Bentonite Hydration observed by Wet-Mode Electron Microscopy (ESEM), AFM force measurements

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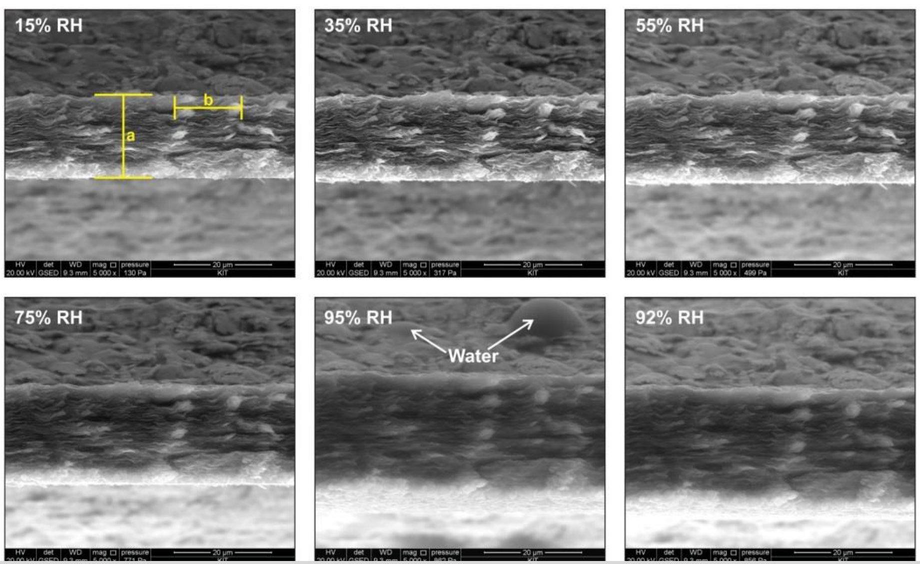
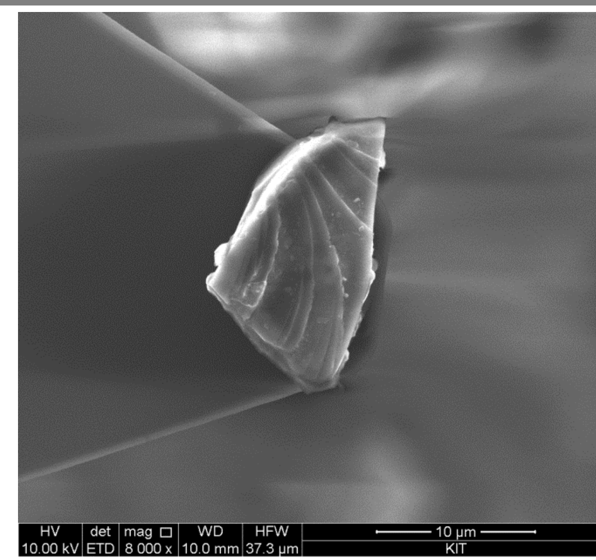
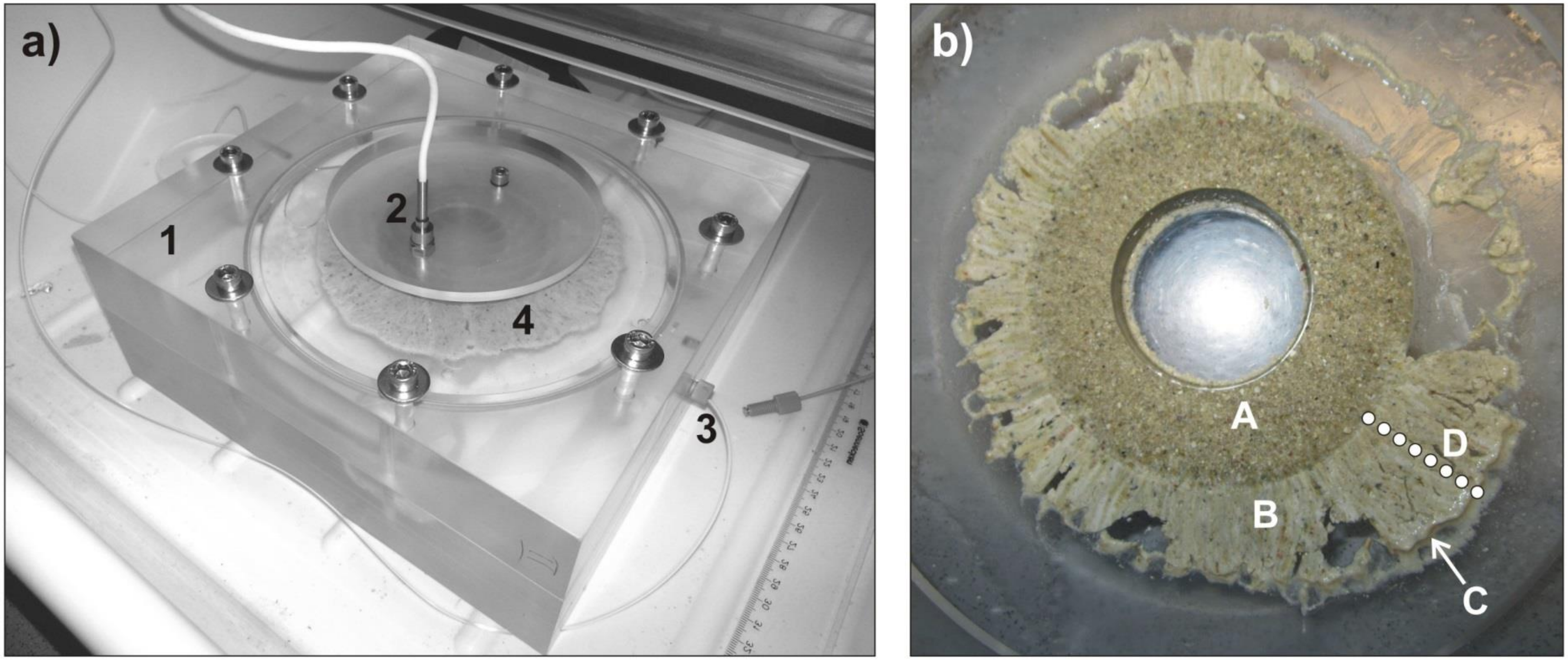




Outline

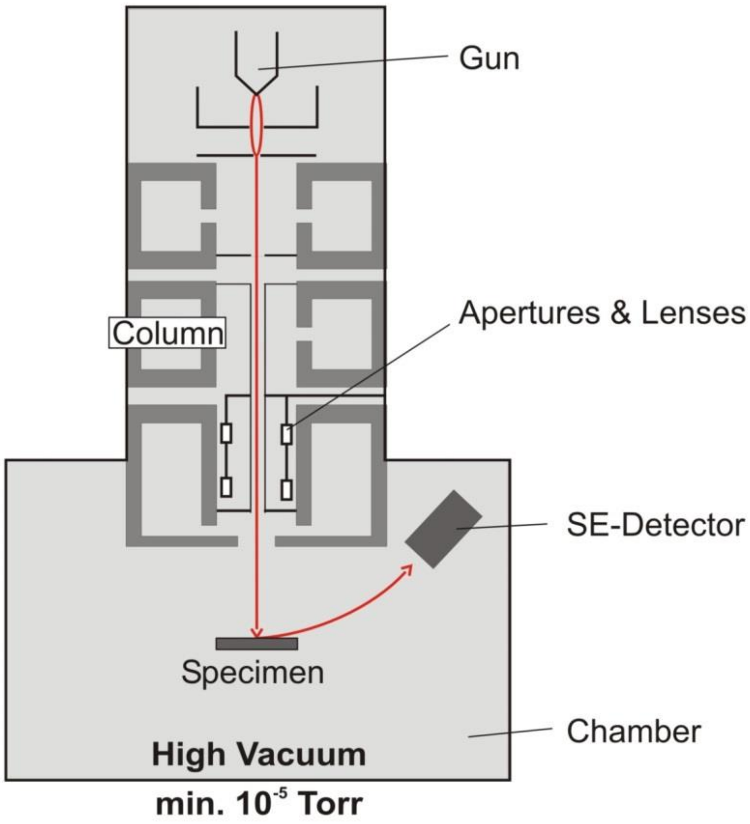
- Motivation
- Basics of Environmental Scanning Electron Microscopy (ESEM)
  - Set-up for in-situ Microsocpy of Hydration Experiments
  - Results
  - Hydration of Febex-Bentonite (raw-material, < 2 µm)
  - Anisotropic swelling behavior of bentonite films
- **A**tomic **F**orce **M**icroscopy colloid probe technique
  - Tests on montmorillonite
  - Step back to kaolinite
- Further Experiments and Outlook

Motivation: Bentonite Erosion Experiments



What happens within the clay during hydration and swelling (into the aperture)?

The Scanning Electron Microscope



Principles

- Electron source produces é-beam (High vacuum: < 10^{-5} Pa) (Acceleration voltages: 1-30 kV)
- Beam is finely focused on the specimen by (condenser and objective) lenses
- Lenses: magnetic fields
- Focused spot is scanned across the specimen
- Interaction beam - sample
- Emitted and scattered electrons (and photons, X-rays) are collected by detectors
- *Sample preparation* (complex) drying procedures, conductive coating (Au, Pt,...)

