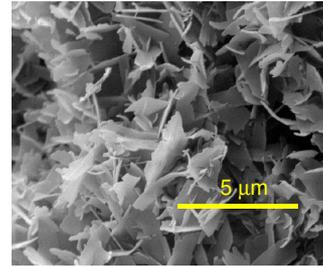
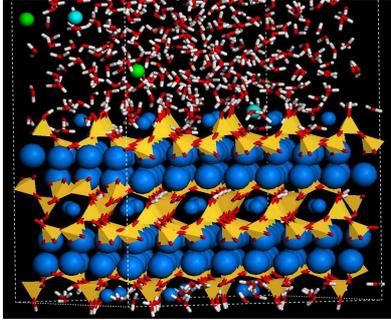


Molecular Modeling of Materials for Nuclear Waste Disposal Applications

Lecture 7 - (Cement Materials and Their Interaction with Metal Ions and Water)

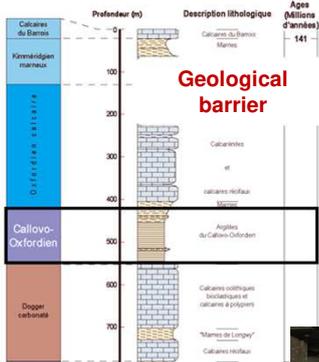
Andrey G. Kalinichev

Laboratoire SUBATECH
IMT-Atlantique



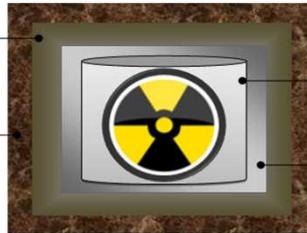
E-mail: kalinich@subatech.in2p3.fr
<https://www.imt-atlantique.fr/en/person/andrey-kalinichev>

Geological Nuclear Waste Disposal



Geological barrier

Multiple barriers around the waste package



Waste package

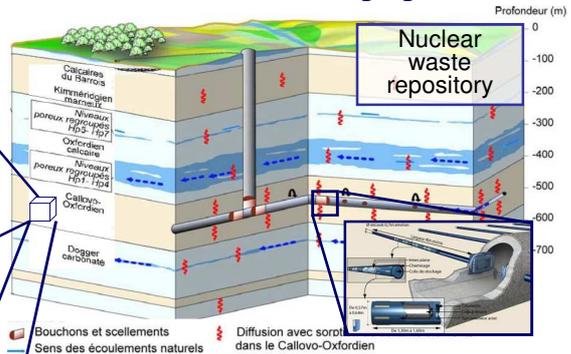
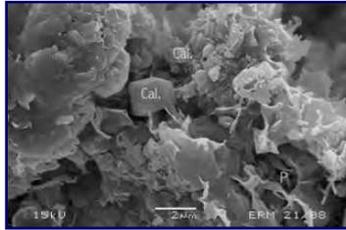
Engineered barrier (steel, concrete)



Disposal cell



Mineral Composition of Callovo-Oxfordian Clayey Formations



- 41% clay (illite, smectite and interstratified I/S)
- 31% calcite
- 25% quartz and feldspar
- 3% other minerals
- ~1% organic matter



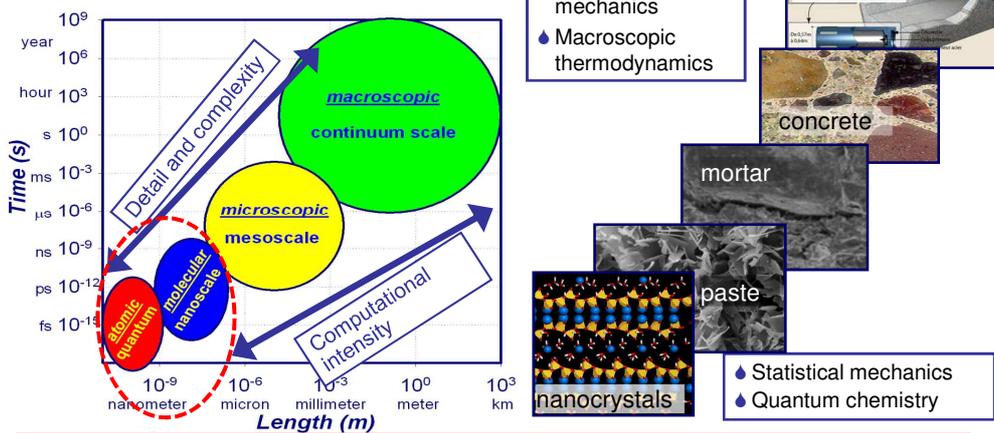
Image source: ANDRA



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 "Molecular modeling of materials for nuclear engineering applications"

3

Time and Length Scales of Cement Materials Modeling



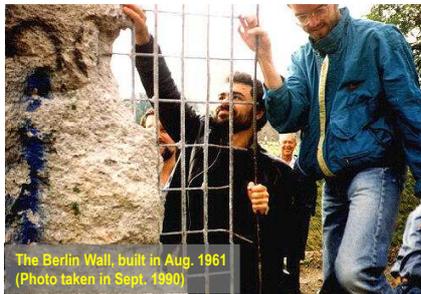
- ◆ Cementitious materials are truly multiscale
- ◆ Need to keep the big picture in mind
- ◆ There are good models for each individual physico-chemical scale
- ◆ The real challenge is to overcome high barriers for linking the models from one scale to another



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 "Molecular modeling of materials for nuclear engineering applications"

4

On the Historical Durability of Cement and Concrete



The Berlin Wall, built in Aug. 1961
(Photo taken in Sept. 1990)



Sept. 1990



May 2009, Grand Rapids, MI, USA



April 2018, Moscow, Russia

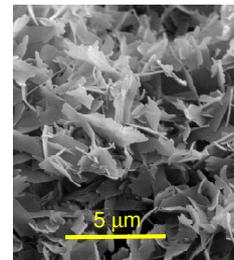
Molecular Modeling of Cement Materials

Current objectives

- ◆ Use statistical mechanics to develop quantitative molecular-level understanding of cement phases, their interfaces, and water in the pores:
 - ◆ Structure and dynamics of aqueous interfacial species
 - ◆ Hydration, adsorption, H-bonding, diffusion
 - ◆ Atomistic mechanisms of interfacial sorption and transport

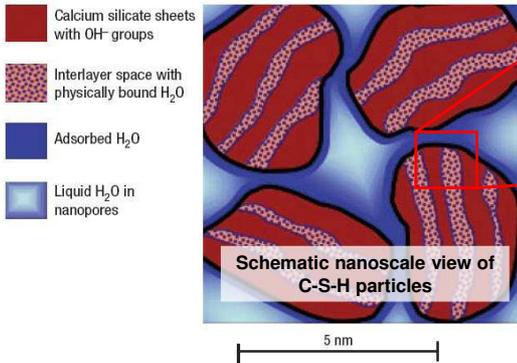
Non-trivial problems

- ◆ Complex crystal structures, low symmetry, variable composition
- ◆ Incompletely and poorly characterized, occur as very fine-grained material
- ◆ Large unit cells, stacking disorder
- ◆ Layered structures with significant electrostatic fields
- ◆ Availability of empirical force-field parameters for realistic molecular modeling

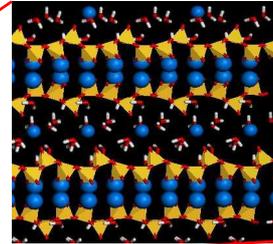


Molecular-Scale Understanding of the Structure of Hydrated Cement

C-S-H: A classic nano-structured material

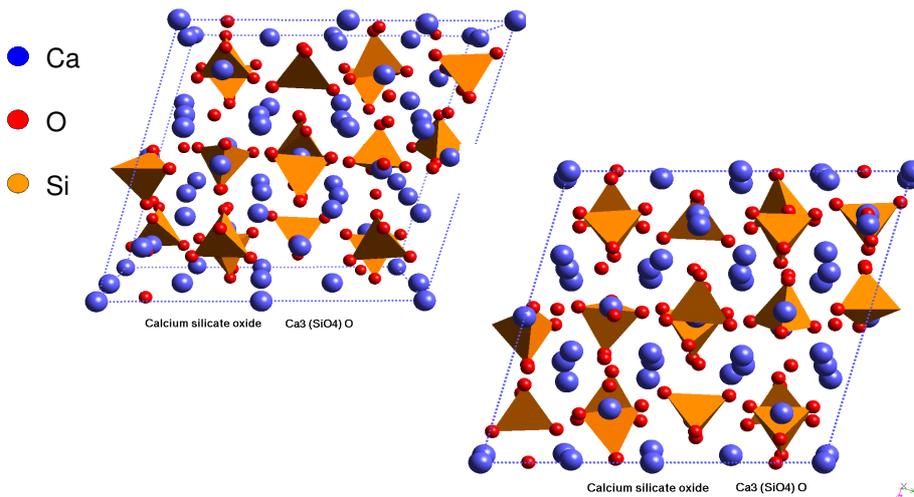


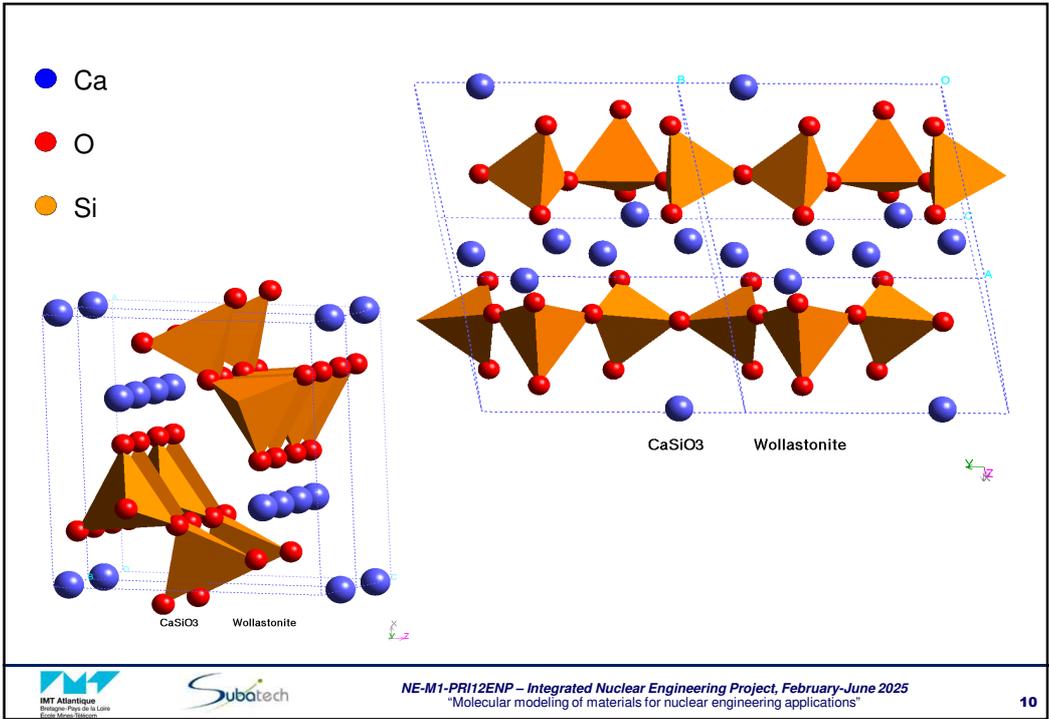
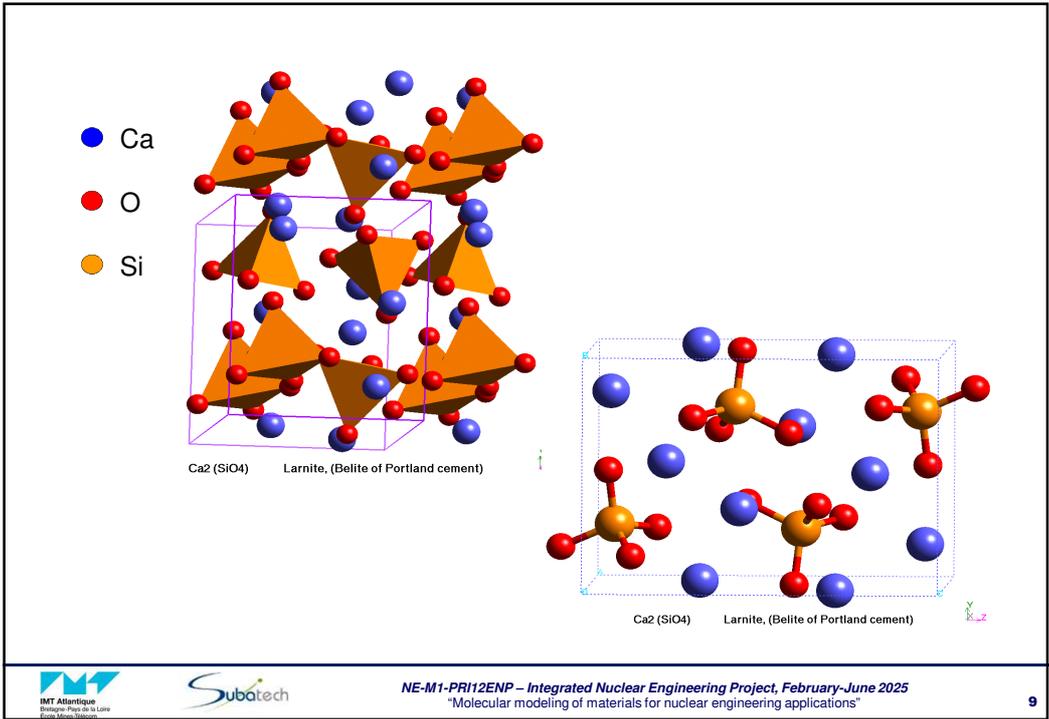
Allen et al., *Nature Materials*, 6, 311-316 (2007)

