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Supplement of

Hydrogeochemical impact of Opalinus Clay system shown in migration lengths of uranium

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Hydrogeochemical impact of Opalinus Clay system shown in migration lengths of uranium

Theresa Hennig[1] and Michael Kühn[1,2]

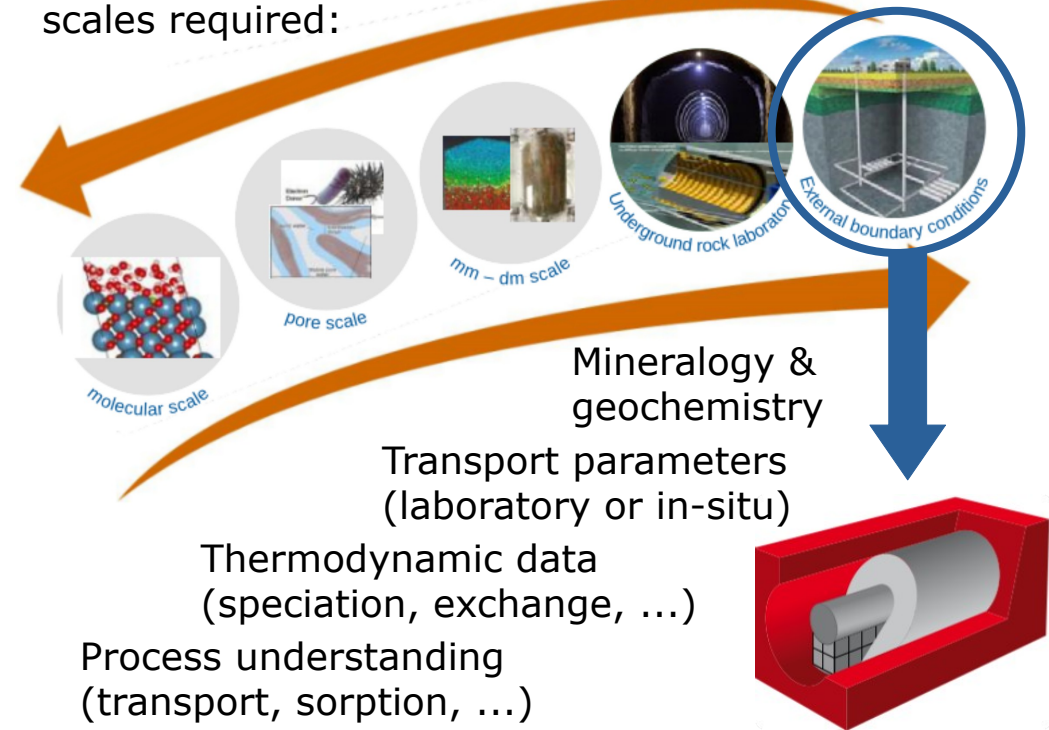[1] GFZ German Research Centre for Geosciences, Potsdam, Germany

[2] University of Potsdam, Institute of Geosciences, Potsdam, Germany
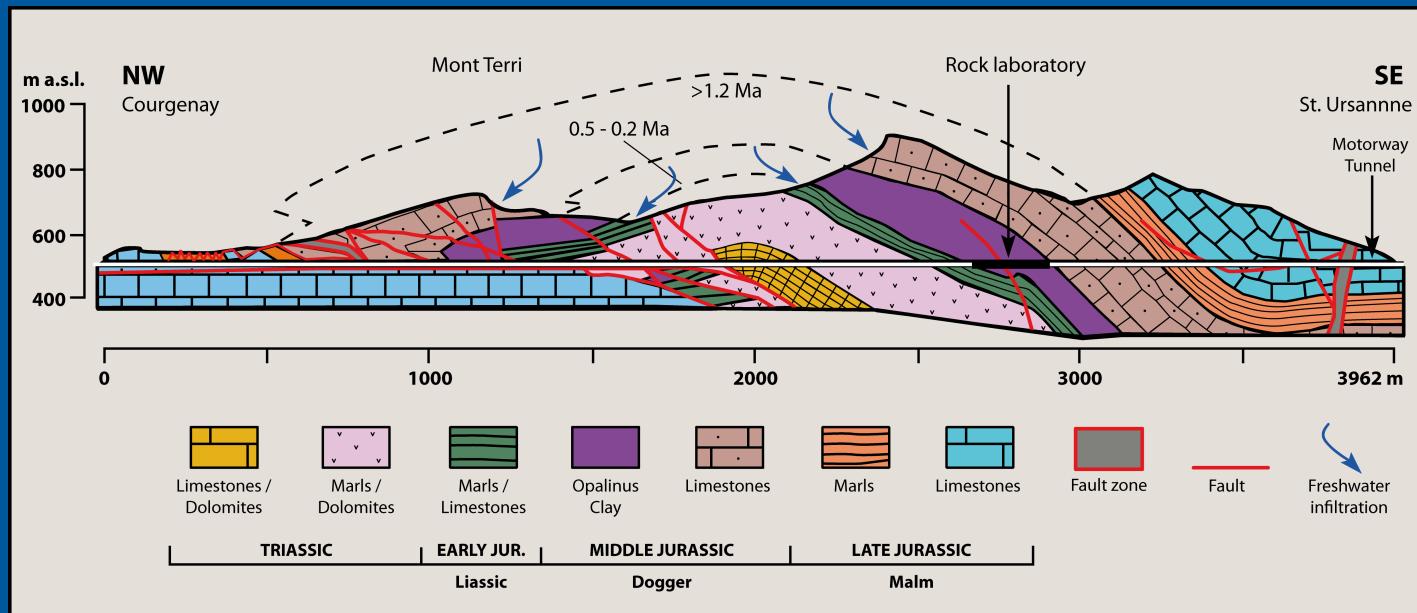
Quantifying radionuclide migration essential for safety assessments of potential nuclear waste disposals

