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

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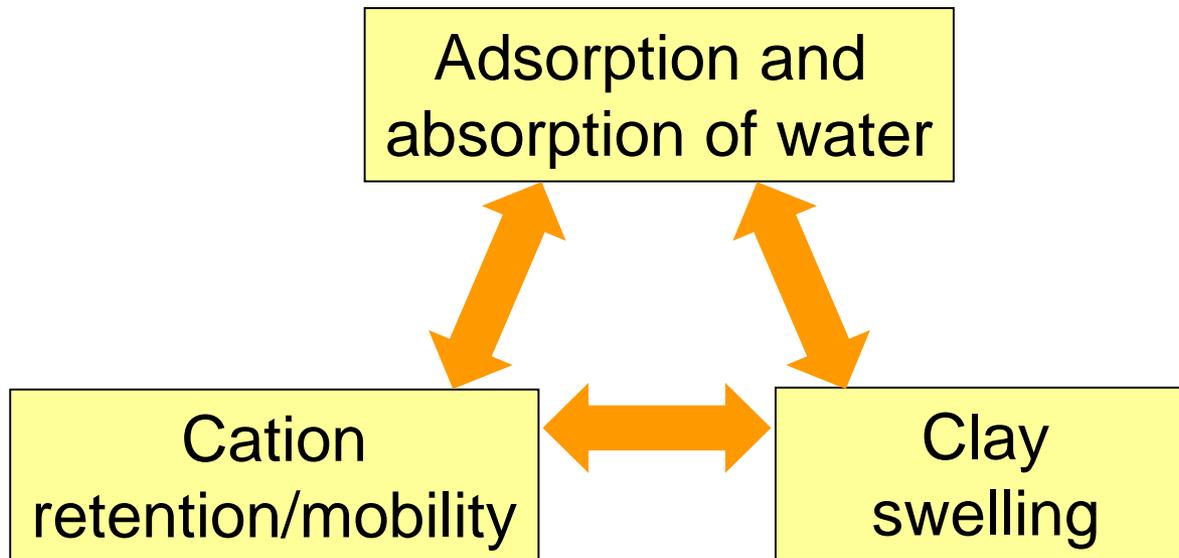
² CEA Cadarache, France

