BELBaR-Training Course: *"Swelling clays: From compacted bentonite to clay colloids in the context of nuclear waste disposal"*

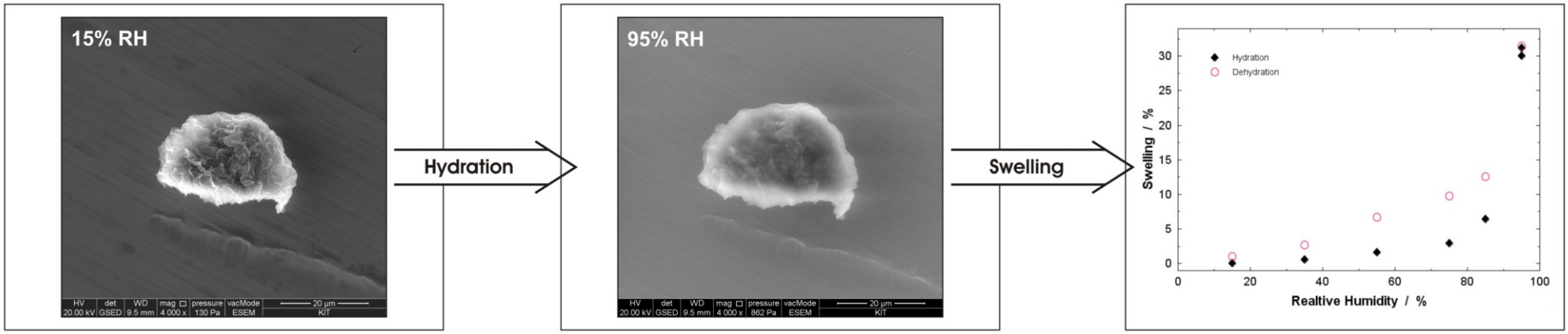
Karlsruhe, 15.10.2015

Environmental Scanning Electron Microscopy (ESEM)

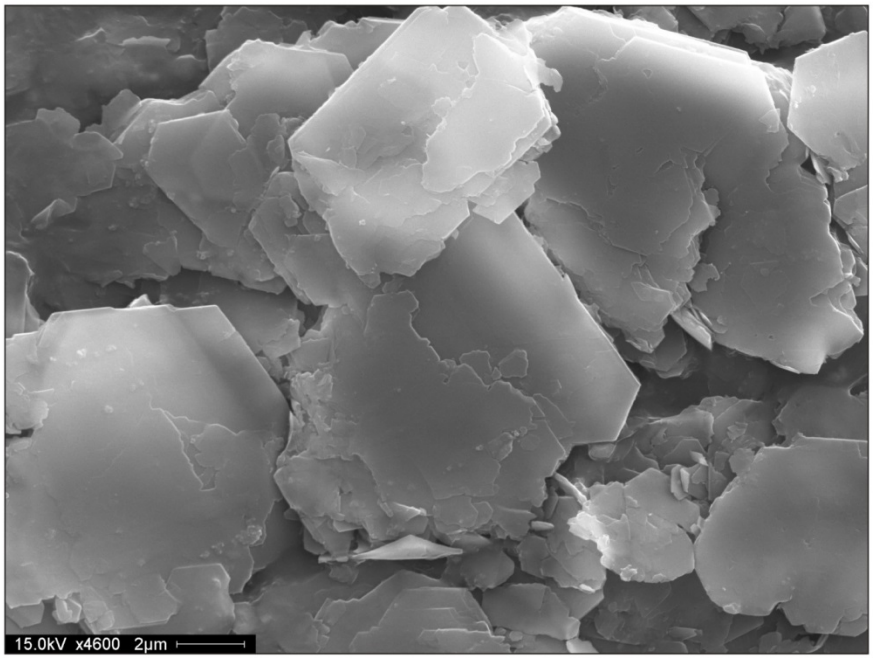
Investigation of (wet) Clays

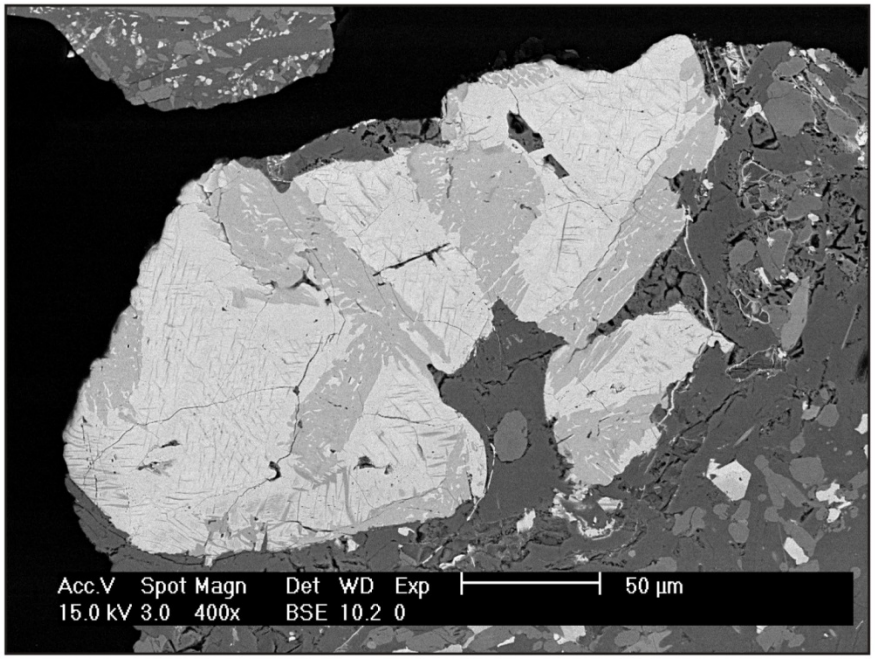
Frank Friedrich

INSTITUTE FOR NUCLEAR WASTE DISPOSAL (INE)

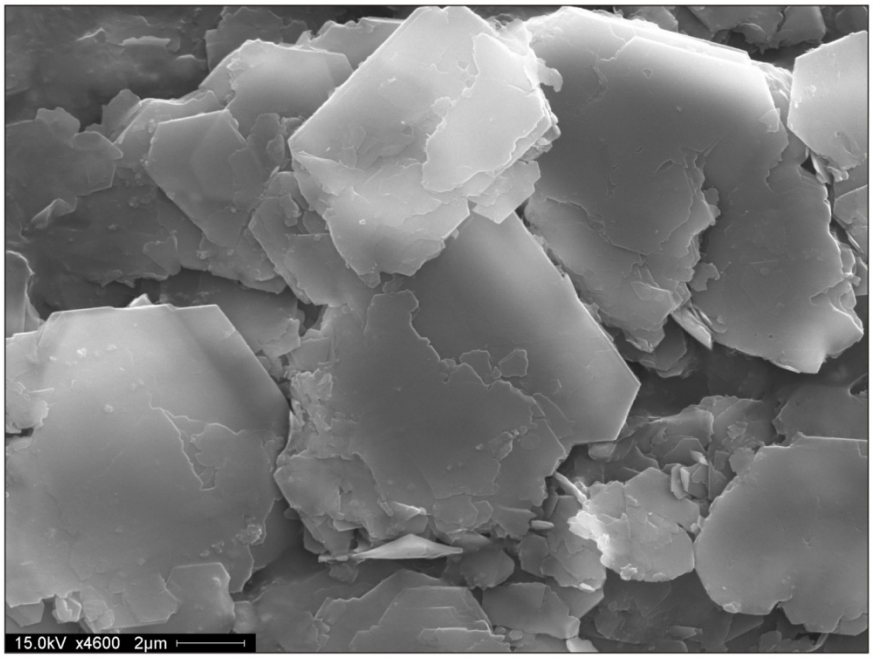


Characteristics of SEM

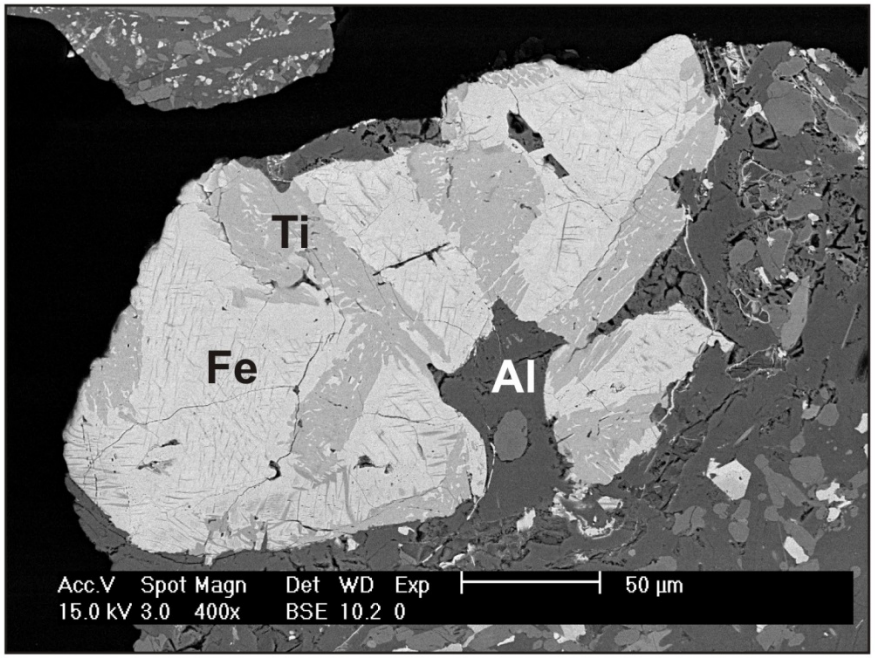




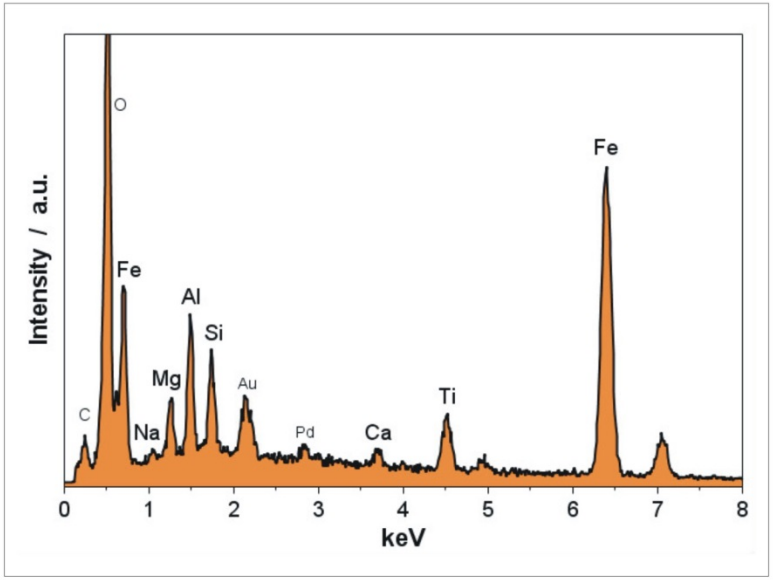
Characteristics of SEM



Imaging
(Secondary electrons, SE)

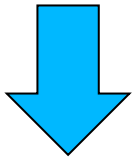


Imaging + Chemical information
(backscattered electrons, BSE)

