



Role of alkali cation in early stage of oligomerization: a molecular dynamics study



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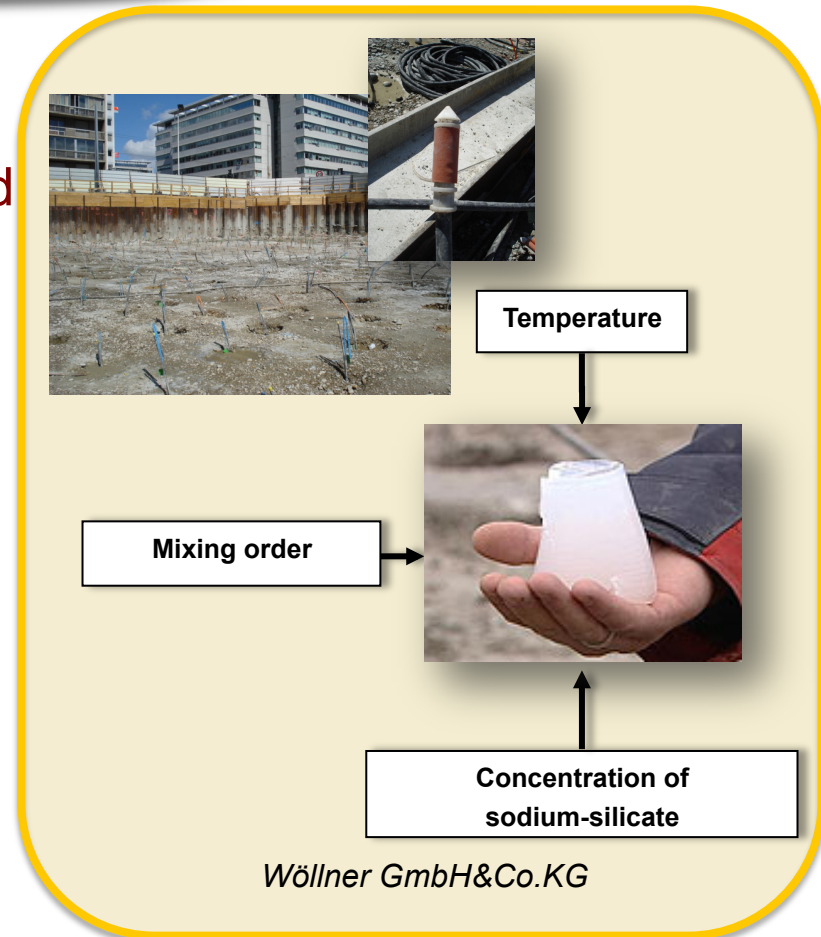
La Grande Motte, France
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Context

- ❑ Solutions of activation (= **concentrated alkali media**) of alumino-silicates are interfacial media involved in many industrial processes and building
- ❑ Complex formulation
- ❑ Alkali impacts gelation process and drives final properties of the gel [1]

Objectives

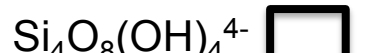
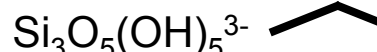
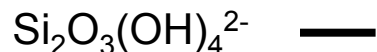
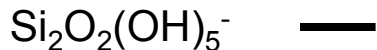
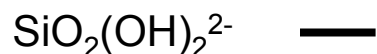
- ❑ Study ion-ion interactions in the early stage of oligomerization
- ❑ Predict structure of the system to improve the formulation



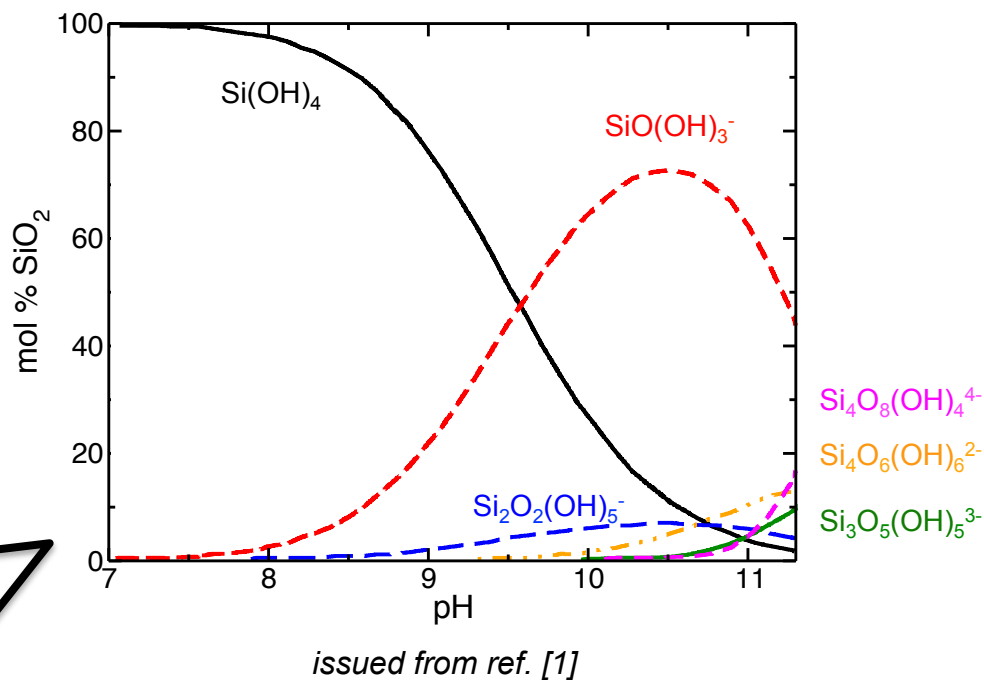
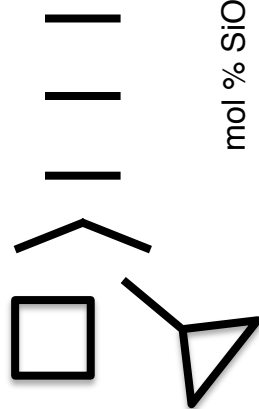
Complex media

Media impacted by the concentration and the nature of the alkali (Li^+ , Na^+ , K^+ and Cs^+)

Formation of anionic species:



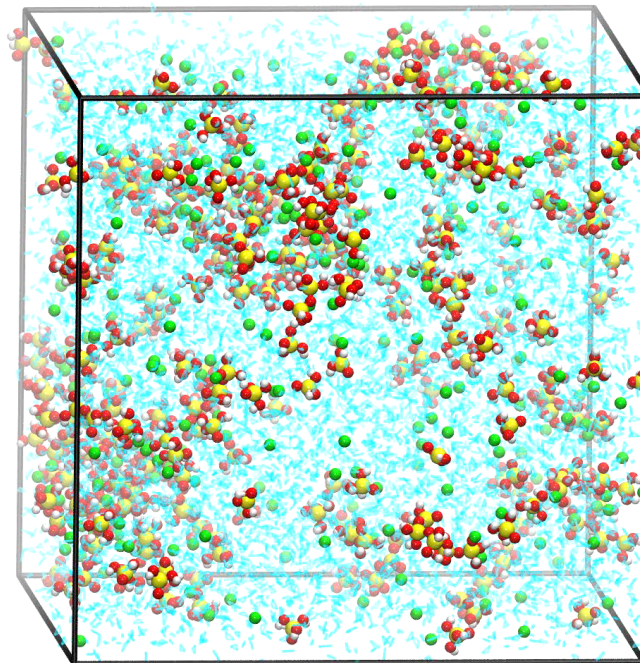
etc...



