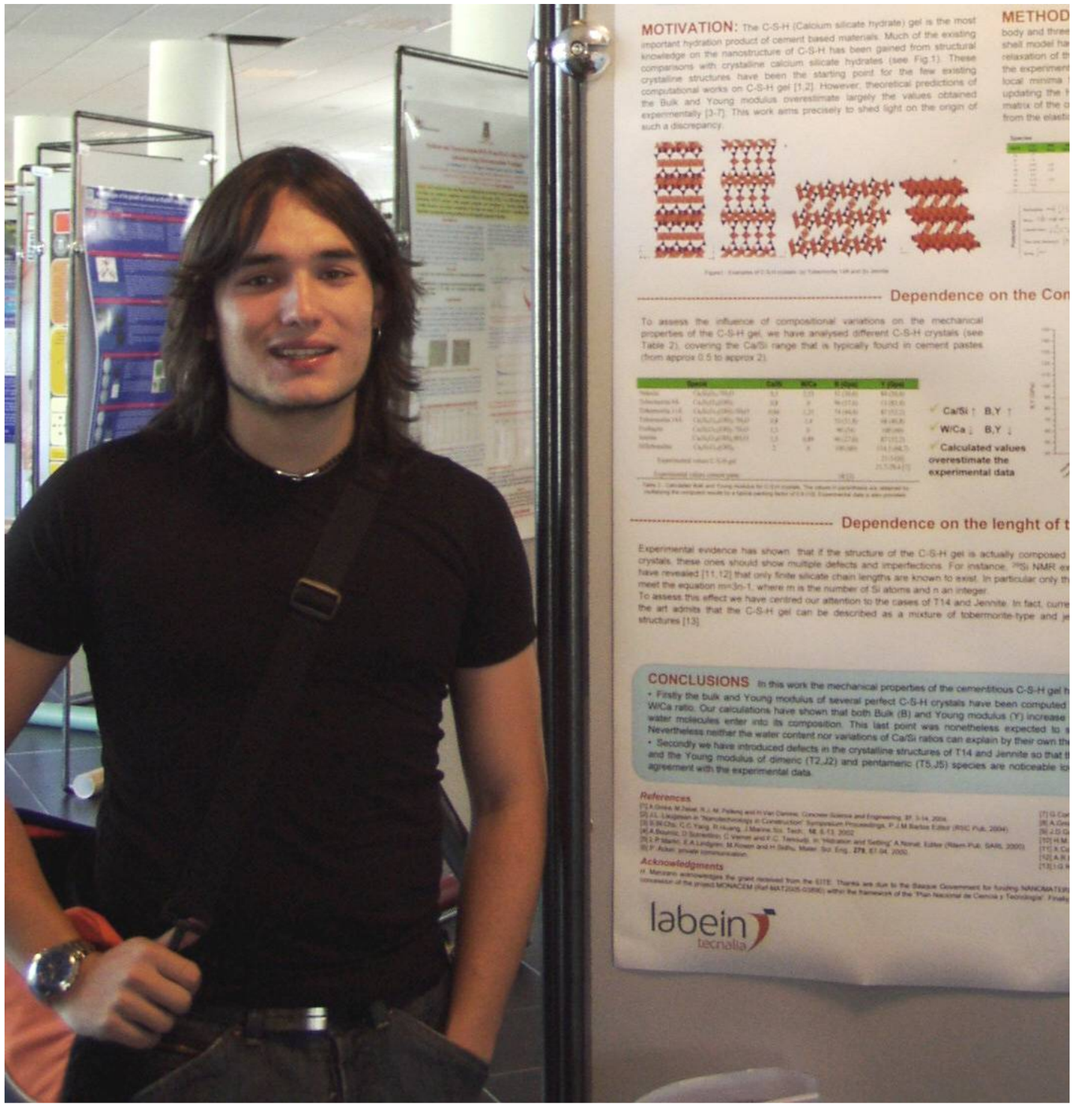
Universidad del País Vasco
Euskal Herriko Unibertsitatea
FACULTY OF SCIENCE AND TECHNOLOGY
UNIVERSITY OF THE BASQUE COUNTRY

20 years of atomistic simulation in cement

Hegoi Manzano

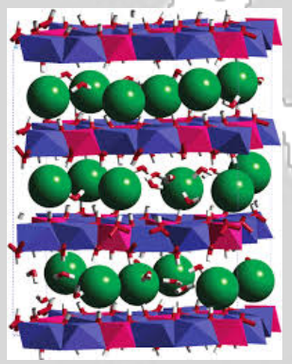
Department of Physics
Faculty of Science and Engineering
University of the Basque Country UPV/EHU

