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

F. Salles<sup>1</sup>, O. Bildstein<sup>2</sup>, H. Van Damme<sup>3</sup>

<sup>1</sup> ICGM, Université Montpellier, France

<sup>2</sup> CEA Cadarache, France

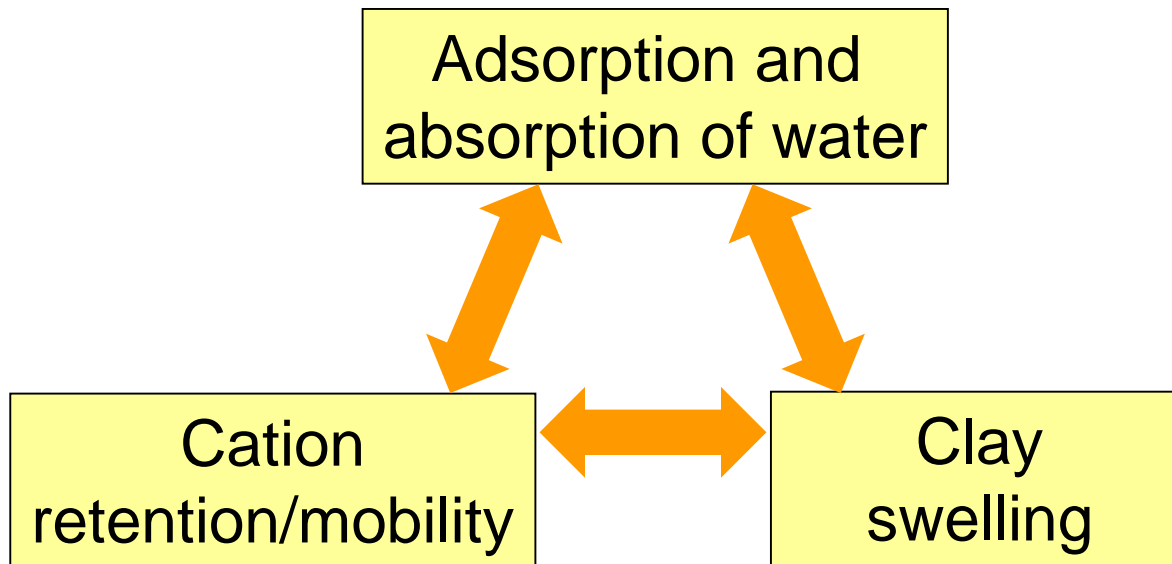
<sup>3</sup> ESPCI, Paris, France & MIT, Boston, USA



# Context of the study

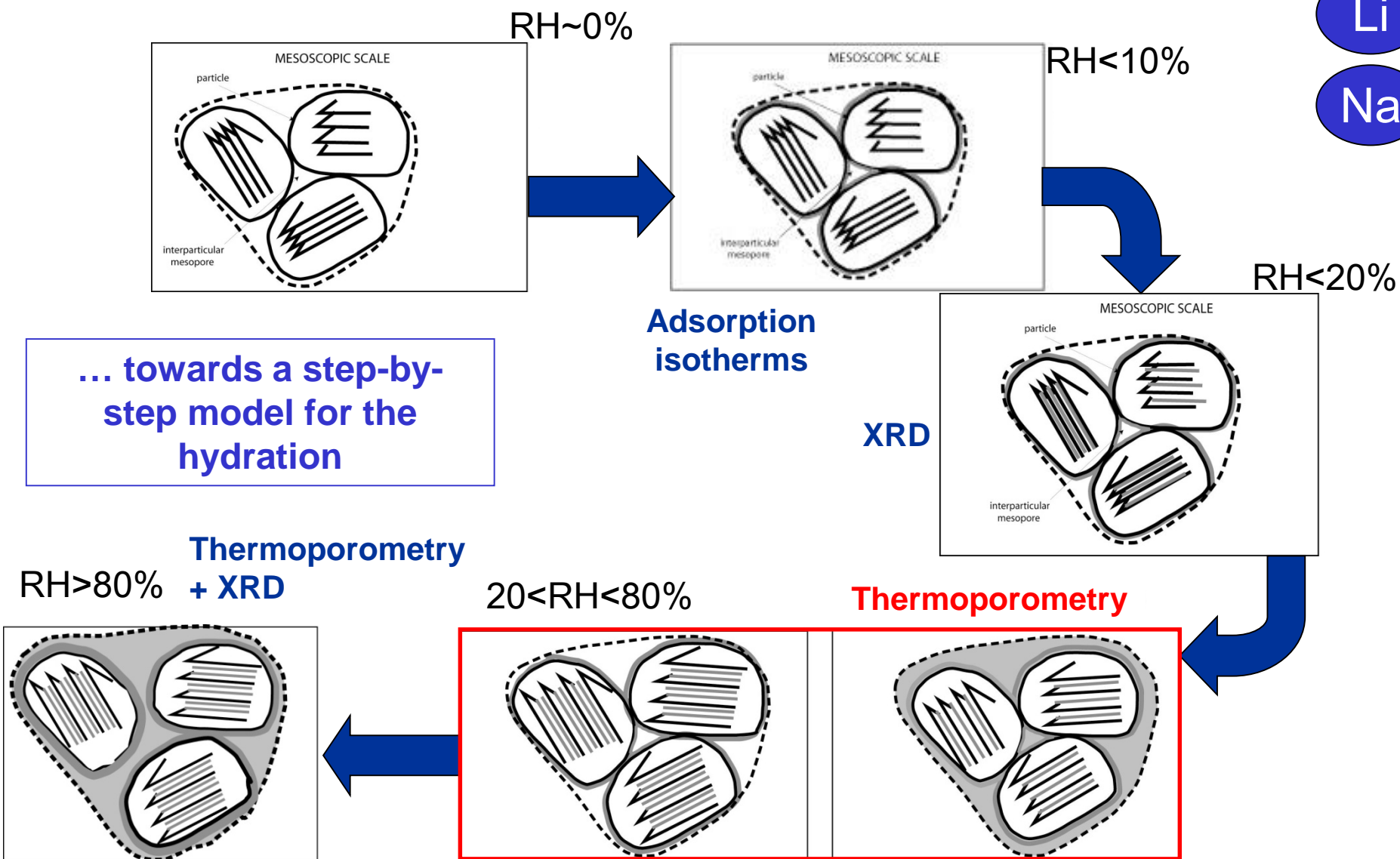
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- Disposal of radioactive wastes in deep geological repositories and multi-barriers concept
- Role of clays:
  - limiting water fluxes in the repository
  - swelling and filling up technical gaps
  - adsorbing RNs (in the interlayer space and onto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