- **Host rocks** are natural and **final barrier** isolating radionuclides from human environment

- **Numerical simulations** are only way to cover spatial (>100 m) and temporal (1 Ma) scales **required**

- Focus on **migration** of **uranium**, the main component of spent fuel, in potential host rock **Opalinus Clay**

iCross-Project

Data from various scales required:

molecular scale

pore scale

mm – dm scale

Underground rock laboratory

External boundary conditions

Mineralogy & geochemistry

Transport parameters (laboratory or in-situ)

Thermodynamic data (speciation, exchange, ...)

Process understanding (transport, sorption, ...)

Nagra (2007)

Opalinus Clay is heterogeneous in mineralogy and pore water geochemistry

How can radionuclide migration be quantified with transport simulations?

→ Classical approaches apply Fick's 2nd law:

Species concentration

Effective diffusion coefficient

$$\frac{\partial C}{\partial t} = \frac{D_e}{(\epsilon + K_d \rho_b)} \cdot \frac{\partial^2 C}{\partial x^2}$$

Time

Accessible porosity

Distribution coefficient

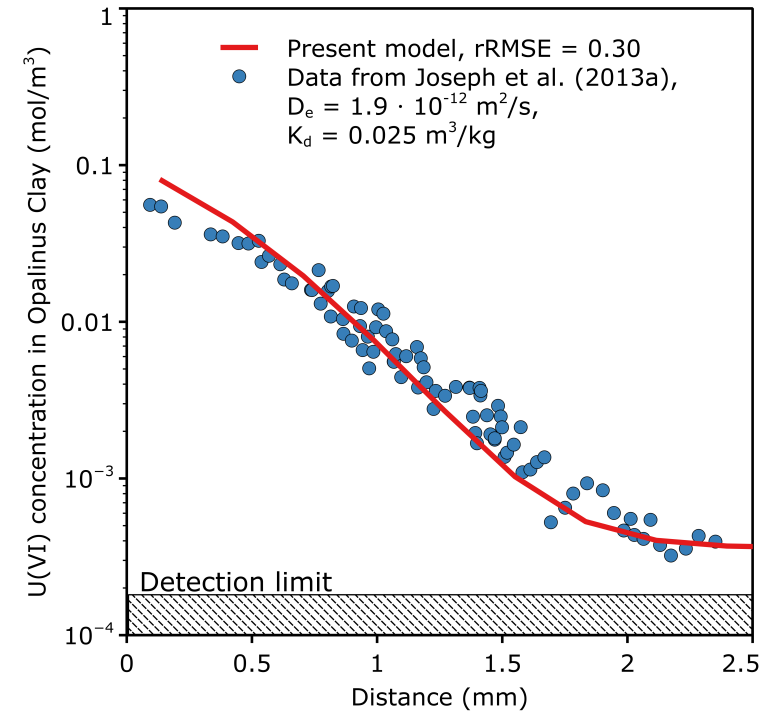Dry bulk density

Spatial coordinate

→ Experimentally determined for geochemically and mineralogically constant boundary conditions
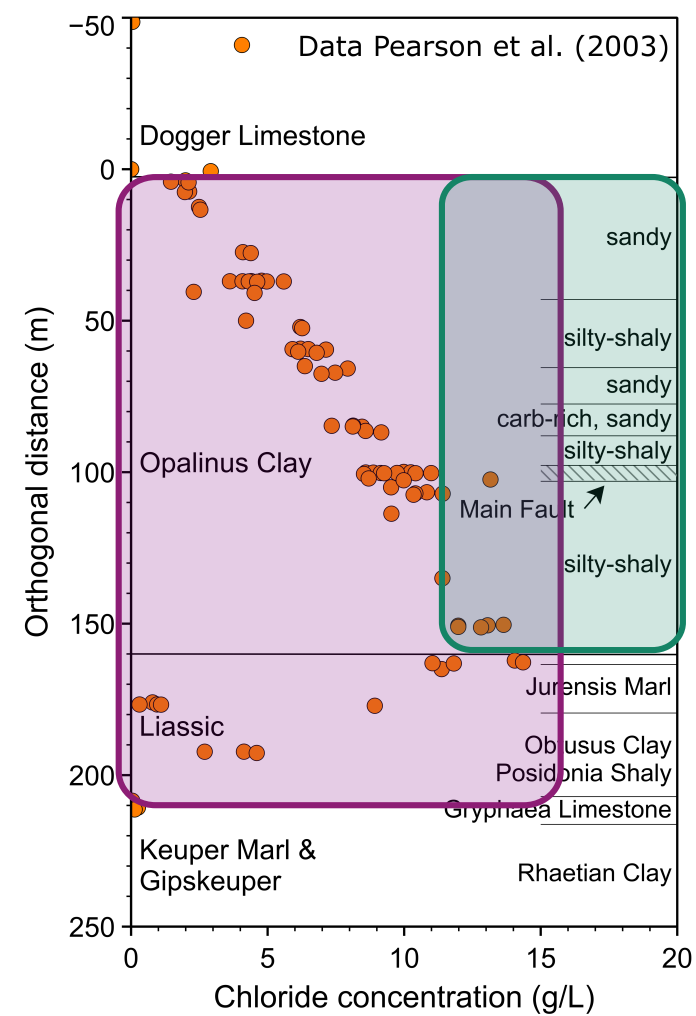
Sorption of uranium species quantified based on competitive effects from individual clay minerals

