VTT TECHNICAL RESEARCH CENTRE OF FINLAND LTD

The fundamentals of clay minerals

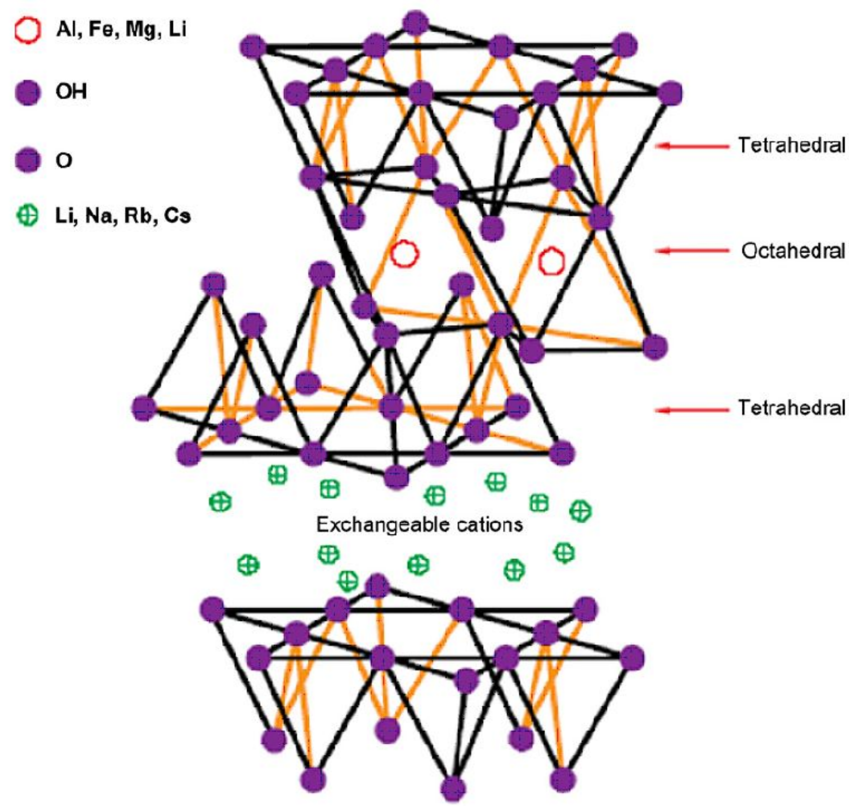
BELBaR Training Course on Clays and Colloids

Markus Olin, Michał Matusewicz,
Anniina Seppälä (VTT)

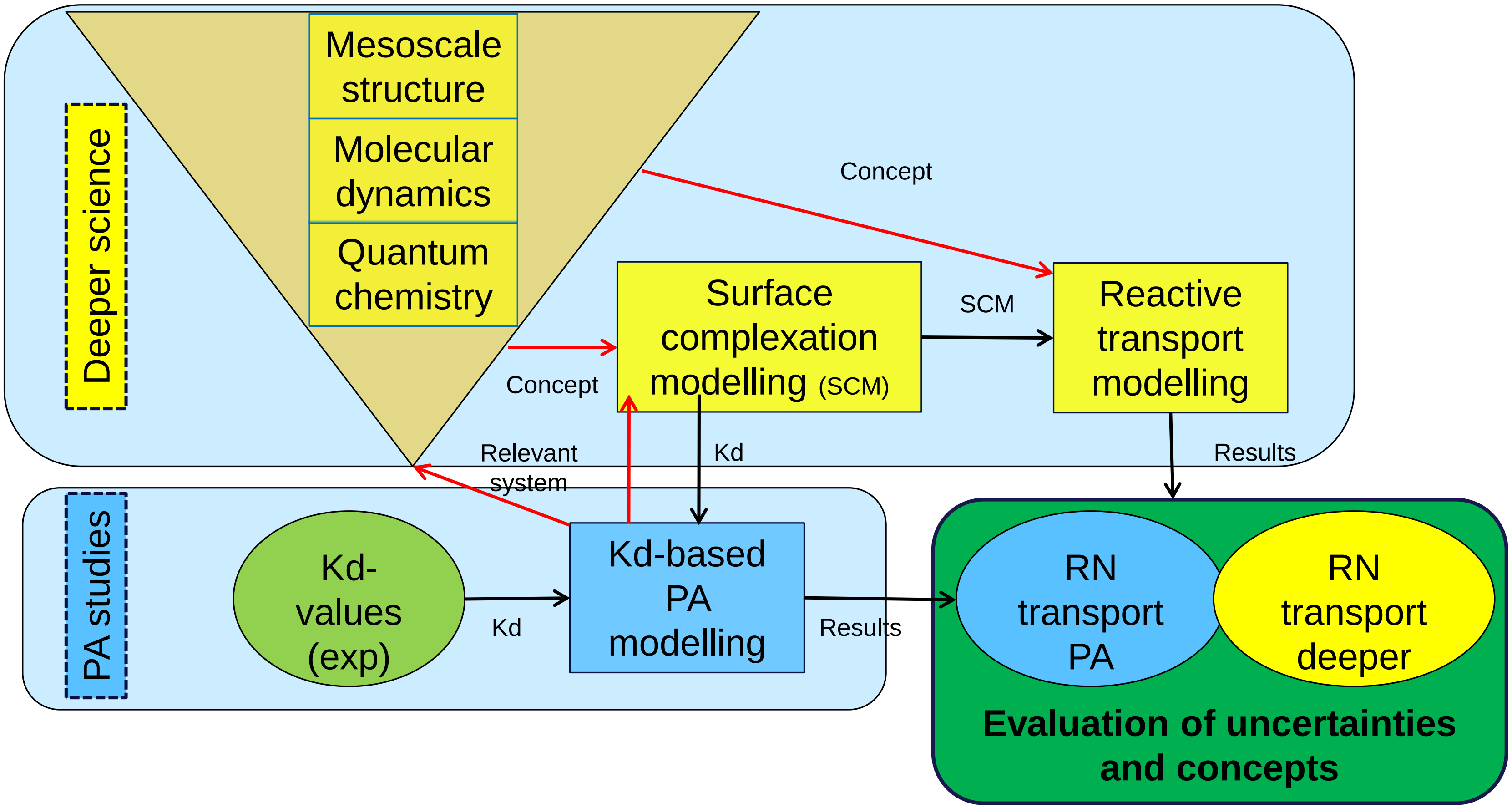
Eini Puhakka (HYRL)

