HAL archives-ouvertes.fr

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

F. Salles, O. Bildstein, J. Douillard, B. Prelot, J. Zajac, H. van Damme

▶ **To cite this version:**

F. Salles, O. Bildstein, J. Douillard, B. Prelot, J. Zajac, et al.. Hydration sequence for swelling clays exchanged with mixed alkali/alkali-earth cations. Scientific Basis for Nuclear Waste Management XXXIX, Nov 2015, Montpellier, France. hal-02445719

HAL Id: hal-02445719

https://hal-cea.archives-ouvertes.fr/hal-02445719

Submitted on 20 Jan 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

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

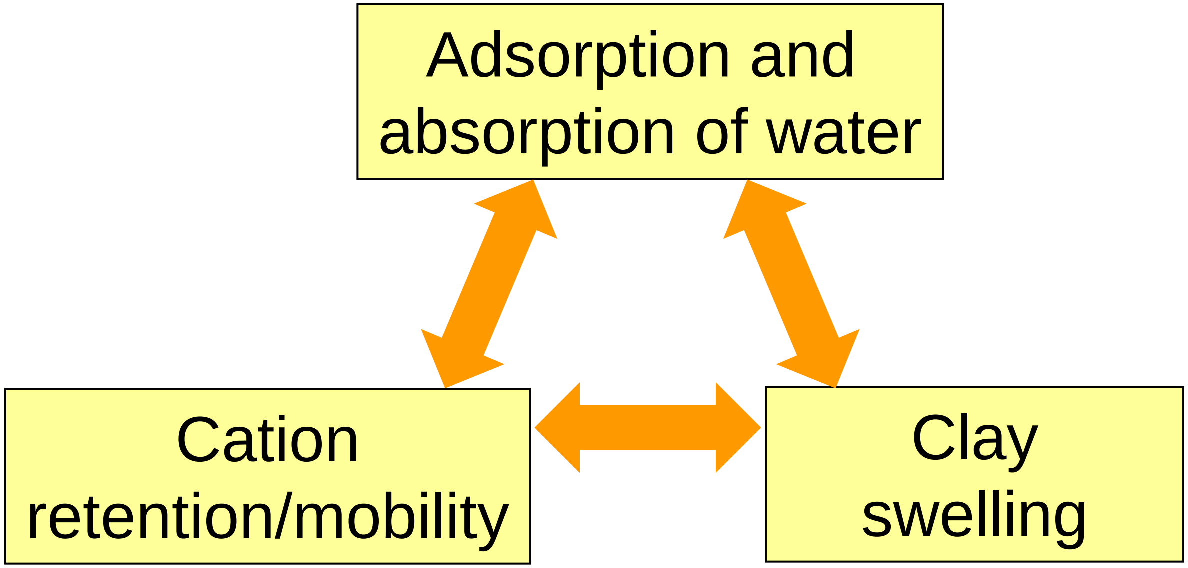
F. Salles[1], O. Bildstein[2], J.M. Douillard[1]
B. Prélot[1], J. Zajac[1], H. Van Damme[3]

[1] ICGM, Université Montpellier, France
[2] CEA Cadarache, France
[3] ESPCI, Paris, France

Context of the study

- 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

- 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

- 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^+, Na^+, K^+, Cs^+ and Ca^{2+} cations & different RH investigated

  → Common practice : DSC on saturated non-swelling samples = all pores are filled

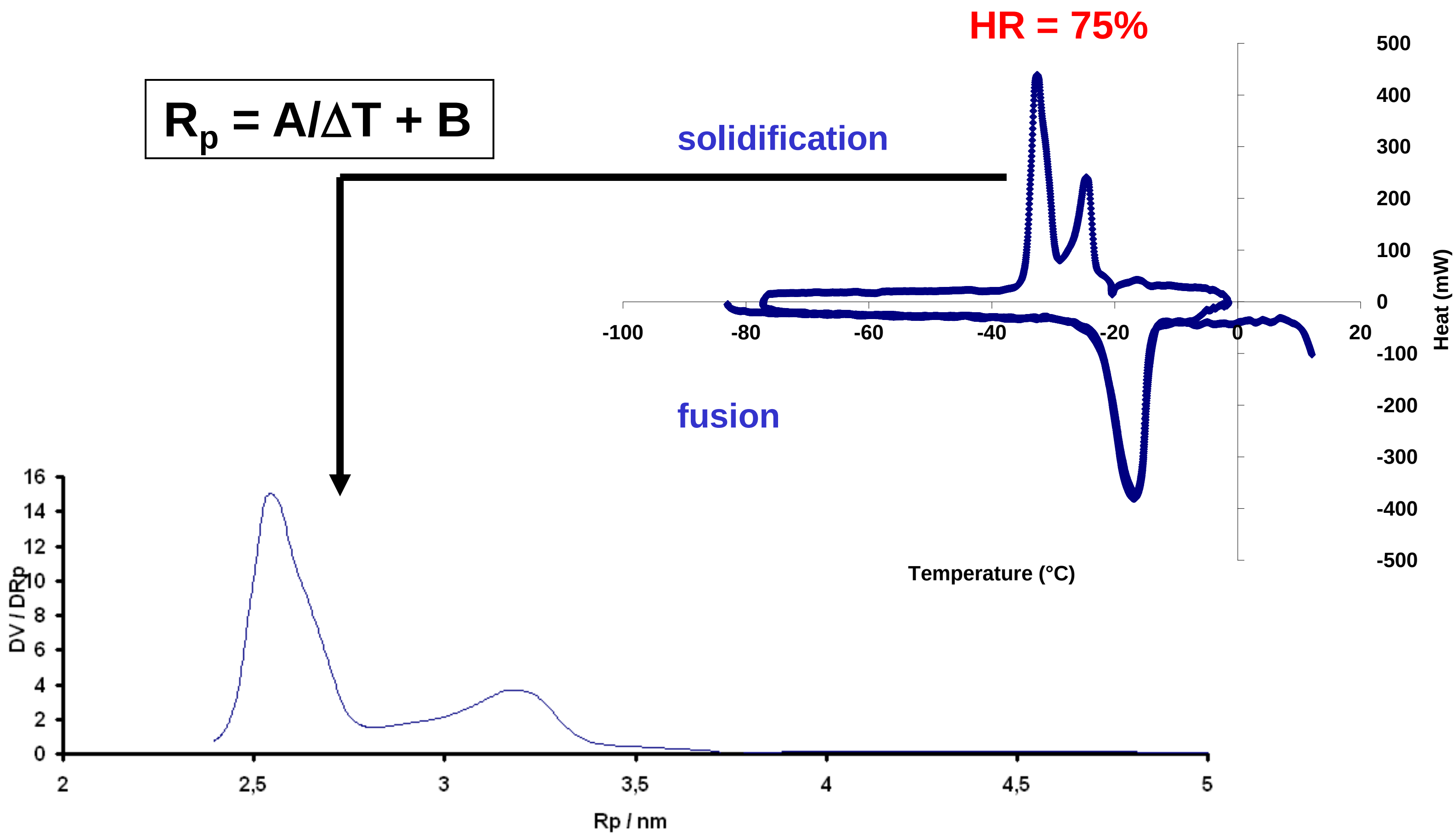
  → Saturation of studied porosity is necessary

- **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)

