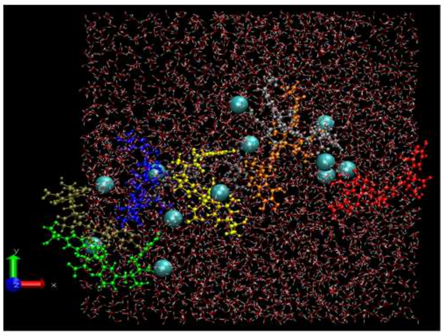
NE-M1-PRI12ENP – Integrated Nuclear Engineering Project

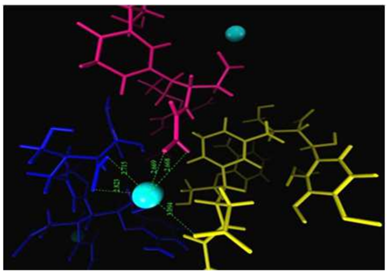
Molecular Modeling of Materials for Nuclear Waste Disposal Applications

Lecture 6 - (Natural Organic Matter and Metal-NOM Interactions)



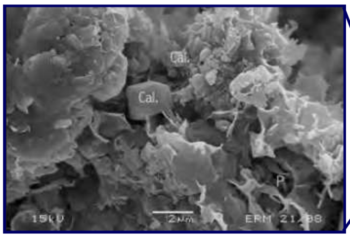
Andrey G. Kalinichev

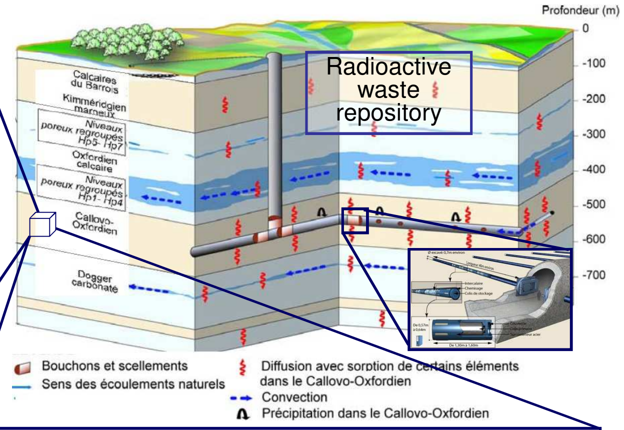
Laboratoire SUBATECH
IMT-Atlantique



E-mail: *kalinich@subatech.in2p3.fr*
https://www.imt-atlantique.fr/en/person/andrey-kalinichev

Mineral Composition of Callovo-Oxfordian (COx) Clayey Formations



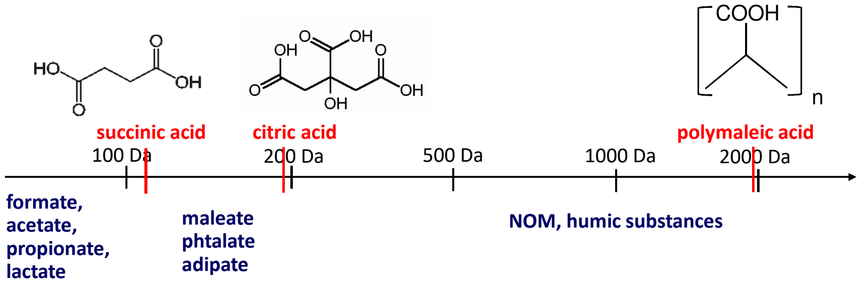


➢ 20-50%	clay (illite-smectite)
➢ 20-40%	calcite
➢ 20-40%	quartz and feldspar
➢ 0.5%	pyrite
➢ 1.5%	organic matter

Adsorption and Mobility of Organic Acids in COx

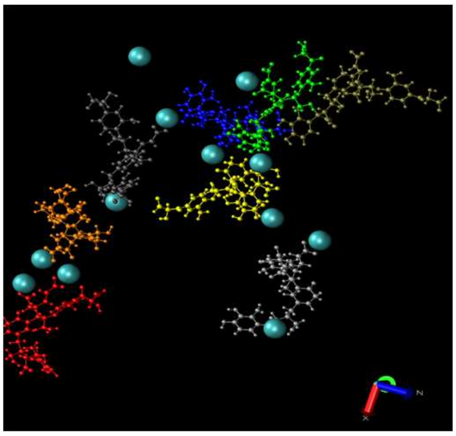
- It has been determined in batch and diffusion experiments with COx samples that organic acids are mobile
- There is a significant degree of irrerversible adsorption, even leading to a complete saturation of the adsorption sites
- There is significant effect of Ca^{2+} on these processes
- Organic molecules can be a potential vector in the transport of radionuclides in COx formations

(D.Durce, PhD thesis, EMN, SUBATECH, 2010)



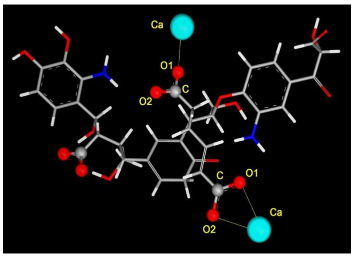
Molecular Modeling of Natural Organic Matter in Aqueous Solutions and in the Environment

- Molecular models of NOM (humic and fulvic acids, humite, kerogene)
- Adsorption of metal cations to natural organic matter (NOM)
- Local electrostatic fields and hydrophobic / hydrophilic sites of the NOM molecules
- Interaction of Na^+, Cs^+, Mg^{2+}, and Ca^{2+} ions with NOM: Structure, energetics and dynamics



Motivation

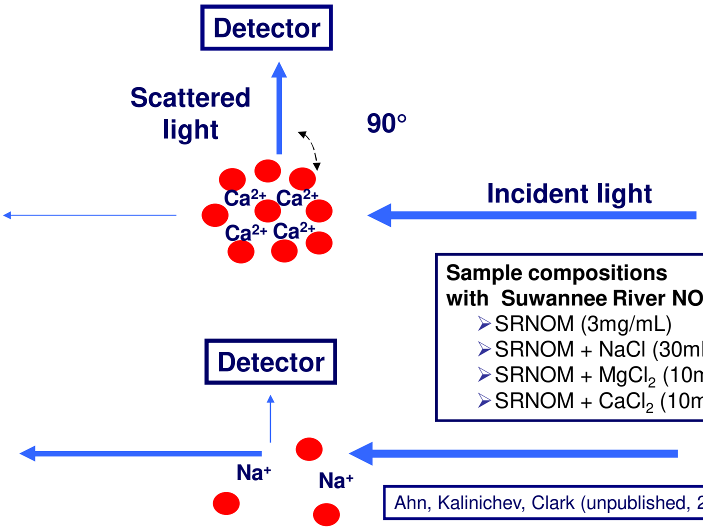
- Natural organic matter (NOM, humic and fulvic acids, humite, kerogene) plays very important role in a wide variety of environmental and geochemical processes:
  - **Sorbents for toxic metals and radionuclides**
  - Catalytically active chemical buffers
  - Sorbents for organic pollutants
  - Mineral dissolution; soil stabilization
  - Water reservoirs and nutrients for plants
  - Foulants in water purification systems



- Metal–NOM interaction induces strong correlations between the NOM concentration and the speciation, solubility and toxicity of many metals in the environment
- NOM solution chemistry controls the charge and conformation of NOM macromolecules and supramolecular aggregates
- Divalent cations, such as Ca^{2+} or Sr^{2+}, may interact with organic molecules to form metal-NOM complexes, resulting in highly compacted supramolecular aggregates and changing the diffusional dynamics of both

---

Experimentally Probing NOM Aggregation by Dynamic Light Scattering (DLS)

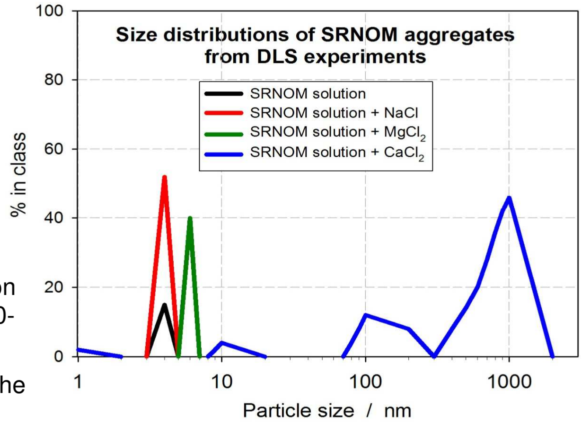


Sample compositions with Suwannee River NOM
- SRNOM (3mg/mL)
- SRNOM + NaCl (30mM)
- SRNOM + $MgCl_2$ (10mM)
- SRNOM + $CaCl_2$ (10mM)

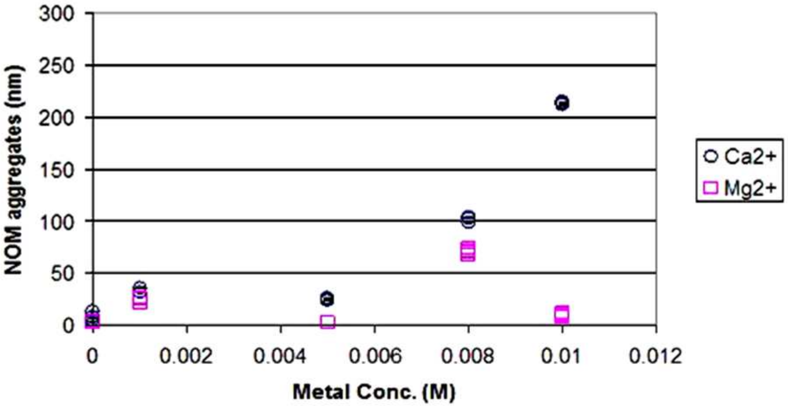
Ahn, Kalinichev, Clark (unpublished, 2007)

Size Distributions of SRNOM Aggregates Probed by Dynamic Light Scattering (DLS)