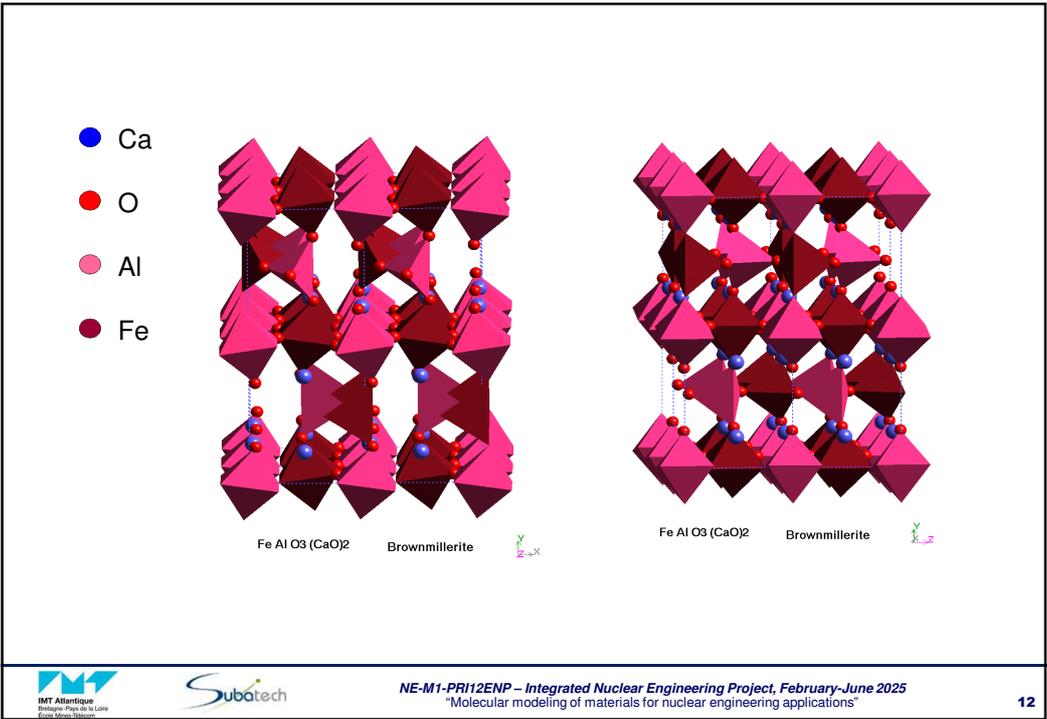
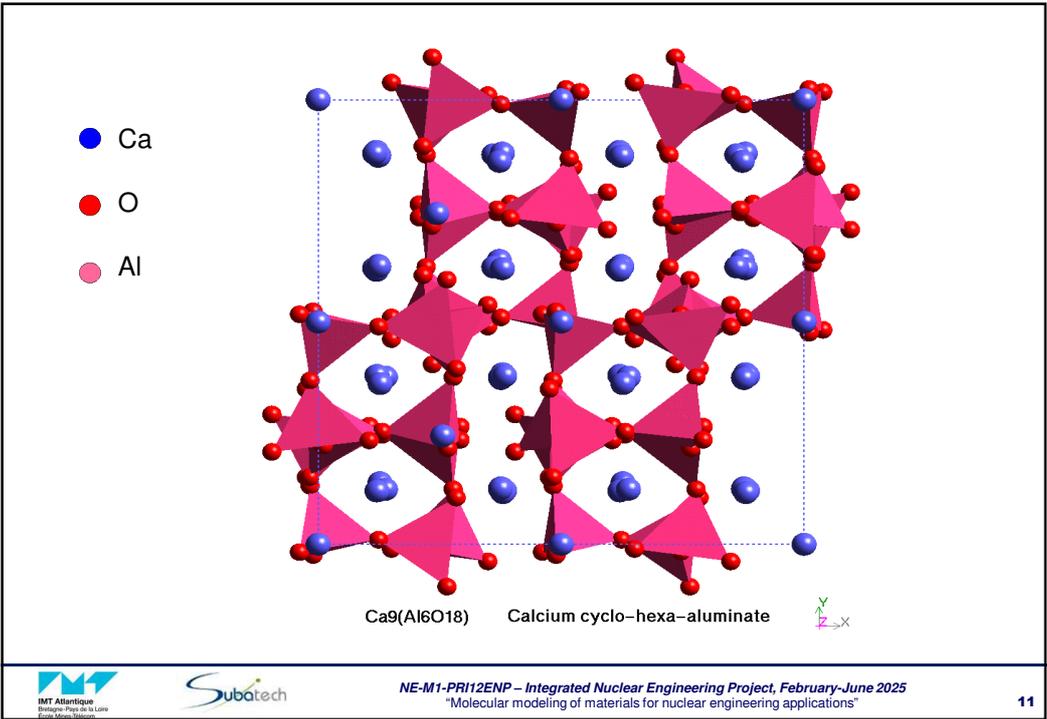


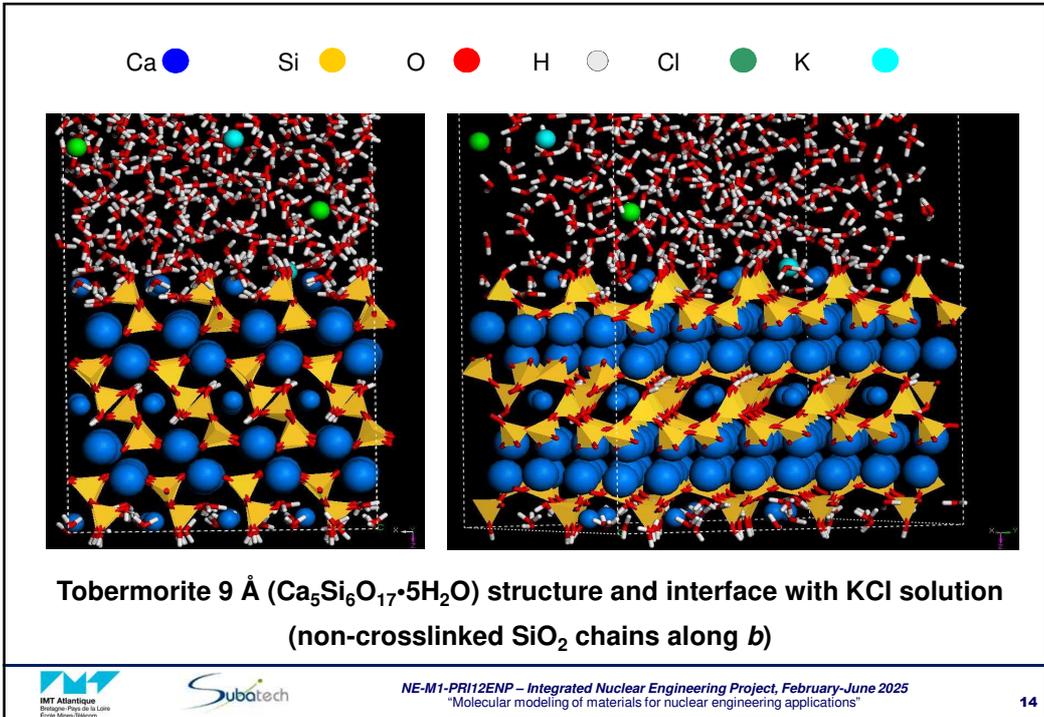
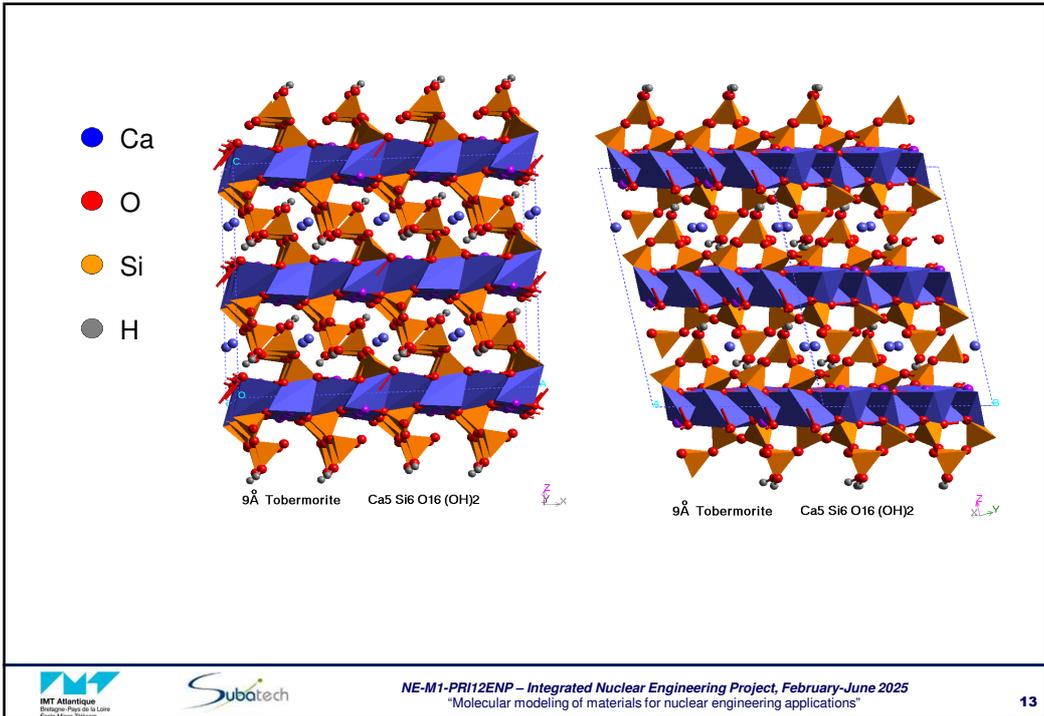
Fundamental Questions

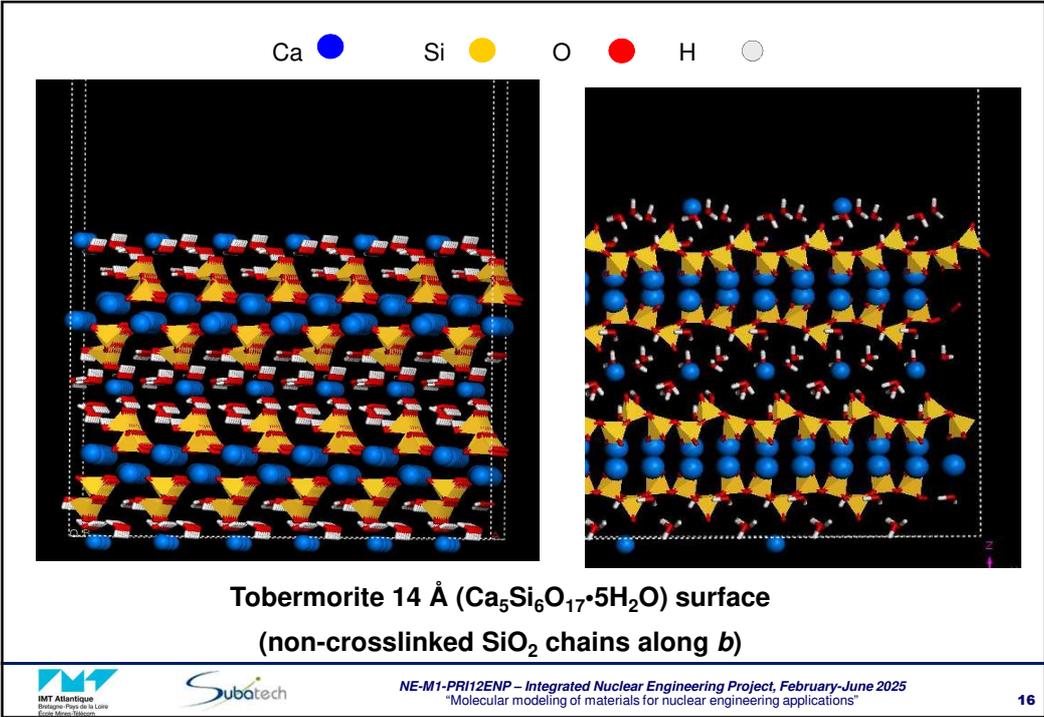
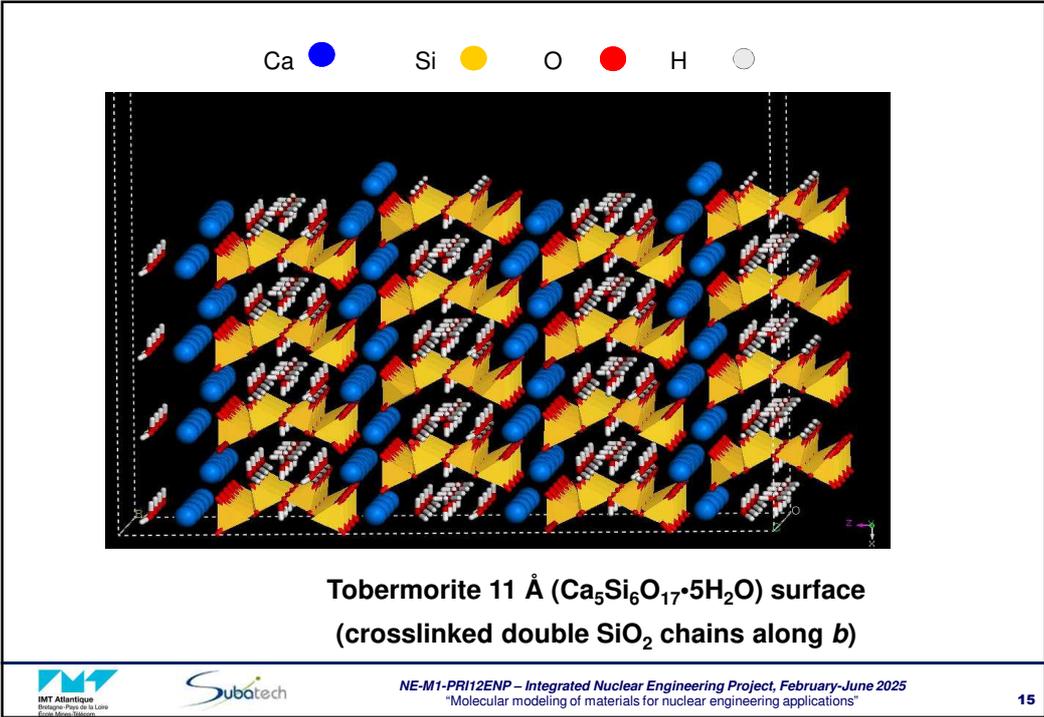
- ◆ Properties of solid-fluid nano-composites
- ◆ Properties of water in confined spaces
- ◆ Precipitation mechanisms?
- ◆ C-S-H structure?
- ◆ Why different morphologies?
- ◆ Why do the particles not coarsen?
- ◆ Role of impurities: e.g., Al?
- ◆ Origin of mechanical properties?



