THE STRUCTURE OF WATER IN CALCIUM-SILICATE-HYDRATES STUDIED BY NEUTRON DIFFRACTION WITH ISOTOPIC SUBSTITUTION

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BRGM Supervisor: Francis Claret
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MOST CONSUMED SUBSTANCES IN THE WORLD

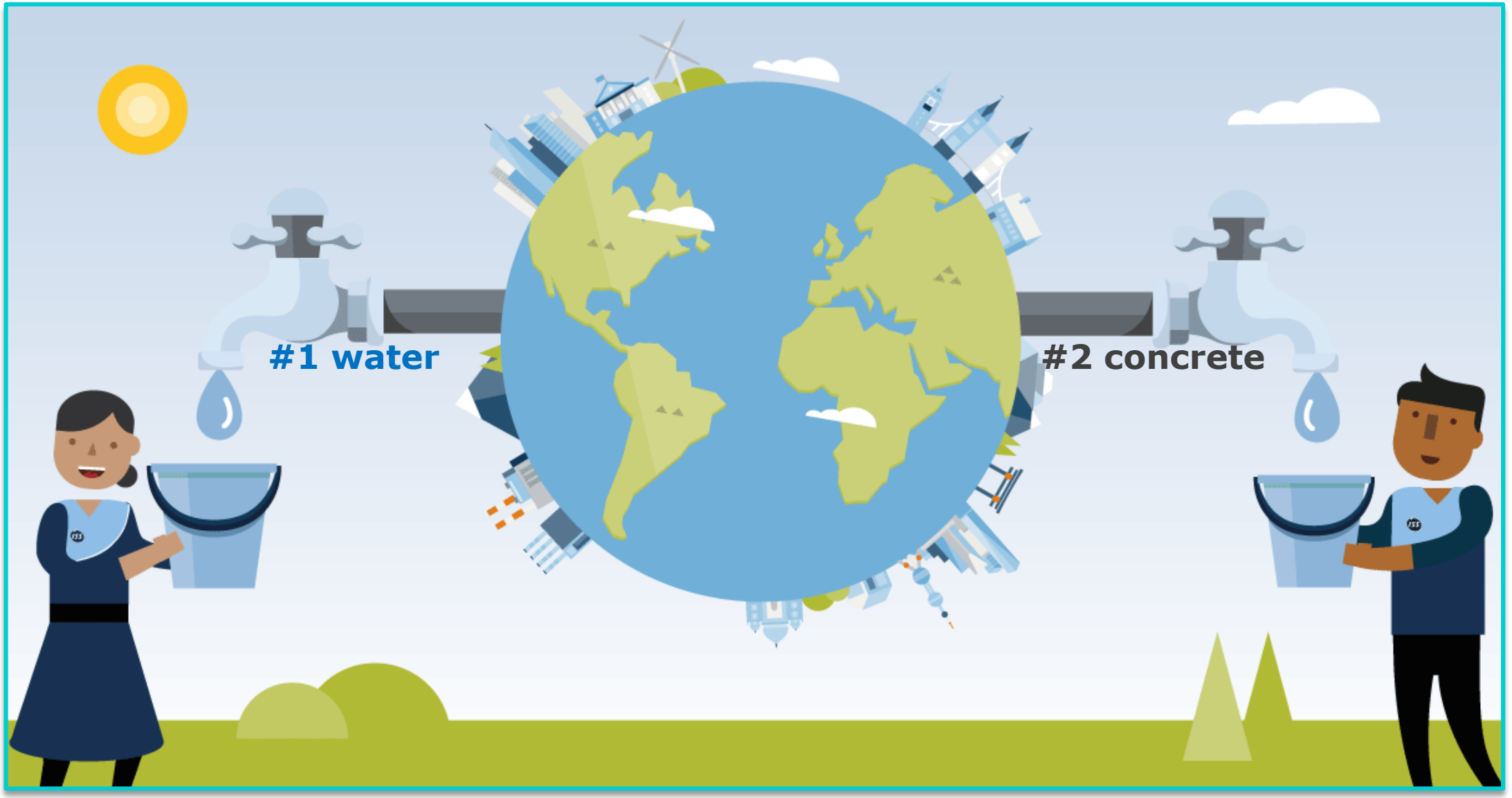
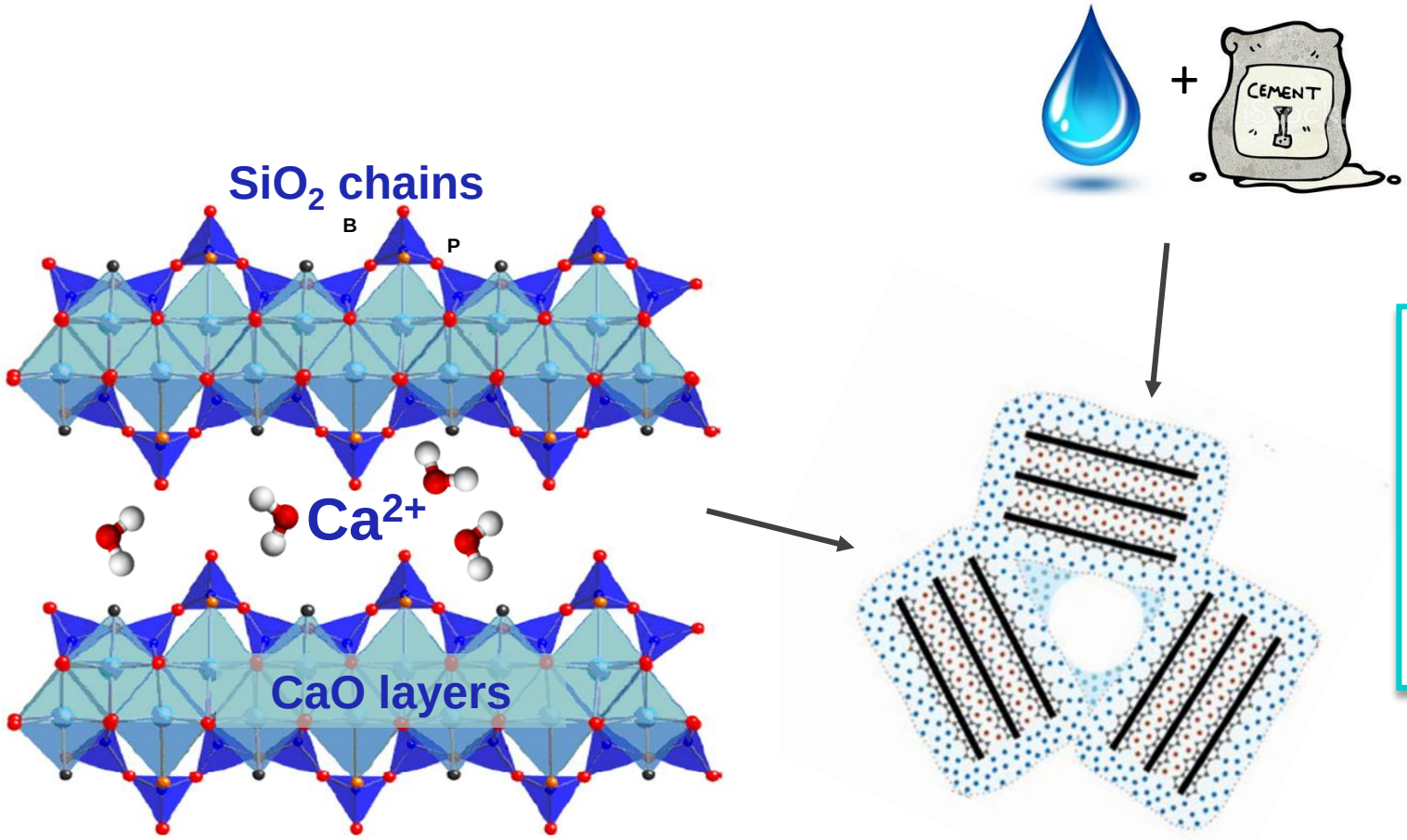