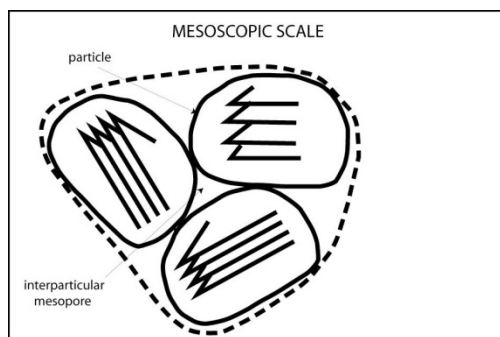
# Hydration sequence for small alkali cations

Li  
Na

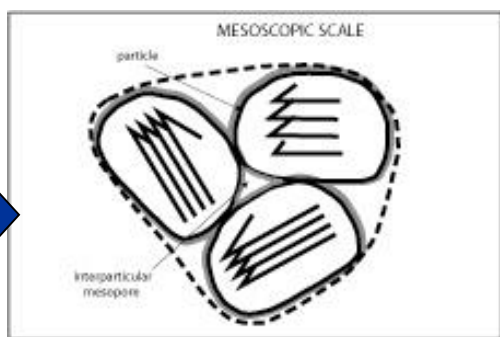


# Hydration sequence for large alkali cations and $\text{Ca}^{2+}$

K  
Ca  
Cs



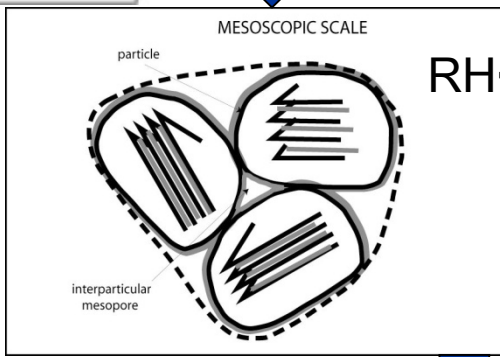
RH ~ 0%



RH < 10%

Water adsorption isotherms

XRD



RH < 20%

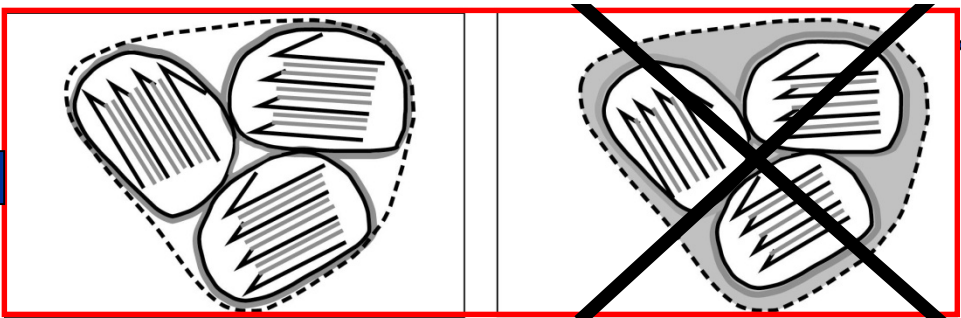
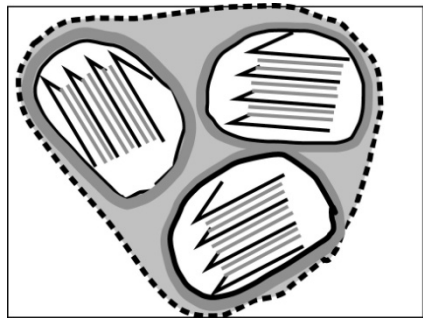
... towards a step-by-step model for the hydration