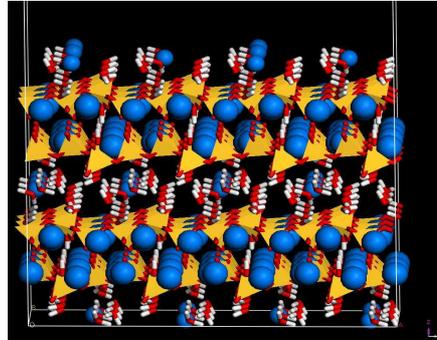
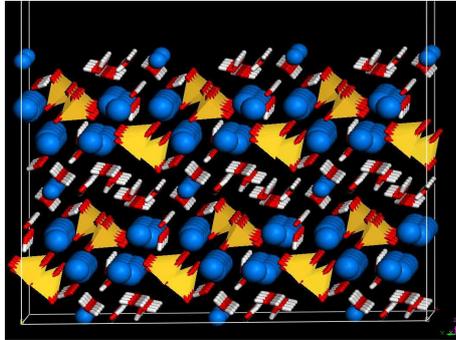








Ca ● Si ● O ● H ●



**Jennite ($\text{Ca}_9\text{Si}_6\text{O}_{18}(\text{OH})_6 \cdot 8\text{H}_2\text{O}$) surface
(non-crosslinked SiO_2 chains along b)**

Progress of Atomistic Modeling of Cement Materials



Cement and Concrete Research

Volume 102, December 2017, Pages 68-89



cemff: A force field database for cementitious materials including validations, applications and opportunities

Ratan K. Mishra ^{a,*,} Aslam Kunhi Mohamed ^{b,} David Geissbühler ^{b,} Hegoi Manzano ^{c,} Tariq Jamil ^{d,} Rouzbeh Shahsavari ^{e,} Andrey G. Kalinichev ^{f,*,} Sandra Galmarini ^{g,} Lei Tao ^{e,} Hendrik Heinz ^{d,} Roland Pellenq ^{h,} Adria C.T. van Duin ^{i,} Stephen C. Parker ^{j,} Robert J. Flatt ^{a,} Paul Bowen ^{b,*,}

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<https://doi.org/10.1016/j.cemconres.2017.09.003>

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Highlights

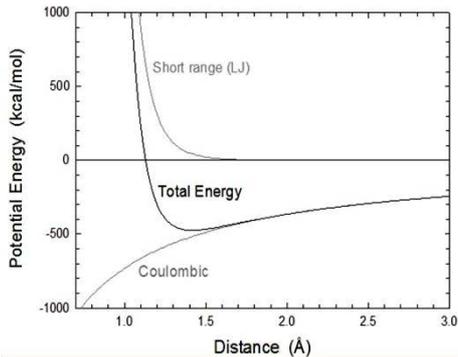
- Development of *cemff* database to improve the accuracy of atomistic simulations and guide in performance optimization of cementitious systems.
- Concepts and atomistic force field parameterizations of cementitious minerals.
- Atomistic model validations and comparison between the computed data and benchmarks (experimental or ab-initio).
- Different force fields (ClayFF, IFF, CementFF, ReaxFF and C-S-H FF) are compared. The benefits and limitations of these approaches are discussed.
- Relationships between structure, properties, and applications are discussed.

ClayFF Force Field

- ClayFF – specialized semi-empirical fully flexible force field model allowing for realistic exchange of momentum and energy among all atoms – solid substrate and aqueous solution (Cygan, Liang, Kalinichev, *J.Phys.Chem. B*, **108** 1255-1266, 2004):

$$U_{ij} = \sum \sum (A_{ij}/r_{ij}^{12} - B_{ij}/r_{ij}^6 + q_i q_j / \epsilon_0 r_{ij}) + \sum \frac{1}{2} k_b (r_{ij} - r_0)^2 + \sum \frac{1}{2} k_\theta (\theta_{ij} - \theta_0)^2$$

Short-range repulsion
v-d-Waals
Coulombic
bond stretching
bond bending



- Simple Point Charge (SPC) flexible model for H₂O
- Structural ions: Si, Ca, Al, Fe, Mg, O, OH with partial charges derived from quantum DFT calculations for a number of simple oxides and hydroxides
- Aqueous species: Na⁺, K⁺, Cs⁺, Mg²⁺, Ca²⁺, Cl⁻, OH⁻, SO₄²⁻, CO₃²⁻, NO₃⁻
- Theoretical models of oxides, hydroxides, clays, C-S-H and other hydrous materials
- Combination with CVFF, AMBER or CHARMM to model mixed organic-inorganic systems

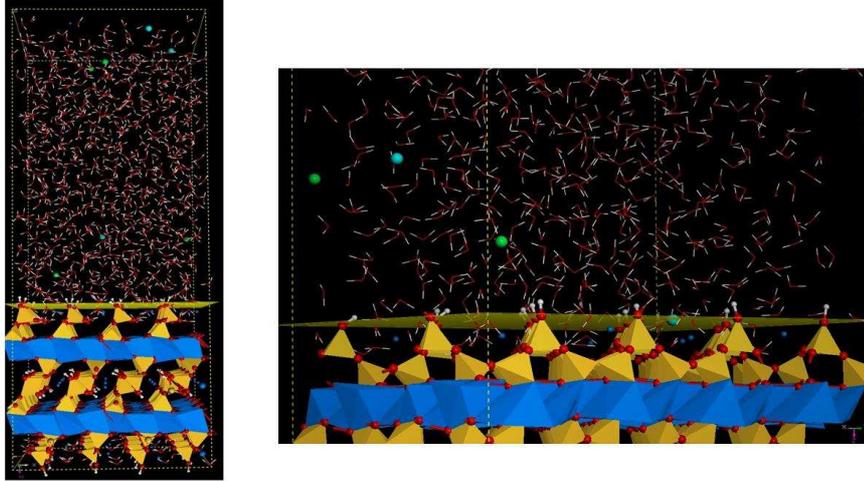
ClayFF and Crystallographic Parameters of Cement-Related Phases

	Portlandite Ca(OH) ₂	Hydrocalumite (AFm) [Ca ₂ Al(OH) ₆]Cl·2H ₂ O	Tobermorite (C-S-H) Ca ₅ Si ₆ O ₁₆ (OH) ₂	Ettringite (C-S-H) Ca ₆ [Al(OH) ₆] ₂ * [SO ₄] ₃ *26H ₂ O	Na-kanemite (ASR gel) NaHSi ₂ O·3H ₂ O	K-kanemite (ASR gel) KHSi ₂ O
<i>a</i> / Å	3.57	10.02	11.16	11.02	5.01	8.13
exp.	3.59	9.979	11.16	11.26	4.95	8.15
<i>b</i> / Å	3.57	5.94	7.26	10.94	19.41	12.54
exp.	3.59	5.751	7.30	11.26	20.50	12.52
<i>c</i> / Å	4.91	15.99	9.61	21.30	7.34	4.76
exp.	4.91	16.320	9.57	21.46	7.28	4.89
<i>α</i> / °	90.01	90.00	103.47	90.50	89.74	90.00
exp.	90.00	90.00	101.08	90.00	90.00	90.00
<i>β</i> / °	89.98	102.89	89.46	89.80	89.63	90.00
exp.	90.00	104.53	92.83	90.00	90.00	90.00
<i>γ</i> / °	120.01	90.00	90.13	119.80	89.81	90.00
exp.	120.00	90.00	89.98	120.00	90.00	90.00
<i>V</i> Å ³	54.3	927.6	757.8	2232.3	714.46	485.28
exp.	54.82	906.64	763.87	2358.53	737.71	498.97

Δ Cell parameters < 2%
Δ Bond distances < 3%

Kalinichev and Kirkpatrick, *Chem. Materials*, **14**, 3539-3549 (2002)
Kirkpatrick, Kalinichev, et al., *Mater. & Struct.*, **38**, 449-458 (2005)
Kalinichev, et al. *Cement & Concrete Res.*, **37**, 337-347 (2007)
Tatarushkin et al. *Cement & Concrete Res.*, **156**, 106759 (2022)

Hydrated Tobermorite as a Model C-S-H Surface



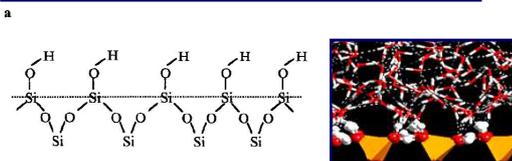
A snapshot from MD simulations (Kalinichev et al., 2002, 2007, 2009)

Ca ● O ● H ● Cl ● K ● Si ●

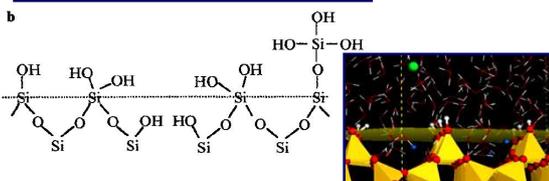
"Real" Hydrated Silica Surface vs Idealized Models

Duval et al. (2002) Evidence of the existence of three types of species at the quartz-aqueous solution interface at pH 0-10. *J. Phys. Chem. B*, **106**, 2937-2945.

Schematic view of idealized atomically smooth (001) quartz surface in contact with water



Schematic view of a real hydrated quartz surface structure

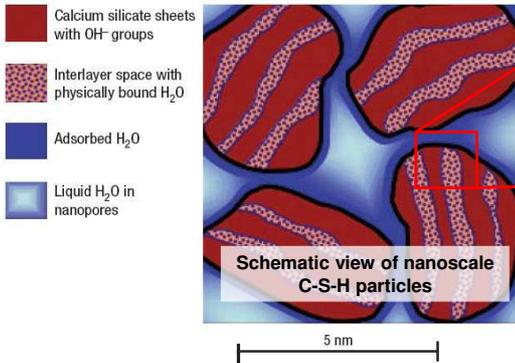


Important implications:

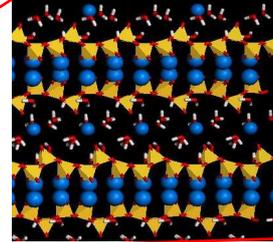
- ◆ Thickness of the interface can be 2-3 times larger than for a smooth surface
- ◆ More H₂O molecules in direct contact with the substrate
- ◆ Much more diverse H-bonding environment can be expected
- ◆ Mobility of interfacial aqueous species can be more restricted
- ◆ Interpretation of surface specific experimental data (SFVS, X-ray reflectivity) can be trickier than usually expected
- ◆ Molecular scale approach to understanding of glass corrosion

Tobermorite - $\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2$ - An Example of Nano-Structured Hydrous Material, a Model of “Real” Surface of Silicates, and a Model of Cement C-S-H Phase

C-S-H: A classic nano-structured material



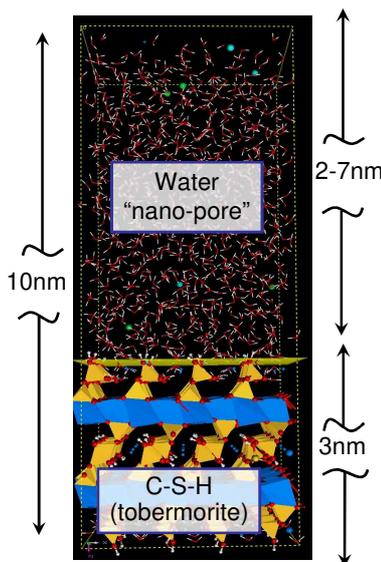
Allen et al., *Nature Materials*, 6, 311-316 (2007)



Fundamental Questions

- ◆ Properties of solid-fluid nano-composites
- ◆ Adsorption of water and ions
- ◆ Precipitation mechanisms?
- ◆ C-S-H structure?
- ◆ Why different morphologies?
- ◆ Why do the particles not coarsen?
- ◆ Role of impurities: e.g., Al, Sr, Fe ?
- ◆ Origin of mechanical properties?

MD Modeling of Cement-Water Interfaces



Classical Newtonian dynamics

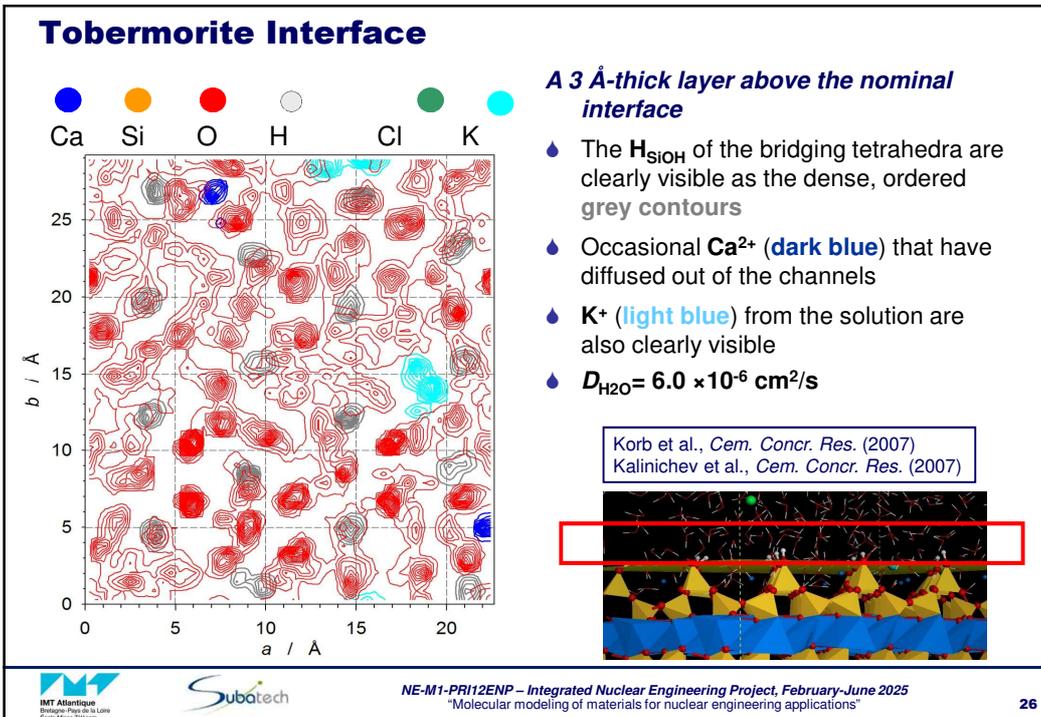
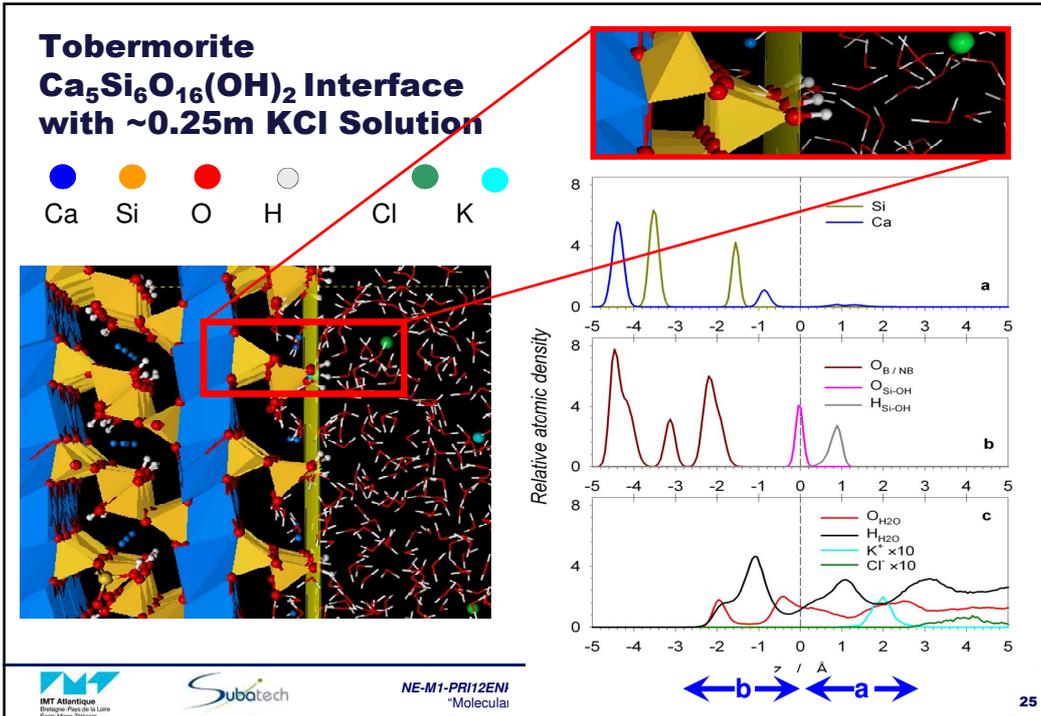
- ◆ $N_{\text{tot}} \sim 3,000 - 100,000$ atoms
- ◆ $N_{\text{H}_2\text{O}} \sim 0 - 10,000$ molecules
- ◆ *ClayFF* force field (Cygan et al., 2004)
- ◆ $a \times b \times c \sim 5 \times 5 \times 10 \text{ nm}^3$
- ◆ Periodic boundary conditions
- ◆ *NVT*- or *NPT*-ensemble $T=300\text{K}$; $P=1 \text{ bar}$
- ◆ $t \sim 200 - 10,000 \text{ ps}$
(equilibration + equilibrium)
- ◆ $\Delta t = 0.5-1.0 \text{ fs}$

