

# Nerudné nerastné suroviny (íly a zeolity)

- charakterizácia, vlastnosti, využitie.

## Industrial minerals (clays and zeolites)

- characterization, properties,  
applications.

Marek Osacký

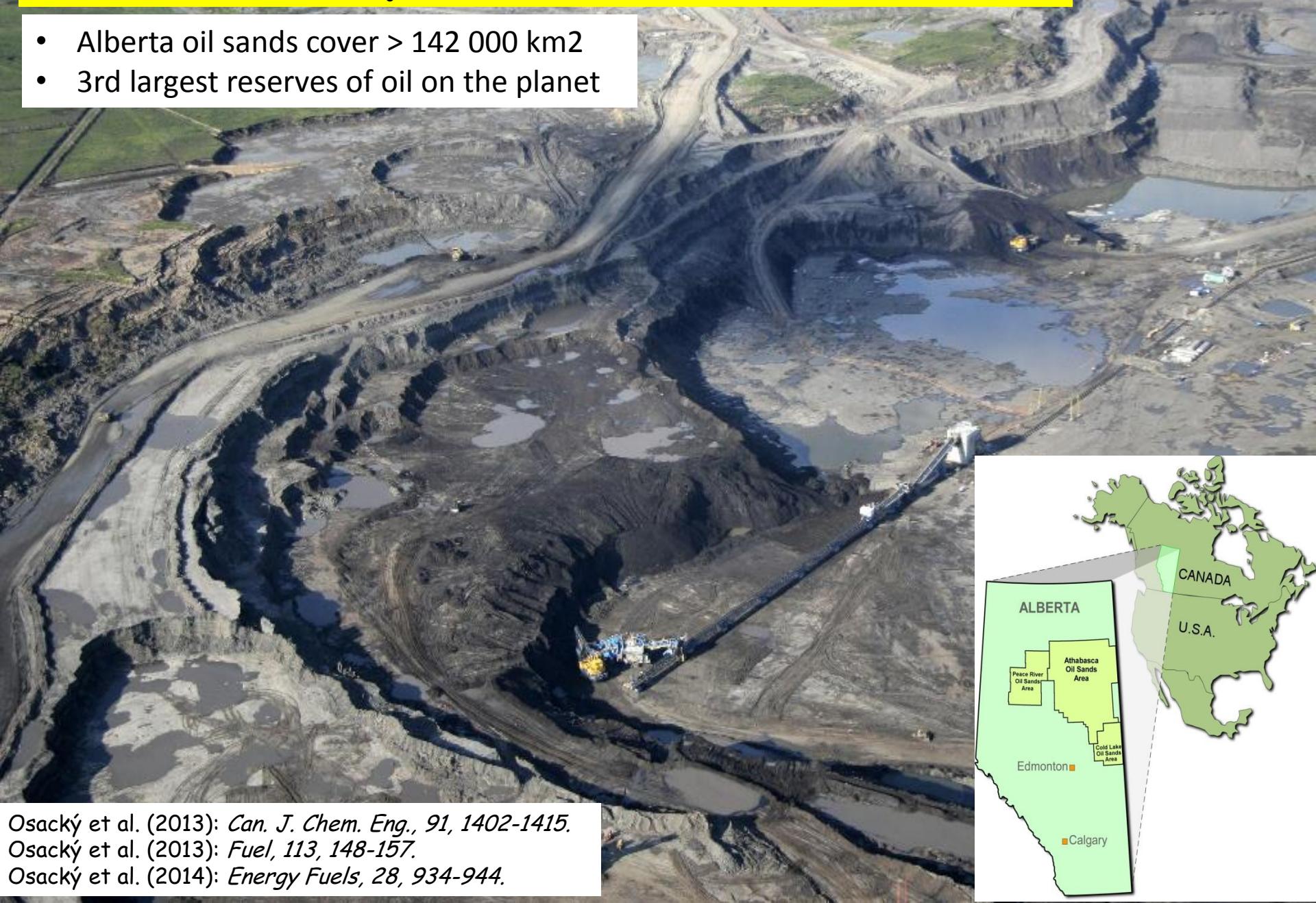
## Research interests:

- Characterization of industrial mineral deposits
- Methods (mineralogy, chemistry, surface properties)
- Applied research related to
  - clay minerals
  - zeolites

# **Characterization of industrial mineral deposits (examples)**

# Oil sands deposit (Alberta, Canada)

- Alberta oil sands cover > 142 000 km<sup>2</sup>
- 3rd largest reserves of oil on the planet



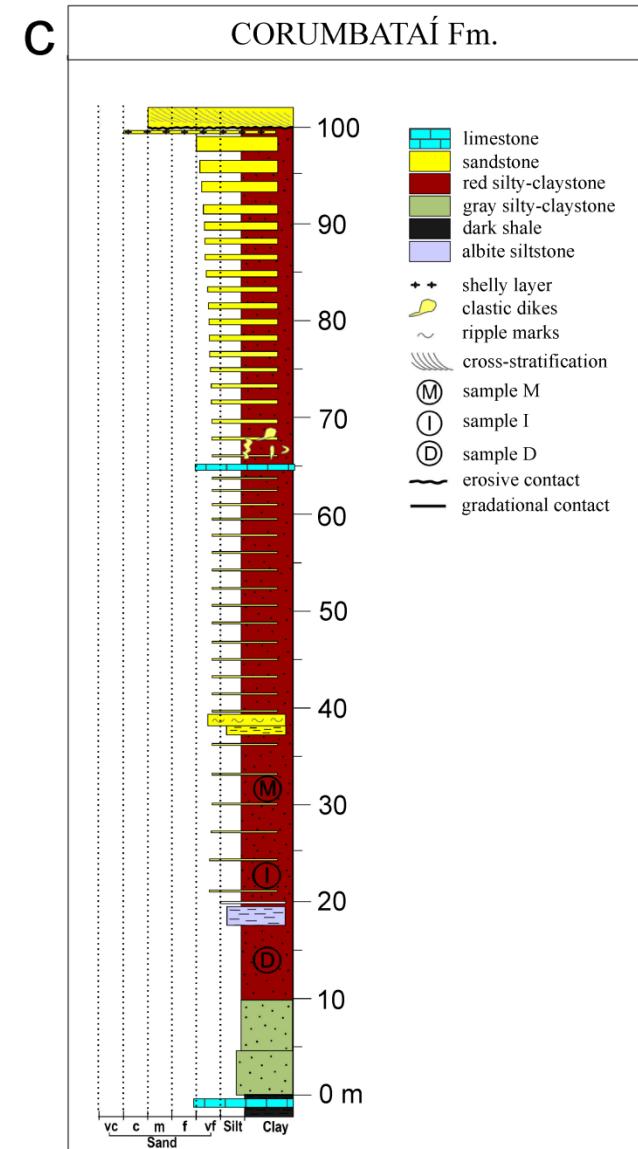
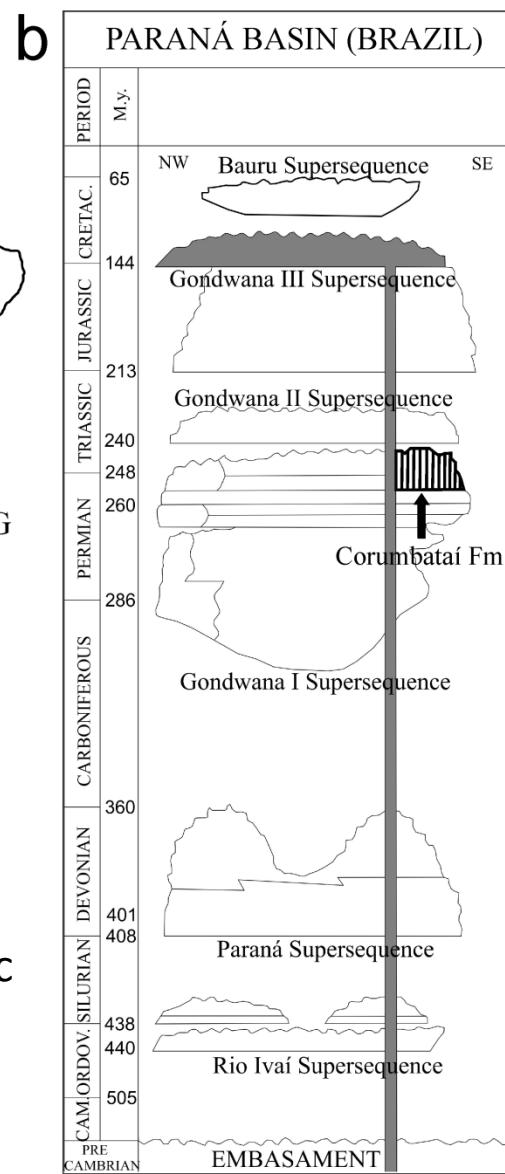
Osacký et al. (2013): *Can. J. Chem. Eng.*, 91, 1402-1415.  
Osacký et al. (2013): *Fuel*, 113, 148-157.  
Osacký et al. (2014): *Energy Fuels*, 28, 934-944.

# Mature fine tailings MFT (Alberta, Canada)

- Environmental issue
- Area of > 250 km<sup>2</sup> (in 2016)
- About 1.3 billion m<sup>3</sup> (in 2020)