- **Sample compositions with Suwannee River NOM**
  - SRNOM (3mg/mL)
  - SRNOM + NaCl (30mM)
  - SRNOM + $MgCl_2$ (10mM)
  - SRNOM + $CaCl_2$ (10mM)
- Addition of Ca^{2+} to SRNOM solution leads to the formation of 100-1,000-nm-sized SRNOM aggregates
- In the presence of Mg^{2+} or Na^+ to the aggregates are less abundant and much smaller, < 10nm

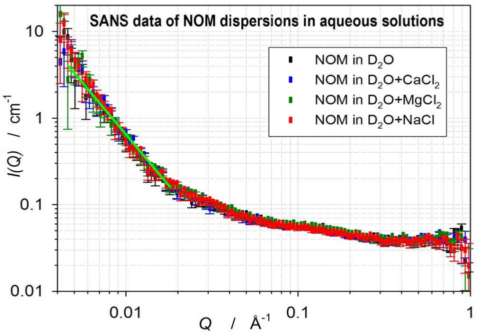


DLS Experiments: Effect of Salt Concentration on the Size of NOM Aggregates



- Strong concentration dependence of NOM aggregation in the presence of Ca^{2+}
- Concentration of Mg^{2+} or Na^+ does not noticeably affect the size of the NOM aggregates

NOM Aggregation in Neat and Salt Solutions Probed by Small Angle Neutron Scattering (SANS)

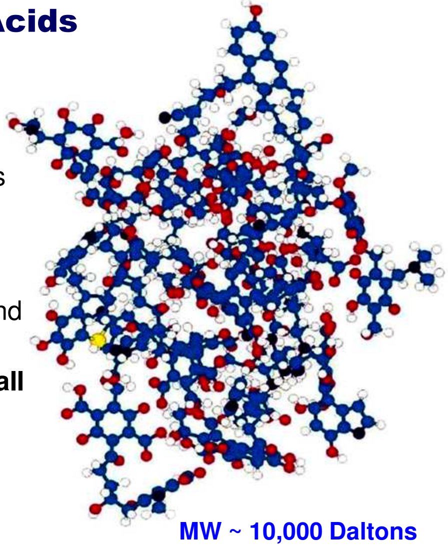


- 4 samples containing NOM in neat and salt solutions in D_2O
- The data are nearly identical for all the samples with a power-law scattering with an exponent of -2.62 at low Q, a slight down turn in the mid-Q region and a flat signal at the high Q that is incoherent background from the H atoms in the NOM and the D atoms in the solvent.
- SANS data can be interpreted as NOM aggregation in a network of small particles. The mid-Q region indicates the presence of smaller length scale moiety.

- The power-law exponent of ~2.62 in the low-Q region implies the presence of a mass fractal aggregate formed presumably through a cluster-cluster aggregation. They are quite large (50 nm) and hence cannot be seen with the finite Q_{min} of the SAND instrument.
- The similarity in the SANS signals of NOM in neat as well as salt solutions suggest that the cations do not affect the structures at the nanoscale probed by SANS.

Molecular Modeling of NOM in Aqueous Solutions: Conceptual Models of Humic Acids

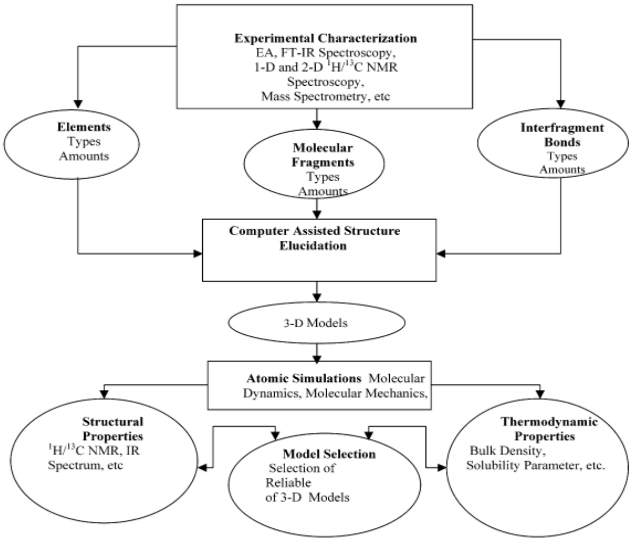
- Not much is known about NOM detailed molecular structure and molecular mechanisms of its activity
- NOM defined only operationally through its aqueous solubility
- Structural modeling for these compounds remains an outstanding problem in environmental chemistry, soil chemistry, and organic geochemistry
- **Large macromolecules or relatively small fragments assembled into supramolecular aggregates?**
- Molecular modeling can be a powerful tool to understand the behavior of NOM in aqueous environments



MW ~ 10,000 Daltons

(Schulten, 1995; Schulten & Leinweber, 2000; Sutton, Sposito, et al., 2005)

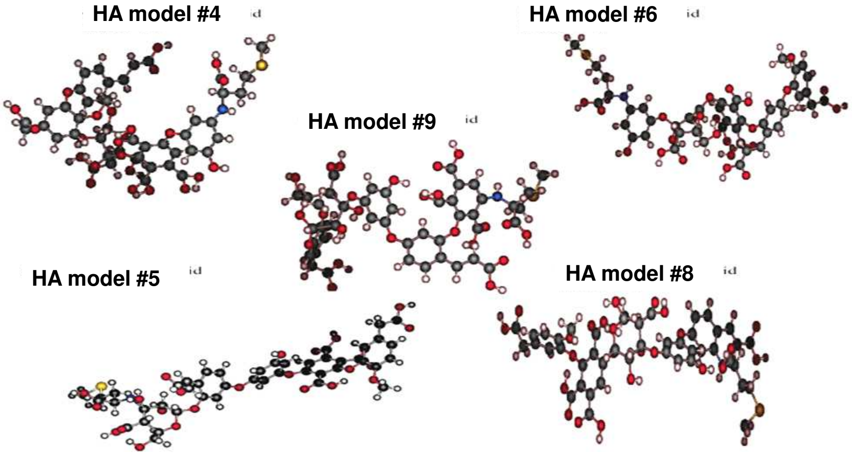
Hierarchical Approach to the Computer Assisted Structure Elucidation (CASE) for the Model 3-D Structures of Humic Substances



- Complex hierarchical fitting procedure based on a set of experimental data from various sources
- Large number of possible 3-D molecular models is generated
- They are rated by the agreement with measured properties

(Diallo et al., 2003)

Resulting Structural Models of Humic Acids

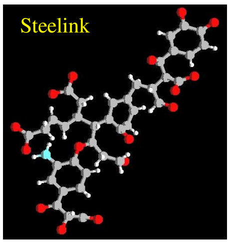


MW ~ 1,000 Dalton

(Diallo et al., 2003)

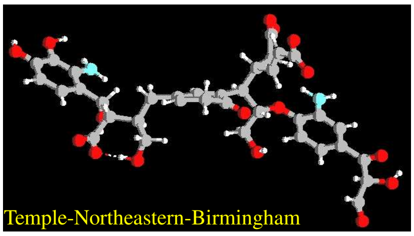
Structural Models of Humic Acids

Structure and composition of two NOM building blocks (Sein et al., 1999)



	C wt%	H wt%	O wt%	N wt%	S wt%	P wt%	carboxyl mol/kg(C)
Steelink	**59.5**	**5.2**	**33.5**	**1.8**	**-**	**-**	**6.6**
TNB	**57.4**	**4.9**	**34.0**	**3.7**	**-**	**-**	**7.0**
Diallo	**53.3**	**4.2**	**37.9**	**1.4**	**3.0**	**-**	**9.3**
Schulten	**51.5**	**4.0**	**41.8**	**2.0**	**0.6**		**14.1**
Exp.(SR)	**52.5**	**4.2**	**42.7**	**1.1**	**0.6**	**0.02**	**9.85**

- "The TNB model incorporates mode fully the results of experimental data and retro-biosynthetic analyses" (Sein et al., 1999)
- 3-D HA models based on an integrated experimental data and CASE (Computer Assisted Structure Elucidation) approach (Diallo et al., 2003)



Simulated NOM Model –
TNB Monomer in Aqueous Salt Solution

TNB model:

Molecular weight - 753 Dalton

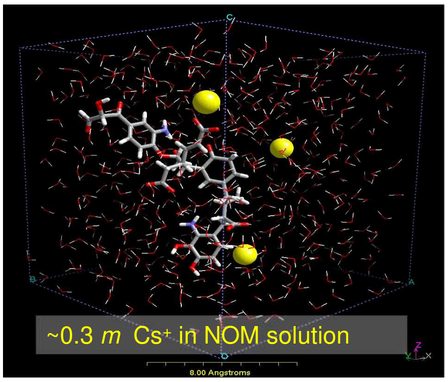
Functional groups:

Carboxyl -	3
Carbonyl -	3
Phenolic -	2
Other R-OH -	4
Amine -	2

Charge - $-3e$

(deprotonated carboxyls; pH ~ 7)