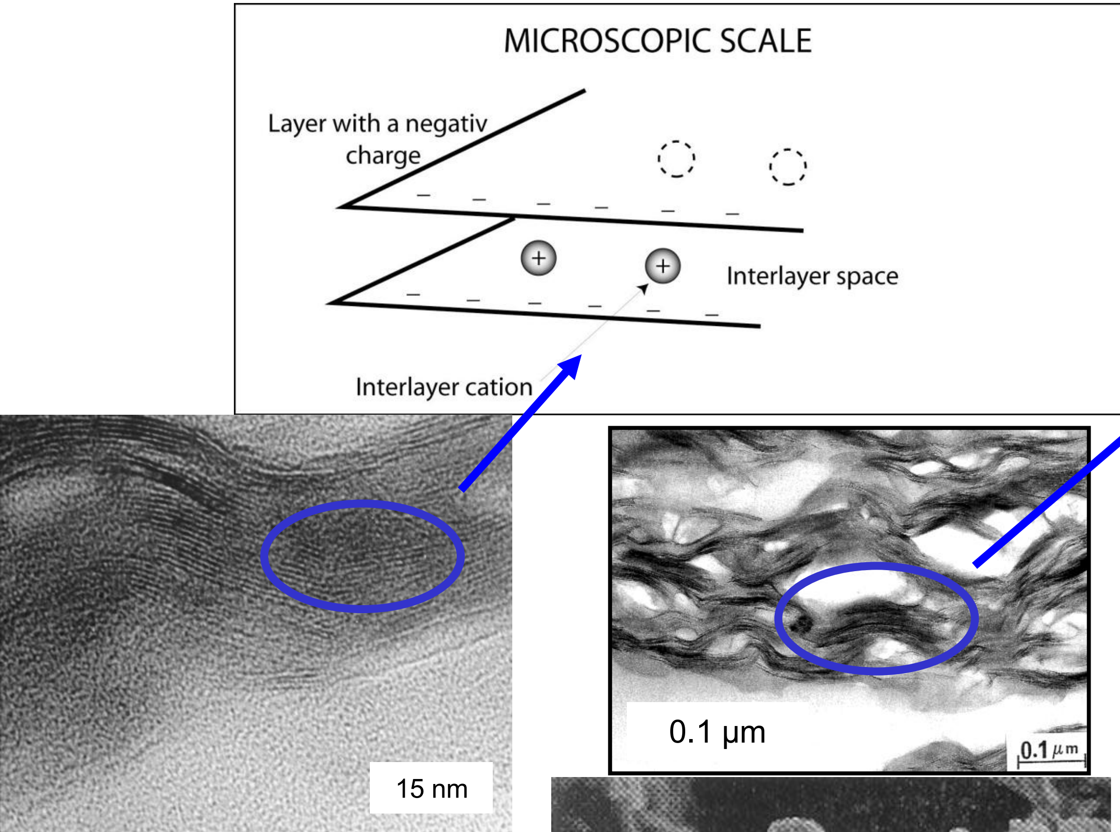
- Pore size distribution obtained with Brun equations **(parameters result from fit with various materials)** :