CONTENT

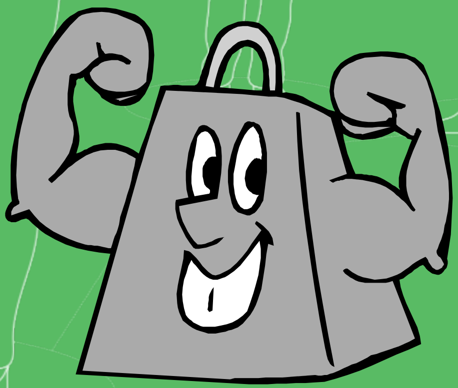
- Mostly about smectites
- Macroscopic properties
  - Low water conductivity vs. capillary phenomena
  - Small grain size (even colloids)
- Molecular level behind macroscopic observations
  - Quantum mechanics
  - Molecular dynamics
  - Mesoscale models
  - Surface complexation
  - Continuum models



Hierarchy of both models and nature itself



- **Not only models, but reactions are also taking place on different scales**
- **Absence of know-how of reactions does not guarantee absence those reactions**
- “Doctors most commonly get mixed up between absence of evidence and evidence of abense” — Nassim Nicholas Taleb

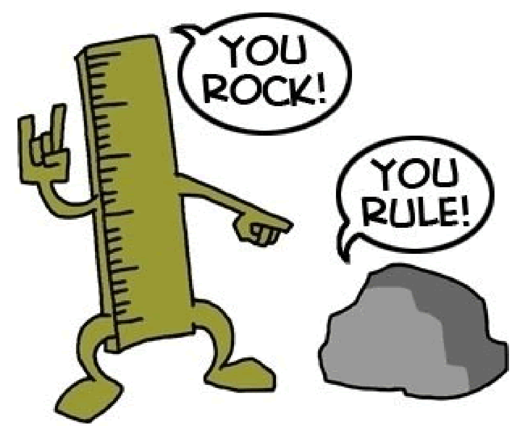


Macroscopic

Rock, crushed rock and compacted bentonite

- Buffer material demands: low hydraulic conductivity (*K*), low diffusion conductivity (D_e) and high enough ductility
- Granitic rock: *low K* and D_e, but it is brittle and difficult to apply
- Crushed rock: *high K* and D_e, porosity is high, easy to use
- Bentonite: *low* D_e for anions, acceptable for cations, and very low *K*, and is ductile
- How highly porous bentonite can have all these properties?
- Why the diffusivity values are different for anions and cations?
- Specific microstructure of bentonite: very small pores, interaction of ions with pore surfaces

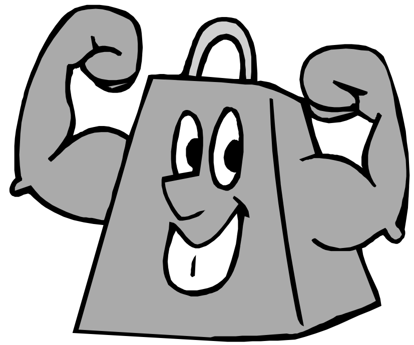
	Dry density (kg/m³)	Porosity (-)	Hydraulic cond. *K* (m/s)	D_e anions (m²/s)	D_e cations (m²/s)
rock	2 650	*0.005*	1.00E-09	*1.00E-13*	*1.00E-13*
crushed rock	1 600	0.4	1.00E-04	6.00E-11	6.00E-11
bentonite	1 600	0.4	*1.00E-12*	*2.00E-13*	8.00E-11



Variation of conditions for bentonite buffer in KBS3 method

Thermodynamic variables

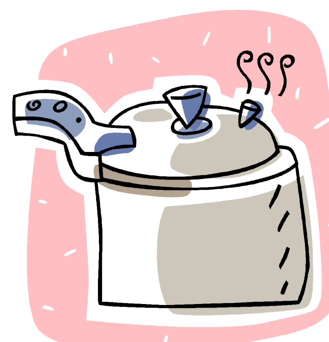
- Temperature, *T*
- Pressure, *P*
- Chemical composition
  - Water, *S*
  - Solid: minerals + exchanged cations, ρ_d
  - Dissolved salts, *I*



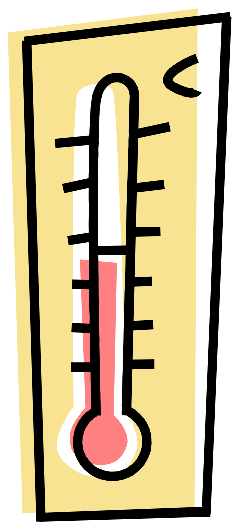
ρ_d: 1…1 700 kg/m^3
Montmorillonite + exchanged cations + other accessory minerals

S: 0.3…1
Dry - fully saturated

I: 0.01 mM…1 M
1 mg/L…100 g/L
Na-Ca-Cl + other ions, microbes, colloids



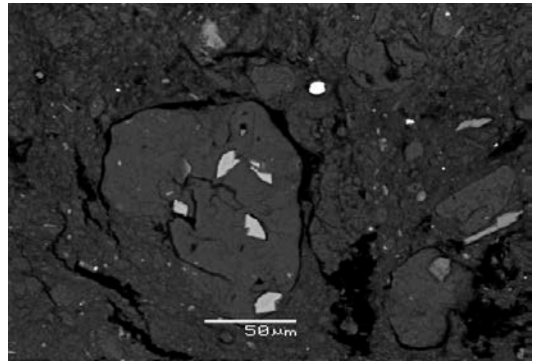
P: 0.1…4 MPa + ice cover



T: -10…100 ºC

Scales, properties of bentonite and water phase

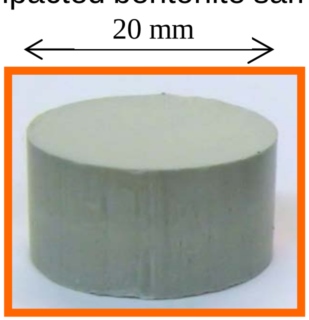
- **Spatial scales**
  - Colloidal size
  - Pore size
  - Laboratory
  - Small scale
  - Pilot scale
  - Repository scale
- **Time scales**
  - Nanoseconds in molecular dynamics
  - Lab = days to years
  - Repository = years to millenia