Thermoporometry + XRD

RH > 90%

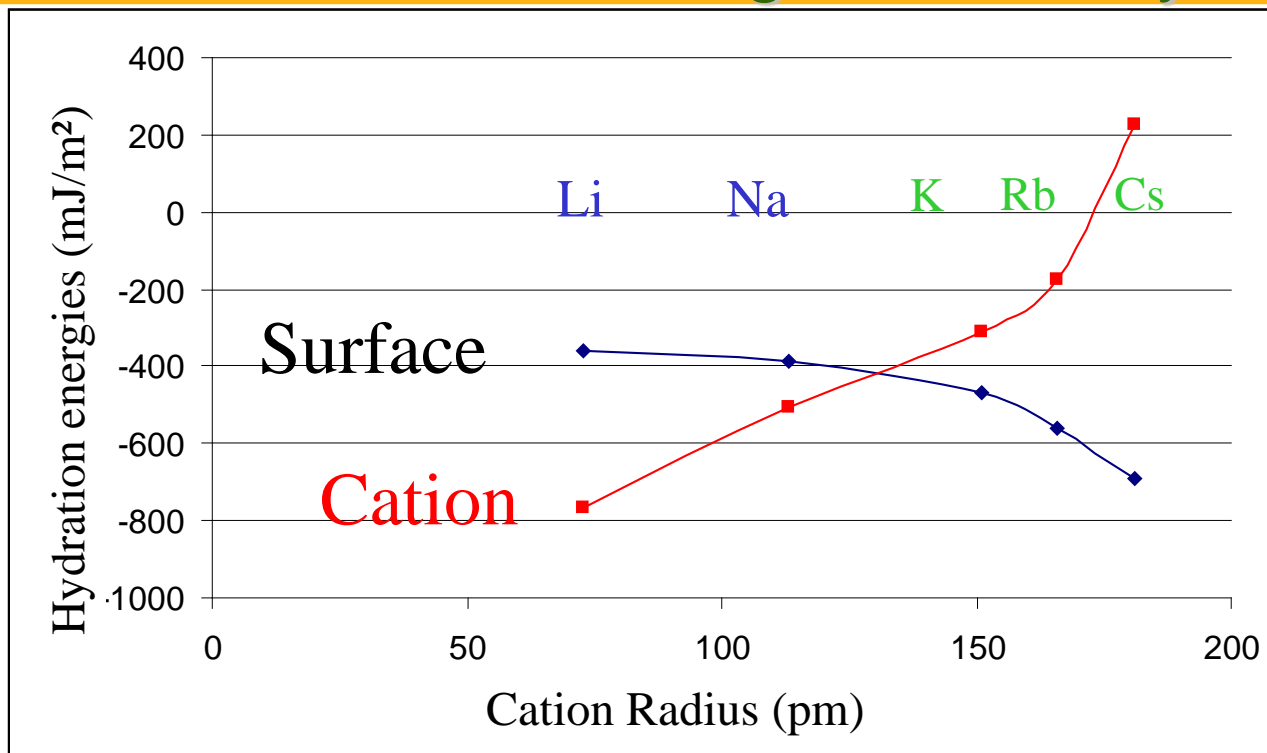
Thermoporometry

20 < RH < 60%