³ ESPCI, Paris, France & MIT, Boston, USA



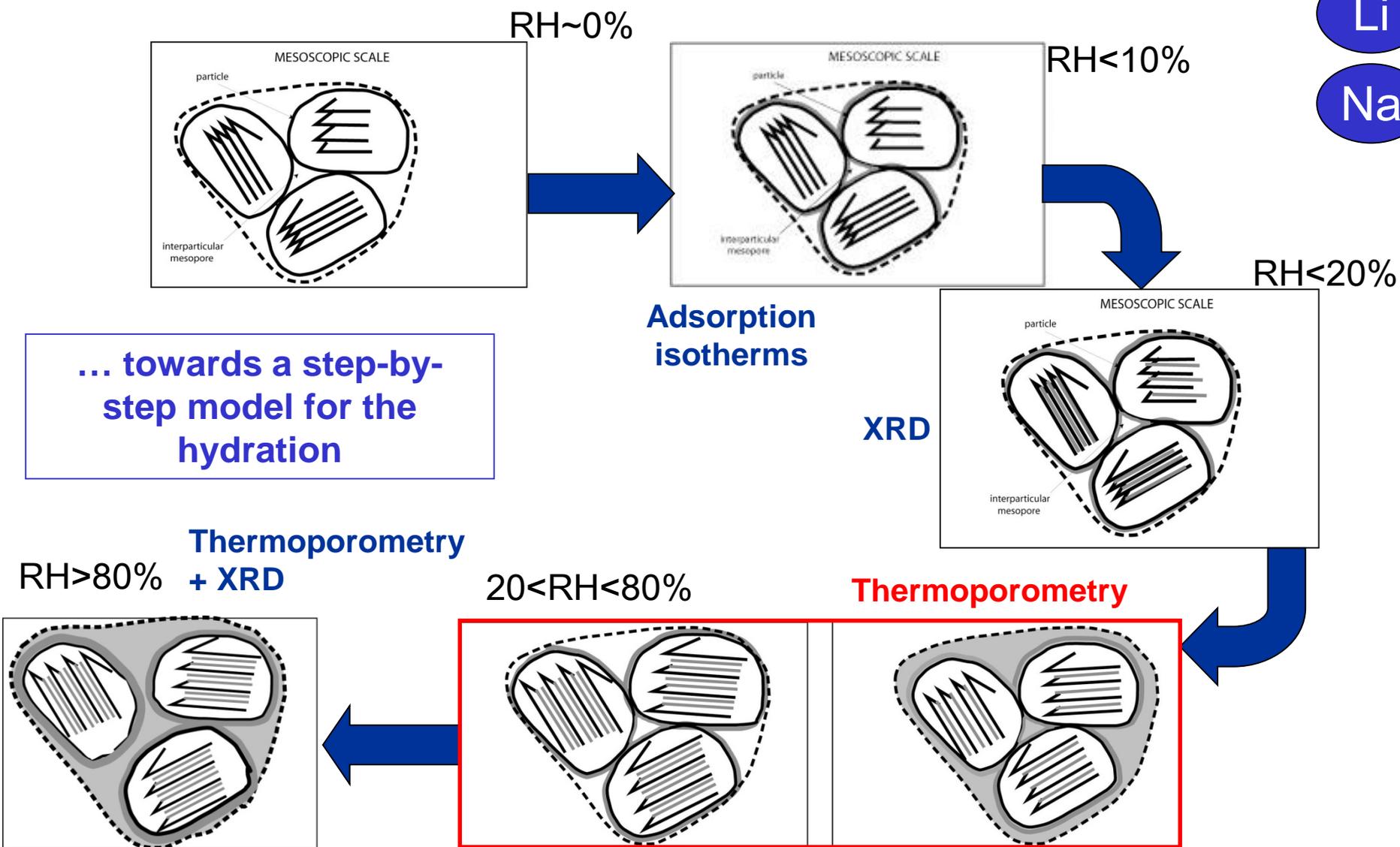
Context of the study

- 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)



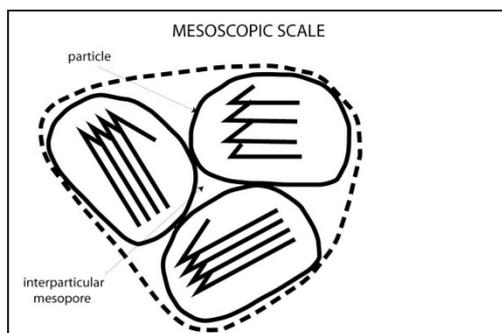
Hydration sequence for small alkali cations

