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# Hydration sequence for swelling clays exchanged with mixed alkali/alkali-earth cations

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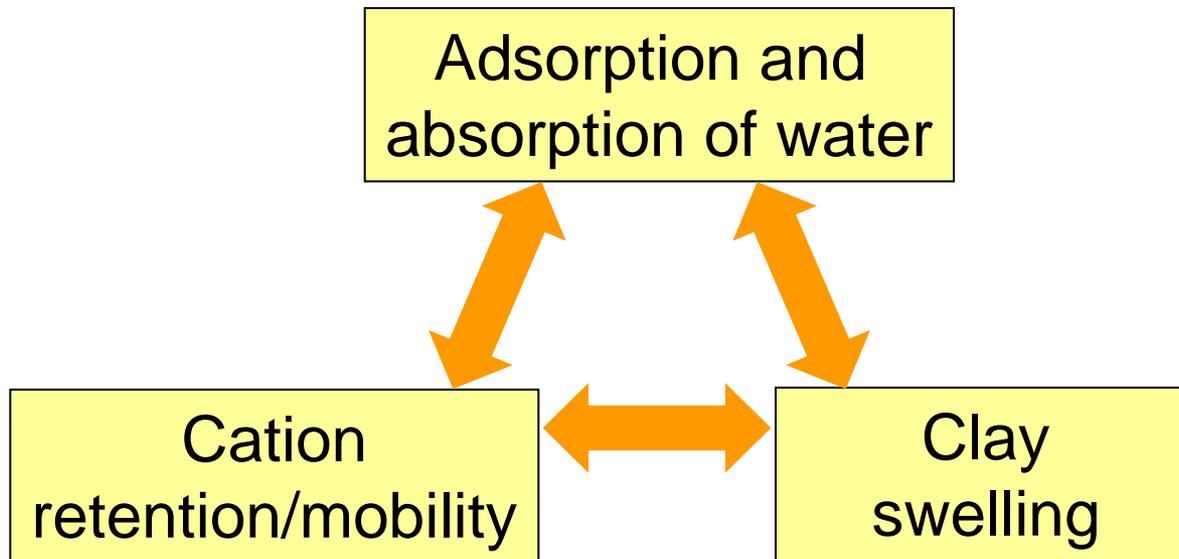
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<sup>3</sup> ESPCI, Paris, France

# Context of the study

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- Disposal of radioactive wastes in deep geological repositories and multi-barriers concept
- Role of clays:
  - limiting water fluxes in the repository
  - swelling and filling up technical gaps
  - adsorbing RNs (in the interlayer space and onto surfaces)



# Outline plan

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- Objectives and experimental approach
- Multi-scale structure of clays
- Thermoporometry results for Montmorillonites samples saturated by alkaline cations: pore size distribution
- Consequences for the hydration sequence in clays as a function of the interlayer cation nature
- Diffusion of the interlayer cation as a function of the hydration state
- Conclusions

# Objectives and experimental approach

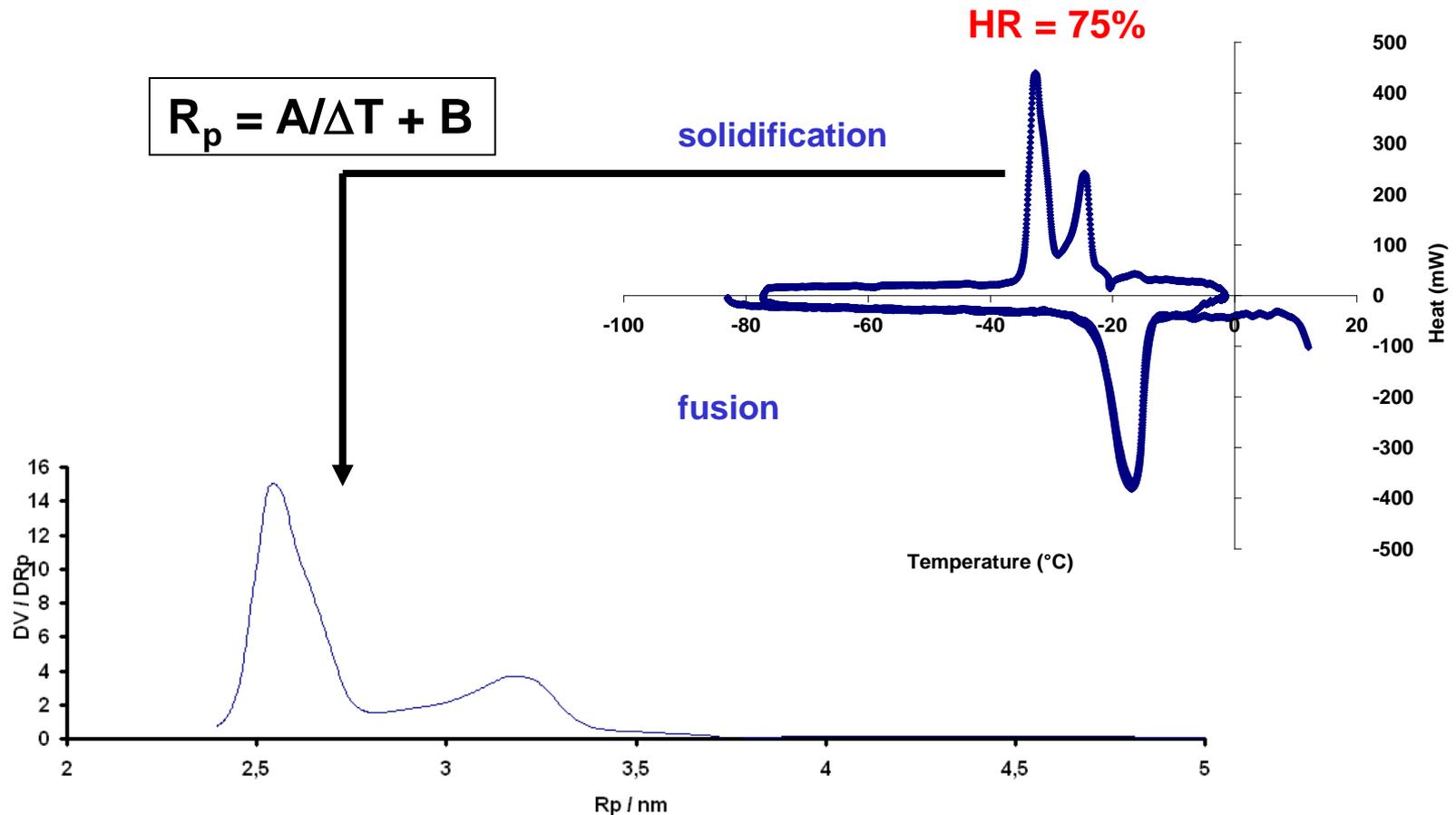
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- Study the “clay-water” system by looking at the modifications of water properties
  - “water in clays” is different from liquid water (or free water)!
- **Thermoporometry** = calorimetric technique sensitive to phase transitions of fluid confined in the porosity → **2 nm < Pore radius < 50 nm (mesoporosity)**
  - Hypothesis: Pore size is the major parameter which influences the properties of the confined fluid
- Originality of these experiments: **swelling material (homoionic Wyoming montmorillonite saturated by Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Cs<sup>+</sup> and Ca<sup>2+</sup> cations & different RH investigated**
  - Common practice : DSC on saturated non-swelling samples  
= all pores are filled
  - Saturation of studied porosity is necessary

- 
- **Quantify the evolution of the mesopore size as a function of RH**
  - **Discuss these results in terms of the sequence of clay hydration**