Limitations of High-Vac SEM

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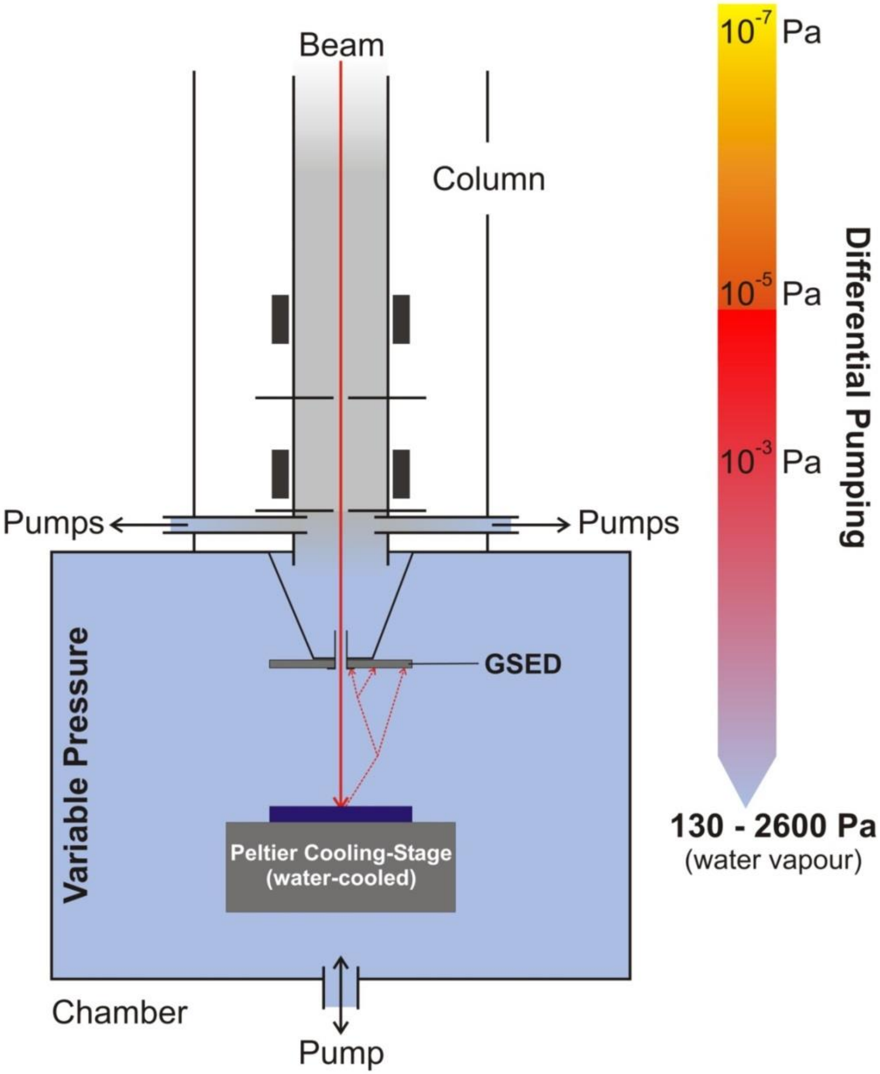
- Insulating specimens have to be covered with conductive material *this avoids electrical charge effects*
- High vacuum (< 10^{-3} Pa) destroys sensitive samples *e.g. hydrated or intercalated clay minerals*
- Gas in the column interferes with the beam *destroys the sensitive high vacuum system*
- Detectors can only be used in high vacuum *electrical breakdown in elevated pressure environments*

Special designed microscopes operated under variable (H_2O-)pressures

Chamber pressures between 100 and 2600 Pa

Environmental Scanning Electron Microscope (ESEM)

The Environmental Scanning Electron Microscope (ESEM)



ESEM-Mode (low-Vac Mode)

– 50 - 200 Pa

– Imaging of beam sensitive samples

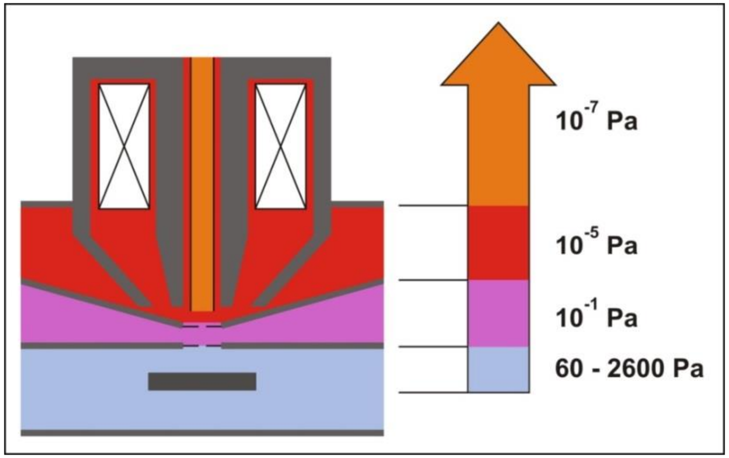
Wet-Mode 130 - 2600 Pa

– Peltier-Stage

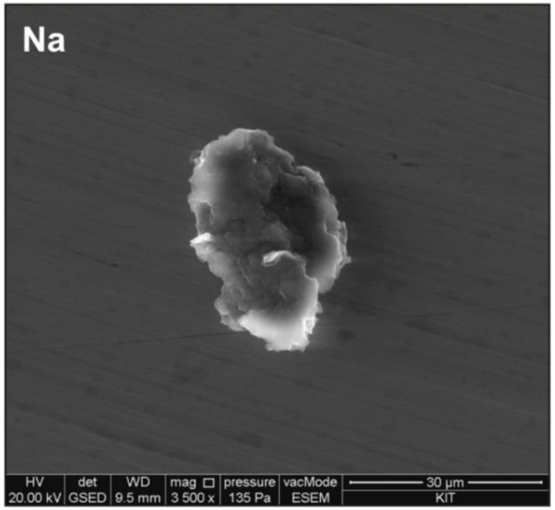
– GSE-Detector

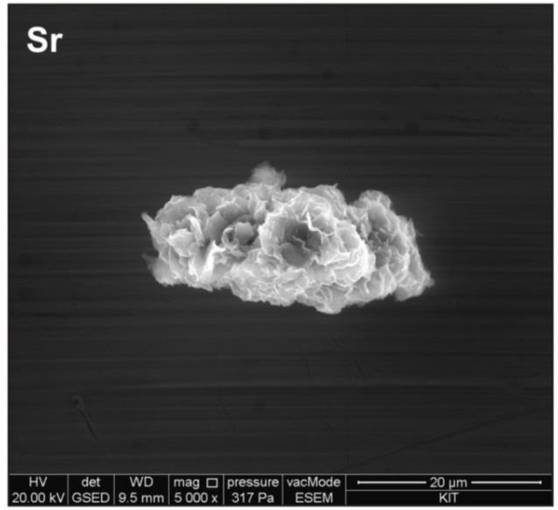
– Precise adjustment of water vapour pressure (= relative humidity) around the sample

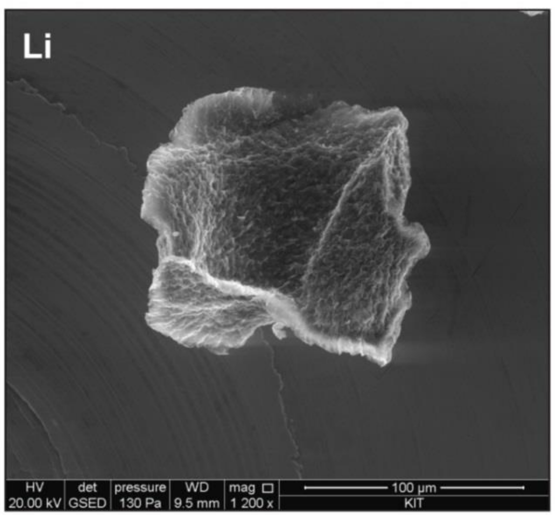
– Even imaging of liquid water is possible!

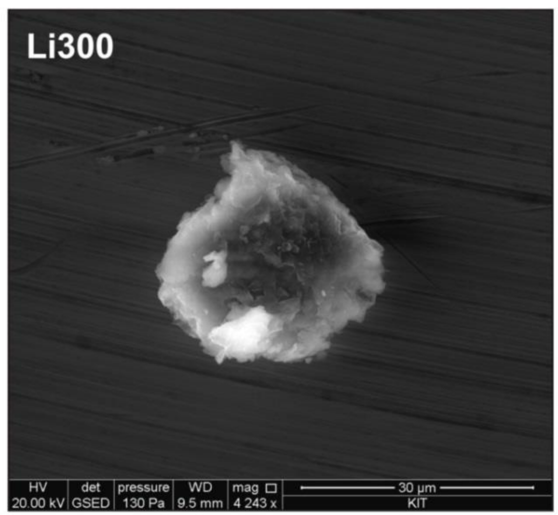


ESEM: Imaging of sensitive materials e.g. cation exchanged bentonite samples









Morphological Differences for FEBEX bentonite

Adjustment of Water Vapour Pressure

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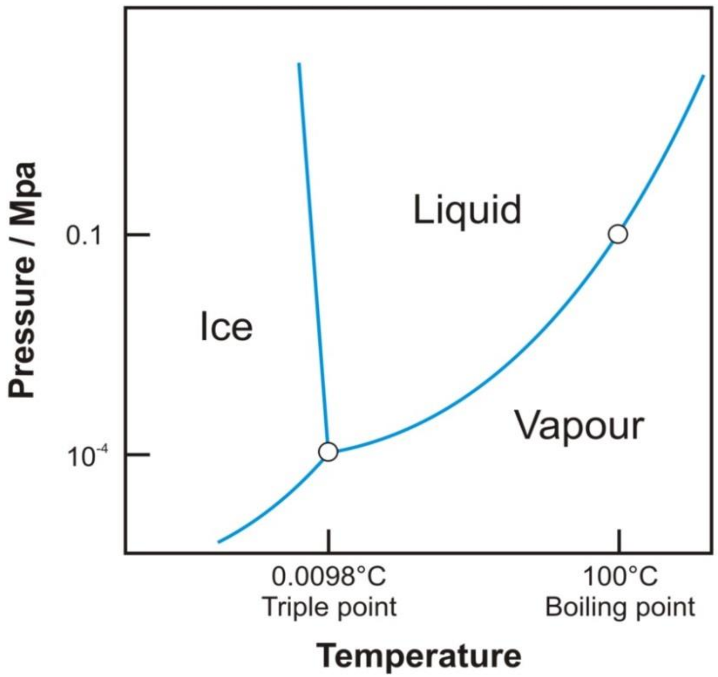
Phase Diagram of Water



