

# HYDRATION SEQUENCE of SWELLING CLAYS EXCHANGED with MIXED ALKALI/ALKALI-EARTH CATIONS

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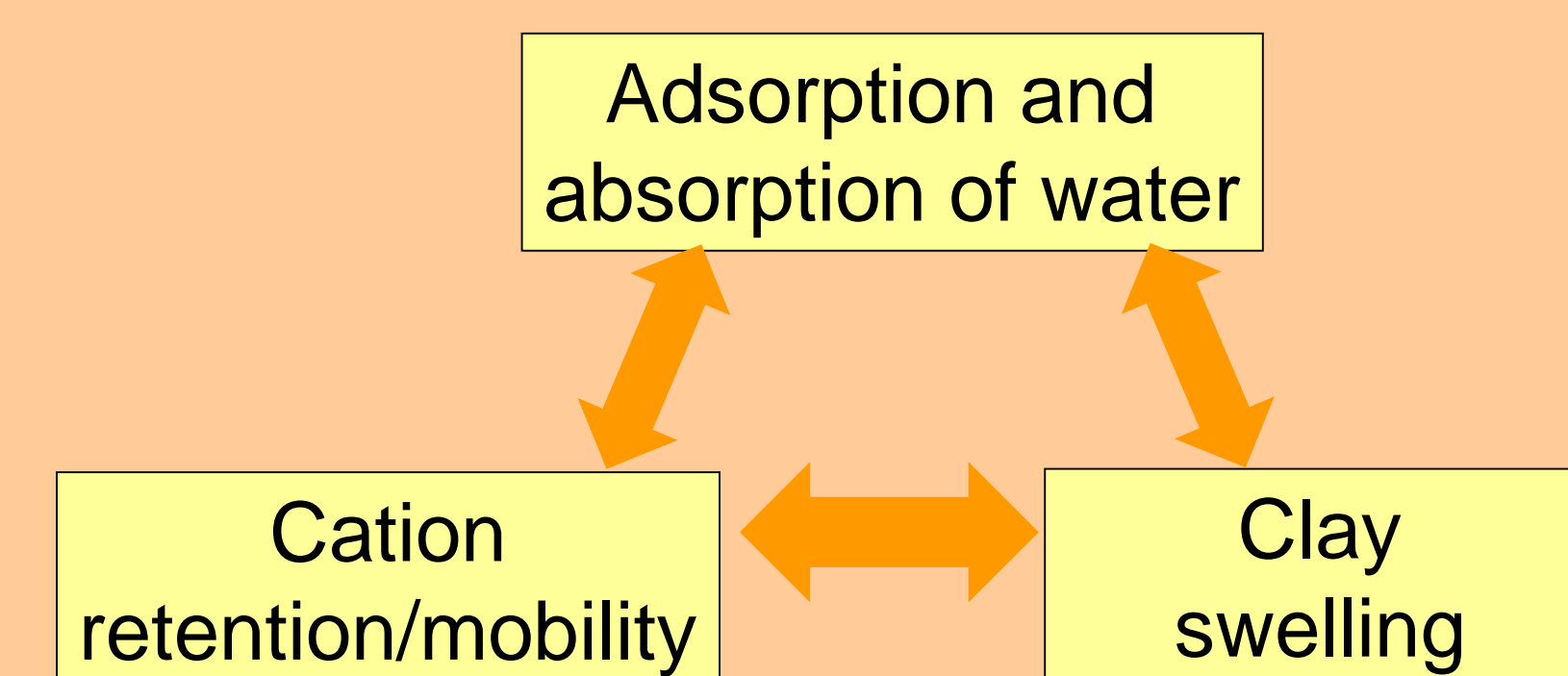
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## Introduction and Principle