- 1D continuum scale simulations are conducted with PHREEQC on laboratory and host rock scale

- Diffusion is quantified with single-component approach following Fick's diffusion

- Sorption processes integrated via cation exchange and mechanistic surface complexation models

- Geochemical and mineralogical data stems from borehole analysis at Mont Terri

  → Pore water geochemistry controlled by equilibrium with carbonates and pyrite

Present model, rRMSE = 0.30
Data from Joseph et al. (2013a),
$D_e = 1.9 \cdot 10^{-12}$ m^2/s,
$K_d = 0.025$ m^3/kg

U(VI) concentration in Opalinus Clay (mol/m^3)

Detection limit

Distance (mm)

Joseph et al. (2013a,b)
Pearson et al. (2003)
Noseck et al. (2018)

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Geochemical behaviour of Opalinus Clay and uranium speciation depend on calcite-carbonate ion system

Aqueous uranium speciation in pore water of sandy facies with background concentration of 2.5 nmol/L.
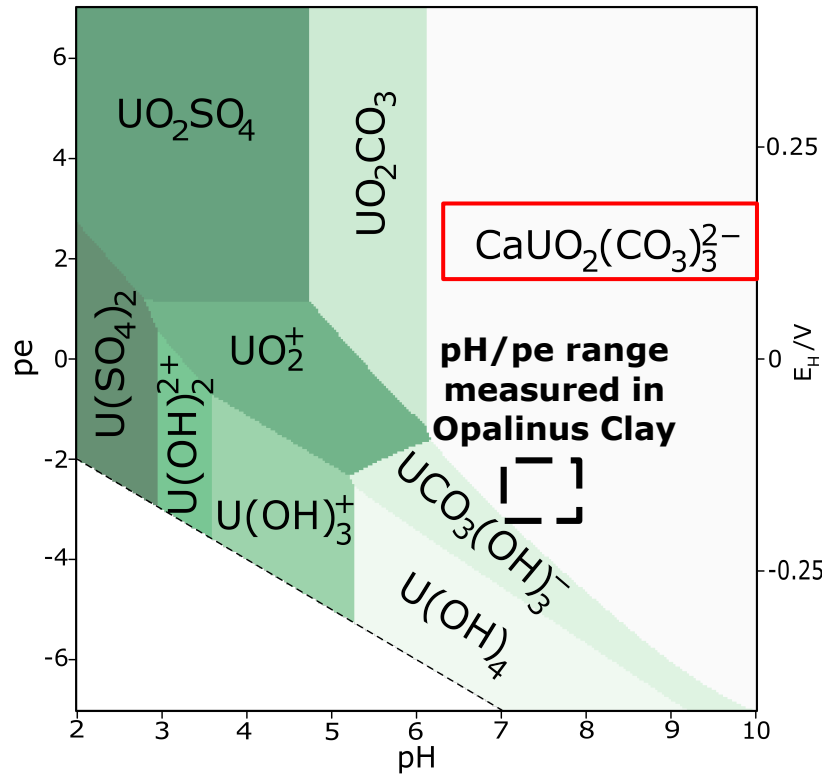
- **Uranium** >90% present as U(VI)

Species	Mol fraction (%)
$CaUO_2(CO_3)_3^{2-}$	70
$MgUO_2(CO_3)_3^{2-}$	16
$Ca_2UO_2(CO_3)_3$	6

→ Regarded as mobile

- **Pore waters equilibrated** for pCO_2 range between -2.5 and -2.0 log bar

→ Correspond to measured values and recommended for clay formations

De Lucia & Kühn (2021)
Hennig et al. (2020)

# Dissolved concentrations of CO_2 and Ca^{2+} more decisive for uranium sorption than pH

- Uranium migrates farther with:
- → decreasing clay mineral quantity
- → increasing pCO_2
- Observed uranium migration varies up to 10 m between individual facies
- Uranium sorption governed by:

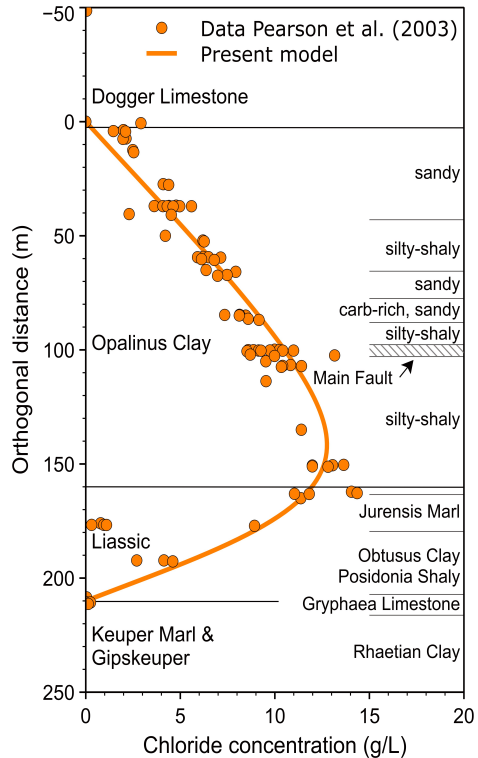1. pCO_2
2. Ca^{2+} concentration
3. pH
4. Clay mineralogy

Geochemistry of pore water controls sorption processes

Lowest sorption **expected**

and **observed**

pH

pCO₂ (log bar)

Facies - wt.% clay minerals
- Shaly - 76
- Shaly - 61
- Sandy - 45
- Carbonate-rich - 26

pCO₂ (log bar)
-2.5   -2.0

	10 m	16 m
	11 m	18 m
	16 m	25 m
	16 m	26 m

5 m

Distance from nuclear waste disposal (m)

Experimental data
— K_d = 0.025 m³/kg (Joseph et al., 2013a)

Uranium concentration pore water (mol/kgw)
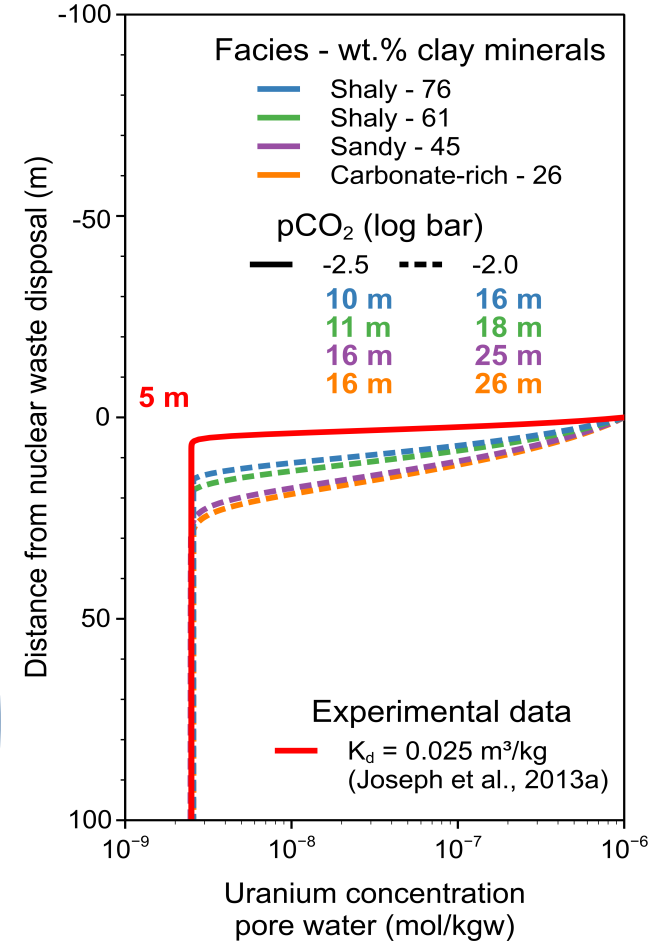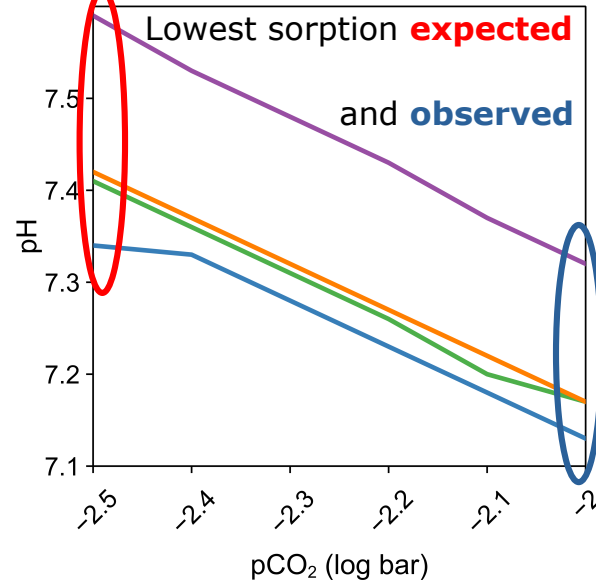
Erosion history of the Mont Terri anticline and associated fresh water infiltration activated the hydrogeological boundaries