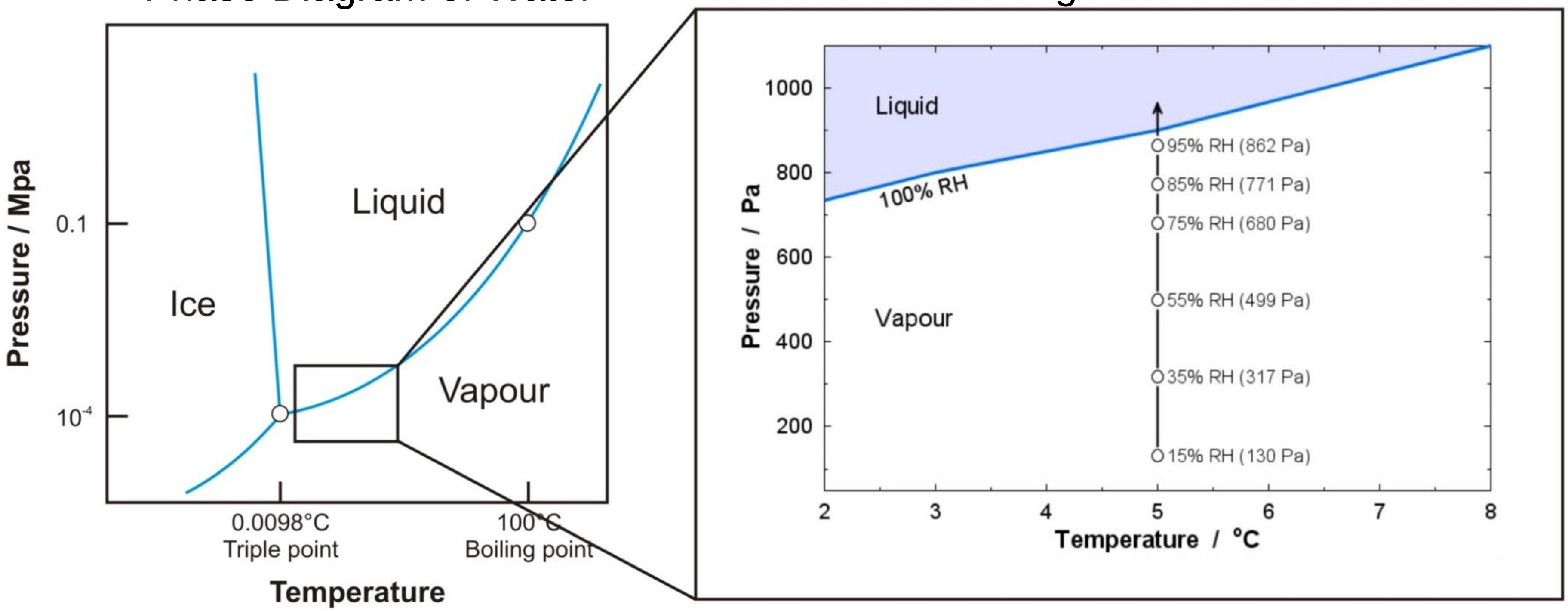
ESEM Wet-Mode (130 - 2600 Pa)

- Peltier-Stage (control of sample T)
- GSE-Detector

Adjustment of Water Vapour Pressure

Phase Diagram of Water

P/T-range in ESEM



ESEM Wet-Mode (130 - 2600 Pa)
- Peltier-Stage (control of sample T)
- GSE-Detector

→ **Precise adjustment of water vapor pressure (= relative humidity) around the sample**

→ **Even imaging of liquid water is possible!**

Literature survey:

- **Carrier, B.; Wang, L.; Vandamme, M.; Pellenq, R. J. M.; Bornert, M.; Tanguy, A.; Van Damme, H., ESEM Study of the Humidity-Induced Swelling of Clay Film. Langmuir 2013, 29, (41), 12823-12833.**
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- Montes-H, G., Swelling–shrinkage measurements of bentonite using coupled environmental scanning electron microscopy and digital image analysis. J. Colloid Interface Sci. 2005, 284, (1), 271-277.
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- Ye, W. M.; Cui, Y. J.; Qian, L. X.; Chen, B., An experimental study of the water transfer through confined compacted GMZ bentonite. Engineering Geology 2009, 108, (3–4), 169-176.
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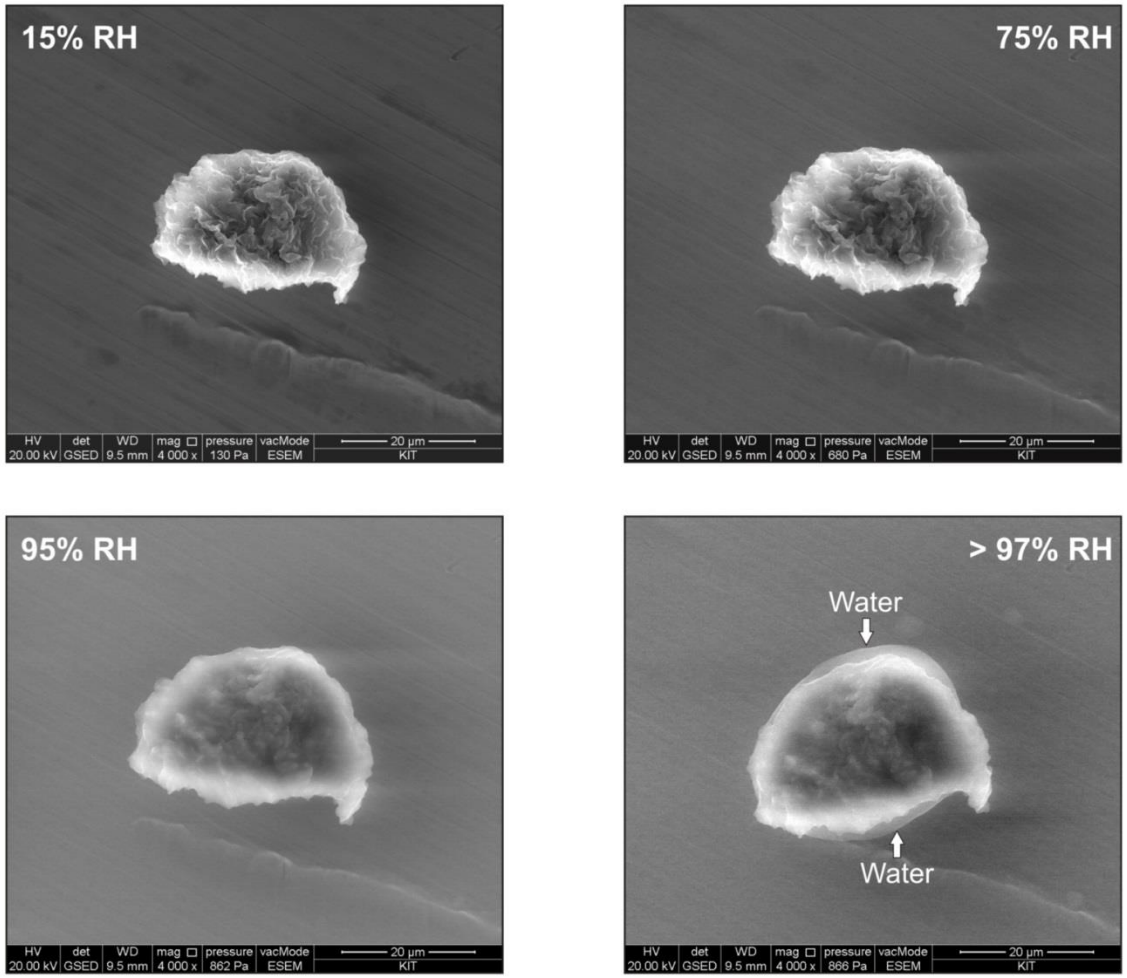
Bentonite Hydration

Hydration of (Febex-) bentonite
(raw-Febex, Fraction < 2 µm)



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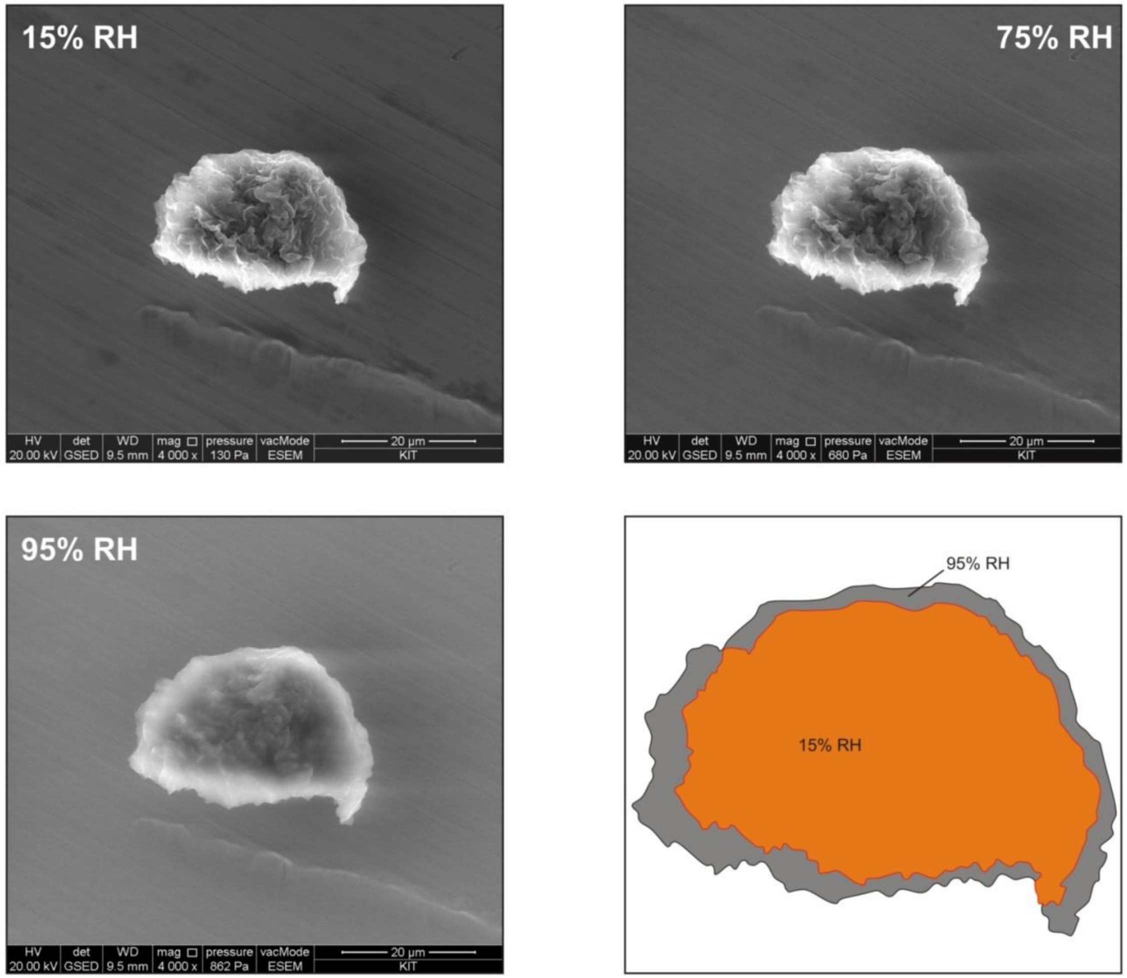
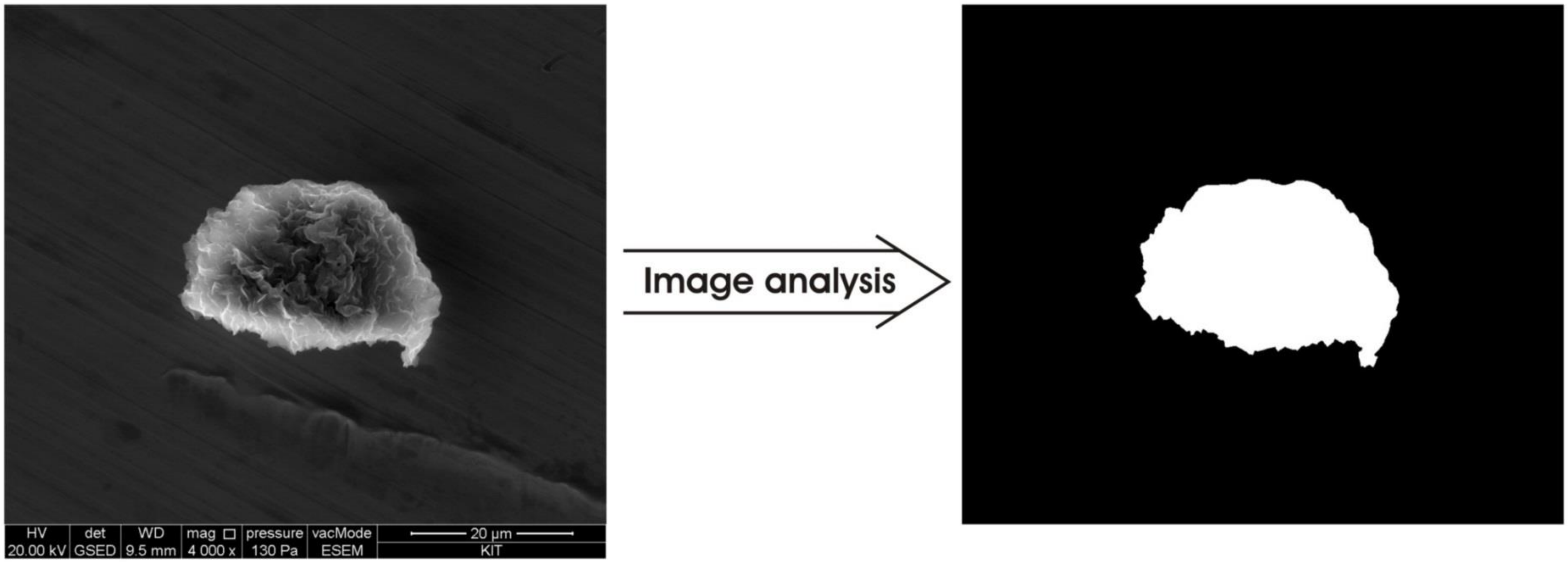