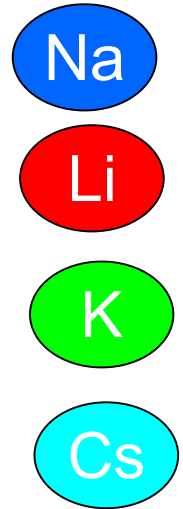
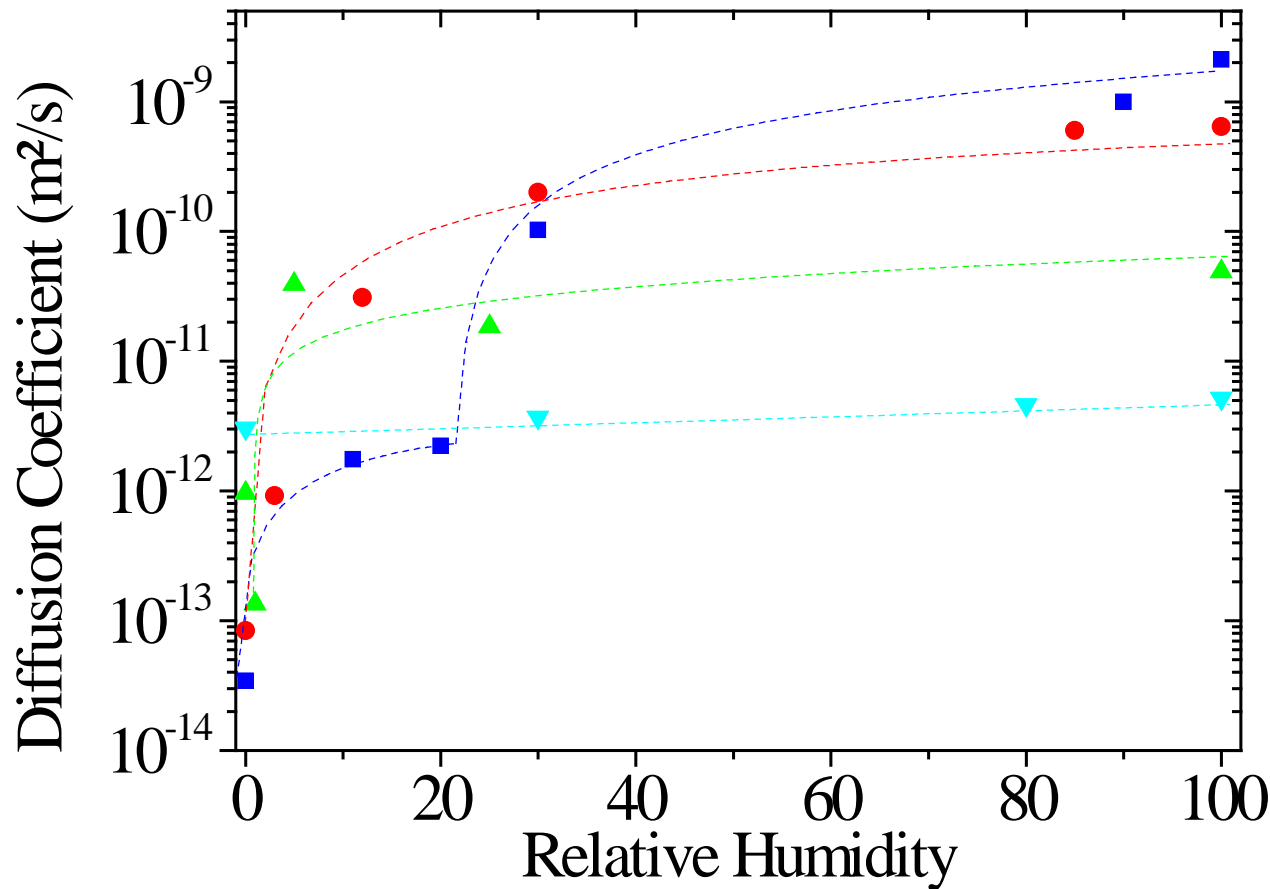
Salles et al., Langmuir, 2010

