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

M. Jullien, F. Salles, Olivier Bildstein, J.-M. Douillard, Bénédicte Prélot, J. Jazac, H. van Damme

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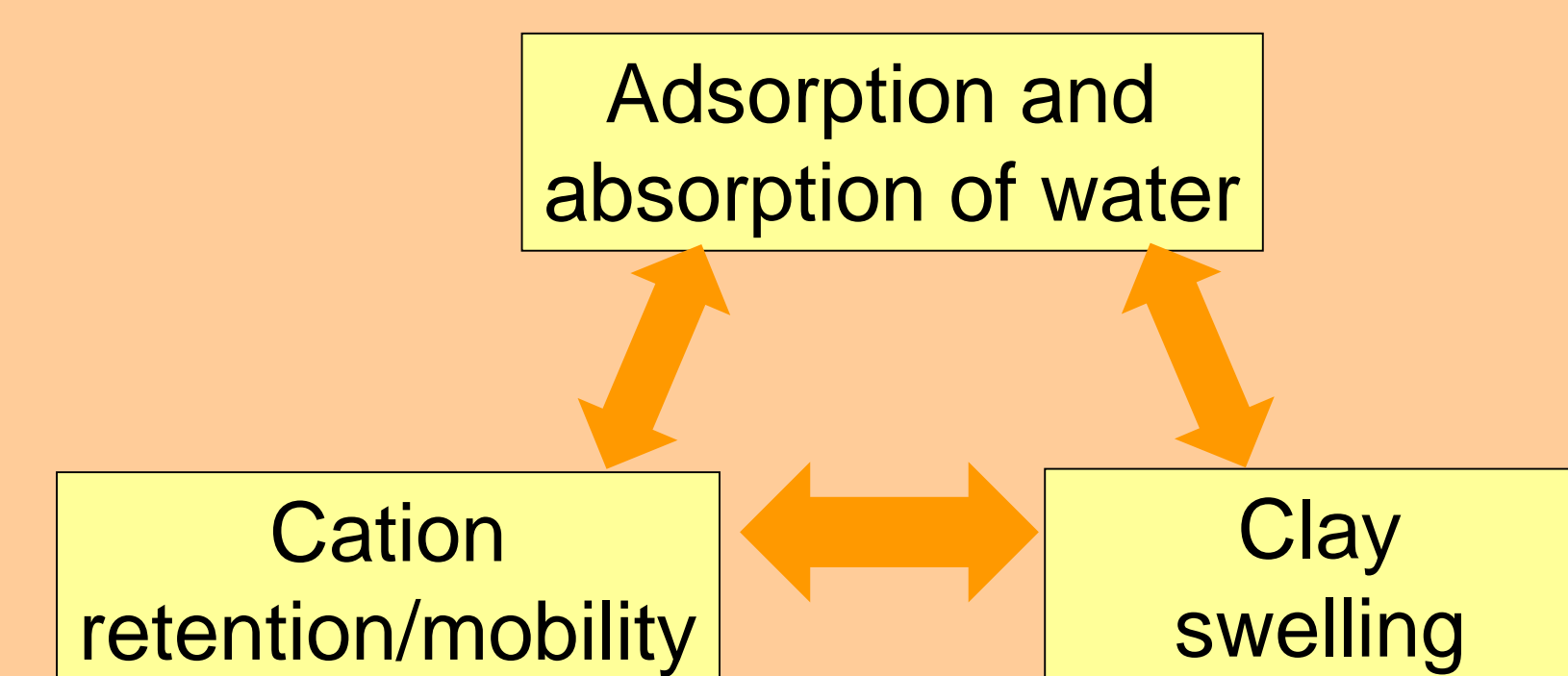
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Introduction and Principle

Swelling clays can absorb/adsorb a great quantity of water inside the **interlayer space** and the **mesoporosity**. This adsorbed quantity of water is strongly dependent on the nature of the **interlayer cation**. In order to probe the hydration sequence in clays as a function of the relative humidity (RH), XRD measurements, water adsorption and calorimetry, thermoporometry and electrical conductivity results are coupled with electrostatic calculations.