Li
Na

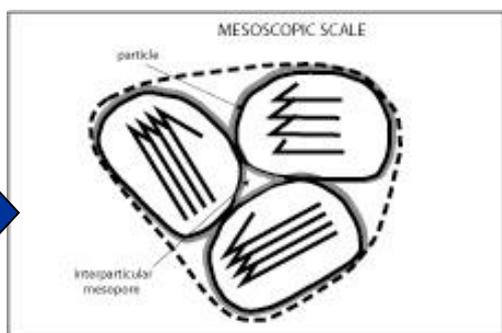


Hydration sequence for large alkali cations and Ca^{2+}

K
Ca
Cs



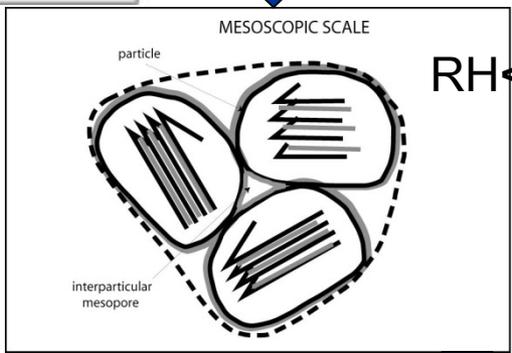
RH ~ 0%



RH < 10%

Water adsorption isotherms

XRD



RH < 20%

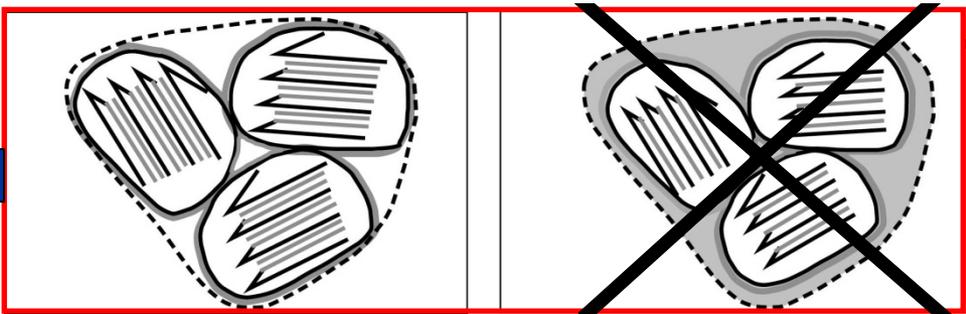
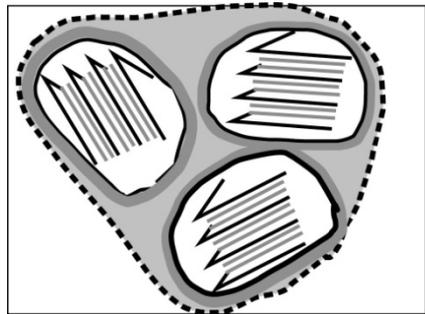
... towards a step-by-step model for the hydration