Speciation of silicate in aqueous phase is complexed [2]: huge variety of structure, total charge of oligomers

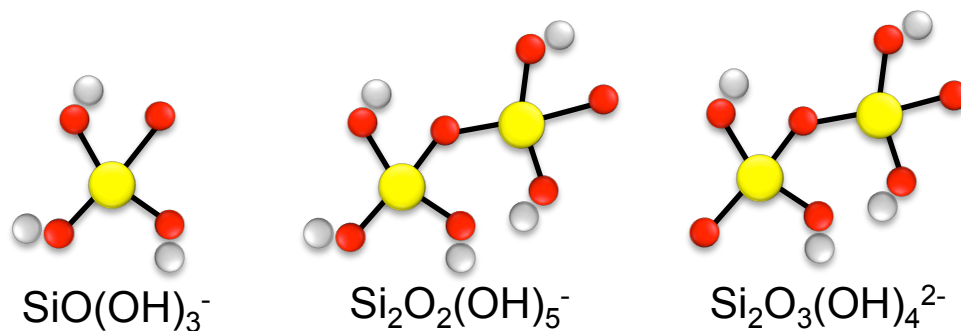
Theoretical approach

- ❑ Classical Molecular Dynamics allow to simulate silicate precursor solutions
- ❑ No formation of covalent bonds in Classical Molecular Dynamics
- ❑ Development of a force field (issued from ref. [1]) for silicate oligomers:



Construction of simulation boxes

- ❑ Silicate solutions at 2.0 mol kg^{-1} of [Si] with a ratio $[\text{Si}]/[\text{Na}^+] = 1$
- ❑ Hydroxide are added for a total charge equal to 0

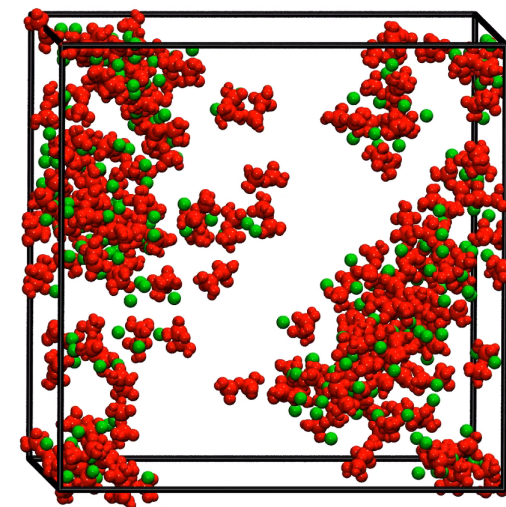
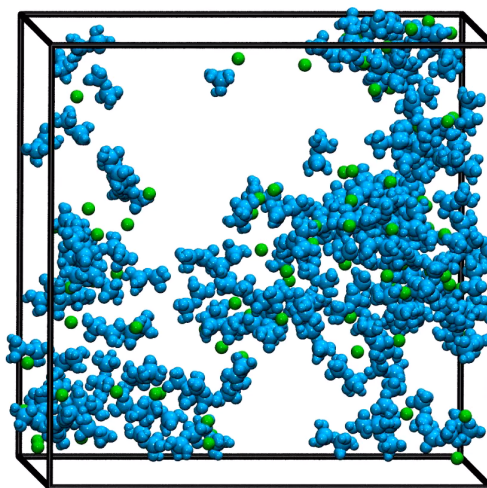
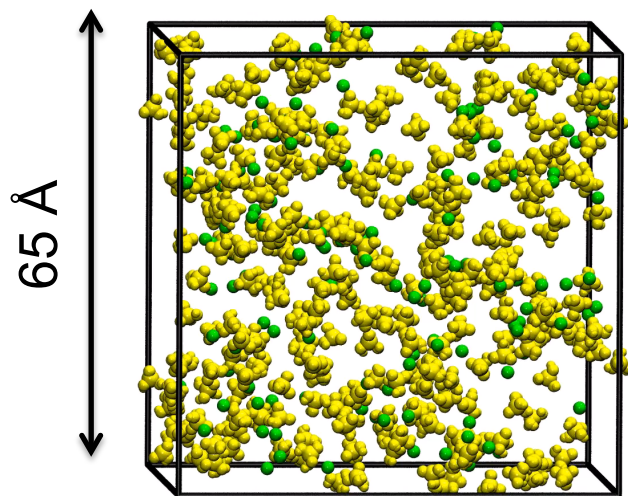