Freivogel & Huggenberger (2003)
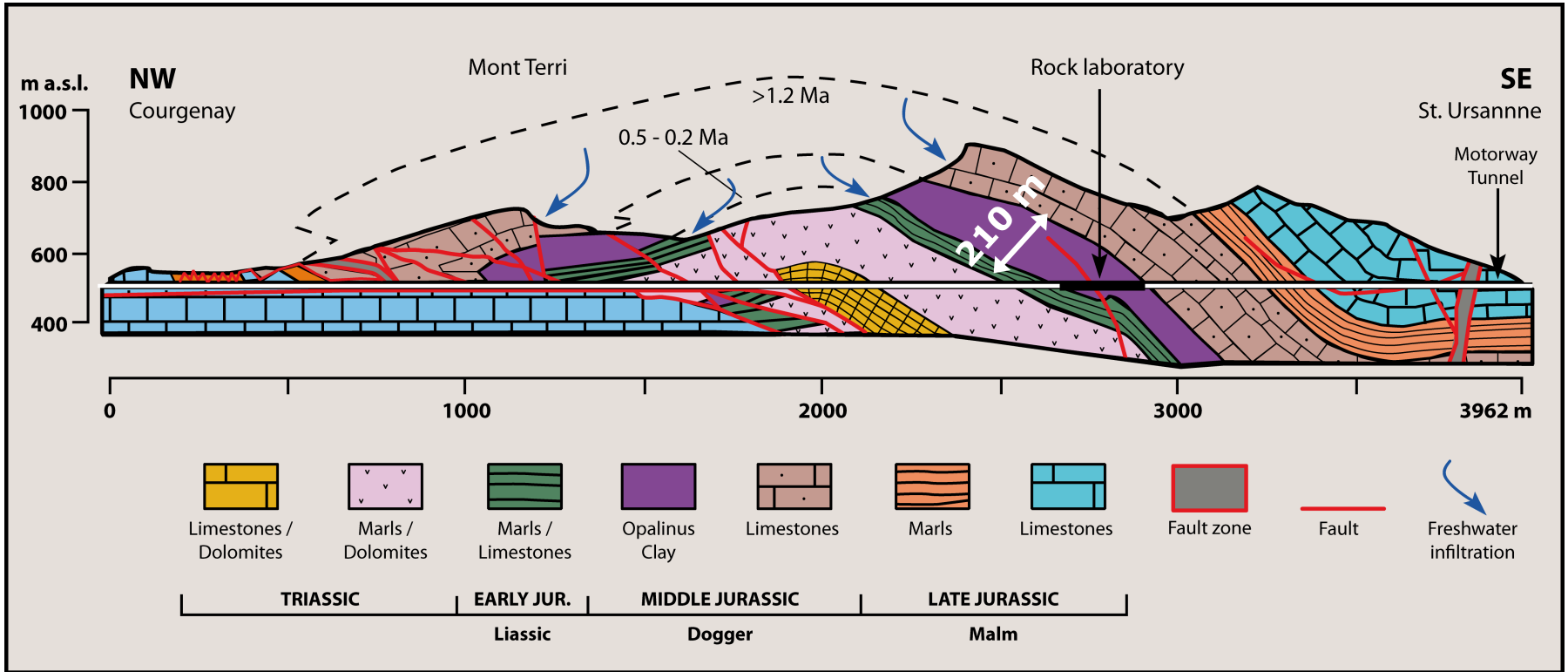
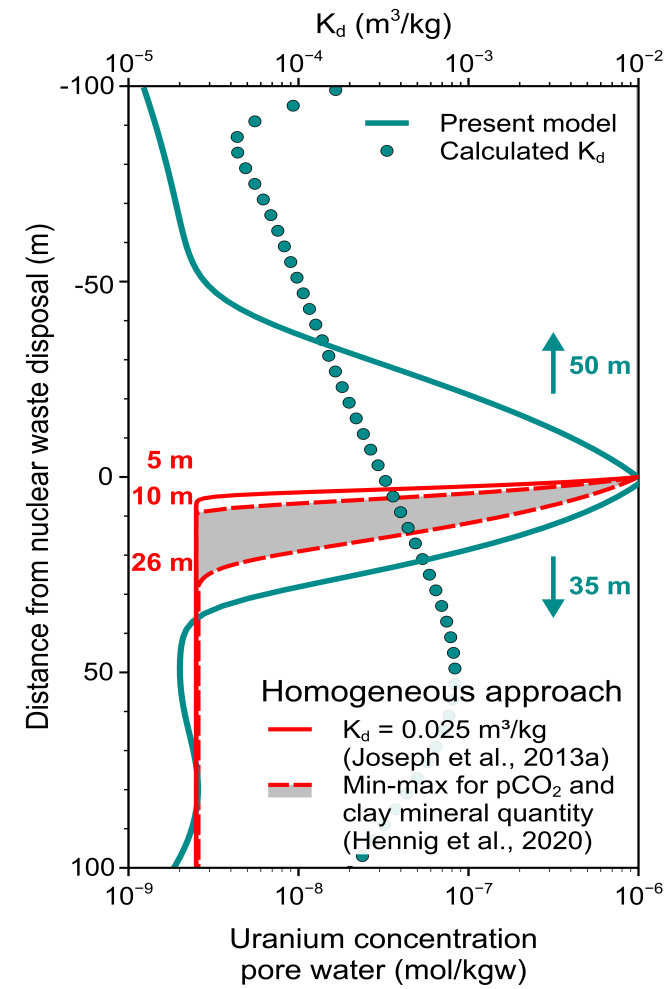# Considering geochemical gradients enhances uranium migration