# Ceramic clays deposit - Santa Gertrudes (São Paulo, Brazil)



CDSG - Ceramic district  
Santa Gertrudes

Largest producer of ceramic  
floor and wall tiles in Brazil

# Ceramic clays deposit - Santa Gertrudes (São Paulo, Brazil)

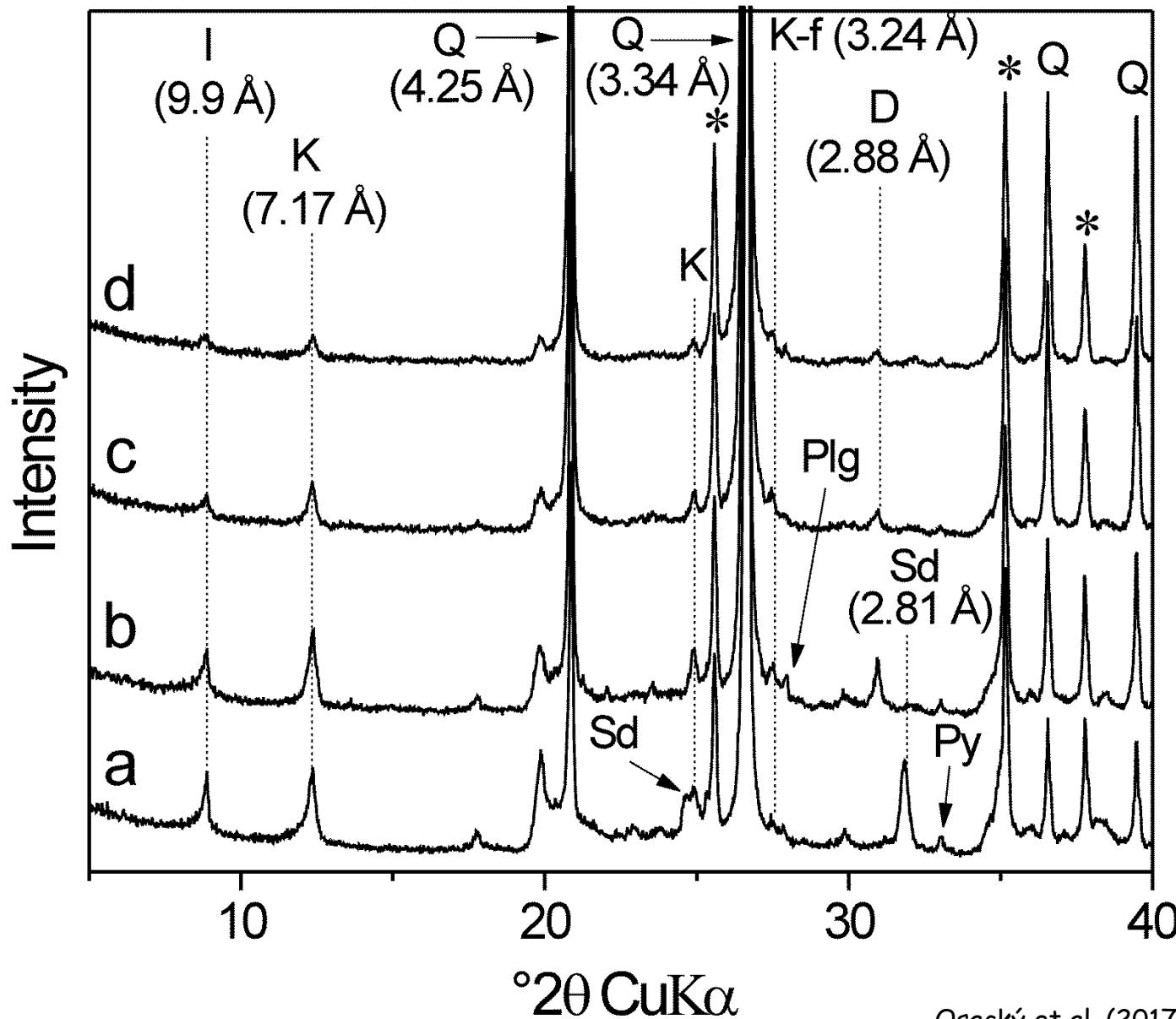


# Bentonite (smectite) K-bentonite (illite-smectite) deposits (Kremnické vrchy Mts., Slovakia)



# Methods (mineralogy, chemistry, surface properties)

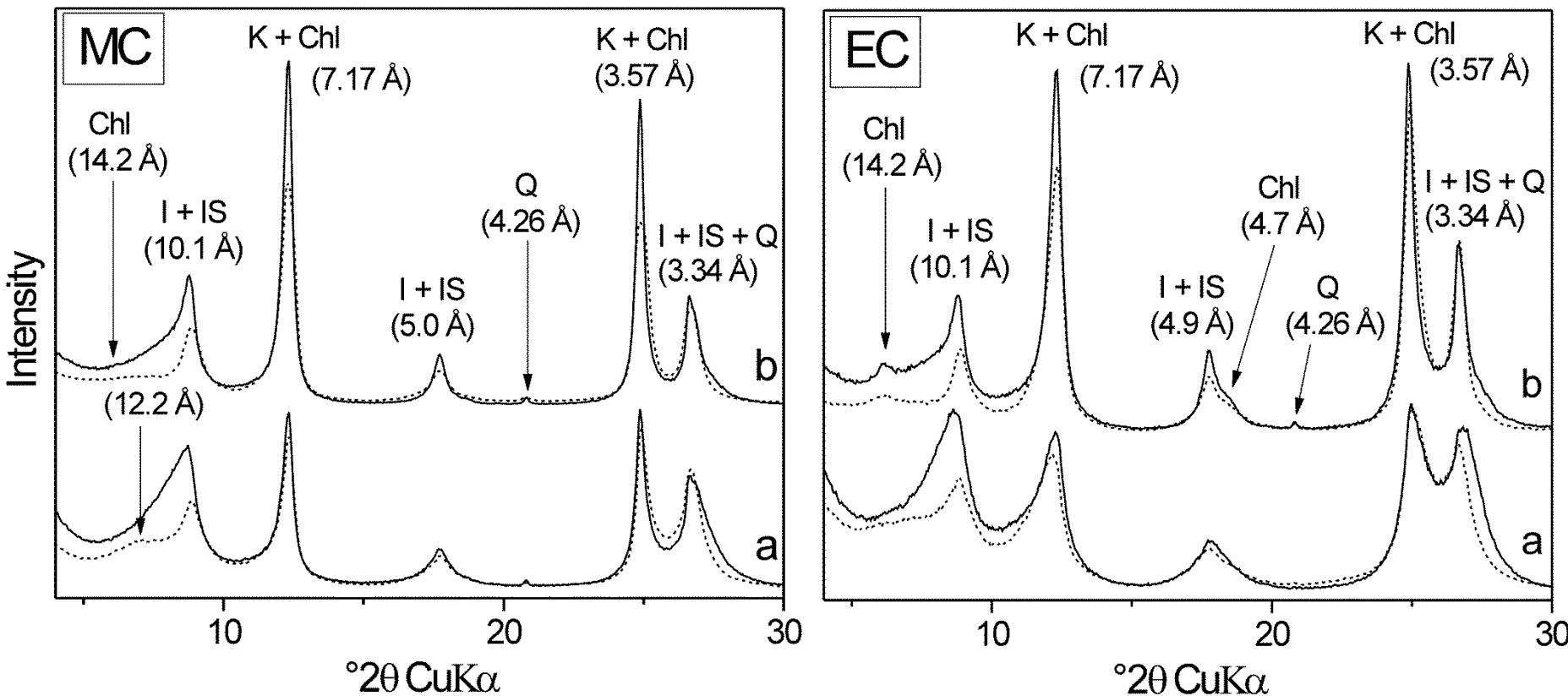
# X-ray diffraction (random preparations)



**Identification of  
Non-clay minerals**  
*hkl  
reflections*

- I – illite
- K – kaolinite
- Q – quartz
- D – dolomite
- Sd – siderite,
- K-f – K-feldspars
- Plg – plagioclases
- Py – pyrite
- \* - internal standard

# X-ray diffraction (oriented preparations)



**Identification of  
clay minerals**

**00l  
basal reflections**

IS – illite-smectite  
I – illite  
Chl - chlorite  
K – kaolinite  
Q – quartz

- **Analysis of clay fraction ( $<2 \mu\text{m}$ )**
- **Diagnostic tests (chemical saturation, heating, etc...)**

# Quantitative X-ray diffraction (random preparations) – RockJock11 software

Sample	Smectite	Quartz	Kaolinite	Illite	Opal-CT	Whole-rocks
						Feldspars
J (Jelšový Potok)	74	6	2	5	0	13
L (Lieskovec)	51	12	17	4	4	12

Osacký et al. (2012): *Clay Miner.*, 47, 465-479.

## Fractions < 2 µm

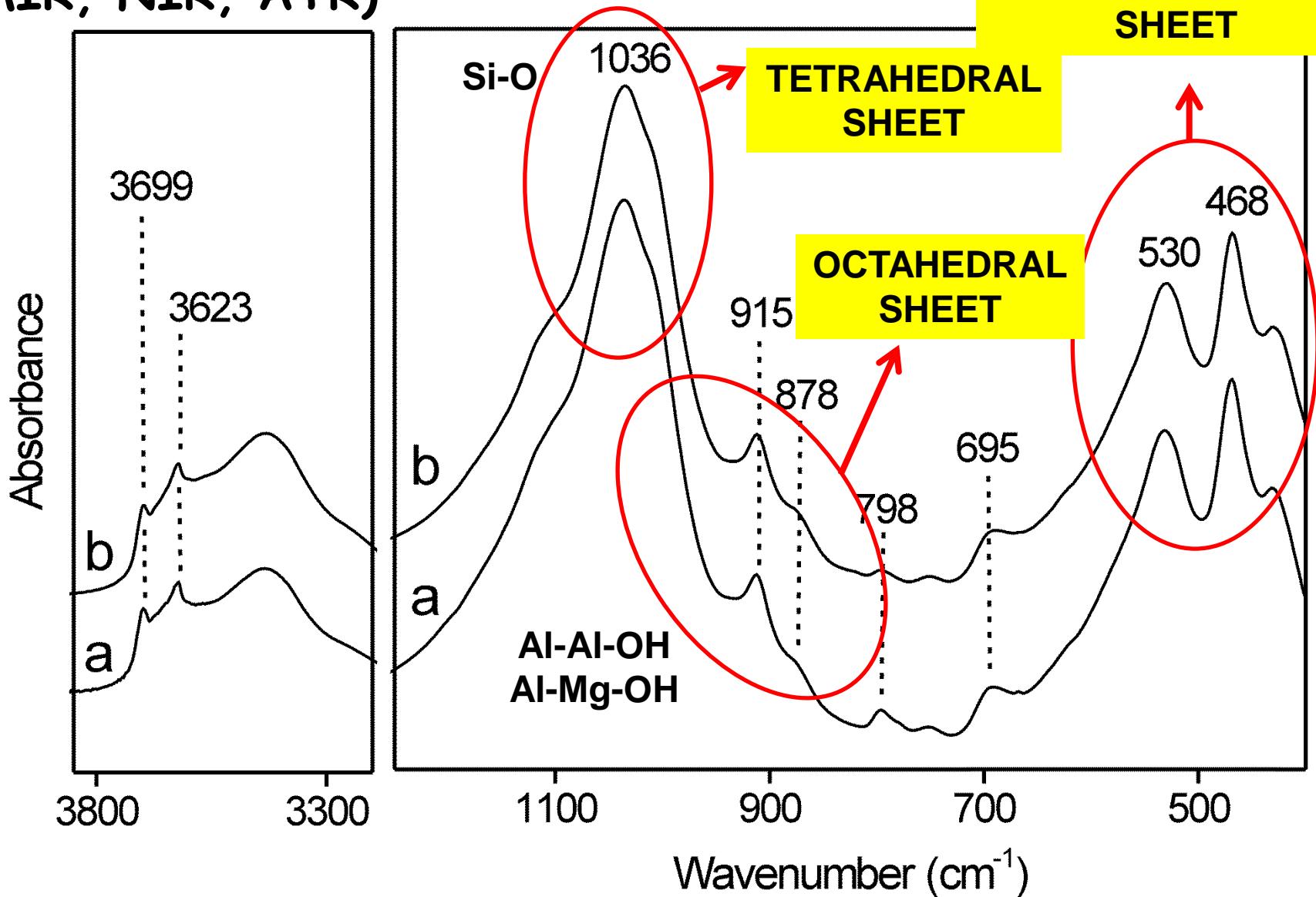
Sample	Smectite	Quartz	Kaolinite	Illite	Opal-CT	Feldspars
J (Jelšový Potok)	89	3	2	0	0	6
L (Lieskovec)	79	1	8	3	2	7
SAz-1	97	tr.	0	2	0	1
SCa-3	93	tr.	tr.	4	0	3
STx-1	70	0	tr.	0	30	tr.
SWa-1	96	tr.	tr.	tr.	0	4

tr. – traces (< 1 mass%)

Osacký et al. (2013): *Appl. Clay Sci.*, 72, 26-36.