Started my phD 10 Oct. 2005



Poster presentation at the Trends in Nanotechnology conference in Grenoble 2006

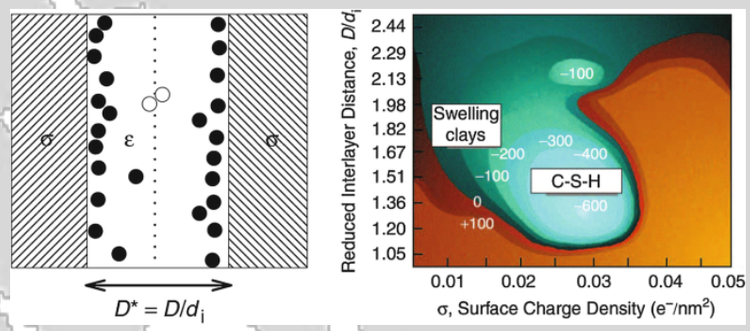
Before 2005: early studies by the clay community



Urbana Champaine
Kirkpatrik & Kalinichev

First MD studies on tobermorite, ettingite, protlandite…

France
Faucon & Nonat,
R.Pellenq, Labbez



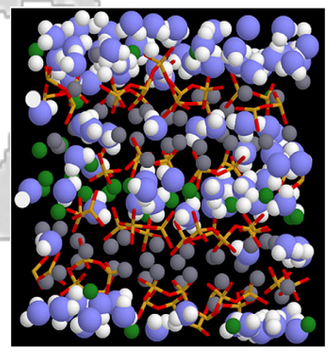
Primitive model to investigate cohesive forces

2005 to 2012: specialised studies

First calculations on hibrid systems

Vandervilt
Florence Sanchez

MIT CSHub
Ulm, Pellenq, et al. (also me)



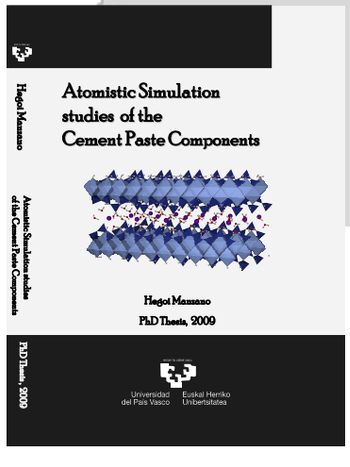
First “realistic” C-S-H model
Disseminate simulations

France
Labbez

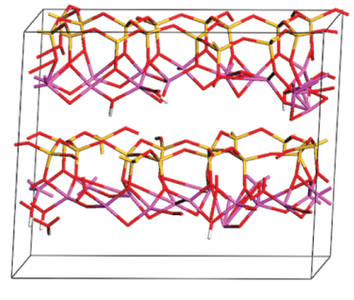
PSI (Switzerlad)
Churakov

Basque Country
Dolado, Ayuela, Manzano

First determination of elastic properties
First calculations on clinker phases
First phD thesis



Melbourne
White and Provis



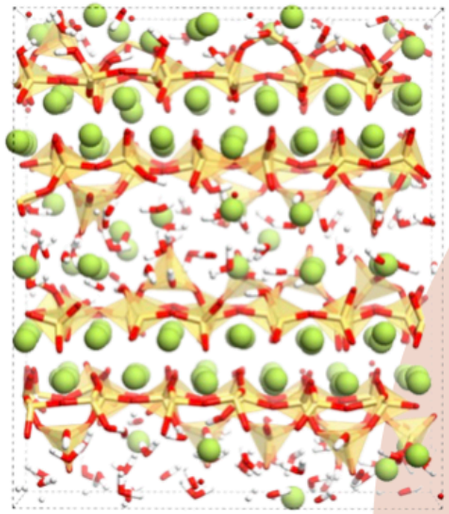
First calculations on SCM

2012 to 2017: generalization of the technique

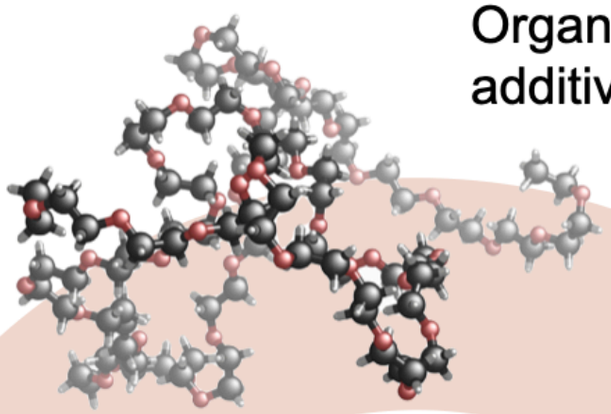
2018 to present: the BOOM!