Sorption capacity (given as calculated K_d values) decreases with gradients,

and thus experimentally determined K_d values are not applicable

Sorption of uranium governed by:
1. pCO_2 (± 10 m)
2. Hydrogeology (± 25 m)
3. Clay mineralogy (± 10 m)


Simulation time = 1 Ma

Thermodynamic data influence speciation and migration models

NEA published update of thermodynamic data:

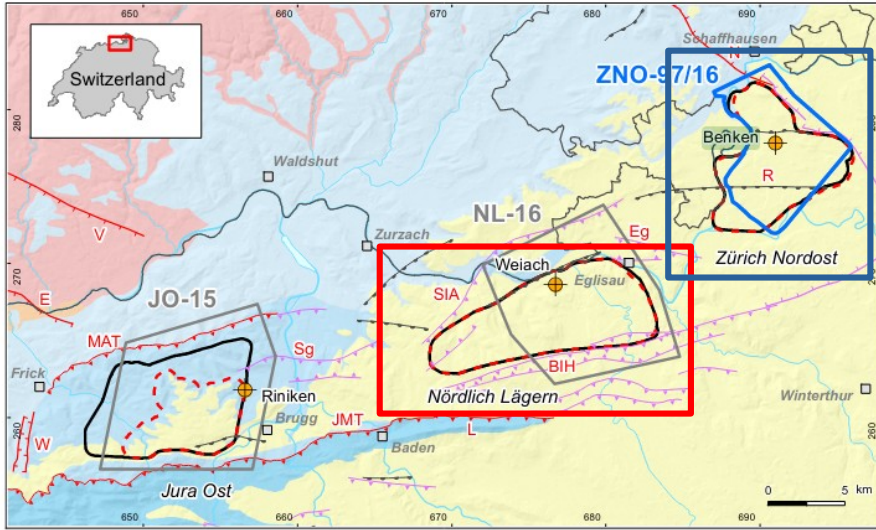| Species	Mol fraction (%) using NEA data of	
	Guillaumont et al. (2003)	Grenthe et al. (2020)
$CaUO_2(CO_3)_3^{2-}$	70	10
$MgUO_2(CO_3)_3^{2-}$	16	2
$Ca_2UO_2(CO_3)_3$	6	88

→ Stronger complexation with carbonate and calcium decreases proportion of uranium available for sorption
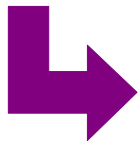
Sorption of uranium governed by:
0. Thermodynamic data (± 30 m)
1. pCO_2 (± 10 m)
2. Hydrogeology (± 25 m)
3. Clay mineralogy (± 10 m)

K_d (m³/kg)

NEA-Data according to
Guillaumont et al. (2003)
Grenthe et al. (2020)
Simulated uranium background concentration

Distance from nuclear waste disposal (m)

80 m

5 m
10 m

26 m

65 m

Homogeneous approach
K_d = 0.025 m³/kg (Joseph et al., 2013a)
Min-max for pCO_2 and clay mineral quantity (Hennig et al., 2020)

Uranium concentration pore water (mol/kgw)

Simulation time = 1 Ma

Hennig & Kühn (2021, 2022)
Hennig (2022)