# Infrared spectroscopy (MIR, NIR, ATR)

BONDING  
TETRAHEDRAL AND  
OCTAHEDRAL  
SHEET



# Chemical analysis

Chemical composition in wt.% (ICP, XRF, ....),  
bentonites, < 2 µm

Sample	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	LOI	Total
J	55.66	18.78	2.40	0.21	2.84	2.12	1.31	0.20	14.31	97.83
L	54.44	19.26	7.51	0.14	1.53	2.12	0.87	0.49	15.29	101.65
SAz-1	56.04	15.60	1.37	0.08	5.17	2.92	0.12	0.24	18.49	100.03
SCa-3	55.30	14.85	1.63	0.17	5.73	3.06	0.24	0.40	18.70	100.08
STx-1	62.74	13.90	0.58	1.01	2.96	1.00	0.09	0.24	17.74	100.26
SWa-1	48.24	9.10	19.71	0.22	1.18	2.39	0.14	0.69	16.97	98.64

# Structural formulas calculation

ICP analysis corrected for mineral impurities (QXRD)

Smectites - structural formulae per  $O_{20}(OH)_4$ :



SWa-1



SAz-1

# BWA (Bertaut-Warren-Averbach) analysis

Mean crystallite thickness - smectites, < 2  $\mu\text{m}$

**STx-1**      7.9 nm

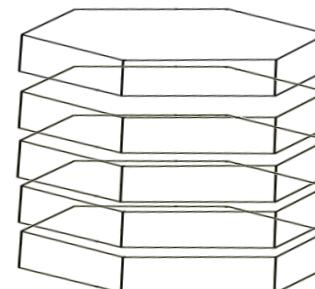
**J**                7.1 nm

**SAz-1**        6.9 nm

**SCa-3**        6.5 nm

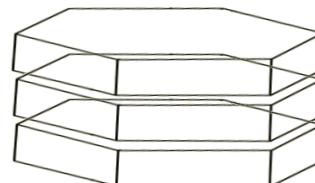
**SWa-1**       6.1 nm

**L**                6.0 nm



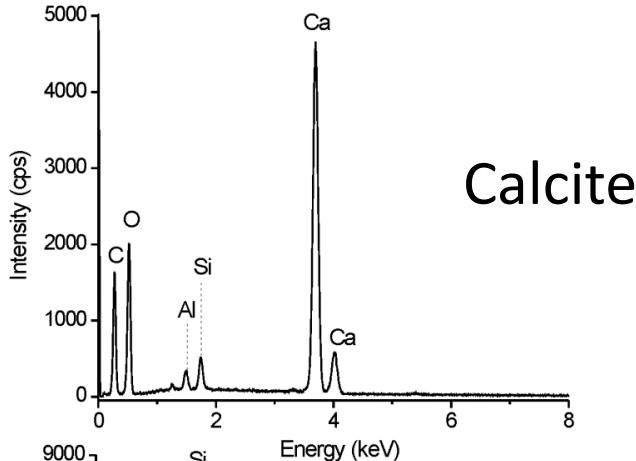
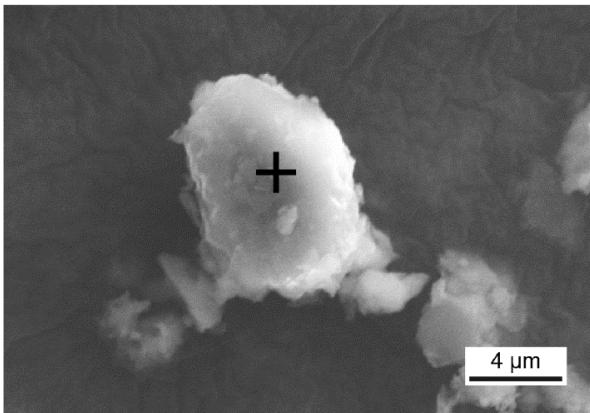
} crystallite thickness

coherent scattering domains

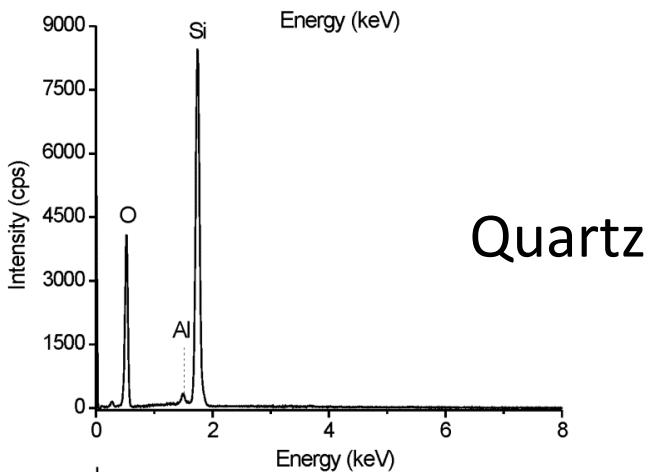
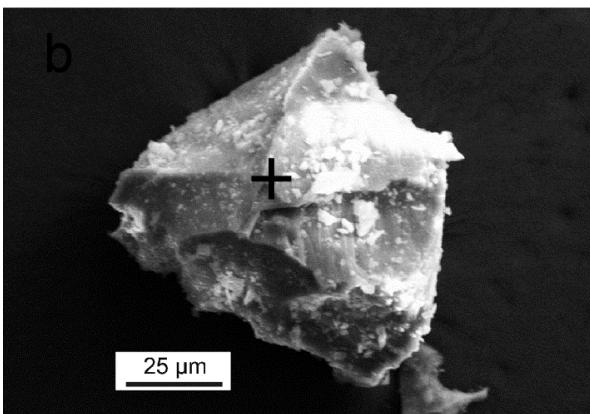


# SEM-EDX

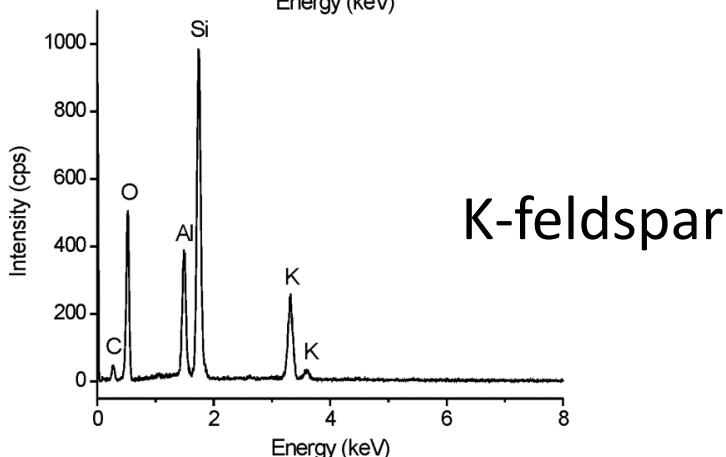
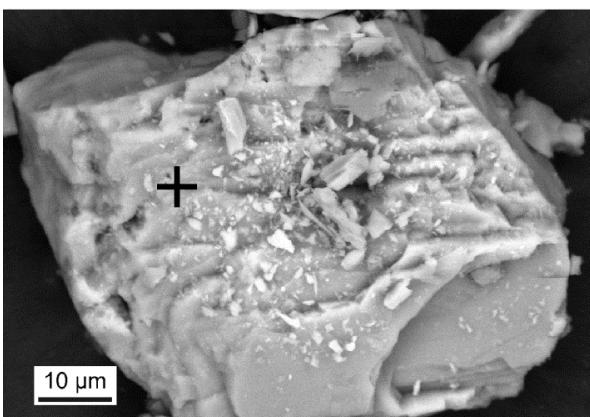
Scanning electron  
microscopy- Energy  
dispersive X-ray  
spectroscopy