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**

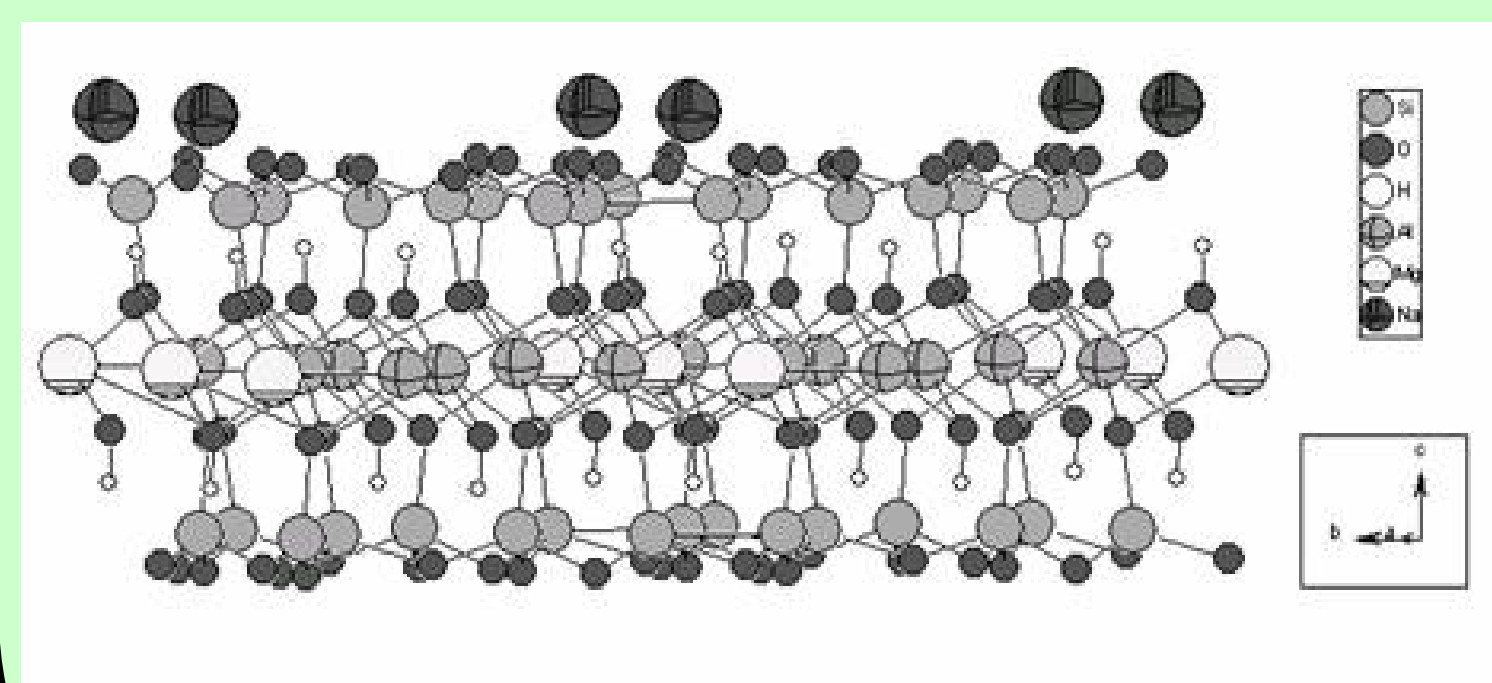
(ii) **To elucidate the mobility process of the interlayer cations as a function of the hydration state**



## 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<sup>-2</sup> Hz – 10<sup>6</sup> 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)!