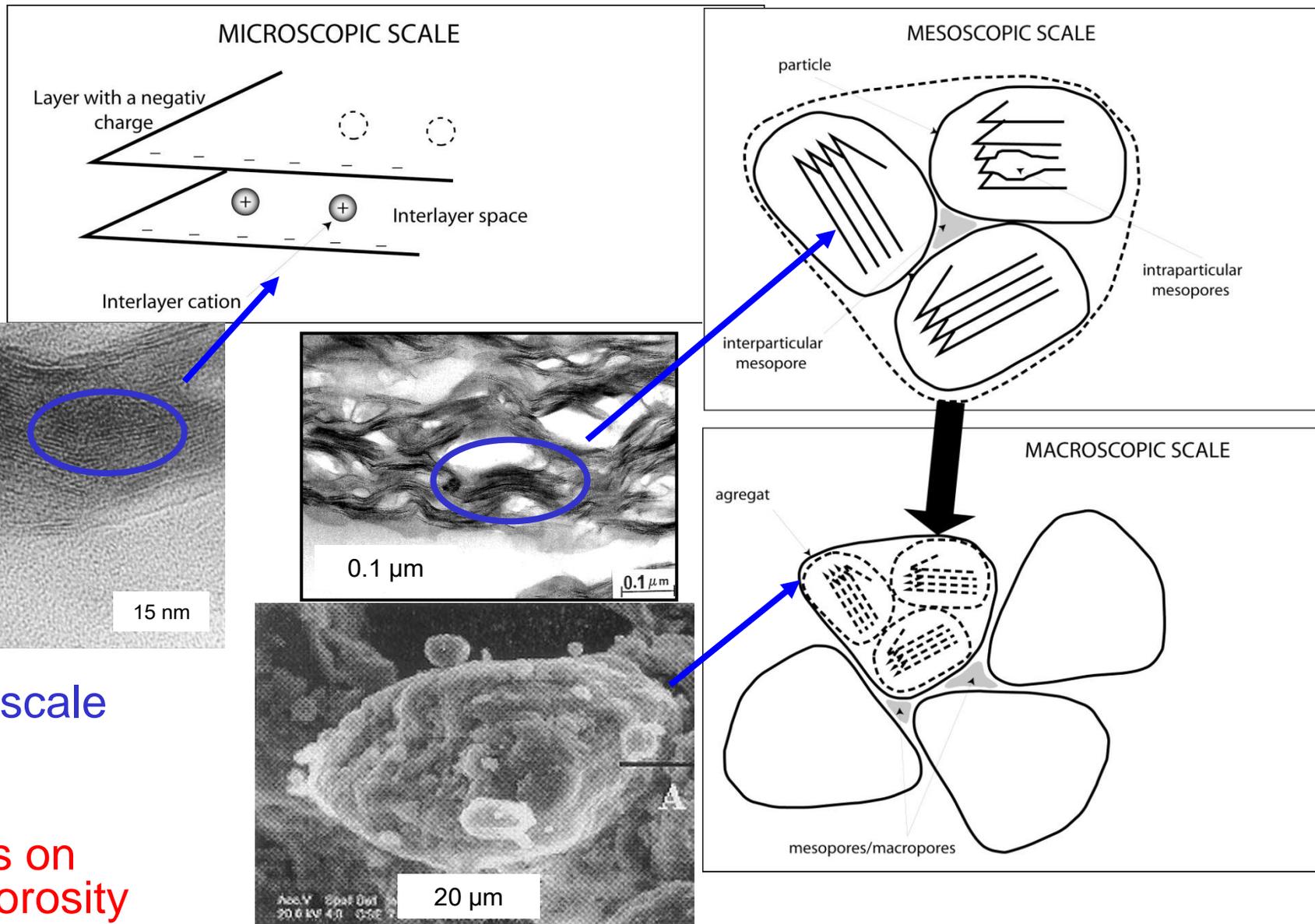
# Pore size distribution (PSD)

- Pore size distribution obtained with Brun equations (parameters result from fit with various materials) :



- 2 peaks = 2 well-defined families of pore size

# Multi-scale structure of clays

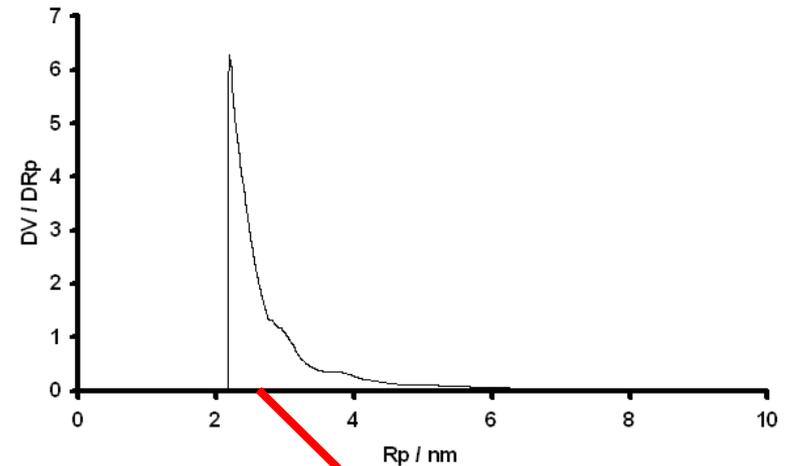
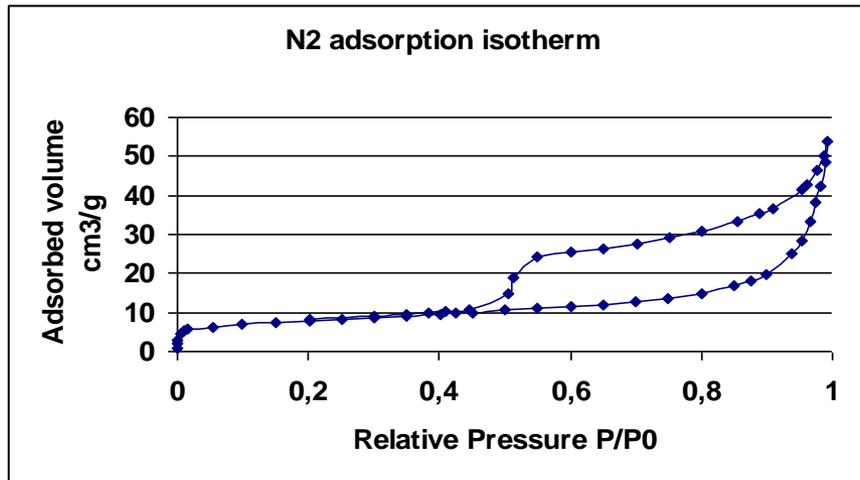


- Multi-scale aspect

- Focus on mesoporosity

# Results for $RH \leq 54\%$

- Na-mont (purified and exchanged MX80 Wyoming) → **powder**
- $RH < 54\%$  → **no interpretable signal** (pores not filled with water? not enough water?)
- Results for  $RH = 54\%$ :



➤ **BJH calculations from N<sub>2</sub> adsorption data**

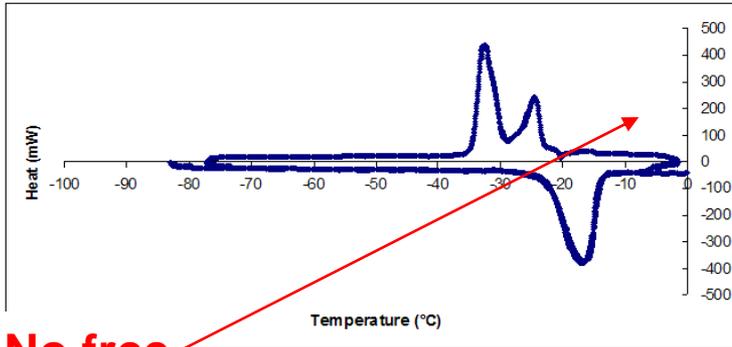
~ 2.5 nm

- Thermoporometry not conclusive alone but same results as BJH: pores filled at 54%
- We verify that the effect of Rp is dominant