Thermoporometry + XRD

RH > 90%

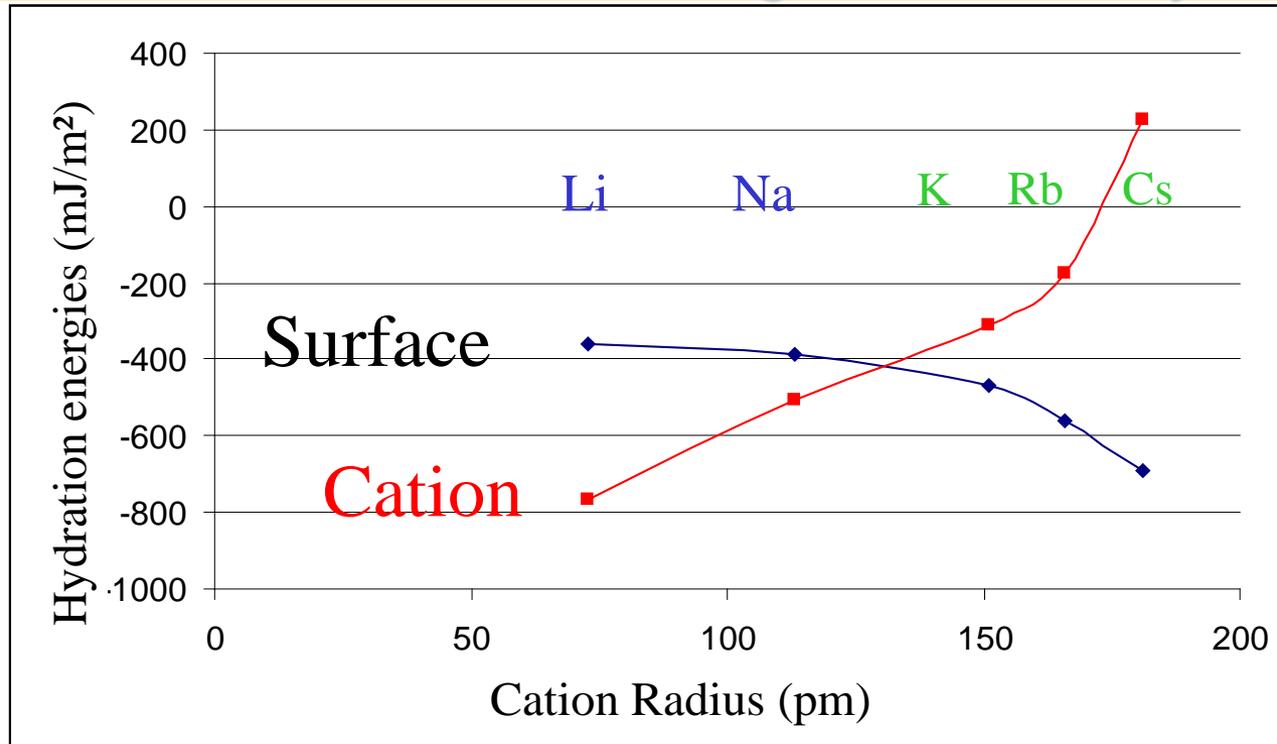
Thermoporometry

20 < RH < 60%



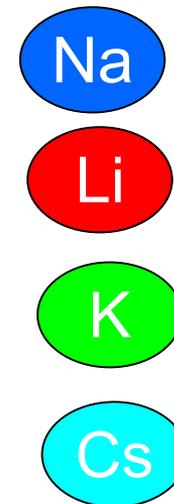
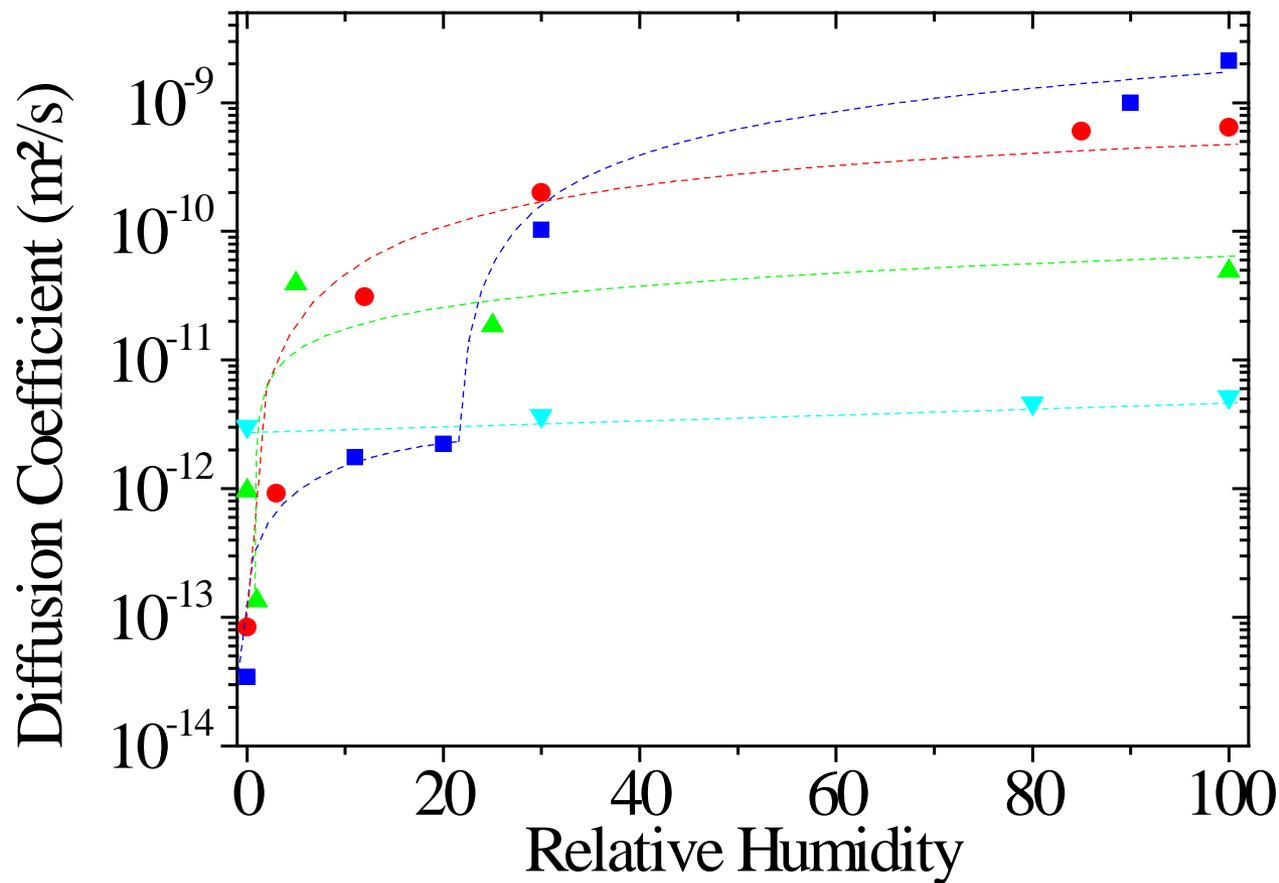
Salles et al., Langmuir, 2010

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:

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

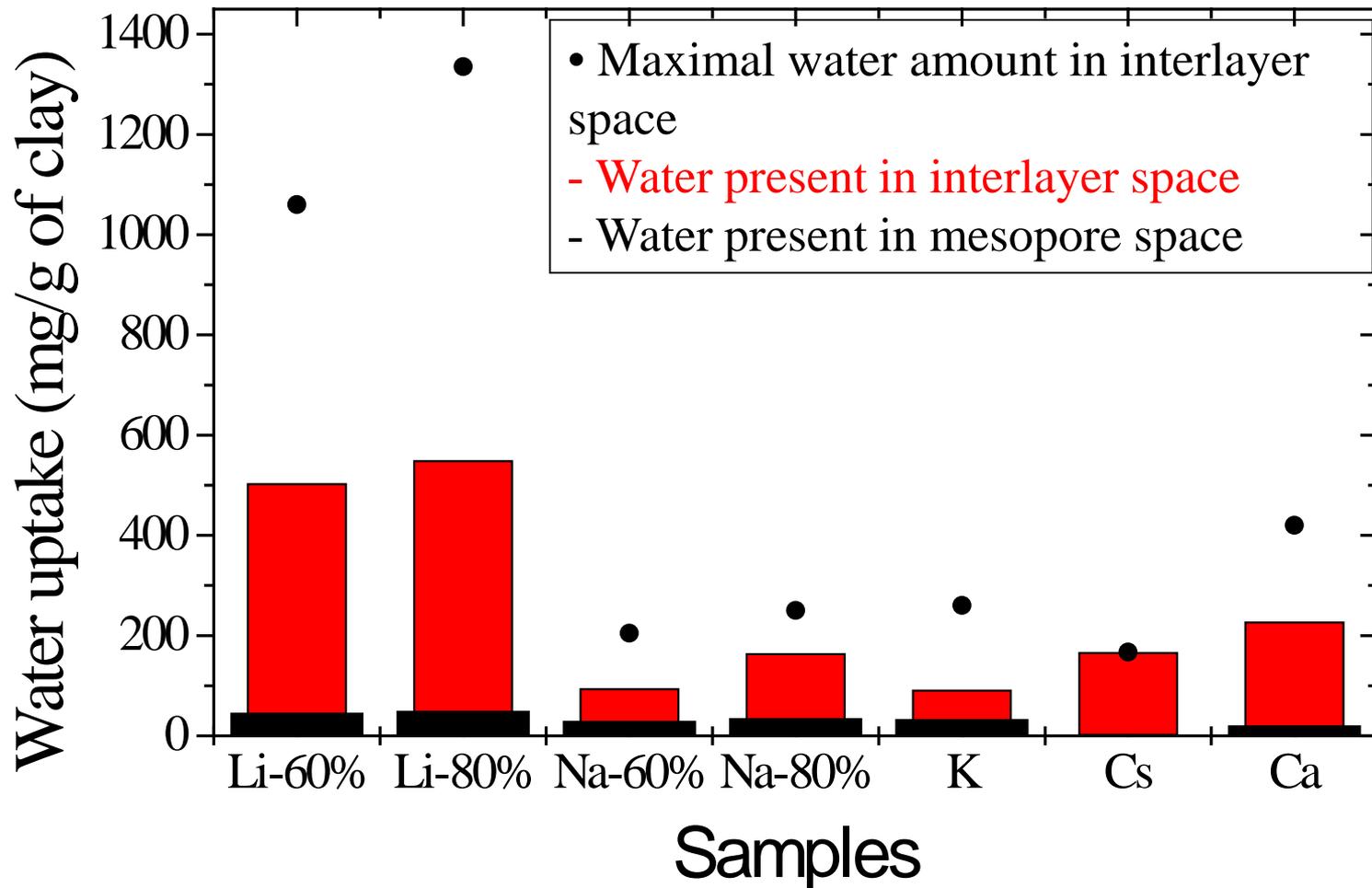
- The theoretical quantity of water (=maximal amount) present in interlayer space can be determined from the following equation:

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

where $S_{\text{H}_2\text{O}}$ and S_{N_2} 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*

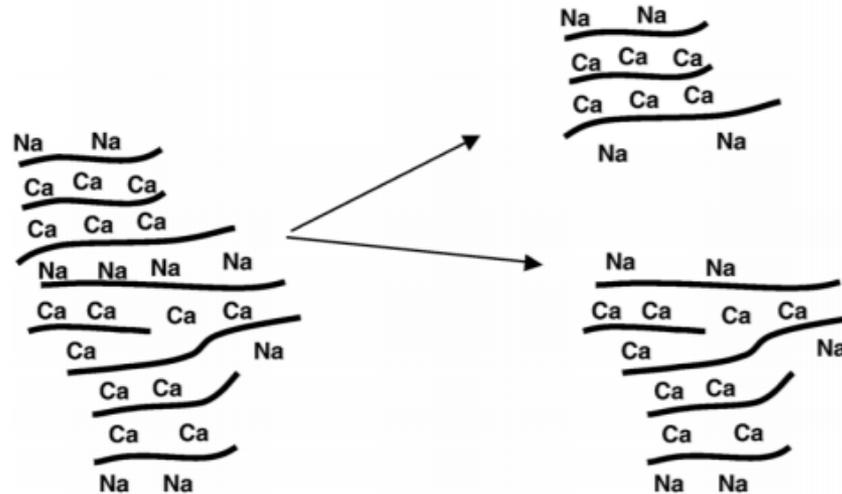
Distinction of interlayer and mesopore water