Image modified from www.servicefutures.com

CALCIUM SILICATE HYDRATES (C-S-H)



mesoscale view of C-S-H

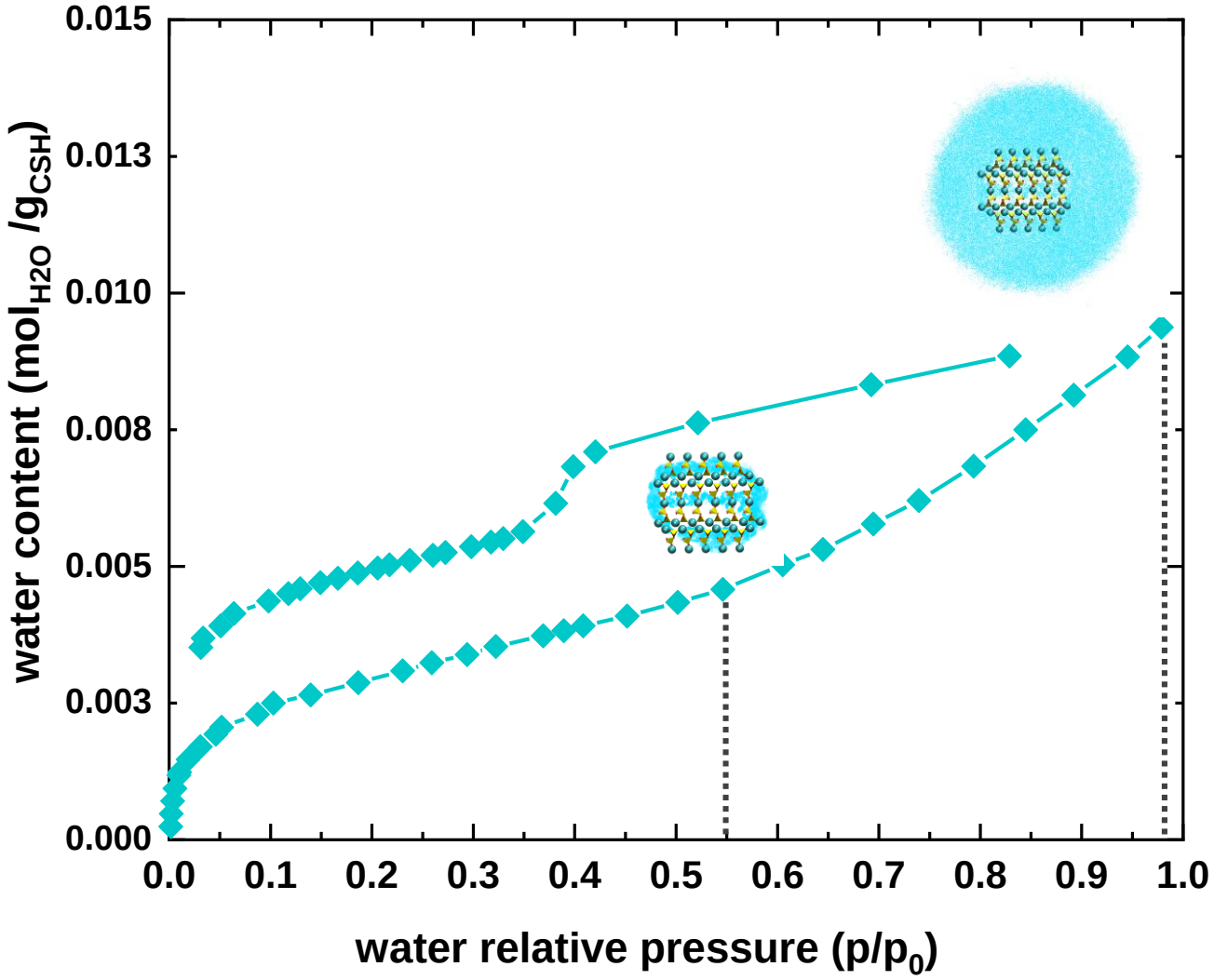
- 1° strength-giving phase
- Nanocrystalline, disordered
- Ca/Si=0.7-1.5 synthetic CSH
- Ca/Si=1.6-2 cement paste

atomic structure of tobermorite mineral

Modified from Richardson (2008); Roosz et al. (2017)

WHY STUDY WATER?

structure of water in C-S-H is still unresolved!



- dissolution and recrystallization of cement
- transport and diffusion of ions
- carbonation of cement
- mechanical properties of cement