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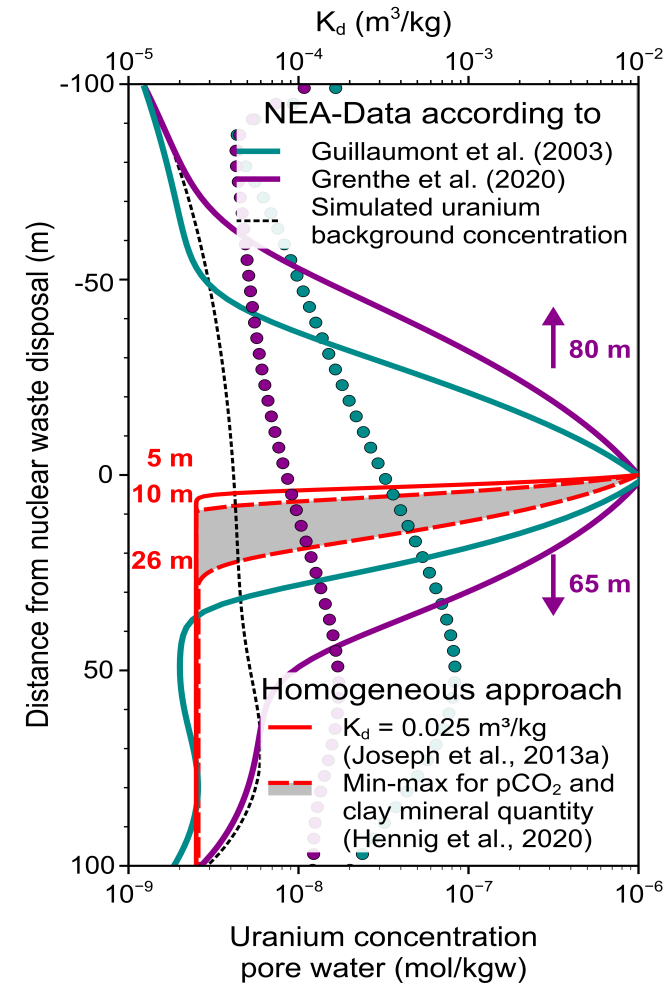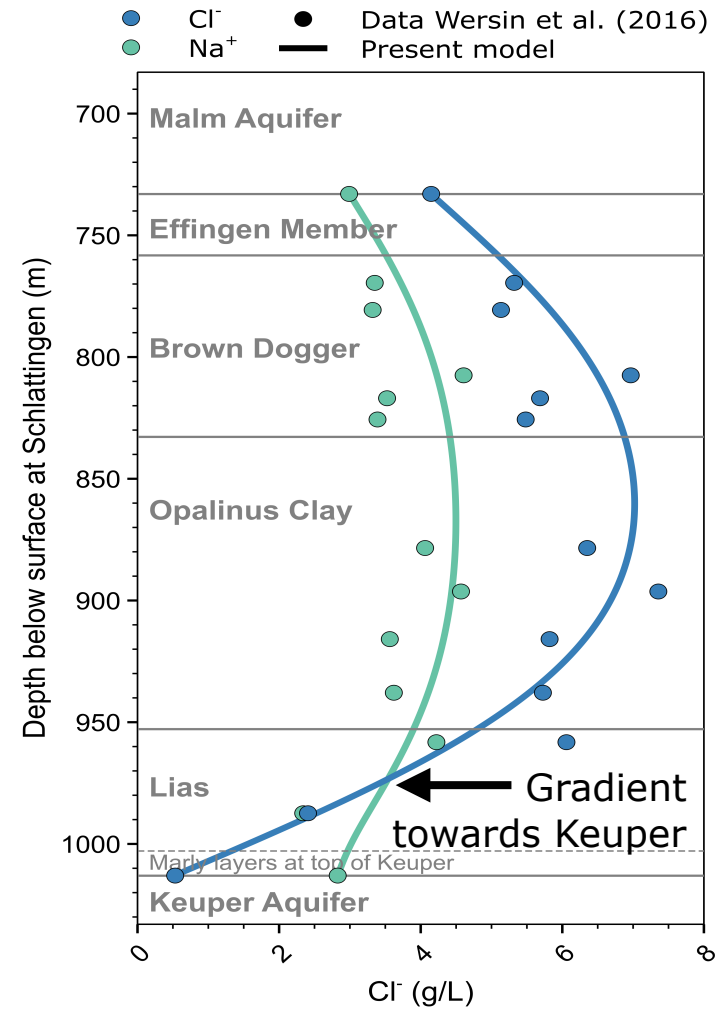
Are geochemical gradients present at the potential disposal sites?

Sorption of uranium governed by:
0. Thermodynamic data (± 30 m)   !
1. pCO₂ (± 10 m)   !
2. Hydrogeology (± 25 m)   √
3. Clay mineralogy (± 10 m)   √

Legend:
- Cl⁻
- Na⁺
- Data Wersin et al. (2016)
- Present model

Gradient towards Keuper

Depth below surface at Schlattingen (m)
Cl⁻ (g/L)

Malm Aquifer
Effingen Member
Brown Dogger
Opalinus Clay
Lias
Marly layers at top of Keuper
Keuper Aquifer

What does the hydrogeological situation at Schlattingen mean for uranium migration?

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Uranium migration depends on pore water composition, geochemical gradients and source term concentration
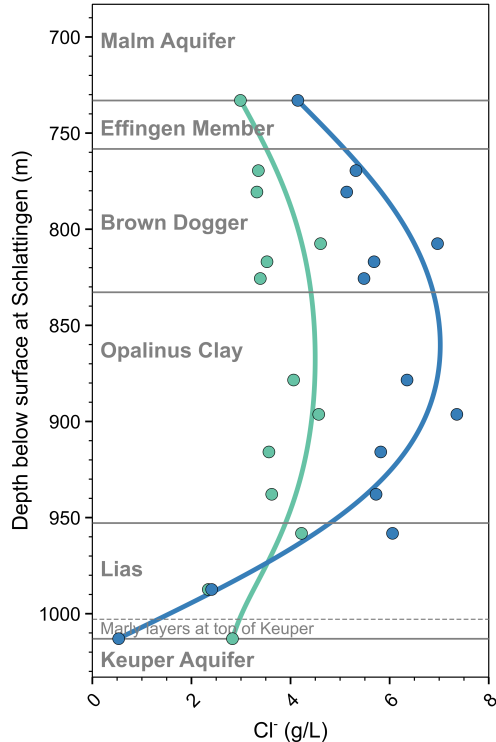
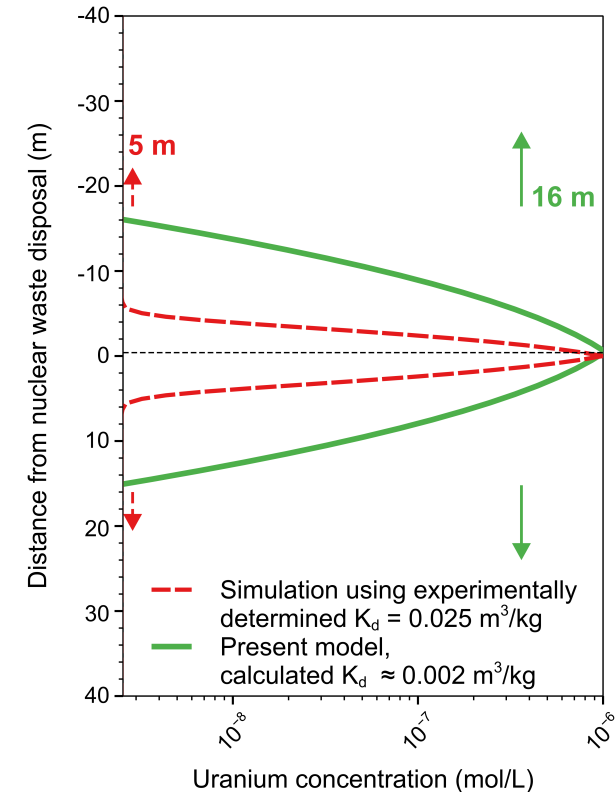Maximum chloride concentration at Mont Terri ~ 15 g/L