Bentonite Hydration

Data Evaluation with digital image analysis (open source software *ImageJ*)

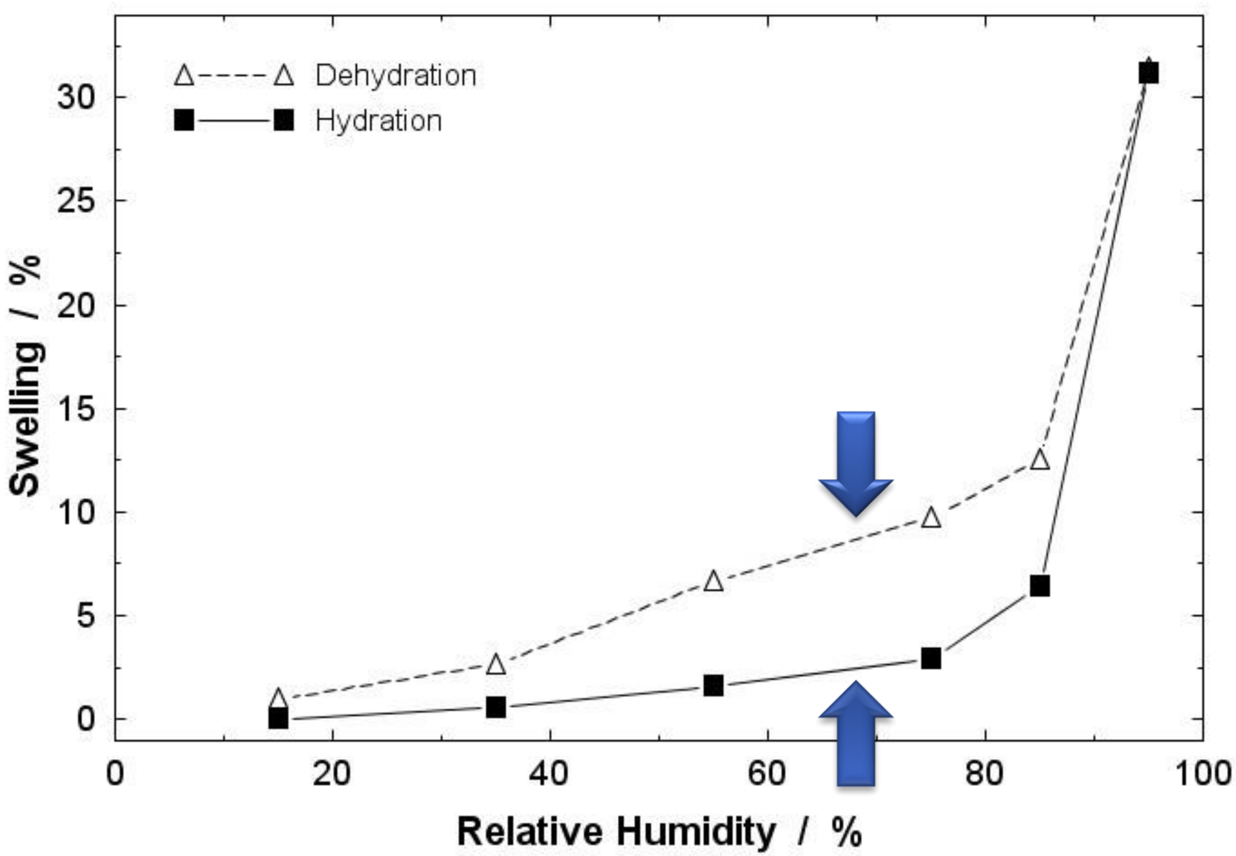


Process:

Defining an area of interest
Selection of gray scale threshold
Calculation of area
Calculation of swelling rate (%) or (linear) coefficient of expansion

Febex Bentonite Hydration / Dehydration Results

Hydration vs. Dehydration Cycle



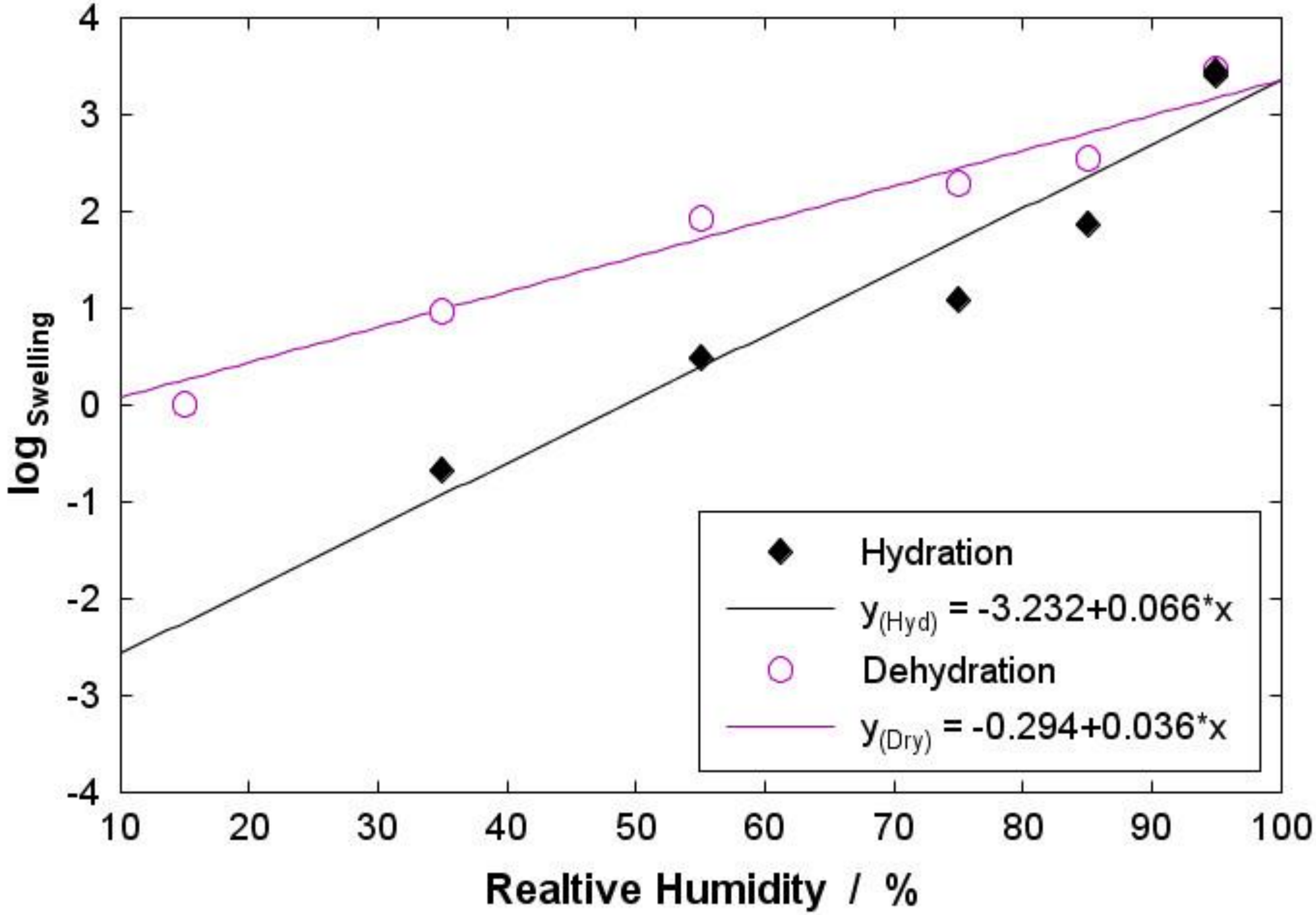
Dehydration path at higher swelling percentages

→ **Hysteresis:** typical for plate-like particles with slit shaped pores

*Sing et al. (1985) Pure and Applied Chemistry, **57**, 603.*

Febex Bentonite Hydration / Dehydration Results

Logarithmic representation (1st order kinetics):