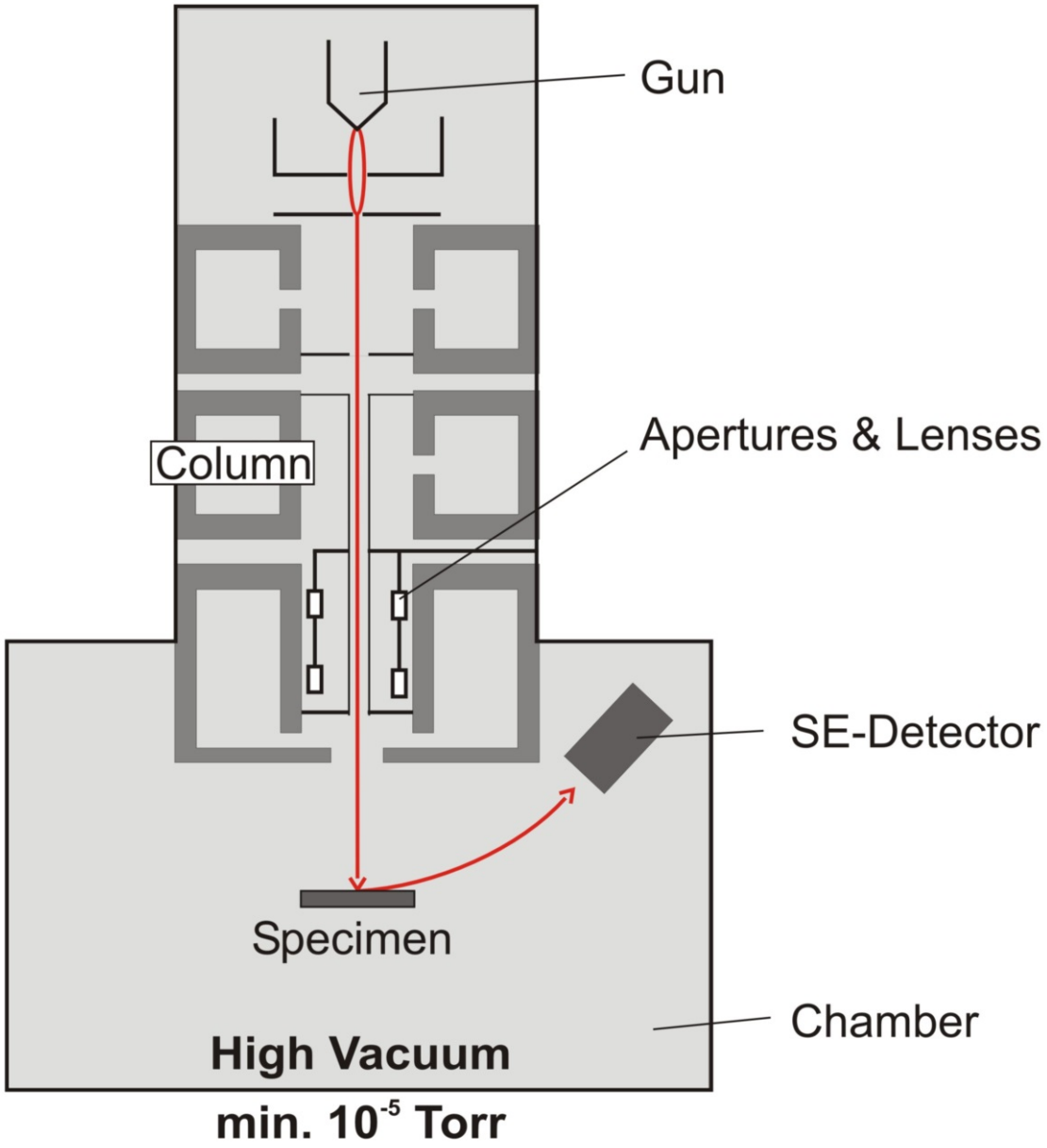


Chemical information
(X-rays)

- Imaging of topography / morphology of massive specimen
- **Three-dimensional look of images – high depth of field**
- **Simultaneous imaging and chemical information (X-rays, BSE)**
- Chemical composition (material contrast)
- Imaging of various kinds of materials, even "wet" and "sensitive" (biological) samples
- High resolution (1 nm)



Result of the Interaction between
é-Beam and Sample Material

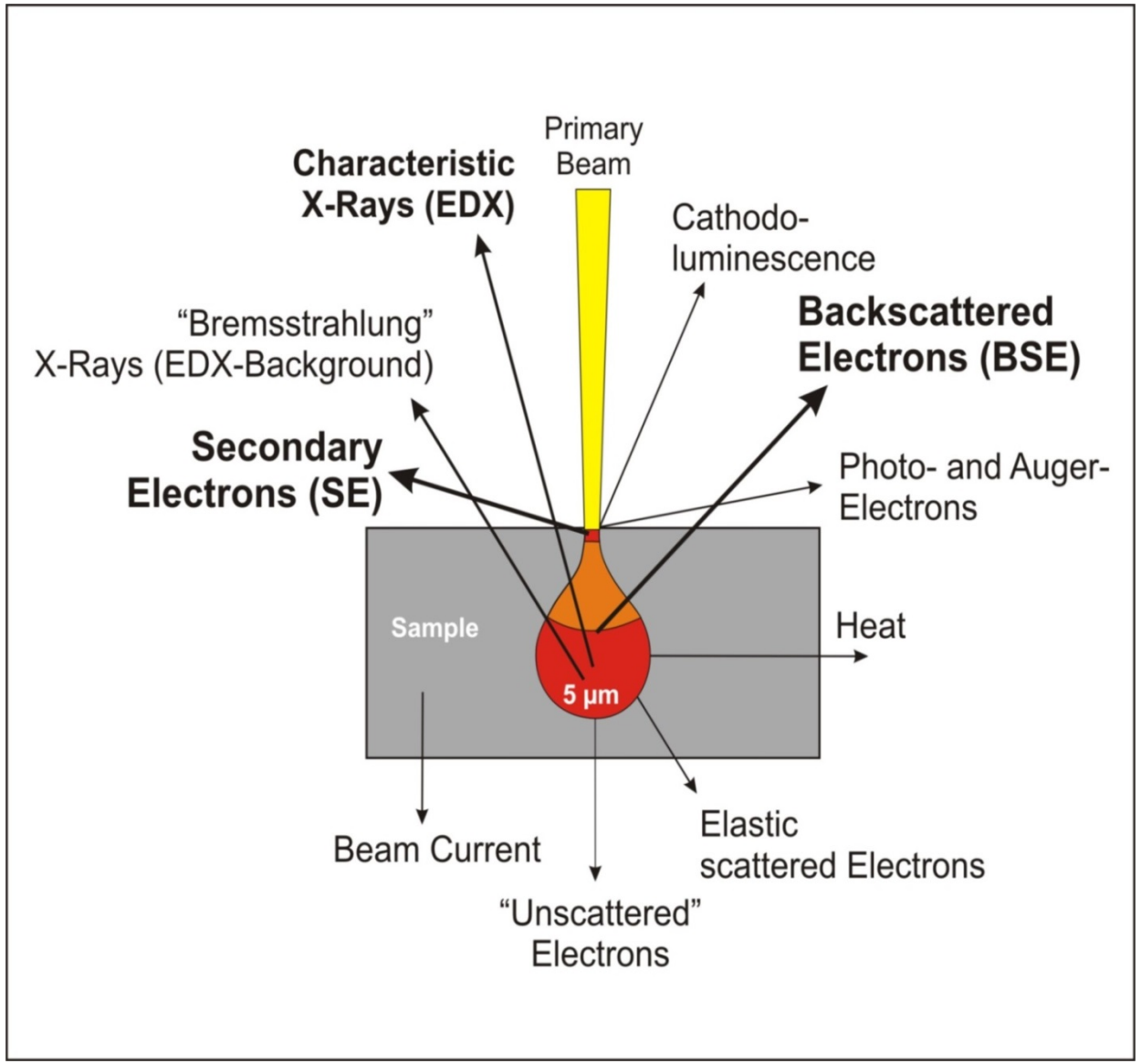


SEM-Principles

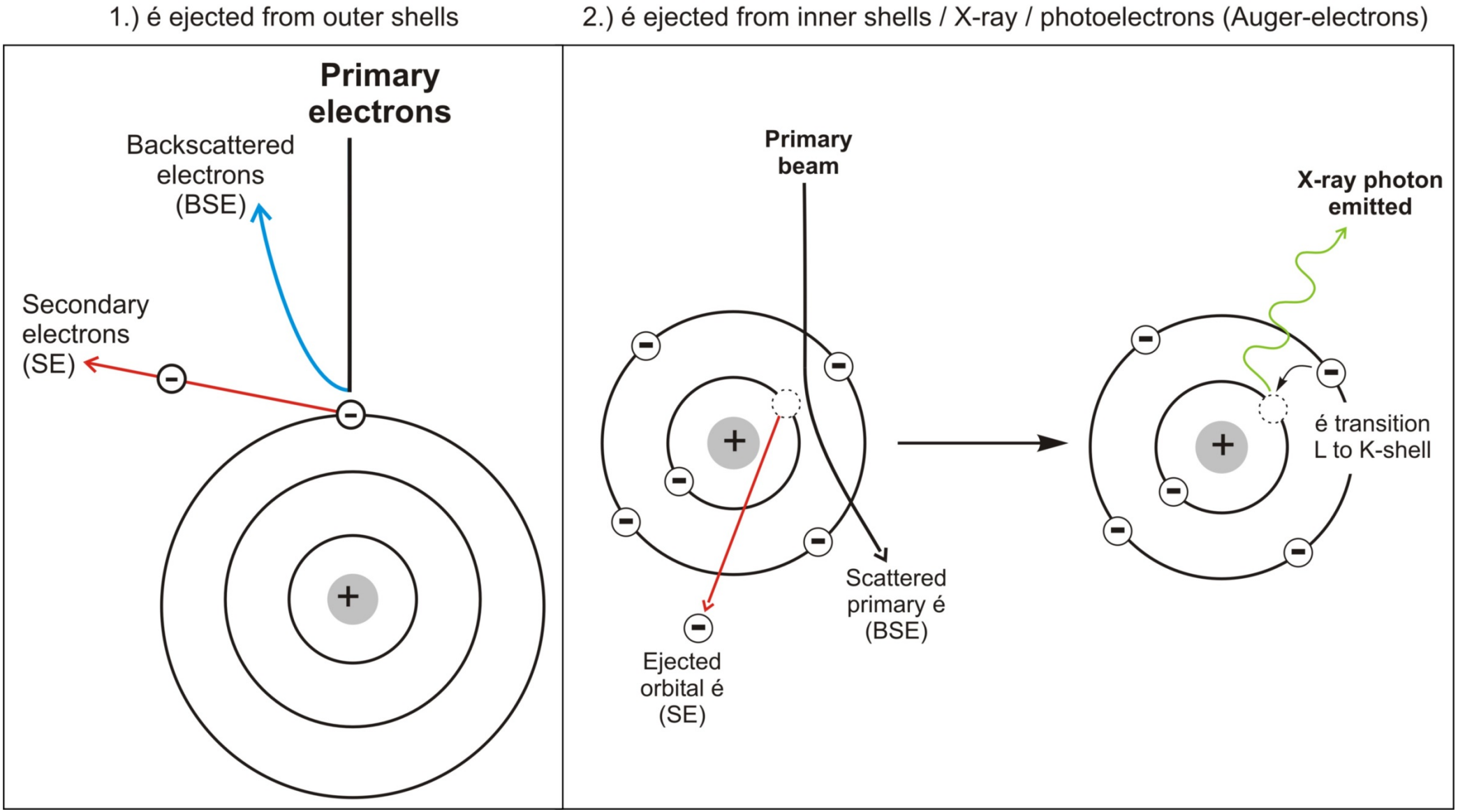
- Electron source produces é-beam (High vacuum: < 10^{-5} Pa) (Acceleration voltages: 1-30 kV)
- Beam is finely focused on the specimen by (condenser and objective) lenses
- Lenses: magnetic fields
- Focused spot is scanned across the specimen
- Interaction beam - sample
- Emitted and scattered electrons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

Goldstein J. (2003) "Scanning Electron Microscopy and X-Ray Microanalysis."