◆ Solution structure:

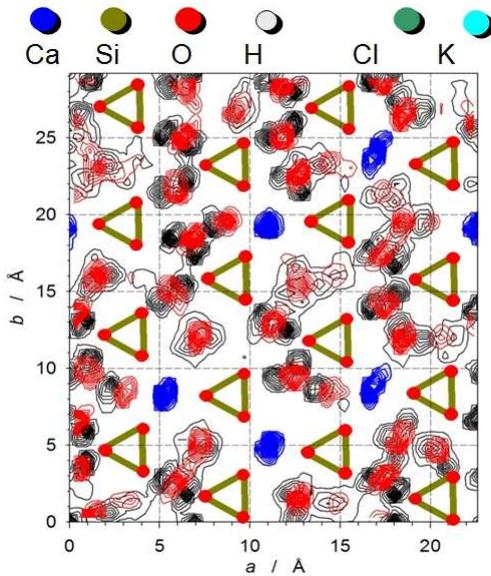
- ✓ Atomic density profiles (\perp)
- ✓ Atomic density surface distributions (\parallel)

◆ Dynamics:

- ✓ Diffusion coefficients (longer time scale)
- ✓ Spectra of vibrational and rotational dynamics (shorter time scale)



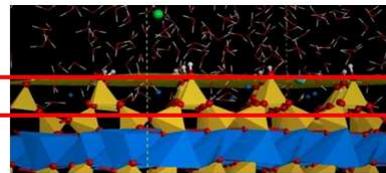
Tobermorite Interface



A 3 Å-thick layer into the crystal (below the nominal interface)

- The chains of SiO₄ tetrahedra run top to bottom in this view, with triangles of oxygens (**dark red dots**) clearly visible
- Ca²⁺ (**blue**) and H₂O (O – **red**, H – **dashed black**) occur in the channels between the tetrahedra
- $D_{\text{H}_2\text{O}} = 5.0 \times 10^{-7} \text{ cm}^2/\text{s}$

Korb et al., *Cem. Concr. Res.* (2007)
Kalinichev et al., *Cem. Concr. Res.* (2007)

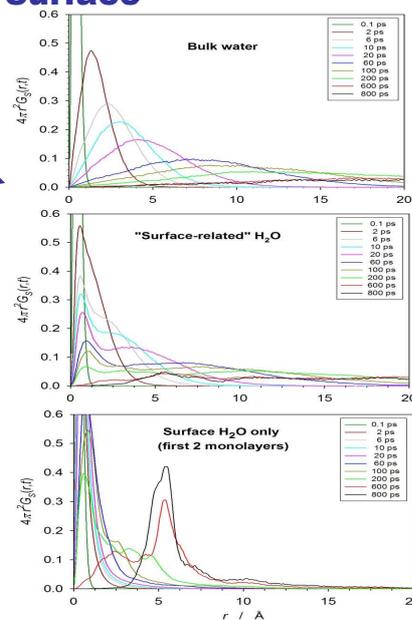


Mobility of Water at Tobermorite Surface

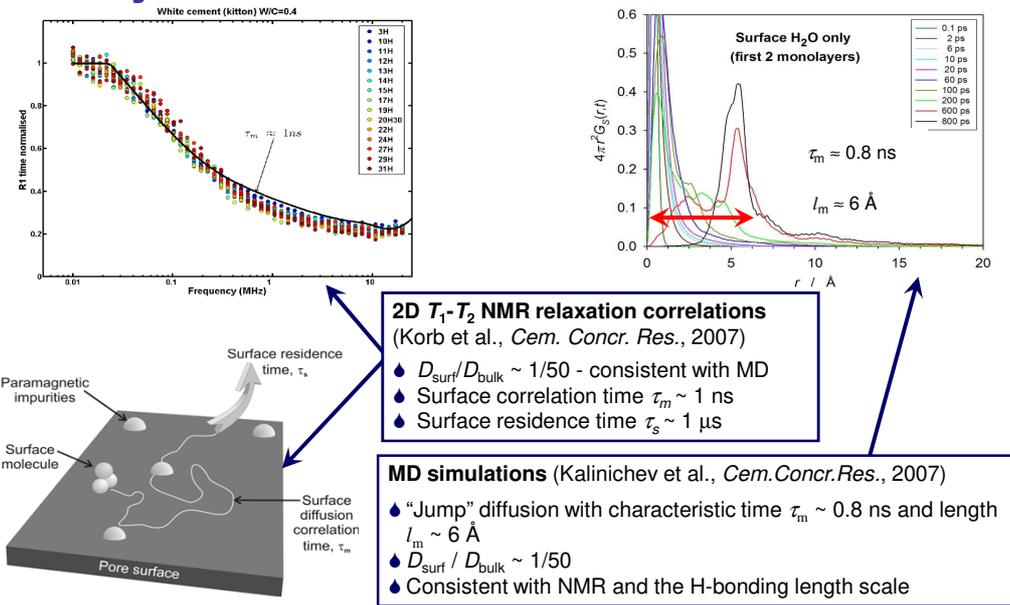
Van Hove self-correlation functions

$$G_S(r, t) = \frac{1}{N} \left\langle \sum_{i=1}^N \delta[r + r_i(0) - r_i(t)] \right\rangle$$

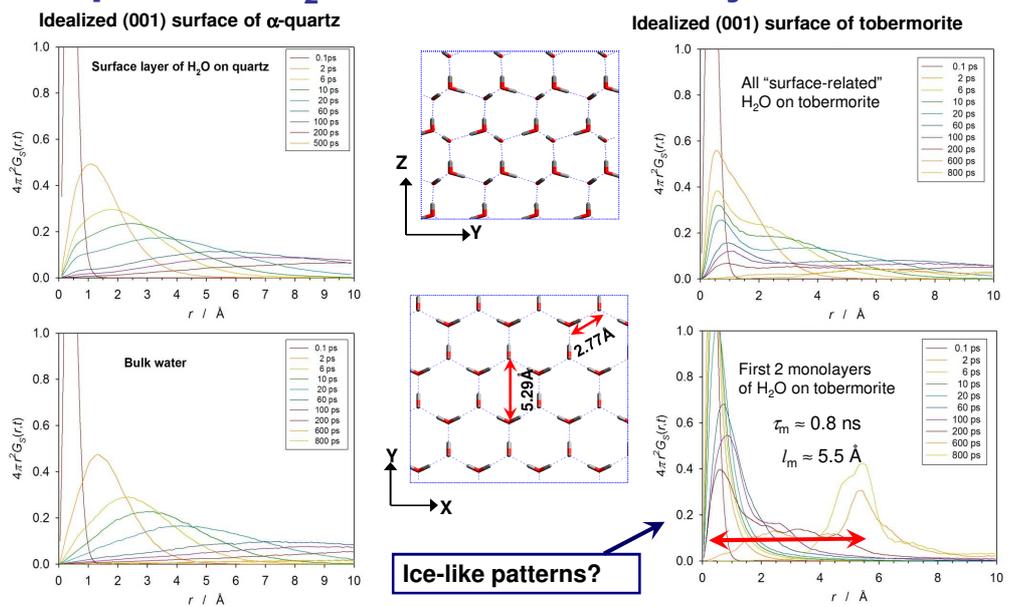
- $4\pi r^2 G_S(r, t) dr$ is the probability to find an atom at distance r after a time t if the position of this atom was at the origin $r = 0$ at time $t = 0$
- Fourier transform of $G_S(r, t)$ is the incoherent scattering function, $I_{\text{inc}}(Q, t)$, which is measured in **incoherent quasi-elastic neutron scattering experiments** and contains detailed information concerning the single-particle dynamics



Mobility of Water at Tobermorite Surface



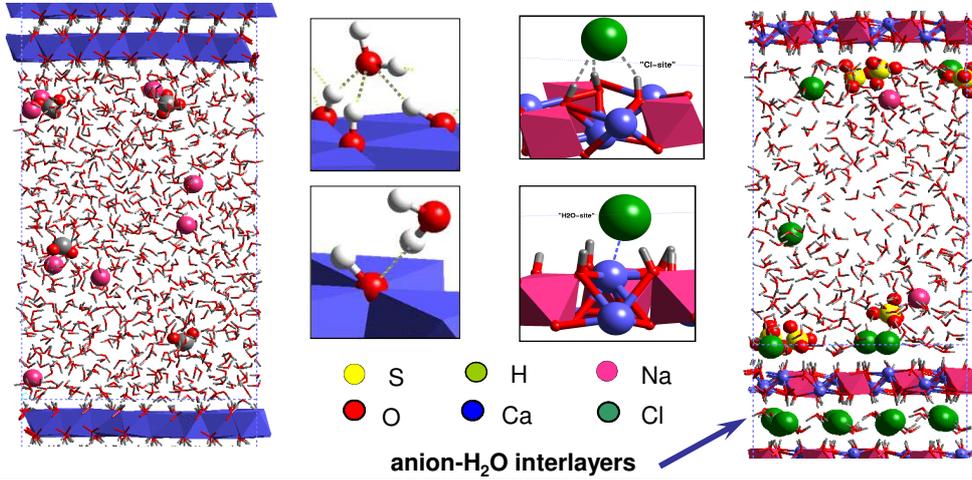
Comparison of H₂O Surface Diffusional Dynamics



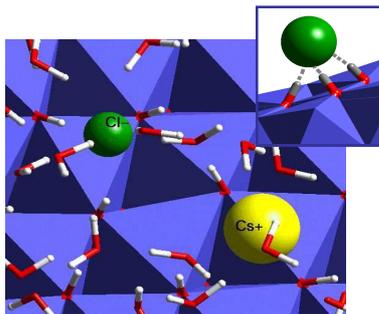
Effect of Surface Charge on Water Structure – Metal Hydroxide Interfaces

$\text{Ca}(\text{OH})_2$
Zero Structural Charge

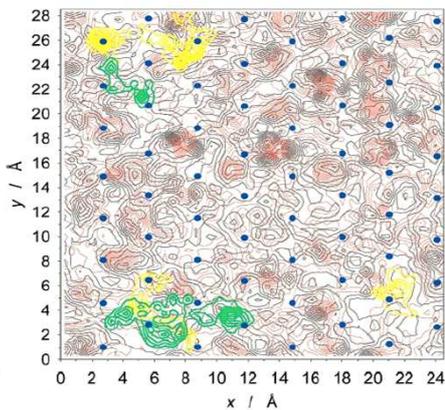
$\text{Ca}_2\text{Al}(\text{OH})_6\text{Cl}\cdot\text{H}_2\text{O}$ - LDH
Positive Structural Charge



Adsorption of Cs^+ and Cl^- Ions at the Surface of Ca-Hydroxide (Portlandite)

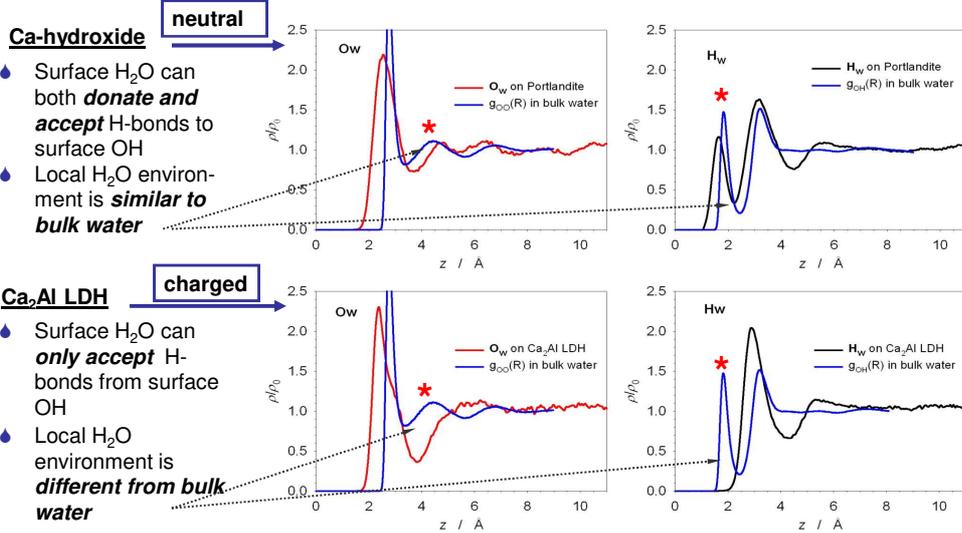


Atomic density maps of the adsorbed surface species ("inner sphere" complexing)