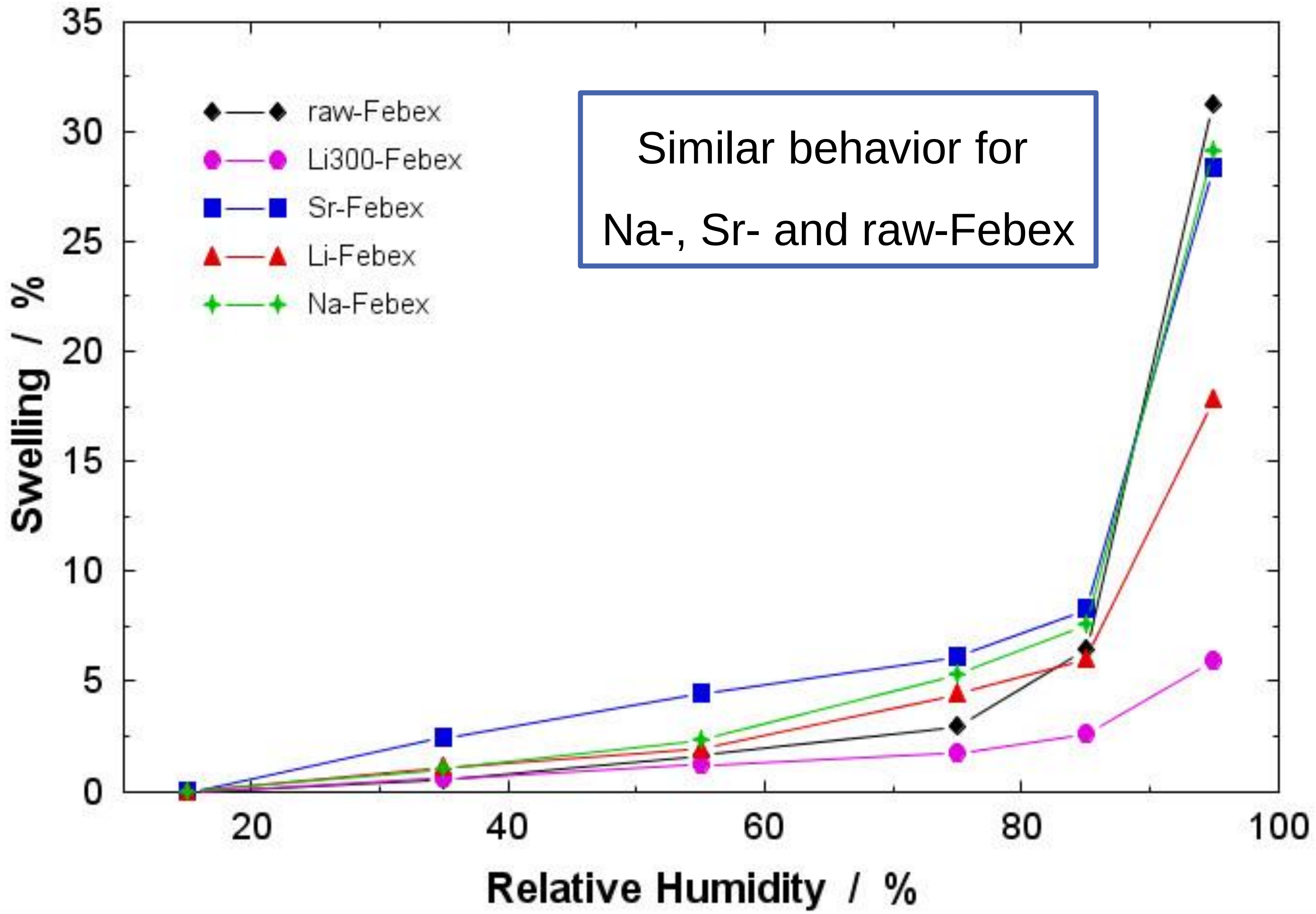


Water adsorption >> Water desorption

Due to geometrical factors (changes in particle arrangement and interlayer distances)

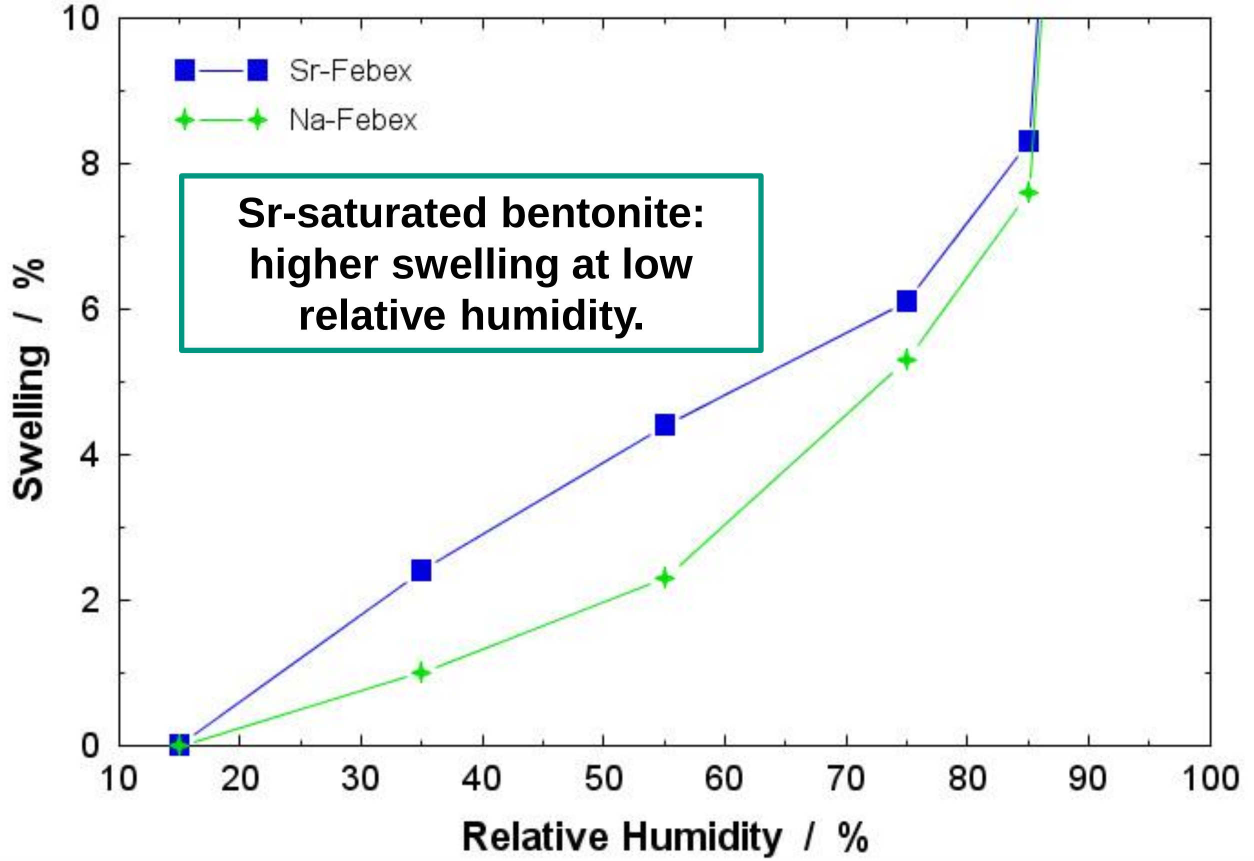
Febex Bentonite Hydration Results

Influence of Interlayer Cations



Raw-Febex contains mono- and divalent cations in interlayer spaces

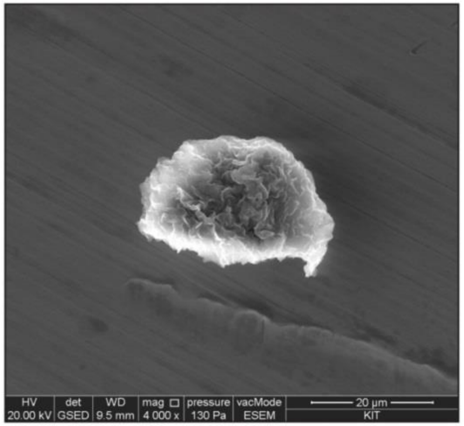
Behavior of divalent interlayer cations

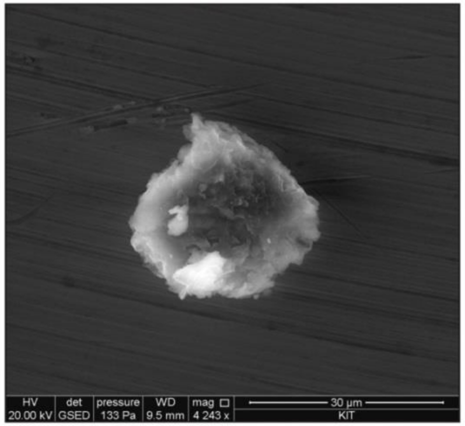


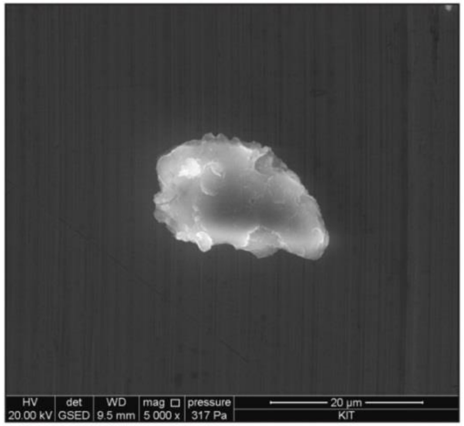
→ **due to higher hydration energy of divalent cations (e.g. Sr^{2+}: - 1415 kJ/mol, Na^{+}: - 390 kJ/mol)**
→ **increase of hydration force within the clay interlayers**
→ **resulting in large water spheres around the cations**

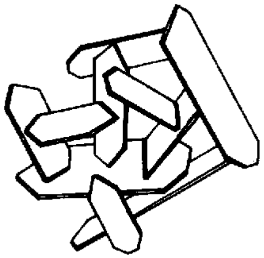
*Keren & Shainberg (1975) Clays and Clay Minerals, **23**, 193.*

Bentonite “flacs” => Bentonite Film



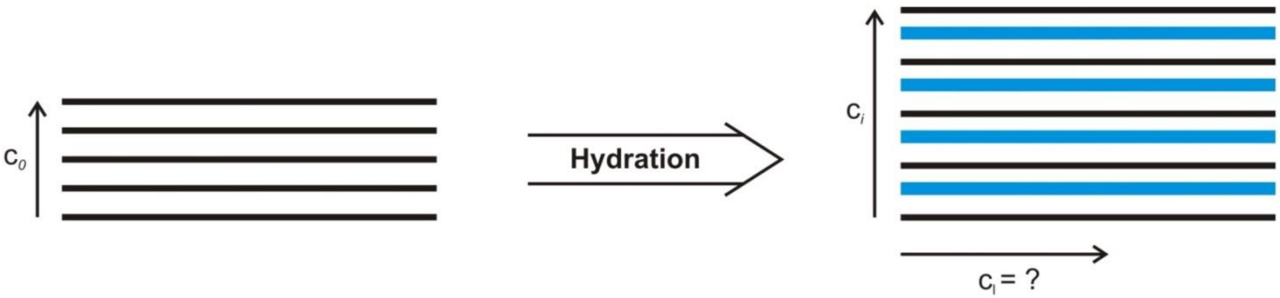






Clay particle

Hydrated particle



Swelling contribution along *ab*-axis?