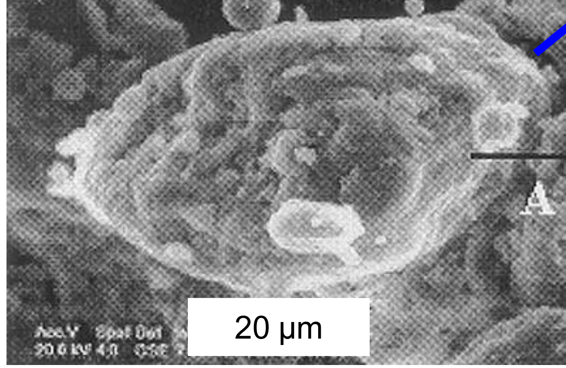
$$R_p = A/\Delta T + B$$

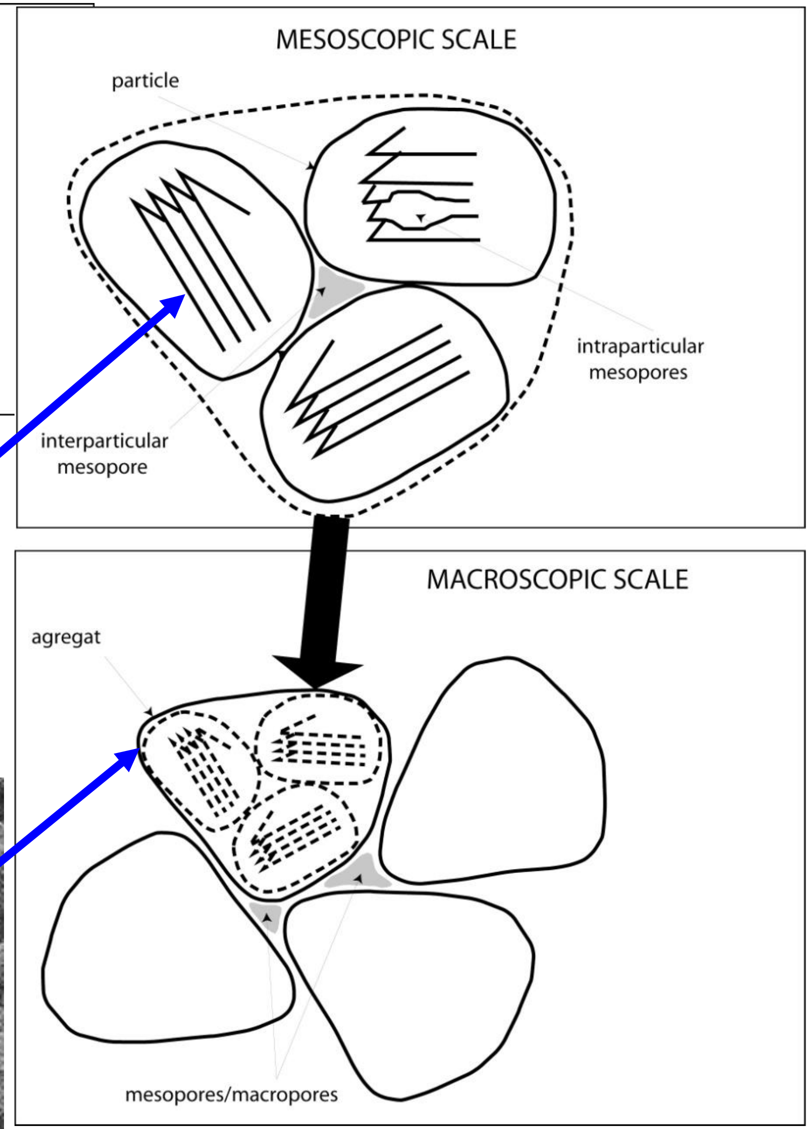


➢ 2 peaks = **2 well-defined families of pore size**

Multi-scale structure of clays





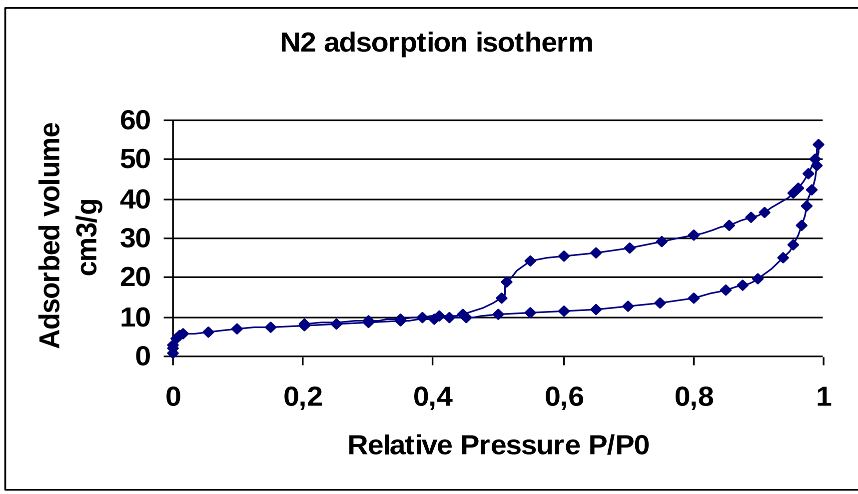


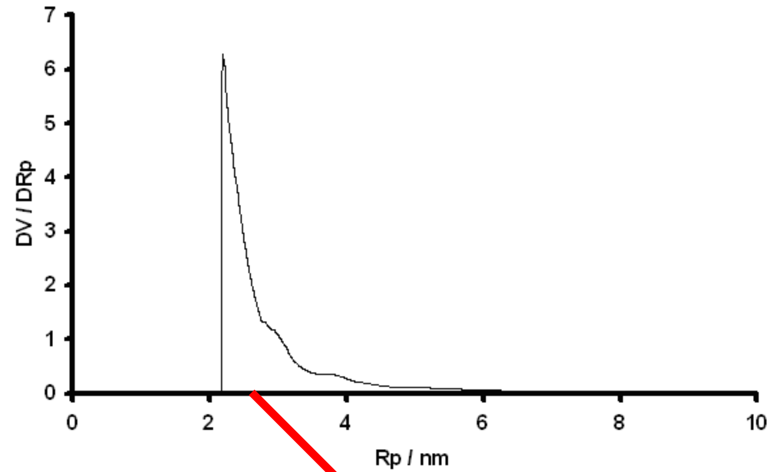
- Multi-scale aspect

- Focus on mesoporosity

Results for RH ≤ 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%:**





~ 2.5 nm

BJH calculations from N_2 adsorption data

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

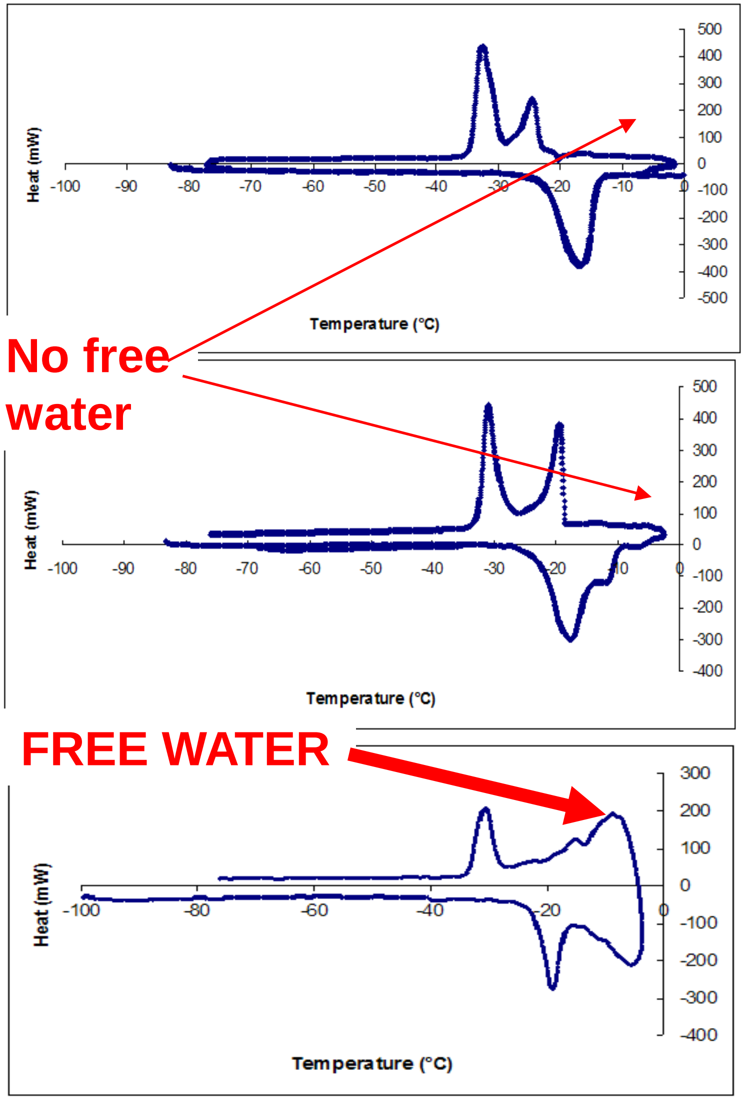
Results for RH > 54%

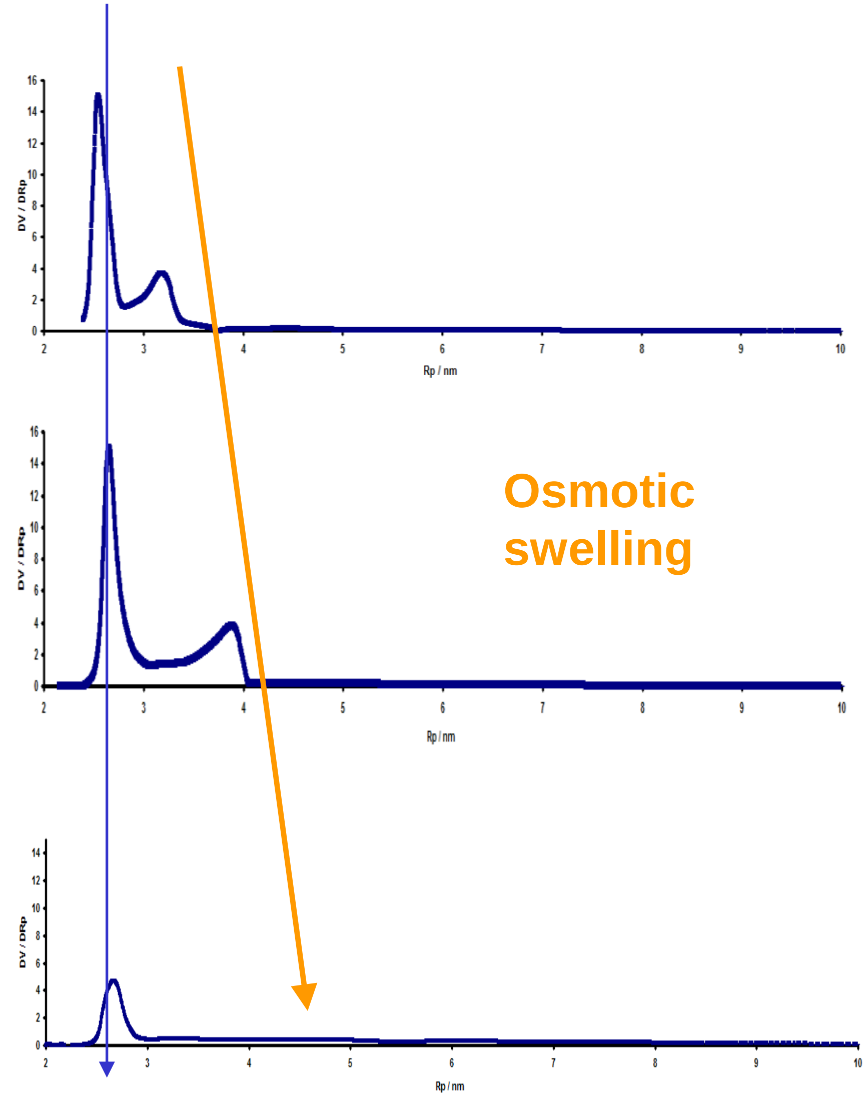
- Results for RH ranging from 75% to saturation