- Study of each oligomer separately

300 Na⁺
 300 SiO(OH)₃⁻
 8236 H₂O

300 Na⁺
 150 Si₂O₂(OH)₅⁻
 8236 H₂O
 150 OH⁻

300 Na⁺
 150 Si₂O₃(OH)₄²⁻
 8236 H₂O

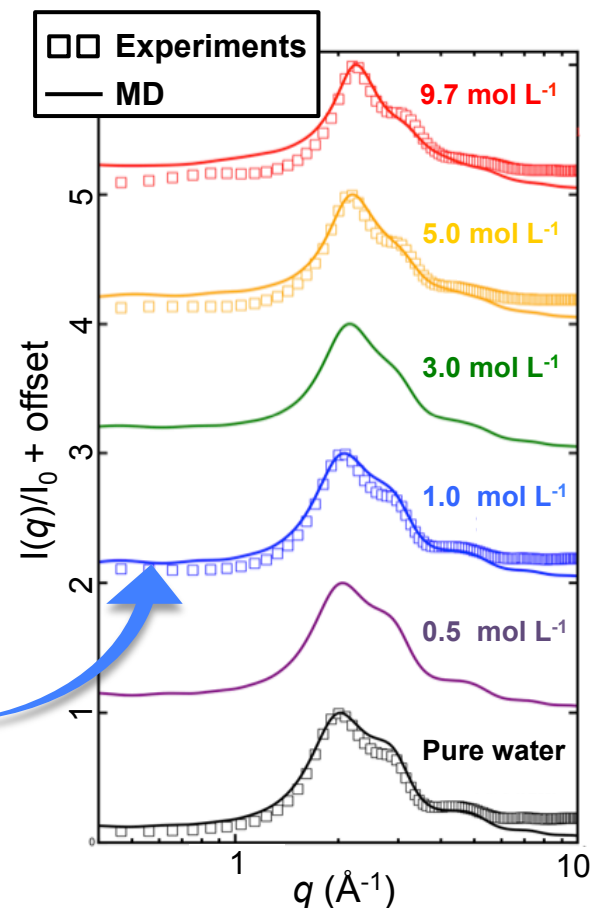
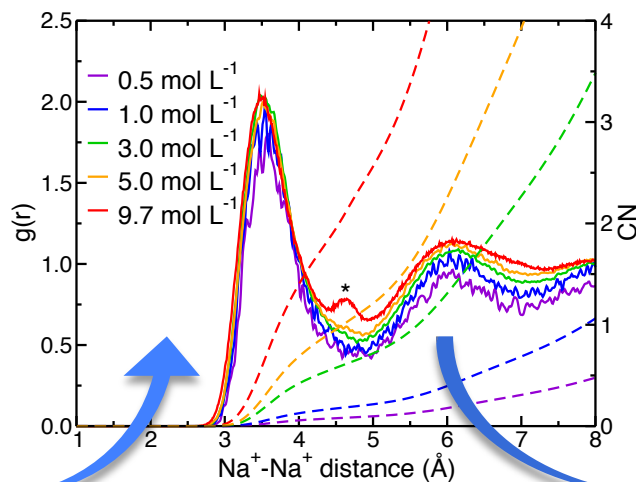
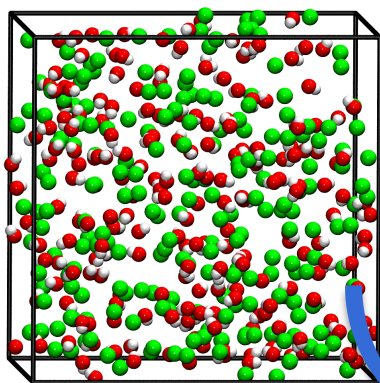


- “Homogenous” structure for the monomer solutions
- Dimer solutions tend to the demixtion

Example for NaOH solution

$$S_{\alpha\beta}(q) = \delta_{\alpha\beta} + \sqrt{\rho_{\alpha}\rho_{\beta}} \text{FT}_{3\text{D}}(g_{\alpha\beta}(r) - 1)$$

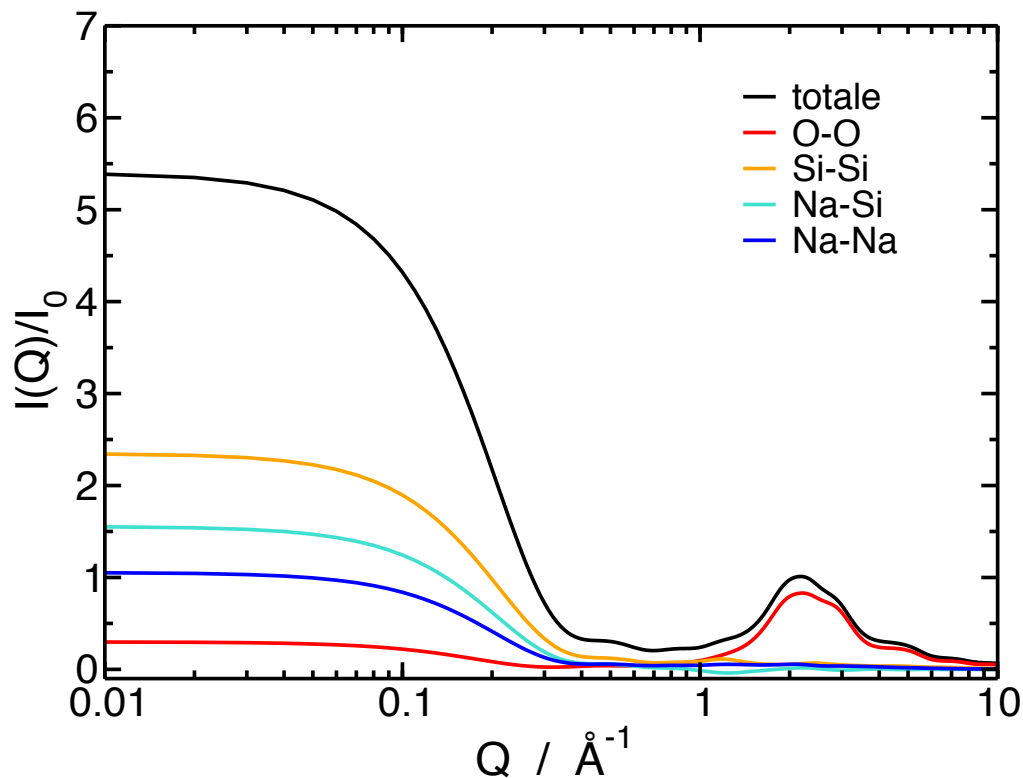
$$I(q) = \sum_{\alpha} \sum_{\beta} f_{\alpha}(q) f_{\beta}(q) \sqrt{N_{\alpha} N_{\beta}} S_{\alpha\beta}(q)$$



NaOH (ex. 5.0 mol L⁻¹)