# 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

# 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*

# 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:

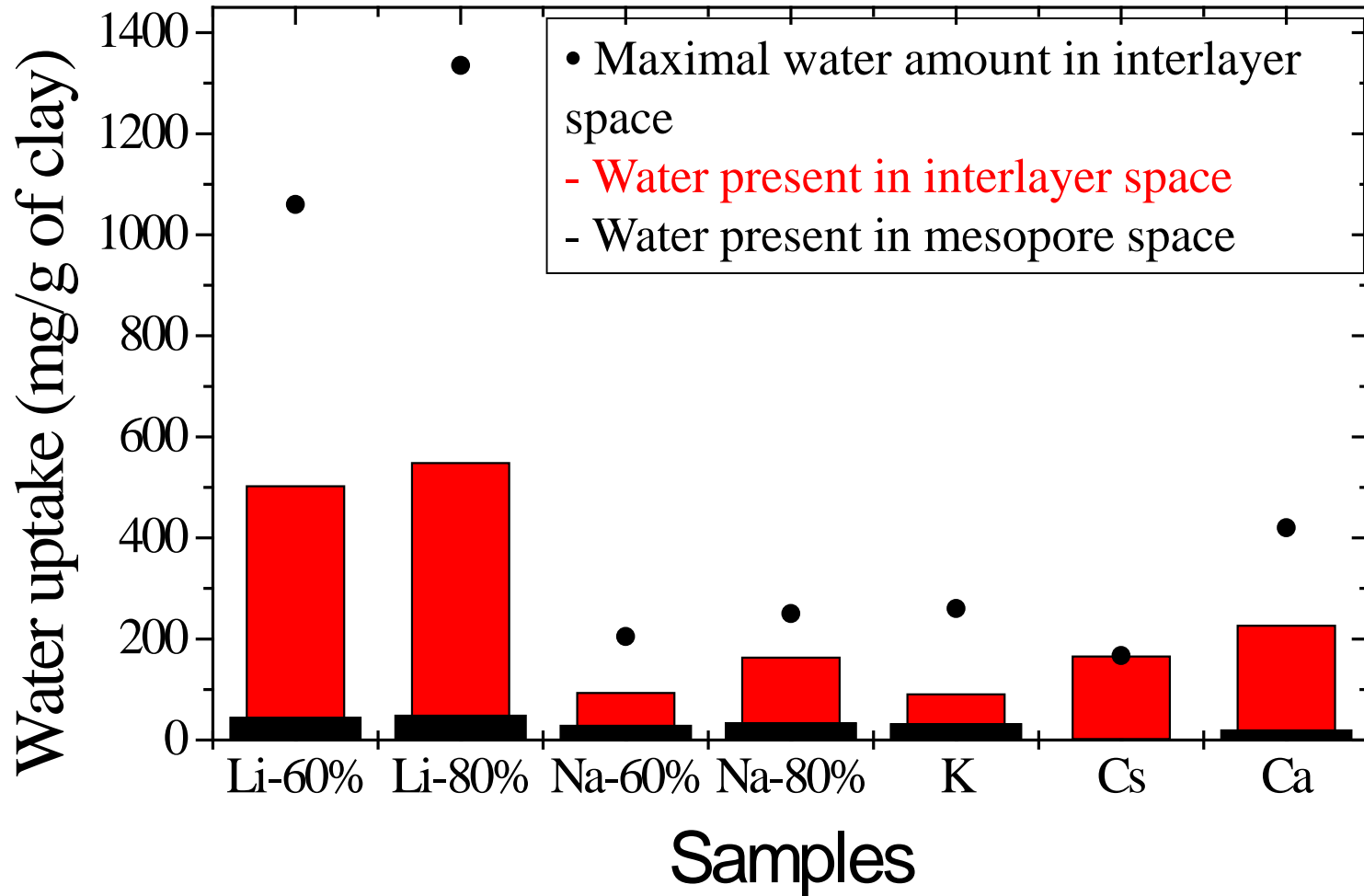
$$m_{\text{theoretical interlayer water}} = d_{001} * (S_{\text{H}_2\text{O}} - S_{\text{N}_2})$$

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*



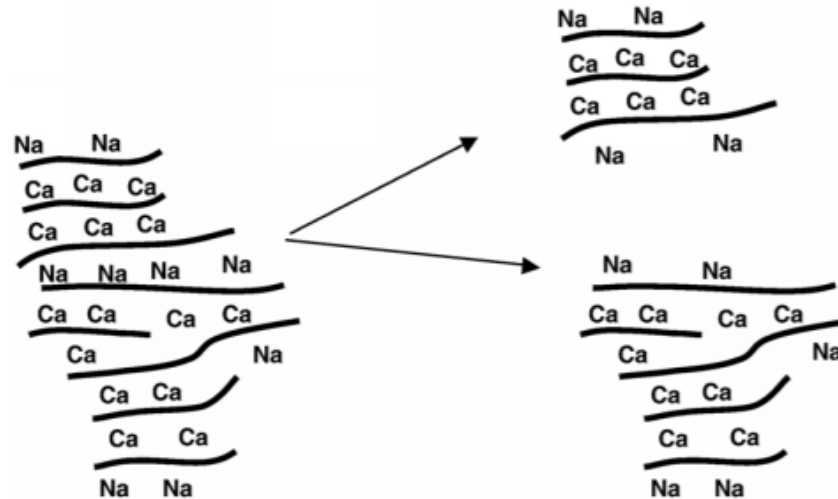
## Distinction of interlayer and mesopore water



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

*Salles et al., Langmuir, 2010*

# What happens in the case of a mixture of interlayer cations??



*Laird, Applied Clay Science, 2006*

# Results for textural properties

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Classical characterisation techniques: XRD & BET