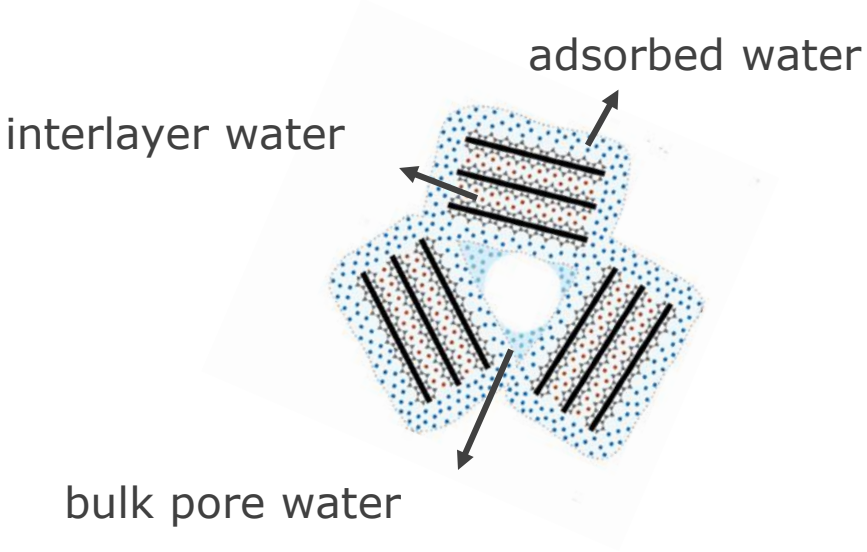
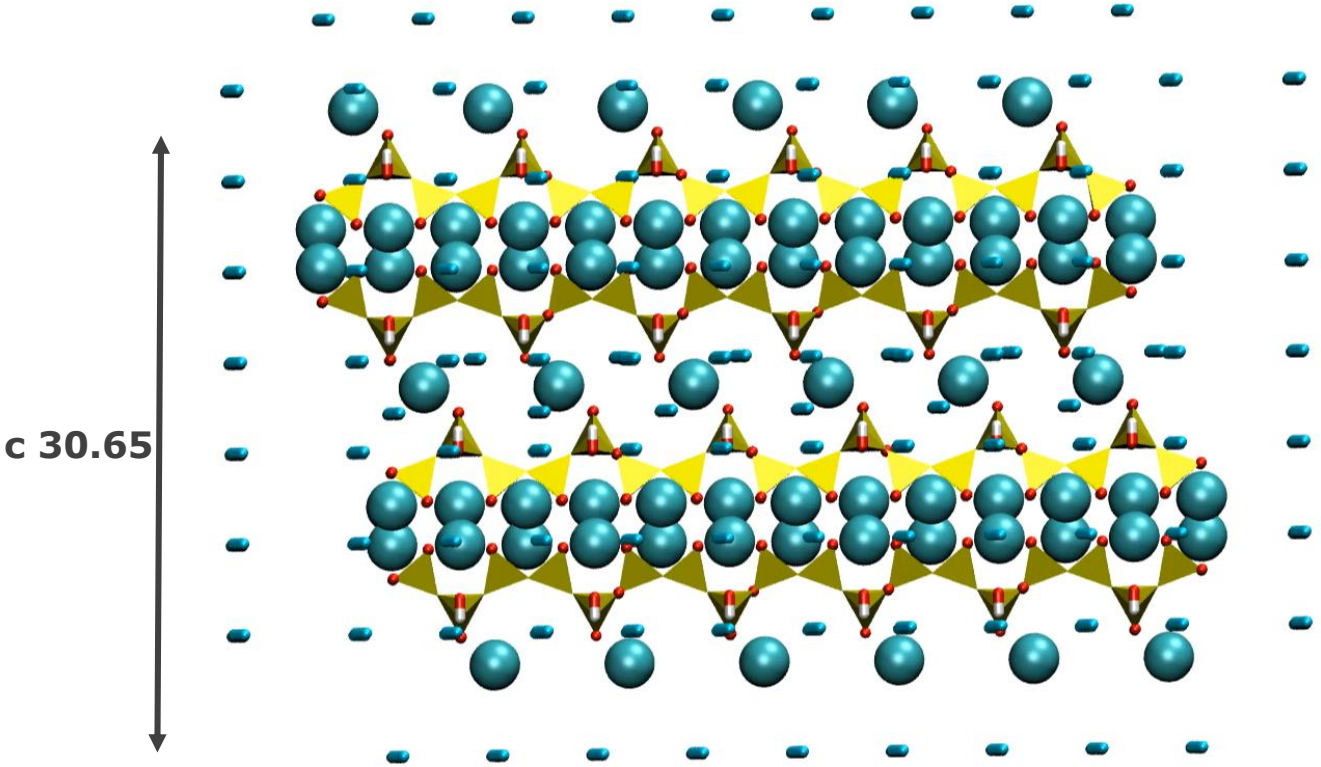


Image from Roosz et al. (2017)

CALCIUM-SILICATE-HYDRATE NANOPARTICLE Ca/Si=1 55% R.H.



- ClayFF, SPC/E
- 14Å tobermorite model by Bonaccorsi et al.
- Ca/Si=1 by removing $Si_{bridging}$
- Nanoparticle – 6x * 6y * 2z, cleaved in 3D
- Partial charges of silanol O – calculated from Lammers & Bourg (2017)
- Water amount from WSI, XRD, TGA to match 55% R.H.

H_2O Ca >Si-O^- >Si-OH

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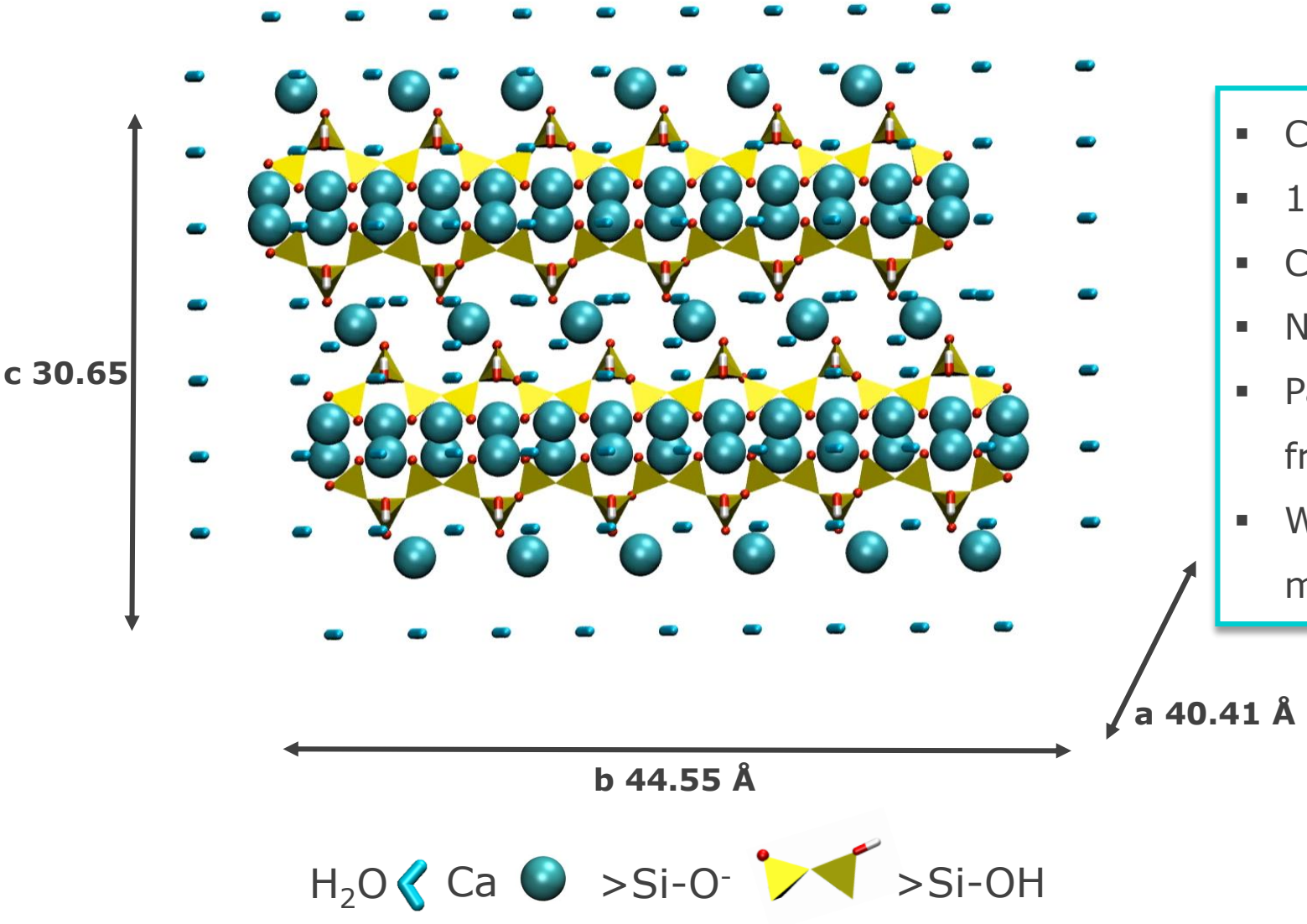