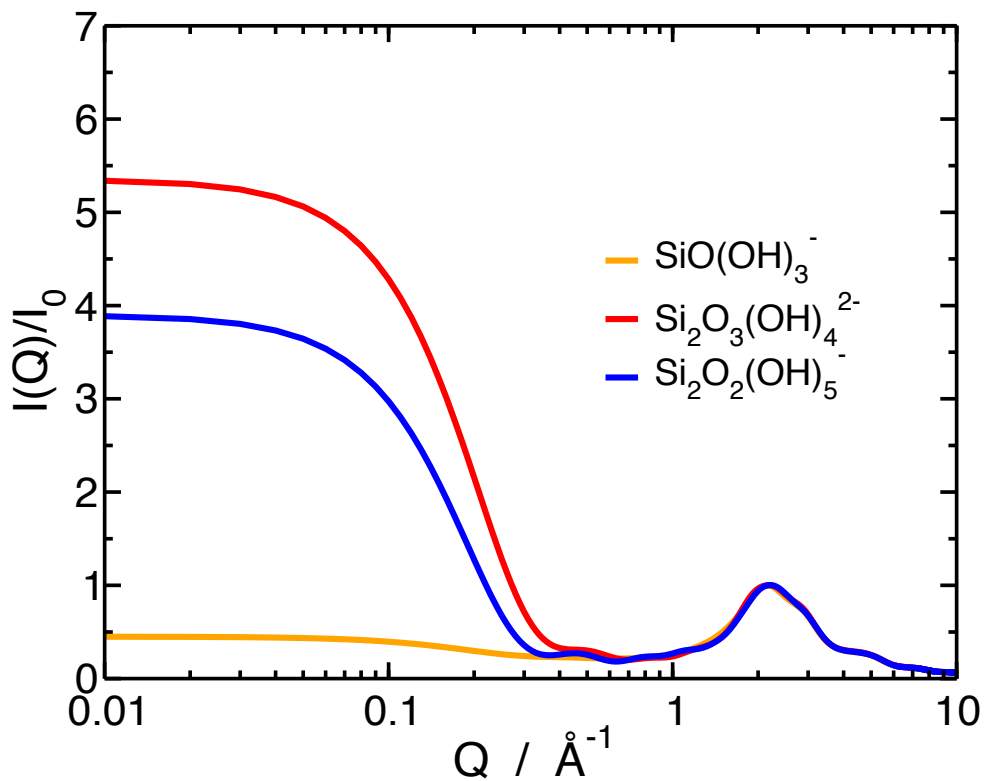
SWAXS spectra

150 Si₂O₃(OH)₄²⁻
 300 Na⁺
 8263 H₂O



- Double peak around 2-3 Å⁻¹ is characteristic of the solvent
- Rise at small angle due to aggregation
- O-O major for Q > 1 Å⁻¹
- Si-Si interaction major for Q < 1 Å⁻¹
- Na-Si and Na-Na Interactions are important

Comparison of WAXS spectra



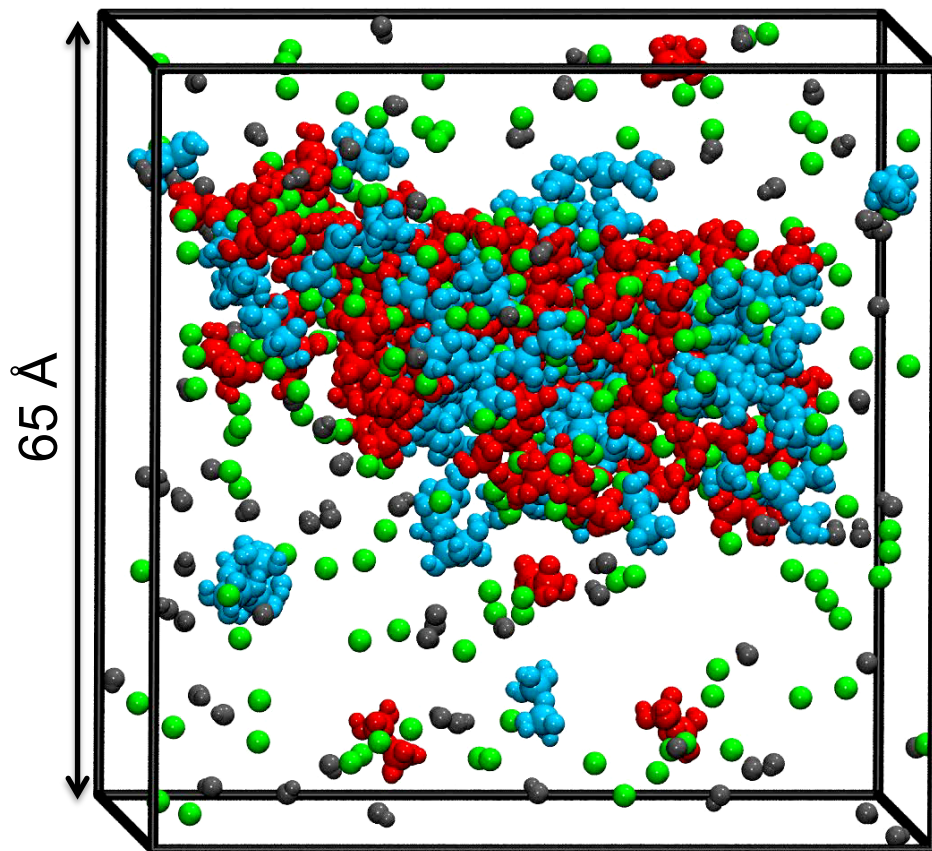
- Same intensity for $Q > 1 \text{ \AA}^{-1}$
- Intensity of the peak at 0.45 \AA^{-1} different
- Different rise at small angle