HR = 75%

HR = 90%

HR sat

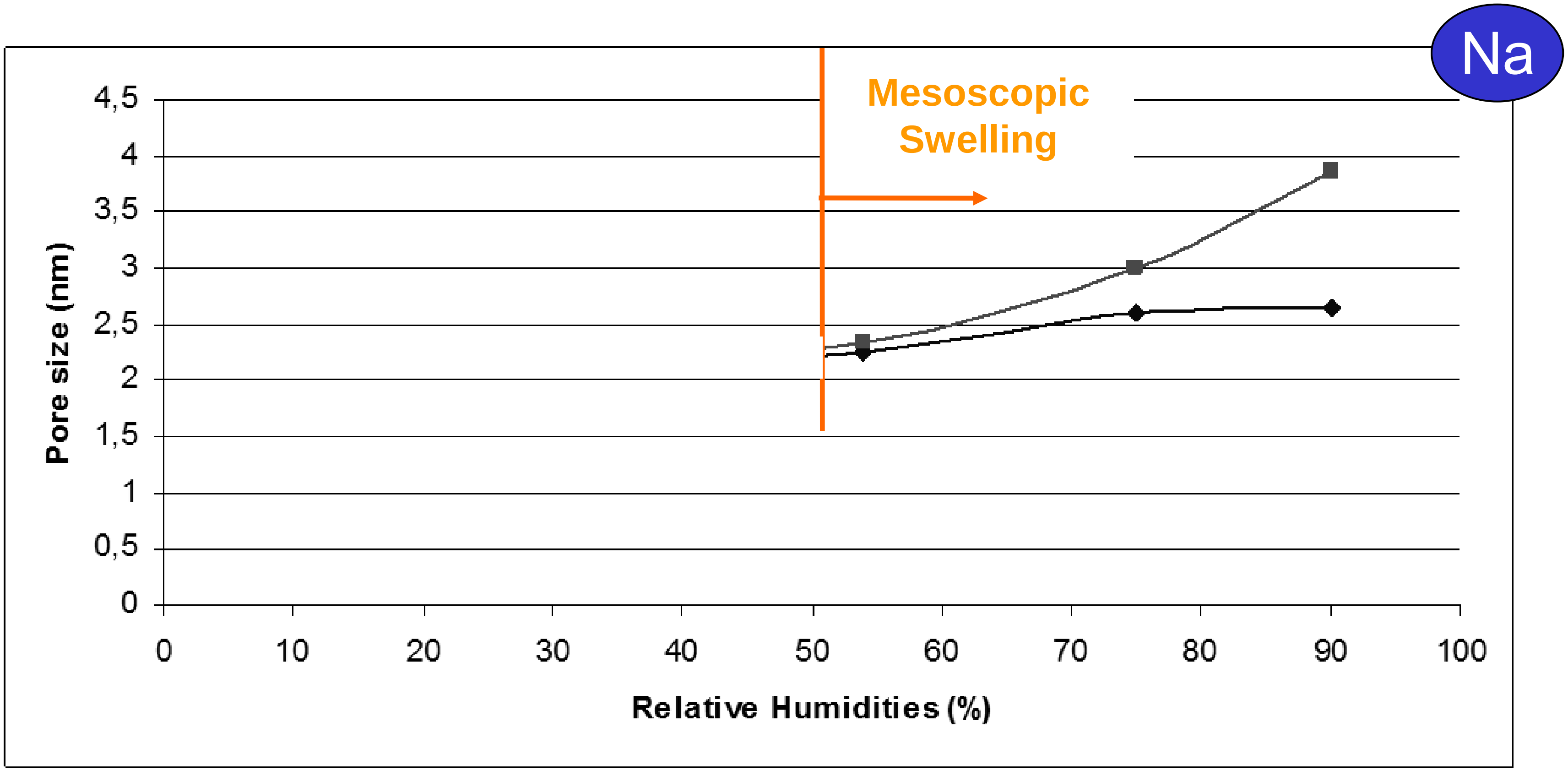




- ➢ No free water at RH < 90%

Interpretation(1): evidence for osmotic swelling in mesopores

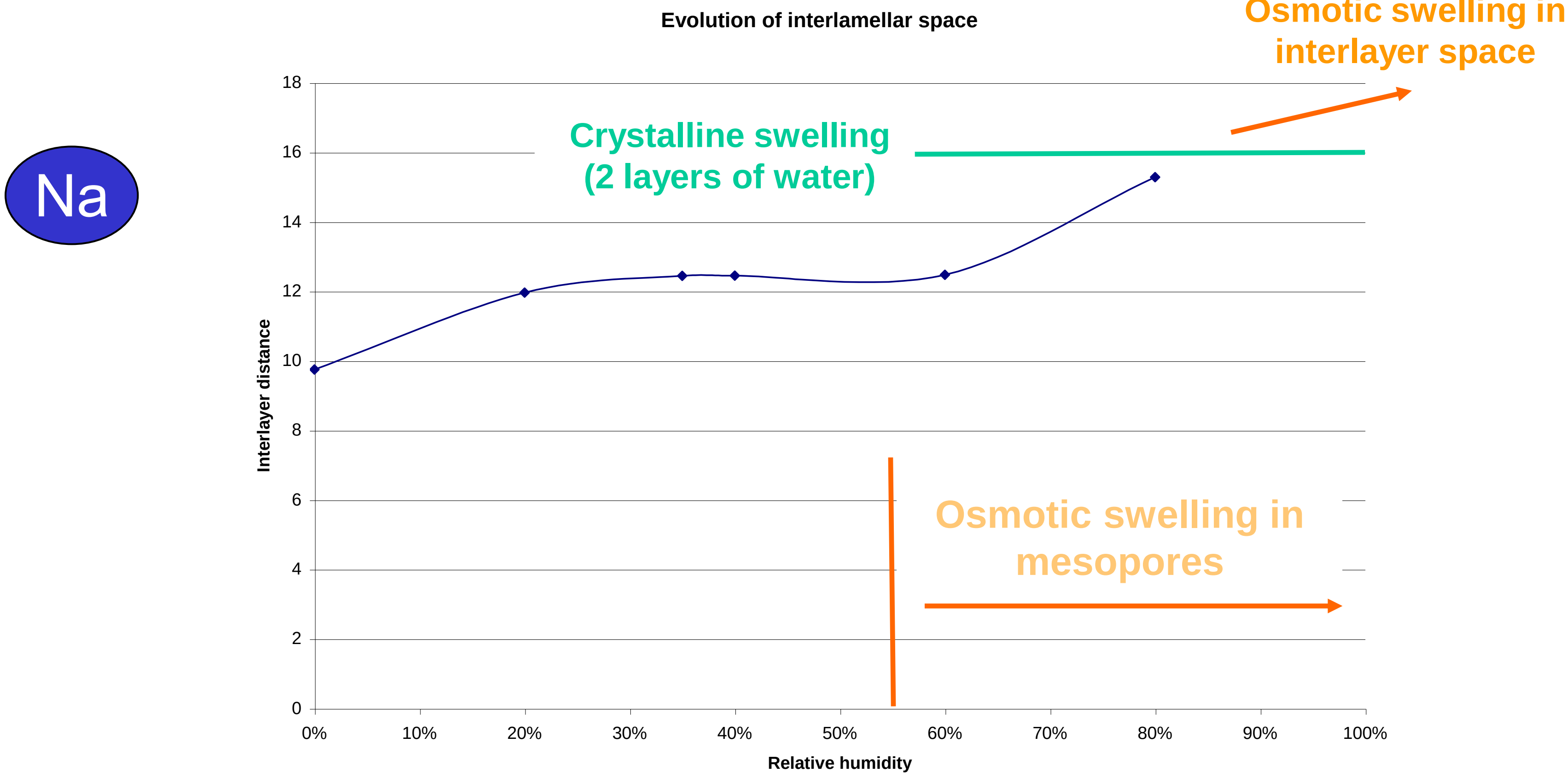
- **pore size in mesopores (for the 2 families)**



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

Interpretation (2)