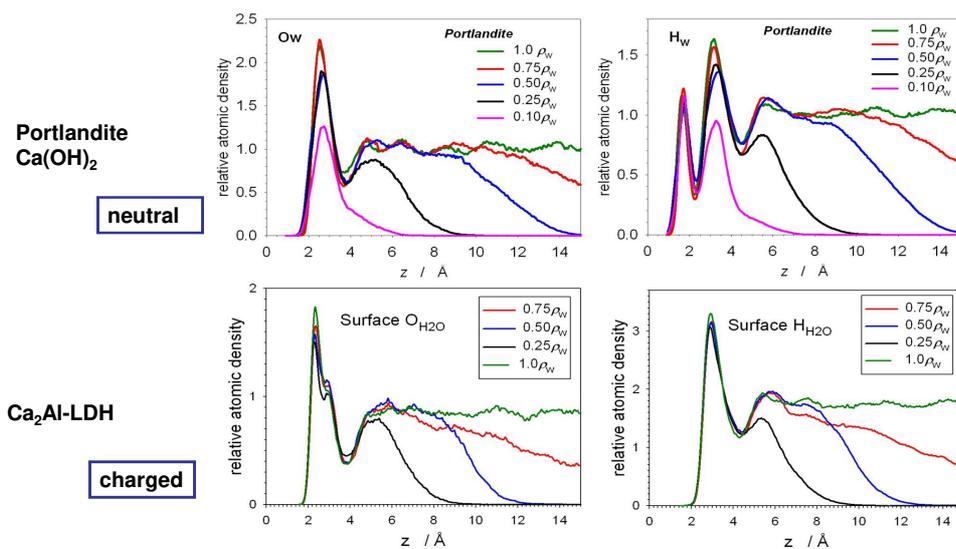


Mobility of surface OH groups is important for realistic modeling of H-bonding at the sorption sites

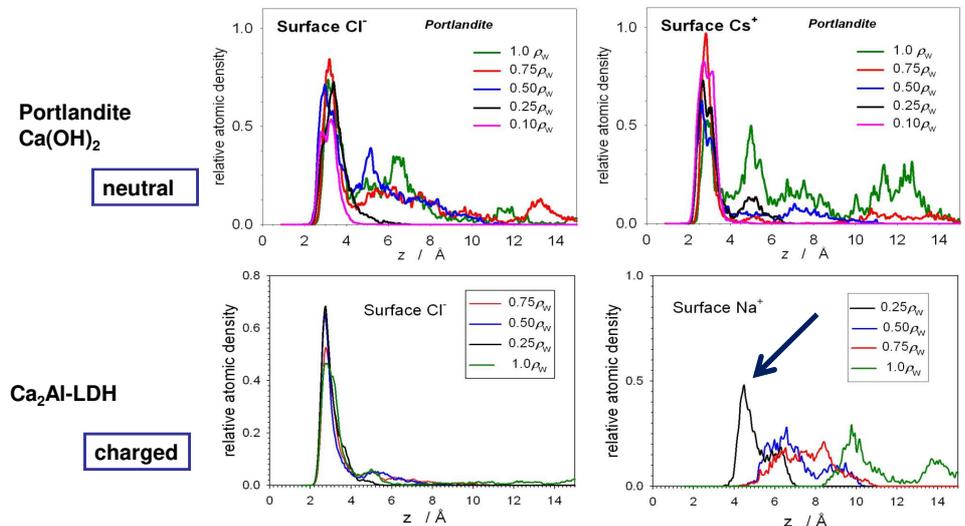
H₂O Density Profiles and H-Bond Network at Water-Hydroxide Interfaces



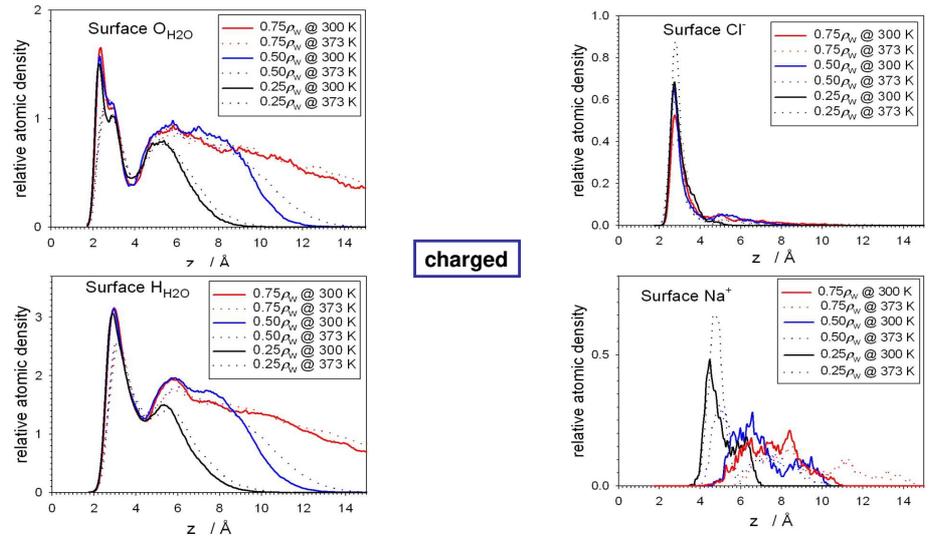
Fluid Structure as Function of Water Density in a Nanopore (proxy of RH)



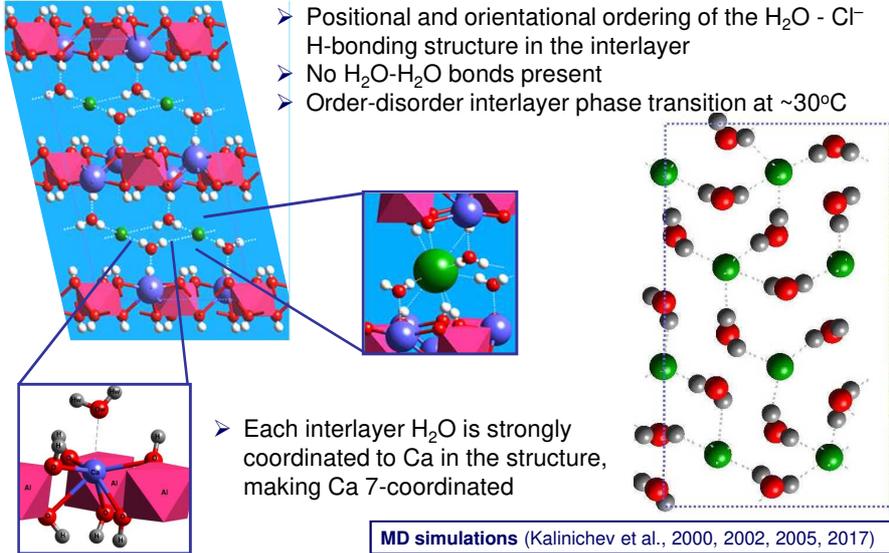
Ion Adsorption as Function of Water Density in a Nanopore (*proxy of RH*)



Effects of Temperature on the Adsorbed Water and Ions Density Profiles at the $\text{Ca}_2\text{Al LDH}$ Interface

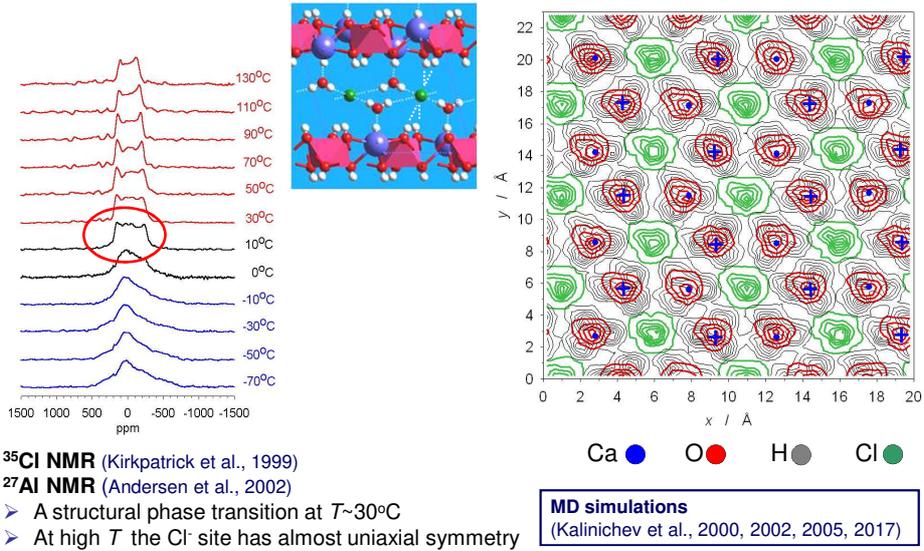


Interlayer Structure of Hydrocalumite, Friedel's Salt, $[\text{Ca}_2\text{Al}(\text{OH})_6]\text{Cl} \cdot 2\text{H}_2\text{O}$ – (AFm)



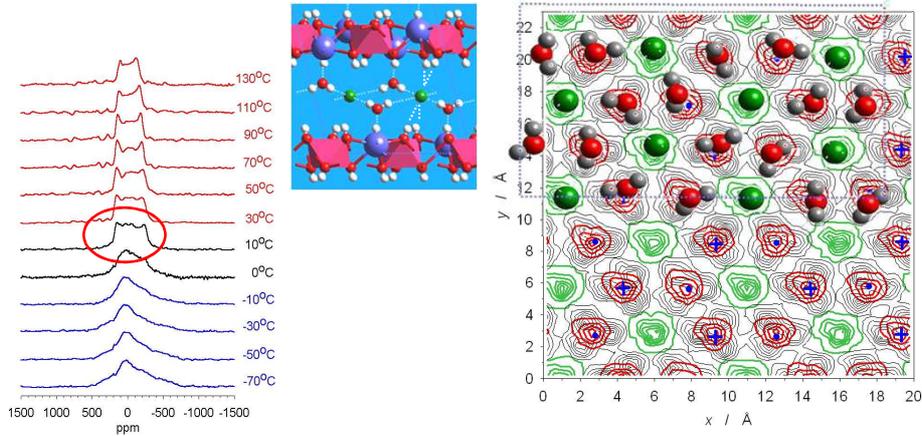
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 "Molecular modeling of materials for nuclear engineering applications"

Time- and Space Averaged Interlayer Structure of Hydrocalumite (AFm) – MD vs NMR



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 "Molecular modeling of materials for nuclear engineering applications"

Time- and Space Averaged Interlayer Structure of Hydrocalumite (AFm) – MD vs NMR



³⁵Cl NMR (Kirkpatrick et al., 1999)

²⁷Al NMR (Andersen et al., 2002)

- A structural phase transition at $T \sim 30^\circ\text{C}$
- At higher T the Cl⁻ site has almost uniaxial symmetry

MD simulations

(Kalinichev et al., 2000, 2002, 2005, 2017)

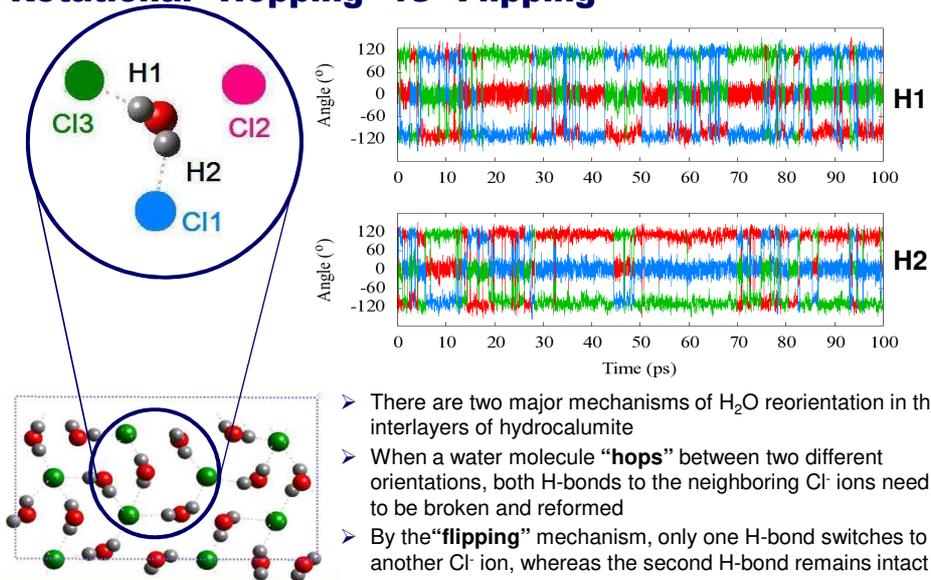


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“Molecular modeling of materials for nuclear engineering applications”

Librational Dynamics of H₂O in Hydrocalumite (AFm): Rotational “Hopping” vs “Flipping”



- There are two major mechanisms of H₂O reorientation in the interlayers of hydrocalumite
- When a water molecule “hops” between two different orientations, both H-bonds to the neighboring Cl⁻ ions need to be broken and reformed
- By the “flipping” mechanism, only one H-bond switches to another Cl⁻ ion, whereas the second H-bond remains intact



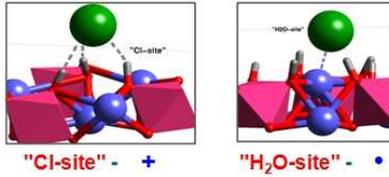
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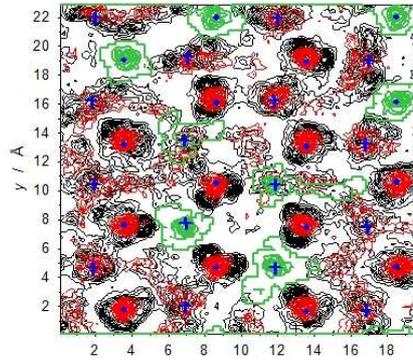
NE-M1-PRI12ENP – Integrated Nuclear Engineering Project, February-June 2025
“Molecular modeling of materials for nuclear engineering applications”

Chloride Sorption and Dynamics on the Surface of the AFm Hydrocalumite $[\text{Ca}_2\text{Al}(\text{OH})_6]\text{Cl}\cdot 2\text{H}_2\text{O}$

Two types of surface sites



	Ca-hydroxide	Ca ₂ Al-hydroxide
Fraction of surface-bound Cl ⁻	65%	85%
Fraction of surface-bound counterions	60-85%	0%
Cl ⁻ surface lifetime	~20 ps	~50 ps
Cl ⁻ surface diffusion (cm ² /s)	1×10^{-5}	2×10^{-6}



Atomic density maps of the first surface layer ("inner-sphere" complexing)