Characteristics of SEM

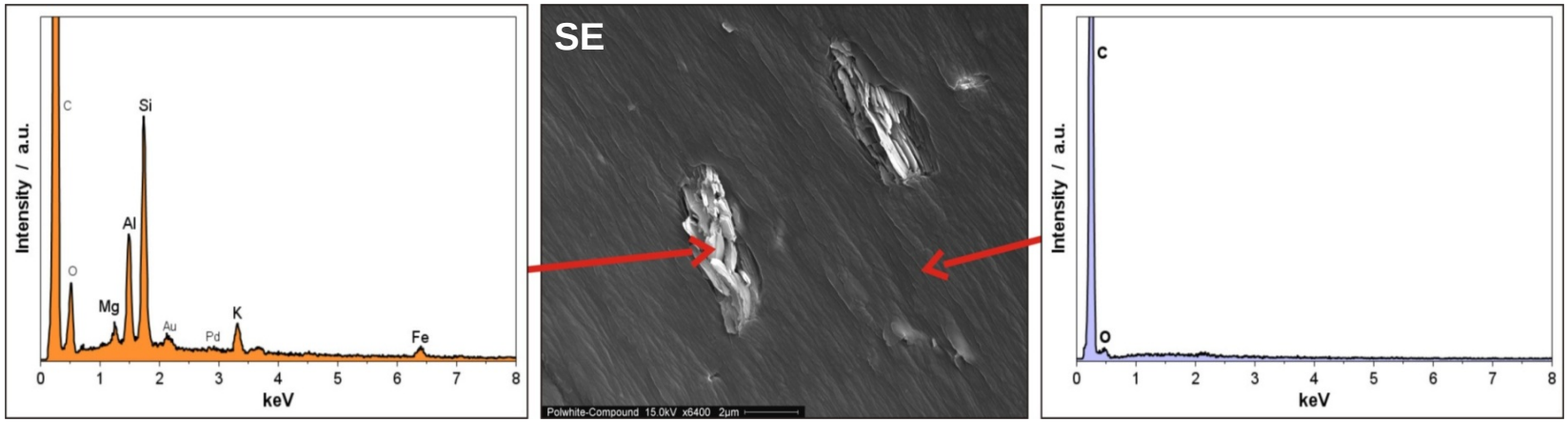


Electron Matter Interaction

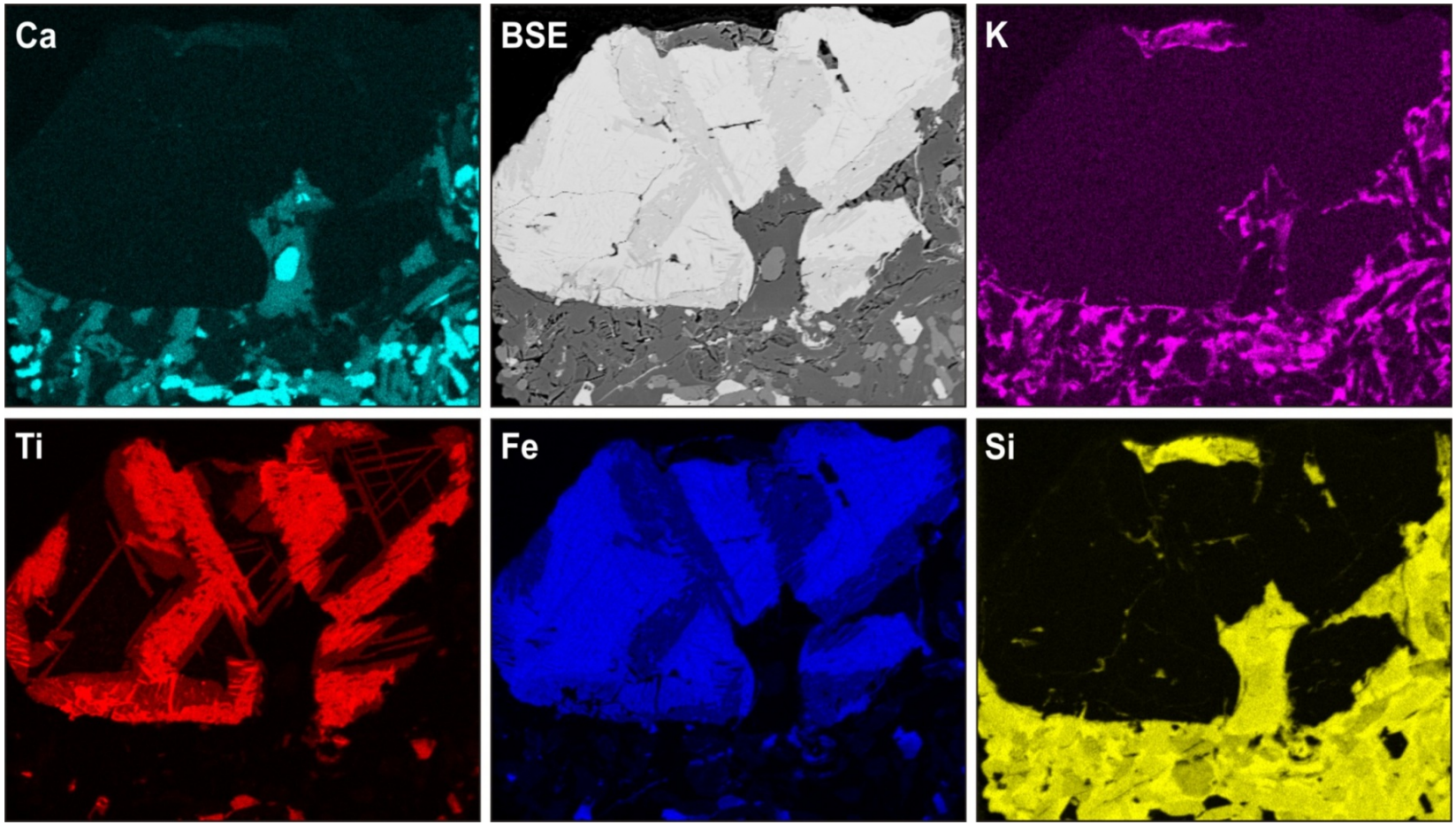


Electron Matter Interaction

Spectra

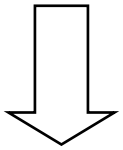


Elemental Mapping



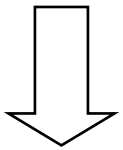
Limitations of High-Vac SEM

- Insulating specimens have to be covered with conductive material
  this avoids electrical charge effects
- High vacuum (< 10^{-5} 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



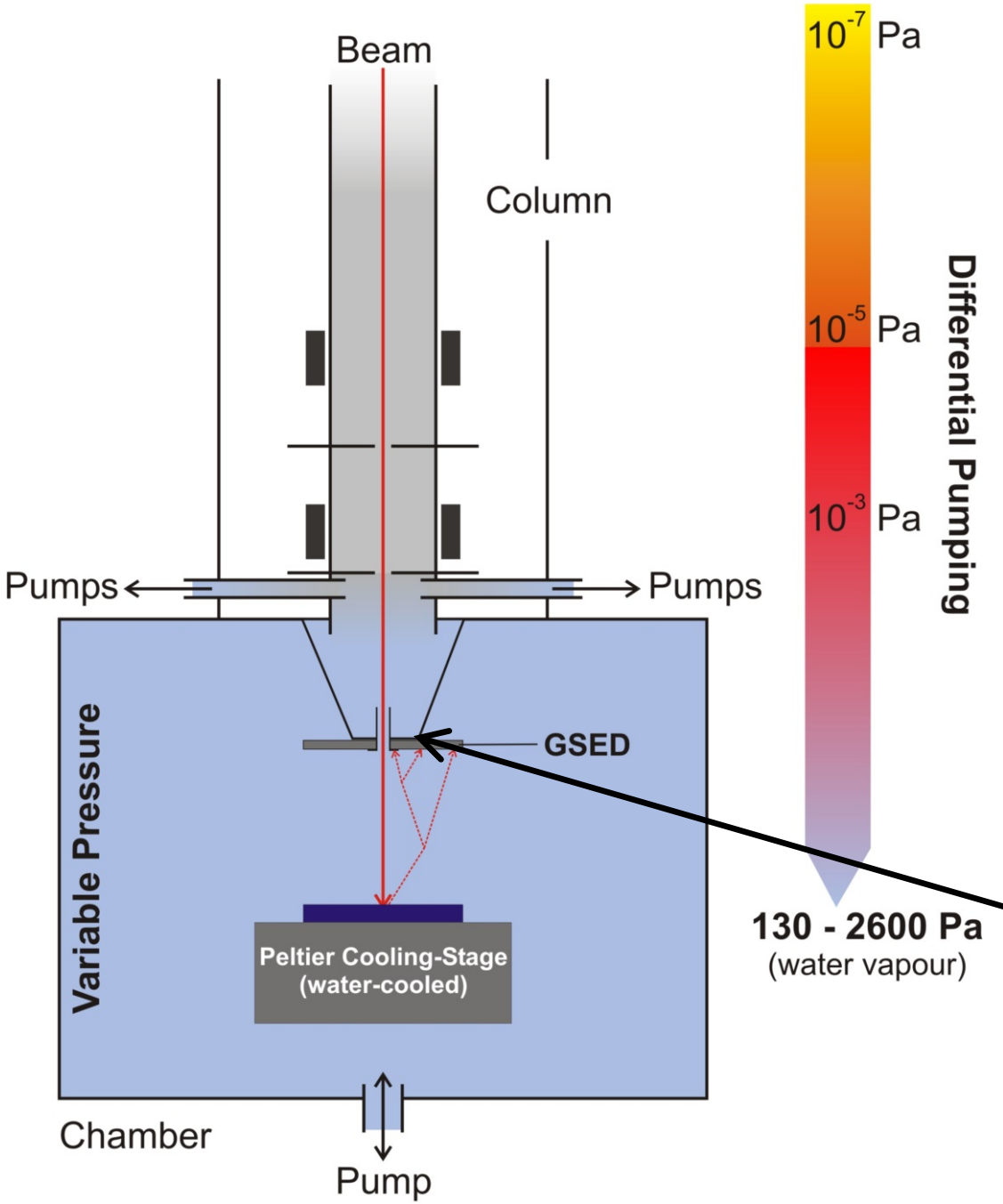
Special designed microscopes operated under variable (H_2O-)pressures

Chamber pressures between 100 and 2600 Pa



Environmental Scanning Electron Microscope (ESEM)

The Environmental Scanning Electron Microscope

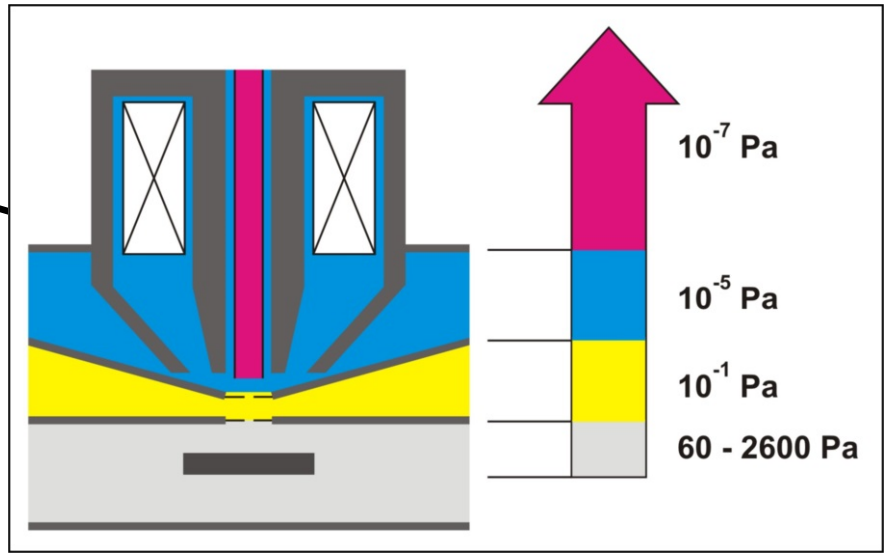


1. ESEM-Mode (low-Vac Mode)

- 50 - 200 Pa
- Imaging of beam sensitive samples

2. Wet-Mode 130 - 2600 Pa

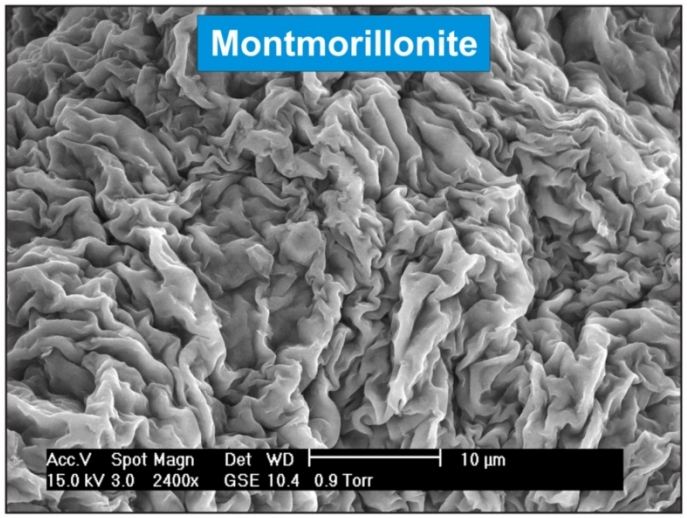
- Peltier-Stage
- GSE-Detector

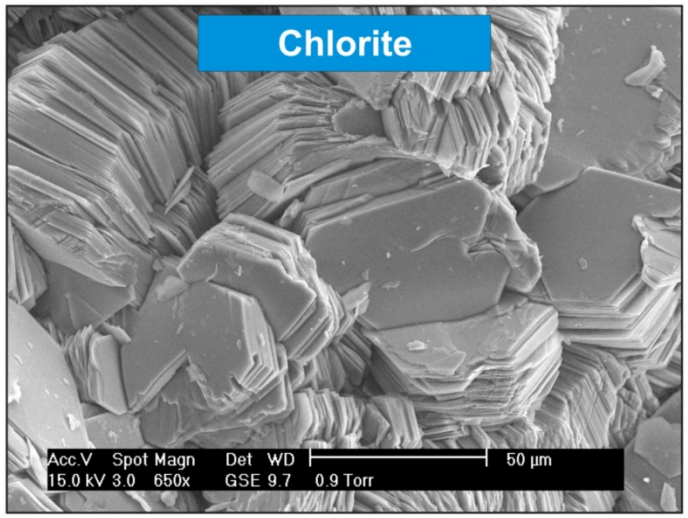


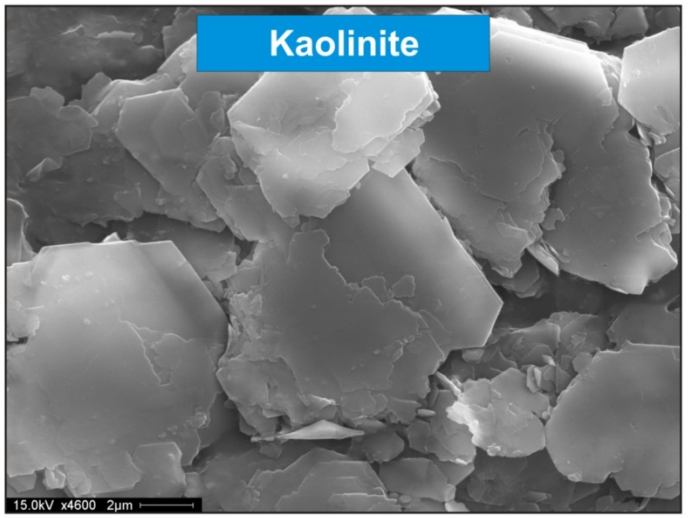
"Differential Pumping"