Calcite



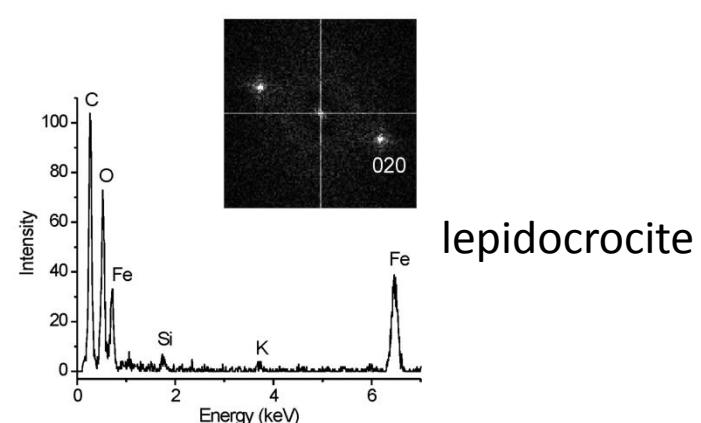
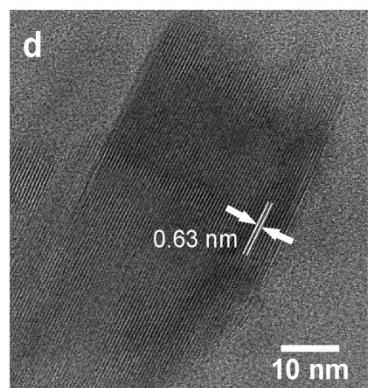
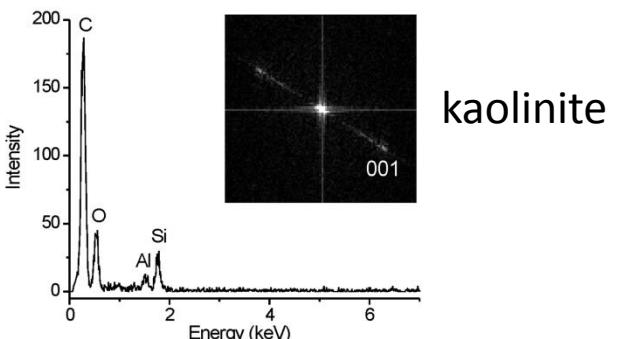
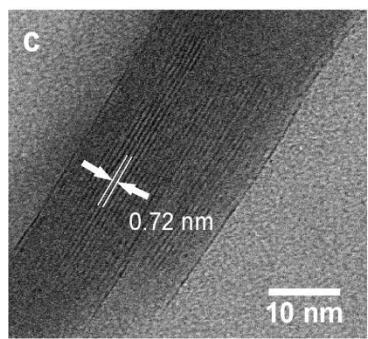
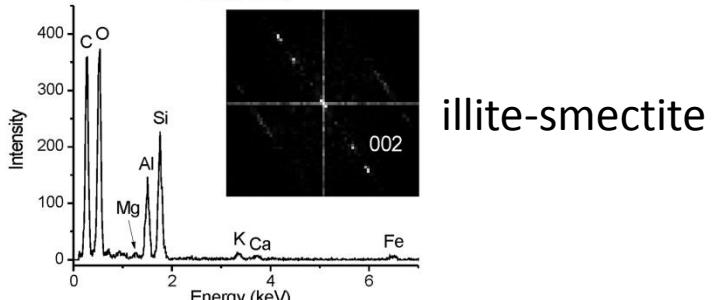
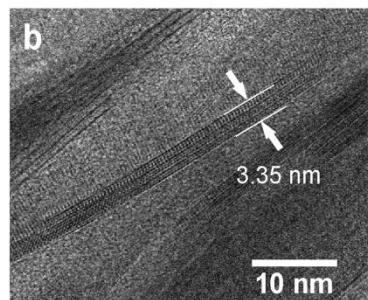
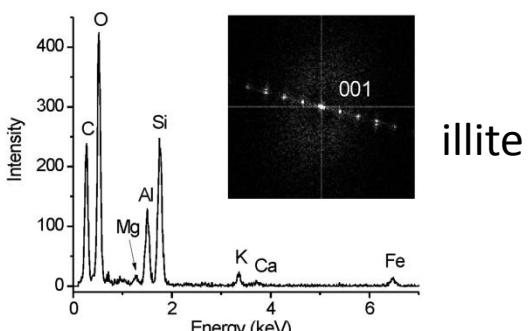
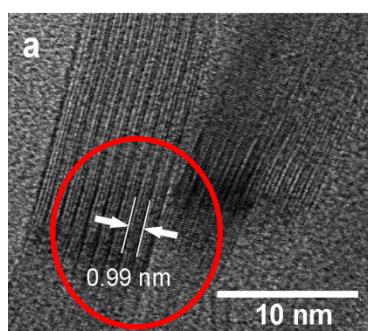
Quartz



K-feldspar

# STEM-HAADF

Scanning-transmission electron microscopy- High angle annular dark field

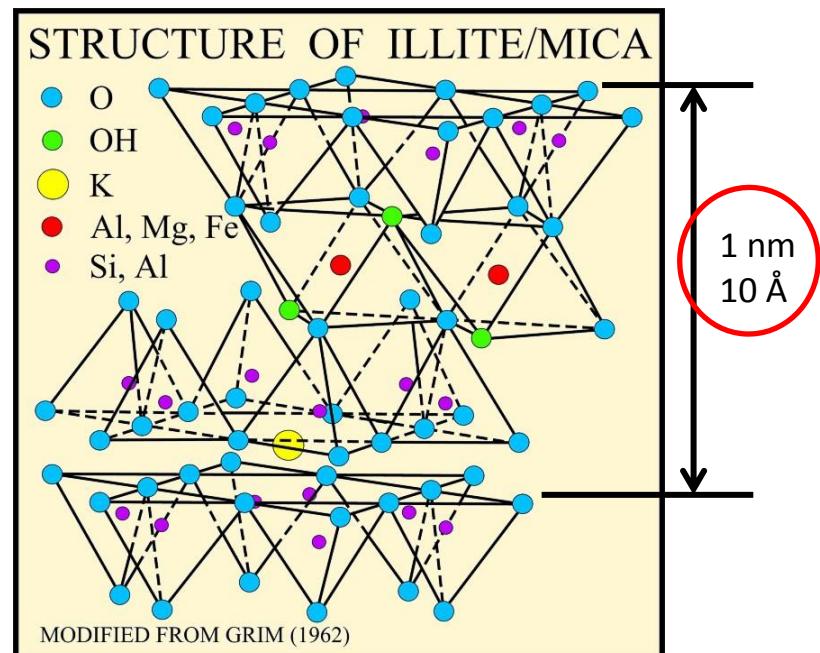


# EDX spectra

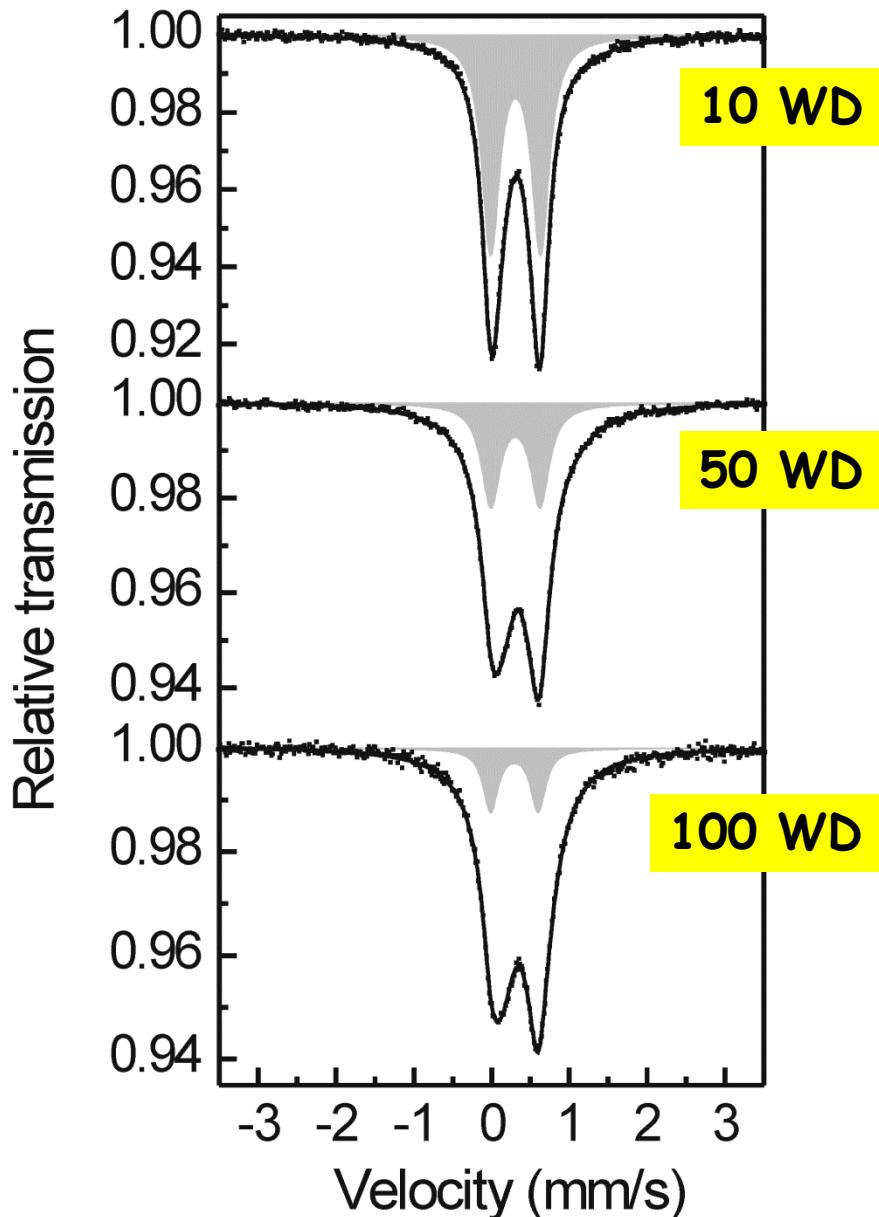
Energy dispersive X-ray spectroscopy

# FFT images

Fast Fourier transform



# Mössbauer spectroscopy (RT, 77 K, 4 K)

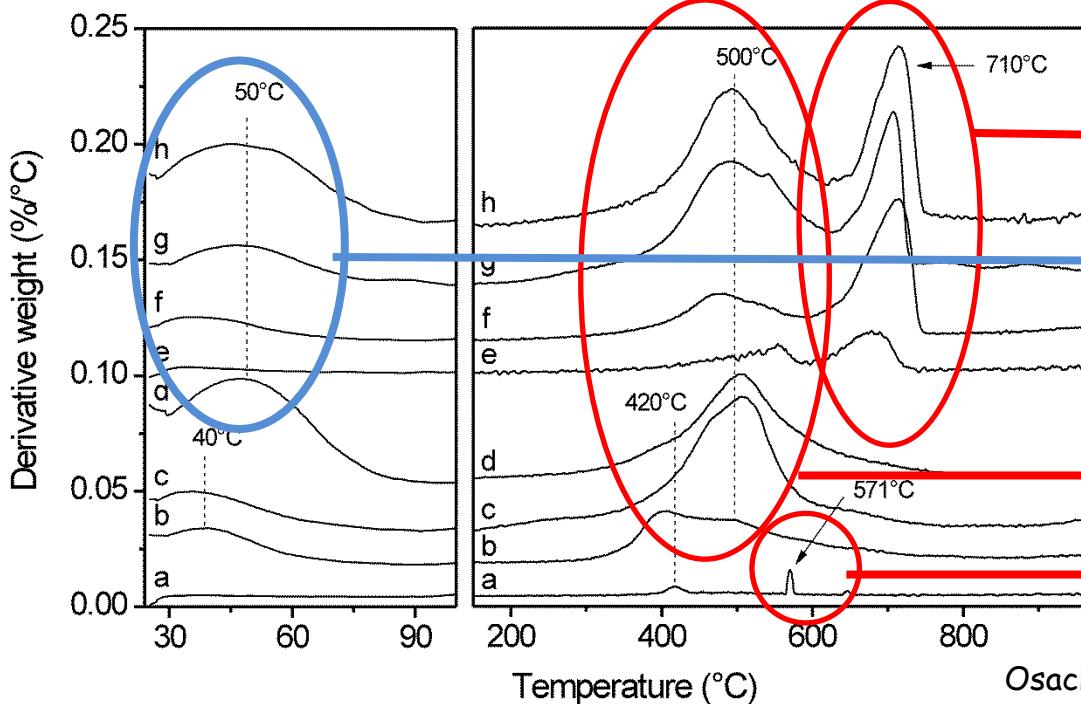
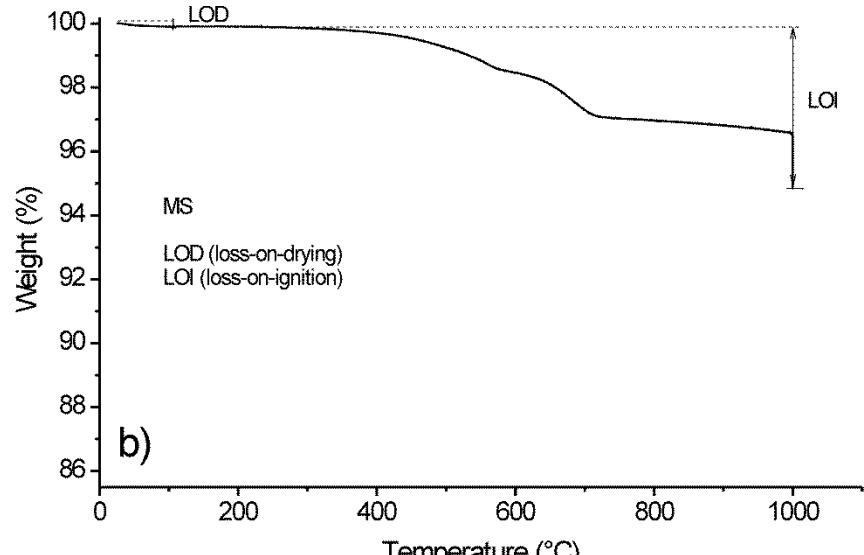
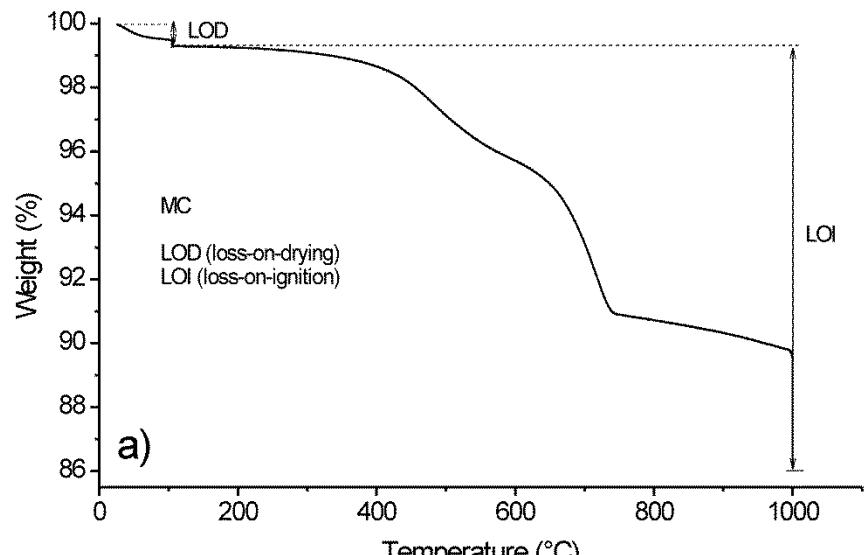