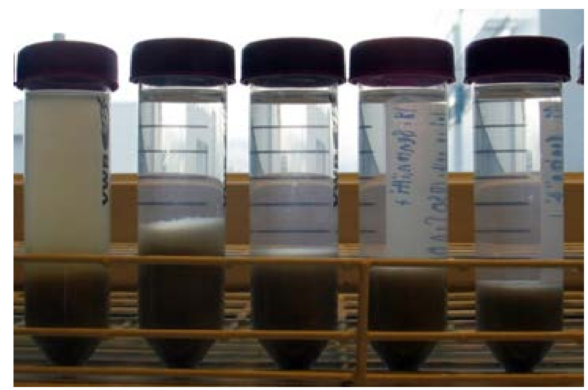


- **Bentonite properties**
  - Relative amount of montmorillonite
  - Cationic form of montmorillonite
  - Accessory minerals
  - Grain size
  - Initial water content
  - “History” of the samples
    - Production
    - Transport
    - Processing

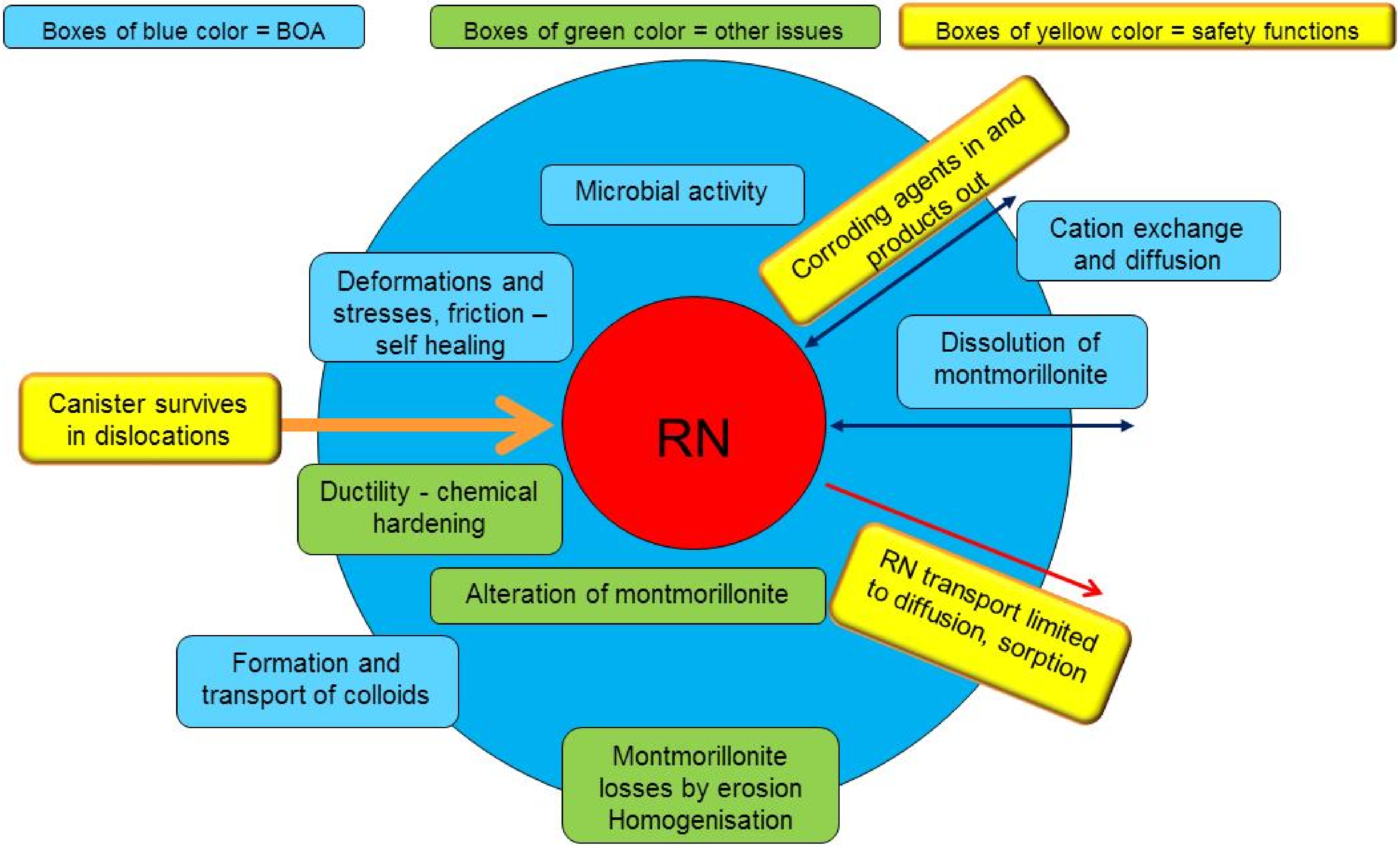
- Water
  - Humidity or saturation
  - Composition
    - Electrolyte
    - Groundwater simulant
  - Gases
  - Colloids
  - Microbes