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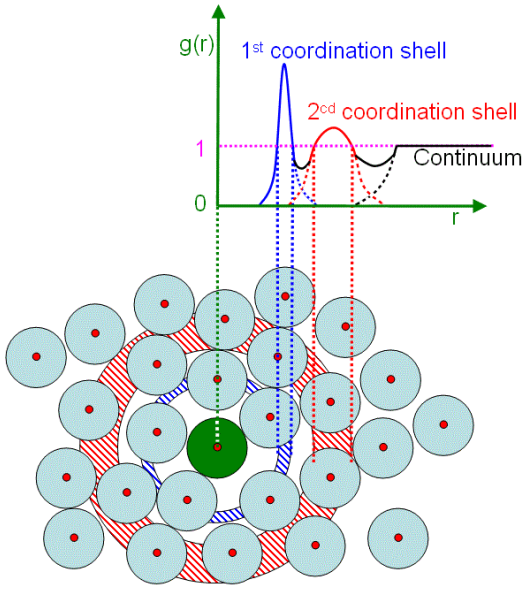
NEUTRON DIFFRACTION WITH ISOTOPIC SUBSTITUTION
WHY NEUTRONS?

Information about local ordering of water

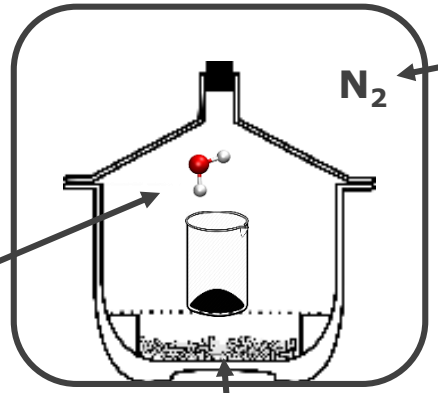
H neutron cross-section

H X-ray cross-section



oven dried C-S-H

Equilibration with H_2O or D_2O at controlled humidity



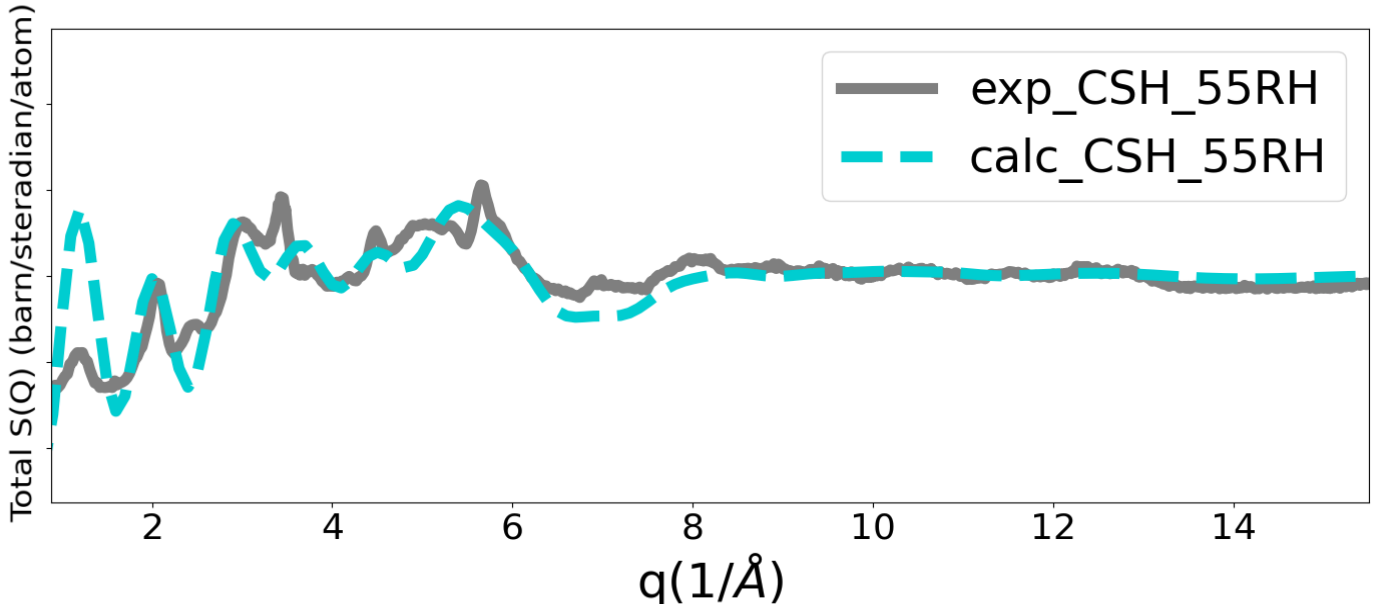
Inert atmosphere (C_{CO2} < 50ppm)

Water vapor = H_2O or D_2O

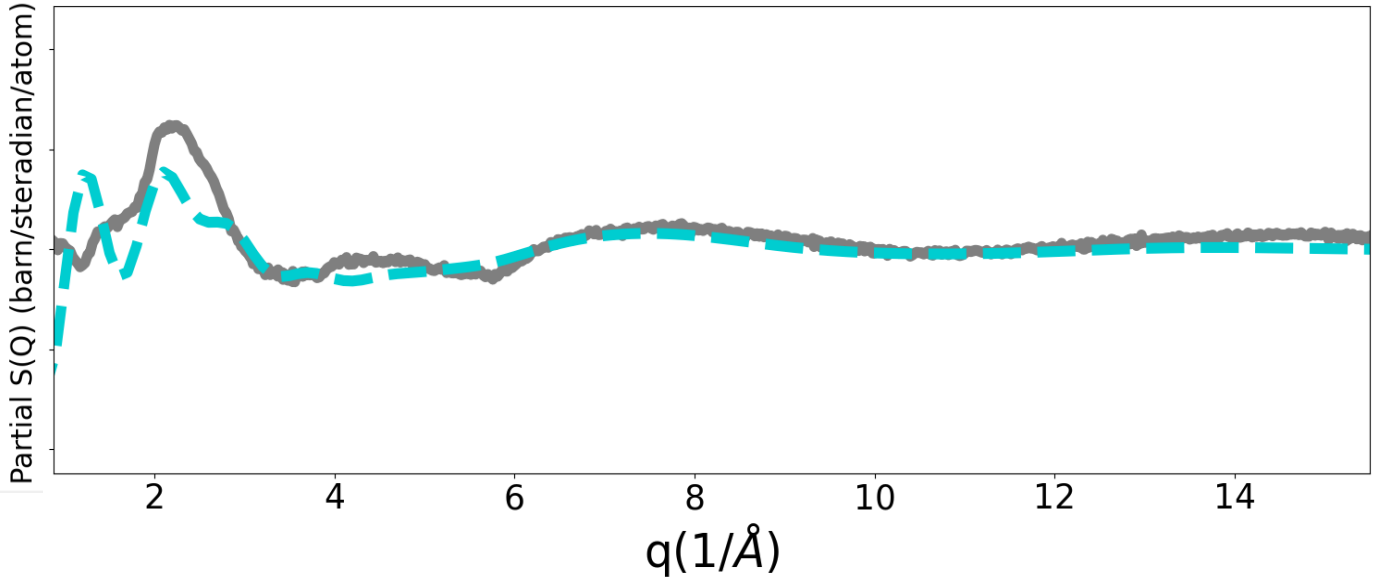
Humidity controlled by a saturated solution of K_2SO_4 (~98% RH) or $Mg(NO_3)_2*6H_2O$ (~55% RH)