Monomer: disperse media
Dimer: phase separation

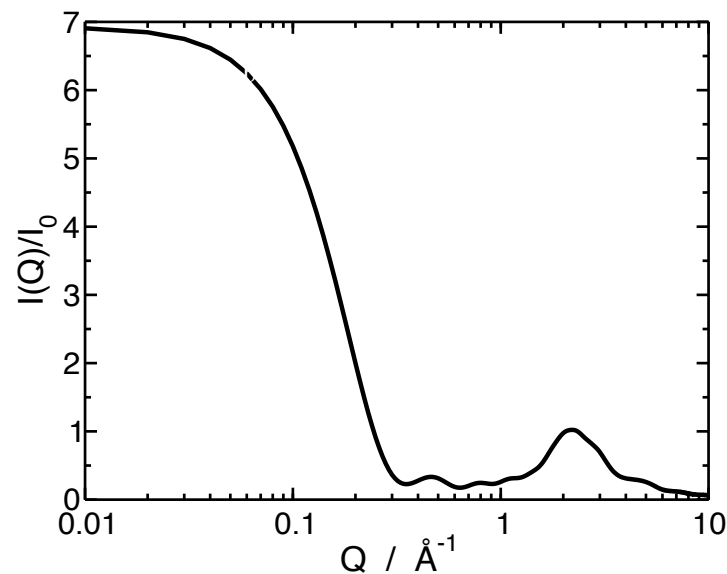
WAXS spectra

300 Na ⁺	75 Si ₂ O ₃ (OH) ₄ ²⁻
75 Si ₂ O ₂ (OH) ₅ ⁻	150 OH ⁻ = 150



Dimer mixture after 26 ns

Formation of a big aggregate



Adsorption of Na⁺ on the aggregate surface

OH⁻ in the bulk

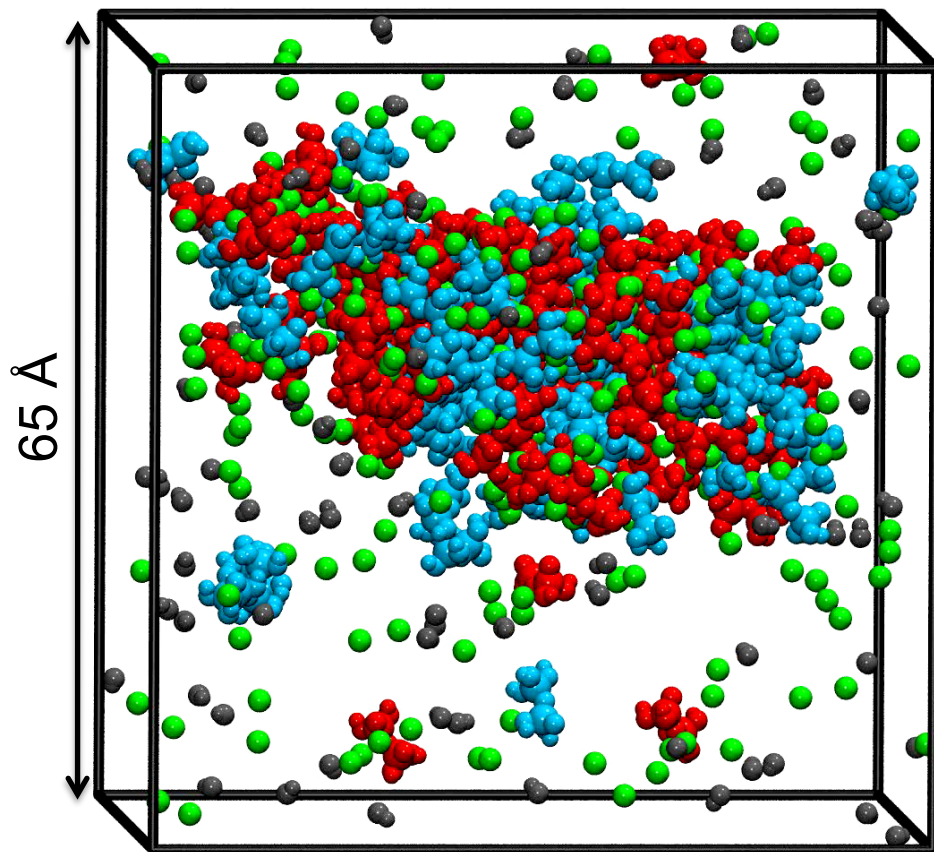
WAXS

300 Na⁺

75 Si₂O₂(OH)₅⁻

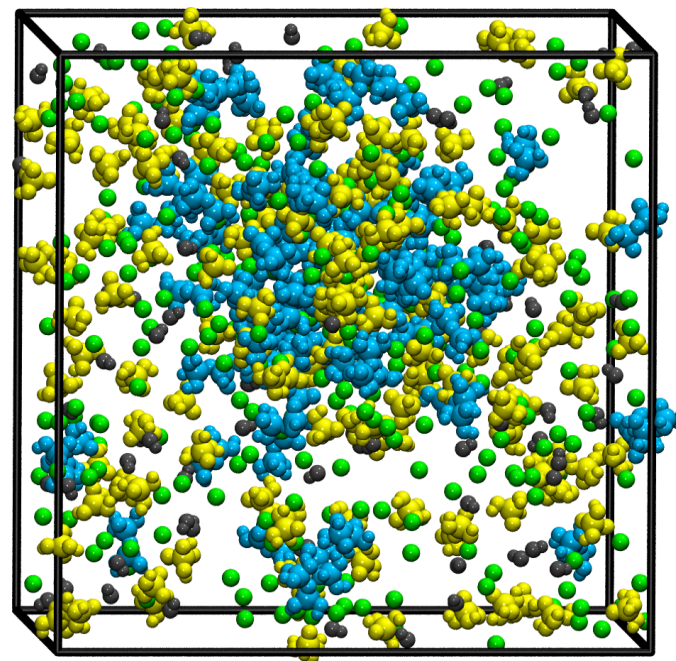
75 Si₂O₃(OH)₄²⁻

150 OH⁻ = 150



Dimer mixture after 26 ns

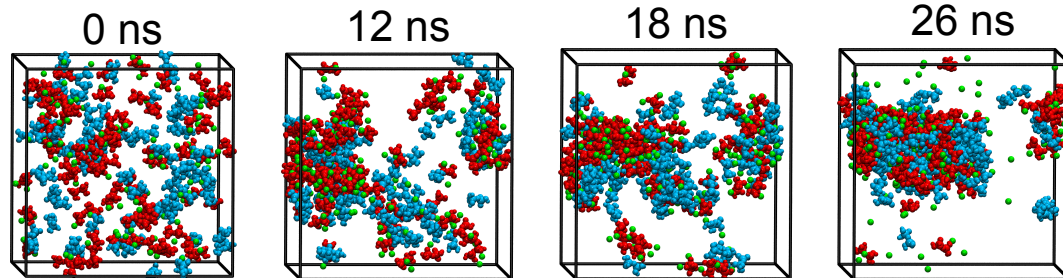
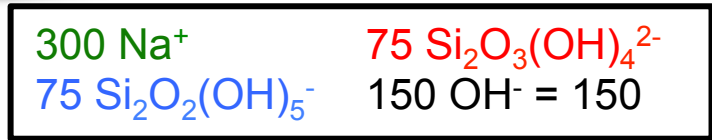
By replacing Si₂O₃(OH)₄²⁻ by 2 Si(OH)₃⁻