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



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

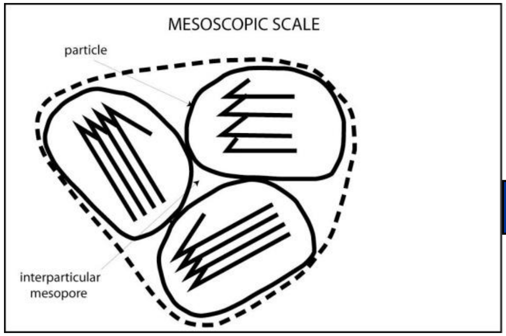
Salles et al., Appl. Clay Sci., 2008

Interpretation (3): hydration sequence

Li

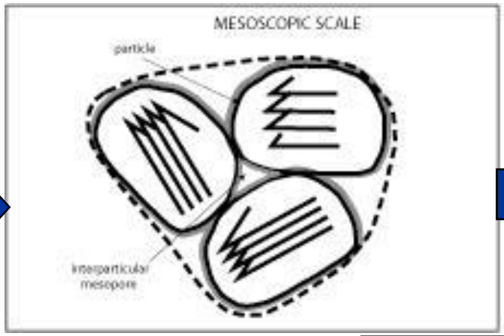
Na

RH~0%



RH ~0%

RH<10%

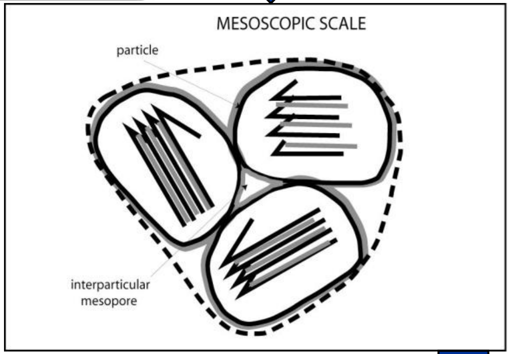


RH < 10%

Adsorption isotherms

RH<20%

XRD

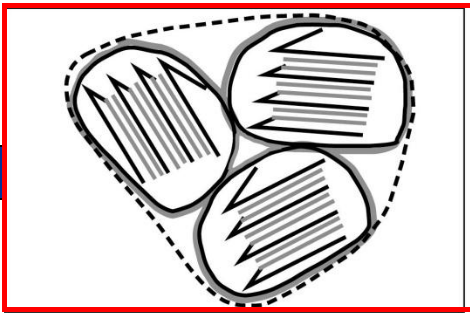


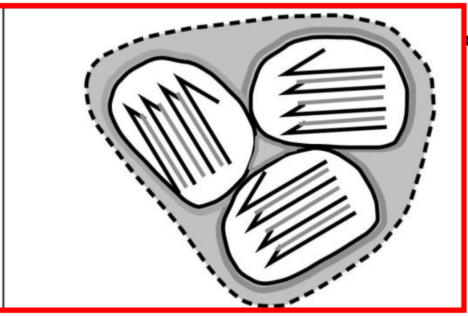
RH <20%

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

Thermoporometry

20<RH<80%

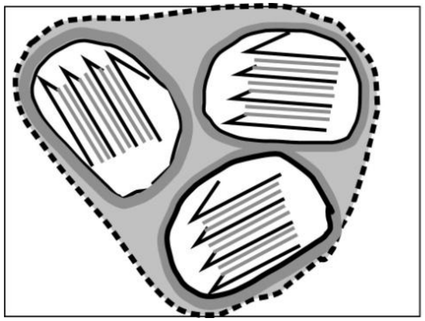




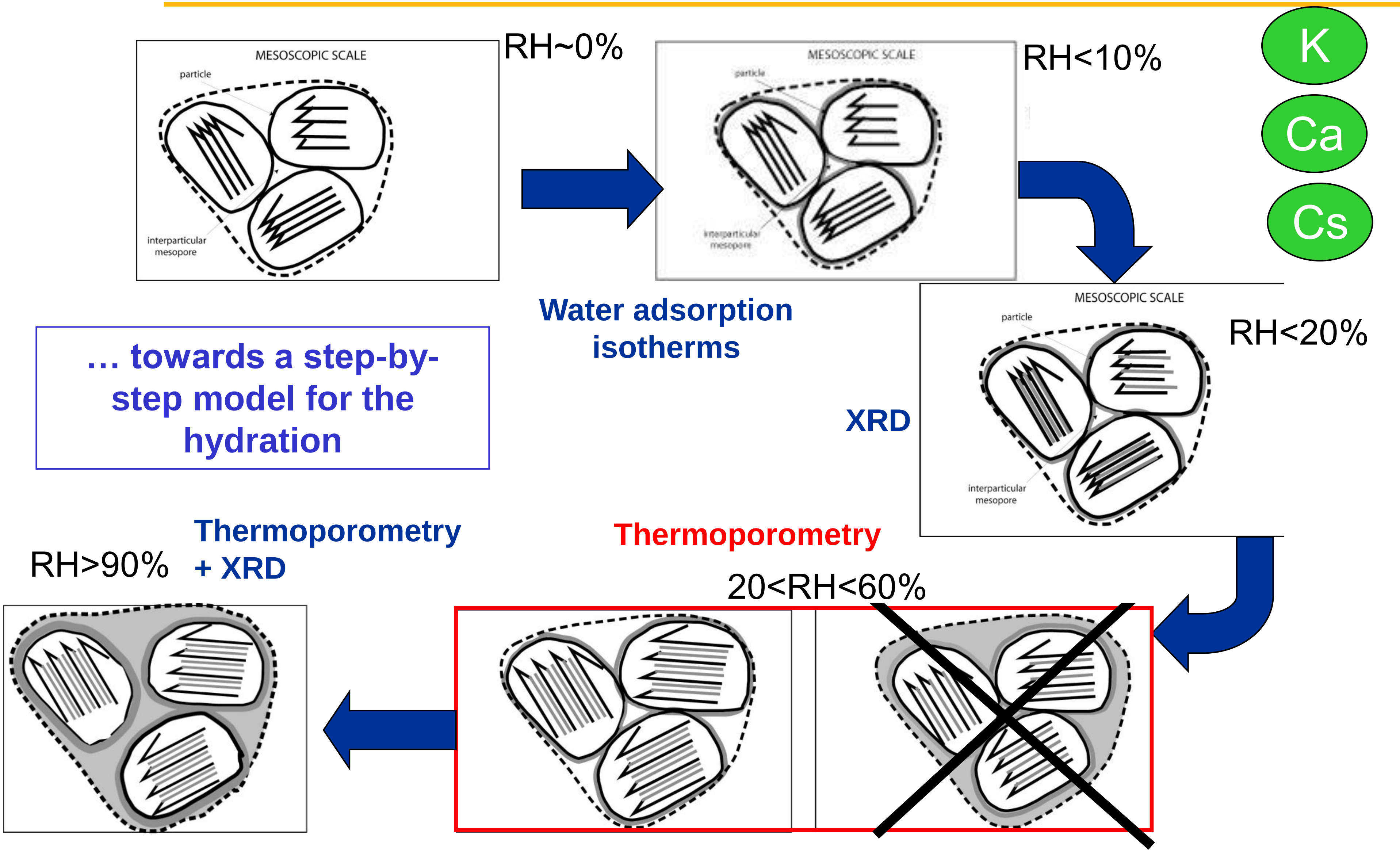
RH> 60%

RH>80%

Thermoporometry + XRD



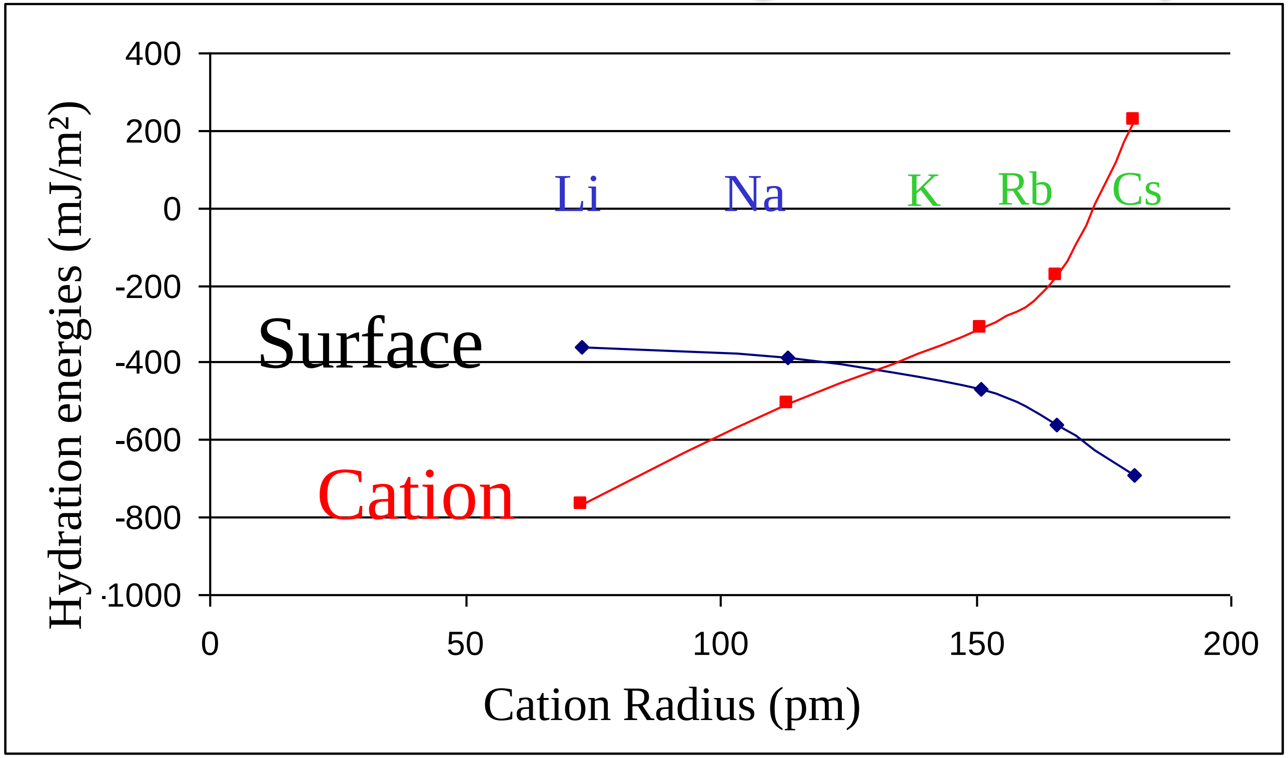