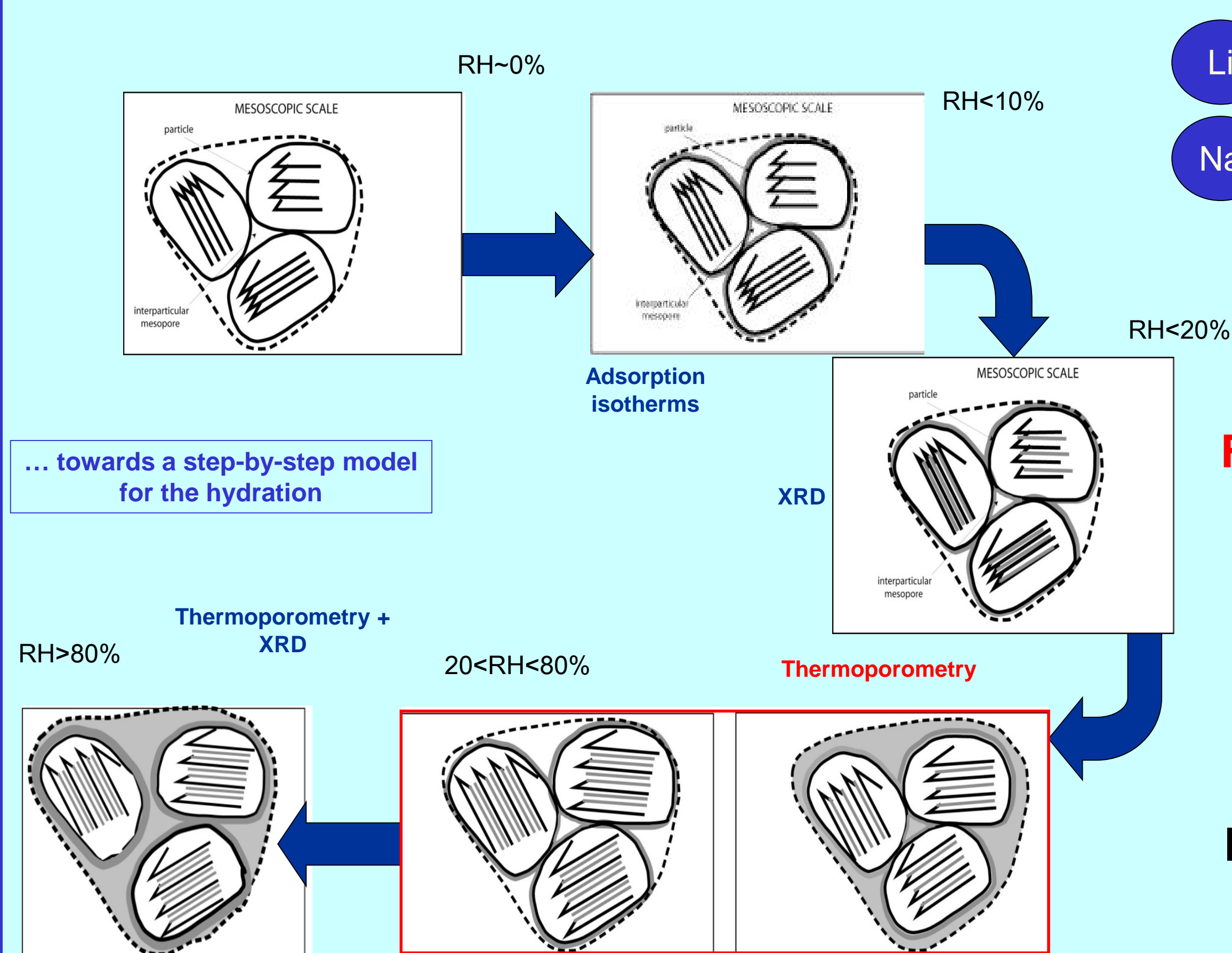
• **Thermoporometry** = calorimetric technique sensitive to phase transitions of fluid confined in the porosity → 2 nm < Pore radius < 50 nm (mesoporosity)

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