# Results for RH > 54%

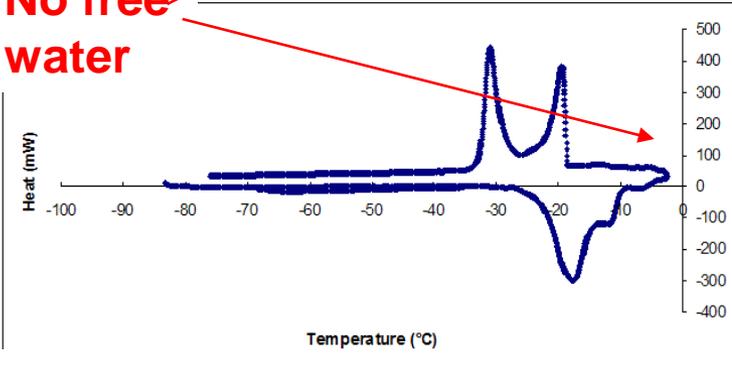
- Results for RH ranging from 75% to saturation

HR = 75%



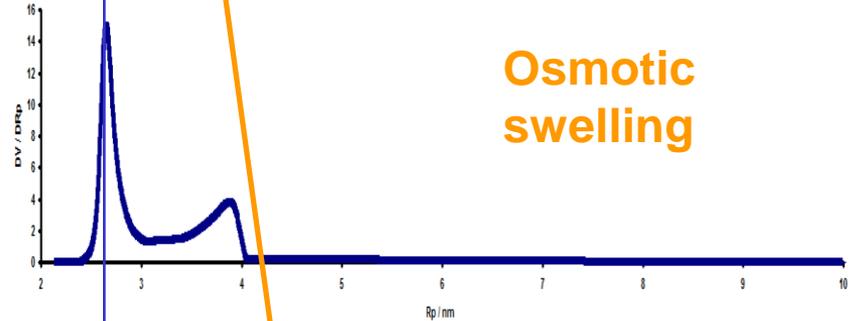
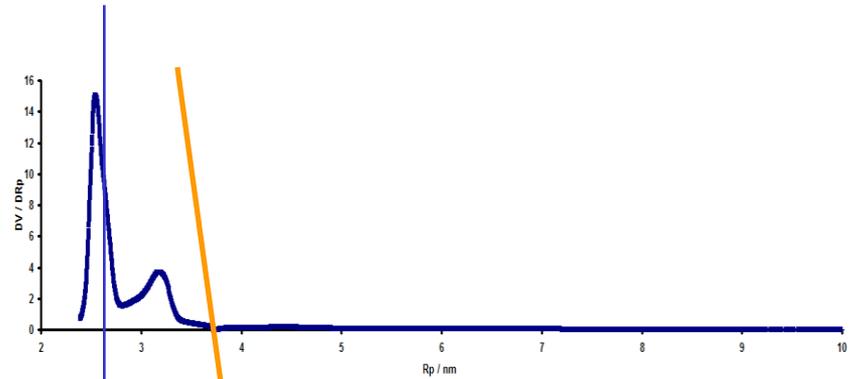
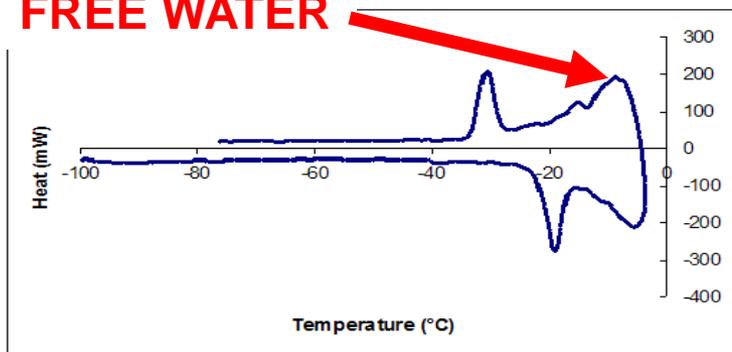
No free water

HR = 90%

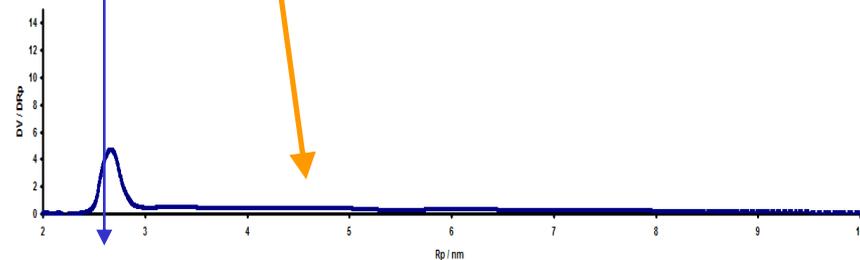


FREE WATER

HR sat



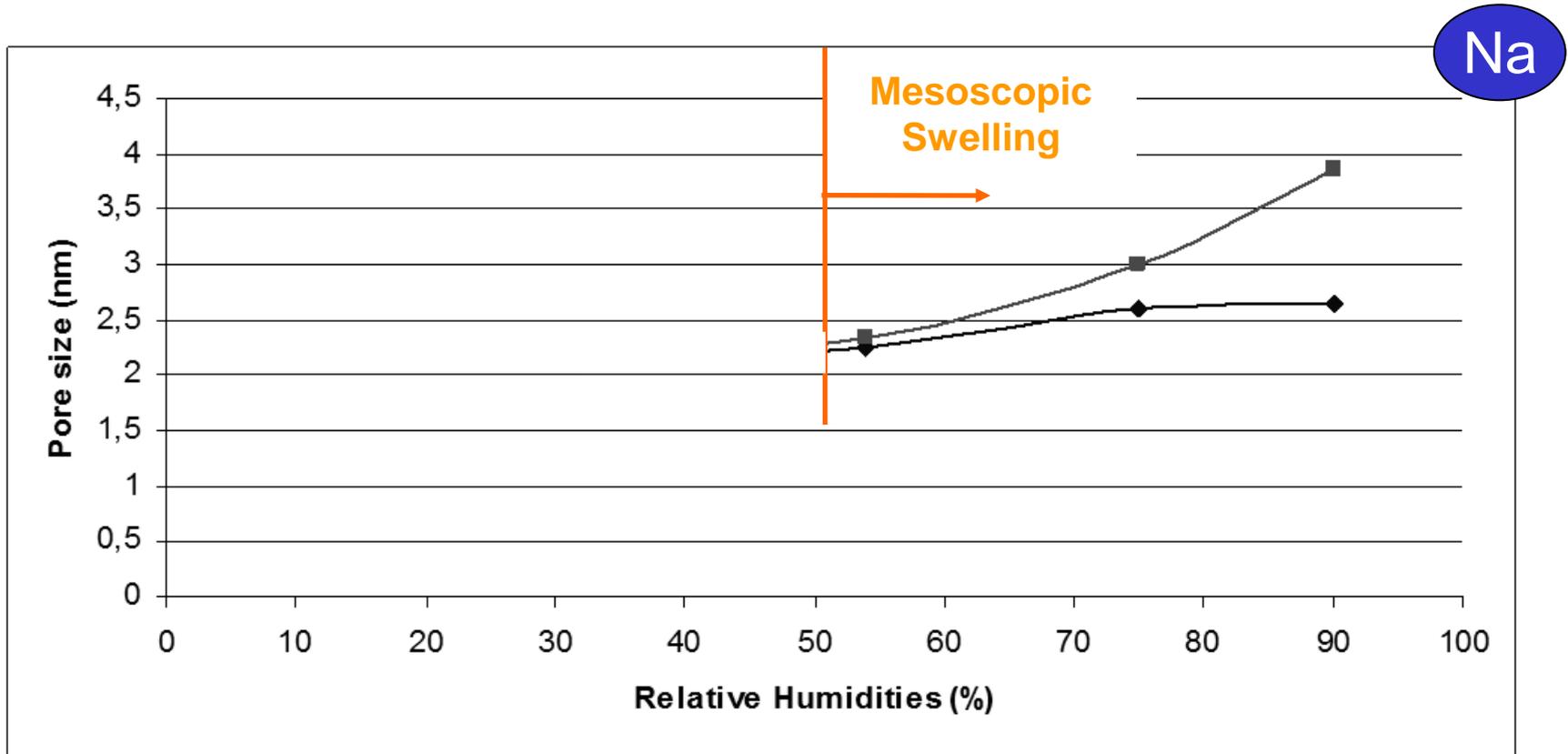
Osmotic swelling



➤ No free water at RH < 90%

# Interpretation(1): evidence for osmotic swelling in mesopores

- pore size in mesopores (for the 2 families)