Aim of this study : (i) **determination of the hydration sequence of swelling clays as a function of the nature of the interlayer cations**

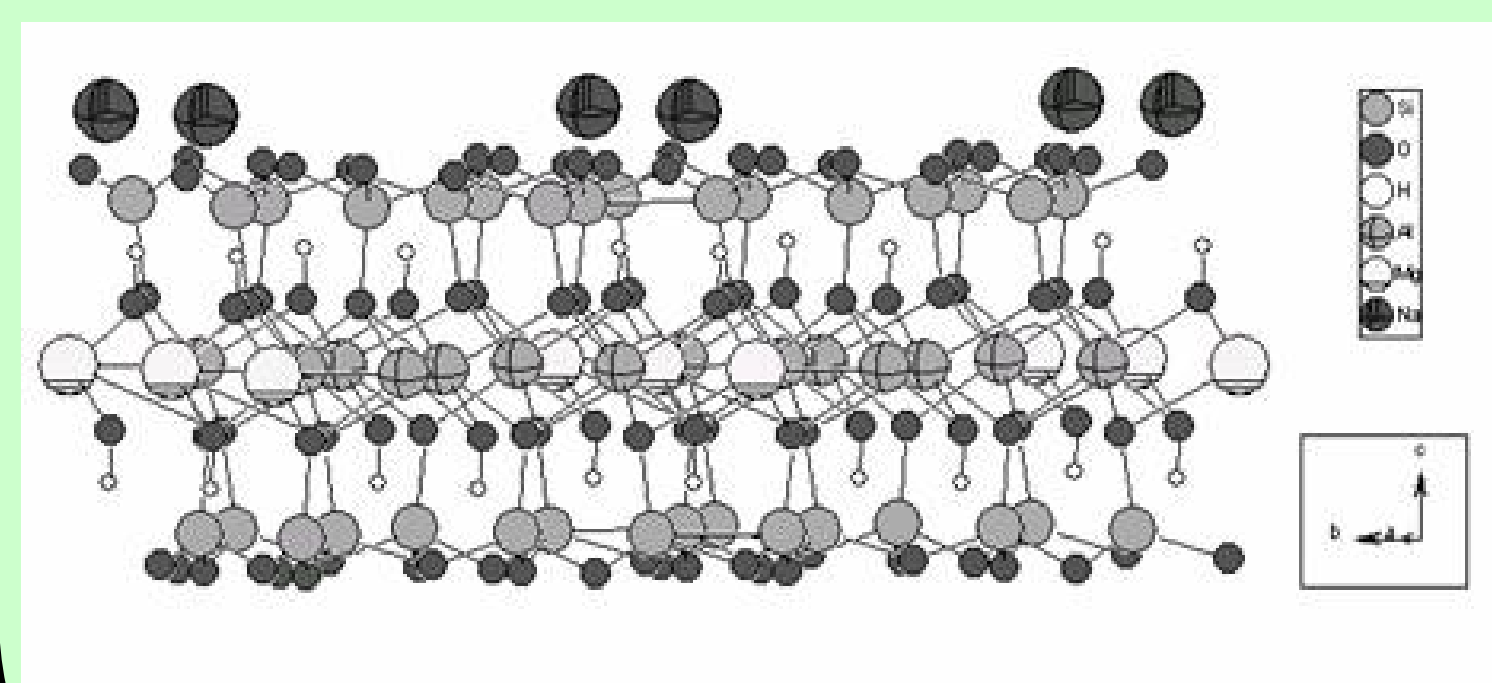
(ii) **To elucidate the mobility process of the interlayer cations as a function of the hydration state**



Material and Method Experiments

Material

Purified and exchanged powders of **montmorillonites (Mont) from the MX80 bentonite (octahedral substitutions - saturated with a large majority of Na as interlayer cations)**



Water adsorption and calorimetry on powder → F. Salles, J.M. Douillard, R. Denoyel, O. Bildstein, M. Jullien, I. Beurroies, H. Van Damme, Journal of Colloid and Interface Science, 2009, 333(2), 510-522

Thermoporometry measurements at different relative humidity values → F. Salles, I. Beurroies, O. Bildstein, M. Jullien, J. Raynal, R. Denoyel, H. Van Damme, Applied Clay Science, 39(3-4), 186-201, 2008.

