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

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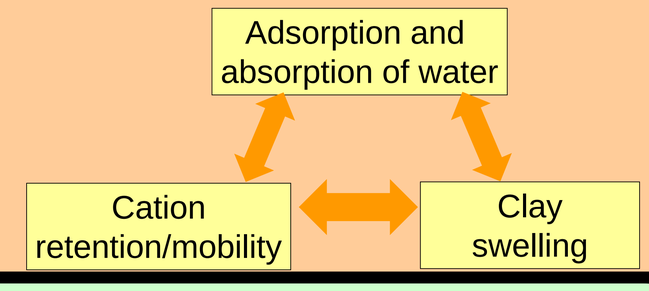
(1) ICGM, Université Montpellier – France (2) CEA, DEN, LMTE – Cadarache – 13108 St Paul lez Durance – France (3) Ecogeosafe – Aix-en-Provence (4) ESPCI – 75231 Paris -France

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

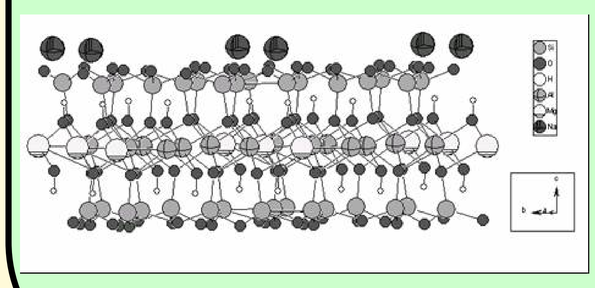
(ii) To elucidate the mobility process of the interlayer cations as a function of the hydration state



Material and Method

Material

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



Experiments

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 – 10^{6} Hz) at different temperatures (200°C-50°C for dry state and -120°C-20°C for hydrated state) with a Novocontrol impedancemeter

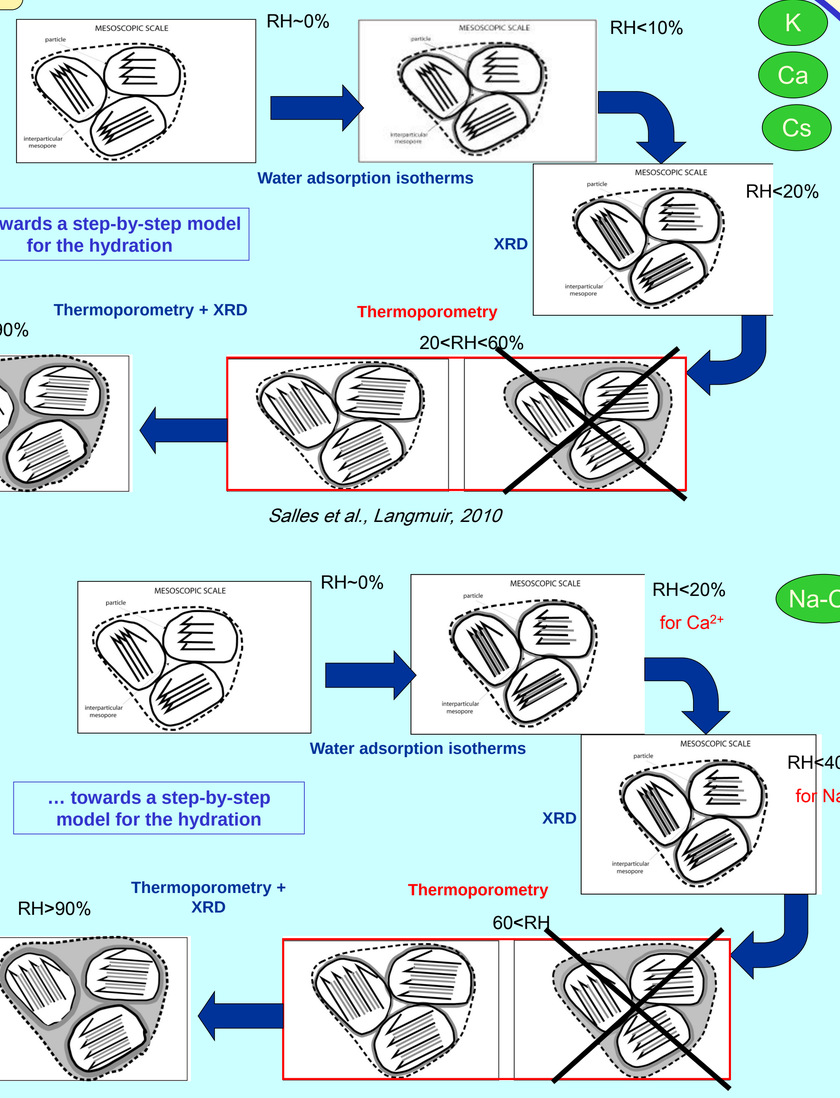
- **Study the "clay-water" system by looking at the modifications of water properties**
  → "water inside clays" is different from liquid water (or free water)!
- **Thermoporometry = calorimetric technique sensitive to phase transitions of fluid confined in the porosity →** 2 nm < Pore radius < 50 nm (mesoporosity)