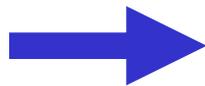
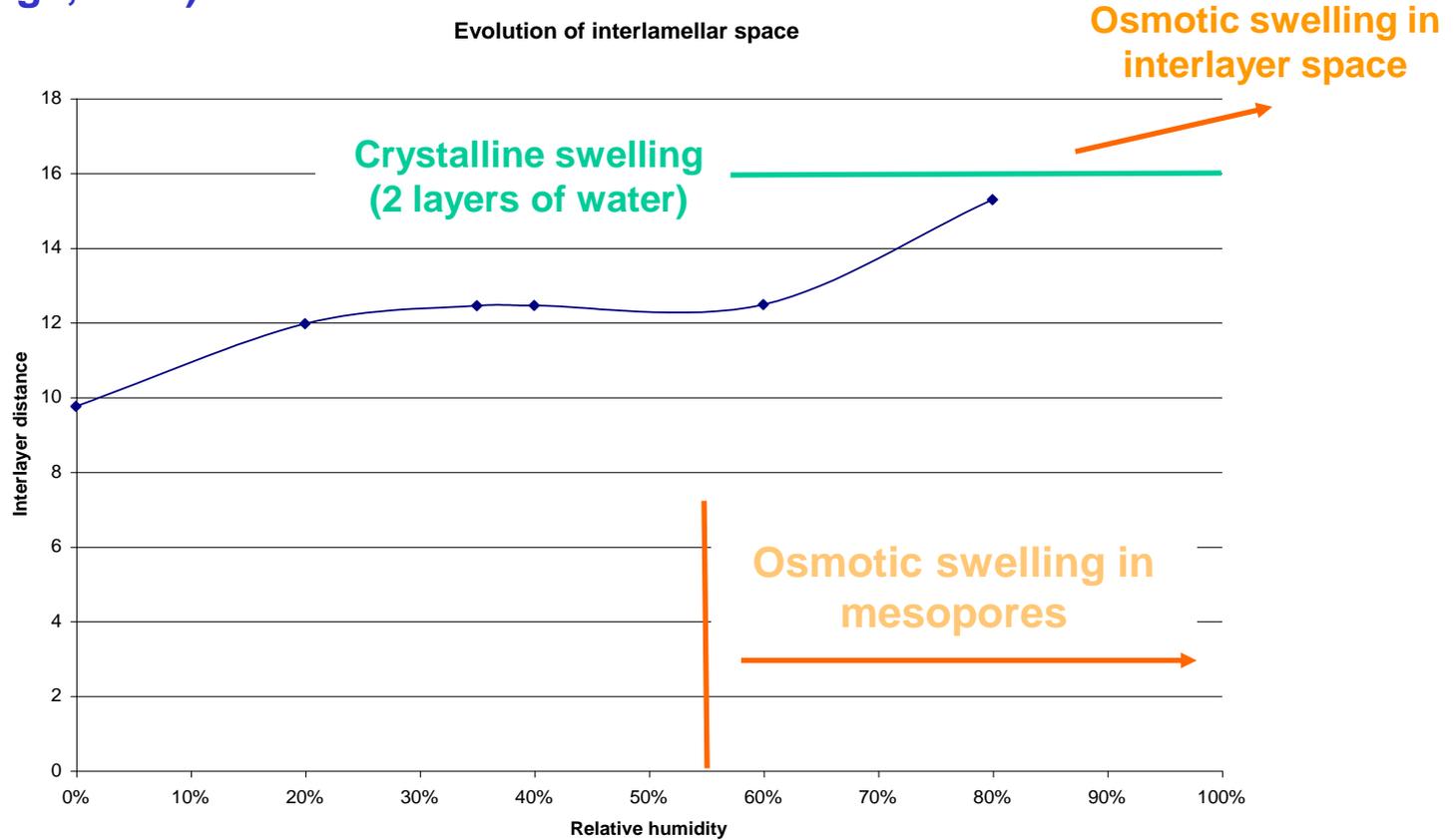


➤ Osmotic swelling in the mesopores occurs starting at RH ~ 54%

# Interpretation (2)

- Comparison with interlayer space (d001) measurements with XRD (Ferrage, 2005)