Textured Bentonite Films

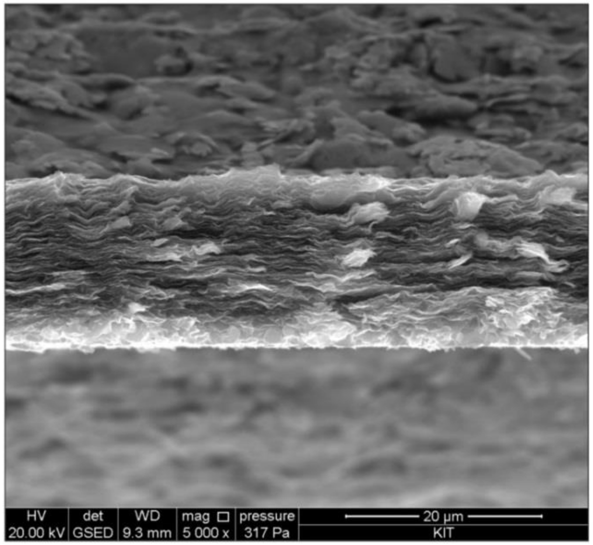
Clay film preparation

clay film

Sample preparation

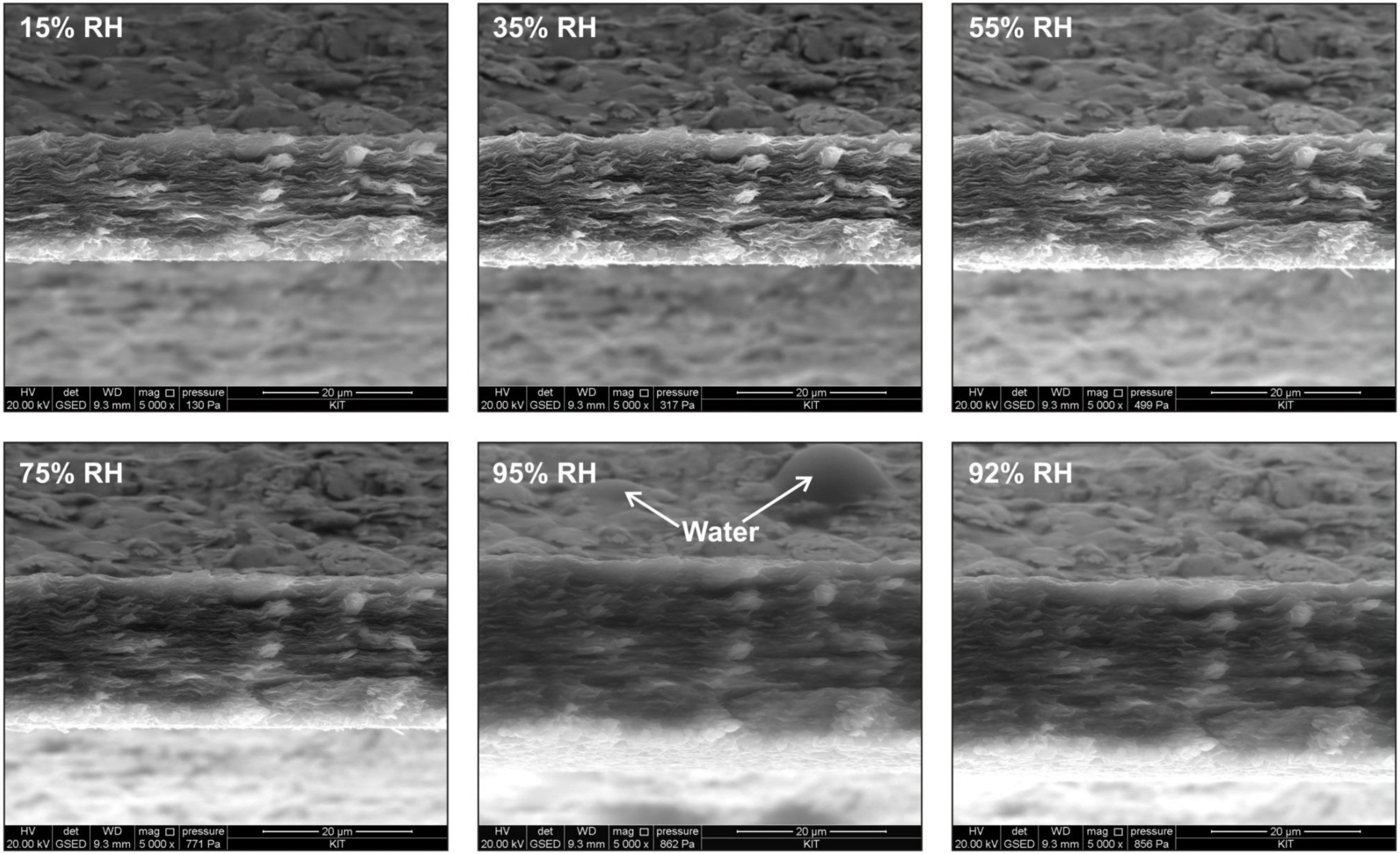
film parallel to beam

Imaging

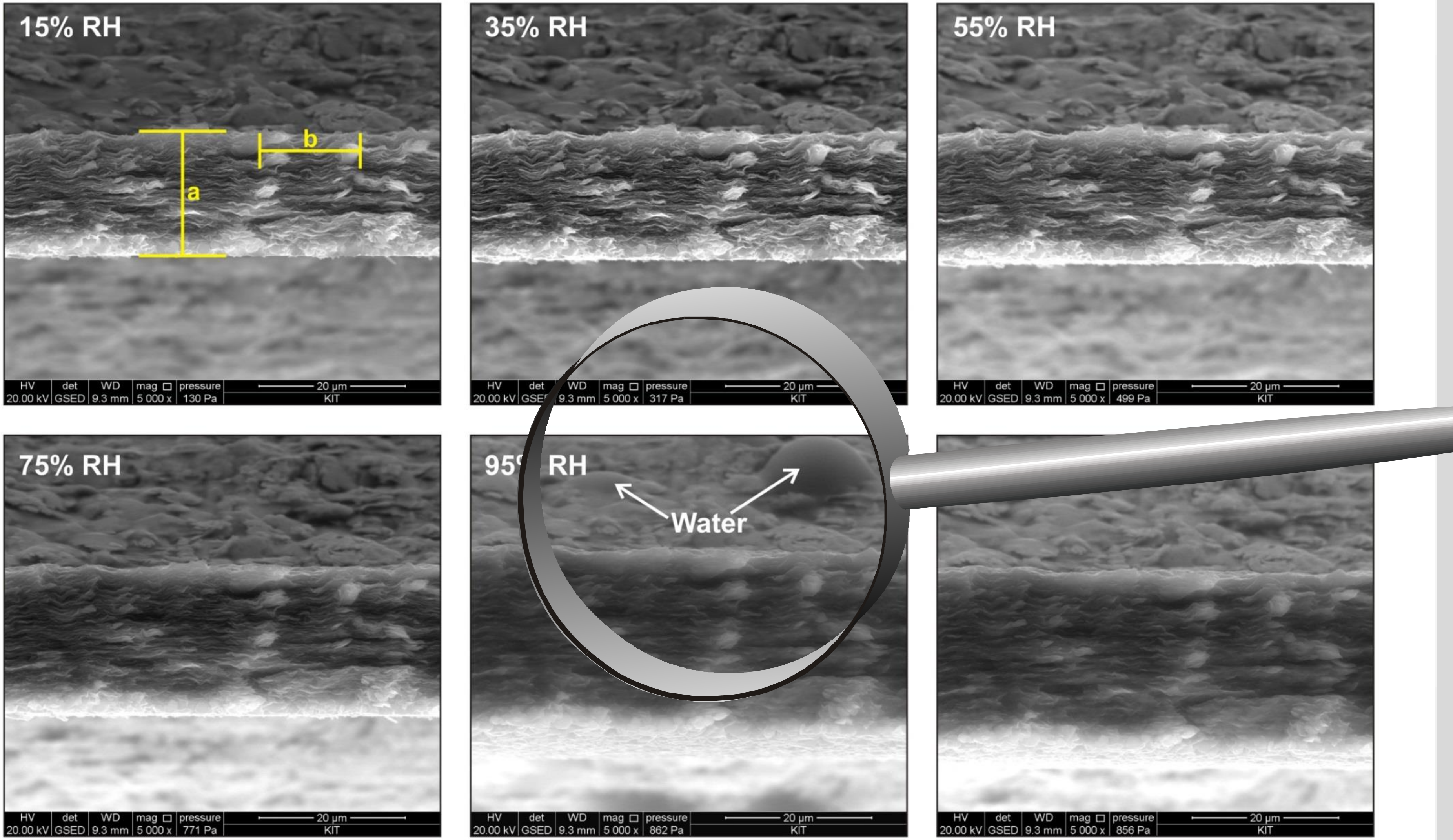


ESEM image

Textured Bentonite Films

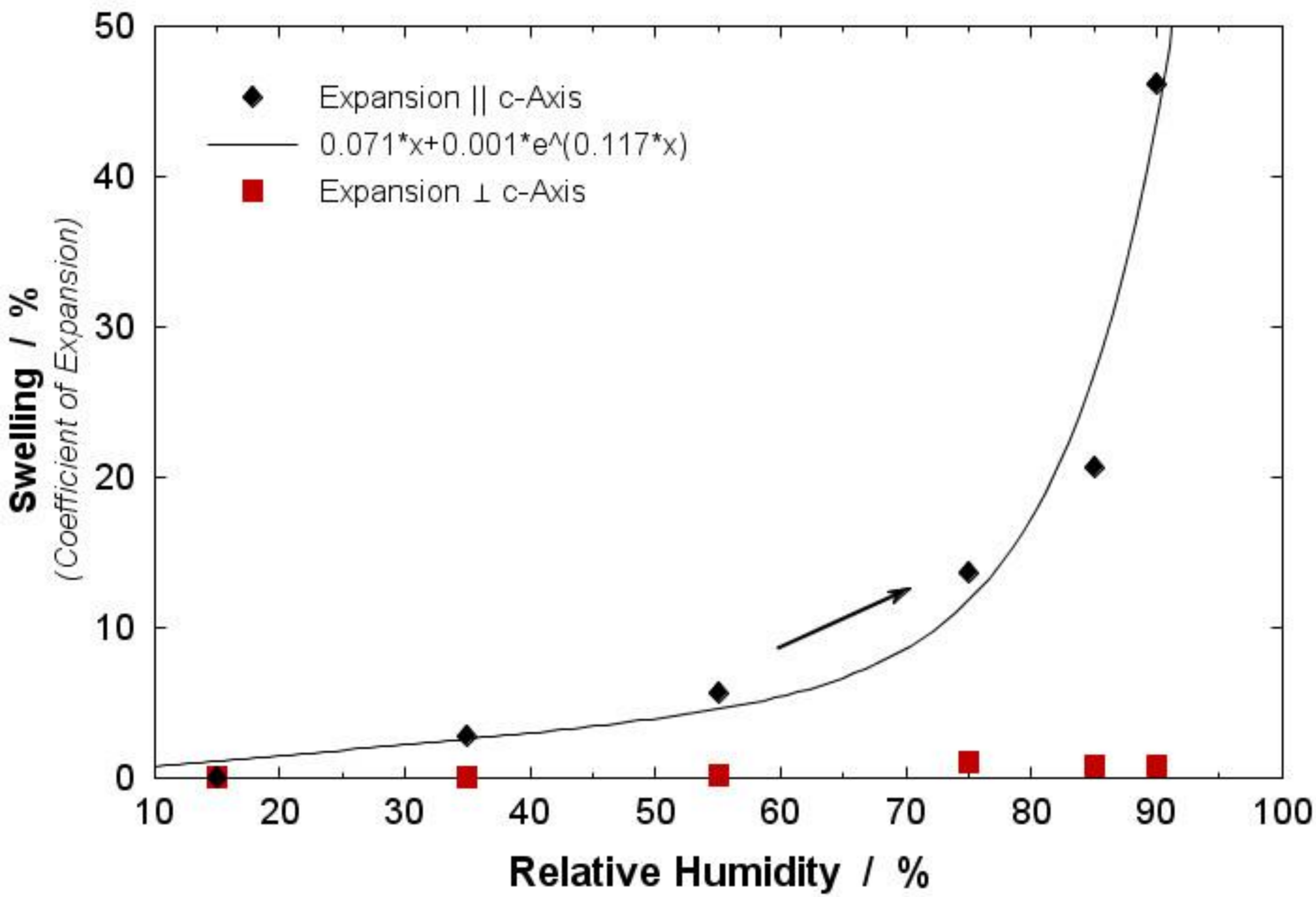


Textured Bentonite Films

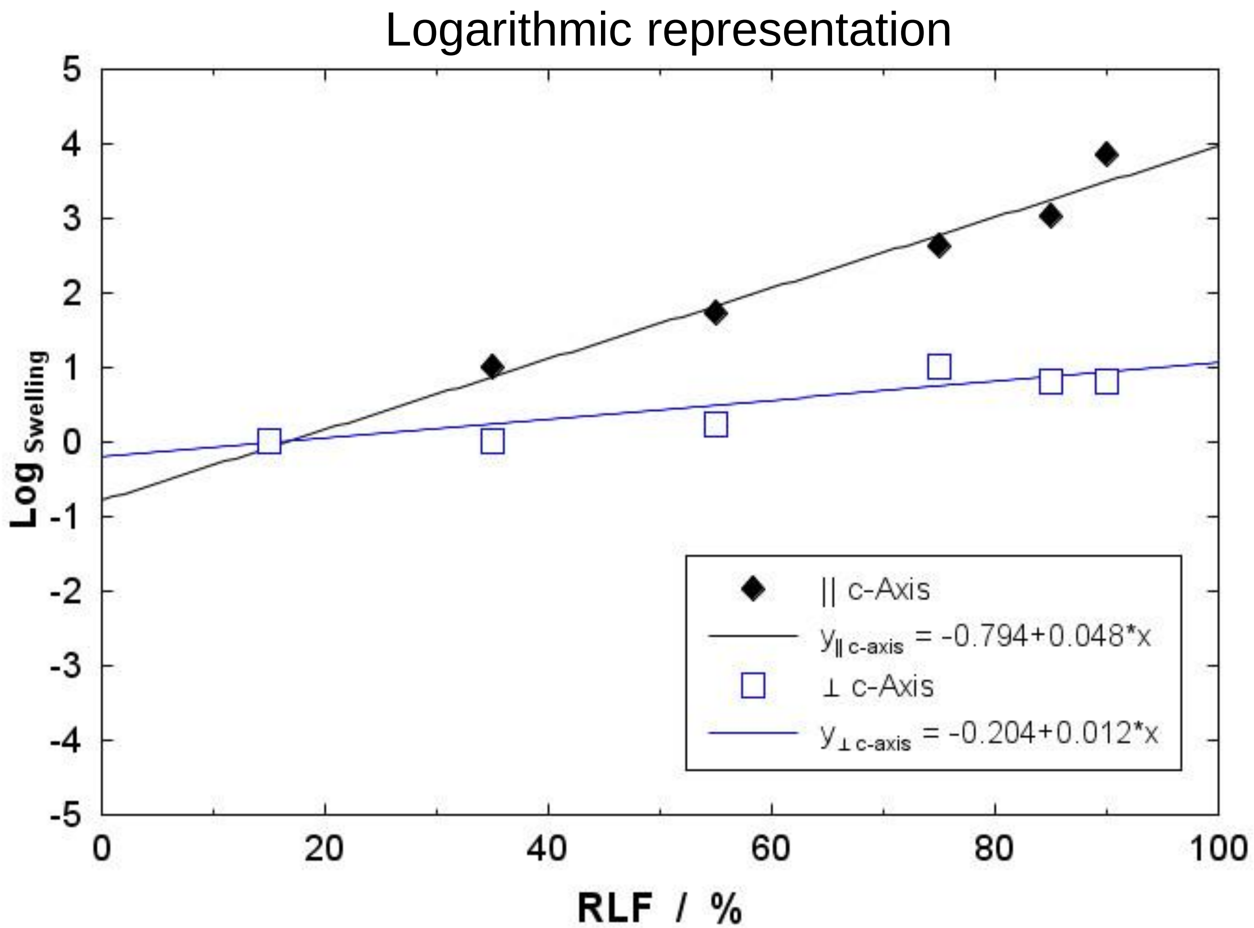


a) Expansion ‖ c-axis
b) Expansion ⊥ c-axis

Textured Bentonite Films



Textured Bentonite Films



Anisotropic behaviour of bentonite during hydration!