20 years of research

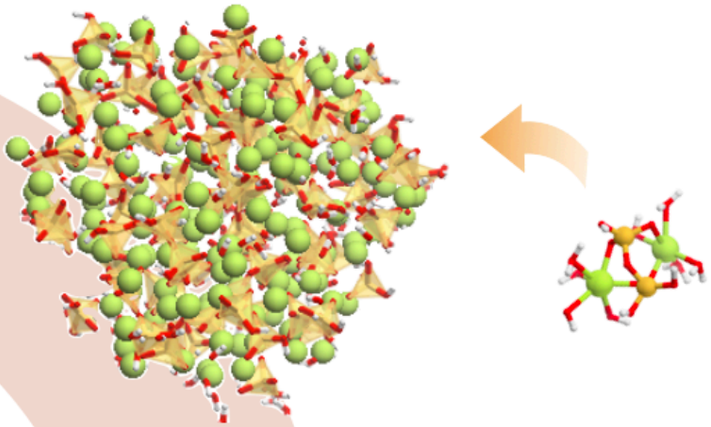
C-S-H structure and properties: confined water, ion transport, etc



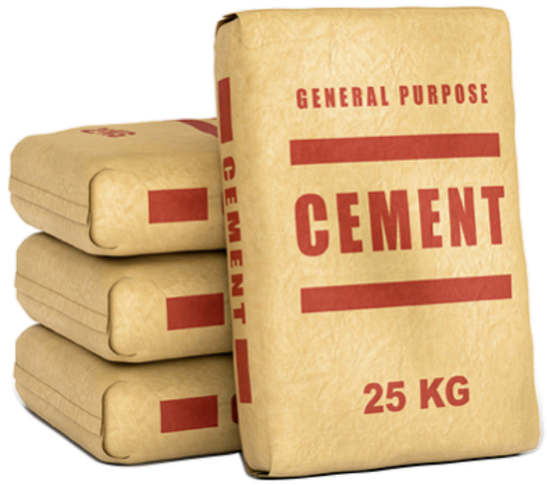
Organic additives

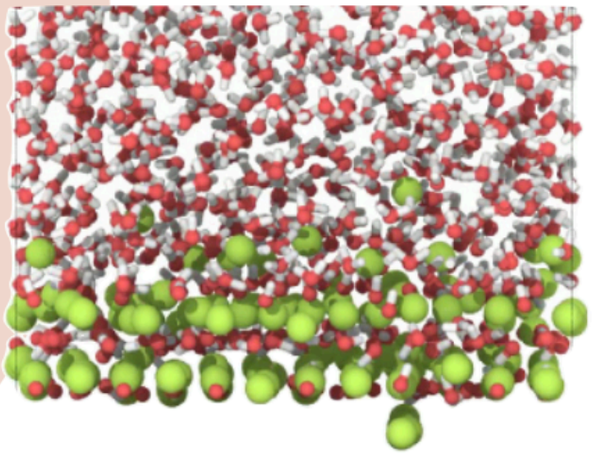


Nucleation and growth of hydrates

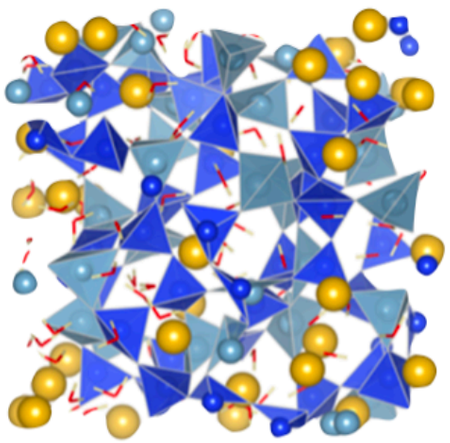


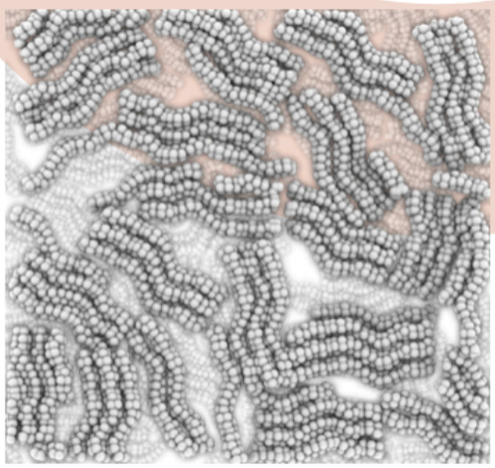
Water/solid interfaces, hydration and dissolution