MD MODEL VALIDATION – EXPERIMENTAL S(Q) VS CALCULATED

MD model is validated by structure factors



total S(Q) C-S-$H_{hydrogenated}$



S(Q)C-S-$H_{deuterated}$

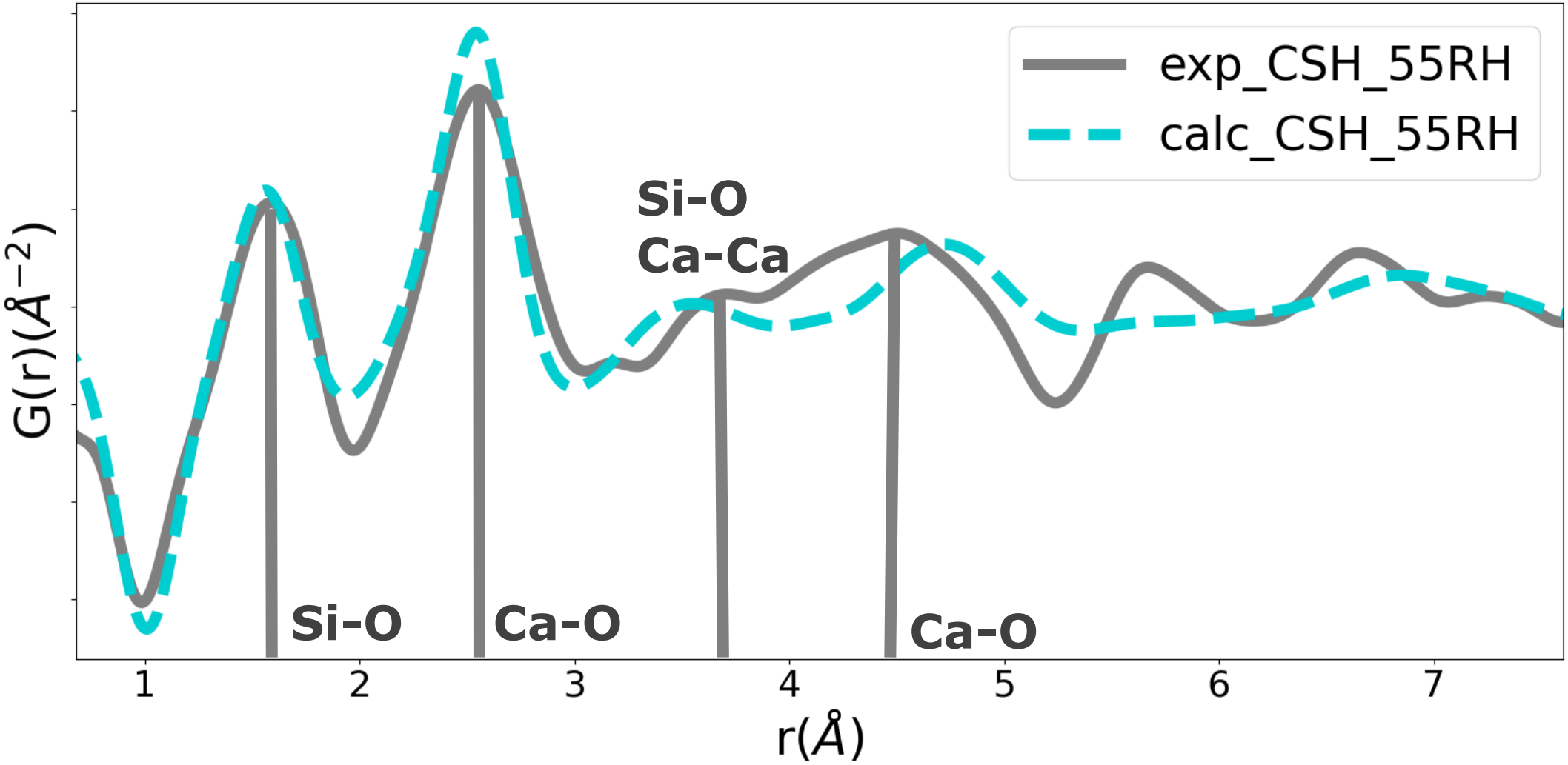
S(Q)C-S-$H_{hydrogenated}$

partial ΔS(Q)

MD MODEL VALIDATION – EXPERIMENTAL TOTAL G(R) VS CALCULATED

MD model is validated by total pdf

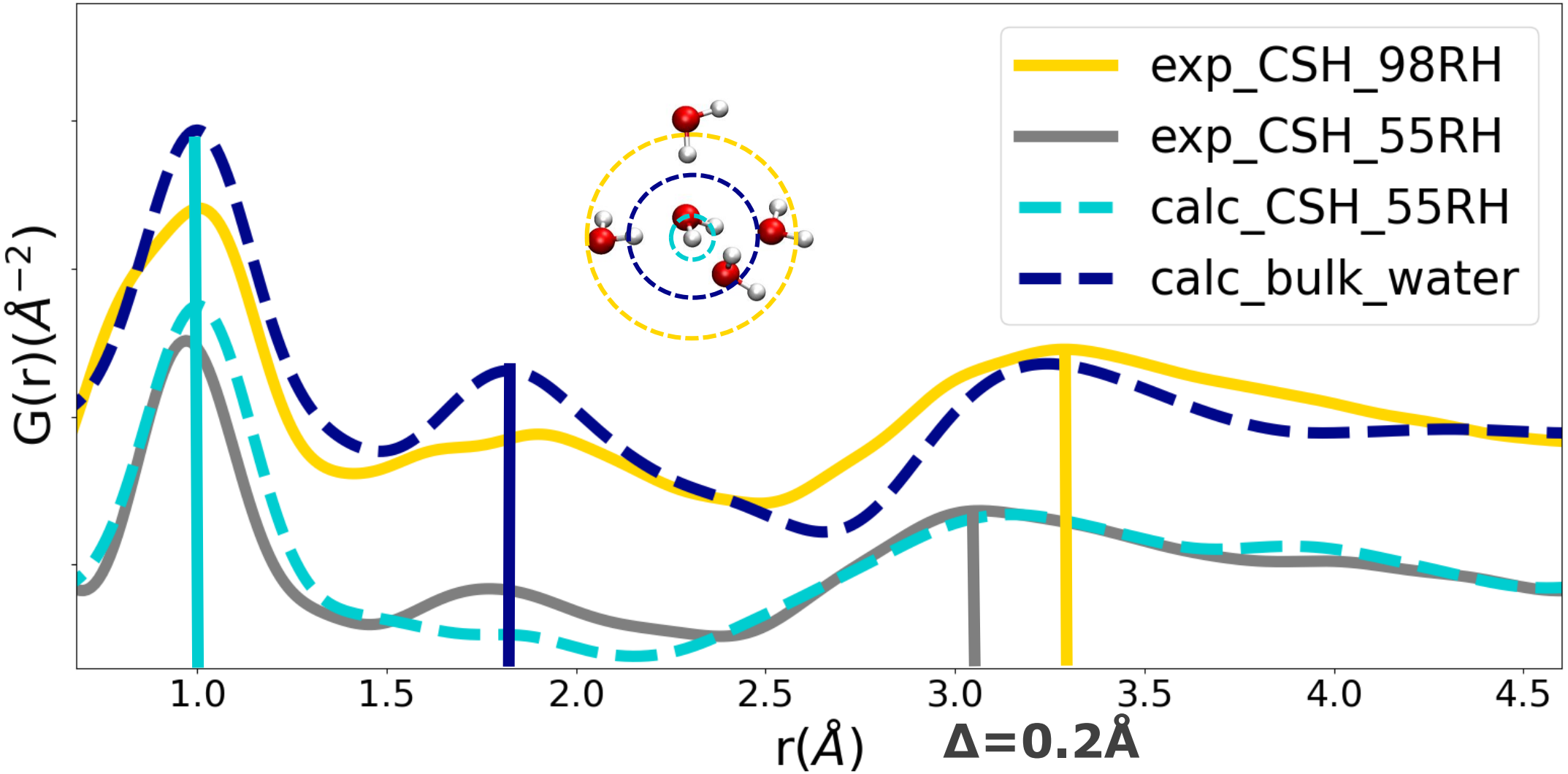
S(Q) hydrogenated $\xrightarrow{FT}$ G(r) distances between all atom pairs