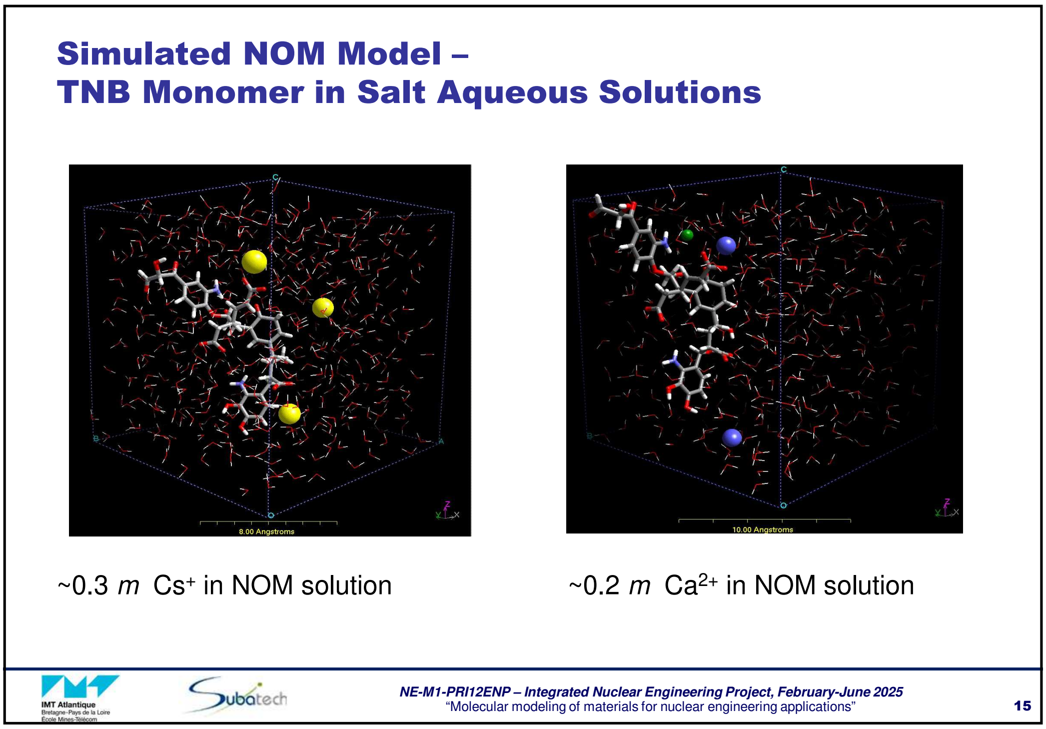
Salt concentration - from 0.0 to 4.0m


~0.3 m Cs^+ in NOM solution

NVT-ensemble $T = 300$K $P \sim 1$bar clayff_cvff (Cygan et al., 2004)

N_{H2O} ~500 N_{tot} ~1800 $t = 100+100$ps $\Delta t = 0.001$ps

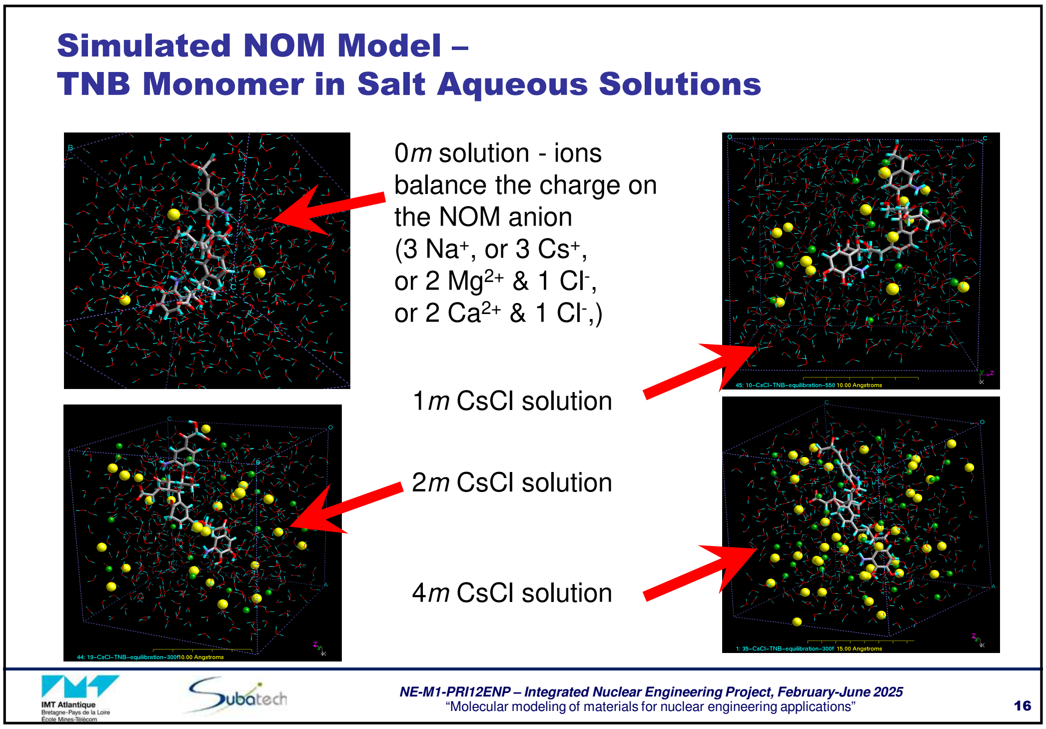
Total of ~20 MD runs for NOM-salt mixtures and neat H_2O-salt solutions



Simulated NOM Model – TNB Monomer in Salt Aqueous Solutions

~0.3 *m* Cs^+ in NOM solution

~0.2 *m* Ca^{2+} in NOM solution



Simulated NOM Model – TNB Monomer in Salt Aqueous Solutions

0*m* solution - ions balance the charge on the NOM anion ($3\ Na^+$, or $3\ Cs^+$, or $2\ Mg^{2+}$ & $1\ Cl^-$, or $2\ Ca^{2+}$ & $1\ Cl^-$,)

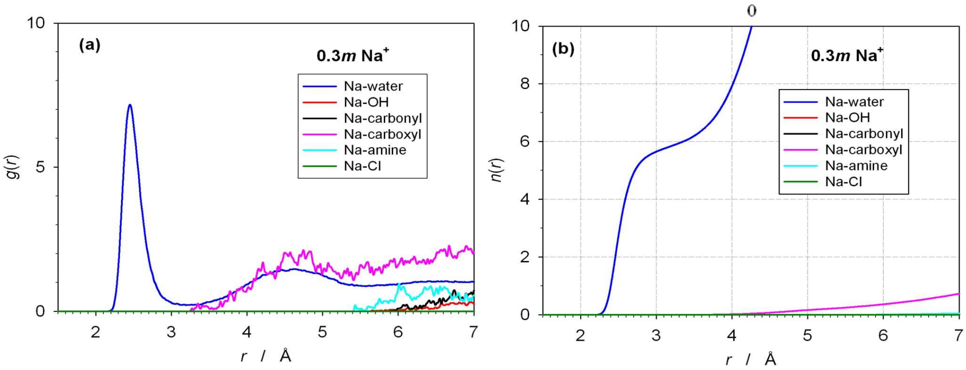
1*m* CsCl solution

2*m* CsCl solution

4*m* CsCl solution

NOM-Na⁺ - Radial Distribution Functions and Running Coordination Numbers

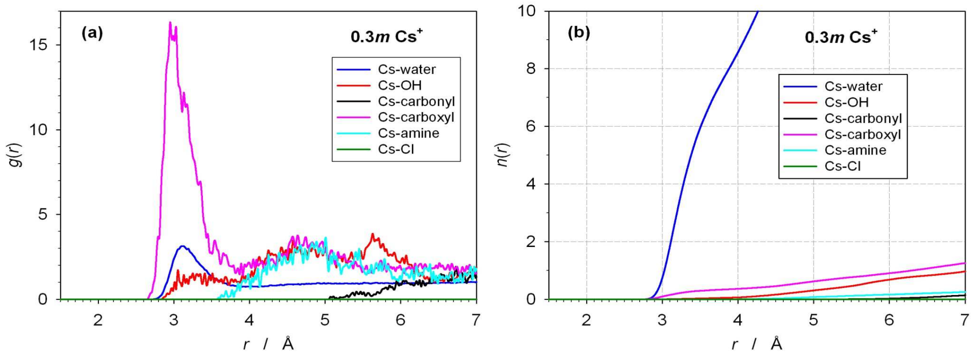
$$n_{ij}(r) = 4\pi\rho_i \int_0^r g_{ij}(r)\, r^2 dr$$



- Only very weak outer-sphere association of Na⁺ with NOM carboxyl groups (pink) is observed.
- No other groups contribute.

NOM-Cs⁺ - Radial Distribution Functions and Running Coordination Numbers

$$n_{ij}(r) = 4\pi\rho_i \int_0^r g_{ij}(r)\, r^2 dr$$



- Some inner-sphere and outer-sphere association of Cs⁺ with NOM carboxyl (pink) and, to a lesser extent, phenolic and other –R-OH functional groups (red) is observed
- No other groups contribute.

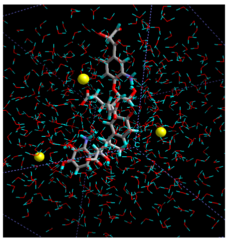
Importance of *g*(*r*) Normalization

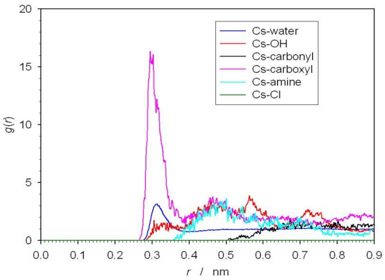
- Hight of the *g*(*r*) peaks is not necessarily an indication of high population
- Average density or concentration of species is equally important