XRD at the dry state

$$\begin{aligned}d_{001} &= 9.75 \text{ \AA} \text{ for Na-sample} \\ &= 10.2 \text{ \AA} \text{ for Ca-sample} \\ &= 10.09 \text{ \AA} \text{ for Na-Ca-sample}\end{aligned}$$

N<sub>2</sub> adsorption

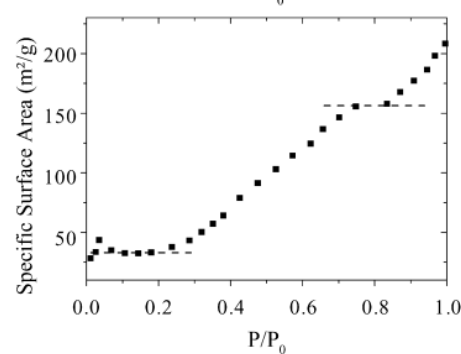
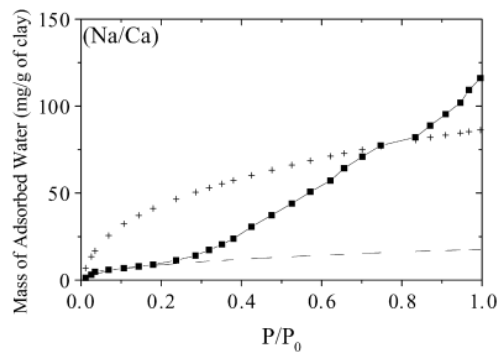
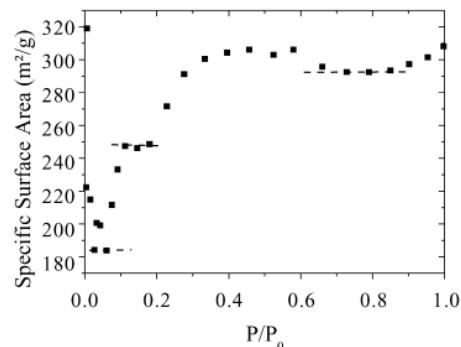
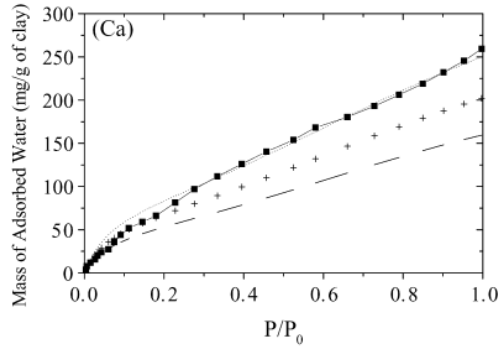
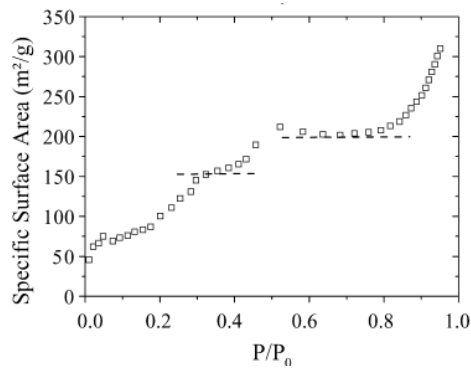
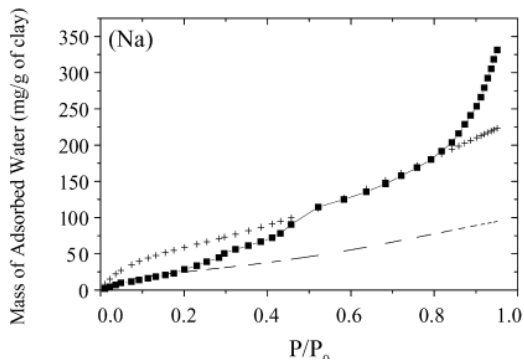
	Na	Ca	Na-Ca
<b>SSA (m<sup>2</sup>.g<sup>-1</sup>)</b>	27	10,4	10,3
<b>C<sub>BET</sub></b>	496	152	167
<b>Monolayer volume (cm<sup>3</sup>.g<sup>-1</sup>)</b>	6,3	2,39	2,4
<b>BJH pore (nm)</b>	2,5	4,5	3



Textural properties of Na-Ca-montmorillonite close to Ca-sample

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# Results for water adsorption