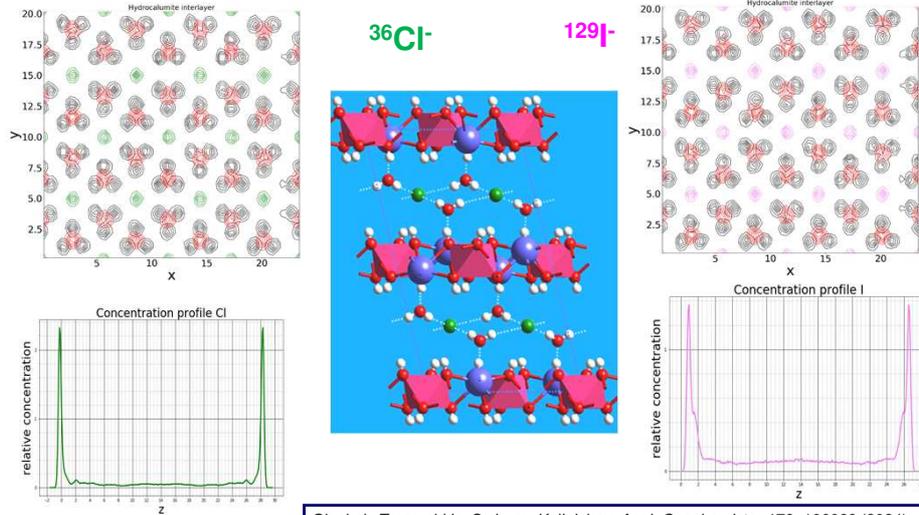
Cl ● O ● H ● Ca ●

Cl⁻ Diffusion Coefficients (cm²/s) under Ambient Conditions

	Portlandite	Hydrocalumite	Ettringite
Interlayer	N / a	$\ll 10^{-7}$	N / a
Surface (inner sphere)	3.6×10^{-6}	1.6×10^{-6}	2×10^{-6}
Surface (outer sphere)	1.5×10^{-5}	7.2×10^{-6}	3.8×10^{-6}
Total surface-bound	1.1×10^{-5}	1.9×10^{-6}	3.5×10^{-6}
In bulk NaCl solution, and in contact with tobermorite	2.3×10^{-5}		

- ◆ No bound Cl⁻ were observed on the surface of tobermorite
- ◆ In ettringite, ~20% of surface SO₄²⁻ can be substituted by Cl⁻

Interlayer and Surface Properties of Hydrocalumite (AFm), $[\text{Ca}_2\text{Al}(\text{OH})_6]_x \cdot 2\text{H}_2\text{O}$ ($x = \text{Cl}^-, \text{I}^-$)

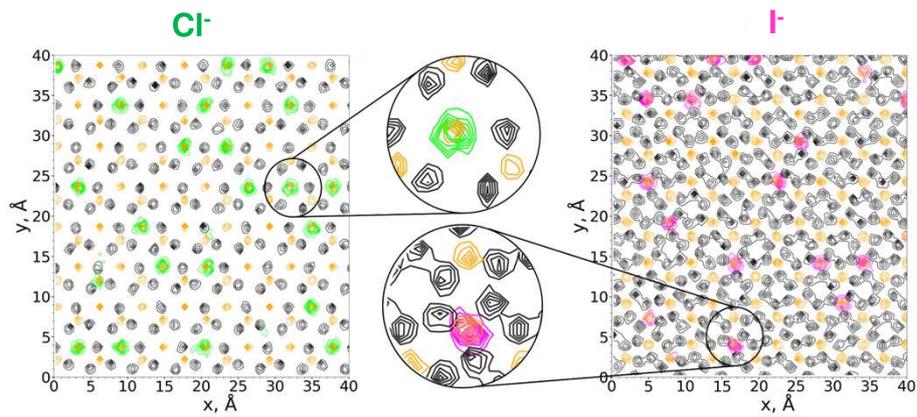


Glushak, Tararushkin, Smirnov, Kalinichev, *Appl. Geochemistry*, **170**, 106089 (2024)



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Adsorption of Cl^- and I^- on the Surface of Hydrocalumite (I)

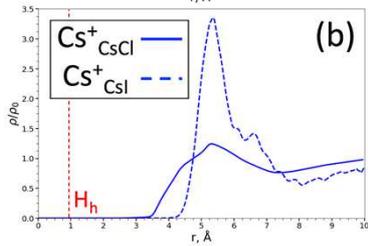
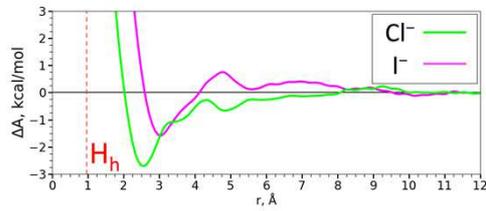
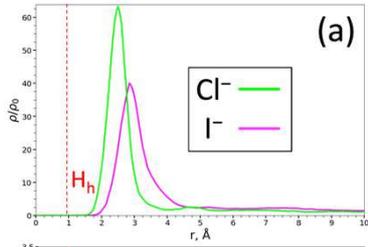


Glushak, Tararushkin, Smirnov, Kalinichev, *Appl. Geochemistry*, **170**, 106089 (2024)



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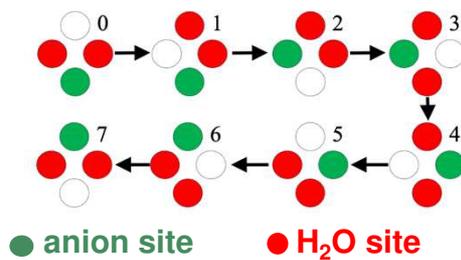
Adsorption of Cl⁻ and I⁻ on the Surface of Hydrocalumite (II)



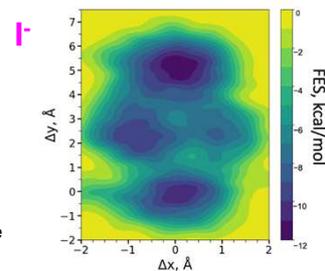
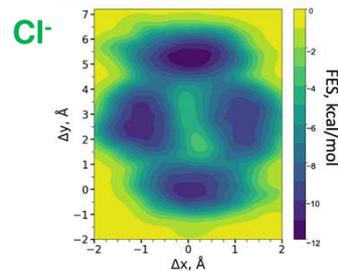
System	$D, 10^{-5} \text{ cm}^2/\text{s}$ CsCl	$D, 10^{-5} \text{ cm}^2/\text{s}$ CsI
Surface	0.25	0.36
Solution	1.15	1.30

Glushak, Tararushkin, Smirnov, Kalinichev, *Appl. Geochemistry*, **170**, 106089 (2024)

Hopping Mechanism of Cl⁻ and I⁻ Interlayer Diffusion in Hydrocalumite



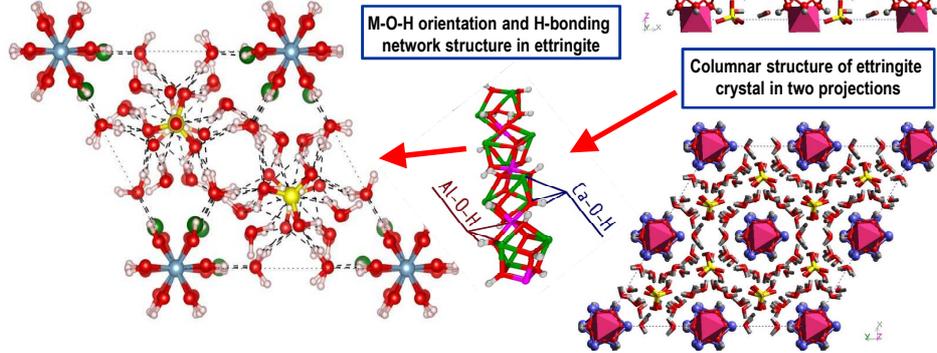
- The height of the energy barrier for the Cl⁻ system at transition points is ~5 kcal/mol for the transition from the Cl⁻ to H₂O site, and for the transition from the H₂O site to the initial vacancy site
- The height of the energy barrier for the I⁻ system at transition points is ~5 kcal/mol for the transition from the I⁻ to H₂O site, but it is only ~4 kcal/mol for the transition from the H₂O site to the vacancy site



Glushak, Tararushkin, Smirnov, Kalinichev, *Appl. Geochemistry*, **170**, 106089 (2024)

Effects of M-O-H Bending Vibrations on the Structure and Properties of Cementitious Hydrous Phases

- **Ettringite**, $\text{Ca}_6[\text{Al}(\text{OH})_6]_2[\text{SO}_4]_3 \cdot 26\text{H}_2\text{O}$, plays an important role in cement chemistry as the primary cause of sulfate corrosion in cement
- Ettringite formation leads to volume expansion, cracking and mechanical damage to concrete



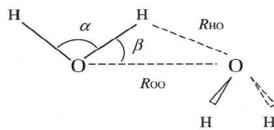
E.V.Tararushkin, V.V.Pisarev, A.G.Kalinichev (2022) *Cement and Concrete Research*, 156, 106759



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Intra-Crystalline Hydrogen Bonding in Ettringite

Geometrical definition for H-bond



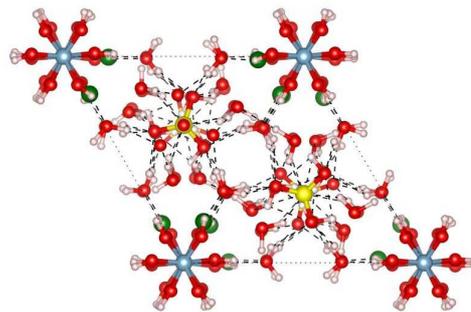
$$R_{\text{OO}} \leq 3.3\text{-}3.5 \text{ \AA}$$

or

$$R_{\text{OH}} \leq 2.45\text{-}2.5 \text{ \AA}$$

and

$$\beta \leq 30^\circ$$



Lifetime of H-bonds

Continuous time autocorrelation functions of H-bonds

$$S(t) = \frac{\langle h(0) \cdot H(t) \rangle}{\langle h \rangle}$$

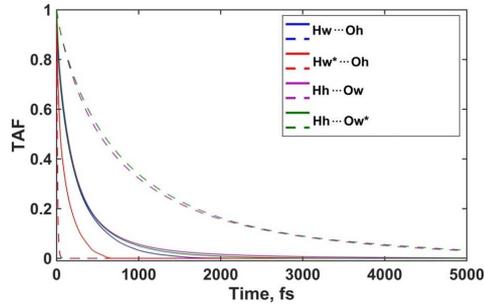
$$\tau = \int_0^\infty S(t) dt$$

Tararushkin, Pisarev, Kalinichev, *Cement and Concrete Research*, 156, 106759 (2022)



NE-M1-PRI12ENP – Integrated Nuclear Engineering Project, February-June 2025
"Molecular modeling of materials for nuclear engineering applications"

H-Bonding Characteristics in Ettringite



Continuous TCF of H-bonds for H₂O molecules and structural -OH groups:

- Solid lines – ClayFF-orig
- Dashed lines – ClayFF-MOH

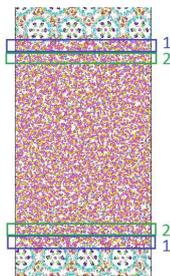
Tararushkin, Pisarev, Kalinichev, *Cement and Concrete Research*, **156**, 106759 (2022)

Average number of H-bonds per donor, n_{HB} , and the average lifetime of H-bond, τ_{HB} , ps

Donor-acceptor pair	n_{HB}		τ_{HB} , ps	
	ClayFF-orig	ClayFF-MOH	ClayFF-orig	ClayFF-MOH
Hw...Ow	0.59	0.58	0.35	0.38
Hw*...Ow*	0.30	0.26	0.43	0.36
Hw...Ow*	0.09	0.09	0.38	0.37
Hw*...Ow	0.75	0.70	0.36	0.38
Hw...Os	1.38	1.38	>10	>10
Hw*...Os	0.81	0.83	>10	>10
Hw...Oh	0.01	~0	0.23	0.01
Hw*...Oh	~0	~0	0.10	0.01
Hh...Ow	0.74	0.89	0.29	>10
Hh...Ow*	0.06	0.05	0.26	>10
Hh...Os	~0	~0	0.06	0.01

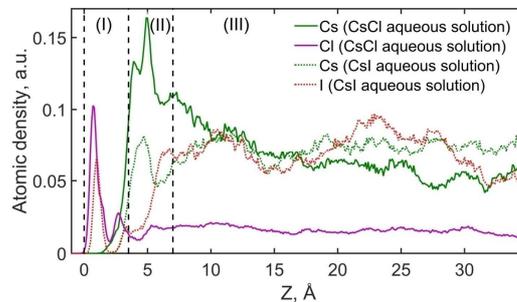
CsCl and CsI Aqueous Solutions on the Ettringite Surface

Ettringite crystal supercell



- Interface of ettringite with aqueous solution
- Numbers and blocks indicate the first 3.5 Å (1) and second 3.5 Å (2) layers of solution next to the surface.

Atomic density profiles for ionic species

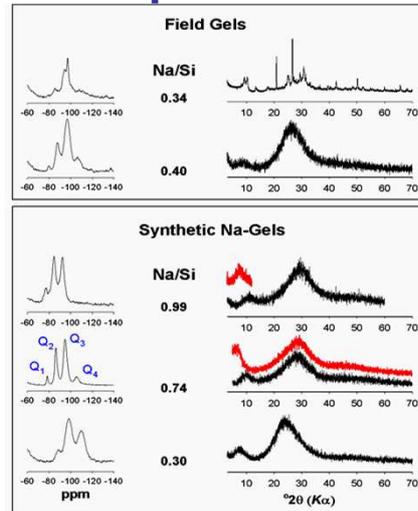


(I) – first slice, (II) – second slice, (III) – bulk of interlayer space.

Alkali-Silica Reaction: Kanemite Model of the Structure and Energetics of ASR Gel Expansion

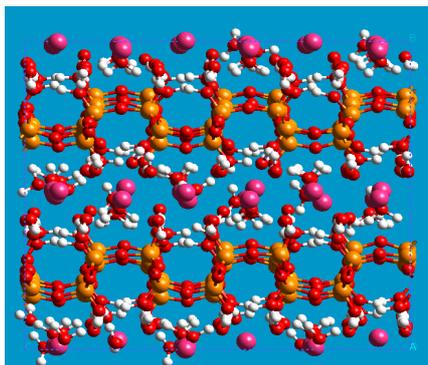
Kirkpatrick, Kalinichev, Hou & Struble,
Mater.Struct.Concr.Sci.Engr., **38**, 449-458 (2005)

- Structure: silicate and hydrated interlayers.
- Energetics.
- Connections to laboratory data: XRD, NMR, and hydration.
- MD computer simulations of the structure and energetics of kanemite, $MHSi_2O_5 \cdot nH_2O$, $M=Na, K, Li, Cs$.
- Evaluate energetics to determine expansion potential.
- Compare to experimental results.
- Evaluate structure to understand origin of behavior.