## Results and Interpretation

### Hydration Sequence

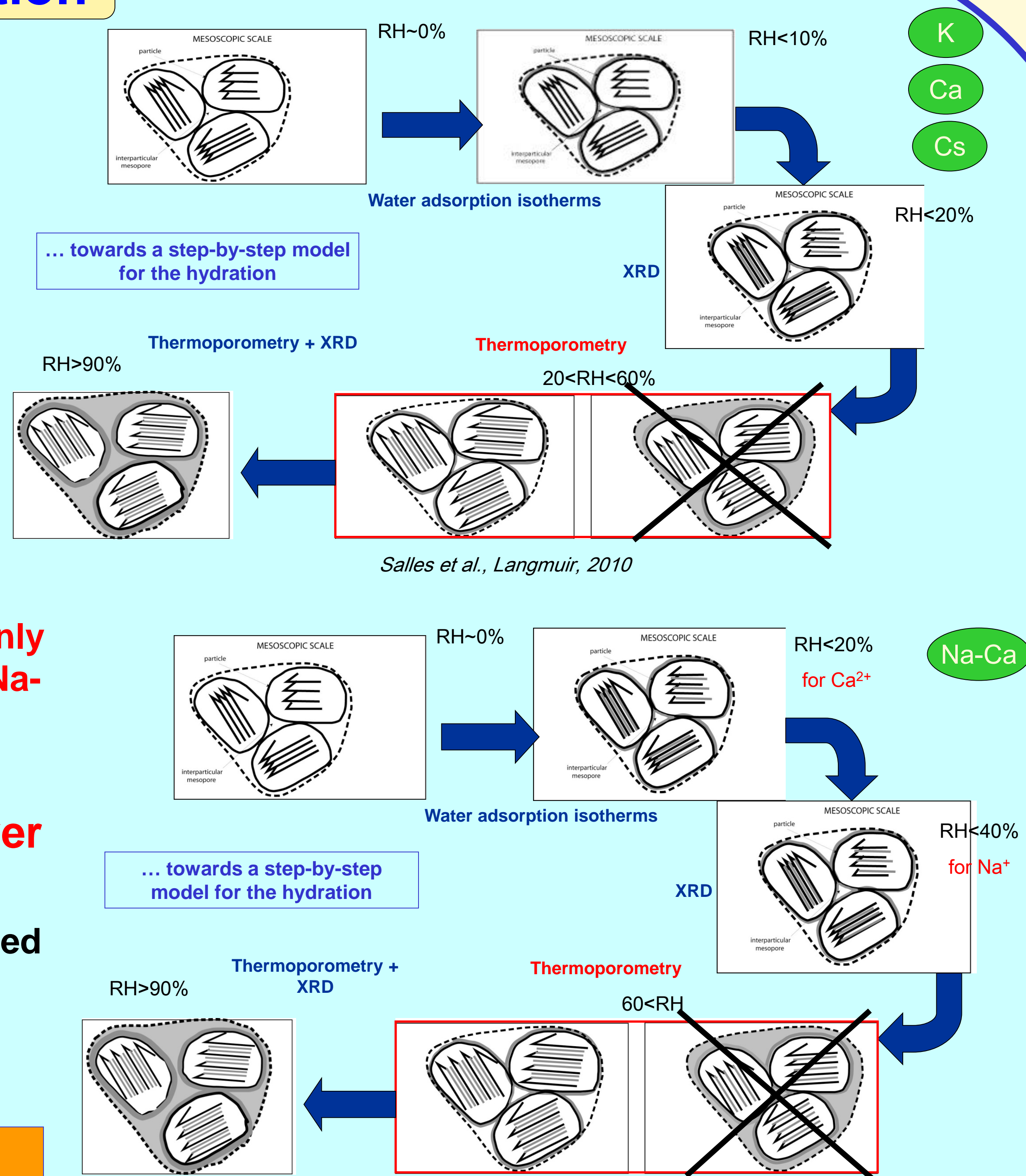
- Quantify the evolution of the mesopore size as a function of RH
- Discuss these results in terms of the sequence of clay hydration
- Comprehensive determination of clay hydration sequence for Na-Ca montmorillonite