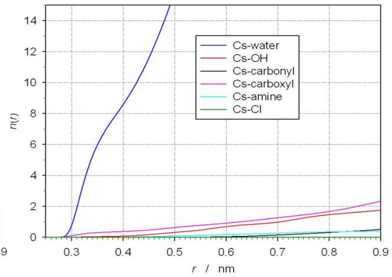
$$g_{ij}(r) = \frac{1}{N_j \rho_i} \left\langle \sum_i \sum_j \delta(\mathbf{r} - \mathbf{r}_{ij}) \right\rangle$$

$$n_{ij}(r) = 4\pi\rho_i \int_0^r g_{ij}(r)\, r^2 dr$$

3 Cs^+ ions in aqueous solution with humic acid (NOM anion)

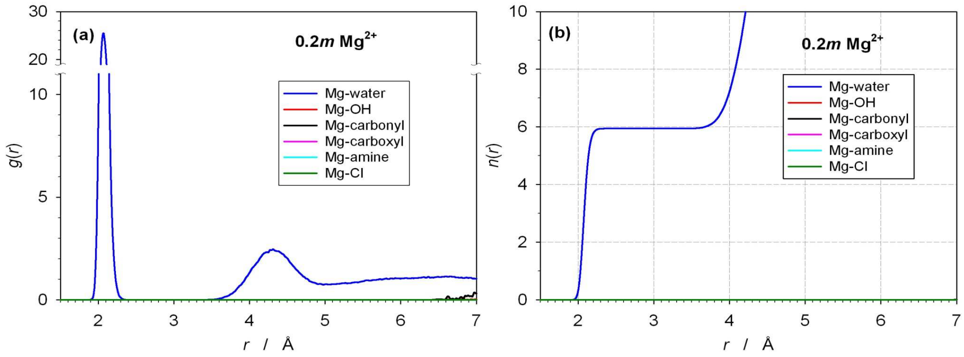






NOM-Mg^{2+} - Radial Distribution Functions and Running Coordination Numbers

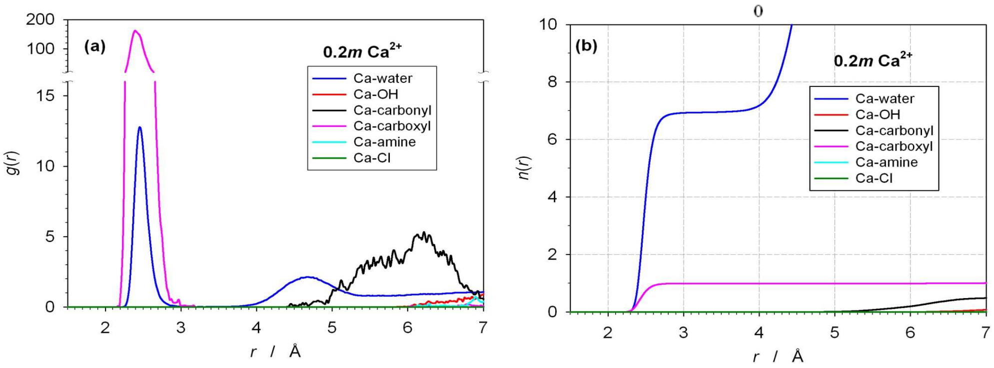
$$n_{ij}(r) = 4\pi\rho_i \int_0^r g_{ij}(r)\, r^2 dr$$



- Mg^{2+} is only coordinated by H_2O, like in neat aqueous solution.
- No association of Mg^{2+} with carboxyl or any other NOM functional groups.
- Very strong second hydration shell of Mg^{2+} is visible

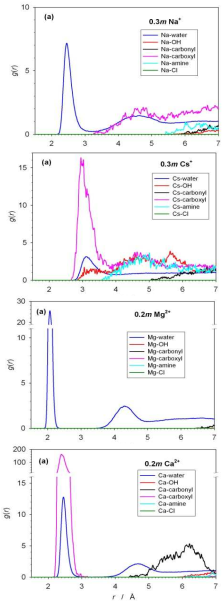
NOM-Ca^{2+} - Radial Distribution Functions and Running Coordination Numbers

$$n_{ij}(r) = 4\pi\rho_i \int_0^r g_{ij}(r)\, r^2 dr$$

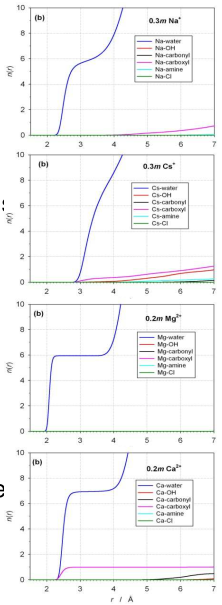


- ~50% of Ca^{2+} ions in strong inner-sphere coordination with NOM carboxyl groups (pink).
- No other groups contribute.
- Strong second hydration shell of Ca^{2+} is visible

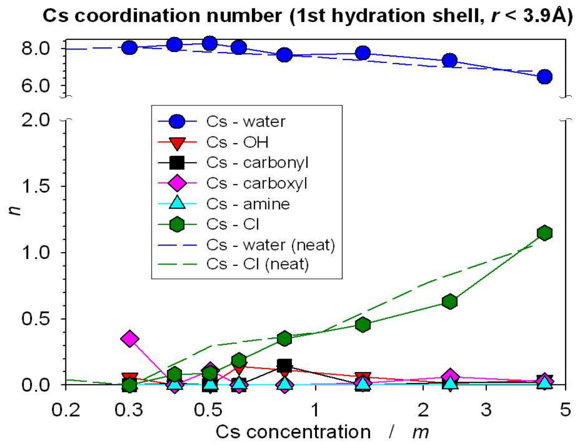
Mechanisms of Cation-NOM Complexation



- Unlike other cations, Mg^{2+} is only coordinated by H_2O, same as in neat aqueous solution
- No association of Mg^{2+} with carboxyl or any other NOM functional groups.
- Very strong second hydration shell of Mg^{2+} i observed
- Cation-NOM complexation is driven by the *z*/*R* ratio for the ions
- For ions of the same size, higher charge results in a stronger association with NOM
- Due to the competition between ionic hydration and cation sorption by the negatively charged NOM (primarily carboxylate groups), larger ions of the same charge have a stronger tendency for NOM association

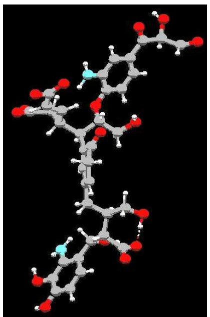


Running Coordination Numbers of Cs⁺ : 1st coordination sphere



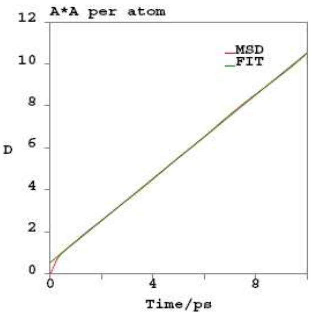
- On average, at the lowest concentration, ~0.3 O atoms of an NOM carboxyl group can be found in the first coordination sphere of Cs⁺ (out of ~8 first neighbors) .
- Another ~0.1 is due to the Cs⁺ coordination to –R-OH groups.
- All other functional groups do not contribute at all to Cs⁺ binding.

- The situation can change somewhat in the presence of sulfate and phosphate NOM functional groups. However, their concentration is typically very low in NOM.

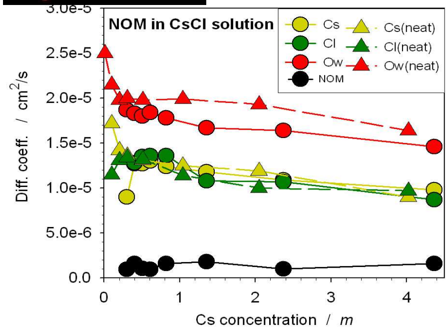


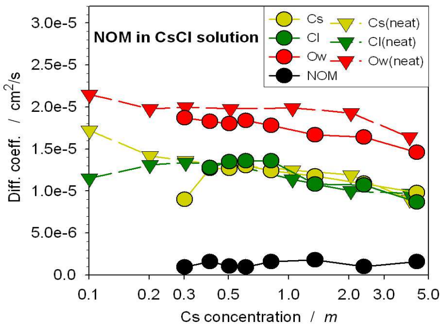
Diffusion Coefficients

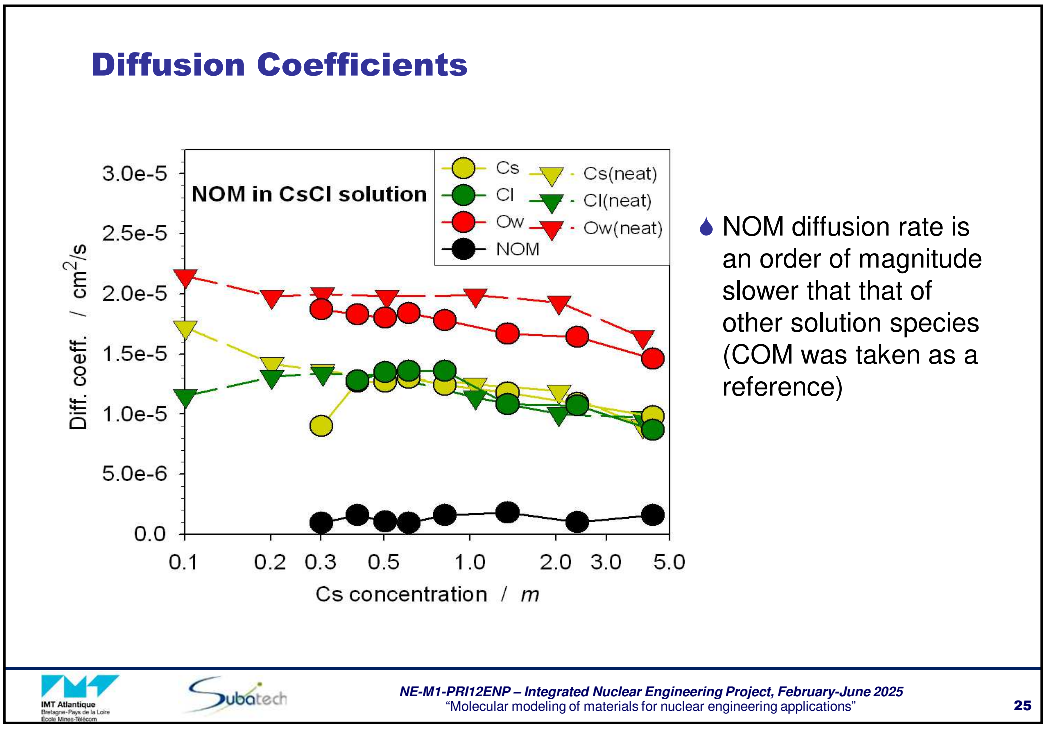
$$D = \lim_{t\to\infty} \frac{1}{6Nt} \underbrace{\left\langle \left|\mathbf{r}(t)-\mathbf{r}(0)\right|^2 \right\rangle}_{\text{MSD}}$$