Conductivity is measured in the frequency range (10⁻² Hz – 10⁶ Hz) at different temperatures (200°C-50°C for dry state and -120°C-20°C for hydrated state) with a Novocontrol impedancemeter

• Study the “clay-water” system by looking at the modifications of water properties
→ “water inside clays” is different from liquid water (or free water)!

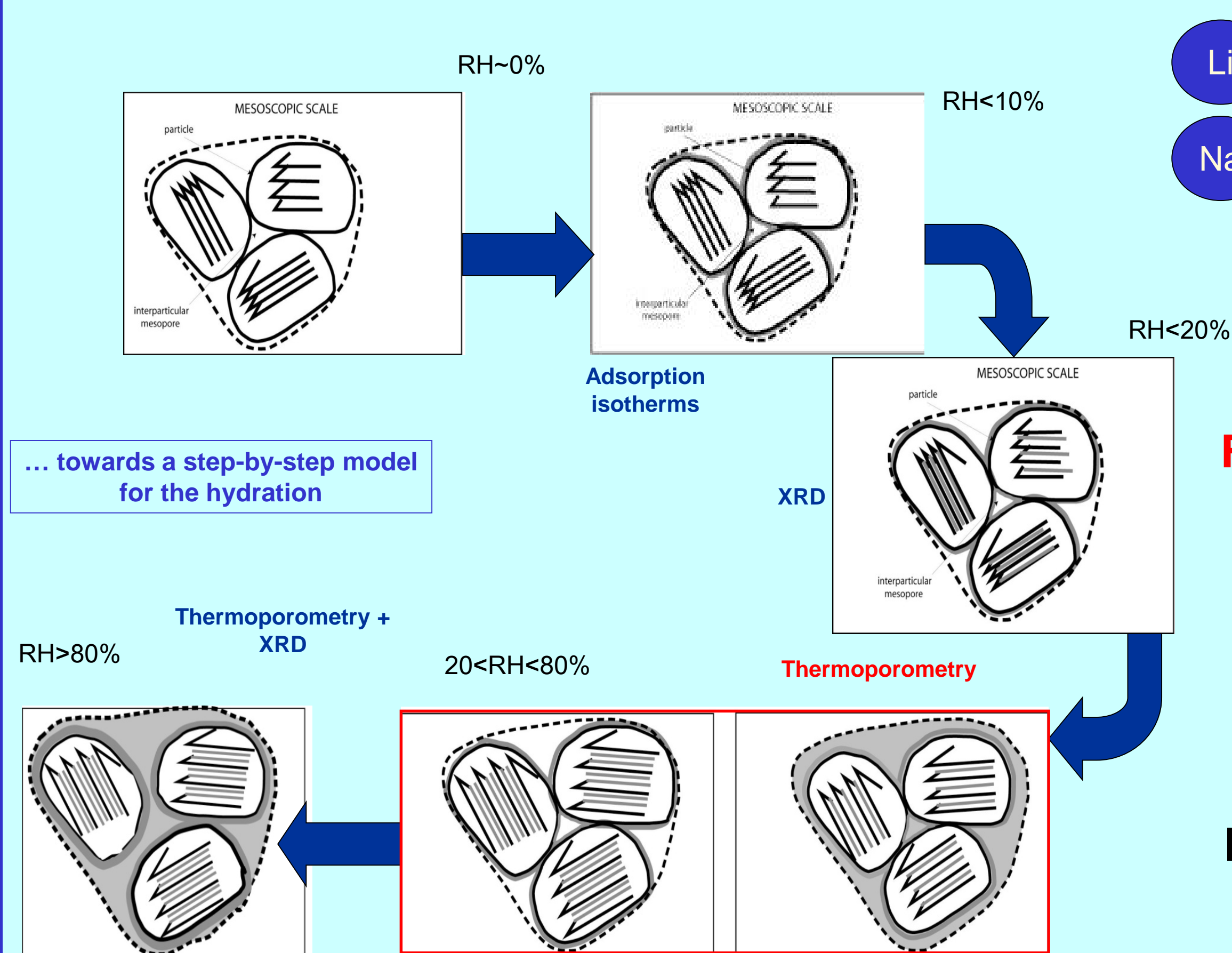
• **Thermoporometry** = calorimetric technique sensitive to phase transitions of fluid confined in the porosity → 2 nm < Pore radius < 50 nm (mesoporosity)