WD = wetting and drying cycles

**Pyrite oxidation**

Shaded spectral components correspond to Fe<sup>2+</sup> bound in pyrite.

# Thermal analysis (TG, DTG, DTA)



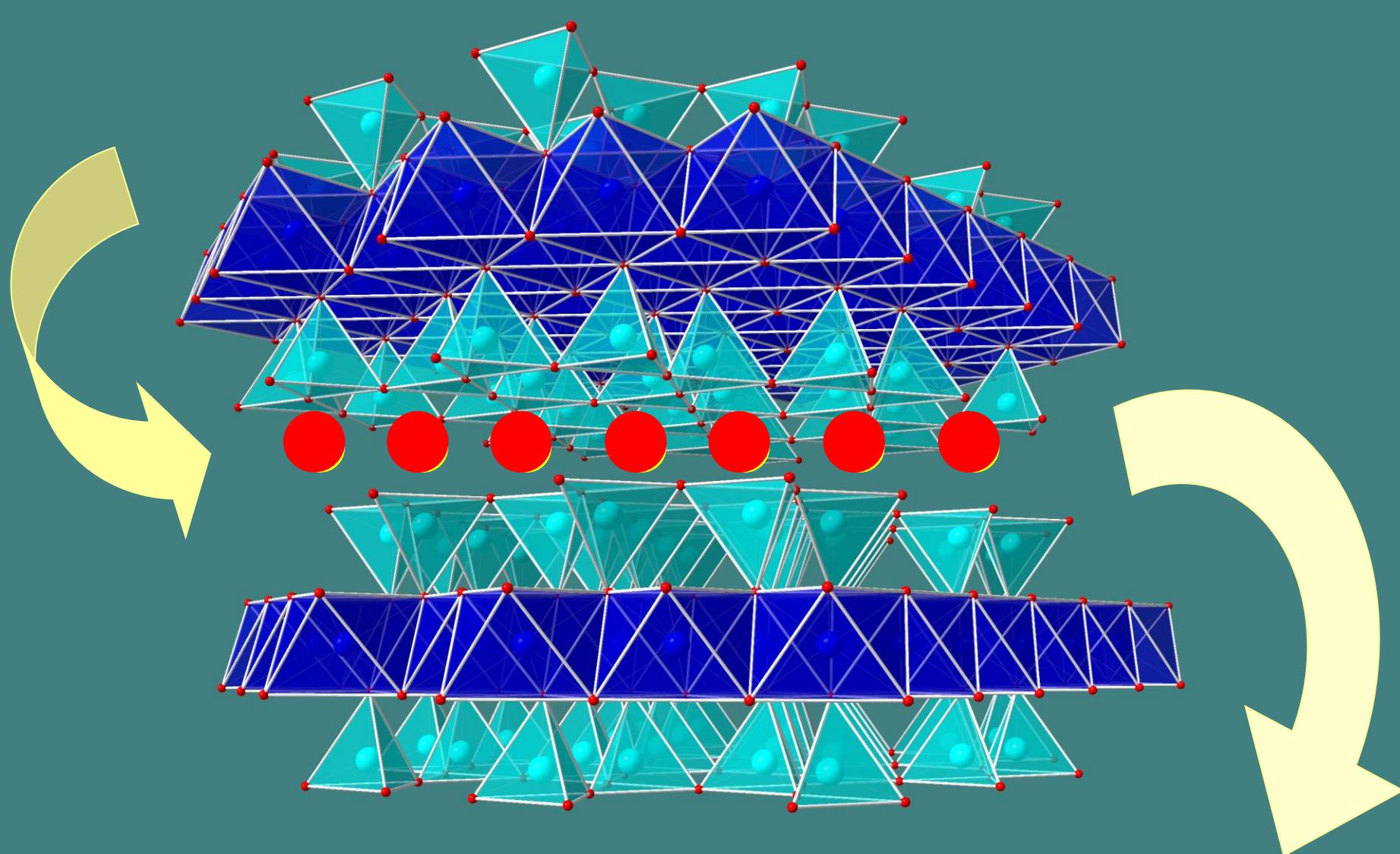
Carbonates decomposition

Release of molecular water

Clay minerals dehydroxylation

Quartz transition ( $\alpha \rightarrow \beta$ )

# Cation exchange capacity (CEC)



# Cation exchange capacity (CEC)

CEC values for pure clay minerals

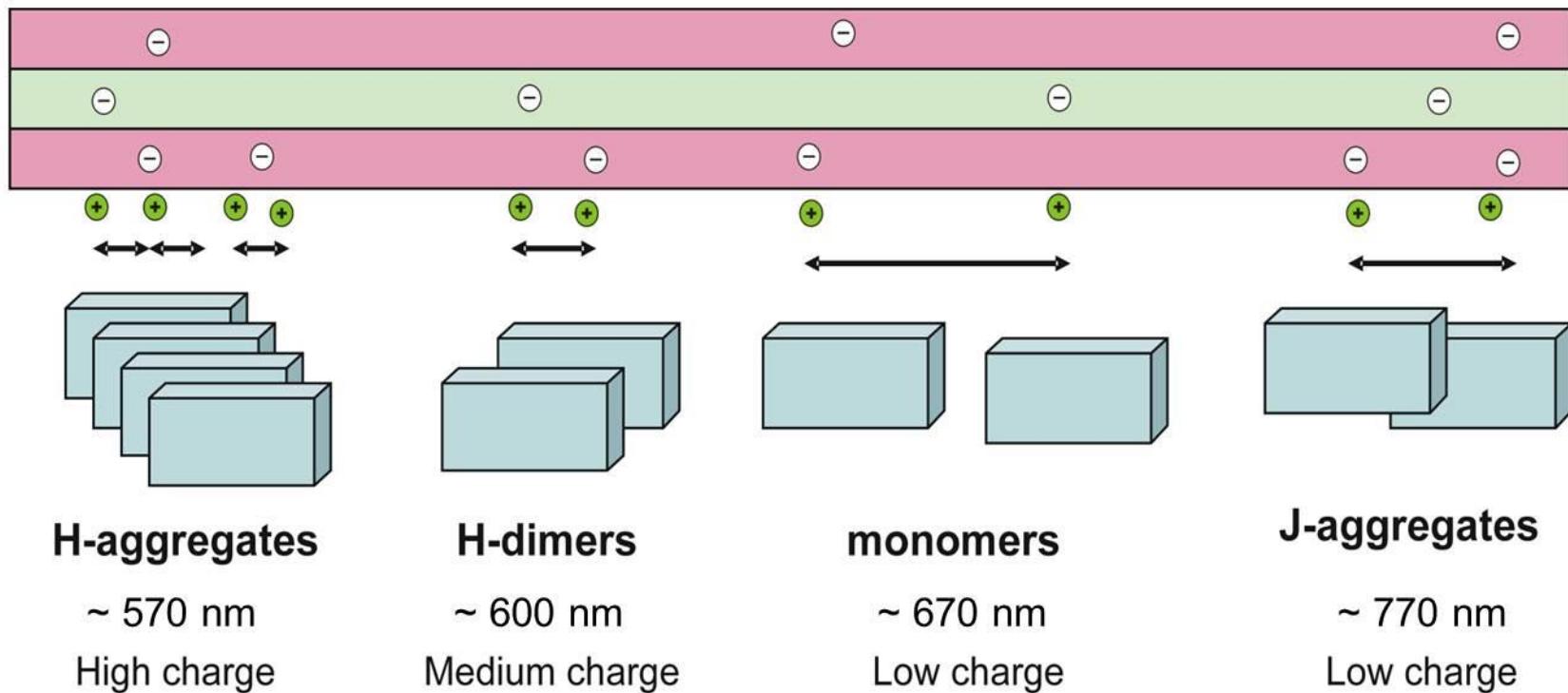
	CEC (meq/100g)
Kaolinite	3 – 15
Illite	10 – 40
Chlorite	10 – 40
Smectite	80 – 150

Methods: Cu-trien, BaCl<sub>2</sub>, Ammonium acetate,..