For large molecules center of mass (COM) diffusion is important

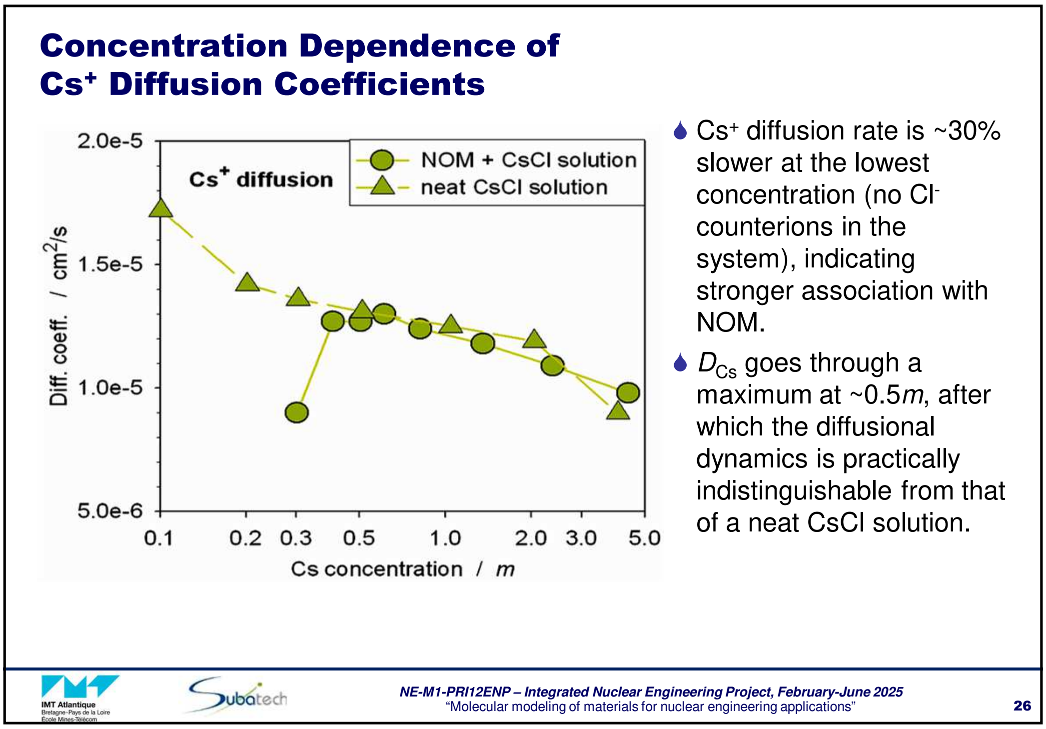






Diffusion Coefficients

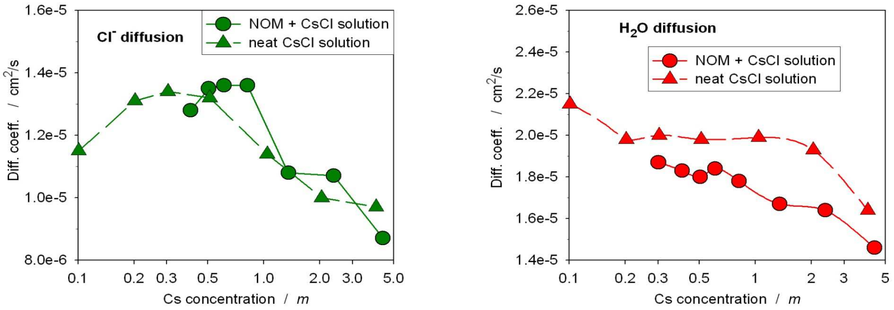
- NOM diffusion rate is an order of magnitude slower that that of other solution species (COM was taken as a reference)



Concentration Dependence of Cs^+ Diffusion Coefficients

- Cs^+ diffusion rate is ~30% slower at the lowest concentration (no Cl^- counterions in the system), indicating stronger association with NOM.
- D_{Cs} goes through a maximum at ~0.5*m*, after which the diffusional dynamics is practically indistinguishable from that of a neat CsCl solution.

Diffusion Coefficients



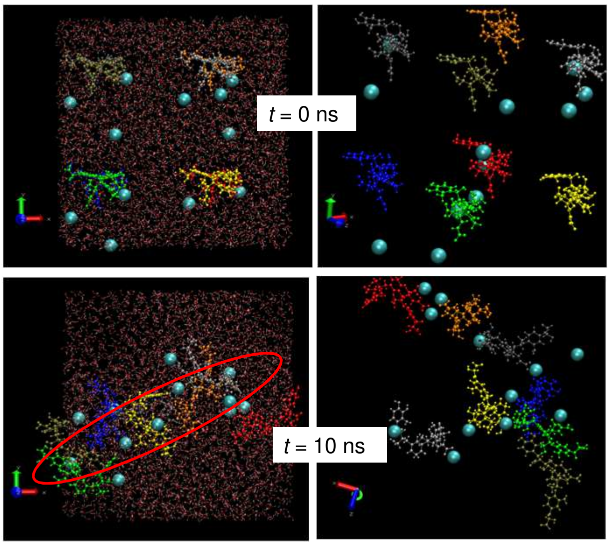
- Cl$^-$ diffusional dynamics is practically indistinguishable from that of a neat CsCl solution in the entire concentration range.
- Average H_2O diffusion coefficients are lower in the presence of NOM because of the close involvement of many water molecules in the NOM hydration.
- The difference between H_2O behavior in NOM and neat solutions fades as the CsCl concentration increases and the effects of Cs$^+$ - Cl$^-$ ion pairing start to prevail.

Diffusion Coefficients of Aqueous Species in NOM Solutions

	D_i (10^{-5} cm^2/s)	D_i^{bulk} (10^{-5} cm^2/s)
Na$^+$	1.0	1.2 1.22^a 1.22^b
Cs$^+$	0.9	1.3 (at 3m CsCl) 1.8 } inf 2.0^b dilution
Mg^{2+}	0.6	0.62^a
Ca^{2+} (average)	0.4	–
Ca^{2+} (inner-sphere)	0.03	–
Ca^{2+} (bulk in NOM soln)	0.7	0.55^a
NOM center of mass	0.05	–

[a] Obst & Bradaczek (1996)
[b] Lee & Rasaiah (1996)

Size Matters! Metal-Organic Interactions in Aqueous Solutions

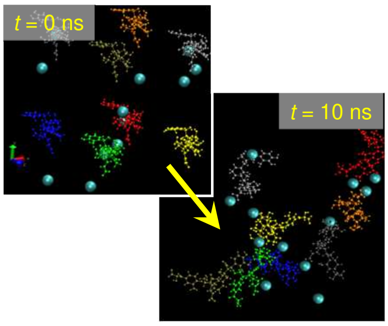


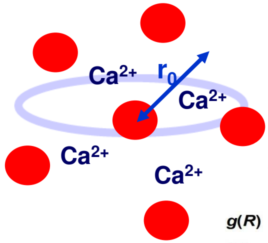
Objective:

to quantify the mechanisms of metal-NOM complexation and colloidal aggregation in aqueous solutions

- Extend MD simulations to much larger systems (~ order of magnitude)
- Extend MD simulations to much longer times (~ 2 orders of magnitude)
- Incorporate as much experimental information as possible

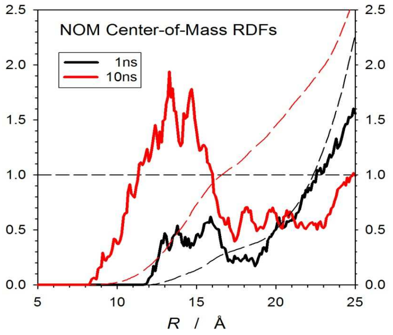
Running Coordination Number of NOM Centers of Mass Probes the Size of the Simulated Aggregates



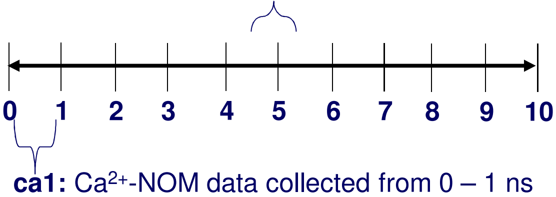


● NOM (TNB) molecule

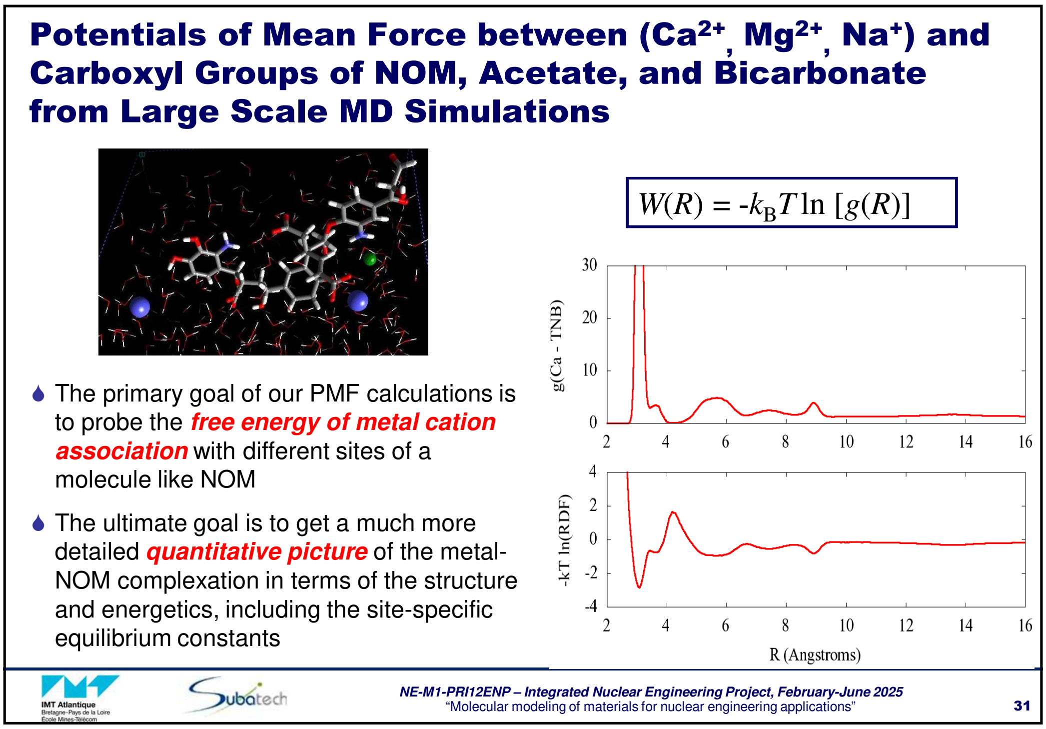
$$n_{ij}(r) = 4\pi\rho_i \int_0^r g_{ij}(r)\, r^2 dr$$