Interpretation (4): hydration sequence



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

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

Salles et al., J. Phys. Chem. C, 2007

Towards the distinction between interlayer or mesopore water

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

- It follows:

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

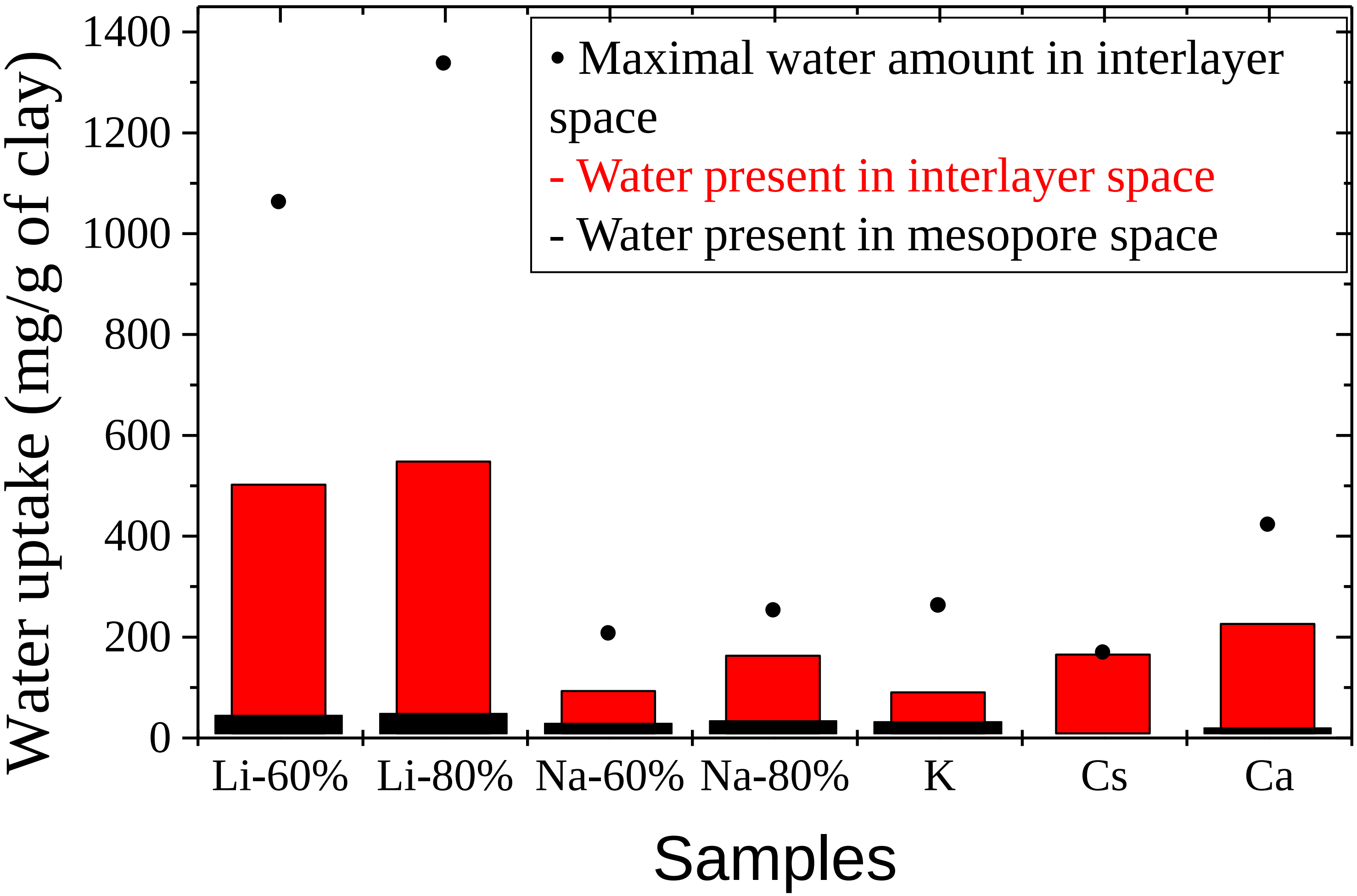
- The theoretical quantity of water (=maximal amount) present in interlayer space can be determined from the following equation:

$$m_{theoretical\ interlayer\ water} = d_{001} * (S_{H2O} - S_{N_2})$$

where S_{H2O} and S_{N2} are the specific surface area as a function of RH* and d_{001} is related to the interlayer space opening