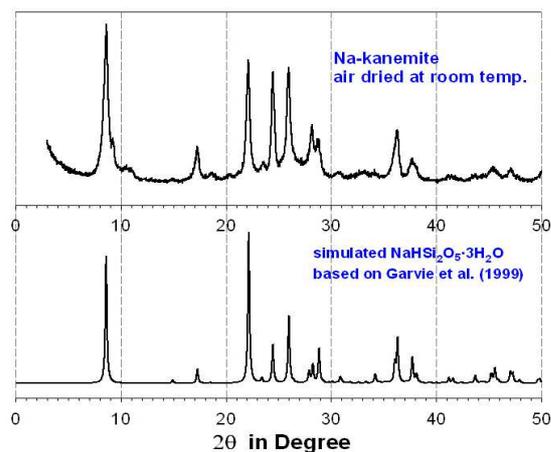


Synthetic and In-Service ASR Gels:
 ^{29}Si NMR and XRD

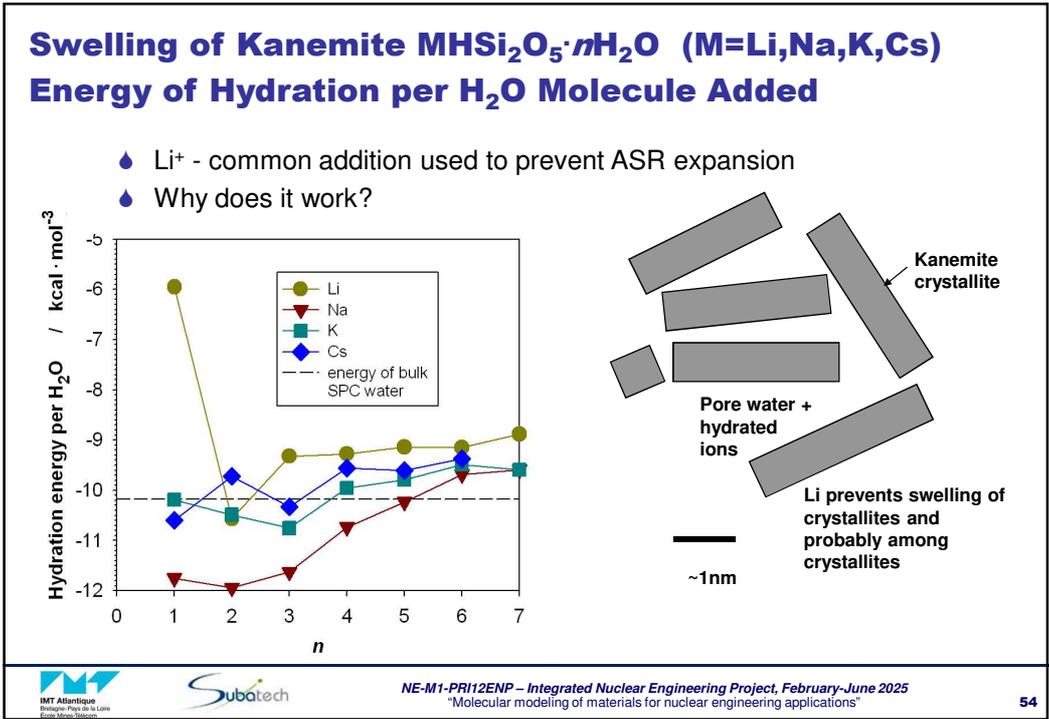
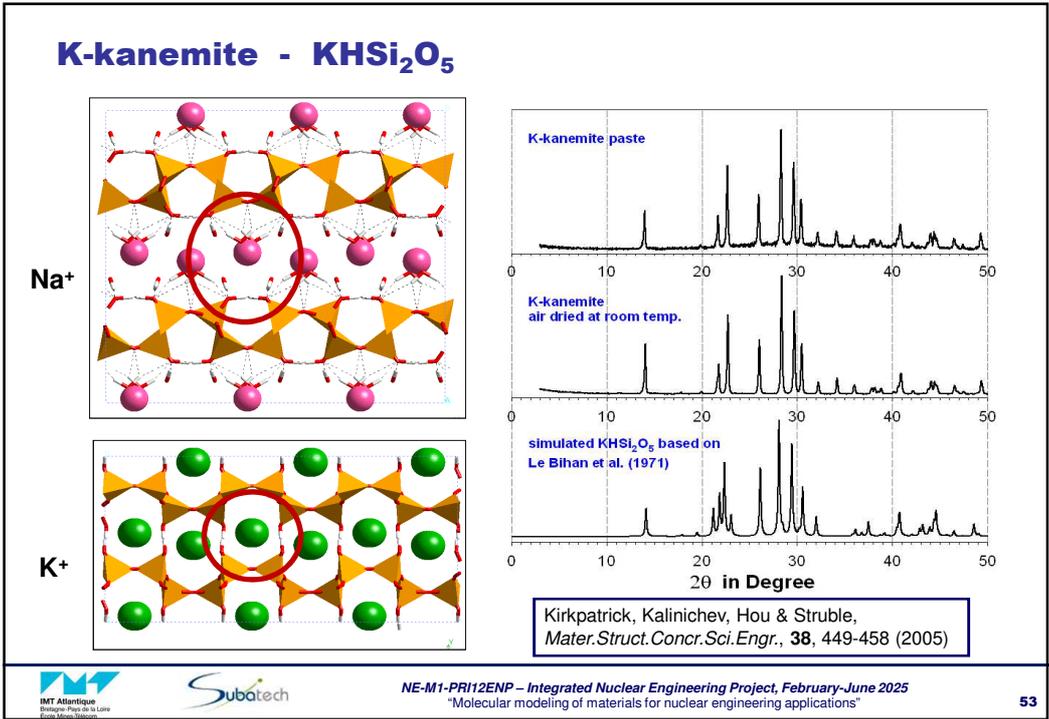
Kanemite Structure: 3 H₂O/Formula Unit In Excellent Agreement with Known Structure



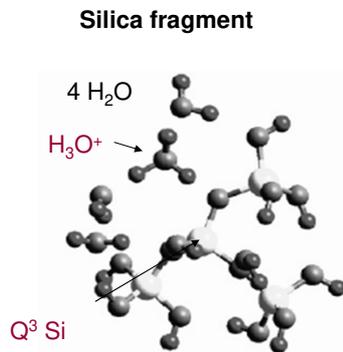
Na⁺



Kirkpatrick, Kalinichev, Hou & Struble,
Mater.Struct.Concr.Sci.Engr., **38**, 449-458 (2005)



Modeling Surface Chemical Reactivity



H⁺ (H₃O⁺) Attack on a Silica Surface:

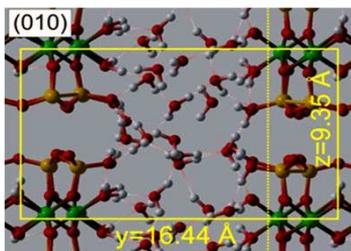
Criscenti et al., *J. Phys Chem. A*, **110**, 198 (2006)

- ◆ Mostly been done using traditional quantum chemical methods
- ◆ Calculations for configurations along a reaction path of optimized structures including solvating H₂O molecules
- ◆ Yields:
 - ◆ Activation energies
 - ◆ Critical reaction steps
- ◆ Limitations:
 - ◆ Very small systems
 - ◆ Cannot account well for effects fluid structure and dynamics

Particle Edges: Quantum (Ab Initio) Molecular Dynamics to Address the Chemical Reactivity

- Use Q.M. to calculate energies at each time step (Schrödinger equation)
- Allows for chemical reaction
- Follow reactions through time
- Very expensive computationally
- ~ $n \times 100$ atoms; ~ $15 \times 15 \times 15$ Å periodic box; $t \sim 10$ -50 ps

Pyrophyllite (010) surface: DFT-AIMD methods



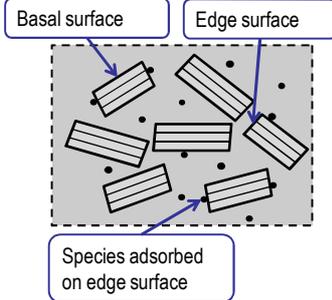
H-Exchange Between Silicate Surface and H₂O

- ◆ H-exchange among surface sites occurs by a proton channel (wire) of H-bonds involving surface –OH⁻ and H₂O
- ◆ Rate of H-exchange controlled by rate of H₂O rearrangement near surface, not individual H-exchange reaction

S.V.Churakov, *Geochim. Cosmochim. Acta*, **71**, 1130-1144 (2007)
S.V.Churakov, P.Mandaliev, *Cem. Concr. Res.*, **38**, 300-311 (2008)

ClayFF Parametrization for Clay Particle Edges

M.Pouvreau, PhD Thesis, Dec. 2016

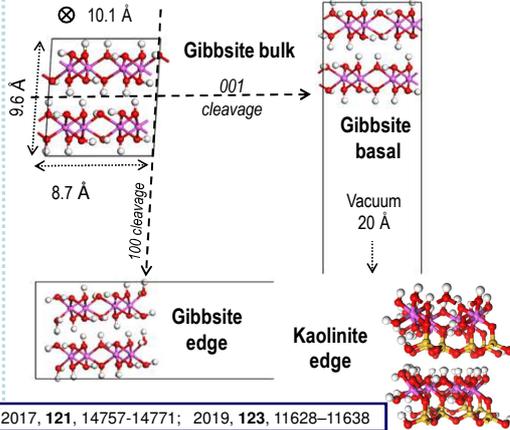


New special ClayFF M-O-H bending terms

$$U_{\text{ClayFF-MOH}} = U_{\text{ClayFF-orig}} + U_{\text{M-O-H}} = U_{\text{ClayFF-orig}} + k(\theta - \theta_0)^2$$

k and θ_0 have to minimize the differences between DFT and ClayFF-MOH results

- *Brucite, gibbsite, kaolinite* edges
- 3D periodic boundary conditions
- Cells size:
 - ✓ $N_{\text{atoms}} \sim 100$ for DFT+parametrization;
 - ✓ $N_{\text{atoms}} \sim 2500$ for classical MD

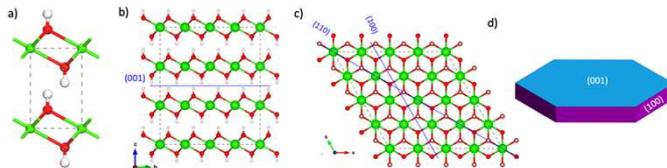
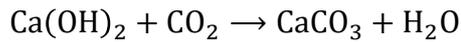


Pouvreau, Greathouse, Cygan, Kalinichev, *J.Phys.Chem.C*, 2017, **121**, 14757-14771; 2019, **123**, 11628-11638

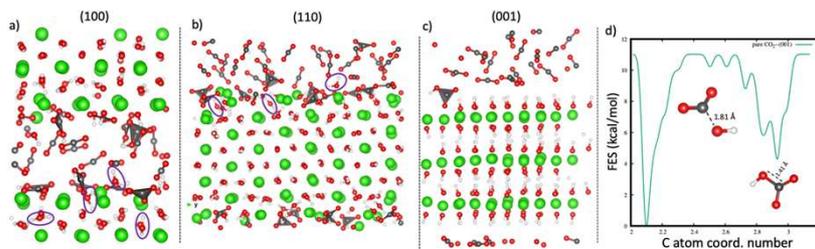


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"Molecular modeling of materials for nuclear engineering applications"

Reactivity of Supercritical CO₂ with Portlandite Surfaces (AIMD + Metadynamics)

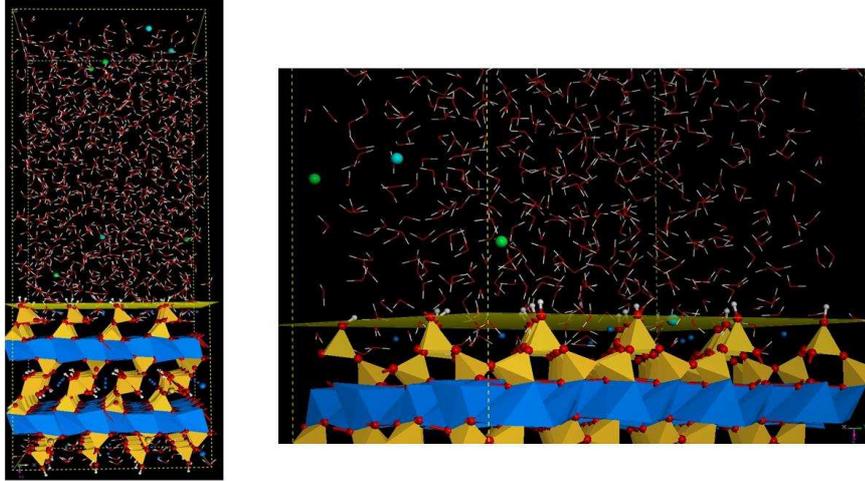


S.Mutisya, A.G.Kalinichev, *Minerals*, **11**, 509 (2021)



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"Molecular modeling of materials for nuclear engineering applications"

Hydrated Tobermorite as a Model C-S-H Surface

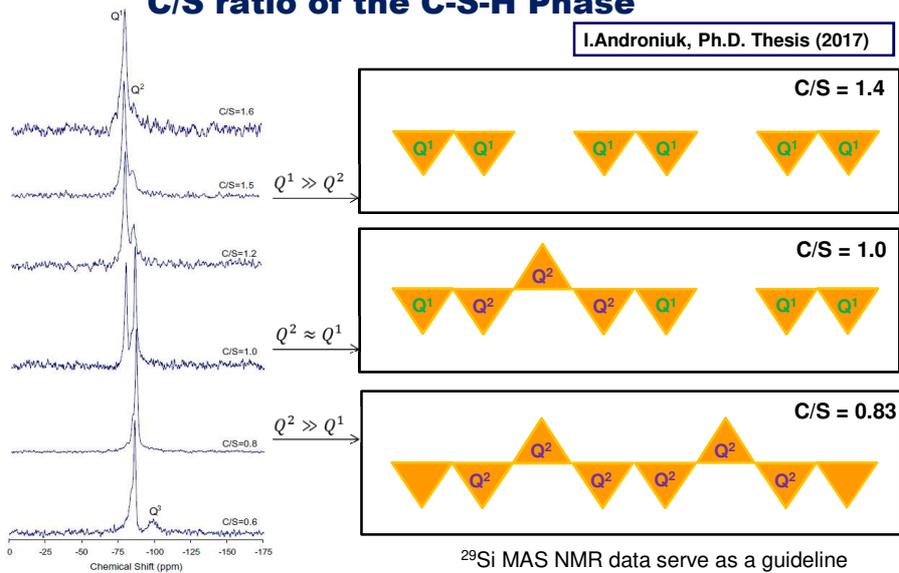


A snapshot from MD simulations (Kalinichev et al., 2002, 2007, 2009)