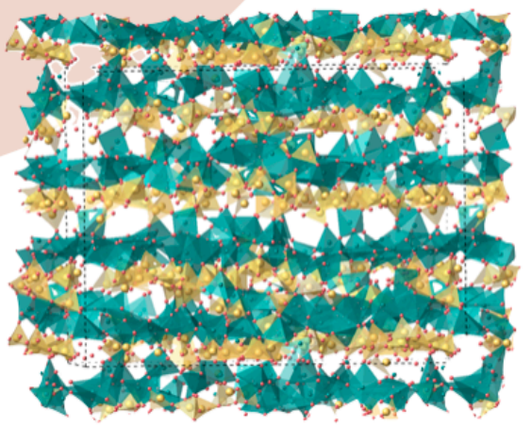


Alternative binders: geopolimers, Mg-based



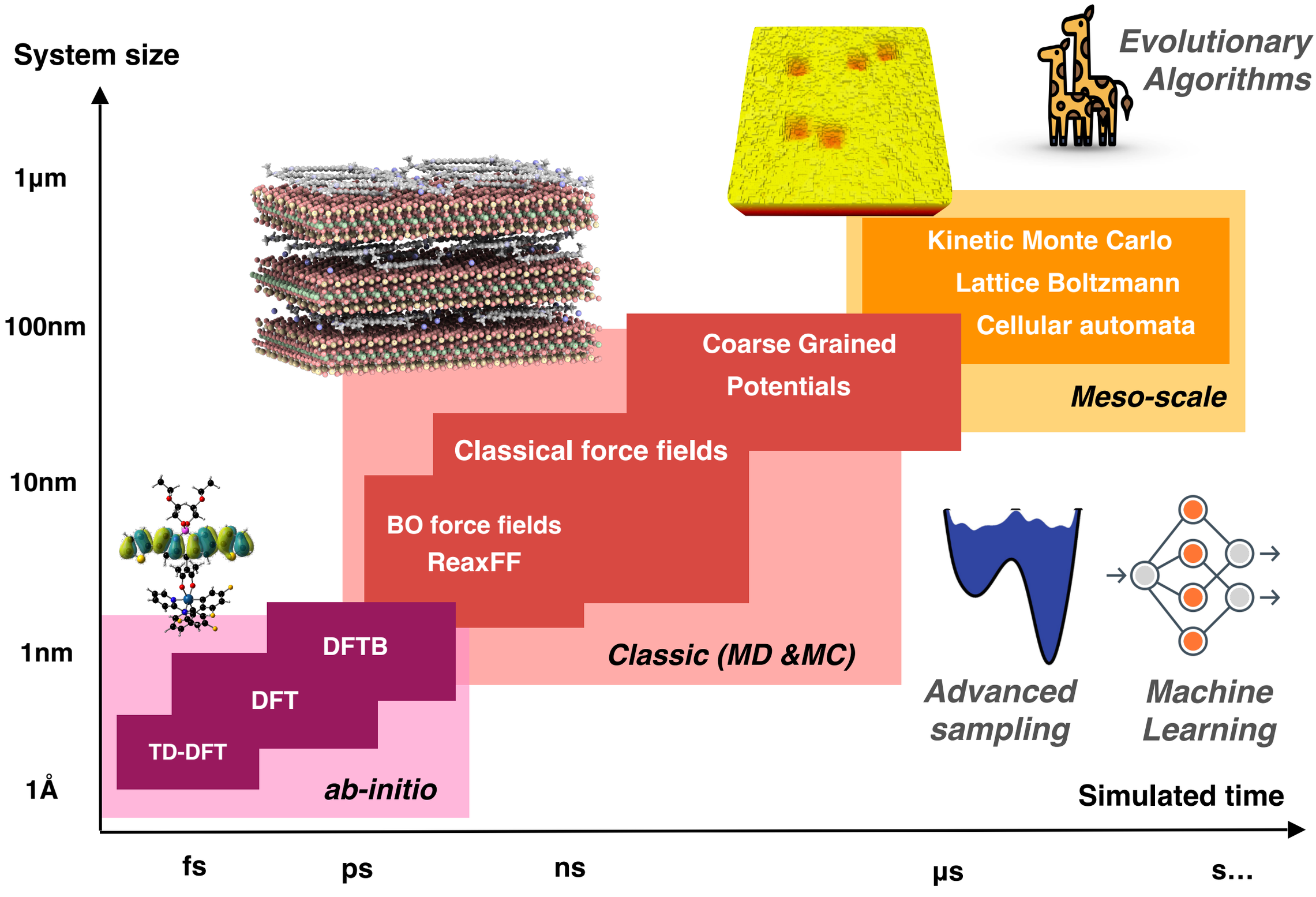


Coarse-grain and mesoscale modelling



SCM: fly ashes, slags, metakaolin

20 years of research



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“We can go beyond laboratory