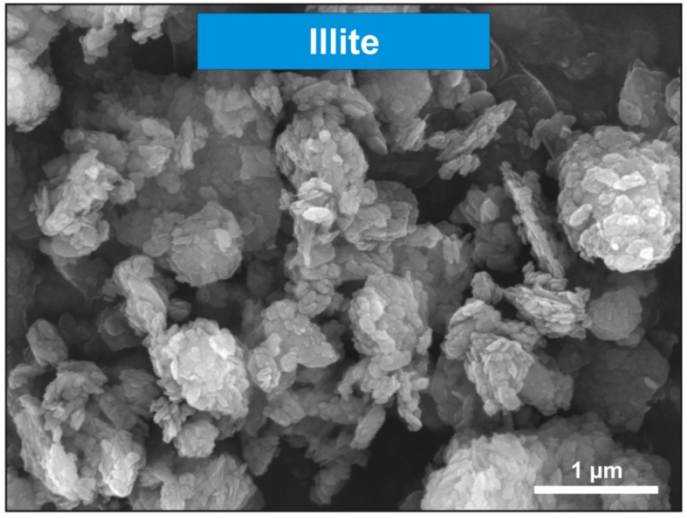
Stokes D. (2008) "Principles and Practice of Variable Pressure / Environmental Scanning Electron Microscopy."

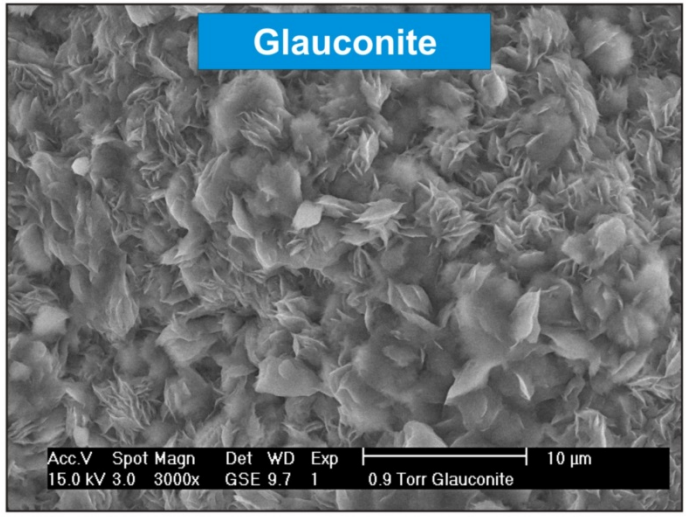
Imaging of Clays

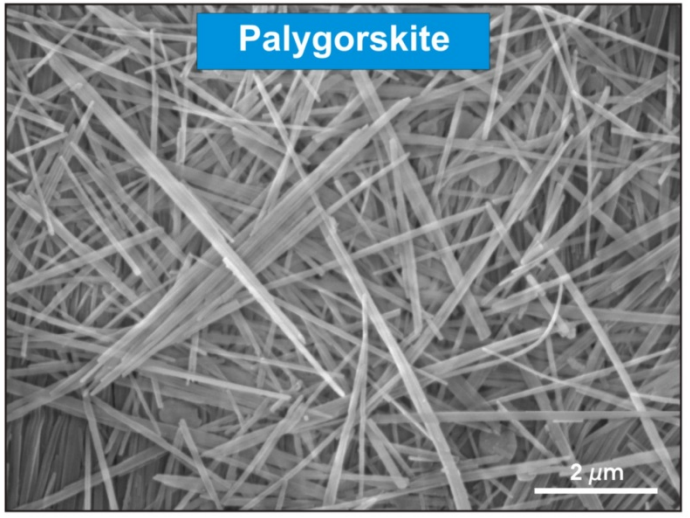






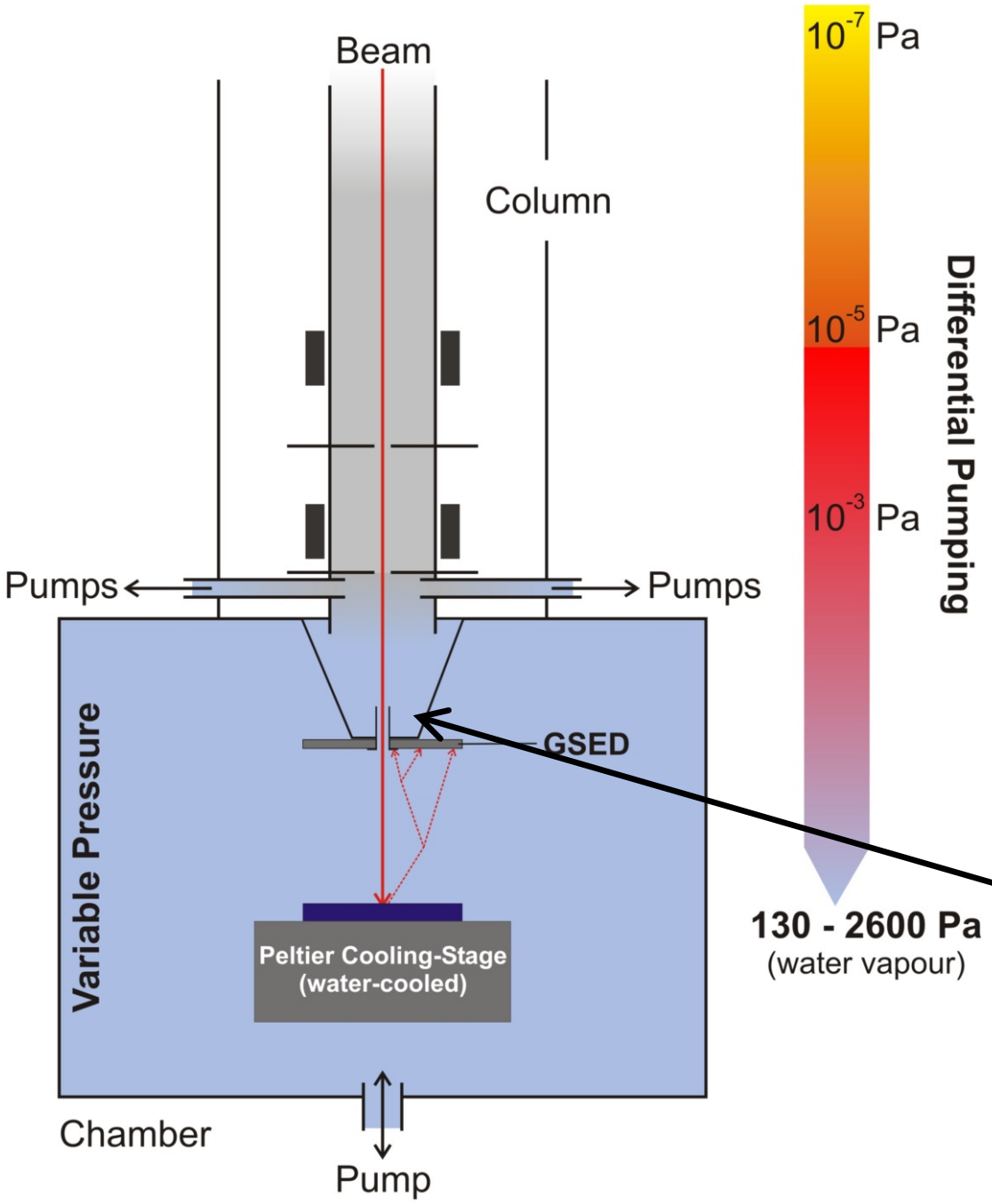






Adushkin V.V., Friedrich F. et al. (2015), Doklady Earth Sciences, 460,137.
Adjdir M., Friedrich F., et al. (2009). Applied Clay Science, 46, 185.
Images: www.minersoc.org/pages/gallery/claypix/index.html & http://www.fei.com/image-contest/2015/

The Environmental Scanning Electron Microscope



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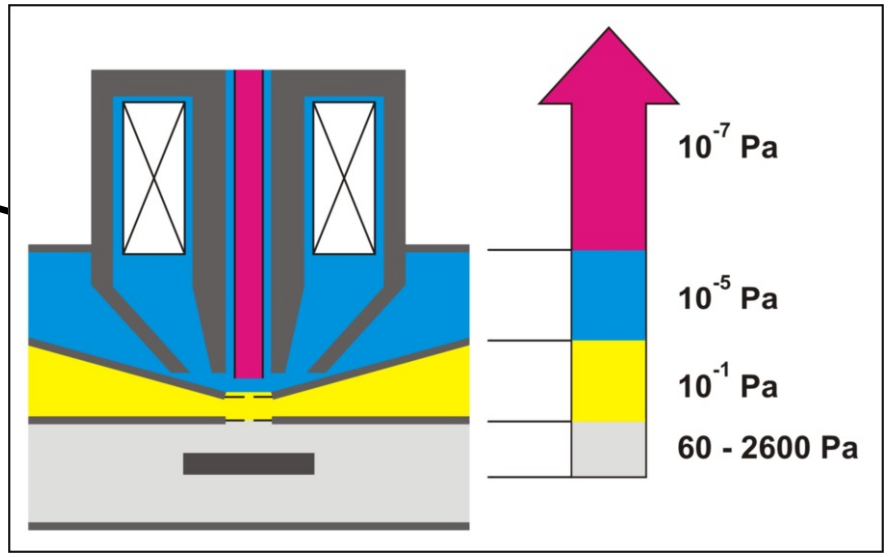
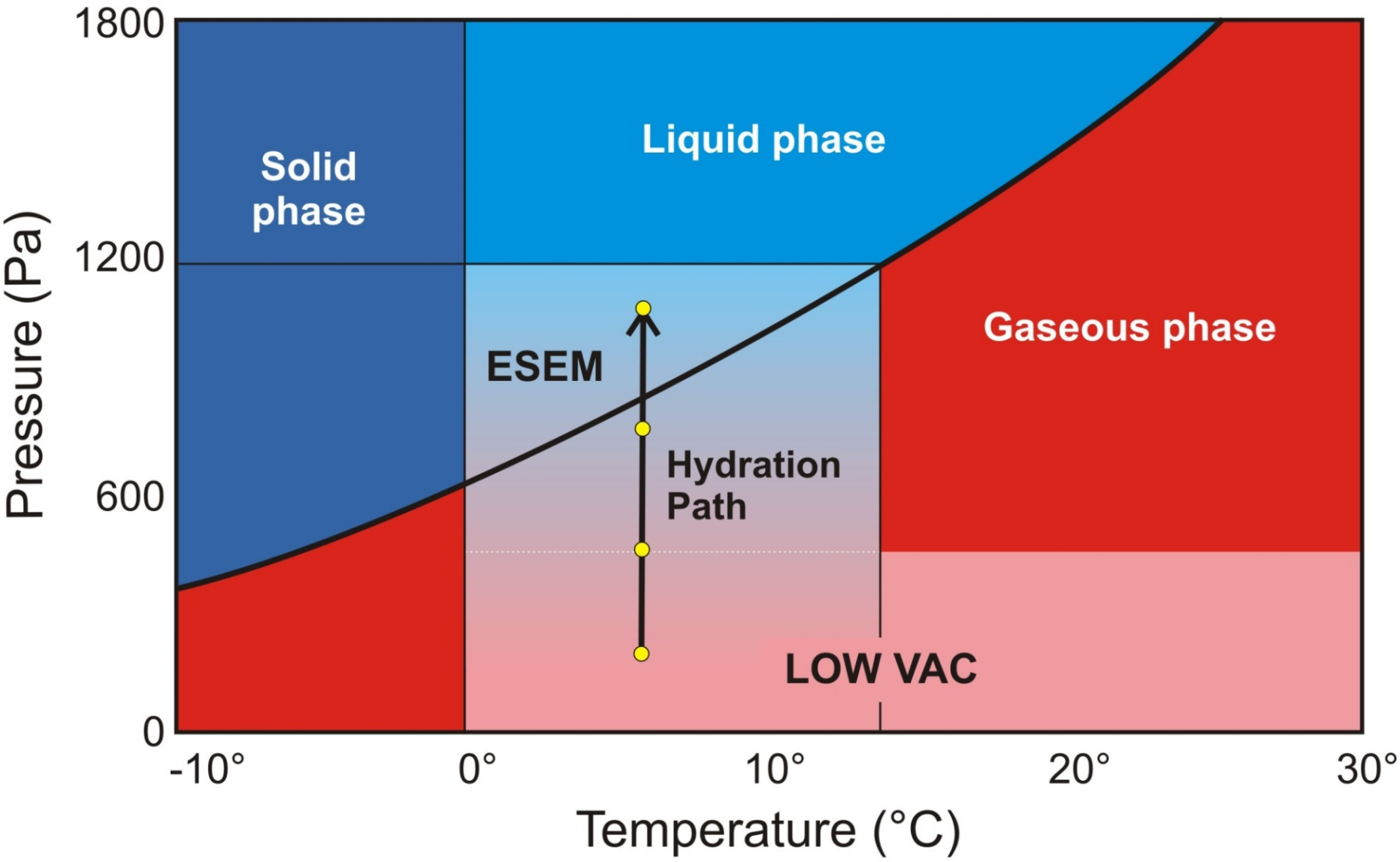