# Layer charge density (LCD)

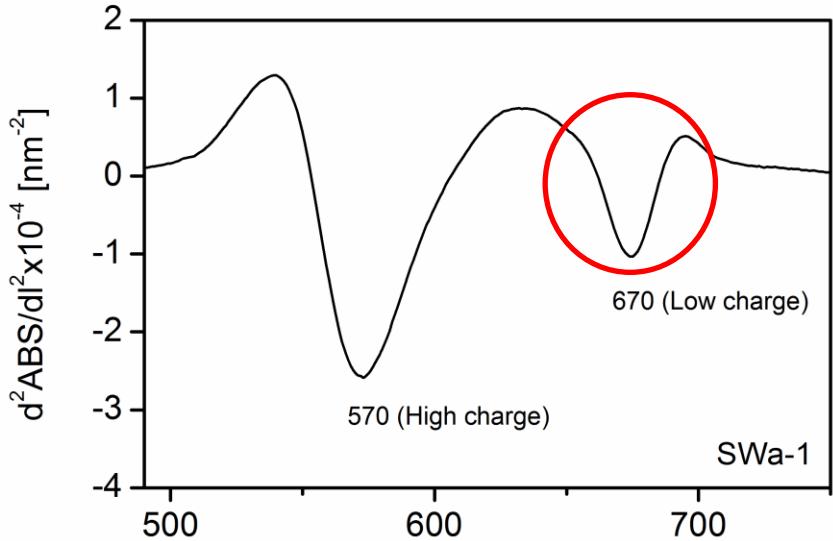
Dye cations (Methylene blue) are adsorbed at the surface of clay minerals by an ion-exchange reaction, at the sites of negative charge.

Pentrák et al. (2012), *Appl. Clay Sci.*, 55, 100-107.



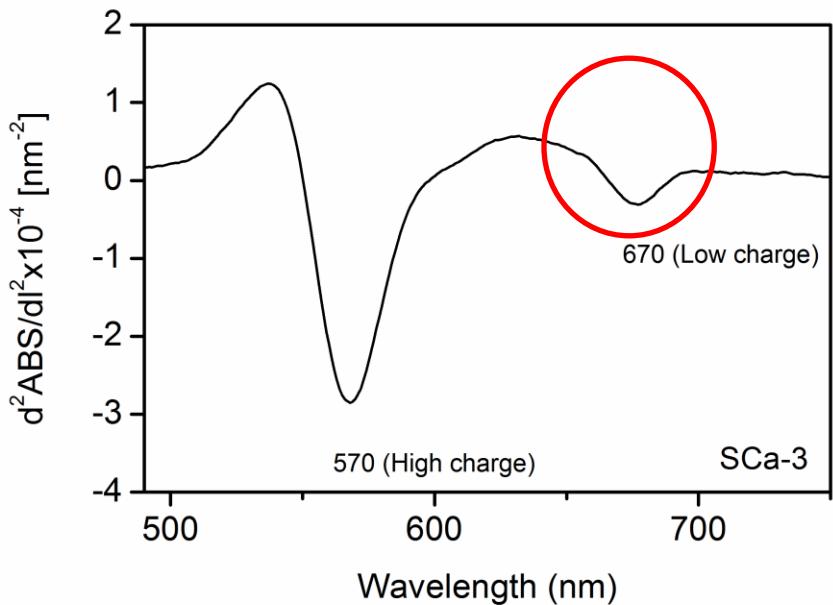
Band position for species of MB – Breen and Rock (1994), *Clay Miner.*, 29, 179-189.

# Layer charge density (LCD)



Low charge smectite

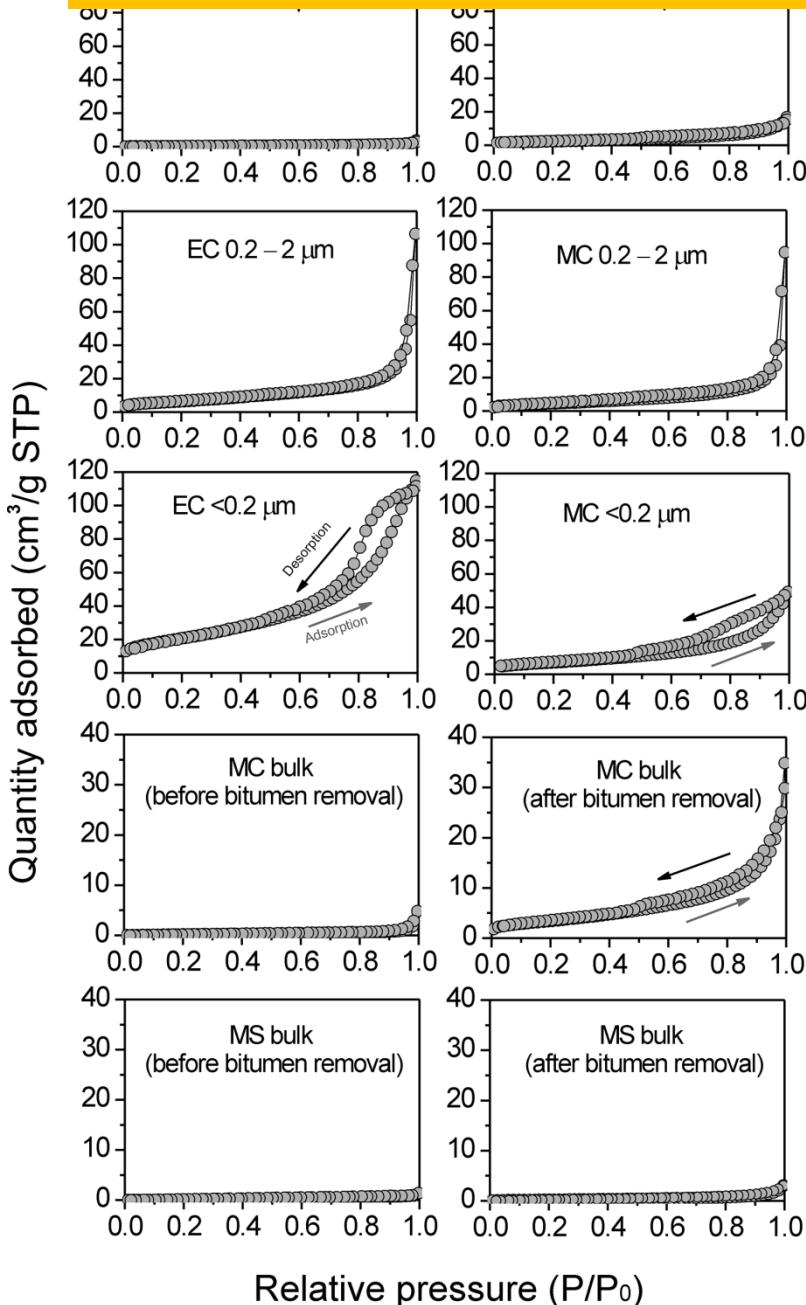
SWa-1



High charge smectite

SCA-3

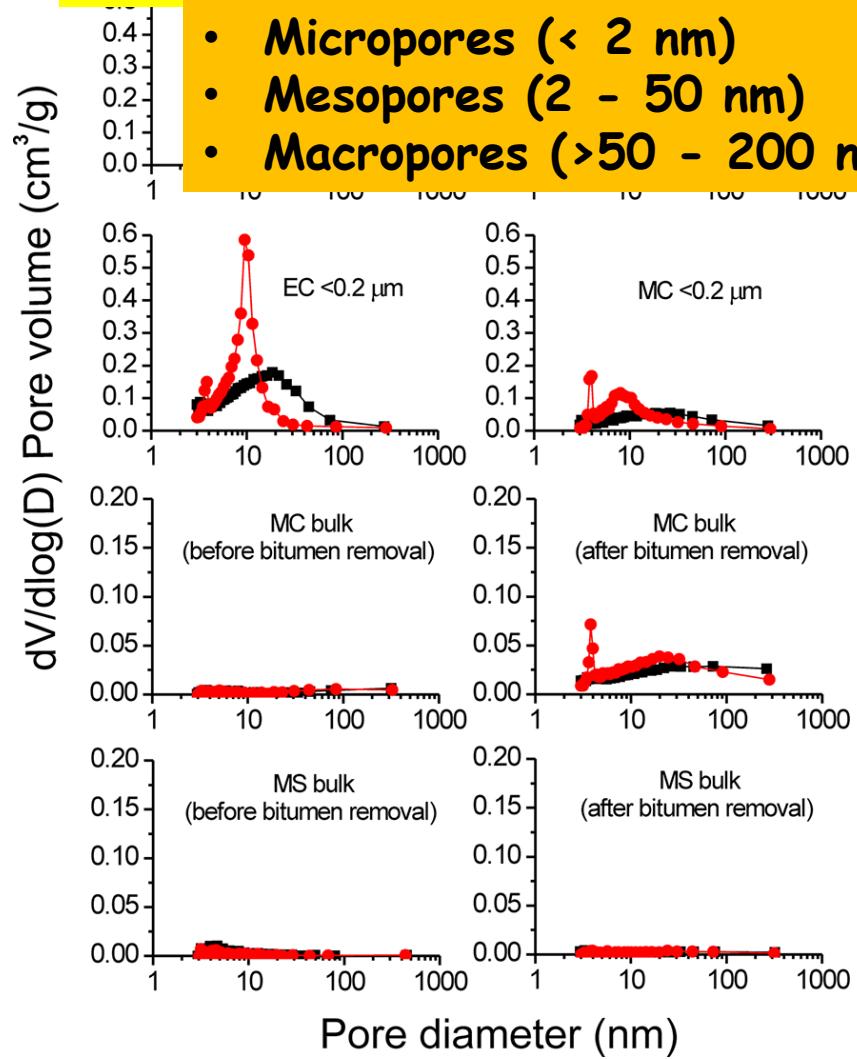
- Specific surface area ( $\text{m}^2/\text{g}$ )



# Pore-structure characteristics

(BET method)

- Micropores ( $< 2 \text{ nm}$ )
- Mesopores ( $2 - 50 \text{ nm}$ )
- Macropores ( $> 50 - 200 \text{ nm}$ )