limitations, do thousands of simulations to test materials and calculate properties, and design cement from electrons to buildings”

The present of atomistic simulations in cement

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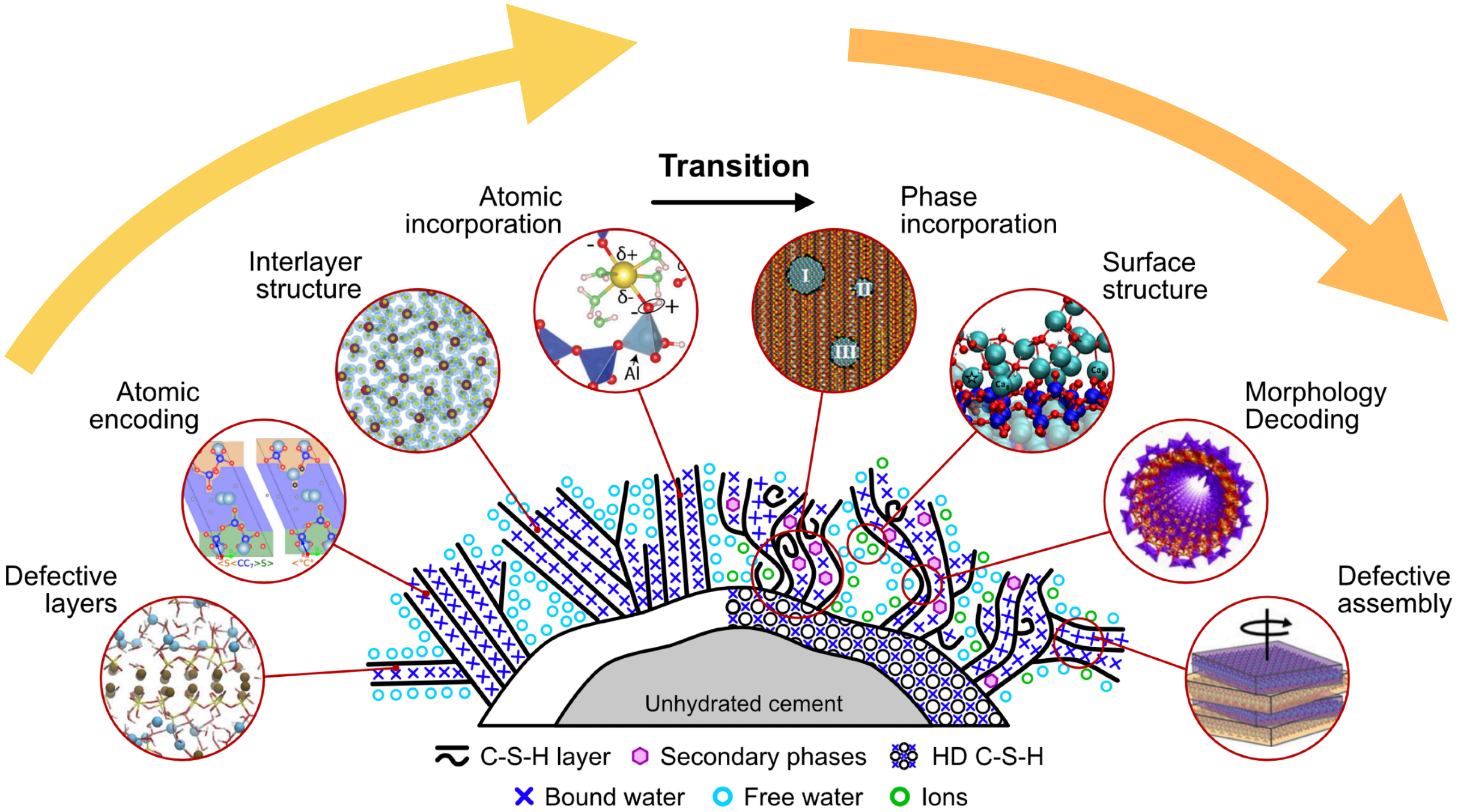
Calcium Silicate Hydrate