Na

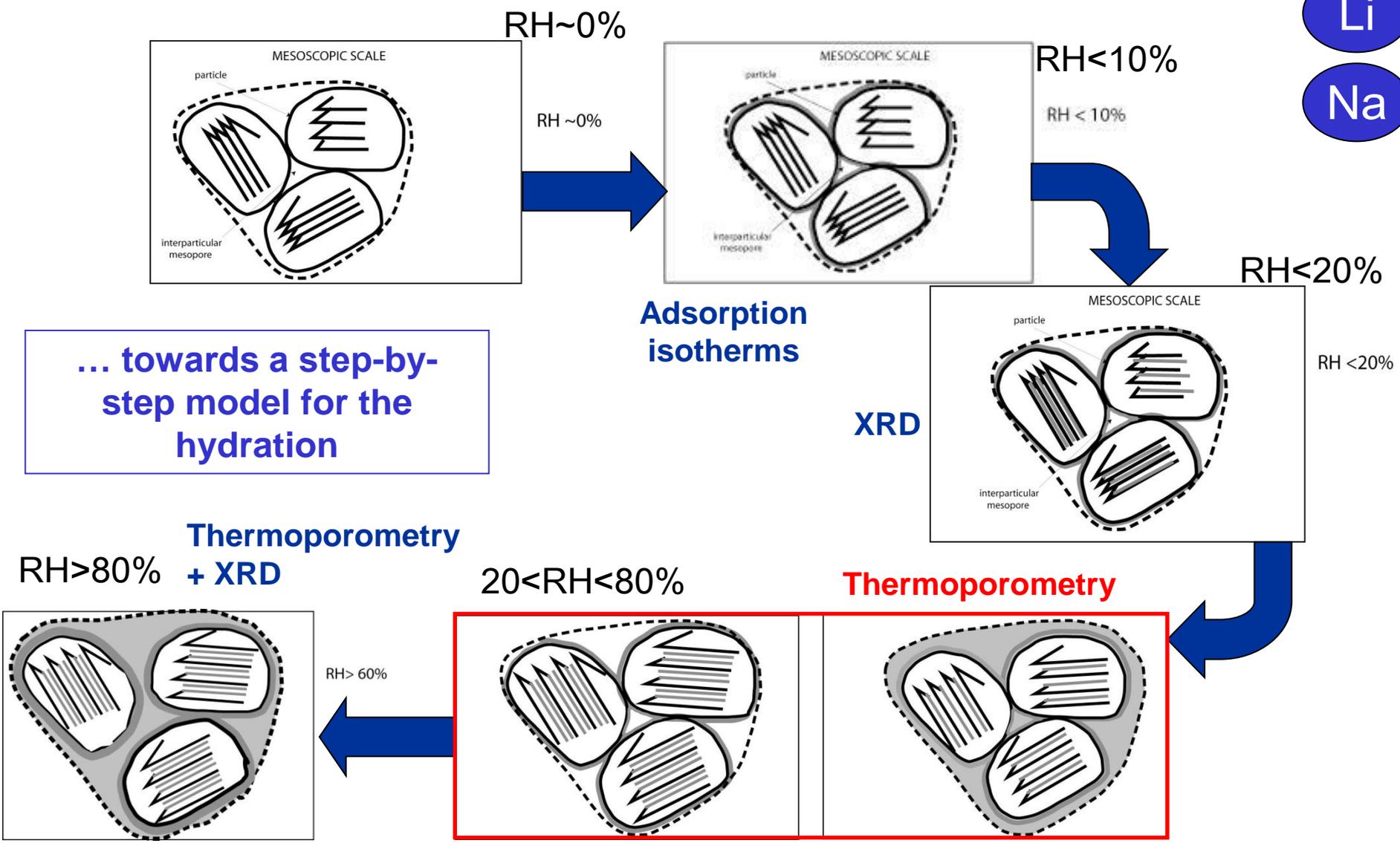


Osmotic swelling occurs at RH > 80% in interlayer space compared to RH ~ 54% in mesopores

*Salles et al., Appl. Clay Sci., 2008*

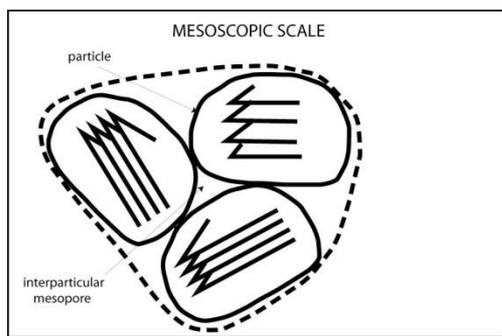
# Interpretation (3): hydration sequence

Li  
Na

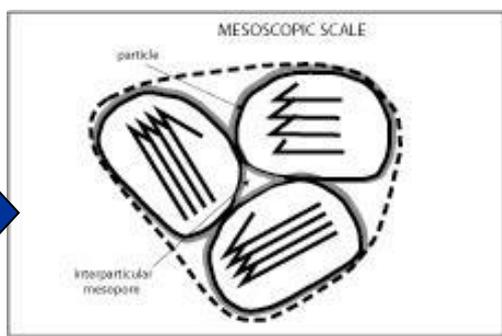


# Interpretation (4): hydration sequence

K  
Ca  
Cs



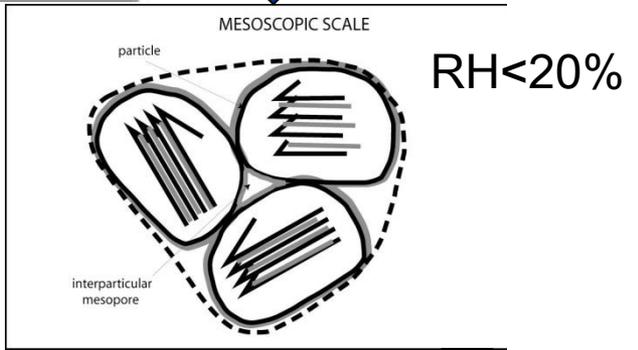
RH ~ 0%



RH < 10%

Water adsorption isotherms

XRD



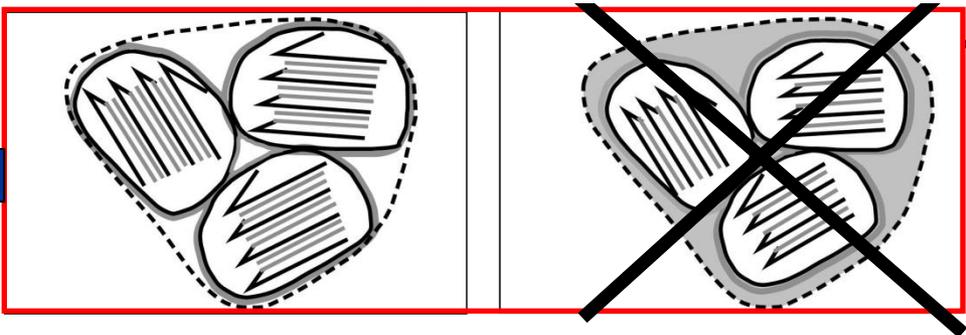
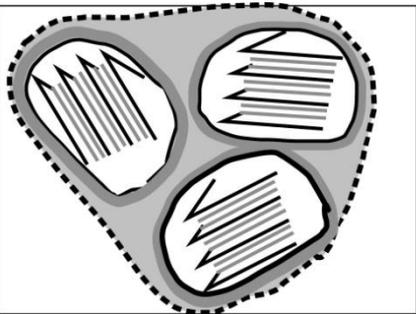
... towards a step-by-step model for the hydration

Thermoporometry

Thermoporometry

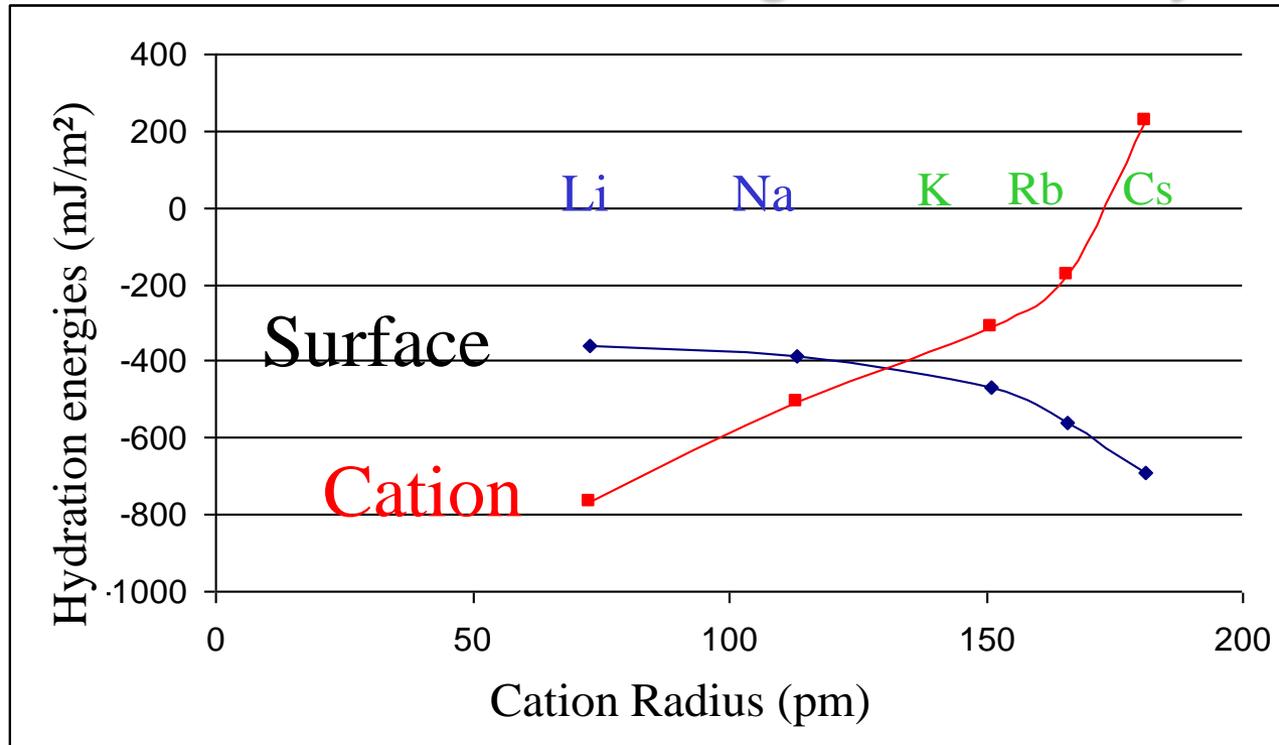
RH > 90% + XRD

20 < RH < 60%



Salles et al., Langmuir, 2010

# Coherence with the driving forces of hydration



- ✓ For Li and Na-samples: Cation Hydration is the driving force
- ✓ For K, Rb and Cs-samples: Surface Hydration is the driving force
- ✓ Changes of leading driving forces in agreement with the experimental behavior varying with the interlayer cation