Different structure of the solution

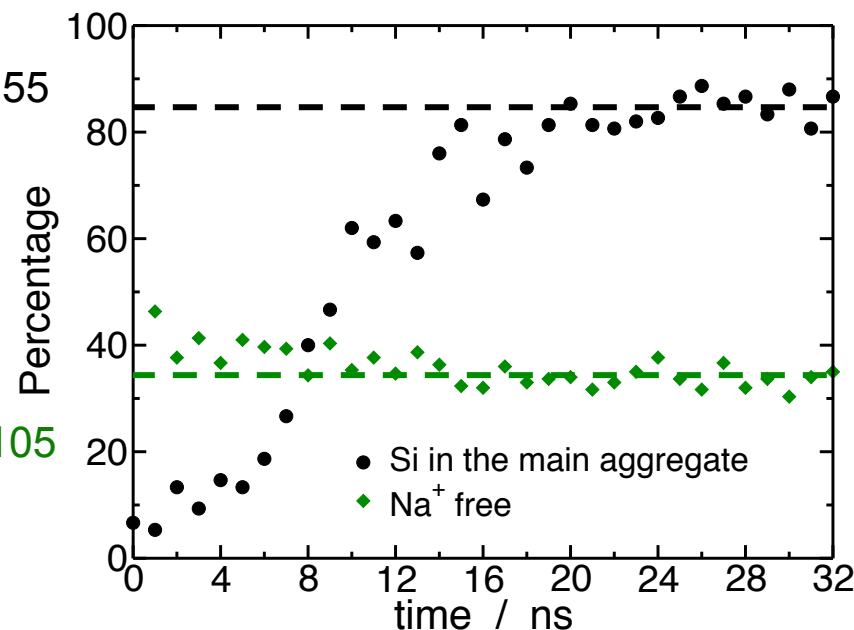
Main aggregate evolution

- ❑ Criteria of affiliation in the same aggregate: Si-Si distance less than 5.7 Å
- ❑ Increase of the size during the simulation
- ❑ Stabilization of the size at 22 ns around (85 % of the Si)
- ❑ Slow decrease of the free Na⁺ concentration
- ❑ Around 40 % of the Na⁺ are in the bulk phase



$N_{Si} = 255$

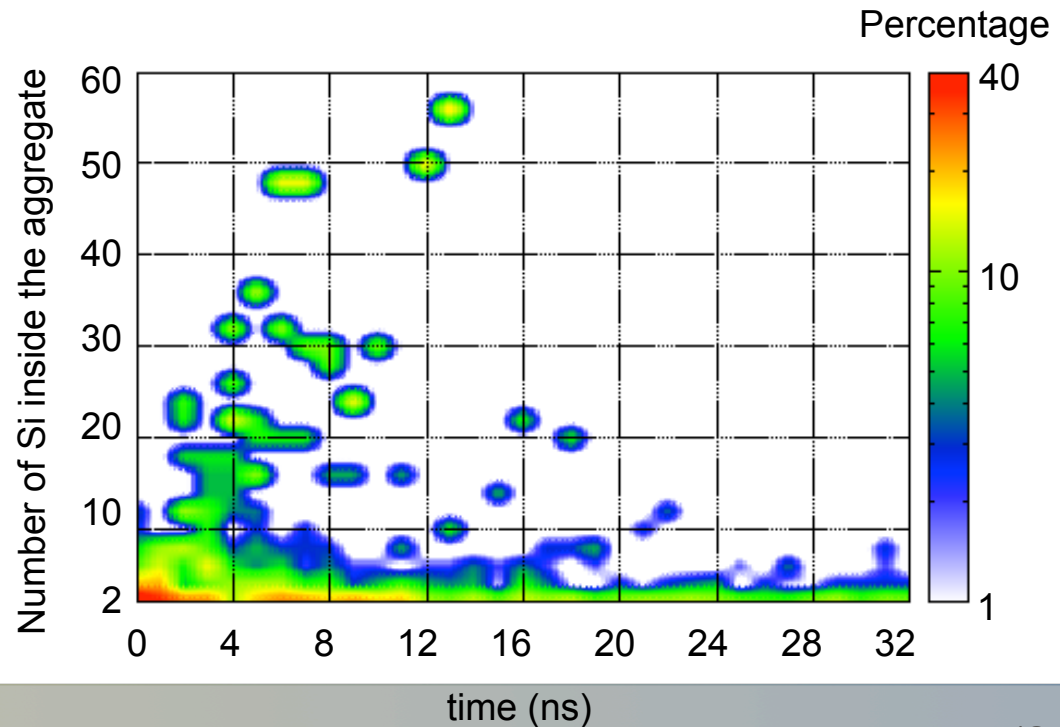
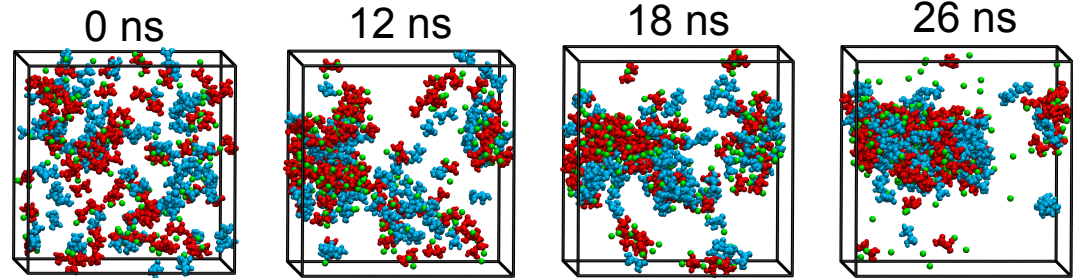
$N_{Na} = 105$



Bulk phase evolution

- ❑ Evolution of the silicates oligomers without the main aggregate
- ❑ Dimers and small cluster predominant at the beginning
- ❑ Time to form the biggest aggregate : 13 ns
- ❑ After 24 ns equilibrium between dimers in the aggregate and the bulk