"Differential Pumping"

Donald A.M. (1998) Current Opinion in Colloid and Interface Science, 3, 143.

Phase Diagram of Water

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



Phase Diagram of Water

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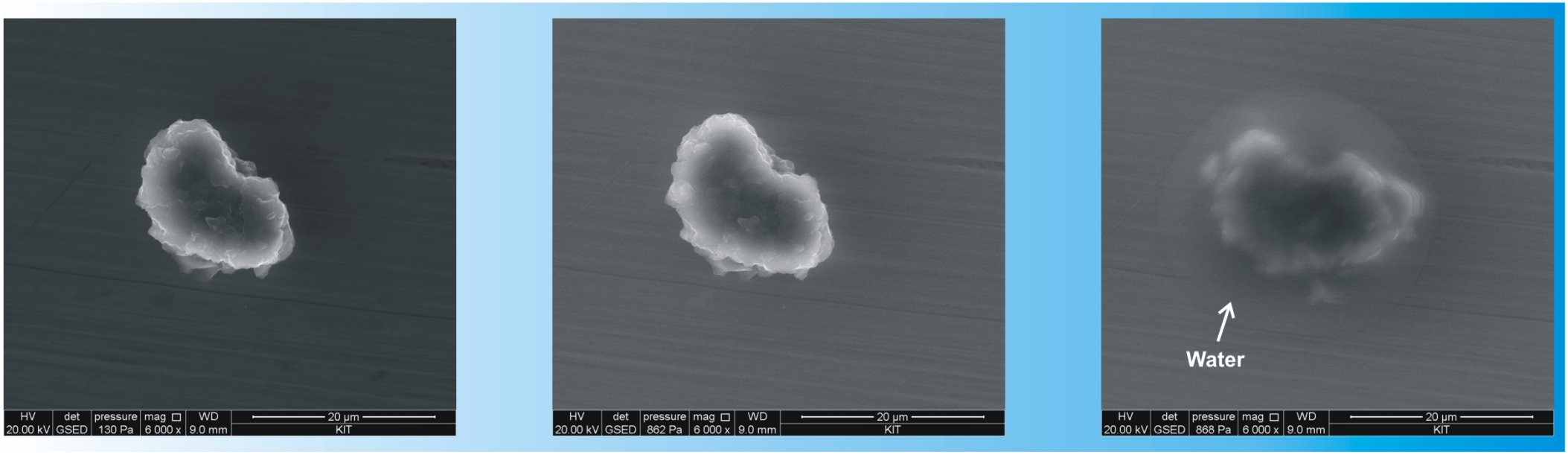
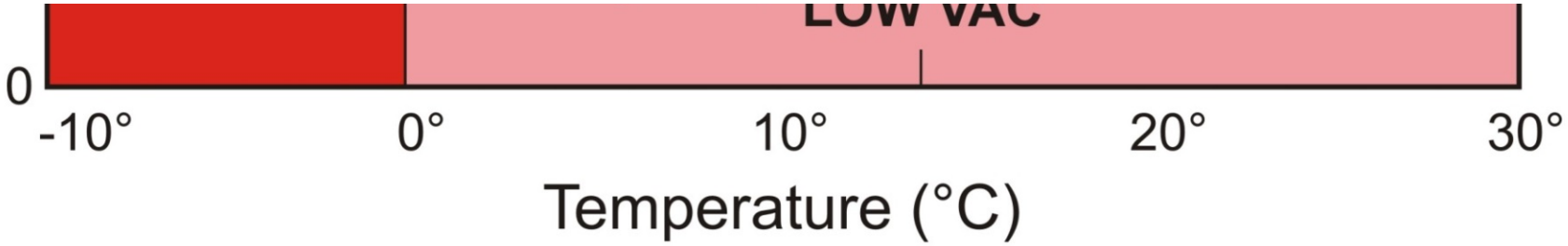
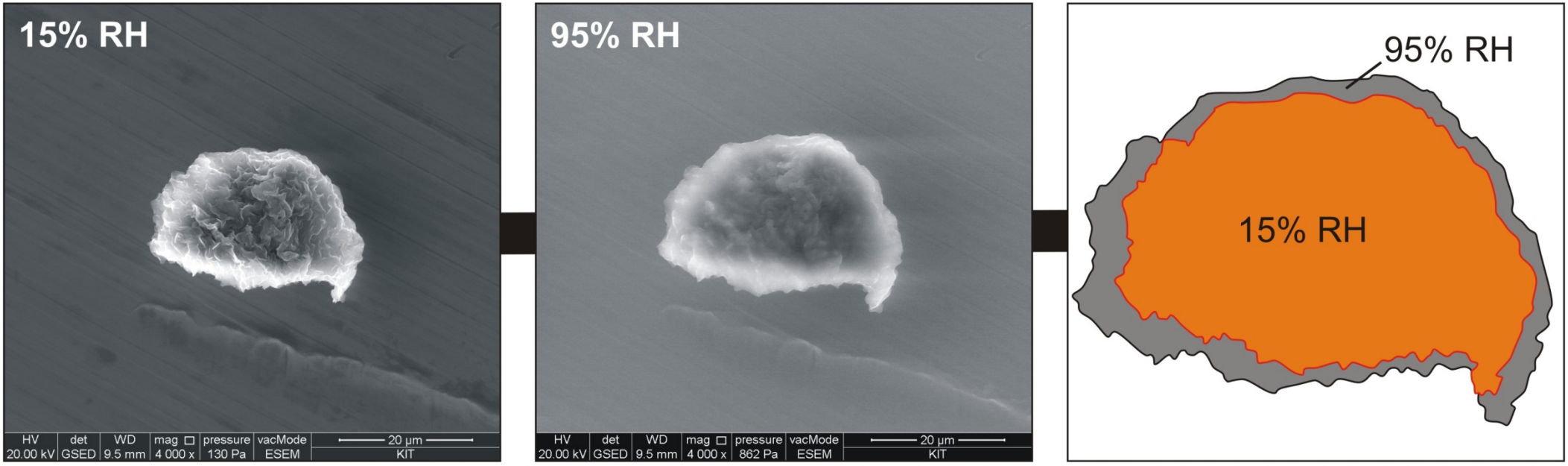


Even imaging of liquid water is possible!

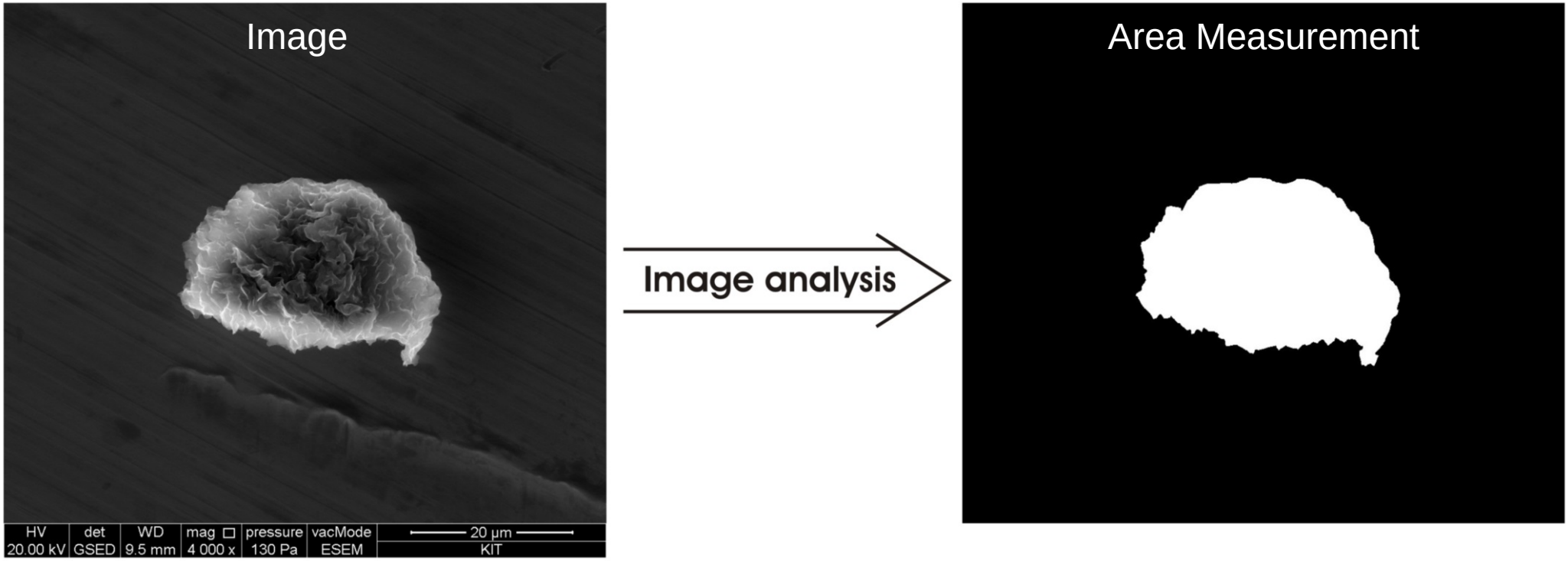


(Febex-)Bentonite Aggregates
(Fraction < 2 µm)



Changes in aggregate morphology and area are visible

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



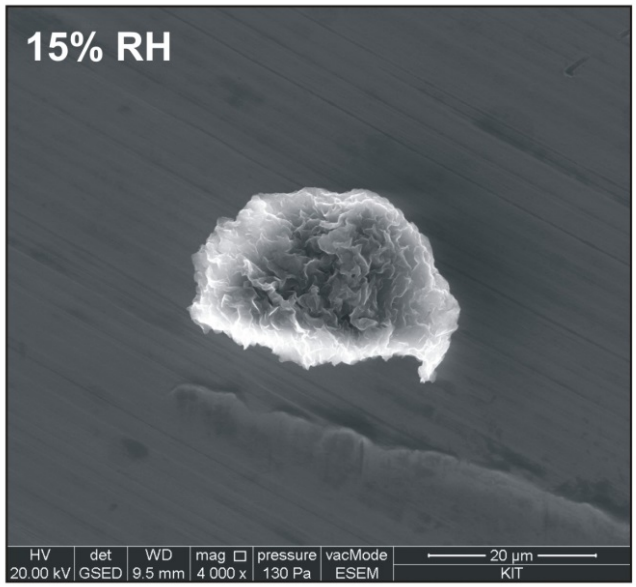
Process:

1. Defining an area of interest
2. Selection of gray scale threshold
3. Measurement of area
4. Calculation of swelling rate (%) or (linear) coefficient of expansion
   Swelling (%) = $((S_i - S_0) / S_0) \times 100$

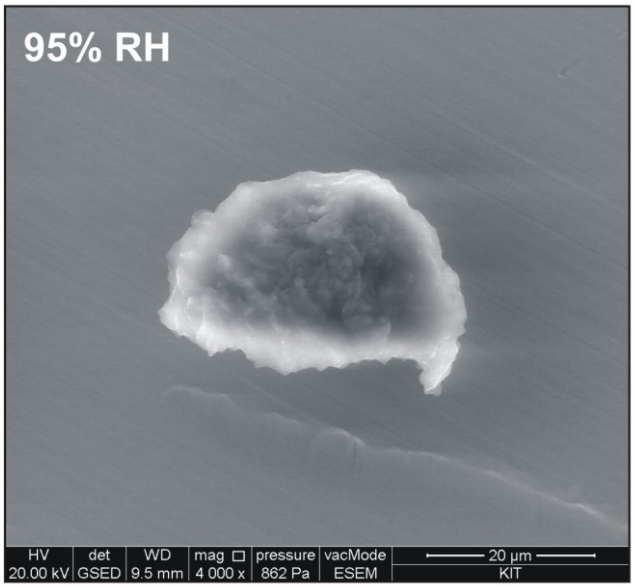
Montes-H et al. (2003). Applied Clay Science, 23, 309.
Friedrich et al. (2015). CMS Workshop Lecture Series, Vol. 19.

Important Questions

- Isotropic or anisotropic swelling behaviour?
- Swelling contribution perpendicular to c-axis?

