduces the colloid desorption as well as smaller size fractions.

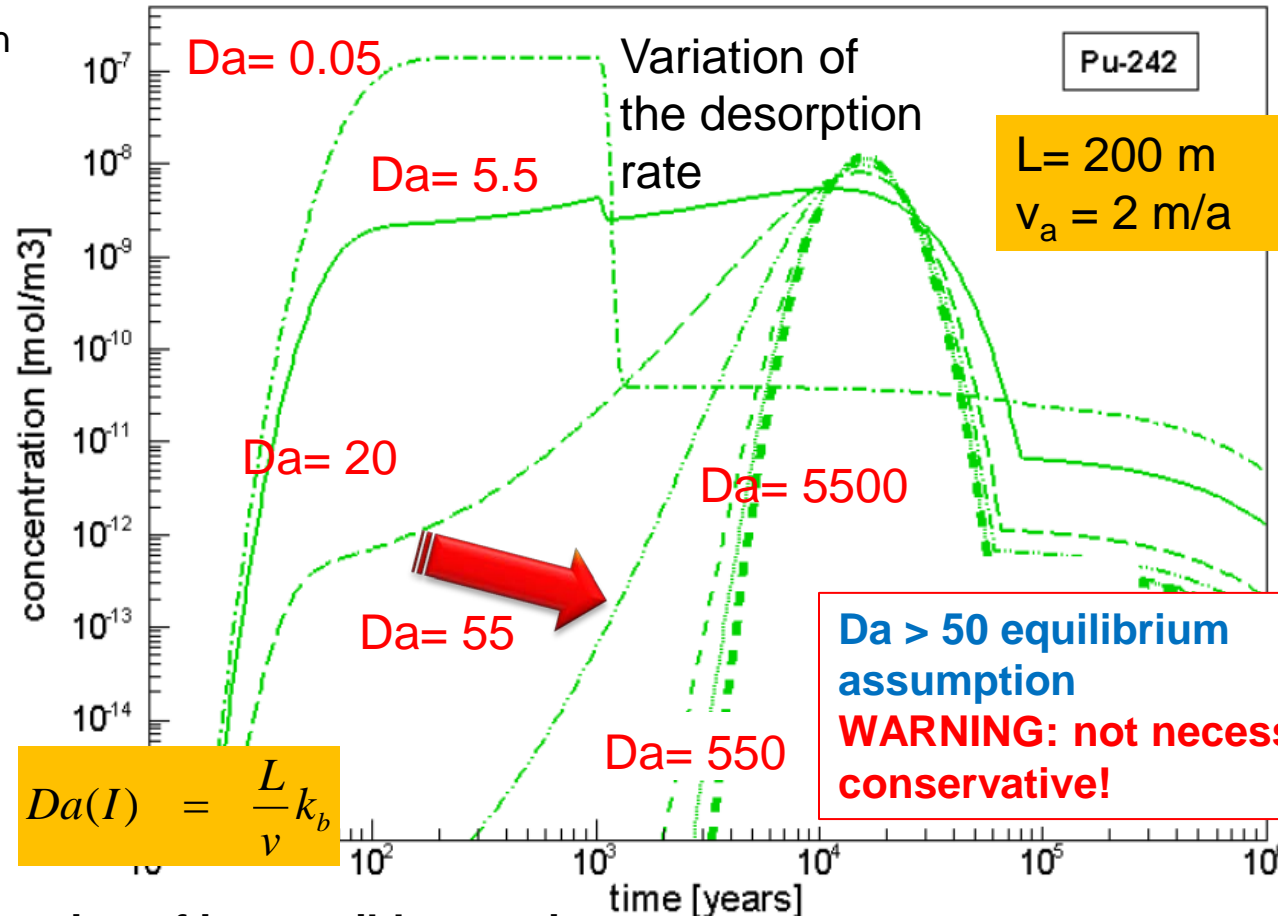
## ■ Addition of FA ( $5 \text{ mg}\cdot\text{L}^{-1}$ ) after different contact time

- No strong desorption (not more than  $10\%$  after 1 year), whatever the clay colloidal size fractions.