→ Originality of these experiments: **investigation of swelling material & various RH**

Results and Interpretation

Hydration Sequence

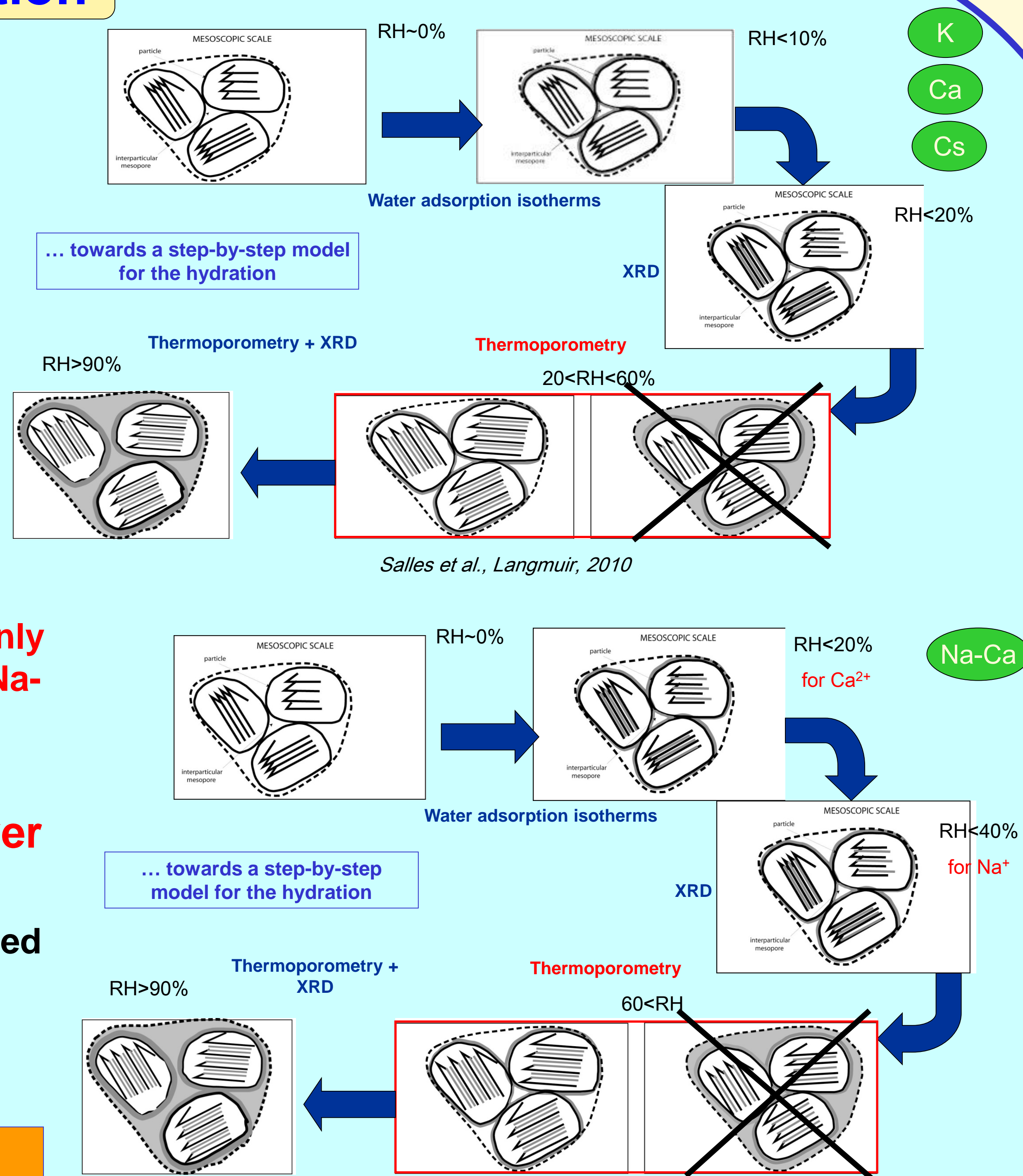
- Quantify the evolution of the mesopore size as a function of RH
- Discuss these results in terms of the sequence of clay hydration
- Comprehensive determination of clay hydration sequence for Na-Ca montmorillonite