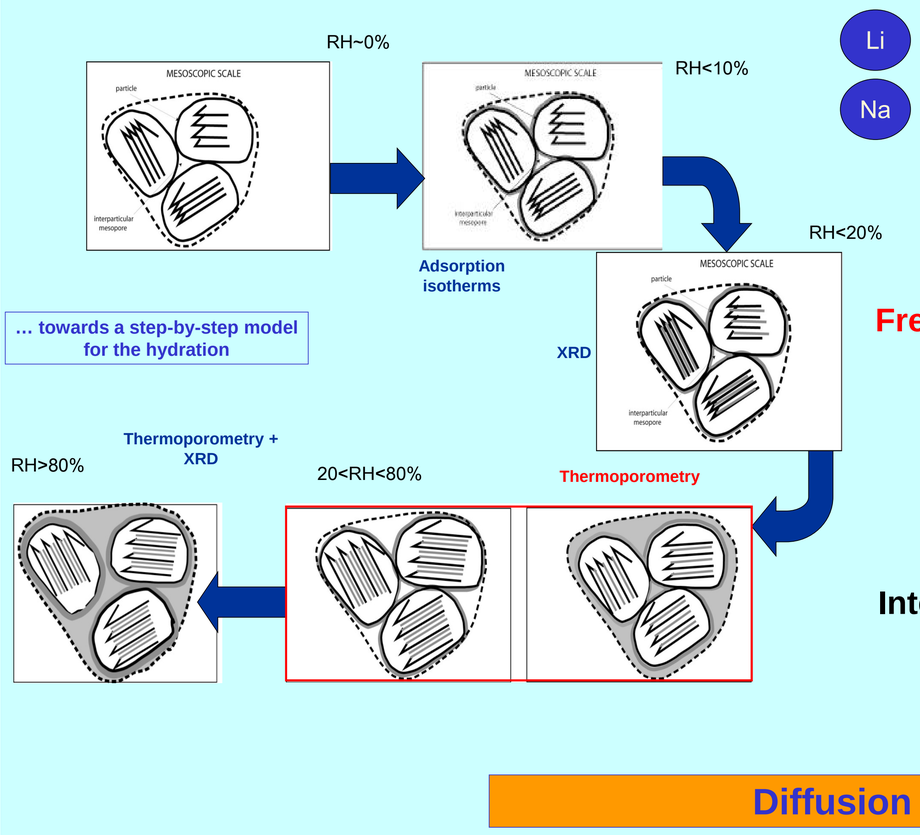
→ Originality of these experiments: investigation of swelling material & various RH

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

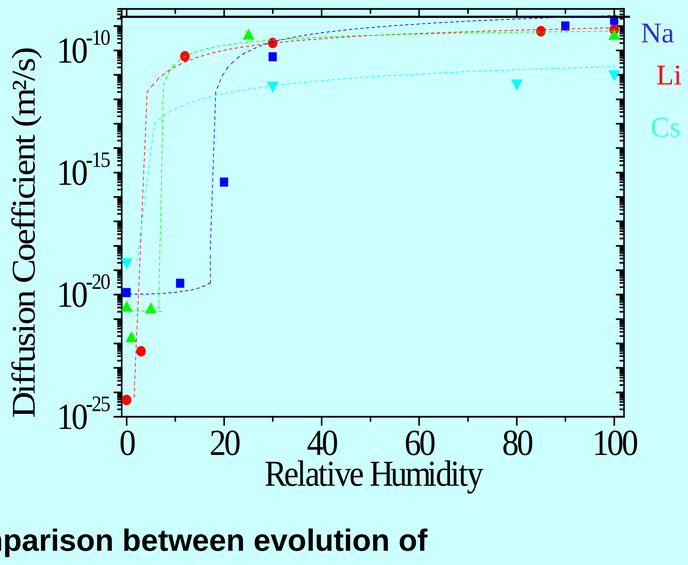
Interlayer space is never completely filled by water at RH<97% for all samples except Cs^+-montmorillonite

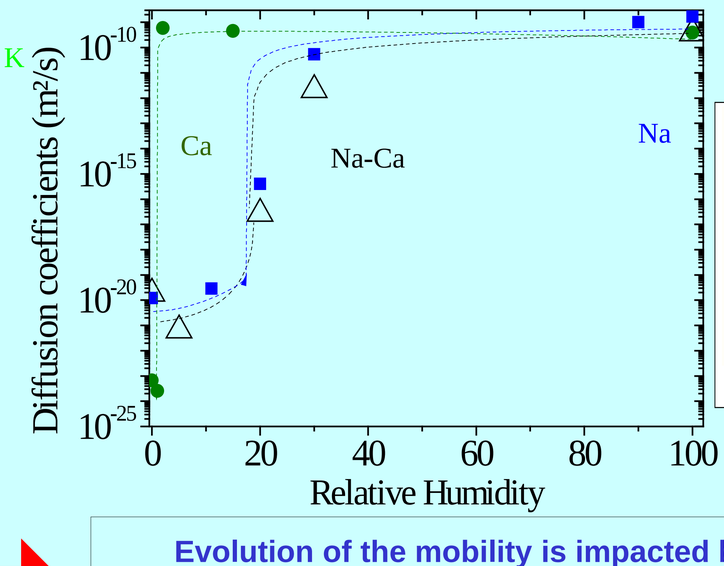
Diffusion coefficients at 20°C

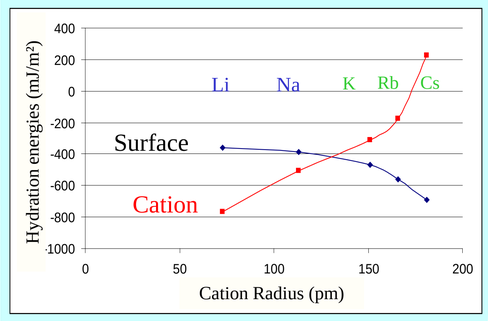
$$D = \sigma kT/(z^2e^2c)$$

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_{001} 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 → Ca^{2+} is hydrated at lower RH than the Na^+ cation as confirmed by adsorption calorimetry**