Compacted bentonite sample

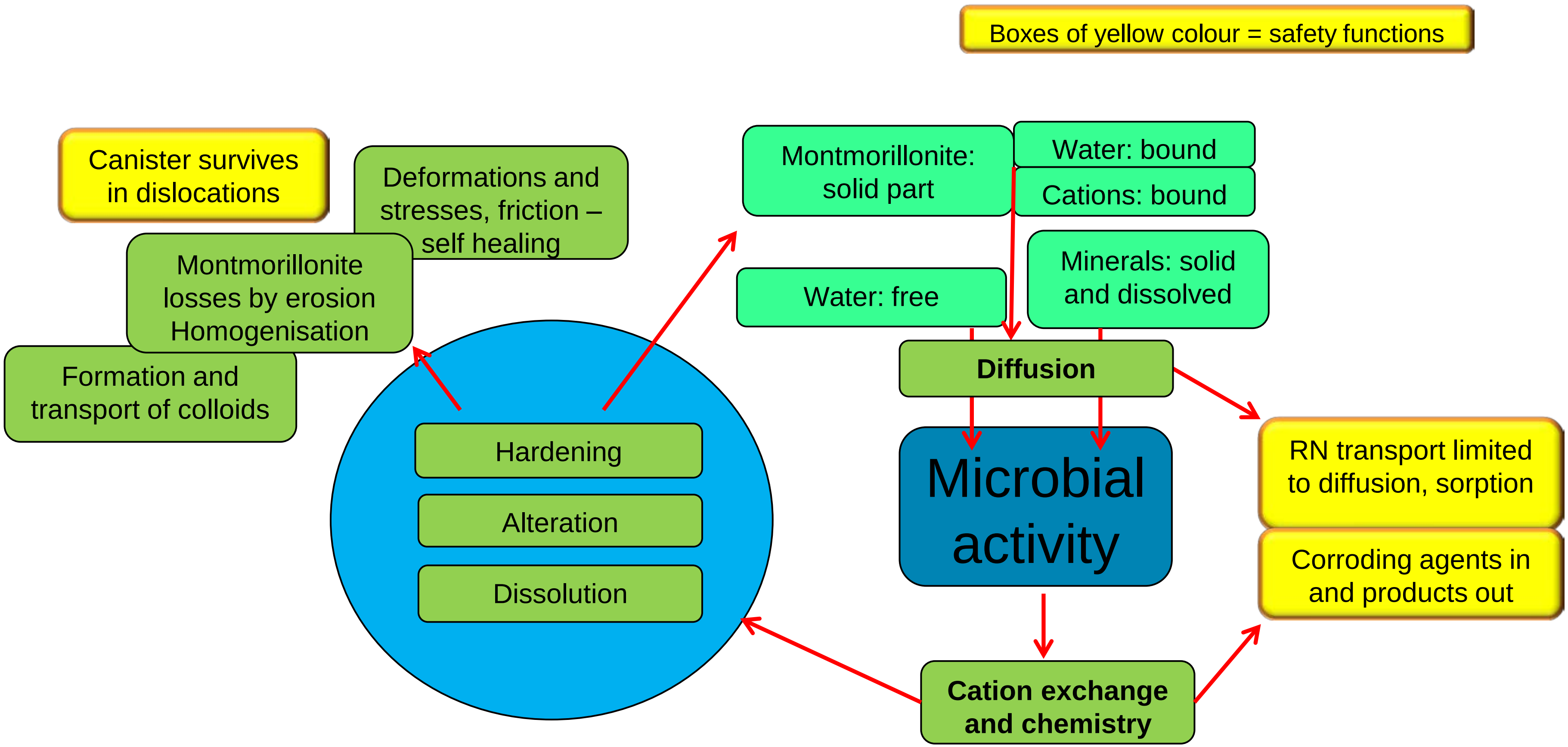




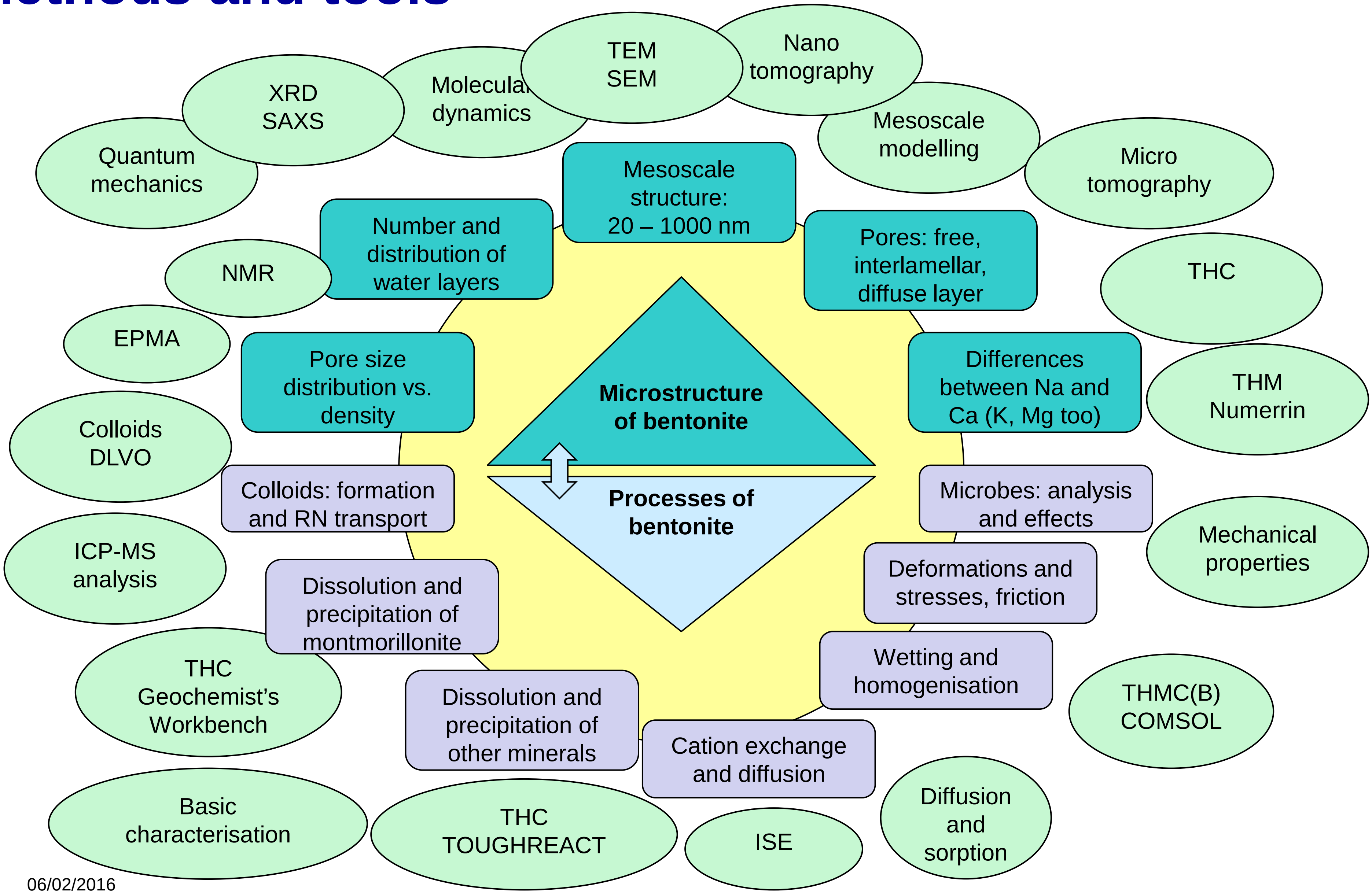
Safety functions (SF): protect canister, and limit and delay release of RN
Processes related to these SFs shown below