# Towards the distinction between interlayer or mesopore water

- From experimental data: it is possible to estimate
  - $m_{\text{water in clay}}$  → from water adsorption isotherm
  - $m_{\text{water in mesopore}}$  → from thermoporometry data

- It follows:

$$m_{\text{interlayer water}} = m_{\text{water in clay}} - m_{\text{water in mesopore}}$$

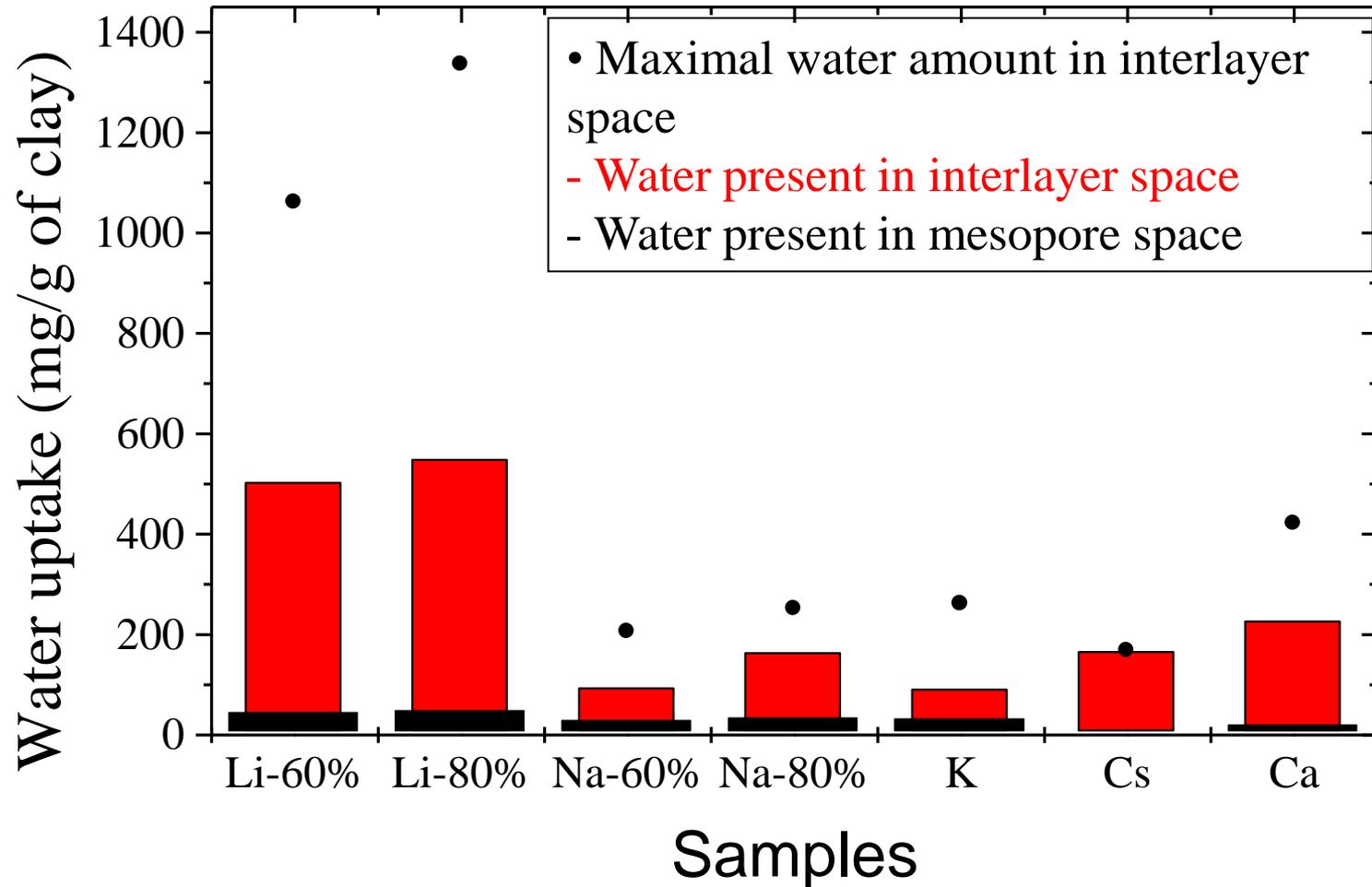
- The theoretical quantity of water (=maximal amount) present in interlayer space can be determined from the following equation:

$$m_{\text{theoretical interlayer water}} = d_{001} * (S_{\text{H}_2\text{O}} - S_{\text{N}_2})$$

where  $S_{\text{H}_2\text{O}}$  and  $S_{\text{N}_2}$  are the specific surface area as a function of  $\text{RH}^*$  and  $d_{001}$  is related to the interlayer space opening

*\* Salles et al., J. Colloid Interf. Sci., 2009*

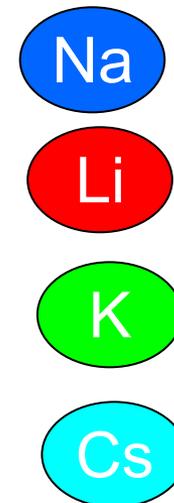
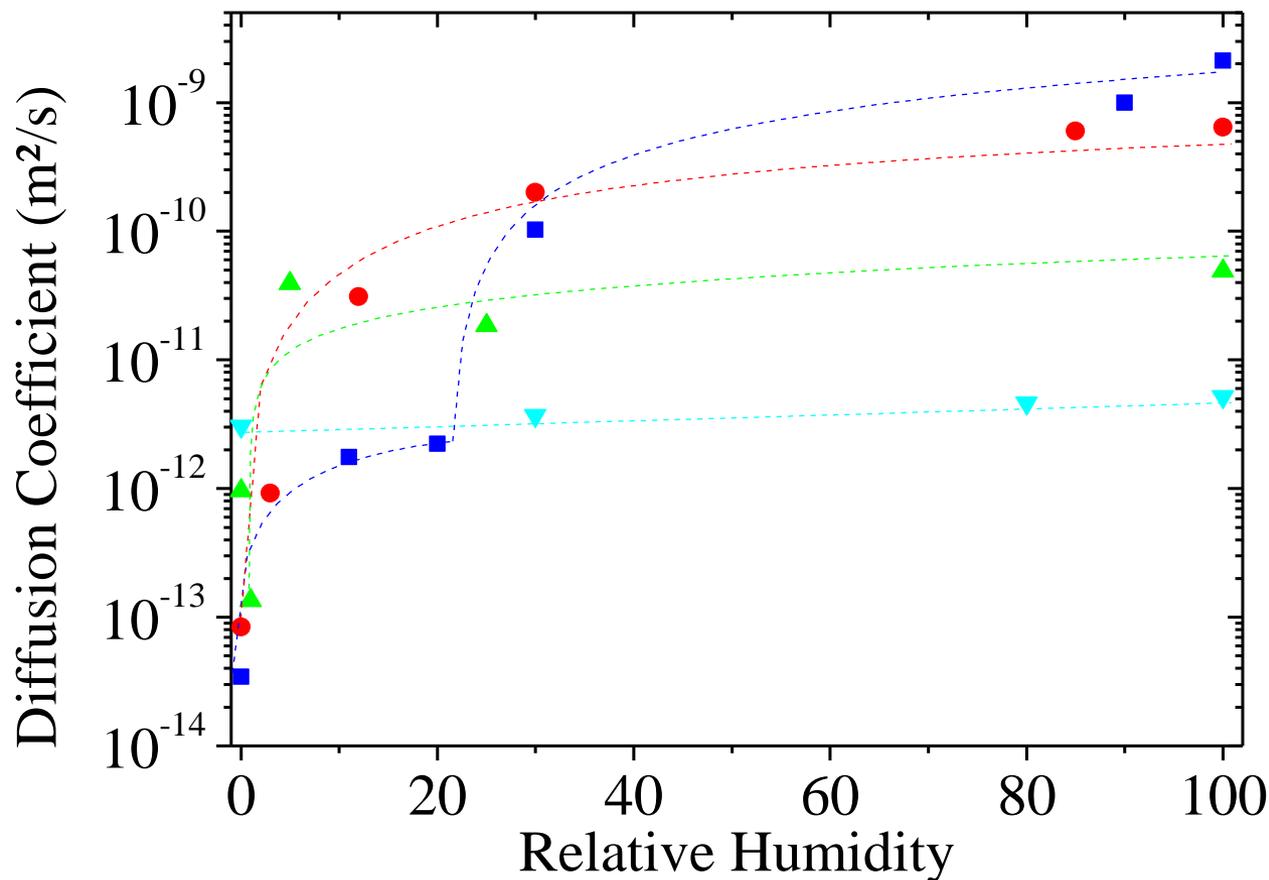
## Distinction of interlayer and mesopore water