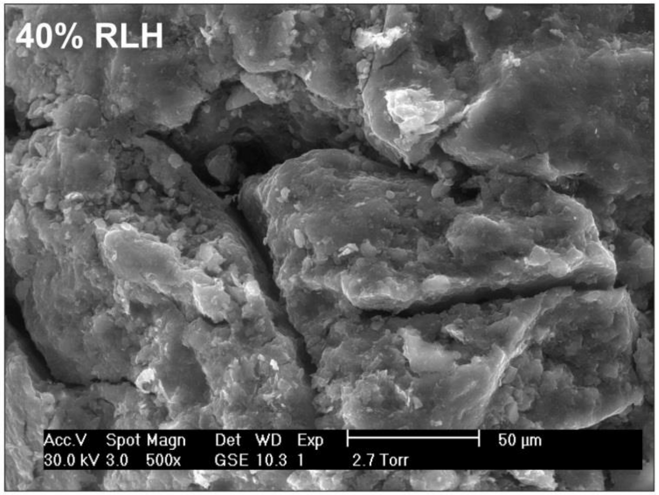
–Strong swelling along c-axis (high gradient)

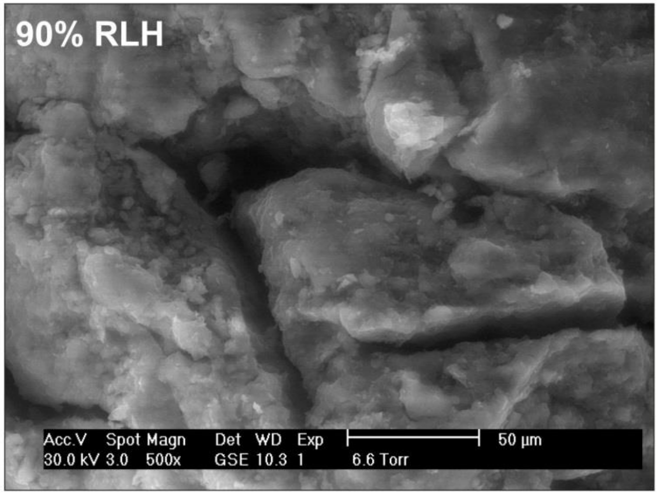
–Low swelling perpendicular to c-axis

Outlook

- Hydration Experiments on compacted samples (correlation of swelling rate to pressure data of erosion experiments possible?)
- Correlation of ESEM-data with:
  - Water content measurements on powdered (+ compacted?) samples
  - XRD-measurements on hydrated textured samples
- Measure hydration isotherms
- Go to water film conditions/ colloid release mechanism measurable?