Total simulation period is 10 ns



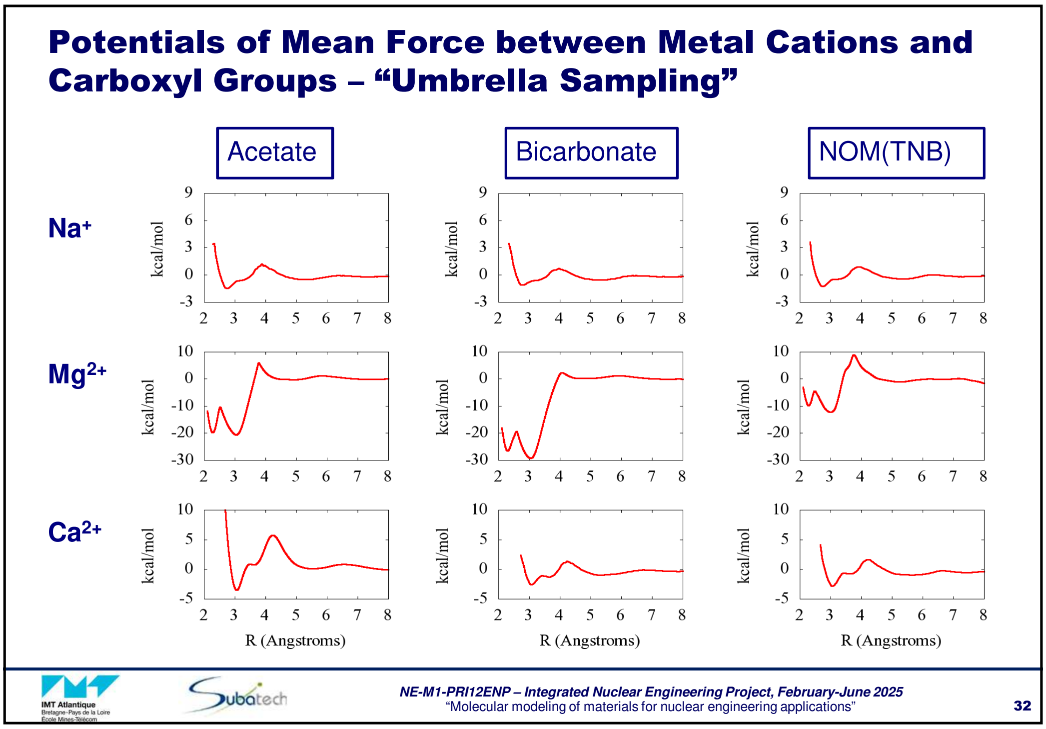
ca1: Ca^{2+}-NOM data collected from 0 – 1 ns



Potentials of Mean Force between (Ca^{2+}, Mg^{2+}, Na^{+}) and Carboxyl Groups of NOM, Acetate, and Bicarbonate from Large Scale MD Simulations

$$W(R) = -k_B T \ln [g(R)]$$

- The primary goal of our PMF calculations is to probe the ***free energy of metal cation association*** with different sites of a molecule like NOM
- The ultimate goal is to get a much more detailed ***quantitative picture*** of the metal-NOM complexation in terms of the structure and energetics, including the site-specific equilibrium constants



Potentials of Mean Force between Metal Cations and Carboxyl Groups – "Umbrella Sampling"

Acetate

Bicarbonate

NOM(TNB)

Na^{+}

Mg^{2+}

Ca^{2+}

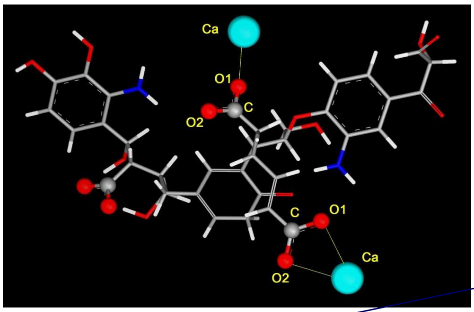
Potentials of Mean Force and Equilibrium Constants

$$K_e = \frac{\rho_{SSIP}}{\rho_{CIP}} = \frac{4\pi \int_{R_L}^{R_U} g_{AB}(r) r^2 dr}{4\pi \int_{0}^{R_L} g_{AB}(r) r^2 dr}$$

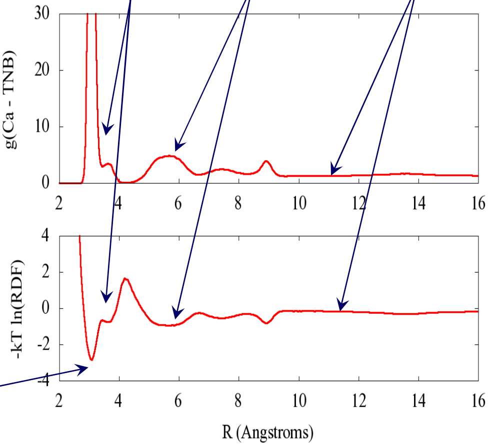
A·B ⇔ A · · · B ⇔ A + B

CIP SSIP free ions

Monodentate

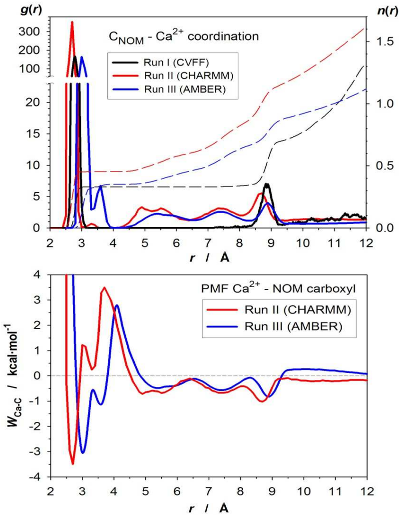


Bidentate



Iskrenova-Tchoukova, Kalinichev, Kirkpatrick (2010) *Langmuir*, **26**, 15909-15919

NOM-Ca^{2+} Coordination in Aqueous Solutions from 3 Different MD Simulations

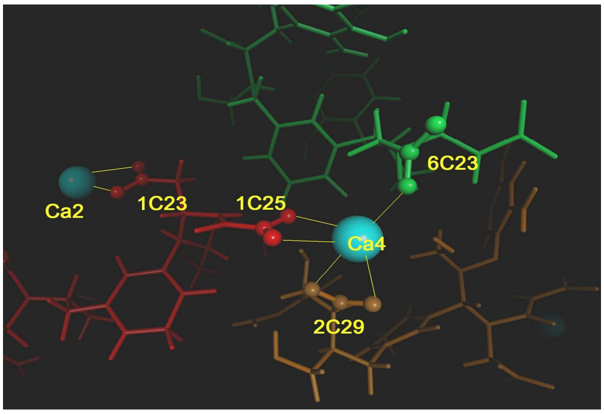


MD run	Force field	Simulation box size (Å)	Duration (ns)	Number of TNB	Number of Ca^{2+}	Total number of atoms
I	CVFF	25.55	0.1	1	2	1753
II	CHARMM27	51.08	10	8	12	13313
III	AMBER FF99	51.32	10	8	12	13385

- 3 different MD simulations using 3 different force field models and different system sizes
- All three simulations are quite robust and consistent
- Approximately 35-50% of Ca^{2+} ions are associated with the NOM carboxylic groups at near-neutral pH
- Strong preference for the stability of bidentate-coordinated contact ion pair complexes

Kalinichev, Iskrenova-Tchoukova, Ahn, Clark, Kirkpatrick (2011) *Geoderma*, **169**, 27-32.

NOM Aggregation in Ca^{2+} and Na^{+} Solutions

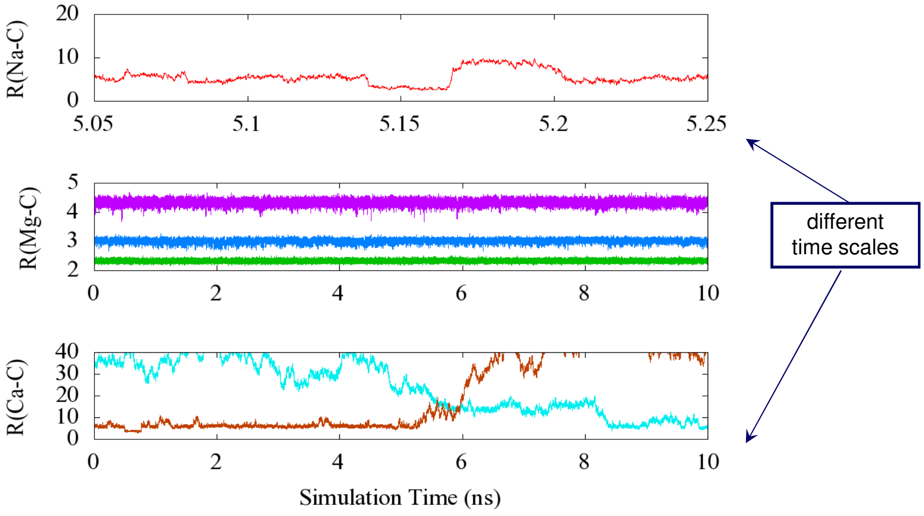


- Ca^{2+} ions connect NOM molecules by Ca^{2+}-NOM inner-sphere complexation ("ionic bridges")
- 5 Ca^{2+} out of total 12 are involved

- Na^{+} ions promote weak NOM aggregation due to the ionic strength effect
- 3 Na^{+} (out of total 24) are involved

Iskrenova-Tchoukova, Kalinichev, Kirkpatrick (2010) *Langmuir*, **26**, 15909-15919
Kalinichev, Iskrenova-Tchoukova, Ahn, Clark, Kirkpatrick (2011) *Geoderma*, **169**, 27-32
Kalinichev (2013) *Pure and Applied Chemistry*, **85**, 149-158.