MD MODEL VALIDATION – EXPERIMENTAL FIRST DIFFERENCE G(R) VS CALCULATED

MD model is validated by partial pdf

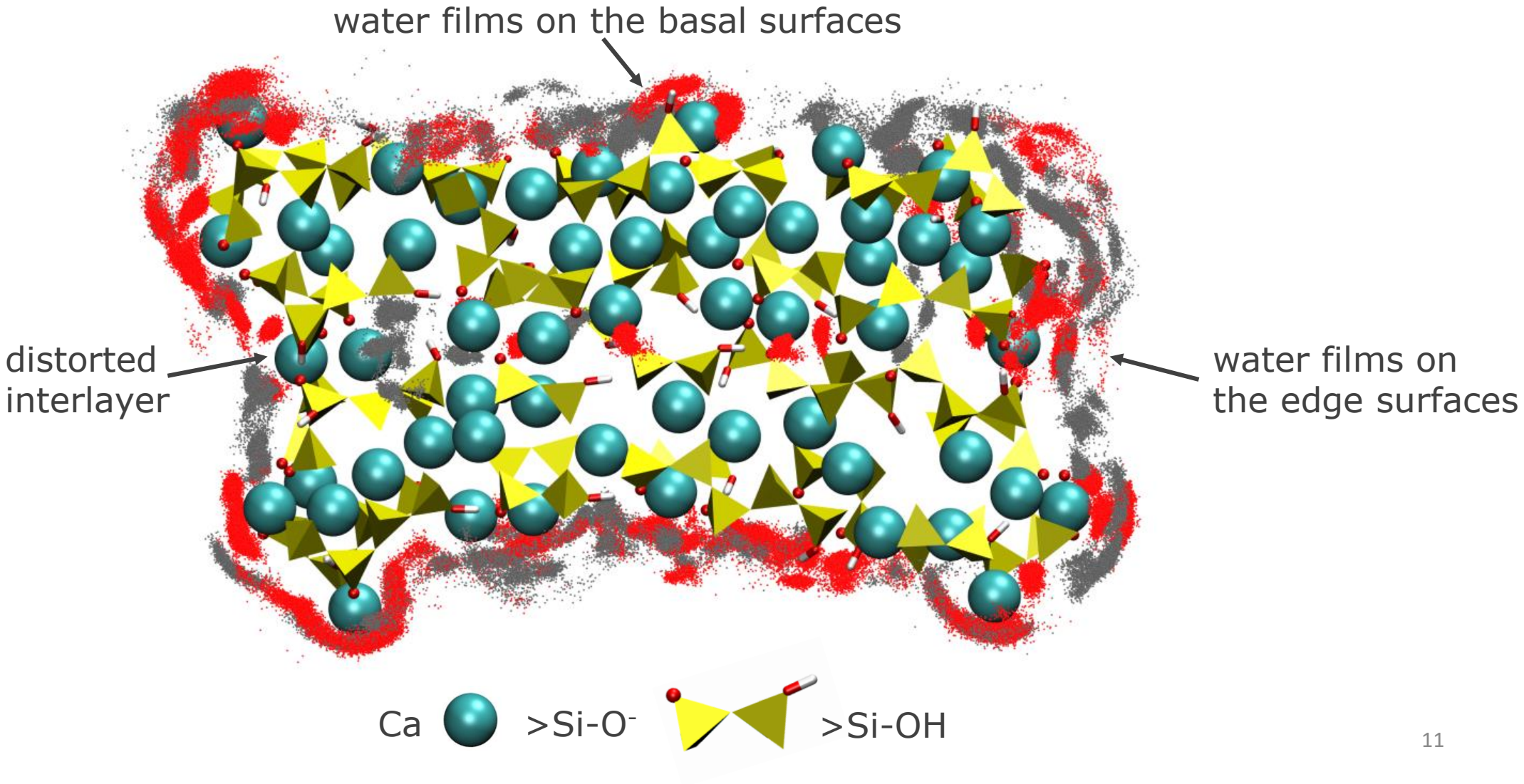
S(Q) hydrogenated – S(Q) deuterated $\xrightarrow{FT}$ G(r) distances between H and Ca, Si, O



CROSS SECTION OF C-S-H 55% R.H.