The interlayer spaces are never completely filled in montmorillonites, except for Cs-sample

*Salles et al., Langmuir, 2010*

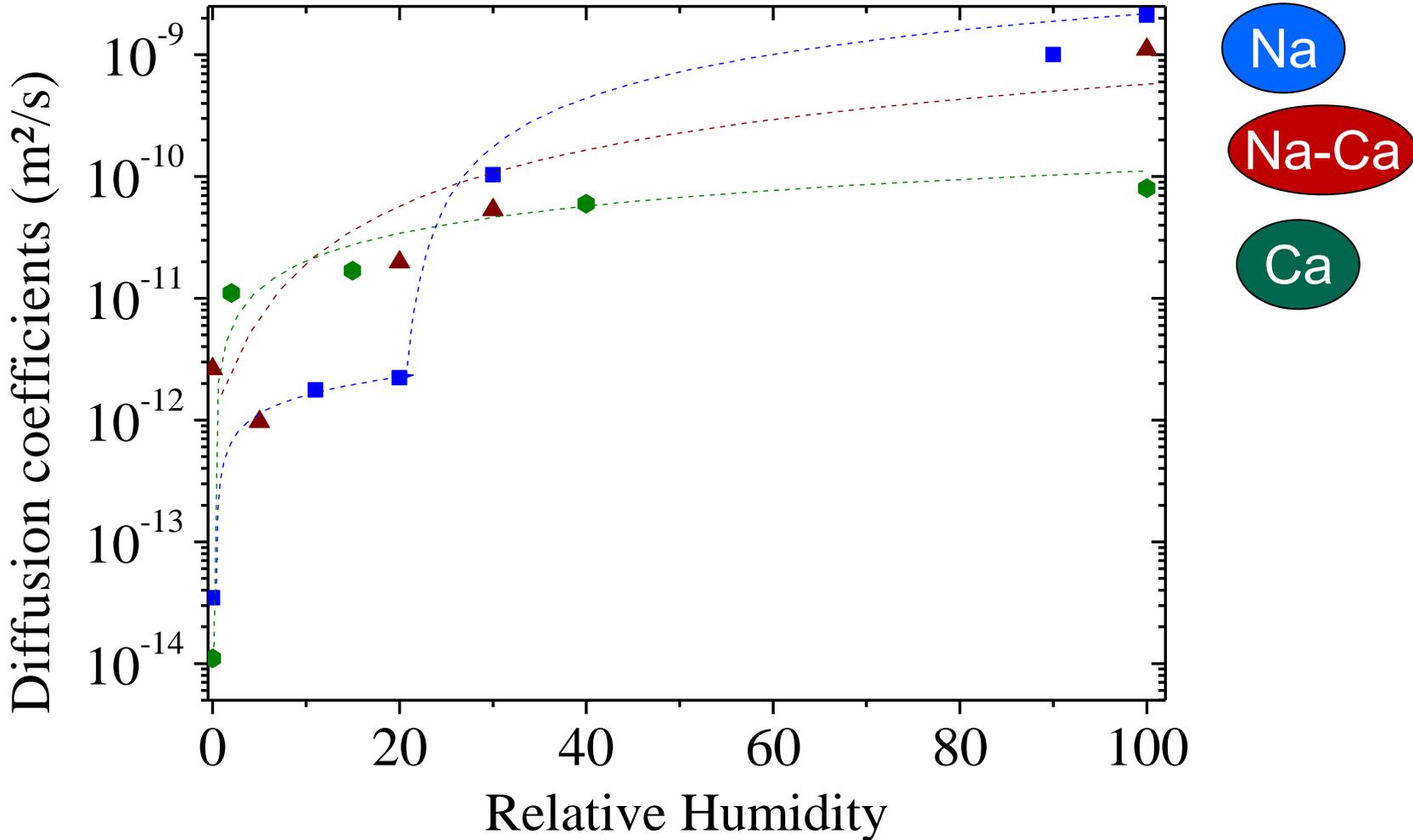
# Diffusion of Cations in swelling clays



- ✓ For Li and Na-samples: Cation diffusion reaches values for bulk water
- ✓ For K, Rb and Cs-samples: Slow diffusion
- ✓ Diffusion behavior is varying with the interlayer cation → osmotic swelling

*Salles et al., J. Phys. Chem. C, 2015*

# Case of Montmorillonites with mixture Na/Ca



- ✓ For Na/Ca-samples: Na<sup>+</sup> diffusion reaches values lower than bulk water
- ✓ Influence of Ca<sup>2+</sup> and repartition of cations ?

# Conclusions

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- Summary:
  - Osmotic swelling in mesopores evidenced by original use of thermoporometry
  - Free water is observed in mesopores only starting at  $RH > 90\%$
  - Osmotic swelling occurs in mesopores before crystalline swelling is finished in the interlayer space (2nd layer of water)
  - Sequence of hydration is depending on the interlayer cation nature
  - Interlayer space water  $>$  mesopore water for all cations
  - Interlayer space is never completely filled by water at  $RH < 97\%$  for all samples except  $Cs^+$ -montmorillonite
  - Impact of  $Na^+$  in the Na/Ca-sample

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**Thank you for your attention!**

# Thermoporometry equations

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- Theoretical equation

$$\frac{1}{(R_p - t)} = -\frac{1}{2\gamma_{sl}} \int_{T_o}^T \Delta S_f \frac{dT}{v}$$