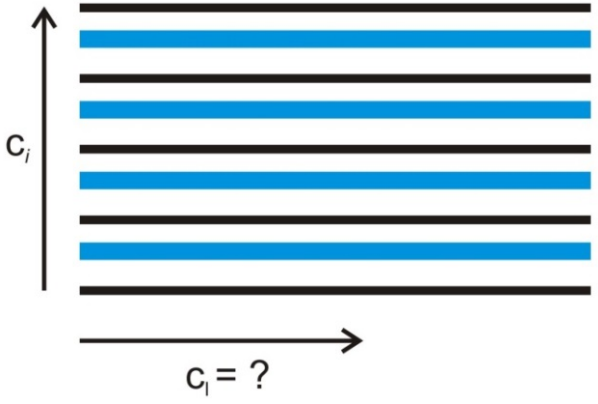


Swelling



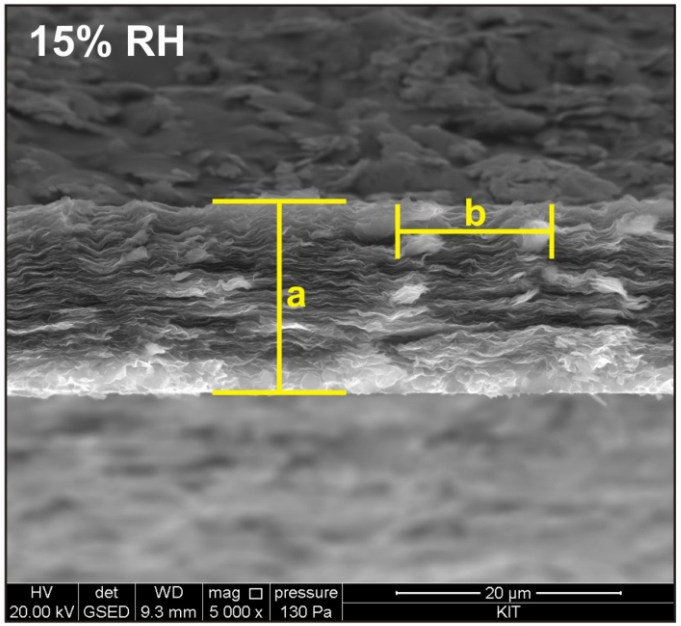
Clay particle

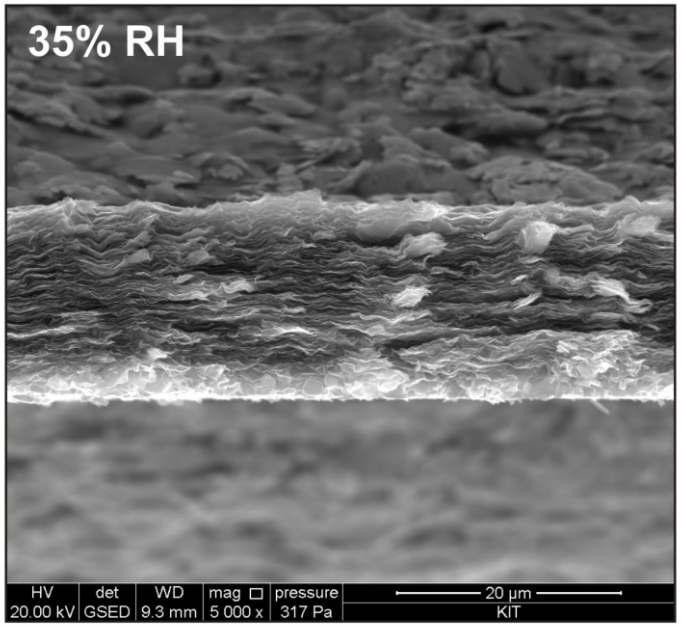
Hydration

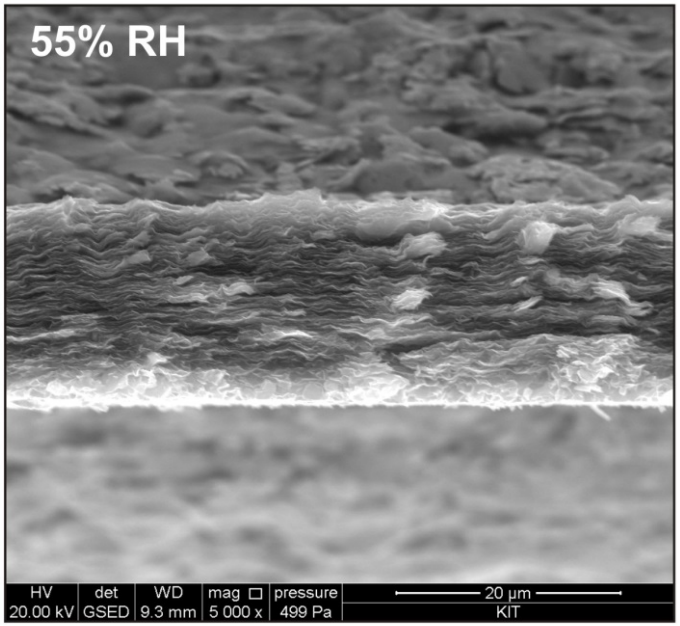


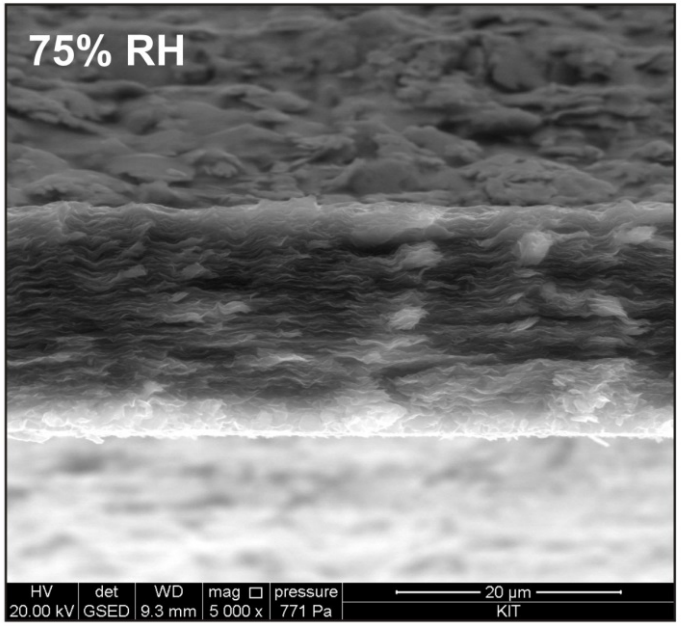
Hydrated particle

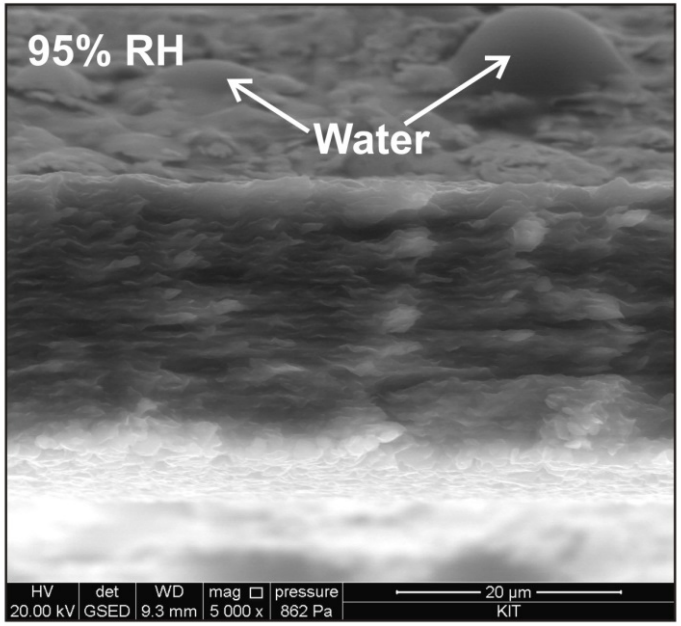
Anisotropic Swelling / Bentonite Films

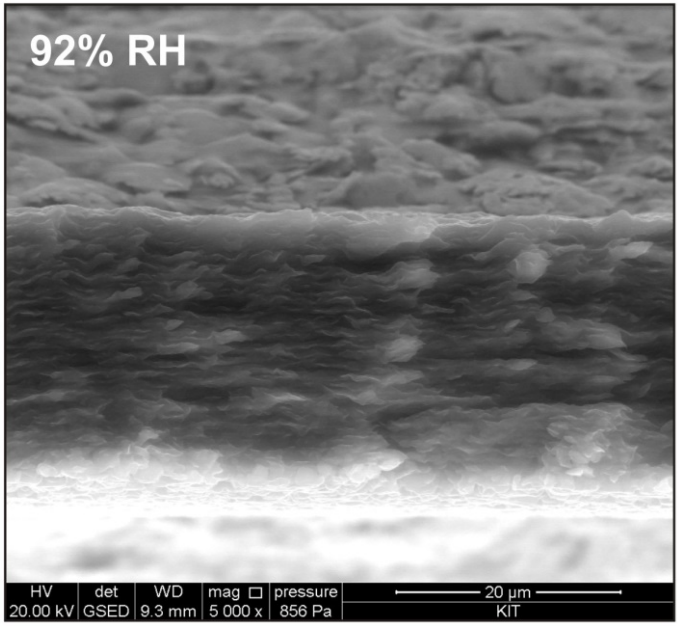








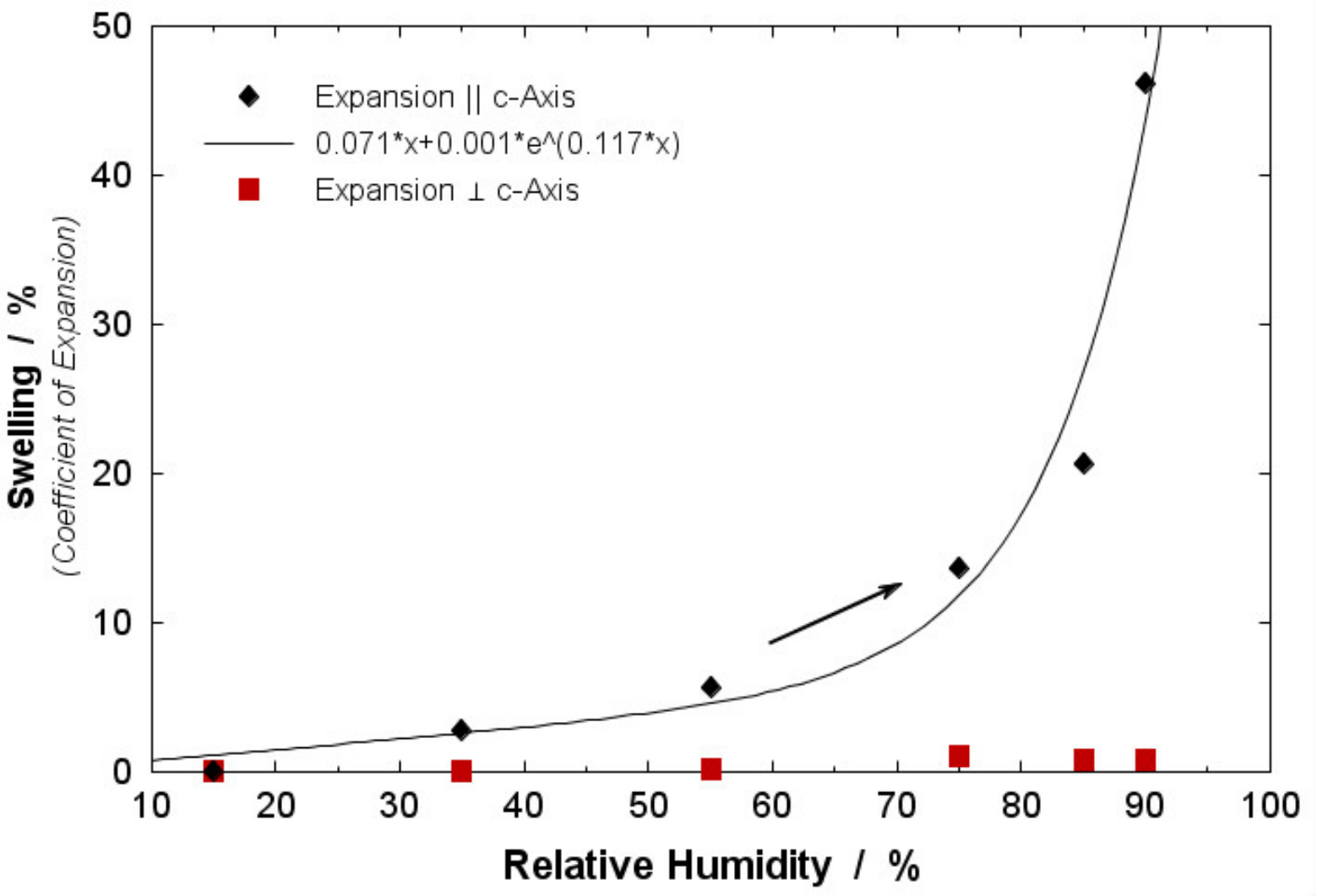




a) Expansion ∥ c-axis
b) Expansion ⊥ c-axis

Carrier et al. (2013), Langmuir, 29, 12823.

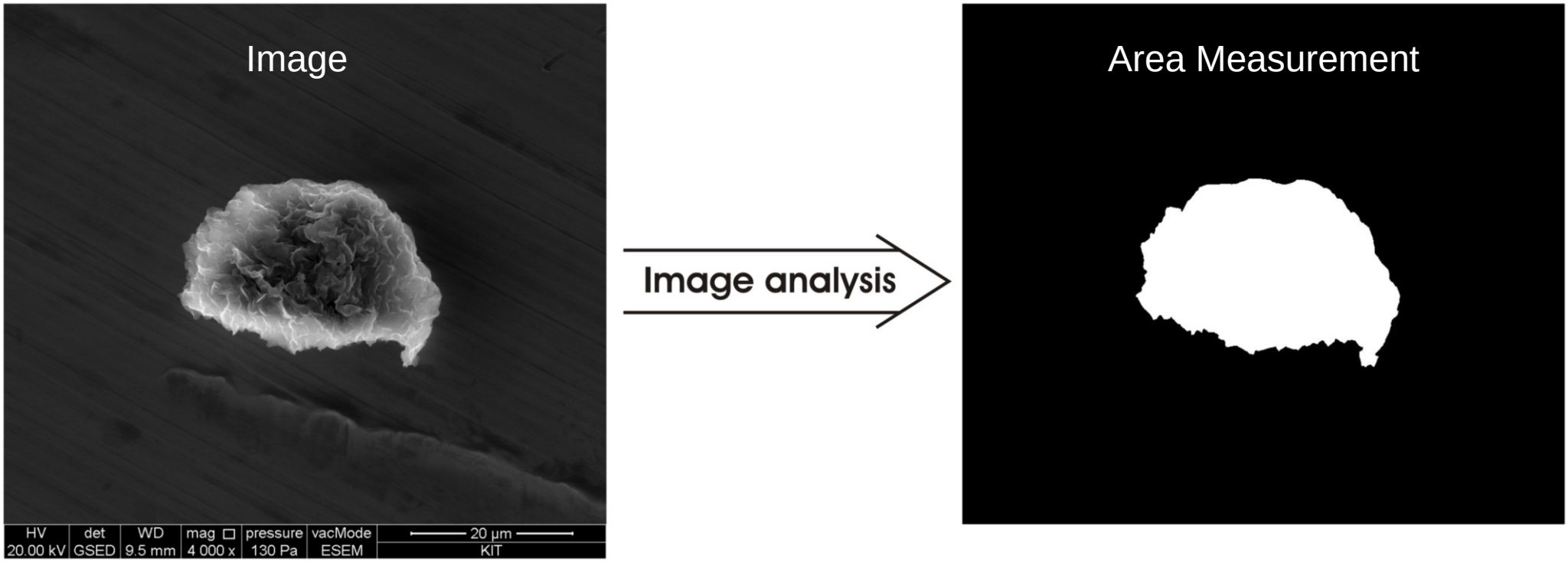
Anisotropic Swelling / Bentonite Films



Strongly anisotropic behaviour of bentonite during hydration!

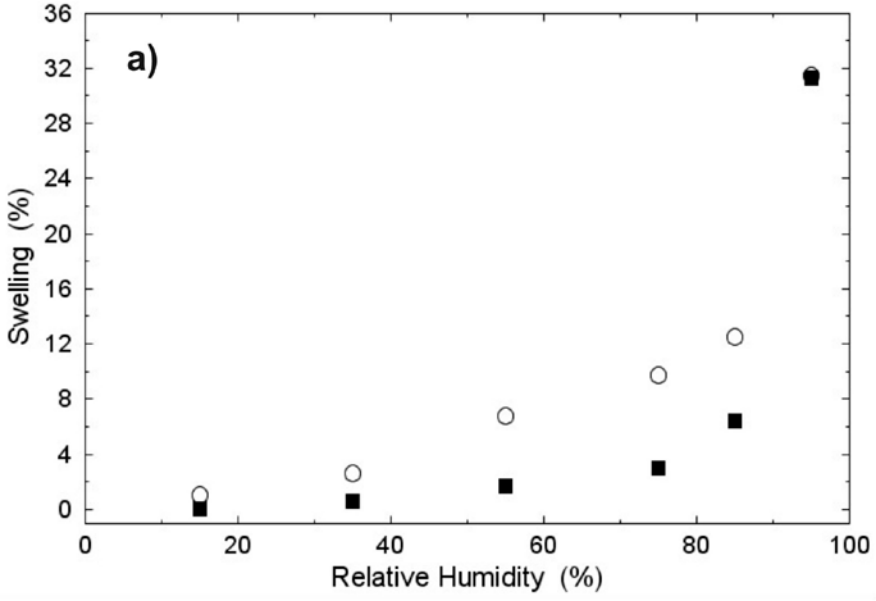
- Strong swelling along c-axis (high gradient)
- Very low swelling perpendicular to c-axis but not equal to zero. (missaligned clay particles not perfectly parallel)

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

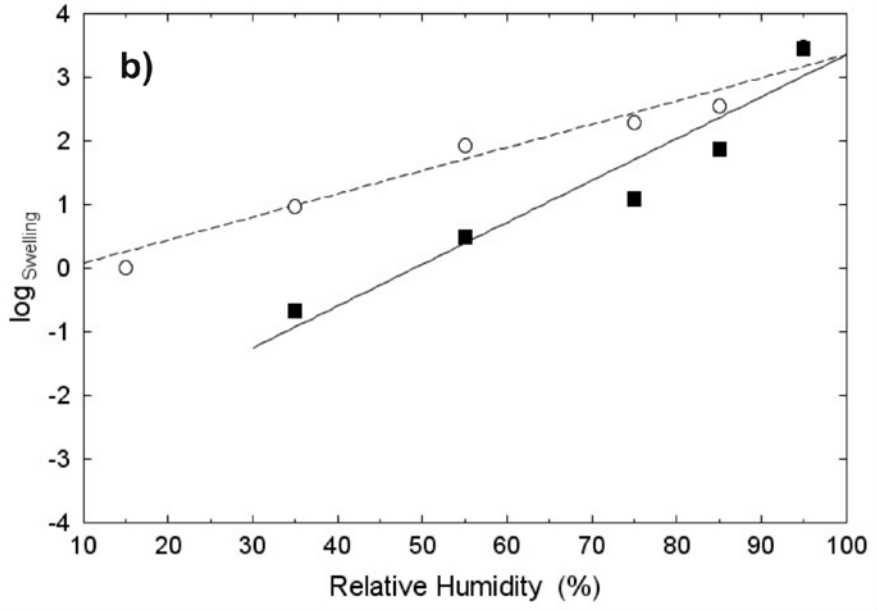


! Data evaluation procedure can be used for clay aggregates with randomly distributed particles !

Isotherm



Logarithmic representation



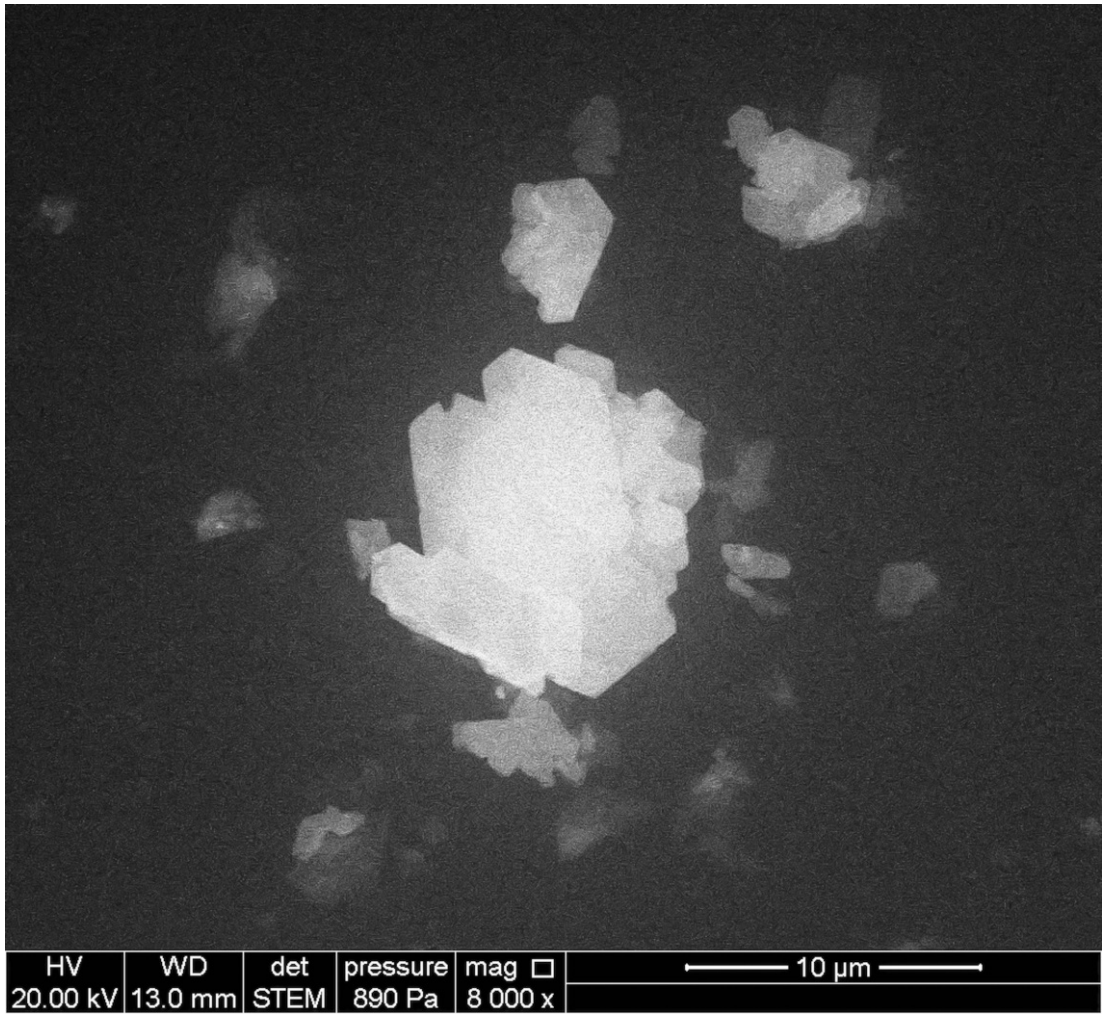
- Swelling rates are very low at the beginning.
- Increase exponentially at high humidities.
- Dehydration path proceeds at slightly higher swelling percentages.
- BET-measurements show similar types of hysteresis (type H3).
- Typical for plate-like particles giving rise to slit shaped pores.