300 Na⁺ 75 Si₂O₃(OH)₄²⁻
 75 Si₂O₂(OH)₅⁻ 150 OH⁻ = 150

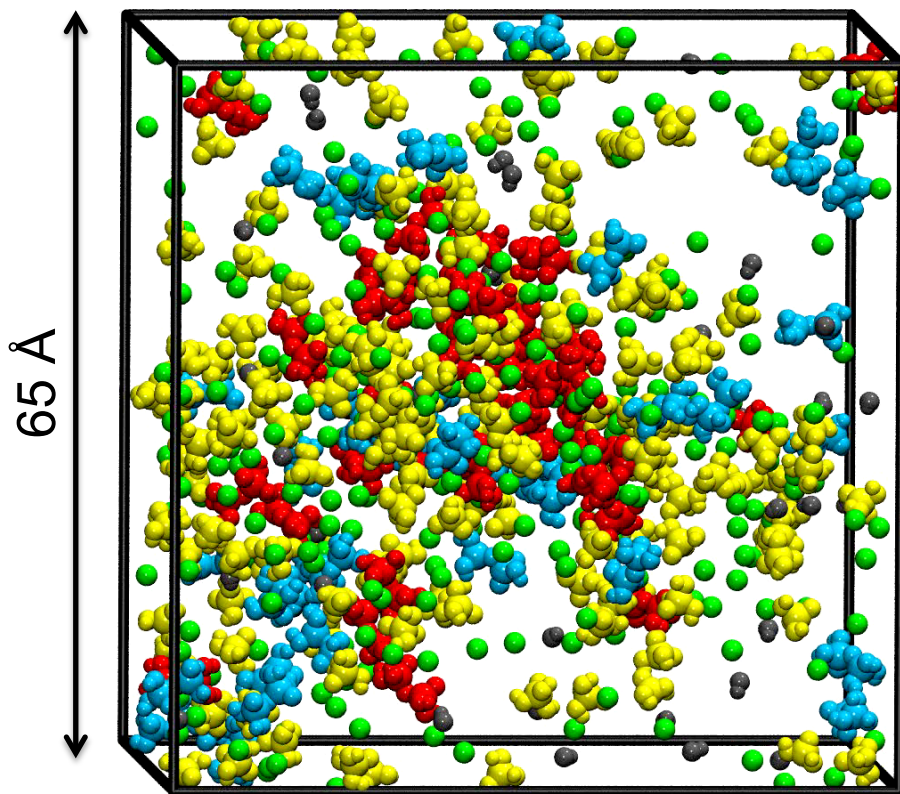


Spectres WAXS

300 Na⁺
37 Si₂O₂(OH)₅⁻

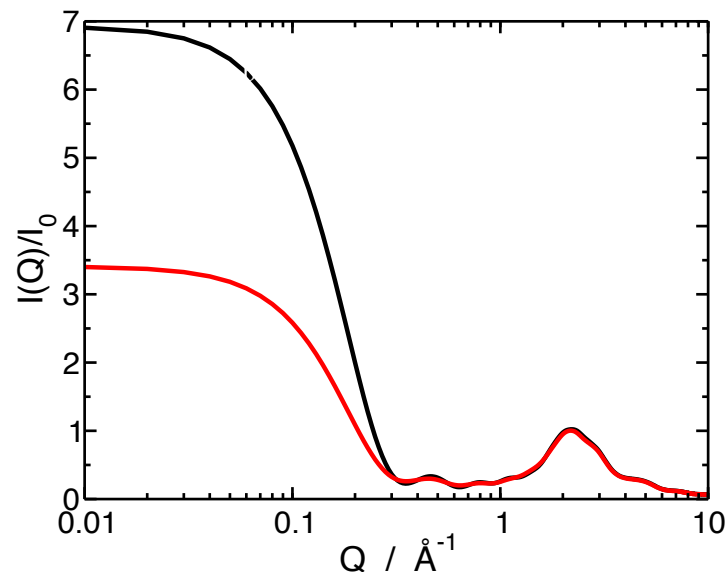
37 Si₂O₃(OH)₄²⁻
37 OH⁻

152 SiO(OH)₃⁻



Mixture of monomers and dimers after 20 ns

Polydispersity of aggregates sizes



SiO(OH)₃⁻ destabilize the aggregate, gain of entropy

Adsorption of Na⁺

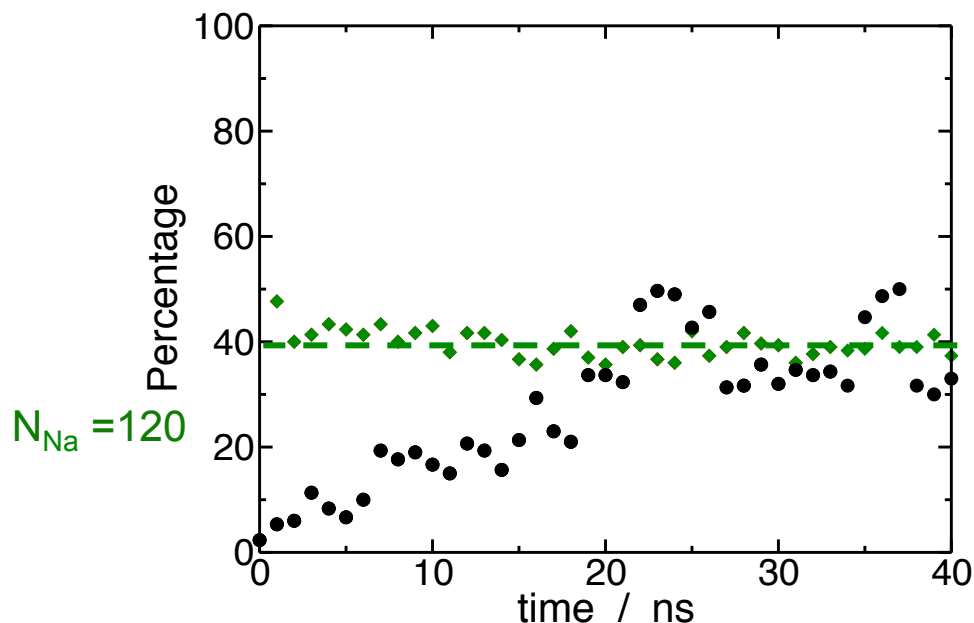
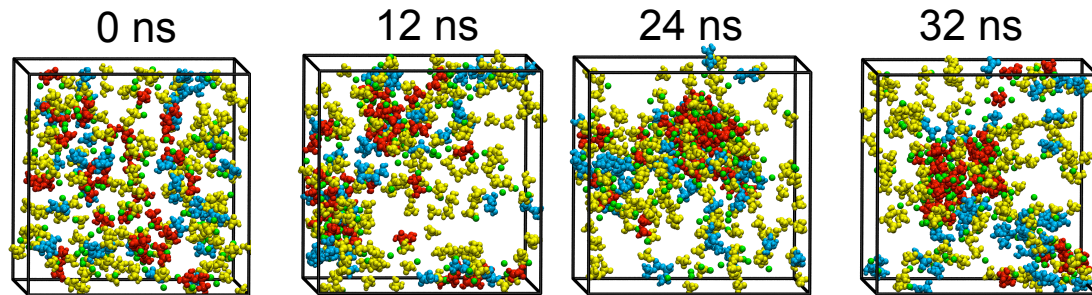
Main aggregate evolution