# Upscaling: Reference case for a generic German repository in crystalline rock TRAPIC/ COFRAME

- No colloid filtration
- 20 mg/L colloids

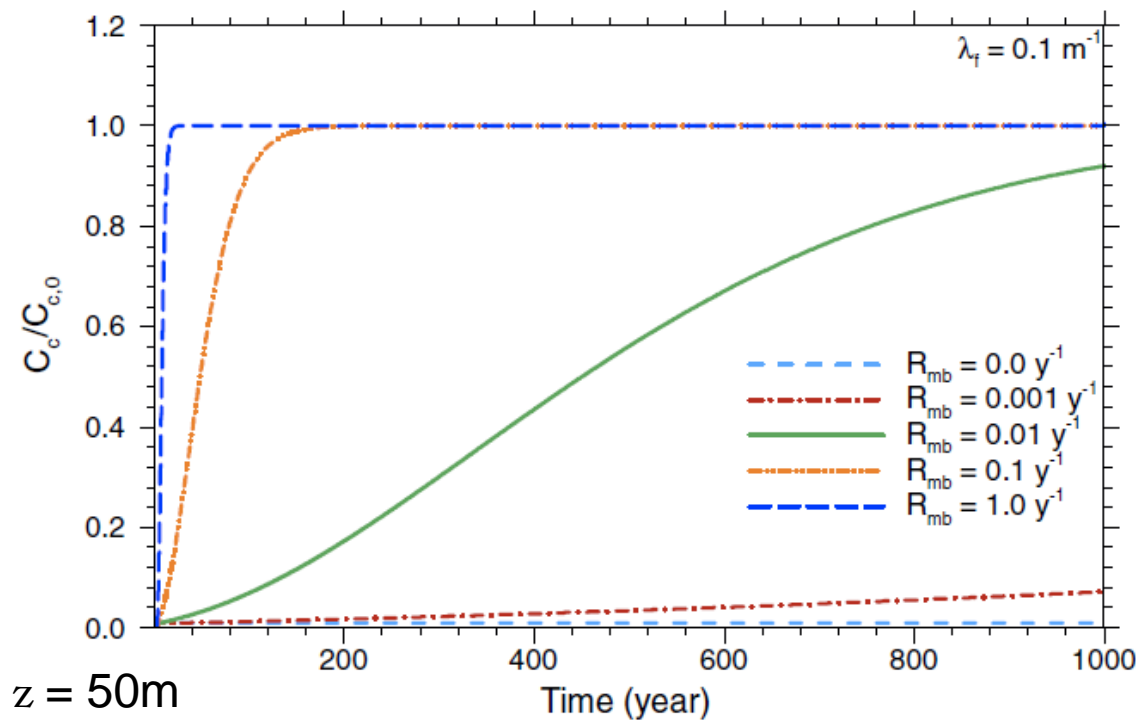


**Da < 1/50: assumption of irreversible sorption**

FZKA report 7515 (2010) & KIT Sci. report 7645 (2014)

# Effect of colloid remobilization

Parameter	Symbol	Value
Fracture aperture	$2b$	0.0001 m
Colloid velocity	$u_c$	13.05 m/year
Filtration coefficient	$\lambda_f$	$0.1 \text{ m}^{-1}$
Longitudinal dispersion length for colloids	$\alpha_c$	0.5 m



Reiche, Noseck & Schäfer,  
*Transport in Porous Media*  
**2016, 111, 143-170.**

## ■ Deliverables

### Work Package 3

D3.1	Progress report on microscale investigations on colloid mobility controlling processes.	MSU, CIEMAT, KIT-INE,	R	PU	15	
D3.2	Macroscale investigations on colloid mobility in near-natural systems	HU, UJV/REZ, CIEMAT, KIT-INE	R	PU	15	✓
D3.3	Process understanding of radionuclide colloid interaction with special emphasis on sorption reversibility	UNIMANCH, CIEMAT, KIT, HU	R	PU	15	✓
D3.4	Progress report on microscale investigations on colloid mobility controlling processes.	MSU, CIEMAT, KIT-INE,	R	PU	27	✓
D3.5	Macroscale investigations on colloid mobility in near-natural systems	HU, UJV/REZ, CIEMAT, KIT-INE	R	PU	27	✓
D3.6	Process understanding of radionuclide colloid interaction with special emphasis on sorption reversibility	UNIMANCH, CIEMAT, KIT, HU	R	PU	27	✓
D3.7	Progress report on microscale investigations on colloid mobility controlling processes.	MSU, CIEMAT, KIT-INE,	R	PU	39	✓
D3.8	Macroscale investigations on colloid mobility in near-natural systems	HU, UJV/REZ, CIEMAT, KIT-INE	R	PU	39	✓
D3.9	Process understanding of radionuclide colloid interaction with special emphasis on sorption reversibility	UNIMANCH, CIEMAT, KIT, HU	R	PU	39	✓
D3.10	Mechanistical model of radionuclide colloid interaction	UNIMANCH, CIEMAT, KIT, HU	R	PU	44	
D3.12	WP3 partners final report on experimental results on micro- to macroscale colloid rock interaction and colloid radionuclide interaction	KIT-INE	R	PU	44	

## Thank you for your attention!

This work has been funded by the European Atomic Energy Community's 7<sup>th</sup> Framework Programme (FP7/2007-2011) under grant agreement no. 295487 (BELBaR Project)



....missed the celebration by one day!!!!