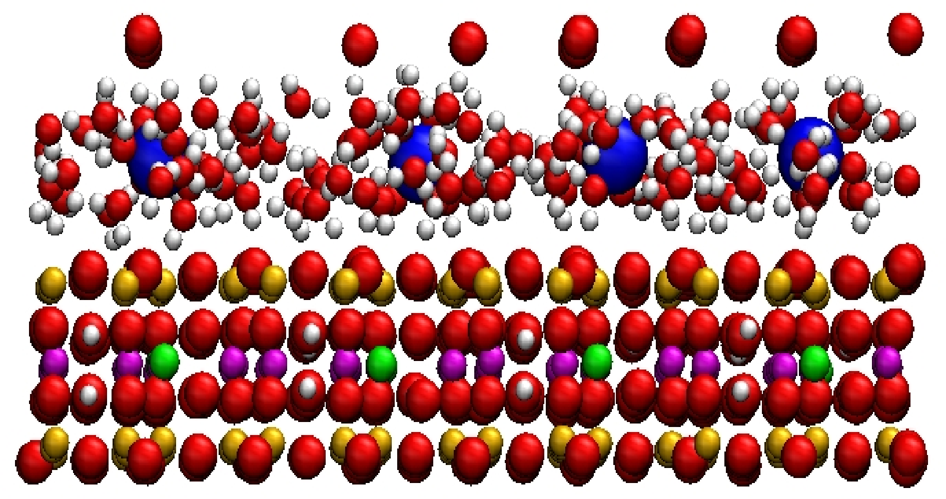


Microbes related to processes and structure



Methods and tools

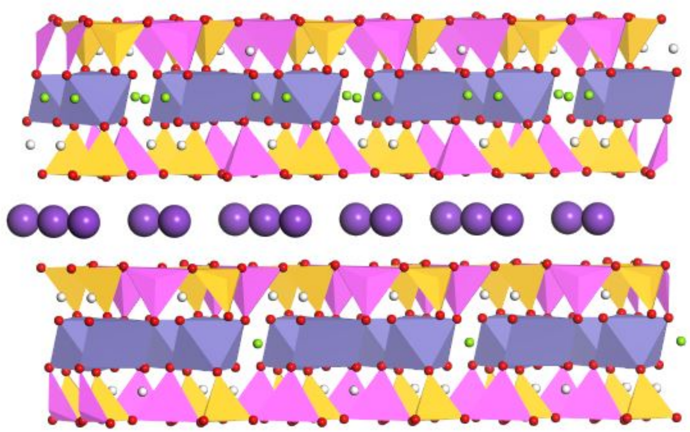




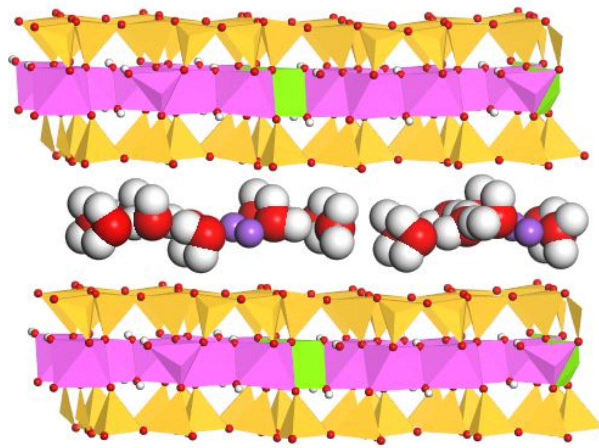
Molecular level

Definitions of clay minerals

- Clay minerals are products of long term weathering of rocks
- Most clay minerals are sheet silicates – phyllosilicates
  - 1:1 phyllosilicates e.g. kaolinite
  - 2:1 phyllosilicates without interlayer sheet e.g. talc
  - 2:1 phyllosilicates with interlayer sheet
    - non-hydrated (e.g. biotite) and hydrated cations (e.g. montmorillonite)
  - 2:1:1 phyllosilicates e.g. chlorite



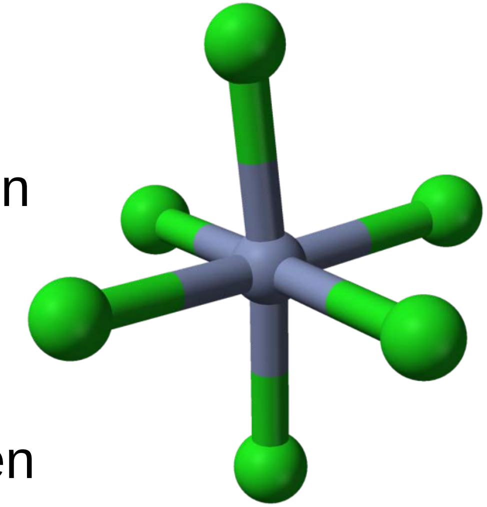
Biotite
Tetrahedral sheet: Si – yellow and Al – aniline red.
Octahedral sheet: Fe – blue, Mg – green.
Interlayer: K – purple.

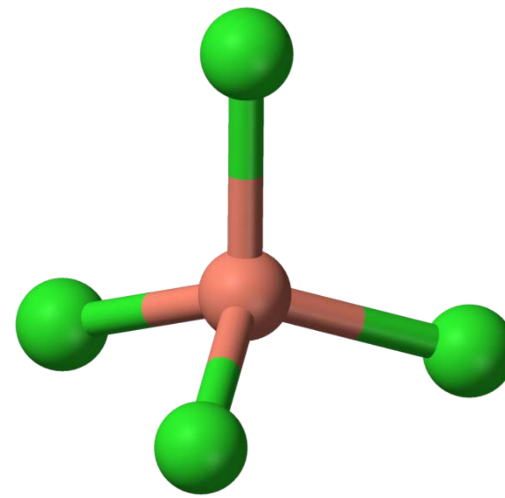


Montmorillonite
Tetrahedral sheet: Si – yellow.
Octahedral sheet: Al – aniline red, Mg – green.
Interlayer: Na – purple, O – red and H – white.