Mobility of Ions in Aqueous NOM Solutions



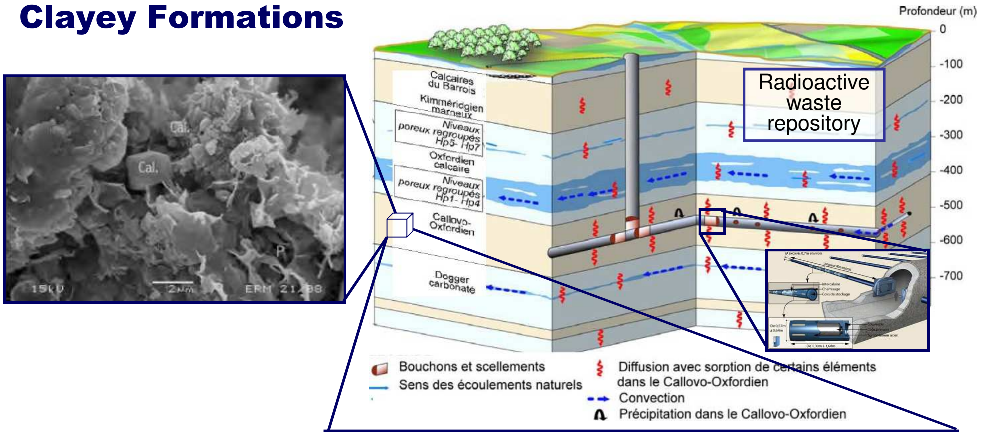
Iskrenova-Tchoukova, Kalinichev, Kirkpatrick (2010) *Langmuir*, **26**, 15909-15919

Conclusions

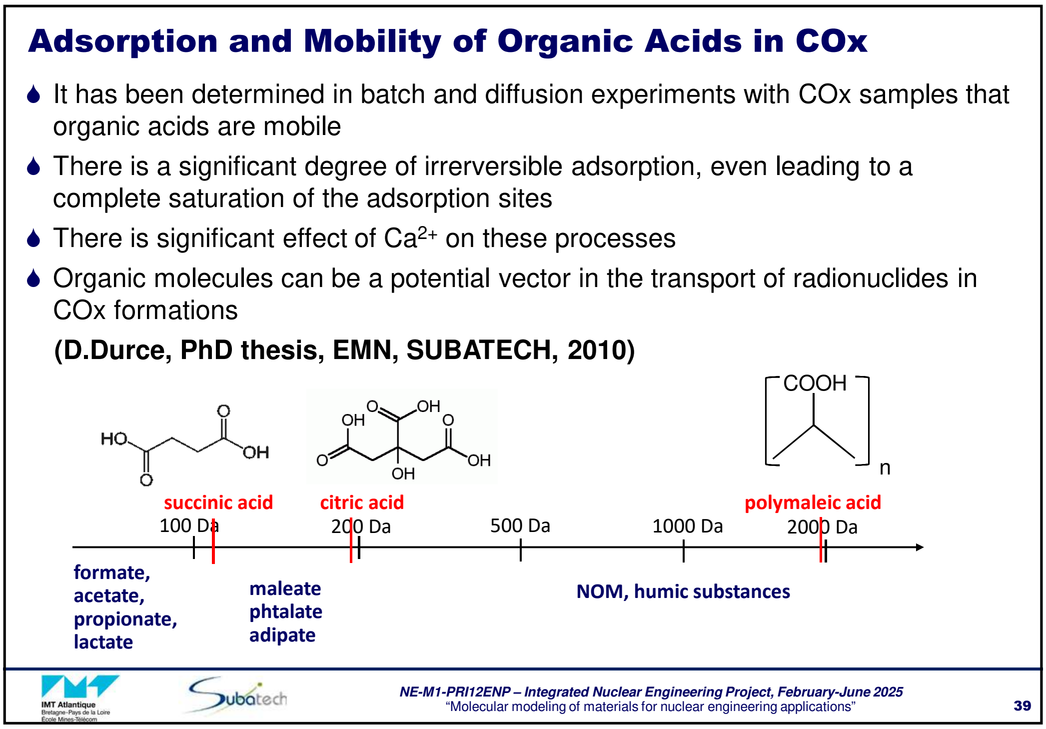
- Good consistency of MD results with NMR, DLS, and SANS experimental data metal-NOM solutions
- ***Charge/size ratio for the ions*** is the main driving force for the cation-NOM complexation, according to our MD simulations and the results of other similar molecular modeling efforts (Sutton et al., 2005)
- Larger ions of the same charge (Cs^+ vs Na^+, or Ca^{2+} vs Mg^{2+}) have a stronger tendency for NOM complexation due to the competition between ionic hydration and adsorption of these cations by the negatively charged NOM functional groups (primarily carboxylate)
- For ions of approximately the same size, higher charge results in a stronger association with NOM
- Diffusion rates of NOM-bound cations are lower by ~30% (NOM-Na^+ outer-sphere complex) to ~2000% (NOM-Ca^{2+} inner-sphere complex) than in neat aqueous solutions
- Ca^{2+} promotes strong NOM aggregation in solution by forming multiple ***metal-carboxylate bridges*** with the NOM molecules
- Na^+ ions promote only weak NOM aggregation through the ionic strength effect and the hydrophobic interactions between the uncharged parts of NOM molecules
- Easy association of metal cations with negatively charged clay particles and negatively charged functional groups of NOM make ***cationic bridging*** the most probable mechanism of NOM association with clays in natural environments

---

Mineral Composition of Callovo-Oxfordian (COx) Clayey Formations



20-50%	clay (illite-smectite)
20-40%	calcite
20-40%	quartz and feldspar
0.5%	pyrite
1.5%	organic matter



Adsorption and Mobility of Organic Acids in COx

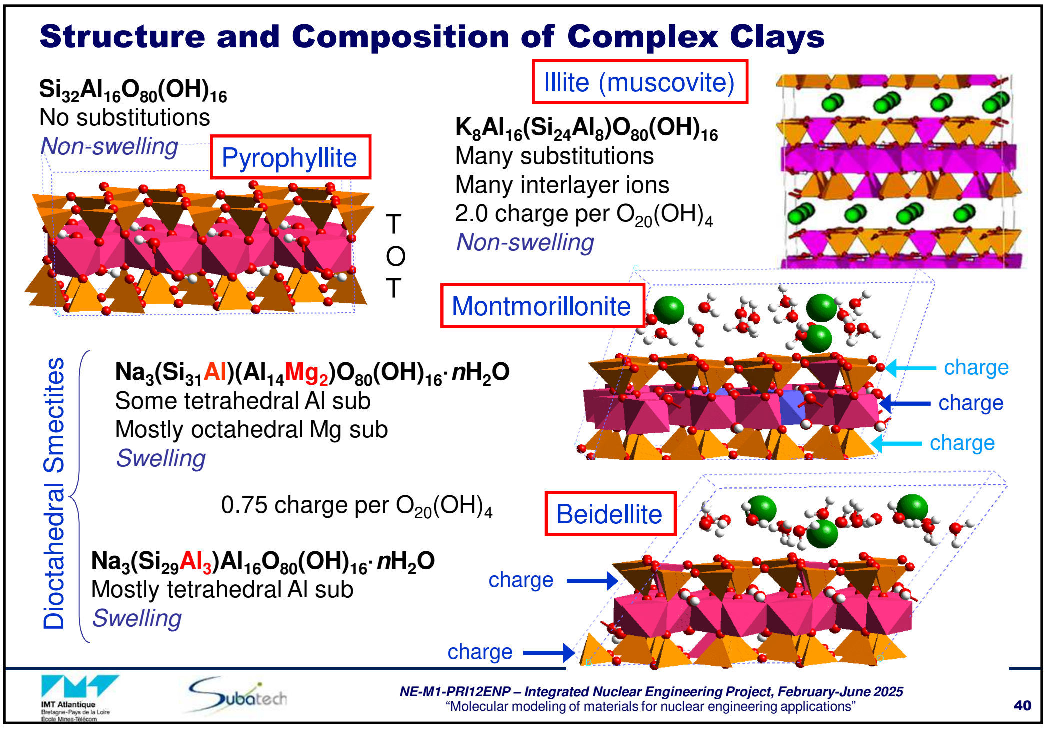
- It has been determined in batch and diffusion experiments with COx samples that organic acids are mobile
- There is a significant degree of irrerversible adsorption, even leading to a complete saturation of the adsorption sites
- There is significant effect of Ca^{2+} on these processes
- Organic molecules can be a potential vector in the transport of radionuclides in COx formations

(D.Durce, PhD thesis, EMN, SUBATECH, 2010)

formate, acetate, propionate, lactate

maleate phtalate adipate

NOM, humic substances



Structure and Composition of Complex Clays

$Si_{32}Al_{16}O_{80}(OH)_{16}$
No substitutions
Non-swelling

Pyrophyllite

Illite (muscovite)

$K_8Al_{16}(Si_{24}Al_8)O_{80}(OH)_{16}$
Many substitutions
Many interlayer ions
2.0 charge per $O_{20}(OH)_4$
Non-swelling