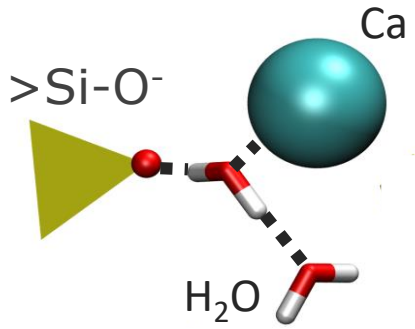
After ~5ns

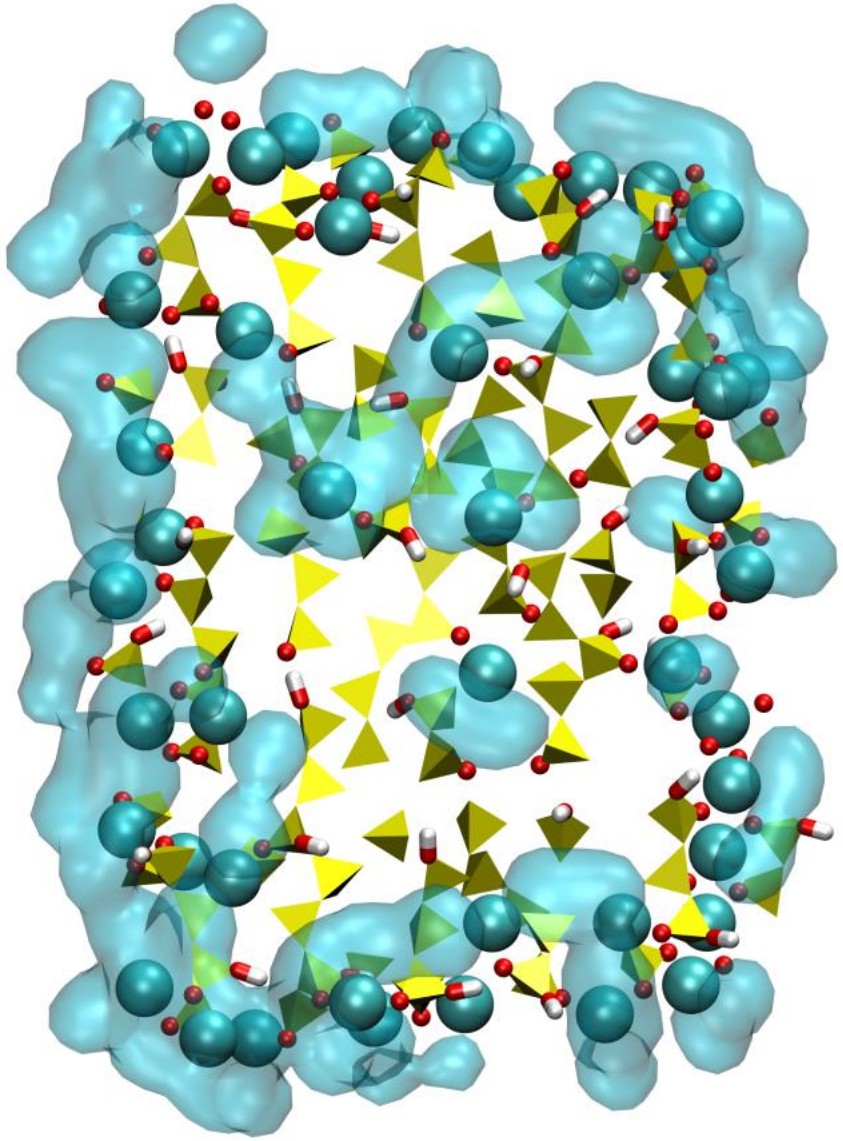
Type I water – coordinated to Ca ions ~61%
Type II water – not coordinated to Ca ions ~39%



CONCLUSION - WATER BONDING

Type I water – coordinated to Ca ions ~61%





basal plane

Type I water donates H-bond equally to the surface >Si-O⁻ and to other H_2O

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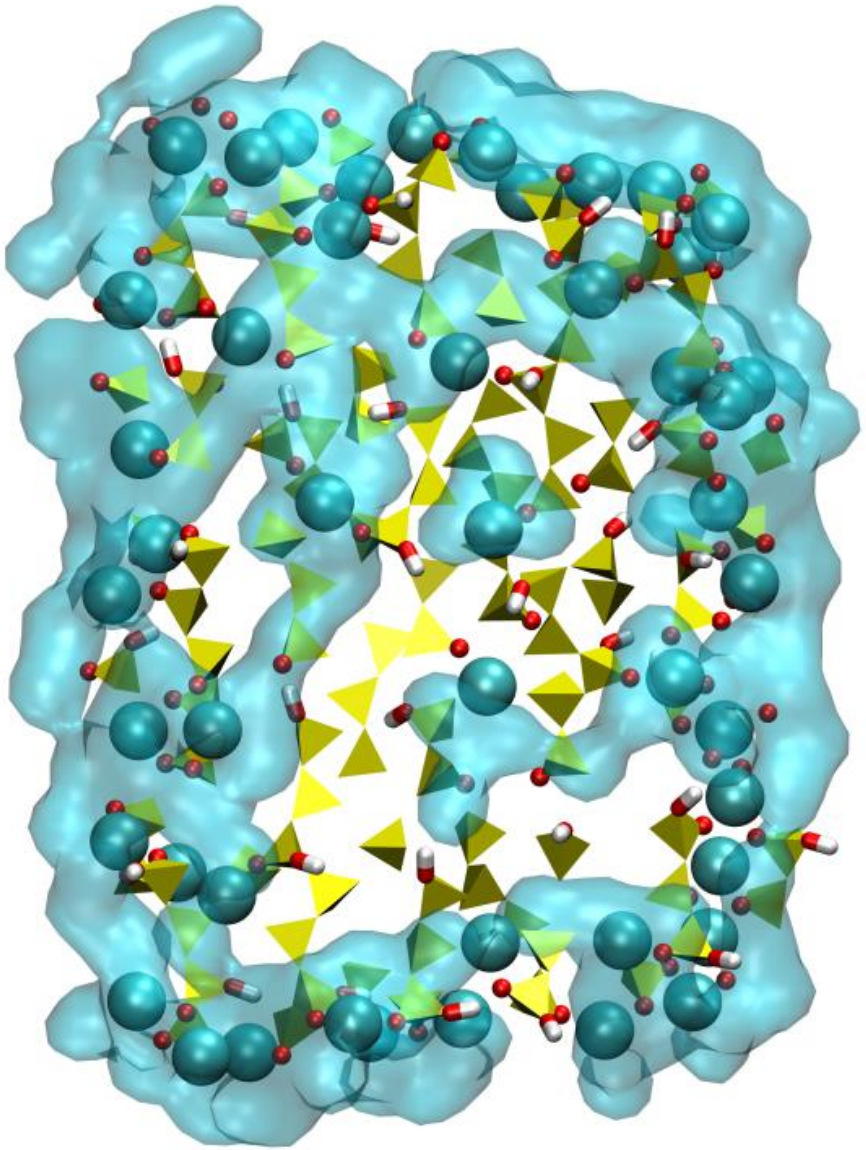

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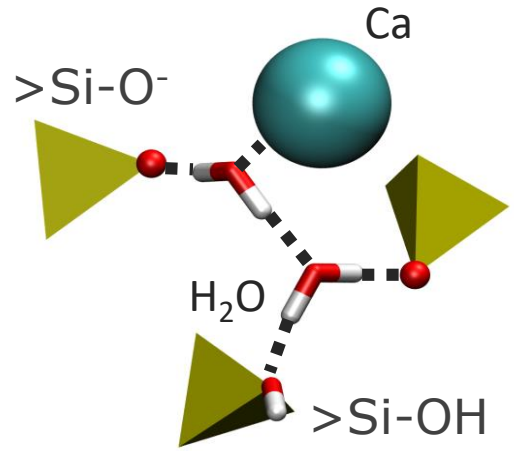

Type I water donates H-bond equally to the surface >Si-O^- and to other H_2O

Type II water donates ~3* more to the surface >Si-O^- than to other H_2O to anchor itself on the surface