Structure of phyllosilicates

- Phyllosilicates are formed by superposed atomic planes parallel to the (001) face of the crystalline structure
- The structure consists of negatively charged layers and cation interlayers which are linked together
- The negatively charged layers consist of tetrahedral (T) and octahedral (O) sheets that stack together to form 2:1 (TOT) layers with a characteristic repeat distance between two negatively charged layers
- The negative framework charge is balanced by equivalent amount of cations on the basal planes and between the silicate TOT-layers
- The cations are exchangeable to ions in external solutions
- The cations can be nonhydrated or hydrated
- The nonhydrated cations are not readily exchangeable, while the hydrated cations are readily exchangeable





Molecular level modelling

Van der Waals methods

- energy of molecules is a sum of Coulombic and van der Waals energies
- optimization of torsion angles (bond lengths and angles are constant)

Molecular mechanics

- force fields (potentials) which are formulated from experimental measurements
- optimization of molecular structures

Molecular dynamics (MD)

- time-dependent simulations at different temperatures and pressures
- generally, the force fields of molecular mechanics are used
    - *Classic and/or reactive MD calculations* – applicable parametrization for clays

Quantum mechanics (QM)

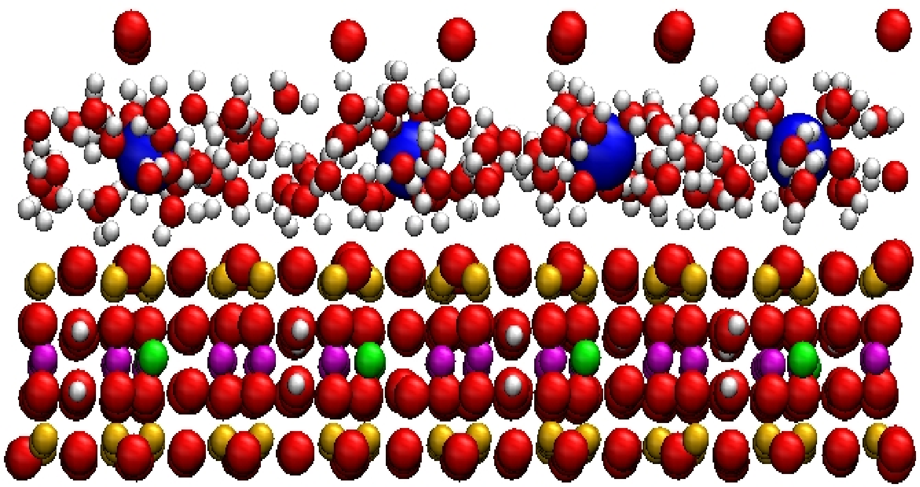
- solution for the time independent Schrödinger equation (molecular orbital theory)
- solution for the ground state of the electron density (density functional theory, DFT)

$$\hat{H} = \sum_{n=1}^{N} \frac{\hat{\mathbf{p}}_n \cdot \hat{\mathbf{p}}_n}{2m_n} + V(\mathbf{r}_1, \mathbf{r}_2, \cdots \mathbf{r}_N)$$

$$= -\frac{\hbar^2}{2} \sum_{n=1}^{N} \frac{1}{m_n} \nabla_n^2 + V(\mathbf{r}_1, \mathbf{r}_2, \cdots \mathbf{r}_N)$$