Osmotic swelling in mesopores
Free water is observed in mesopores only starting at RH > 90% in Li- and Na-montmorillonites

Sequence of hydration is depending on the interlayer cation nature

Interlayer space is never completely filled by water at RH<97% for all samples except Cs+-montmorillonite

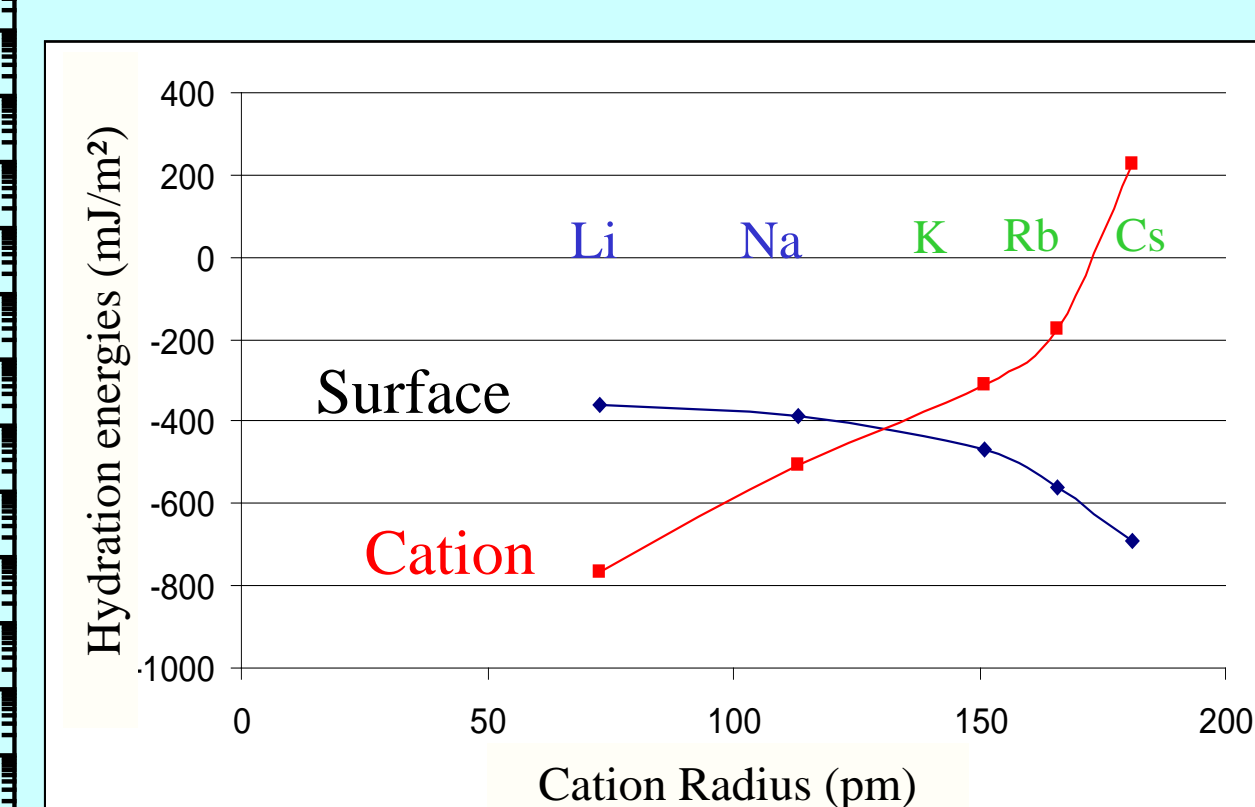
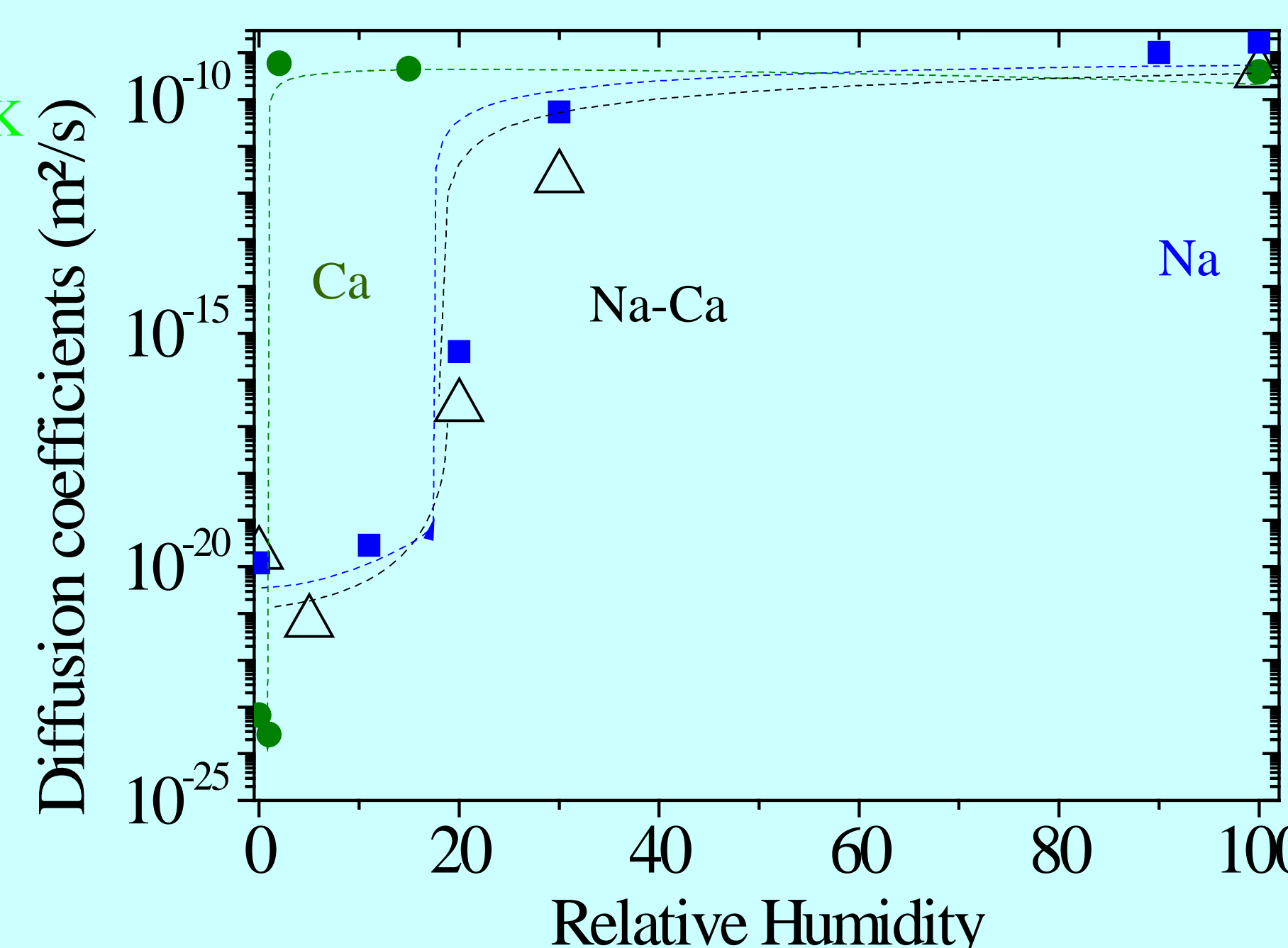
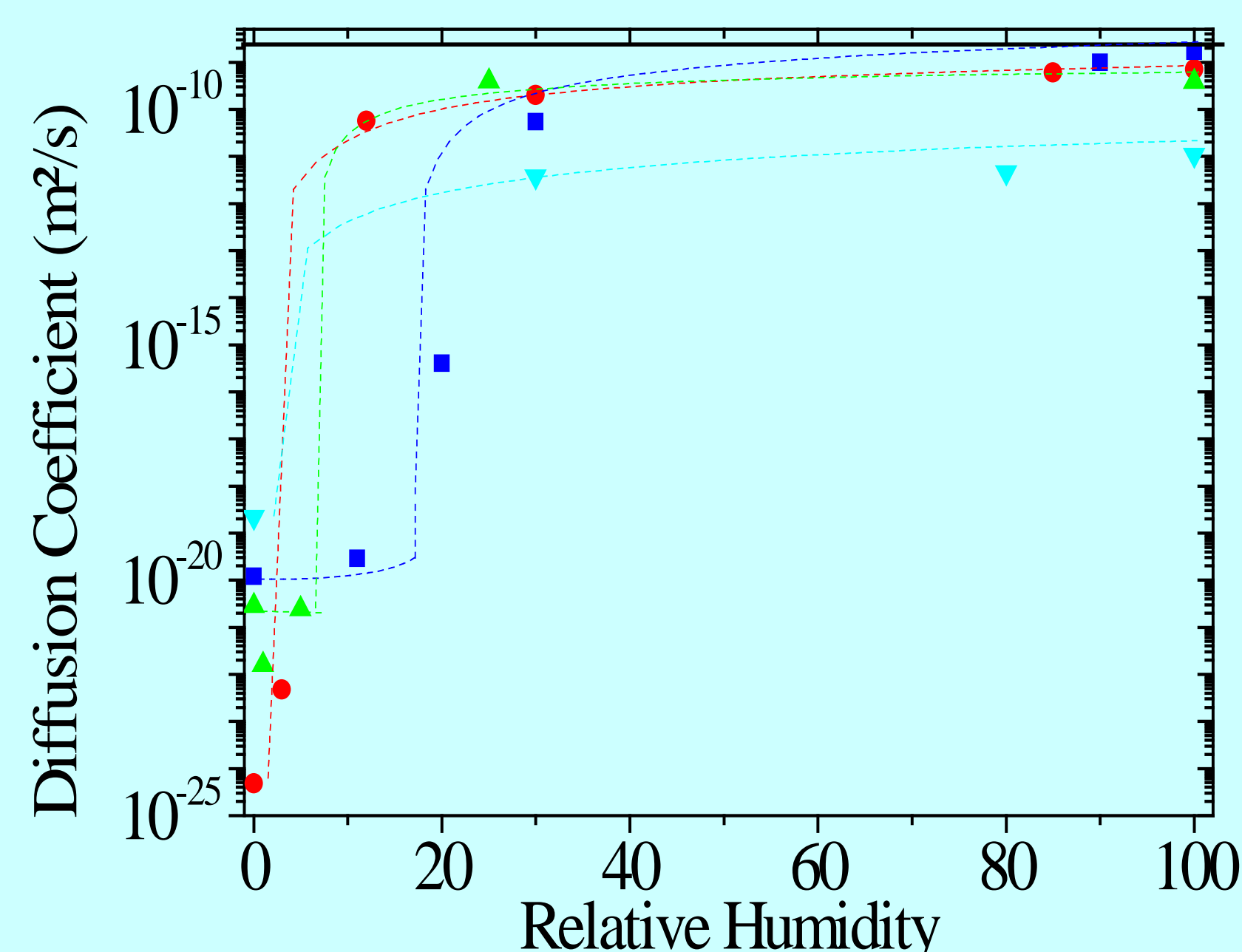


Diffusion coefficients at 20°C

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

D is the diffusion coefficient
σ is the conductivity
k the Boltzmann constant & T the temperature
z the charge of the species & e the electrical charge
c the concentration of the species

The concentration of cations is estimated from the specific surface areas calculated from water adsorption isotherm



Comparison between evolution of d₀₀₁ from X-ray diffraction (see Ferrage et al., 2005) and evolution of the diffusion coefficients

Evolution of the mobility is impacted by both the **interlayer space opening** and the **hydration status of the extra-framework cation**

Conclusion

- Sequence of hydration is depending on the interlayer cation nature.
- High mobility/diffusion of the smaller cations confirms the weak interactions existing between the hydrated Li⁺ and Na⁺ compared to the others cations.
- In the case of the mixture Na/Ca cations → Ca²⁺ is hydrated at lower RH than the Na⁺ cation as confirmed by adsorption calorimetry