- Simplified equation (Brun et al. 1977)

$$R_p = A + \frac{B}{\Delta T}$$

# Material and method

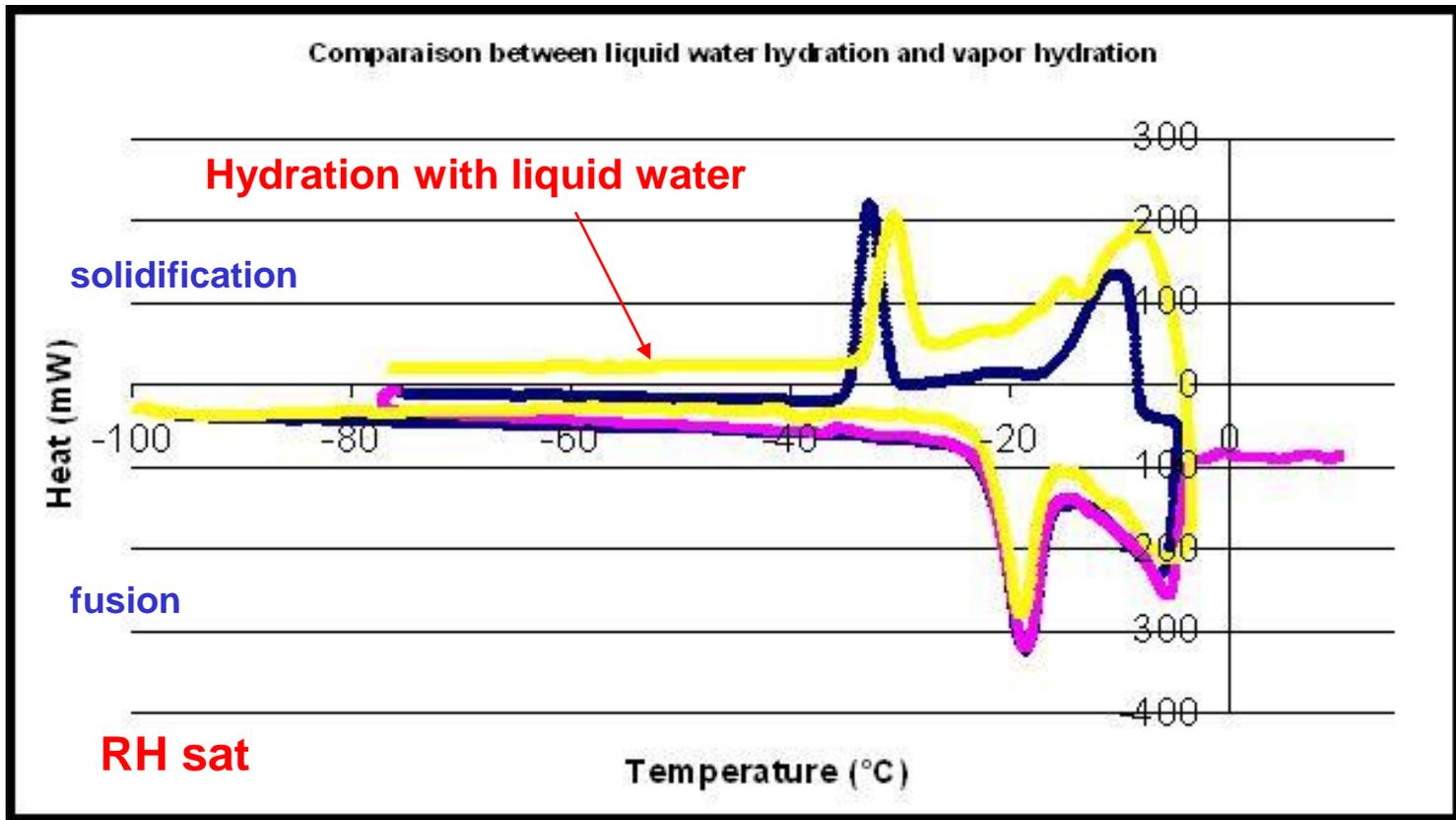
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- Na-mont (purified and exchanged MX80 Wyoming) → **powder**
- Thermoporometry:
  - fusion-solidification-fusion cycles (2°C/min for a range of temperatures between -80°C and 0°C)
  - RH conditions: 11%, 33%, 54%, 75%, 90% (for each RH sample: equilibration for 1 month with saline solutions), saturated material (97% < RH < 99%)
  - Study of hysteresis between adsorption-desorption
  - Hydration with liquid water or with water vapour for saturated samples
- Experiments: samples mass  $\cong$  10mg

# Influence of hydration method

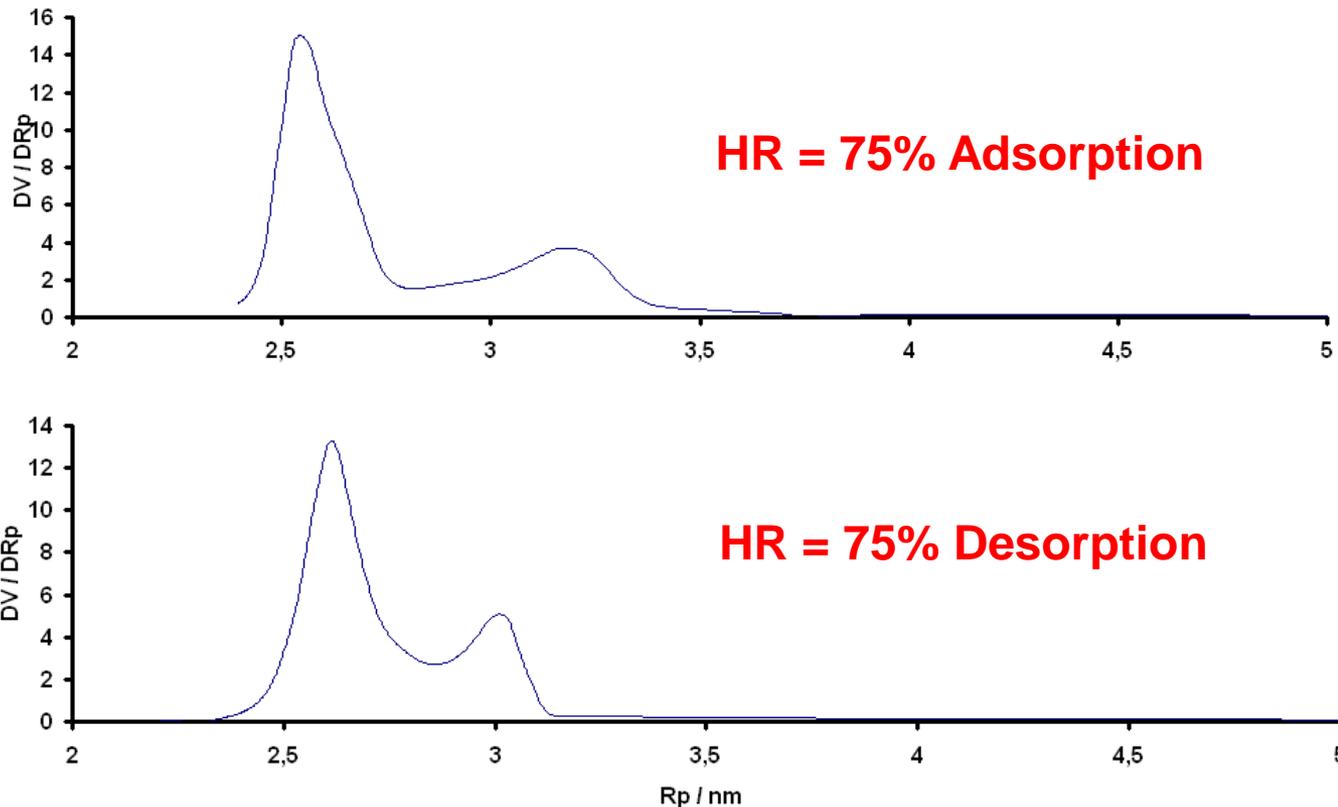
- Liquid water vs. vapour hydration process

Na



- 2 fusion cycles are identical
- 2 solidification cycles slightly different = no significant modification of pore structure
- No influence between the two modes of hydration

# PSD: hysteresis between adsorption and desorption



- No notable differences for the first peak  $< 0.05$  nm (experimental error)
- Difference for the second peak : hysteresis (observed also in water adsorption isotherms)