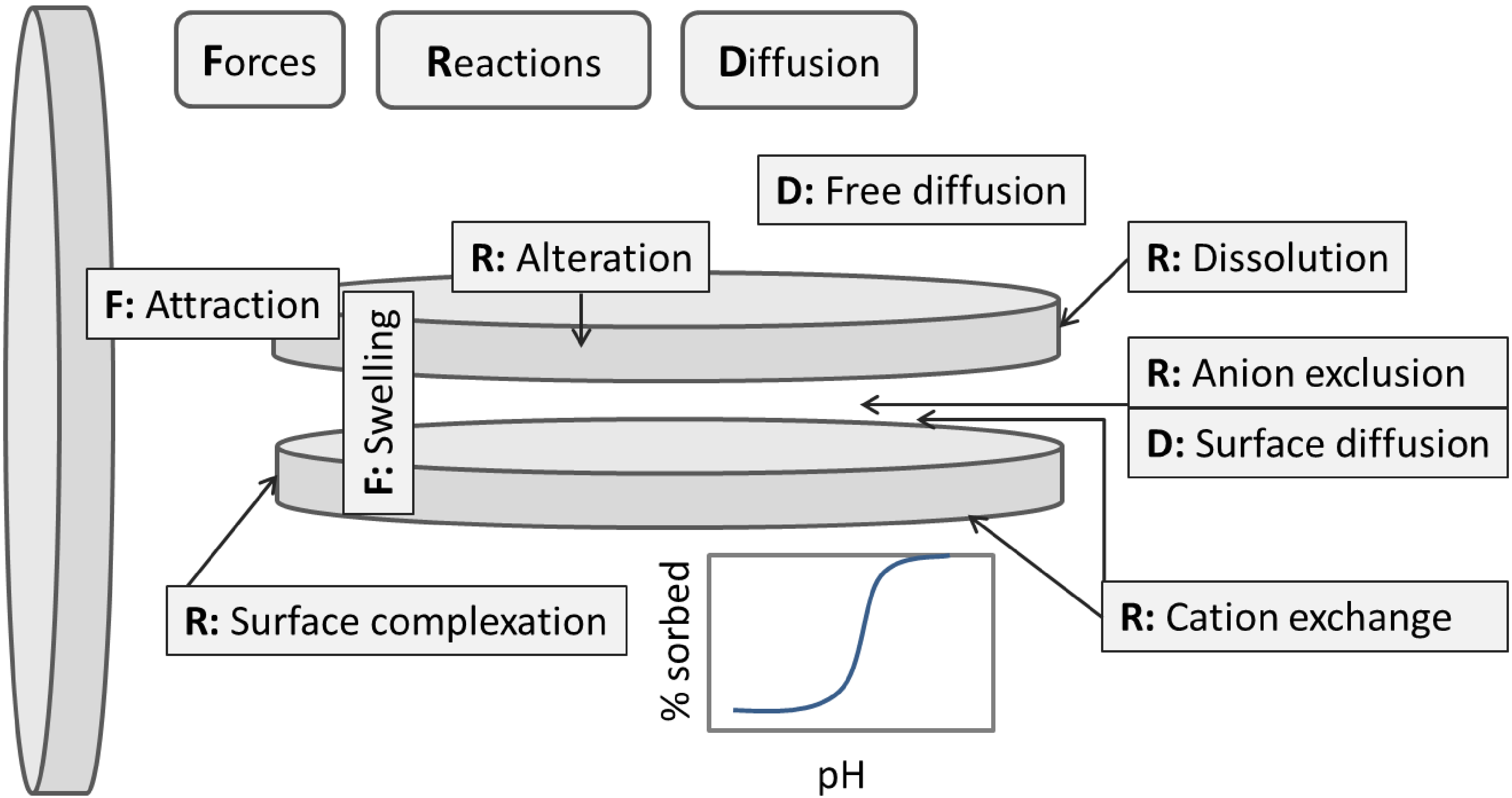
MD simulation of Na-montmorillonite

Formation of interlayer water layers



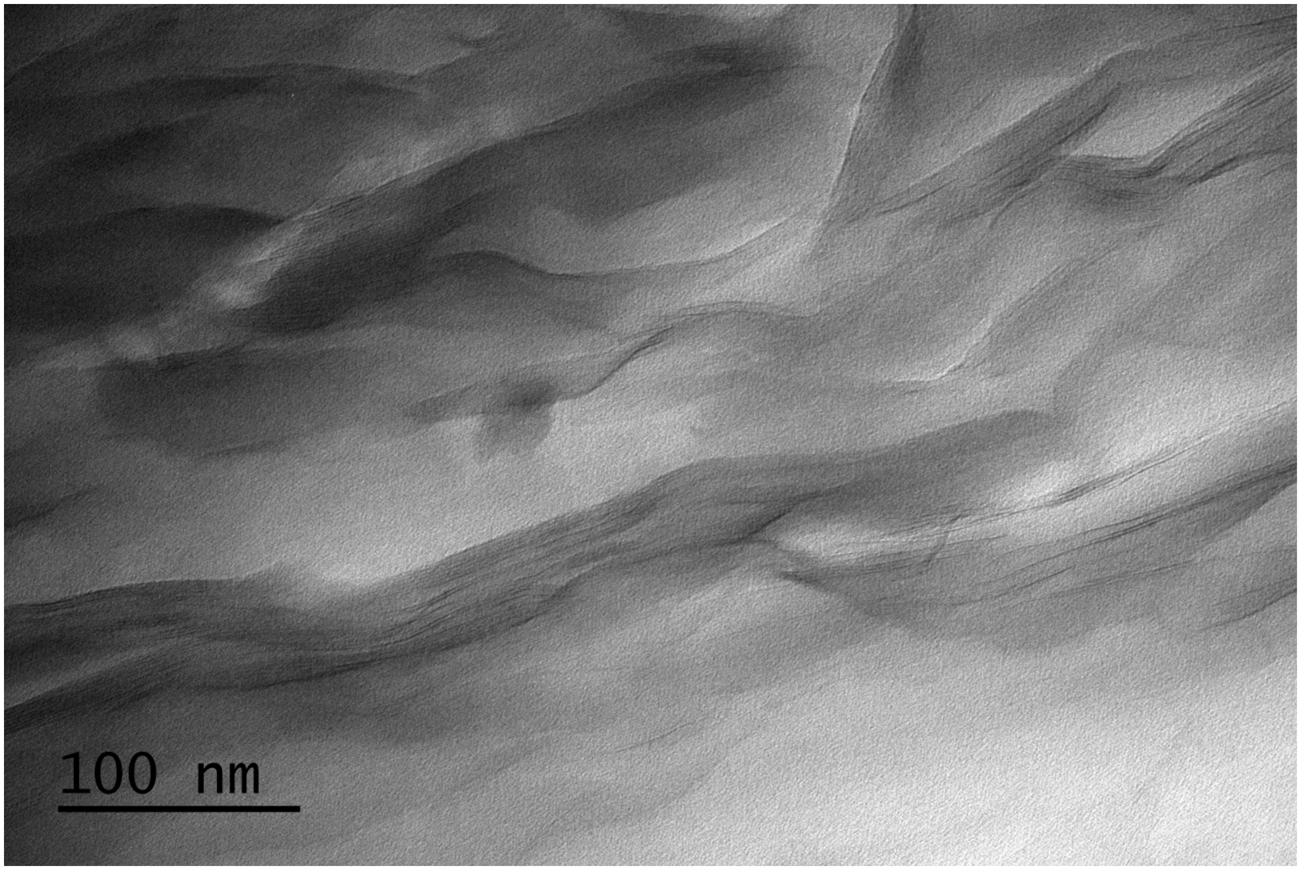
Simulation box with 1 layer of mmt + interlayer (Si = yellow, Al = magenta, Mg = green, O = red, H = white, Na = blue)