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

Salles et al., Langmuir, 2010

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



Laird, Applied Clay Science, 2006

Results for textural properties

Classical characterisation techniques: XRD & BET

XRD at the dry state

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

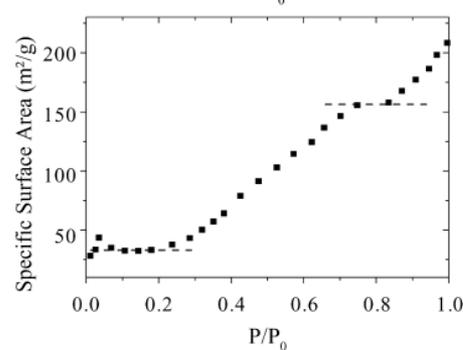
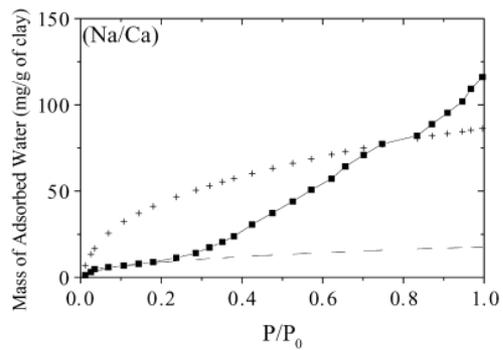
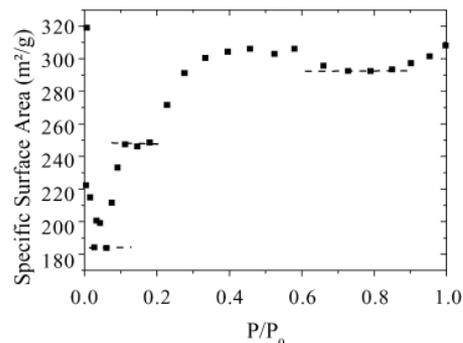
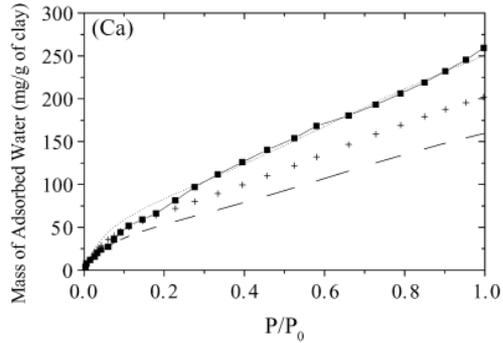
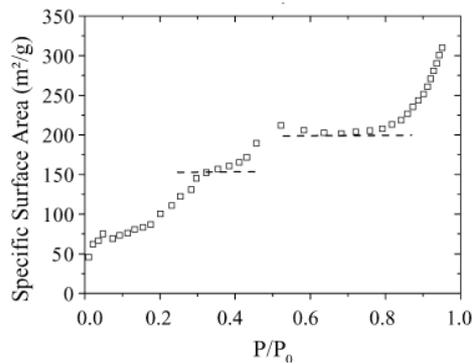
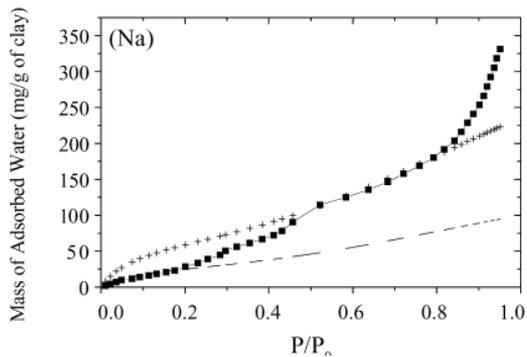
N₂ adsorption

	Na	Ca	Na-Ca
SSA (m².g⁻¹)	27	10,4	10,3
C_{BET}	496	152	167
Monolayer volume (cm³.g⁻¹)	6,3	2,39	2,4
BJH pore (nm)	2,5	4,5	3