Migration lengths depend on spatial and temporal variation of hydrogeology and geochemistry

→ stable conditions enable application of K_d approach to quantify radionuclide migration

→ K_d values need to be determined for in-situ conditions (pCO$_2$)

Simulation using experimentally determined K_d = 0.025 m^3/kg

Present model, calculated K_d ≈ 0.002 m^3/kg

Uranium sorption governed by thermodynamic data and the hydrogeochemical system and less by clay mineralogy

Following points arise due to the range of migration lengths (5 m – 80 m) resulting from reactive transport simulations:

- Hydrogeological system always affects geochemistry and must be considered in safety assessments

- Geological, physical and hydrogeochemical systems are not in a stationary state and constant changes need to be considered

- Coupled models to state questions and formulate hypothesis
  - Geological input data are always inaccurate to a certain degree
  - Experimentally determined data are subject to simplification
  - Data may be missing that is needed for building a model

- Degree of reliability of models derived from comparison with laboratory tests and data from boreholes and underground labs

Thank you very much for your attention!
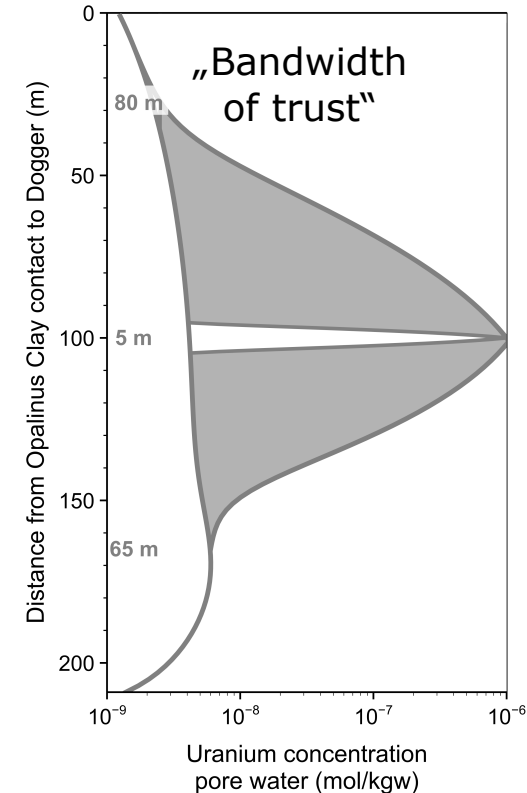
References

De Lucia, M. and Kühn, M. (2021): Advances in Geosciences 56, 33–43. DOI: 10.5194/adgeo-56-33-2021.

Freivogel, M. and Huggenberger, P. (2003): Reports of the FOWG, Geology Series, no 4.: Mont Terri Project – Geology , paleohydrology and stress field of the Mont Terri region, 7–44.

Hennig, T. (2022): Dissertation, University of Potsdam, https://publishup.uni-potsdam.de/frontdoor/index/index/docId/55270.

Hennig, T. and Kühn, M. (2021): Minerals 11 (10), 1087. DOI: 10.3390/min11101087.

Hennig, T. and Kühn, M. (2022): Advances in Geosciences, 58, 11–18, DOI: 10.5194/adgeo-58-11-2022.

Hennig, T. and Kühn, M. (2023): Advances in Geosciences (accepted for publication).

Hennig, T. et al. (2020): Applied Geochemistry 123, 104777. DOI: 10.1016/j.apgeochem.2020.104777.

Joseph, C. et al. (2013a): Geochimica et Cosmochimica Acta 109, 74–89. DOI: 10.1016/j.gca.2013.01.027.

Joseph, C. et al. (2013b): Applied Geochemistry 36, 104–117. DOI: 10.1016/j.apgeochem.2013.06.016.

Nagra (2007): Nagra Themenhefte no. 1. Wettingen, Switzerland: Nagra, https://nagra.ch/downloads/.

Nagra (2022): Nagra Arbeitsbericht NAB 22-01, Wettingen, Switzerland: Nagra, https://nagra.ch/downloads/.

Noseck, U. et al. (2012): GRS-297. Cologne and Dresden, Germany: GRS and HZDR.

Pearson, F. J. et al. (2003): Reports of the FOWG, Geology Series no. 5. Bern, Switzerland: Federal Office for Water and Geology (FOWG).

Wersin, P. et al. (2016): Chemical Geology, 434, 43–61, DOI: 10.1016/j.chemgeo.2016.04.006.