Ca ● O ● H ● Cl ● K ● Si ●

C/S ratio of the C-S-H Phase

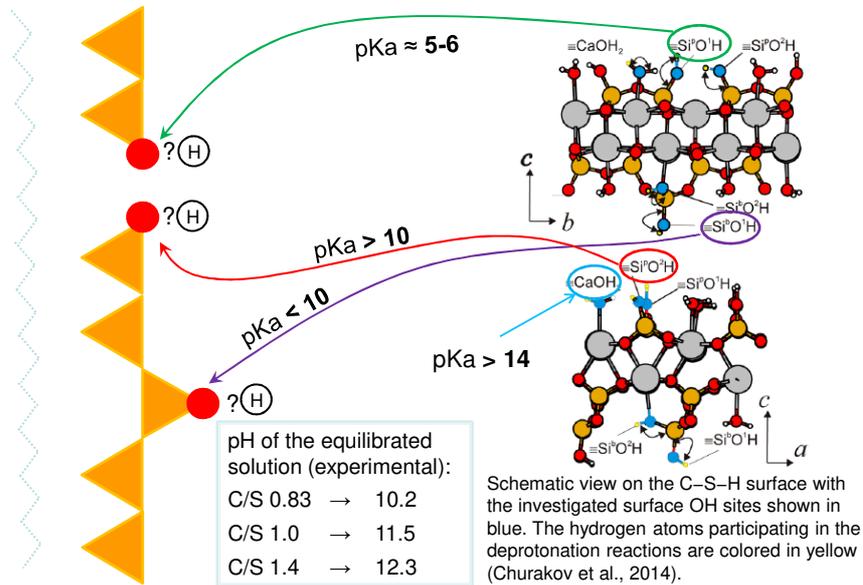
I. Androniuk, Ph.D. Thesis (2017)



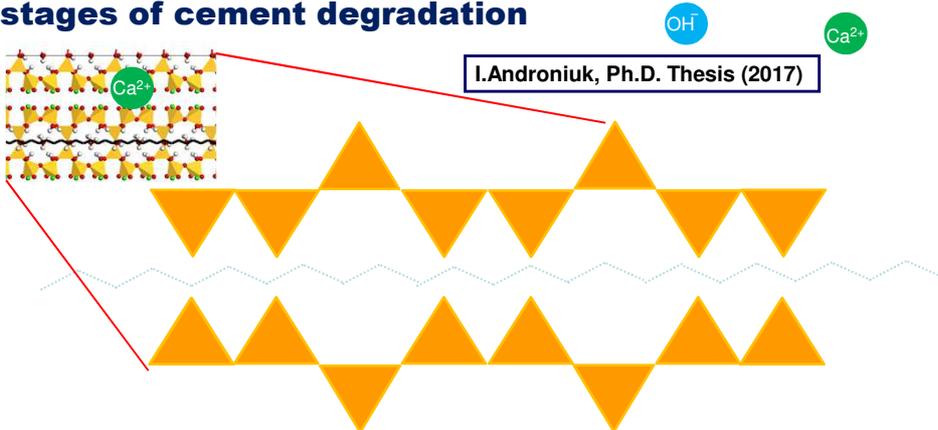
²⁹Si MAS NMR spectra of C-S-H:
C/S = 0.6, 0.8, 1.0, 1.2, 1.5, 1.6 [Beaudoin, 2009]

²⁹Si MAS NMR data serve as a guideline
for elimination of tetrahedra from the Si layer
of initial tobermorite structure.

Protonation of the C-S-H surface

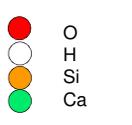


Realistic modeling of C-S-H surfaces at different stages of cement degradation



Realistic C-S-H (tobermorite) surfaces with variable C/S ratios are created by:

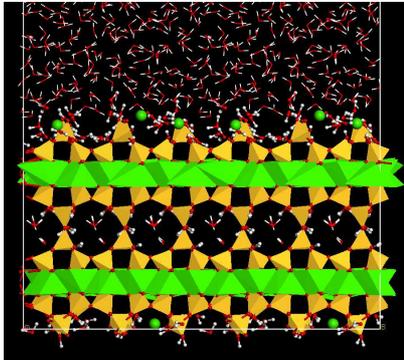
1. Elimination of bridging tetrahedra in the Si layer.
2. Introducing additional Ca^{2+} ions.



New More Realistic C-S-H models

I.Androniuk, Ph.D. Thesis (2017)

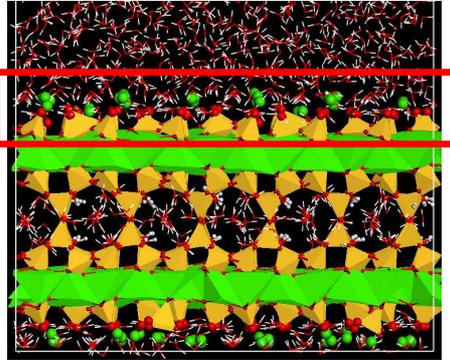
Three computational models of C-S-H surfaces were build representing different C/S ratios (0.83,1.0 and 1.4)



C/S = 0.83

- less defected Si layer
- less Ca^{2+} ions on the surface
- hydroxyls of bridging Si and one of the pairing are deprotonated.

VS.



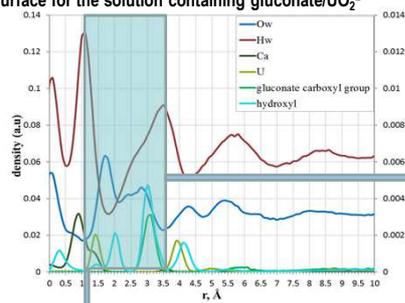
C/S = 1.4

- only dimers in the Si layer
- more Ca^{2+} ions on the surface
- all surface O are deprotonated.

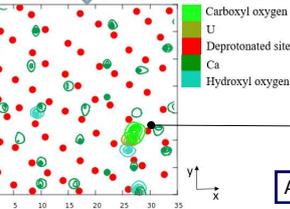
C-S-H / Uranyl / Gluconate System

Ph.D. Thesis of Iuliia Androniuk, Feb. 2017

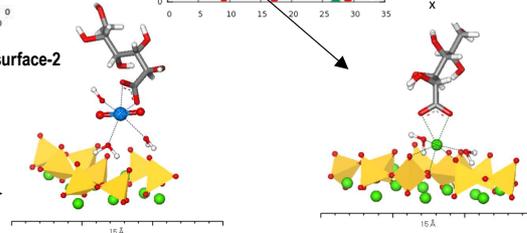
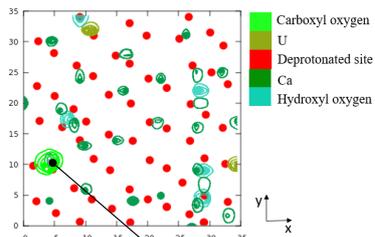
Atomic density profiles normal to the C-S-H-1.4 surface for the solution containing gluconate/ UO_2^{2+}



Distribution of ions on the C-S-H-1.4 surface-2



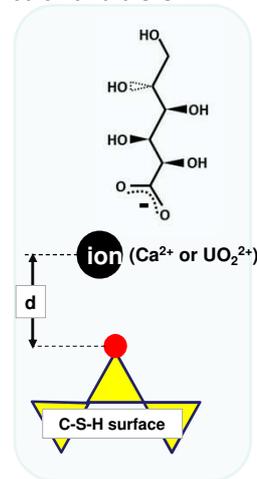
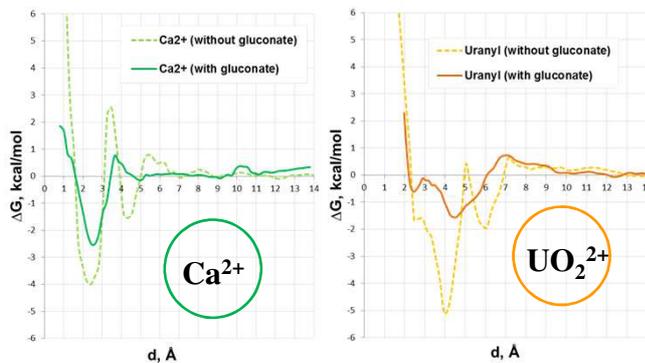
Distribution of ions on the C-S-H-1.4 surface-1



Androniuk et al. *Phys.Chem.Earth A/B/C*, 99, 194-203 (2017)

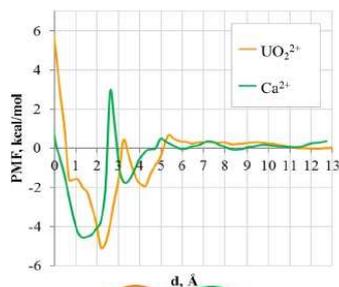
Competition of UO_2^{2+} and Ca^{2+} for Adsorption Sites on the C-S-H Surface

Potential of mean force: adsorption free energy profile between the interfacial Ca^{2+} and UO_2^{2+} ions and a deprotonated silanol group of the bridging Si-tetrahedron on the C-S-H surface with and without a gluconate ion.

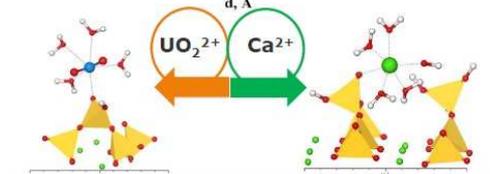


- Presence of gluconate anion in the first coordination sphere of cations significantly weakens the surface binding of both UO_2^{2+} and Ca^{2+}

Competition of UO_2^{2+} and Ca^{2+} for Adsorption Sites on the C-S-H Surface



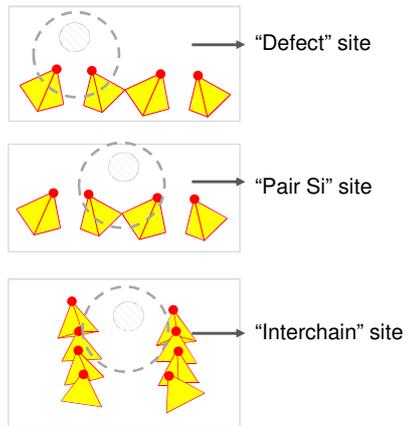
Adsorption free energy (PMF) as a function of distance between UO_2^{2+} , Ca^{2+} and deprotonated silanol group of the bridging Si tetrahedra on the C-S-H surface at C/S = 0.83



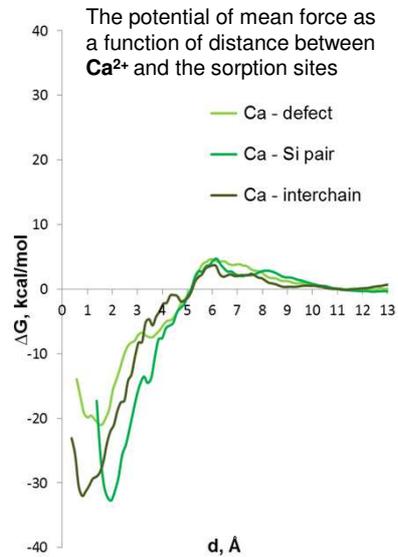
- High energy barrier between the inner-sphere (IS) and outer-sphere (OS) surface complexes
- Approximately the same depth of the potential wells for both IS and OS
- Ion exchange and competition for the same surface sites are very likely

I. Androniuk, A.G.Kalinichev (2020) *Applied Geochemistry*, **113**, 104496.

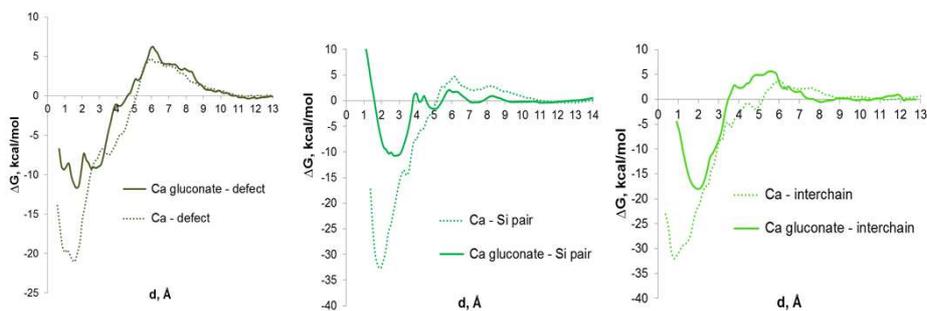
Surface Sorption Sites on C-S-H with High C/S Ratio



- At $C/S > 1.4$, Si chain are mainly built of paired Si, surface silanol groups are deprotonated ($pH > 12$)
- Ca^{2+} is strongly bound to C-S-H surface.
- 3 most important sorption sites were identified.

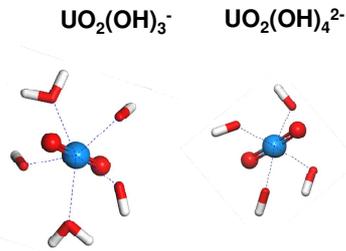


Effect of Gluconate on Ca^{2+} Binding to the C-S-H Surface

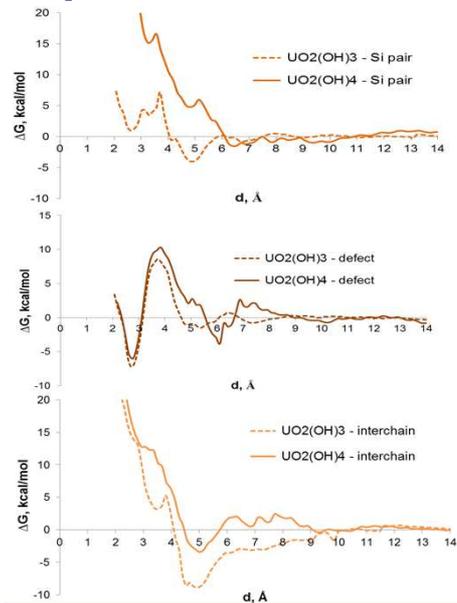


- The binding of Ca^{2+} to the C-S-H surface becomes much weaker and potentially may result in a higher probability of substitution for a competing solution cation (e.g., Na^+ or $UO_2(OH)_3^-$).
- Effect of gluconate is the same for all the sorption sites studied.
- Even though the adsorption energy decreases, complexation between Ca-gluconate and C-S-H surface remains stable.

Sorption of UO_2^{2+} Hydroxo-Complexes on C-S-H at High C/S Ratio



- $\text{UO}_2(\text{OH})_3^-$ and $\text{UO}_2(\text{OH})_4^{2-}$ are the dominating species at high pH range
- $\text{UO}_2(\text{OH})_3^-$ surface binding is more energetically stable for all sorption sites studied
- $\text{UO}_2(\text{OH})_4^{2-}$ has to exchange hydroxyls in order to bind to the C-S-H surface



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.