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

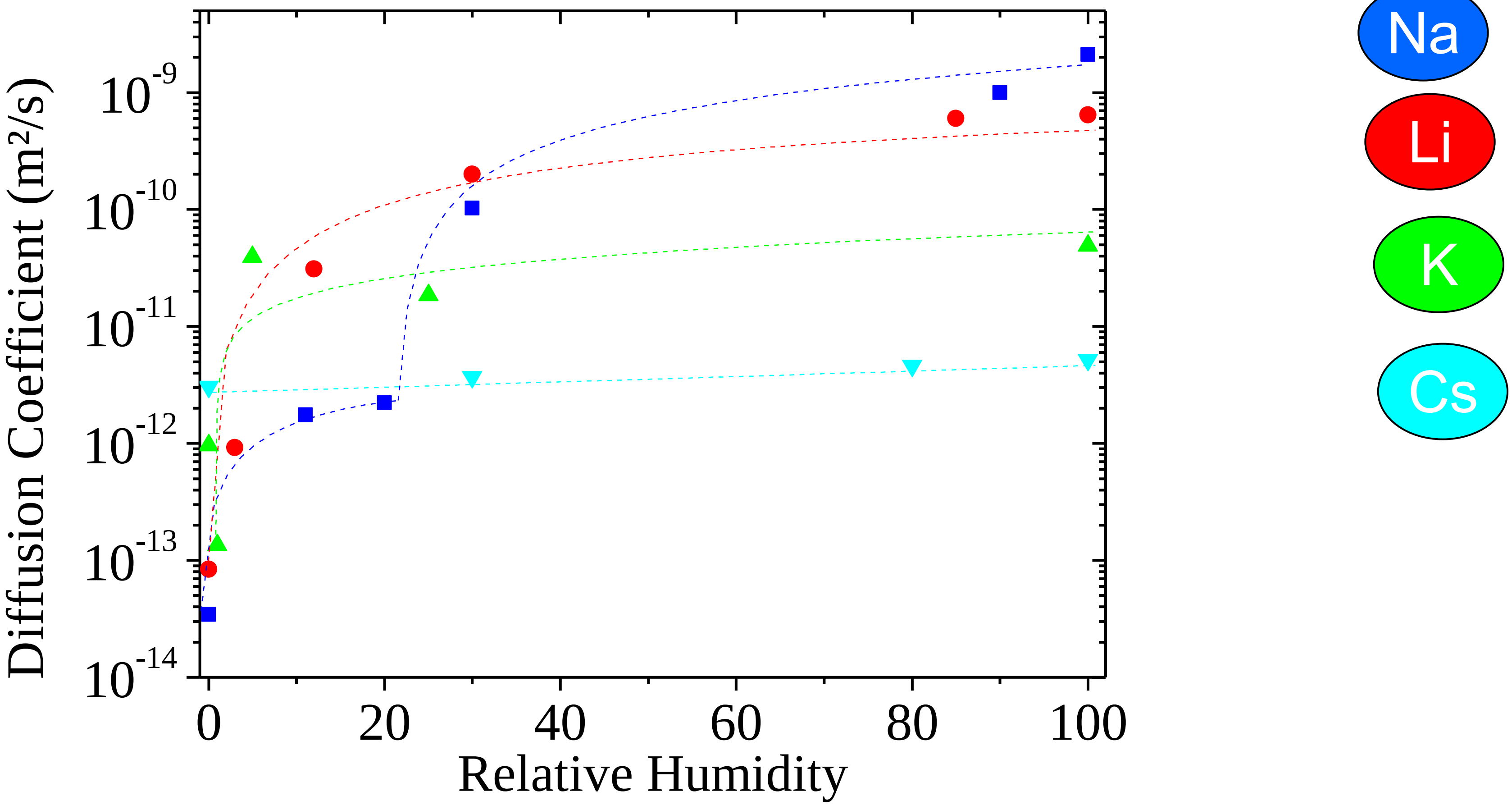
Distinction of interlayer and mesopore water



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

Salles et al., Langmuir, 2010

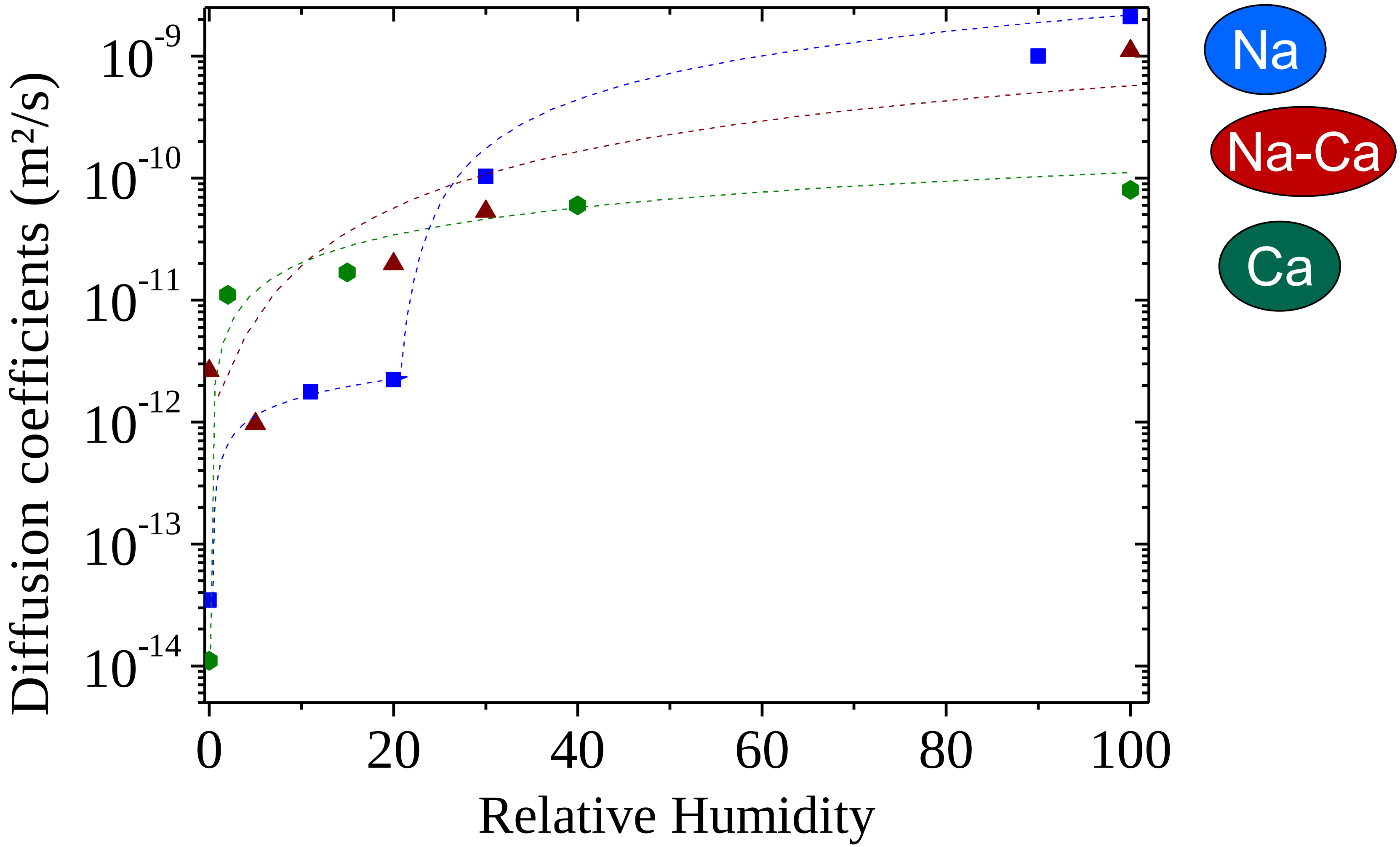
Diffusion of Cations in swelling clays



- 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^+ diffusion reaches values lower than bulk water
- ✓ Influence of Ca^{2+} and repartition of cations ?

Conclusions

- 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

Thank you for your attention!