CONCLUSION - WATER BONDING

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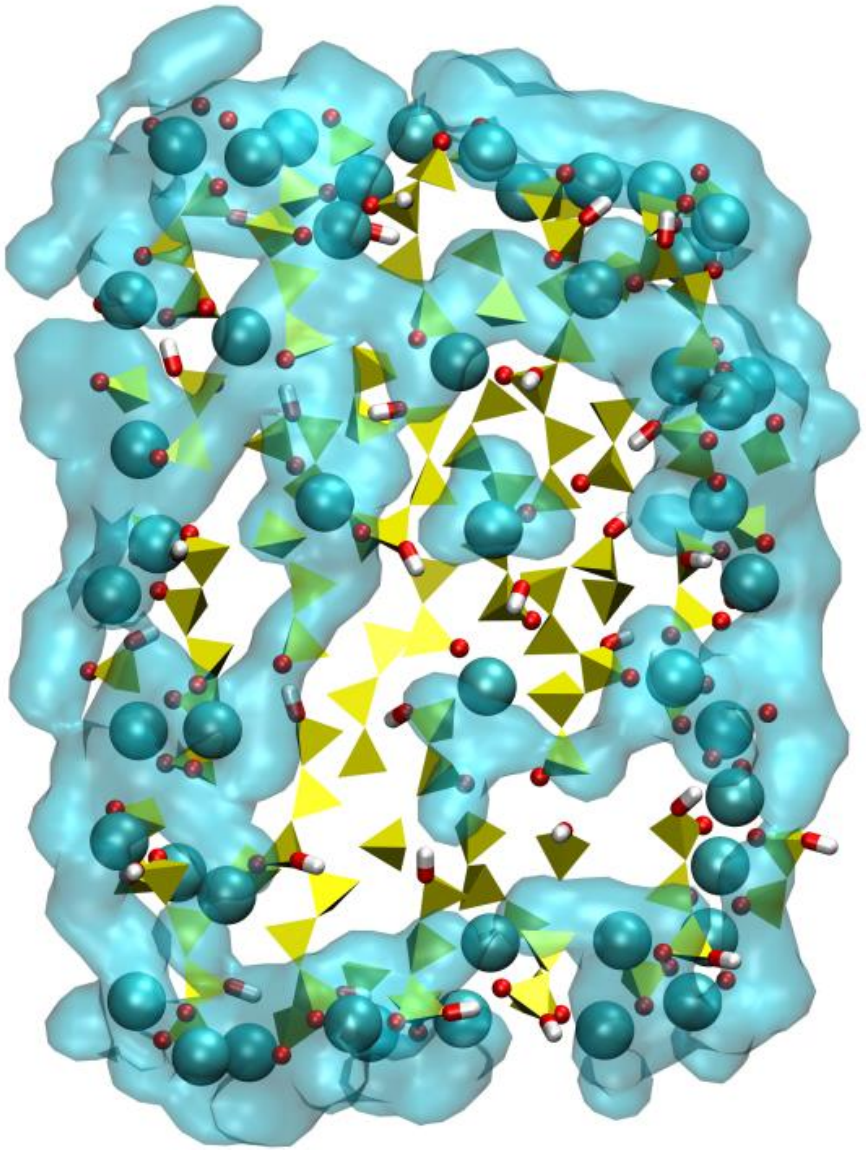

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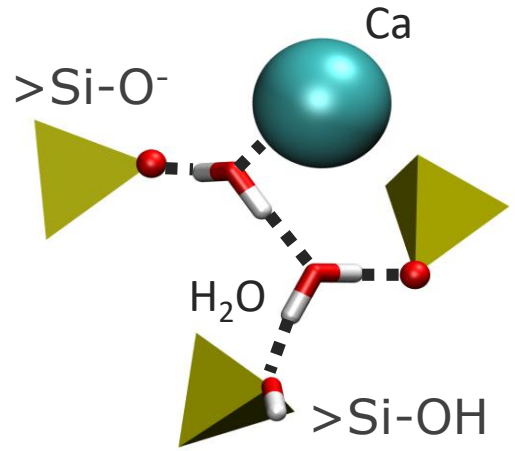

Type I water donates H-bond equally to the surface >Si-O⁻ and to other H_2O

Type II water donates ~3* more to the surface >Si-O⁻ than to other H_2O to anchor itself on the surface

The **wet areas** of the surface are around Ca ions

The **dry areas** are around the surface >Si-OH

THANK YOU FOR YOUR ATTENTION!

Acknowledgements:

Supervisors: Alejandro Fernández-Martínez and Alexander Van Driessche
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ILL collaborator: Henry Fischer
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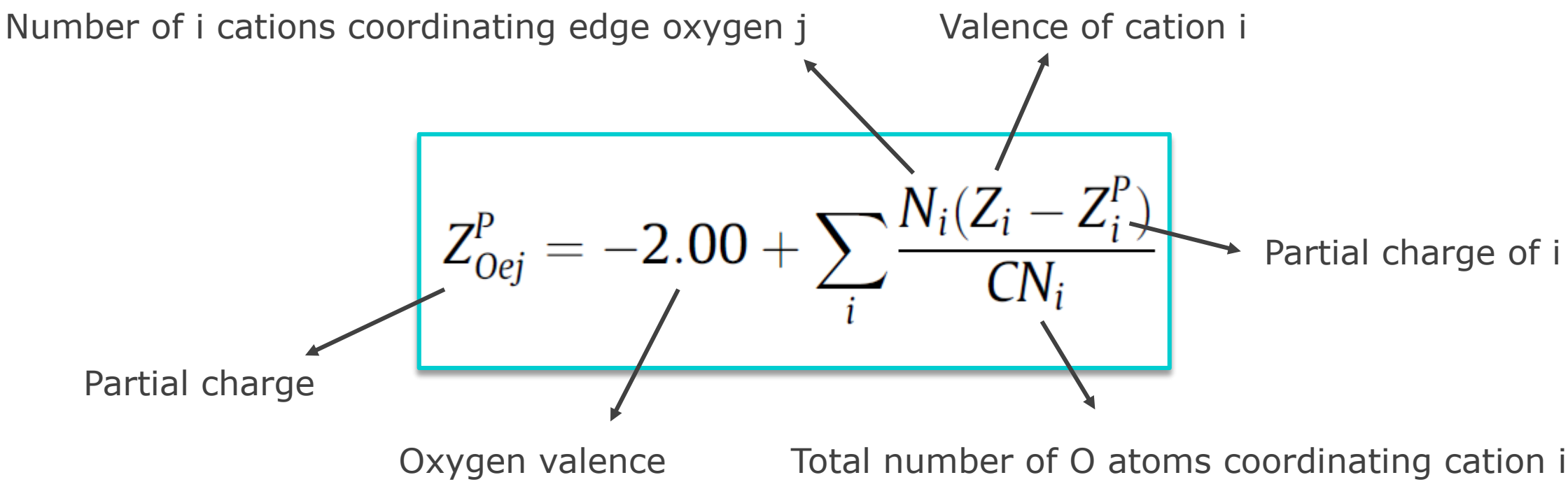
IDEX mobility scholarship from UGA


Number of i cations coordinating edge oxygen j
Valence of cation i
$Z^P_{Oej} = -2.00 + \sum_i \frac{N_i(Z_i - Z^P_i)}{CN_i}$
Partial charge of i
Partial charge
Oxygen valence
Total number of O atoms coordinating cation i