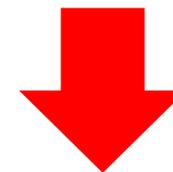


Textural properties of Na-Ca-montmorillonite close to Ca-sample

Results for water adsorption

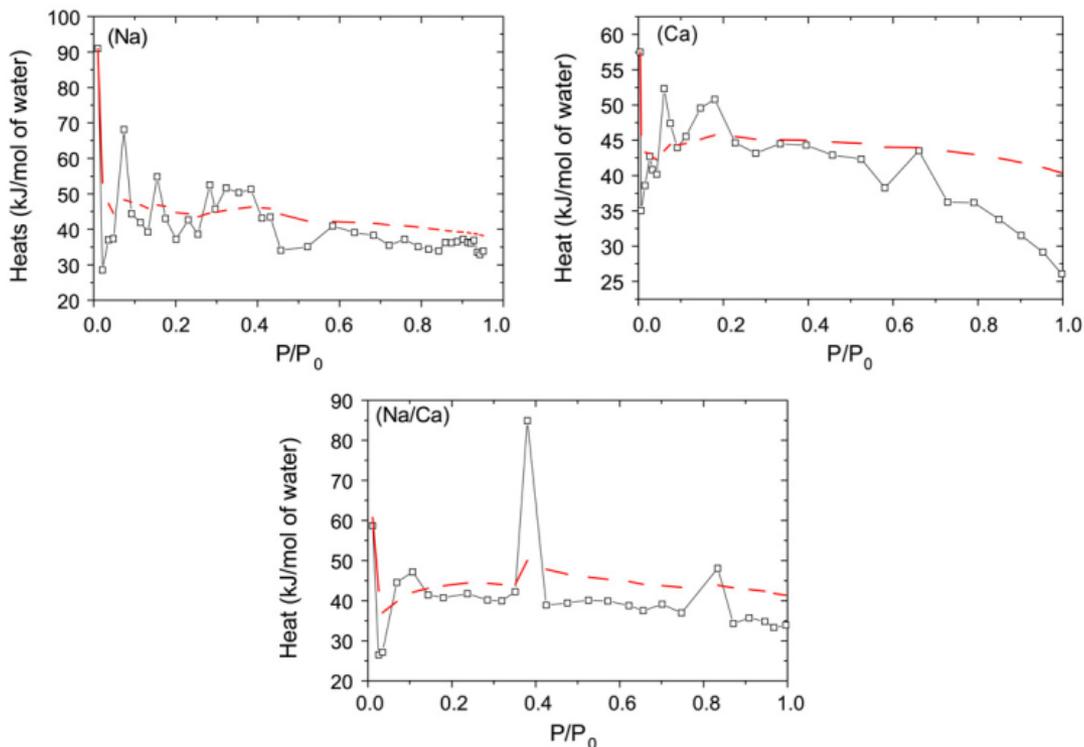


From adsorption isotherms 2 steps can be observed for Na-Ca-sample + SSA are relatively different



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 Ca^{2+} cations are hydrated at lower RH than Na^{+}

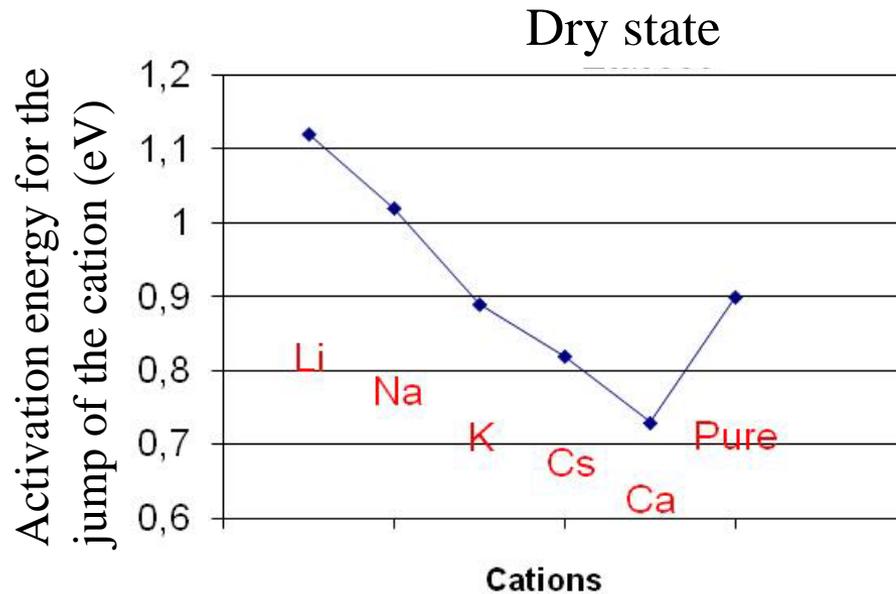
+

No osmotic swelling in the mesopores



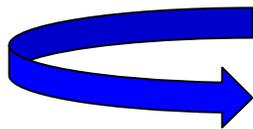
Inexpected in the case of demixion = mixture of cations