300 Na⁺
37 Si₂O₂(OH)₅⁻

37 Si₂O₃(OH)₄²⁻
37 OH⁻

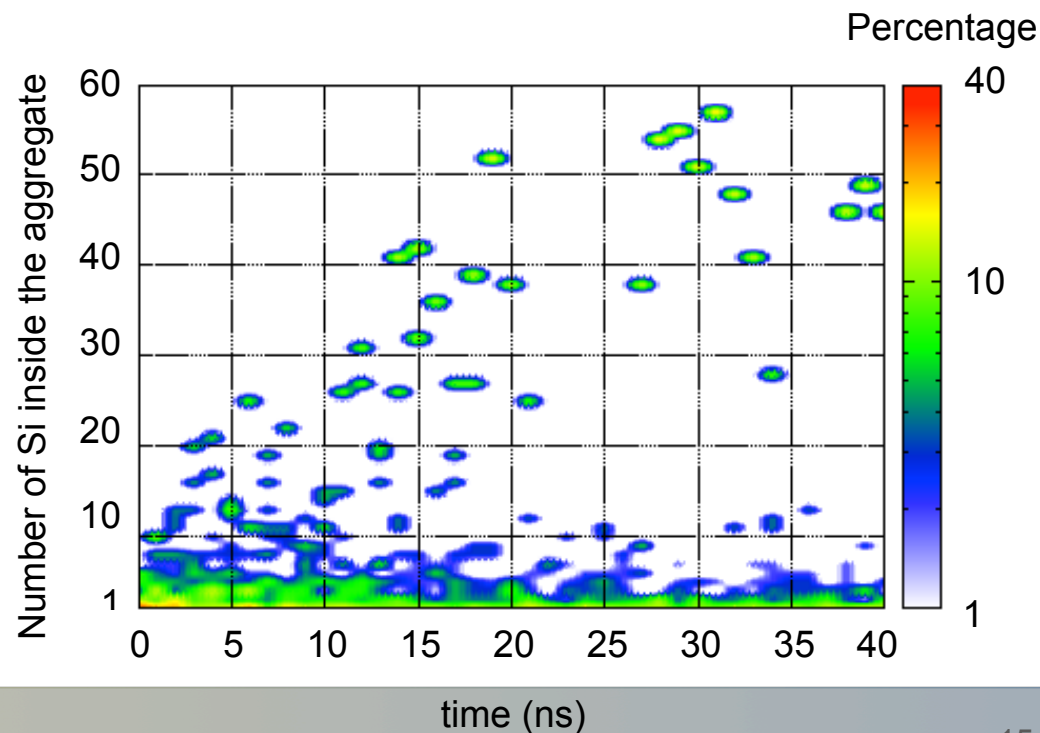
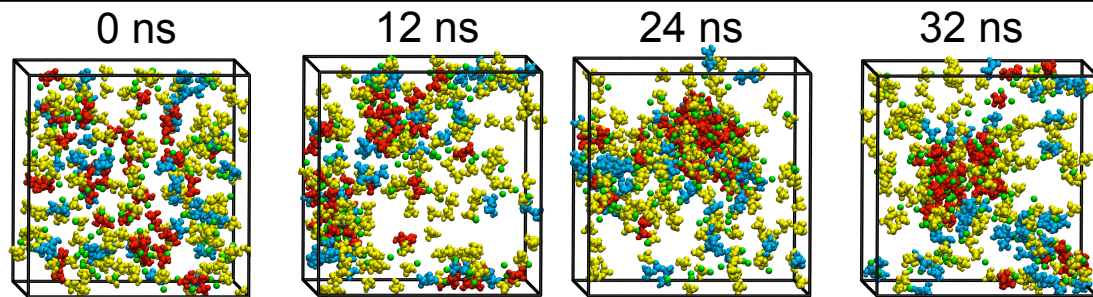
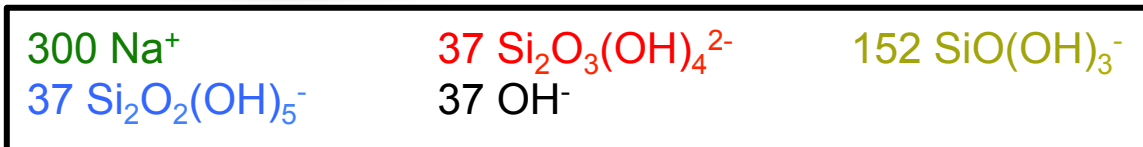
152 SiO(OH)₃⁻

- ❑ Criteria of affiliation in the same aggregate: Si-Si distance less than 5.7 Å
- ❑ Increase of the size during the simulation
- ❑ Slow diminution of the free Na⁺ concentration
- ❑ Around 42 % of the Na⁺ are in the bulk phase



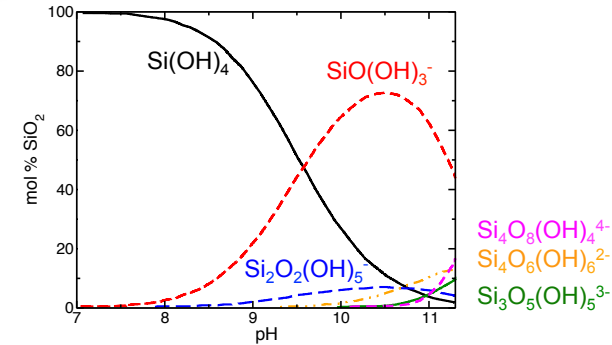
Bulk phase evolution

- Evolution of the silicates oligomers without the main aggregate
- Oligomers and small cluster dominants at the beginning
- Increase of cluster size
- After 20 ns equilibrium between one and two big aggregates



Conclusions

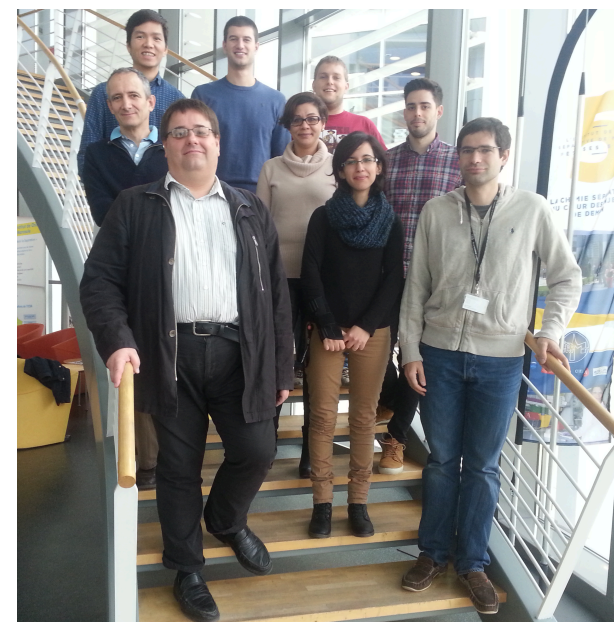
- Structure of the solution depends on oligomer composition
 - Dimers → demixtion of the solution
 - Monomers → destabilization of the aggregate, entropic effect
- Similar behaviours of Na^+ in each simulation, provide a **buffer media** with hydroxide
- Weak interactions between silicate and hydroxide



Outlook

- Comparison to experimental solutions
- Simulations with various ratio of $[\text{Si}]/[\text{Na}]$ and change the alkali nature

ANR DYNAMISTE:



Laboratoire de Modélisation Mésoscopique et Chimie Théorique (LMCT)



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Thanks for your attention!