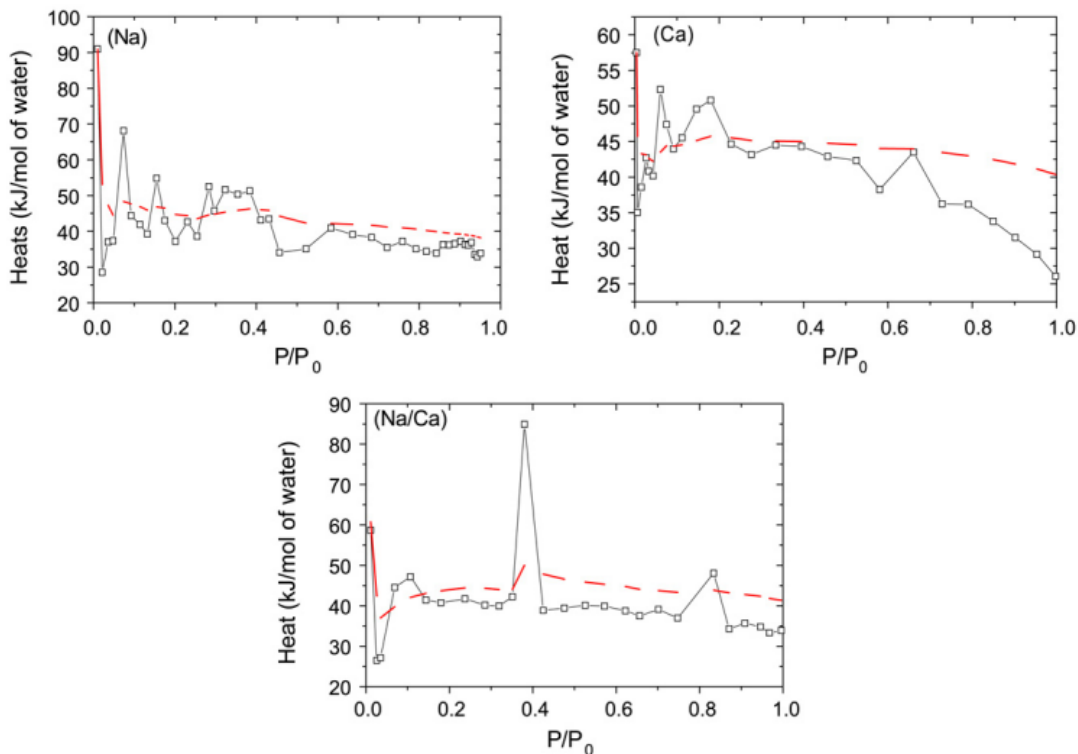


From adsorption isotherms 2 steps can be observed for Na-Ca-sample + SSA are relatively different



It is difficult to affirm which cation is predominant

# Results for water adsorption



The hydration enthalpies for swelling clays measured by calorimetry evidence that the  $\text{Ca}^{2+}$  cations are hydrated at lower RH than  $\text{Na}^{+}$

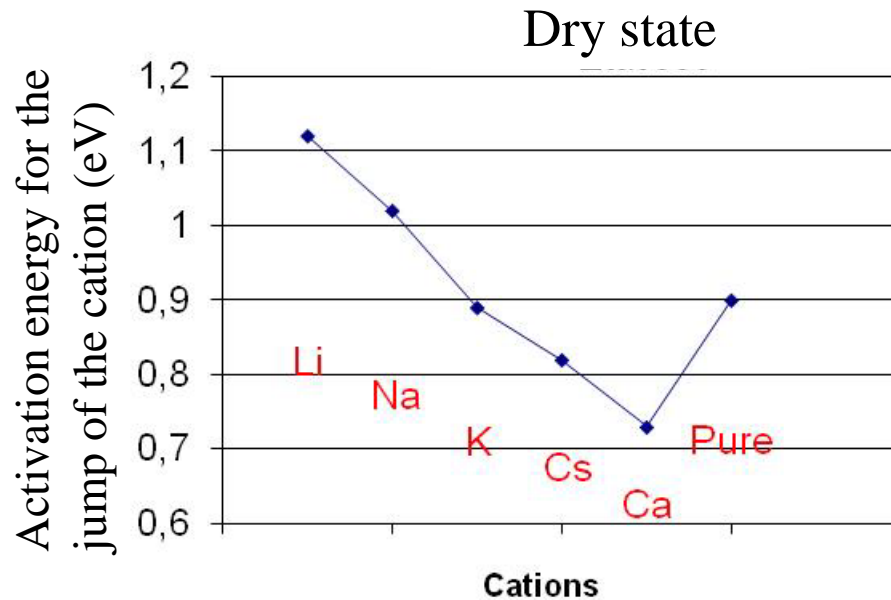
+

No osmotic swelling in the mesopores



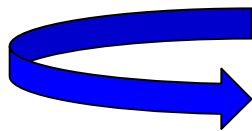
Inexpected in the case of demixion = mixture of cations