Results on conductivity measurements



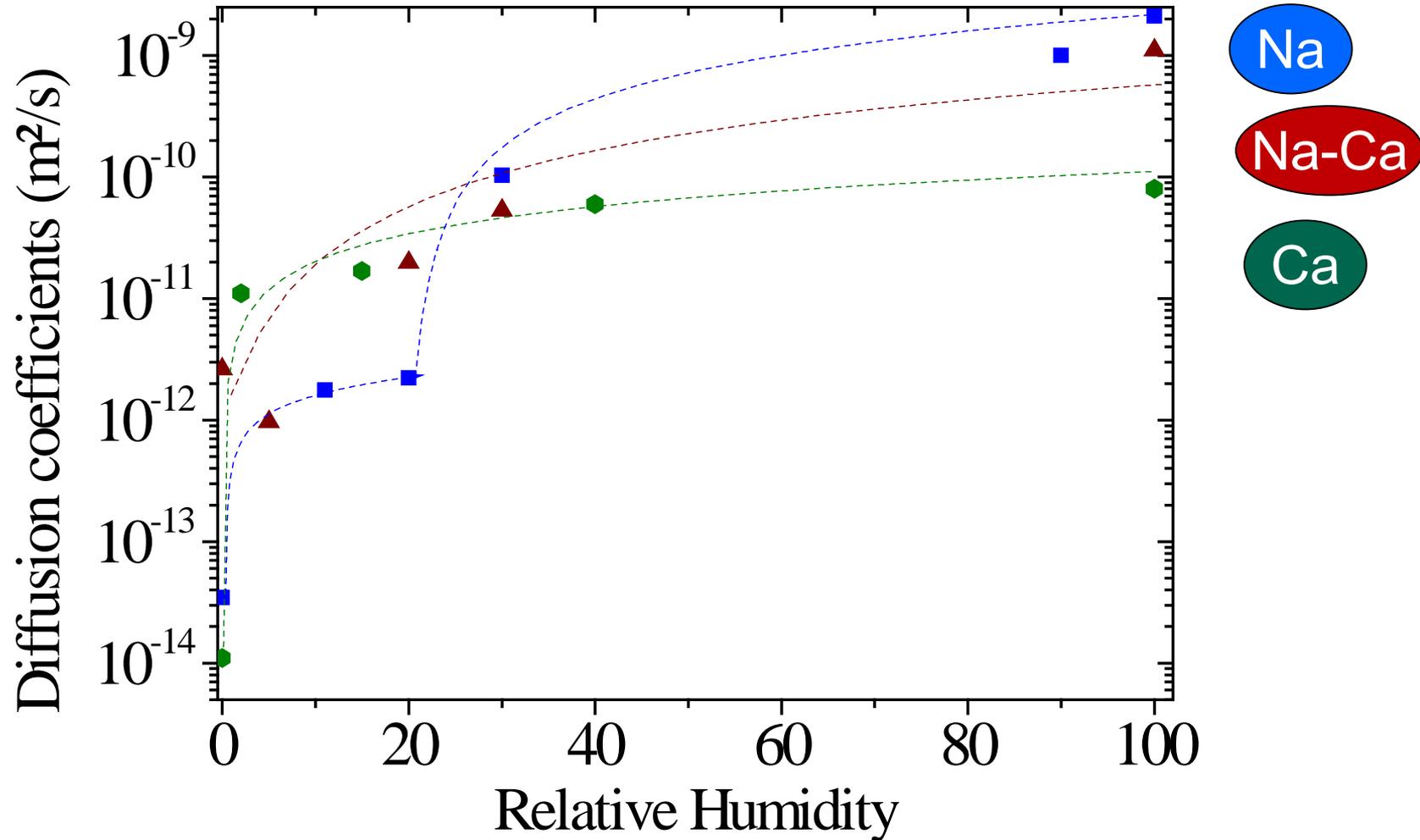
At the dry state, energy required to allow the interlayer cation to jump from an adsorption site to another one in the Na-Ca saturated sample = intermediate value

Mixture in the same interlayer space is confirmed



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

Results for diffusion



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

Conclusions

- 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

Thank you for your attention!