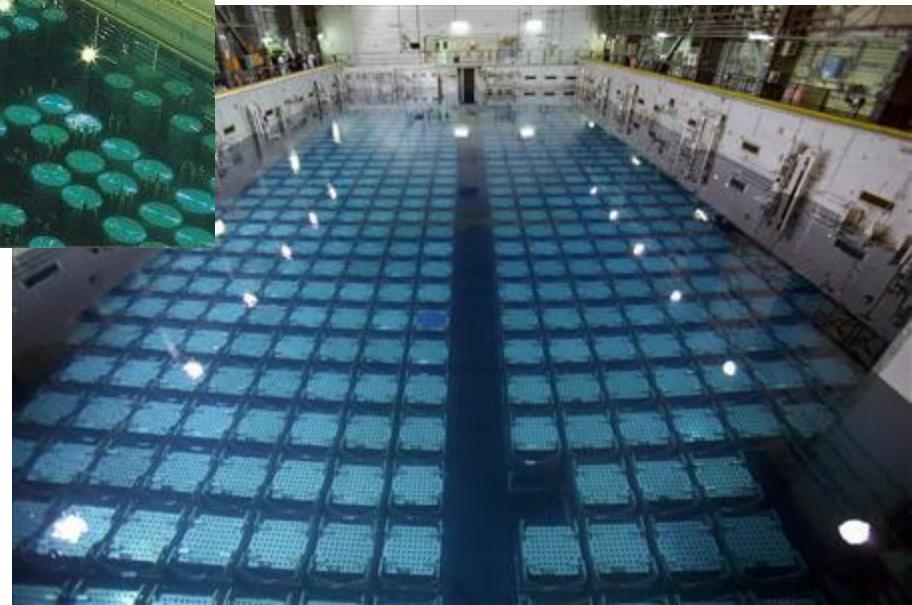
Applied research related to

- clay minerals
- zeolites

# High-level nuclear waste storage



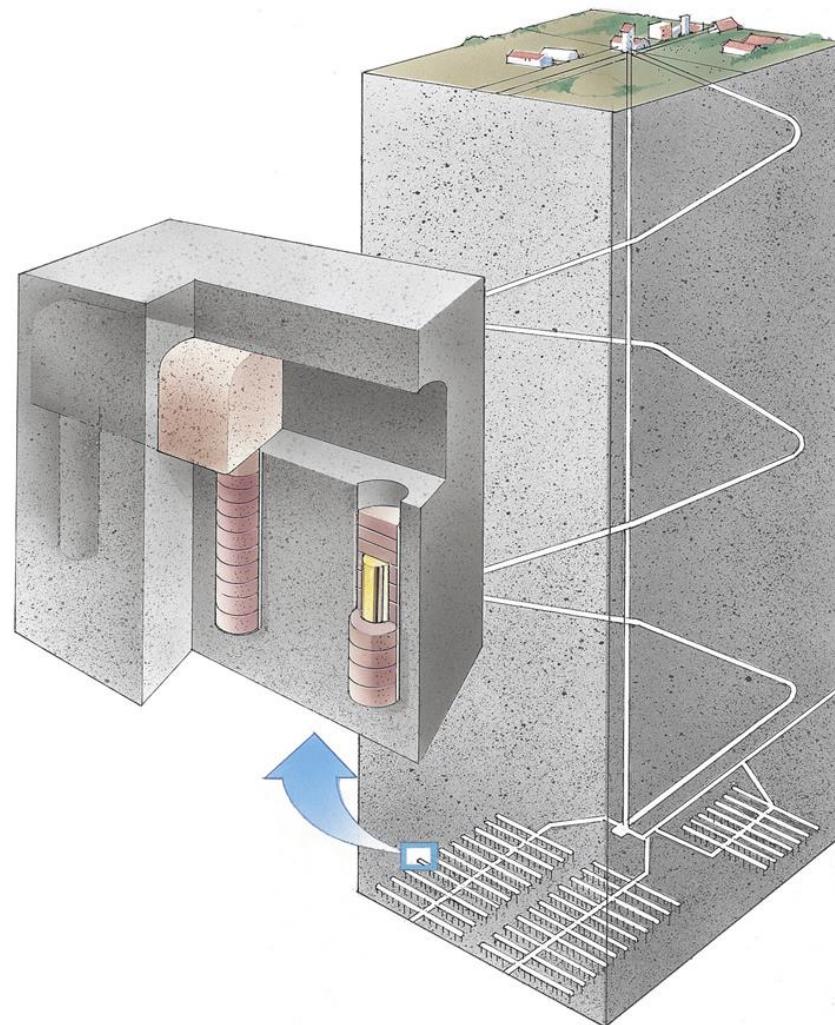
temporarily (present solution)



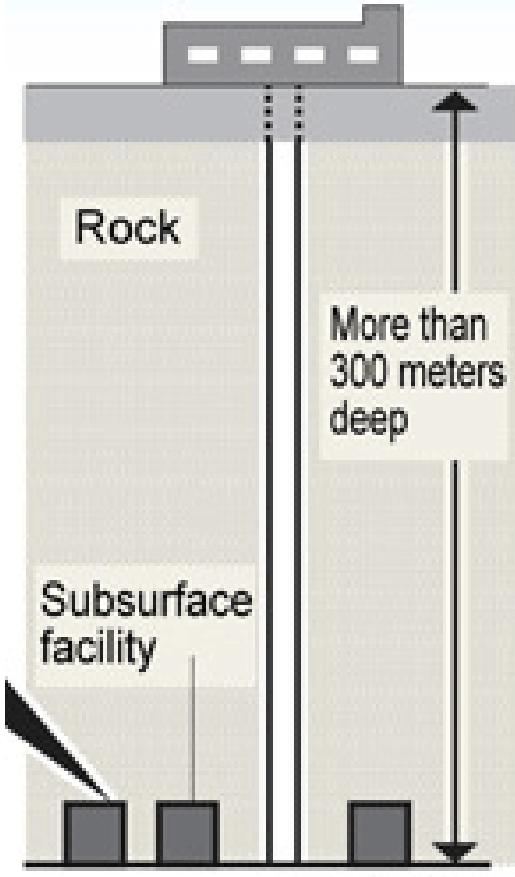
# High-level nuclear waste storage - long-term (future solution)

## High-level radioactive waste disposal site

(based on material provided by Agency for Natural Resources and Energy)



Surface facility



The Asahi Shimbun

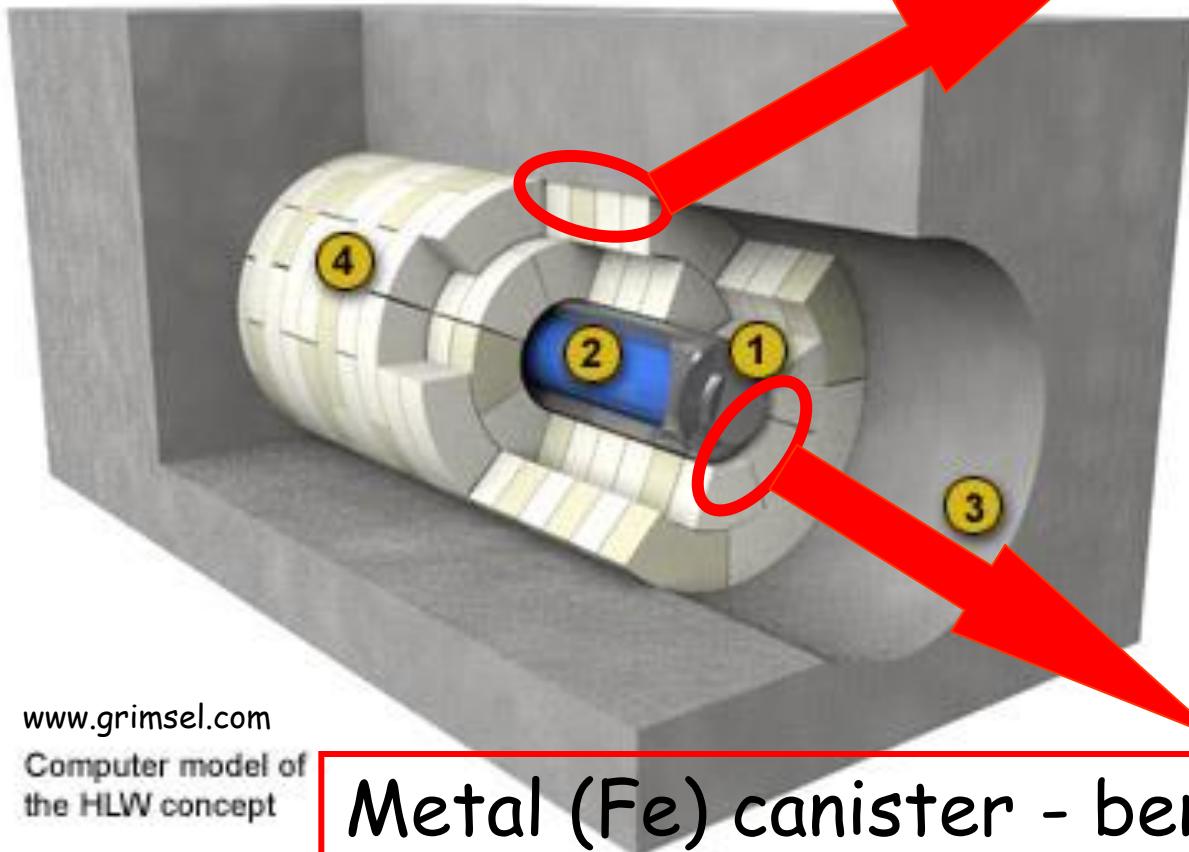
- 1 metal canister
- 2 radioactive waste
- 3 host rock
- 4 bentonite

# Model of HLW repository

HLW = high-level nuclear waste

Bentonite - host rock

Osacký et al. (2012): *Clay Miner.*, 47, 465-479.