- Fitted with a linear function.
- Slope of hydration path is larger than dehydration path.
- Can be assigned to first order reaction (water availability is the driving force)

→ Attributed to changes in particle arrangement and interlayer distances.

Wet-Scanning Transmission Electron Microscopy (Wet-STEM)

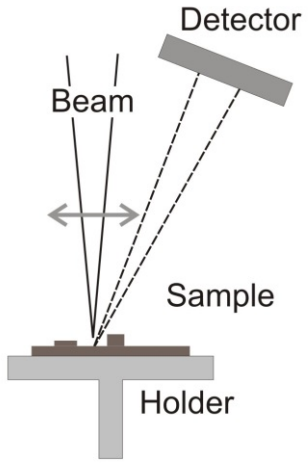
In-*situ* measurement of particles in suspenison



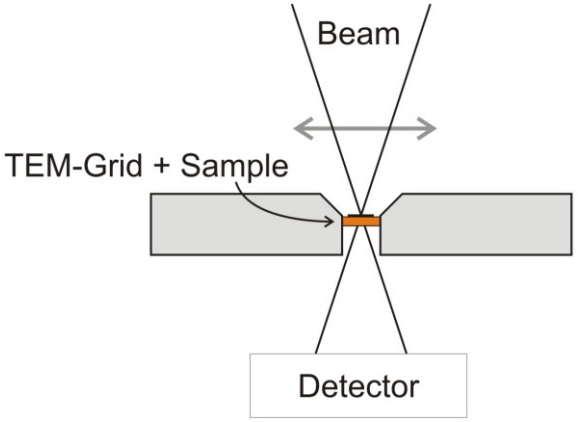
Wet-Mode ESEM vs. Wet-STEM

Principle

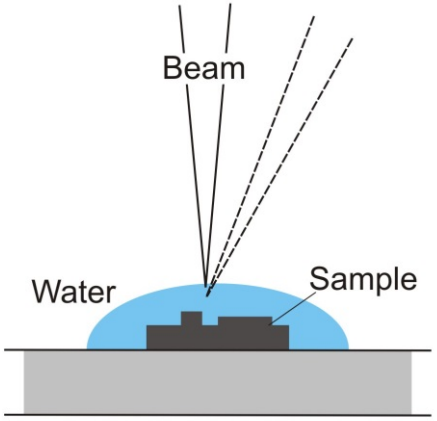
SEM



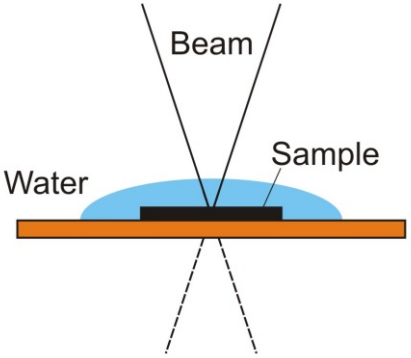
STEM



ESEM wet-Mode



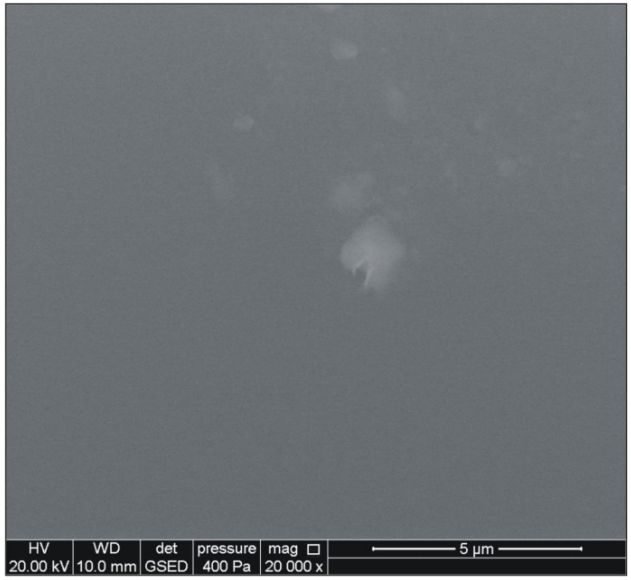
Wet-STEM



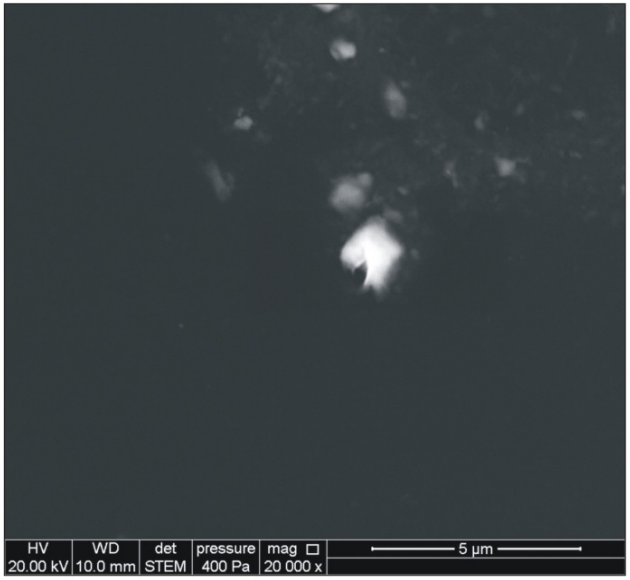
Williams D.B. & Carter C.B. (2009) Transmission Electron Microscopy, Part 2. 2nd Ed., Springer.

Example: Na-Febex-Suspension (< 2 mm)

ESEM wet-Mode



wet-STEM

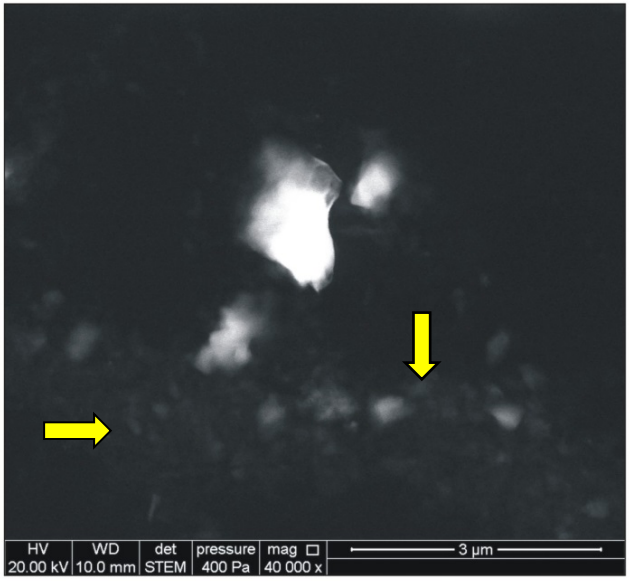


Why wet-STEM?

Imaging of very small and thin single particles in-situ in environments from wet too dry.

Why wet-Mode ESEM?

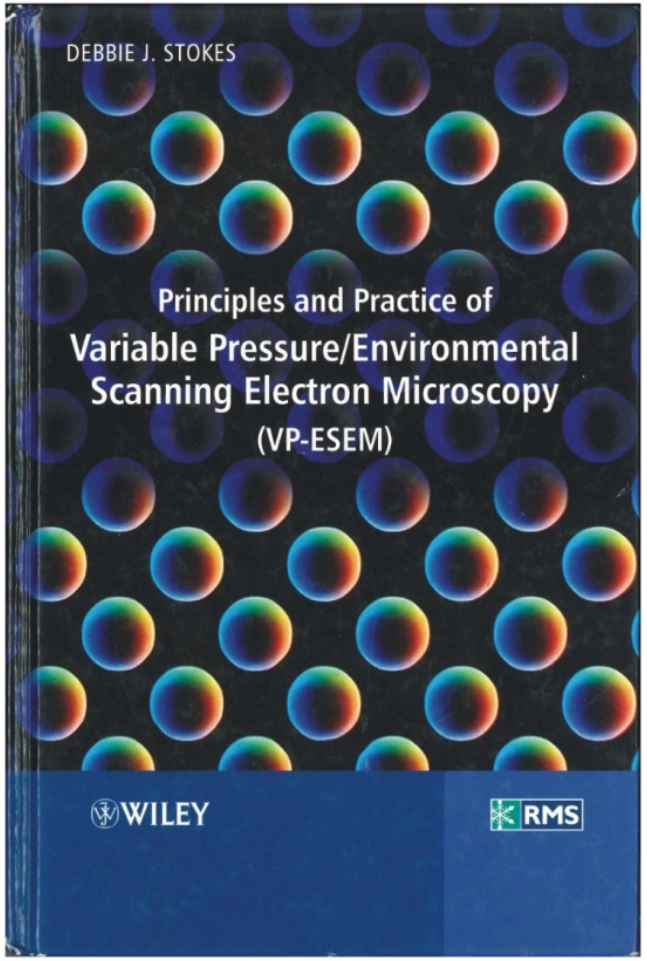
Imaging of particles under humid conditions (no open water).

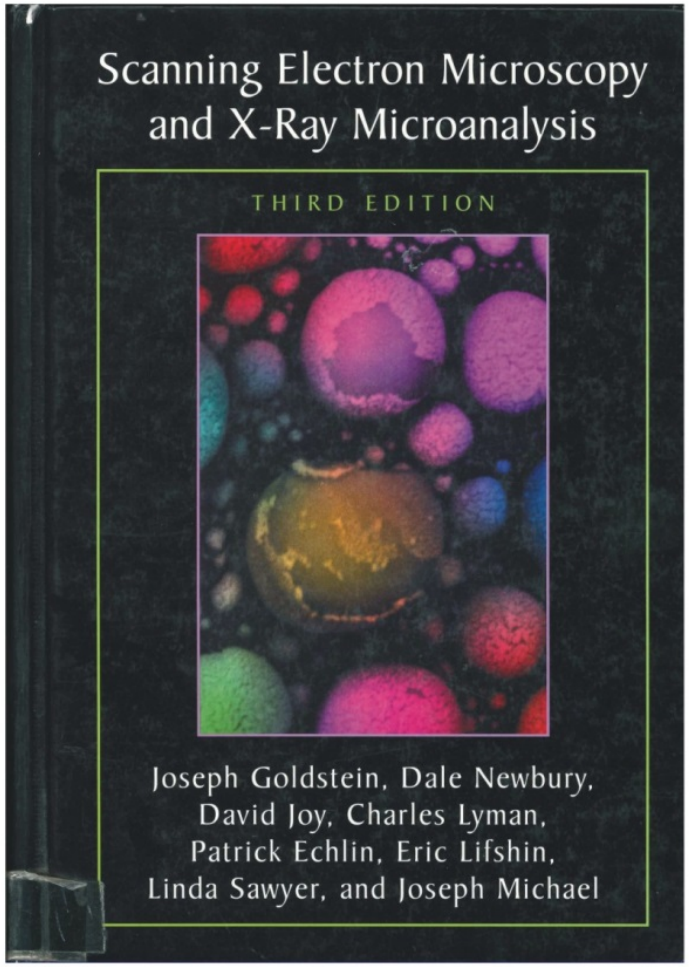


Yellow arrows: particle sizes < 100 nm.

Bogner et al. (2005), Ultramicroscopy, 104, 290.
Bogner et al. (2007), Micron, 38, 390.

Further Reading





Periodicals:

e.g. *Scanning, Ultramicroscopy, Microscopy* (previously *Journal of Electron Microscopy*)

(good & free: Microscopy & Analysis, http://www.microscopy-analysis.com/magazine)