Montmorillonite

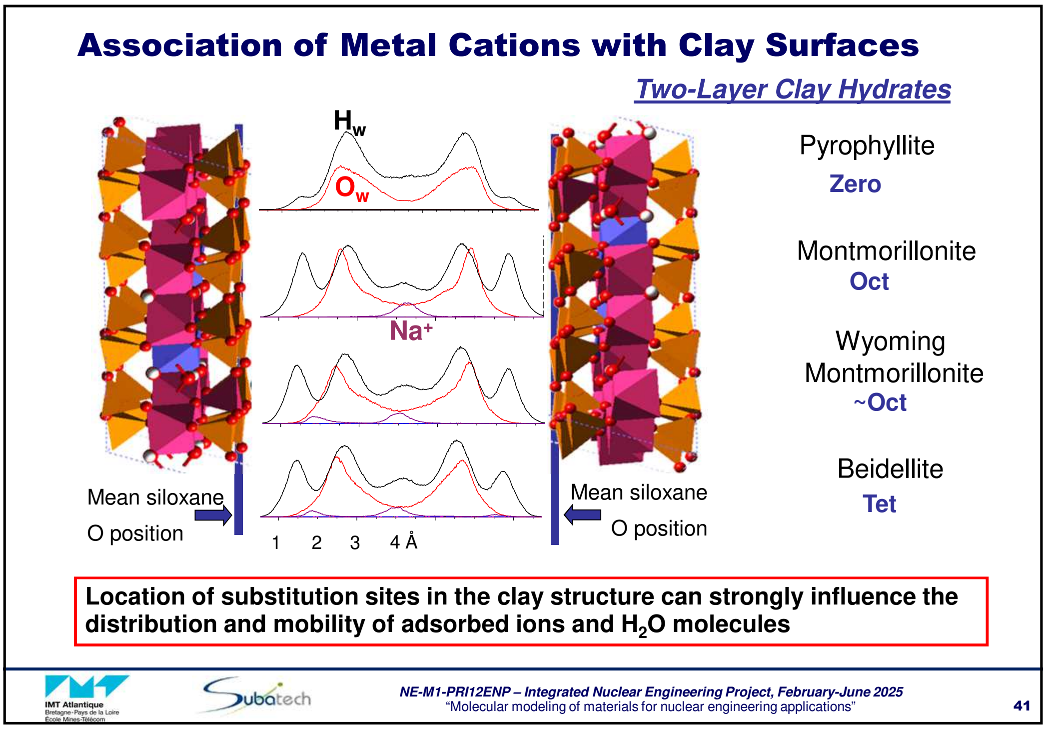
Dioctahedral Smectites

$Na_3(Si_{31}Al)(Al_{14}Mg_2)O_{80}(OH)_{16}\cdot nH_2O$
Some tetrahedral Al sub
Mostly octahedral Mg sub
Swelling

0.75 charge per $O_{20}(OH)_4$

Beidellite

$Na_3(Si_{29}Al_3)Al_{16}O_{80}(OH)_{16}\cdot nH_2O$
Mostly tetrahedral Al sub
Swelling



Association of Metal Cations with Clay Surfaces

Two-Layer Clay Hydrates

Pyrophyllite
Zero

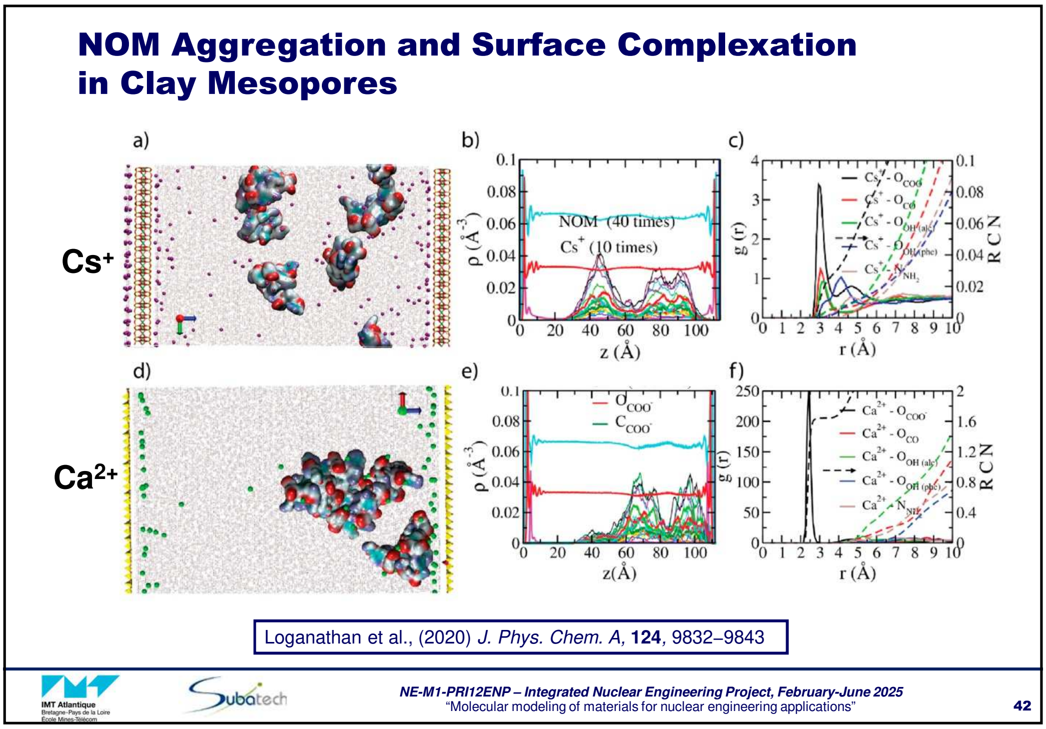
Montmorillonite
Oct

Wyoming
Montmorillonite
~Oct

Beidellite
Tet

Location of substitution sites in the clay structure can strongly influence the distribution and mobility of adsorbed ions and H_2O molecules

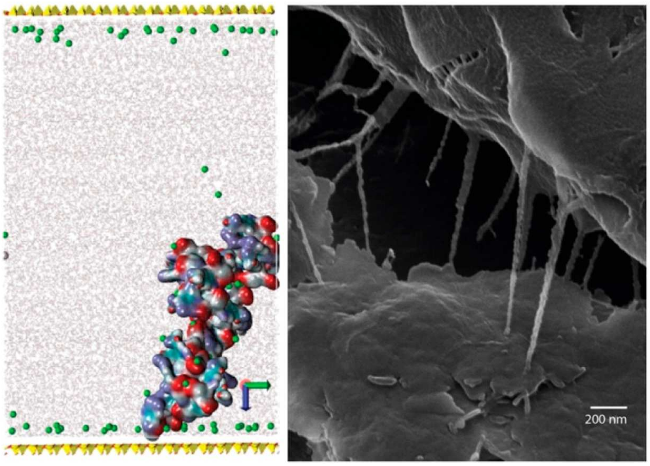
---



NOM Aggregation and Surface Complexation in Clay Mesopores

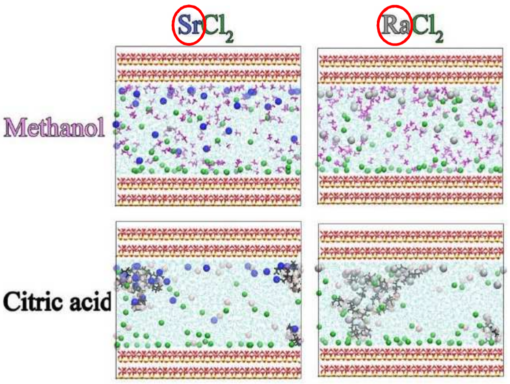
Loganathan et al., (2020) *J. Phys. Chem. A*, **124**, 9832–9843

NOM Aggregation and Surface Complexation in Clay Mesopores



Loganathan et al., (2020) *J. Phys. Chem. A,* **124**, 9832–9843

Naturally Occurring Radioactive Materials (NORM): Aggregation with Organics in Clay Mesopores

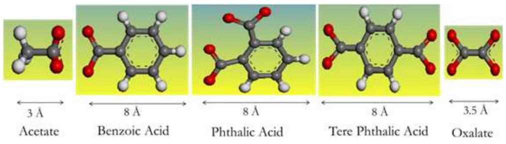


Papavasileiou et al., (2018)
J. Phys. Chem. C, **122**, 17170-17183

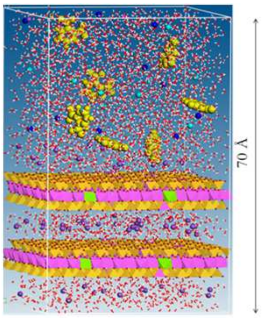
- Snapshots of the equilibrated water-based fracturing fluids with methanol and citric acid additives in kaolinite mesopores
- $SrCl_2$, and $RaCl_2$ salts at approximately 0.3 M concentration

Effects of Small Organic Molecules on the Adsorption and Mobility of Radionuclides in Clay Materials (COx)

PhD projects of D.Banerjee (2017-2021) and Jakub LICKO (2022-2025)



- Fundamental molecular scale understanding of the physical and chemical mechanisms controlling the interactions between radionuclides (Cs^+, Sr^{2+}, UO_2^{2+}, Ni^{2+}), organic molecules and clay rock
- This projects are mainly focused on the computational molecular modeling effects of small organic molecules on the adsorption and transport of radionuclides in clay
- In addition to the interactions with basal surfaces of clay, the interactions with clay nanoparticle edges are also thoroughly quantitatively studied in the projects.



Questions for the final paper / report on one of the ~26 topics, e.g., 1 – clays; 2 – cement; 3 – TiO_2 surfaces; 4 – corrosion; 5 – organics, etc. https://moodle.imt-atlantique.fr/course/view.php?id=407#section-11

(Please use only as a guidance)

- What molecular modeling method was used and why?
- Was it a fully atomistic simulations, or some simplified models were used?
- What other approximations were used in the modeling?
- What was the number of particles in the simulations? Was it big enough for the specific problem? Was it small enough to make the simulations computationally efficient?
- How long-range electrostatic interactions were handled in the simulations? Was it important for the given problem?
- What kind of boundary conditions were applied to the simulation box? Why?
- What properties of the system were calculated from the molecular simulation?
- Make a qualitative assessment of the accuracy for the calculated properties given the number of atoms in the simulated system and the duration of the simulation.
- What other properties would you additionally calculate from the same simulations for the same system?
- Formulate 2 or 3 strong points of the given molecular simulation paper and 2 or 3 weak points of the paper.