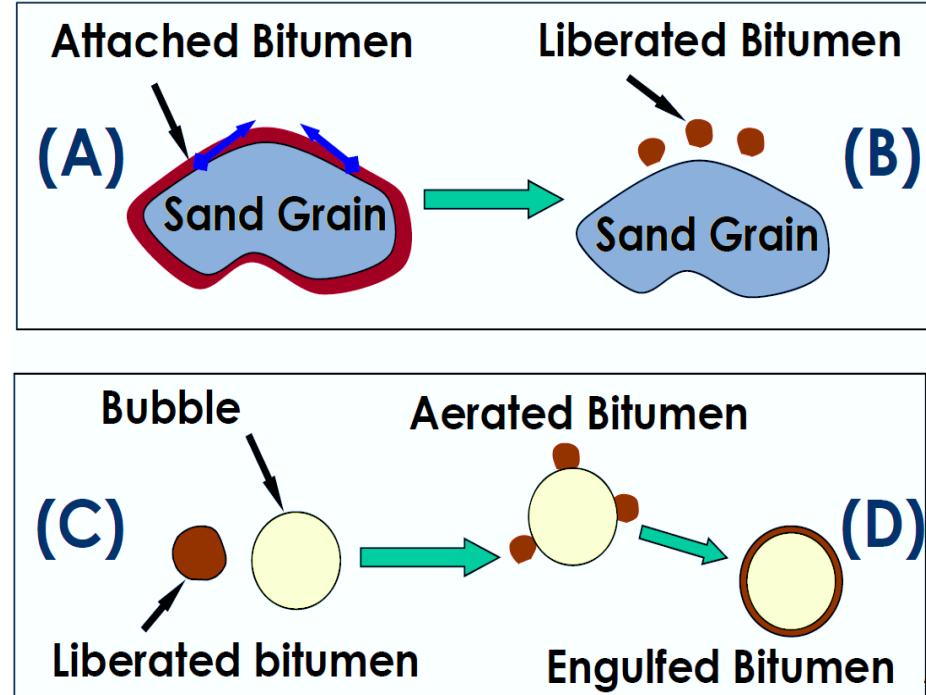
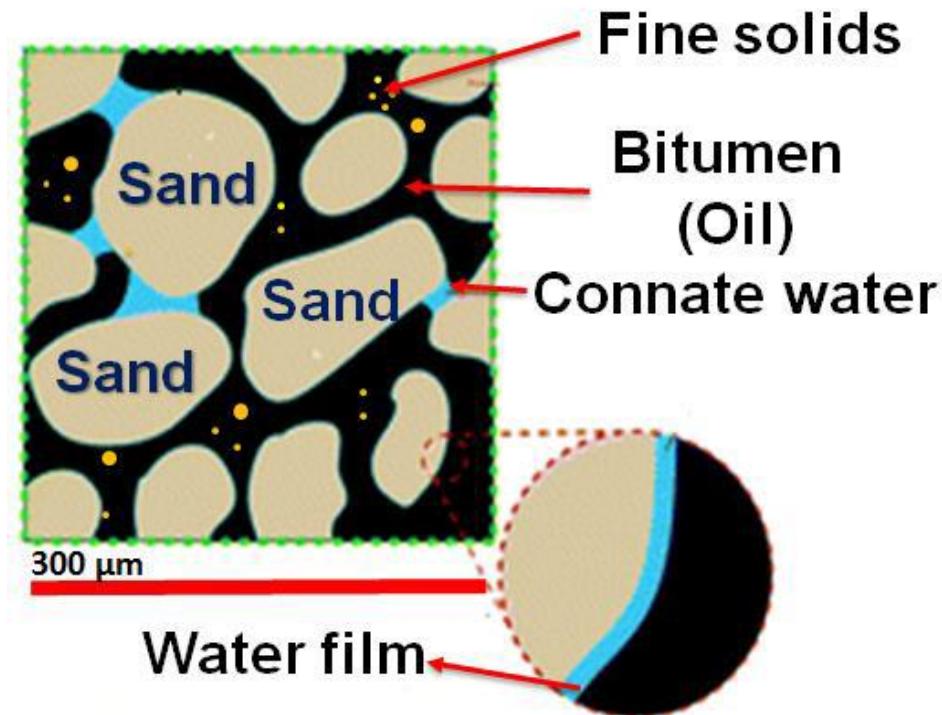
Which  
bentonites are  
suitable?

# Impact of clays on bitumen recovery

Clays have negative effect on bitumen recovery from oil sands. Why?

Which clay minerals are more detrimental?

Osacký et al. (2015): *Energy Fuels*, 29, 4150-4159.  
Geramian et al. (2016): *Energy Fuels*, 30, 8083-8090.  
Osacký et al. (2017): *Energy Fuels*, 31, 8910-8924.



# Impact of clays on tile making process



Problem:  
Raw materials have complex clay mineralogy



- Maturation (tempering effect) of raw materials
- More aggressive milling



- Addition of plastic component (swelling clay minerals)
- Homogenous mixing of plastic and non-plastic components



Azzi et al. (2016): *Appl. Clay Sci.*, 132-133, 232-242.  
Azzi et al. (2018): *Appl. Clay Sci.*, 157, 92-101.

# Zeolite - synthesis - applications

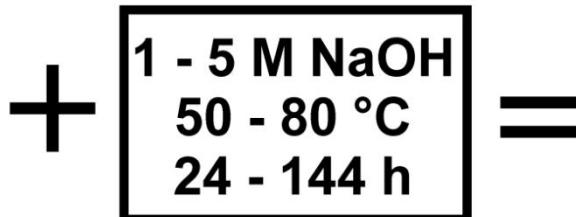
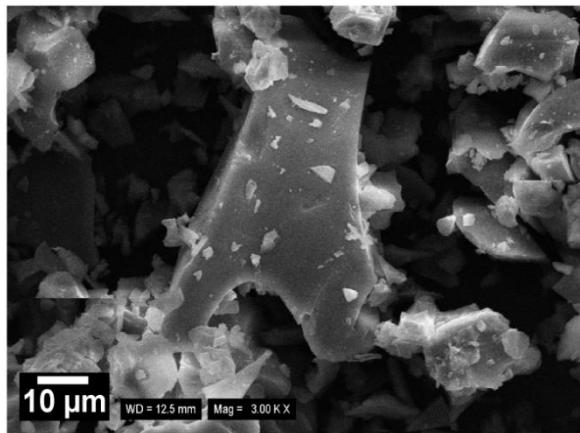


LBK PERLIT Ltd.  
Perlite production:  
30 000 t /year

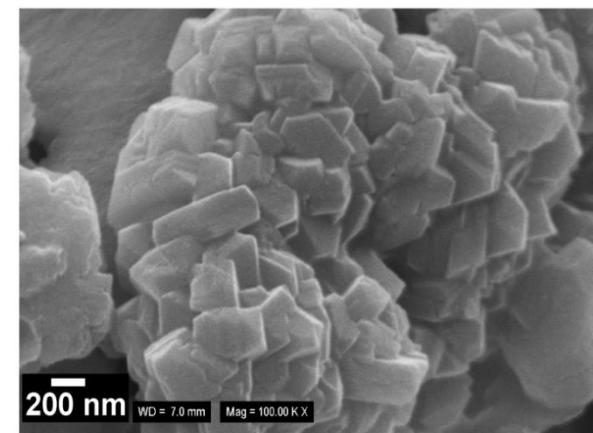
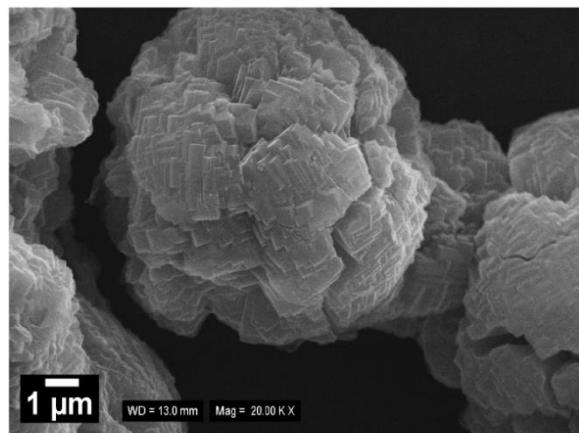
Waste: 5 000 t/year

# Zeolite synthesis (from waste materials)

Perlite by-product material



up to  
77 wt% of zeolites  
  
16 wt% of unaltered  
volcanic glass  
  
7 wt% of accessories  
(mica and feldspars)



Phillipsite (PHI type)

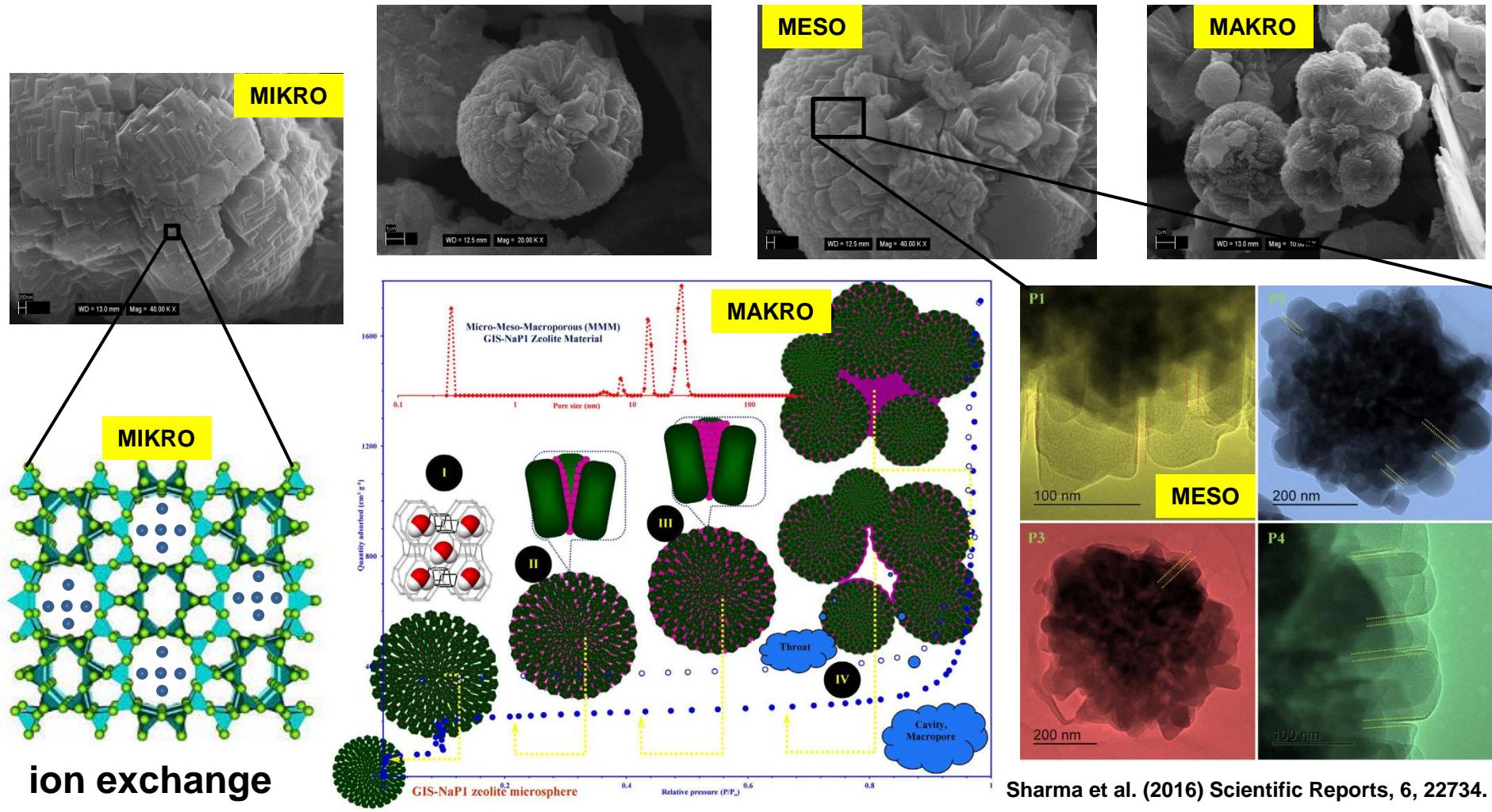
Zeolite P (GIS type)

Zeolite X (FAU type)

# Different binding sites on zeolites

(= different sorption mechanisms)

Hudcová et al. (2021): Micropor. Mesopor. Mater., 317, 111022.



Sharma et al. (2016) Scientific Reports, 6, 22734.

# Application - large scale *in situ* experiment (Smolník acid mine drainage treatment)