Thermoporometry equations

- **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

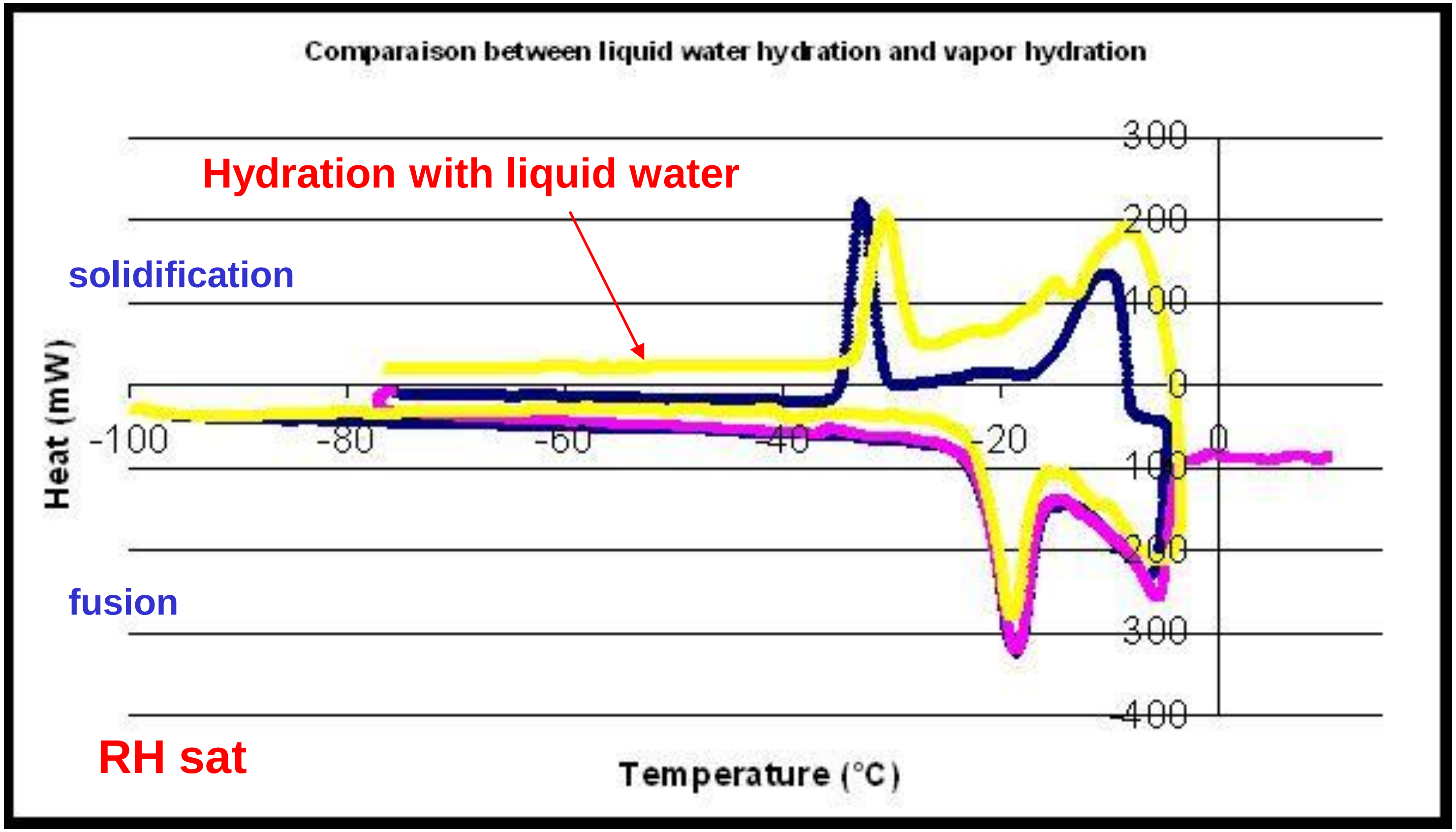
- Na-mont (purified and exchanged MX80 Wyoming) → **powder**

- 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 ≅ 10mg

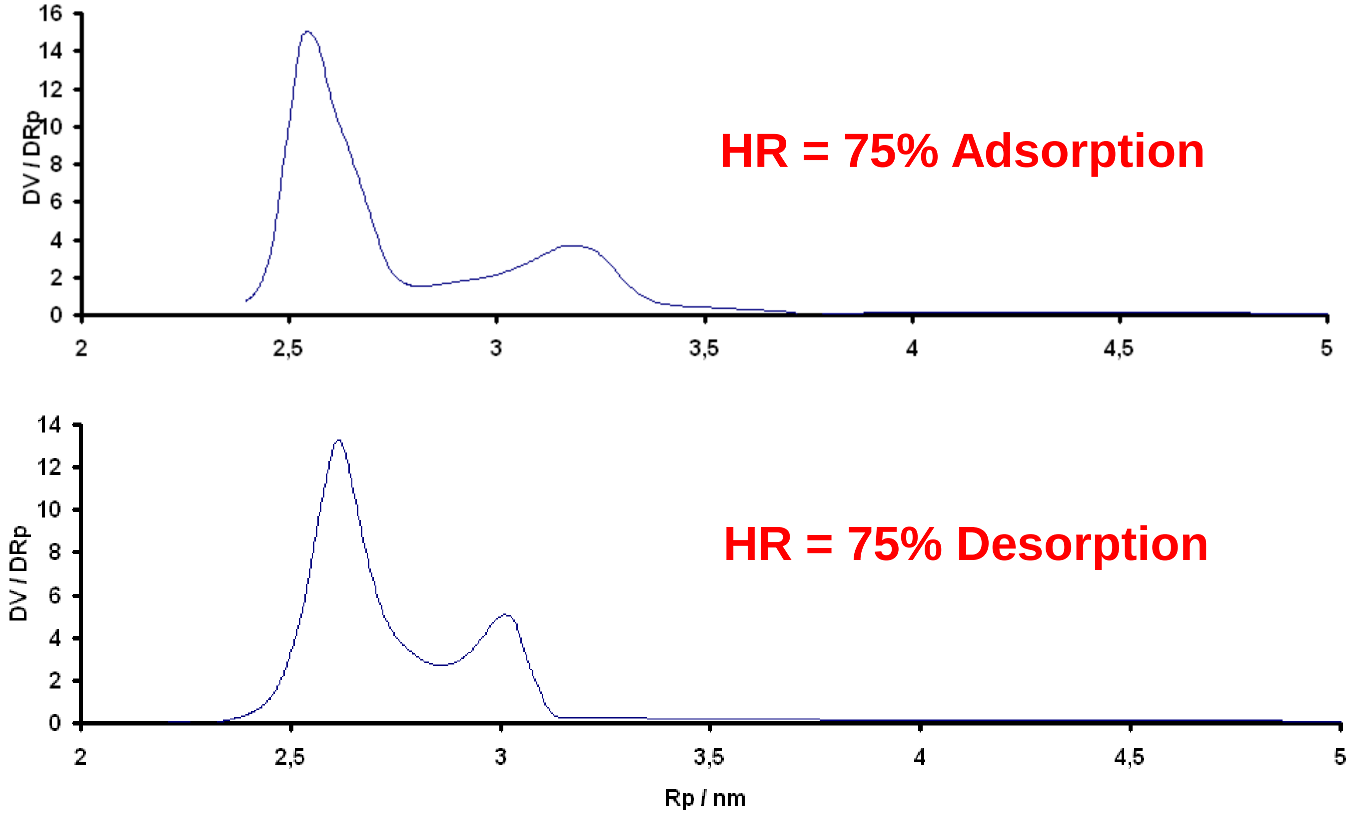
Influence of hydration method

- Liquid water vs. vapour hydration process



- 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)