# Results on conductivity measurements



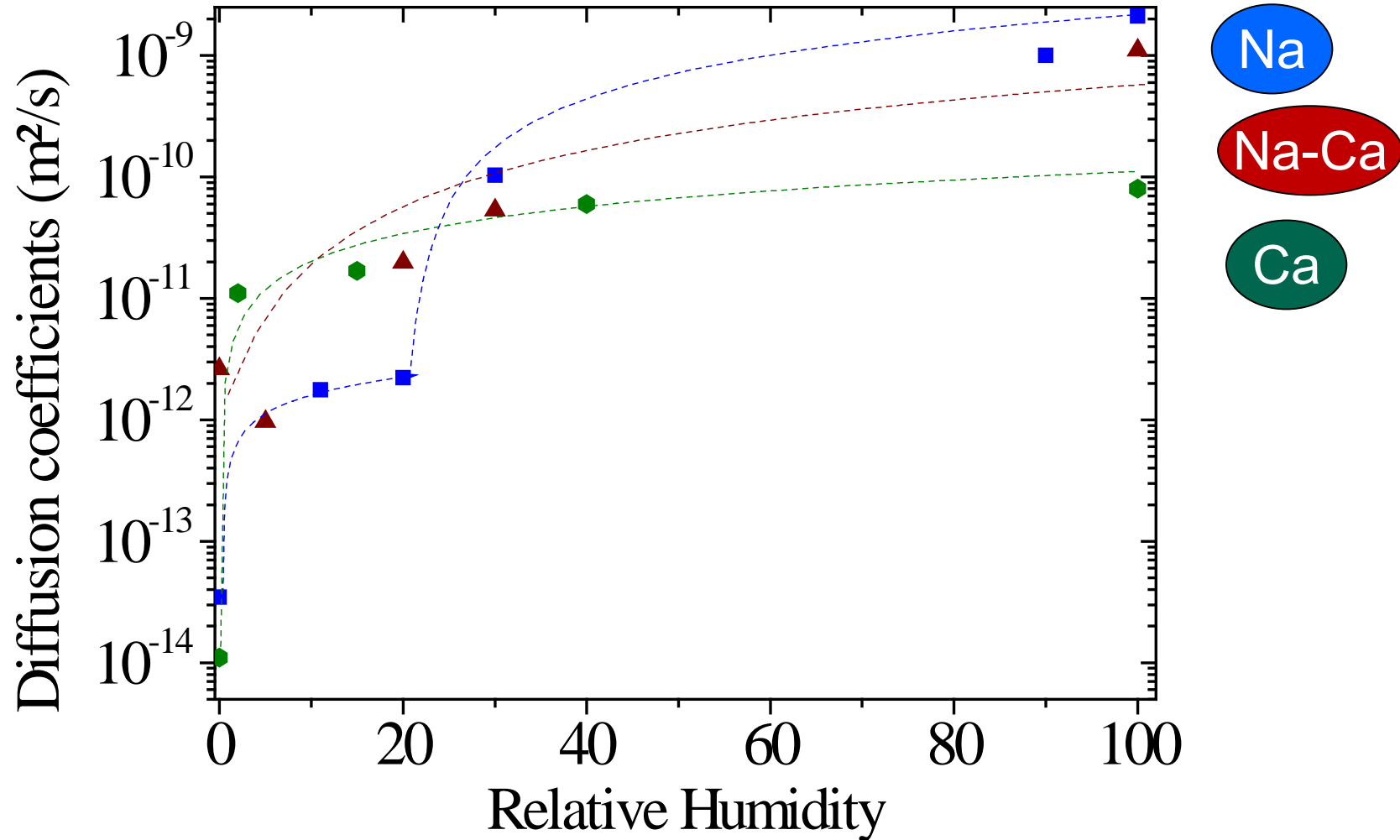
At the dry state, energy required to allow the interlayer cation to jump from an adsorption site to another one in the Na-Ca saturated sample = intermediate value

Mixture in the same interlayer space is confirmed



$$D = \sigma kT / (z^2 e^2 c)$$

# Results for diffusion



- ✓ For Na-Ca-samples:  $\text{Na}^+$  diffusion reaches values lower than bulk water
- ✓ Impact of  $\text{Ca}^{2+}$  on the  $\text{Na}^+$  diffusion in the interlayer space

# Conclusions

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- Summary:
  - Sequence of hydration is strongly depending on the interlayer cation
  - Existence of osmotic swelling in Li- and Na-montmorillonite in mesopores before crystalline swelling is finished in the interlayer space (2nd layer of water)
  - Interlayer space is never completely filled by water at  $RH < 97\%$  for all samples except  $Cs^+$ -montmorillonite
  - Mixtures of compensating cations in the interlayer space leading to modified properties compared to the homoionic samples



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**Thank you for your attention!**