**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<sup>+</sup>-montmorillonite**

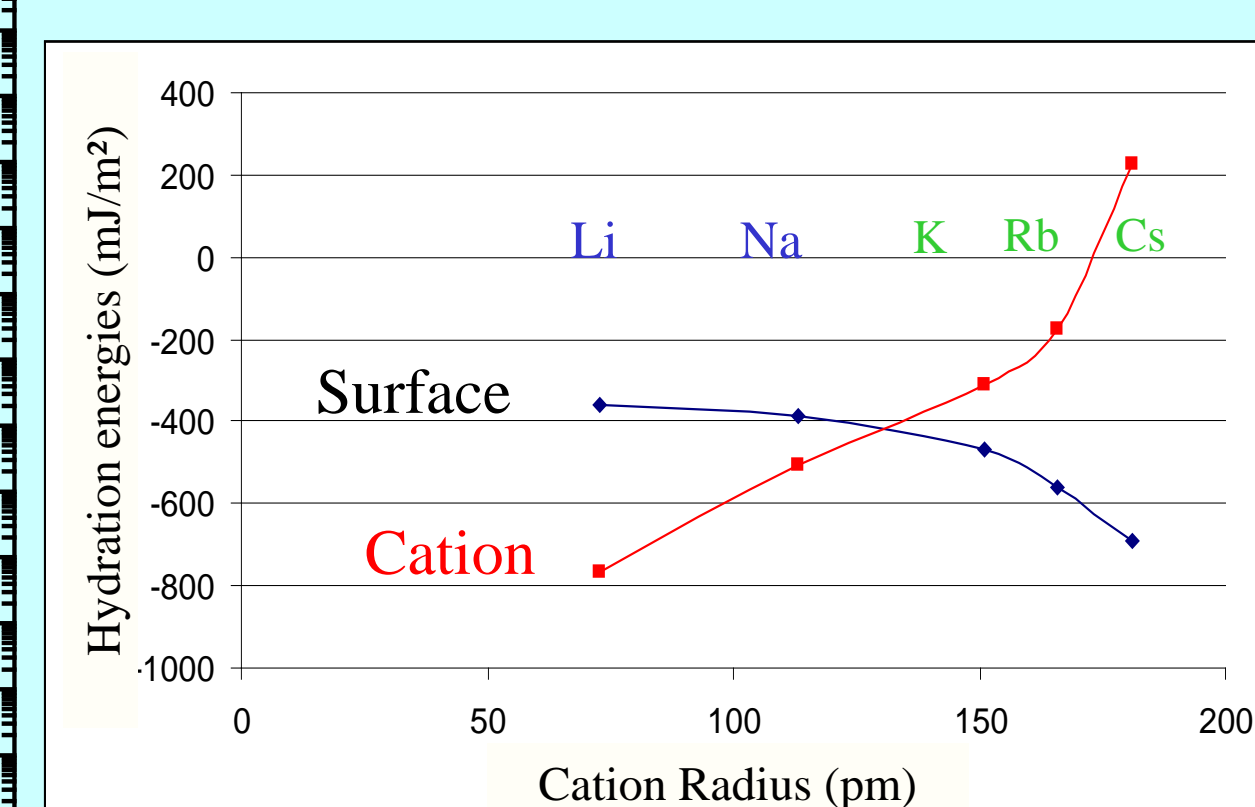
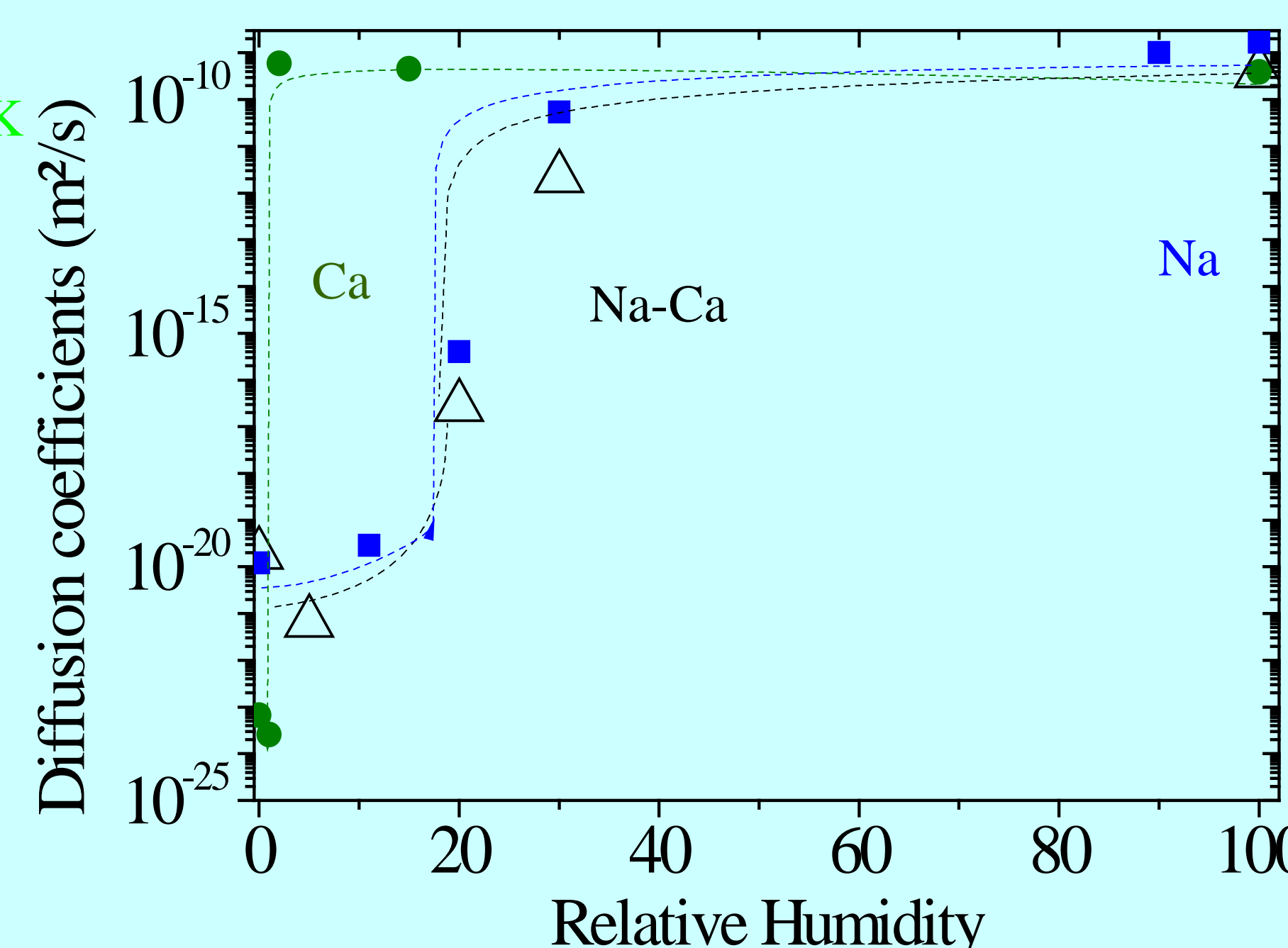
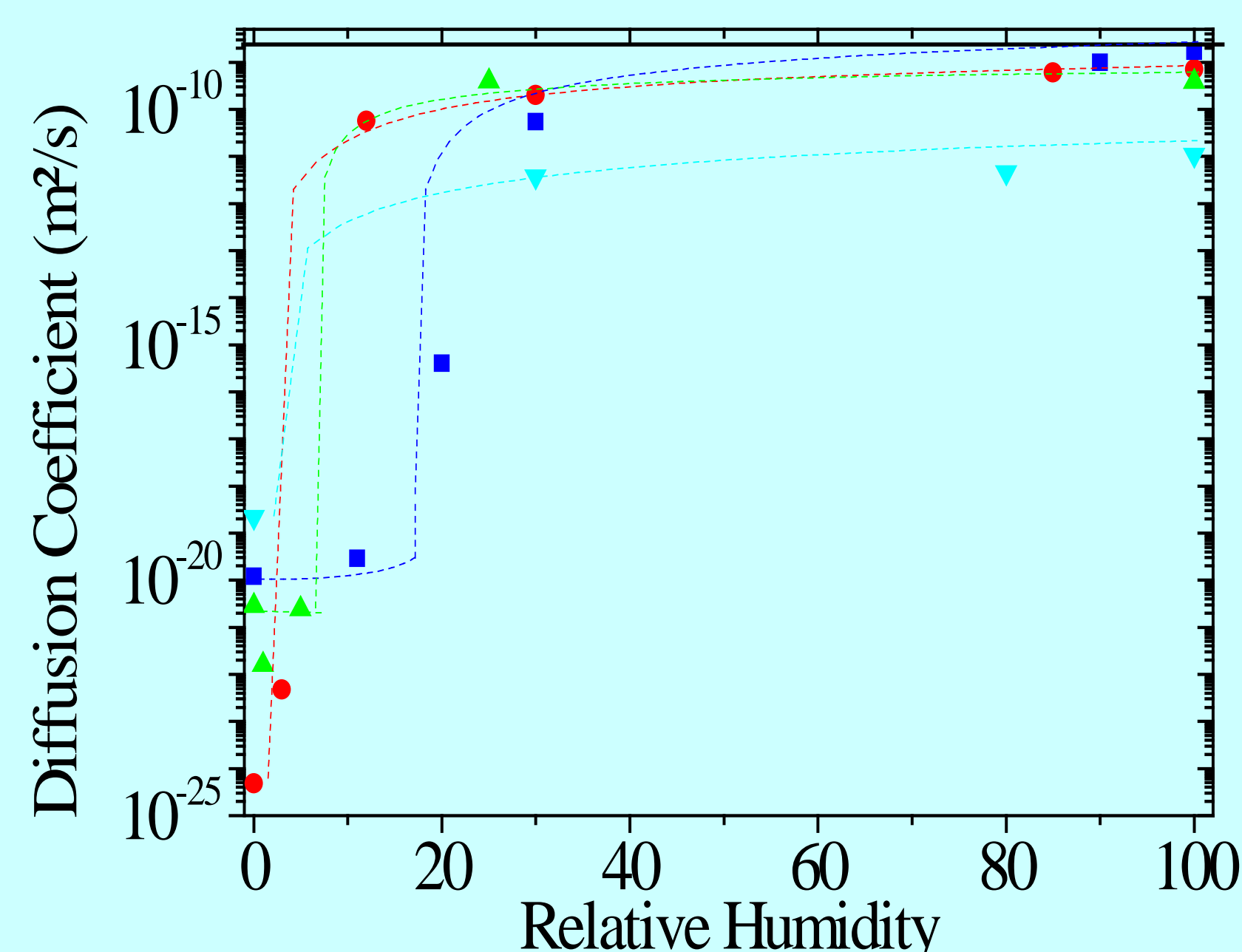


### Diffusion coefficients at 20°C

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

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 d<sub>001</sub> 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<sup>+</sup> and Na<sup>+</sup> compared to the others cations.
- In the case of the mixture Na/Ca cations → Ca<sup>2+</sup> is hydrated at lower RH than the Na<sup>+</sup> cation as confirmed by adsorption calorimetry