Clay interactions



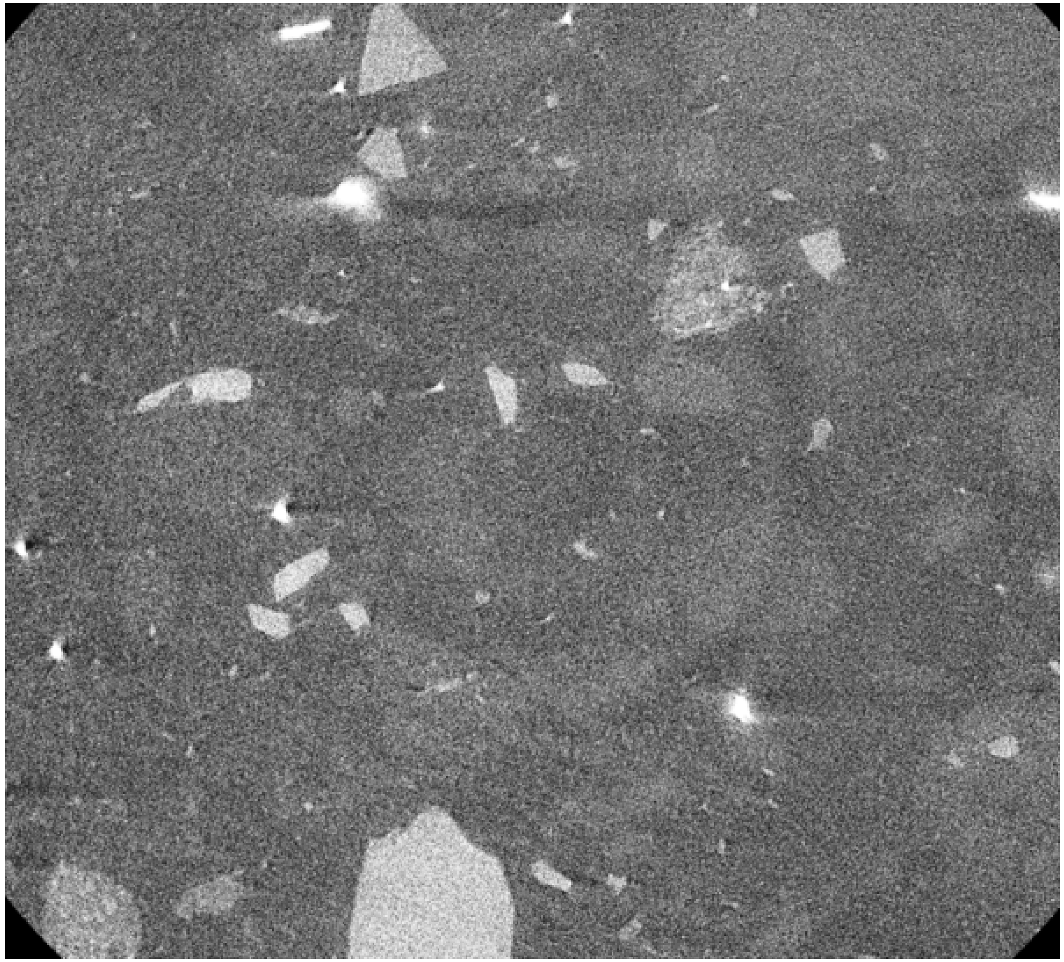
Experimental

TEM imaging



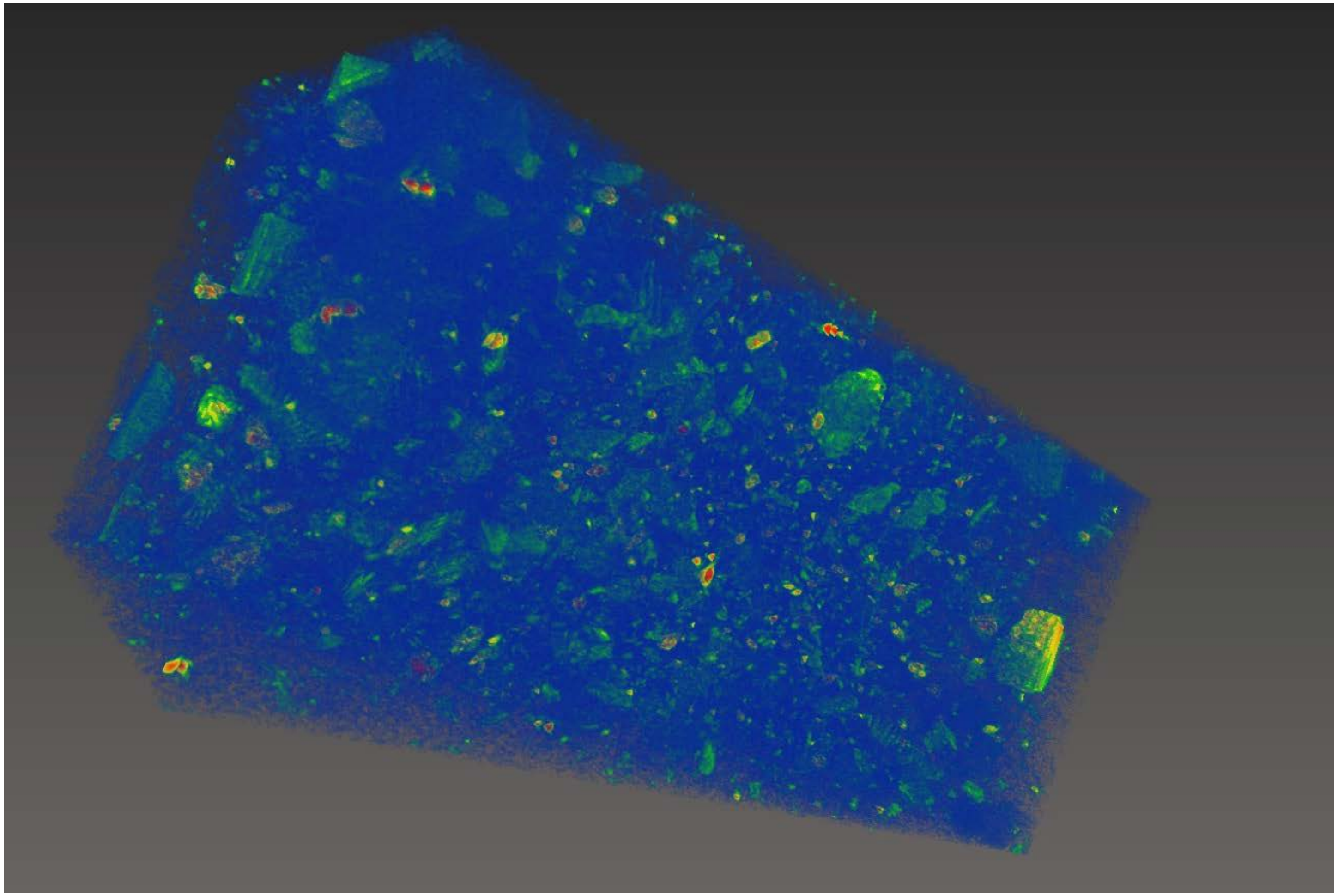
MX-80, dry density 1.56 g/cm^3, equilibrated with MilliQ water

X-ray Tomography



MX-80, dry density 0.7 g/cm^3, saturated with MilliQ water

X-ray Tomography

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