ESEM / Hydration-experiments





Quantification of interaction forces between clay particles and crystalline surfaces using AFM colloid probe technique

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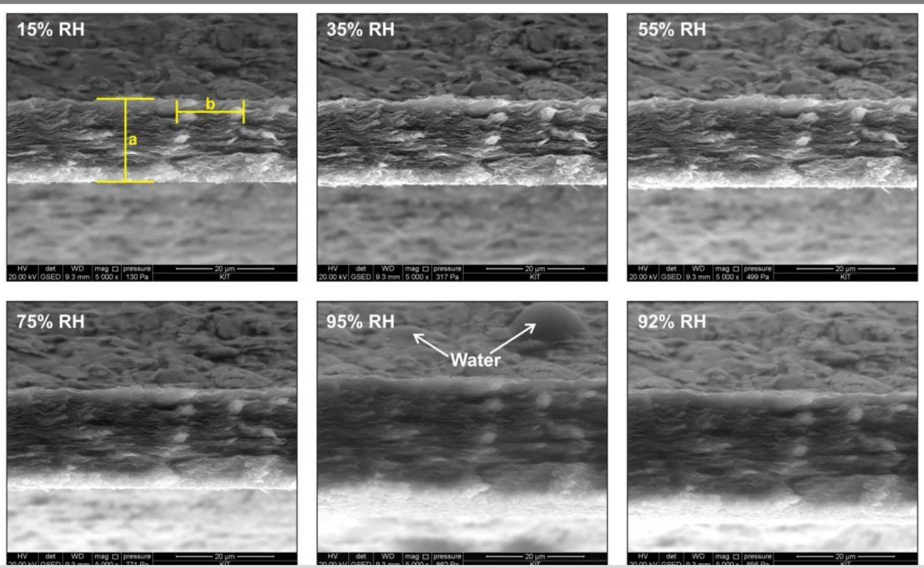
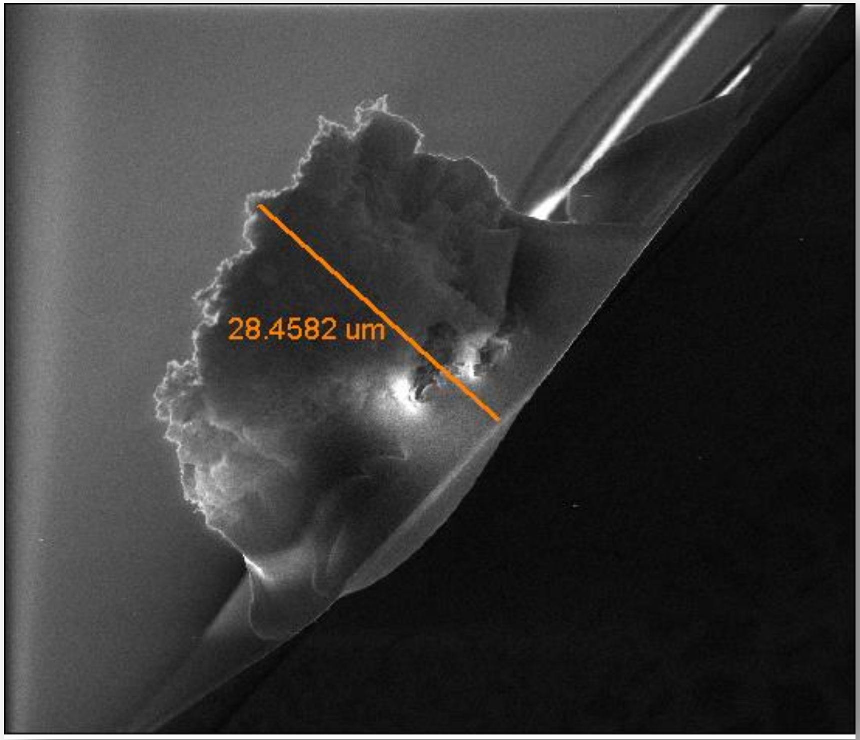


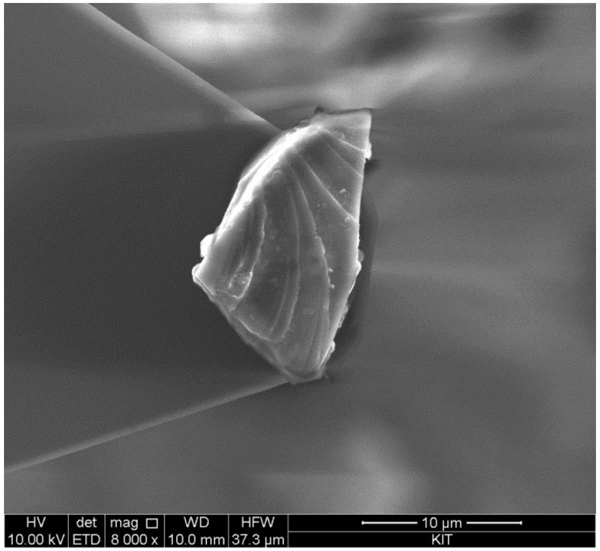
Montmorillionite particle on AFM cantilever tip

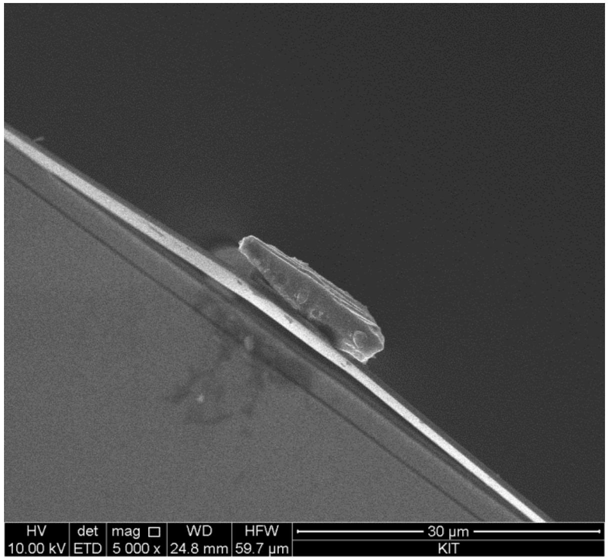
- Attempts were made to attach montmorillonite to the end of an AFM cantilever and measure forces in an electrolyte.
- ***Glue soaks into the clay aggregate***
- ***The difficulty was the particle disintegrates and changes its shape***
- ***Due to swelling changes its size***
- ***The Gel layer is sticky at the interface***
- ***Undetermined roughness of the probe***



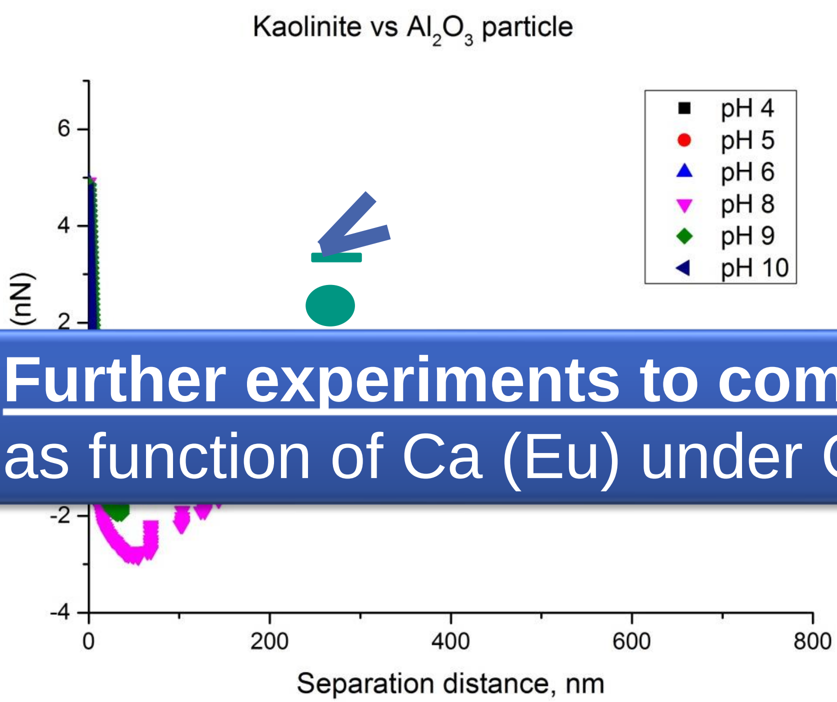
Kaolinite colloid probe

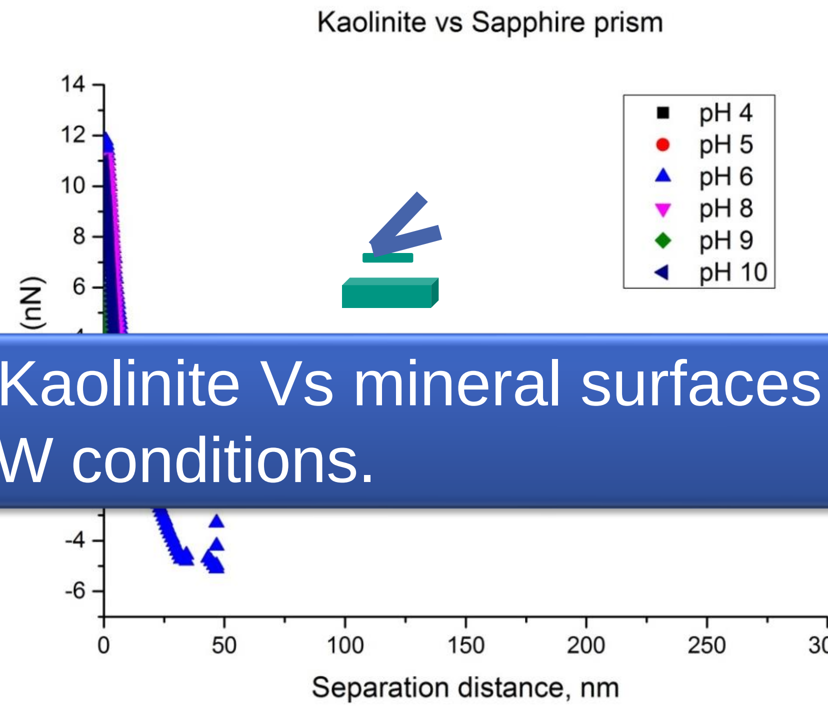
- In continuation to probe the clay edge/face site forces, **kaolinite** was chosen
- Now the question is which face is projected to the measurements (Al-OH's or SiO^- are dominating at the point of contact)?





Kaolinite vs Al_2O_3 & Sapphire





Further experiments to come: Kaolinite Vs mineral surfaces as function of Ca (Eu) under GGW conditions.

- **Forces of adhesion between Kaolinite particle and a) Al_2O_3 and b) sapphire substrates in 1 mM NaCl as function of pH**
- **PZC of Al_2O_3 is pH~8-9 and for sapphire is pH~5-6. This fits very well that the Al-OH functional groups are dominating at the contact point of Kaolinite particle.**

THANK YOU FOR YOUR ATTENTION.

BELBaR Training course & WP meetings

Karlsruhe Institute of Technology

- **When:** **12-16.October 2015 @KIT-INE**
- 2 days Training course ***„Swelling Clays: From compacted bentonite to clay colloids in the context of nuclear waste disposal"***
  - Max. 20 intern. students
  - Lectures given by BELBaR experts on analytics used
  - Invited presentations
  - *Hands-on Training (e.g. LIBD, FFF- ICP-MS, PCS, zeta/streaming potential, ESEM, TRLFS, Synchrotron techniques @ ANKA)*
  - Students poster session with finger food
  - Optional: One day field trip (Clay mines, Westerwald region)
- WP 2-5 meetings in preparation for synthesis report (1-2 days)