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Calcium Silicate Hydrate: interfaces

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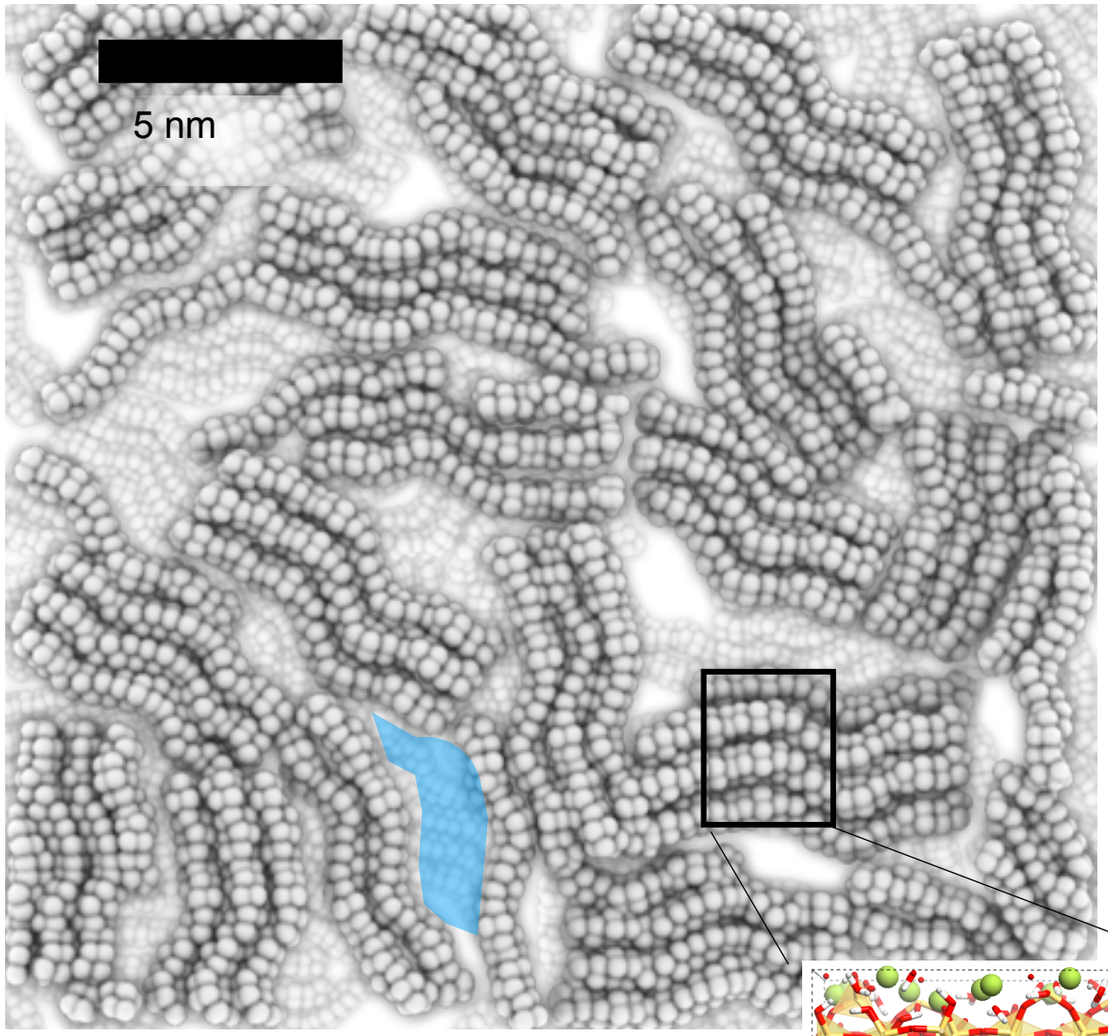

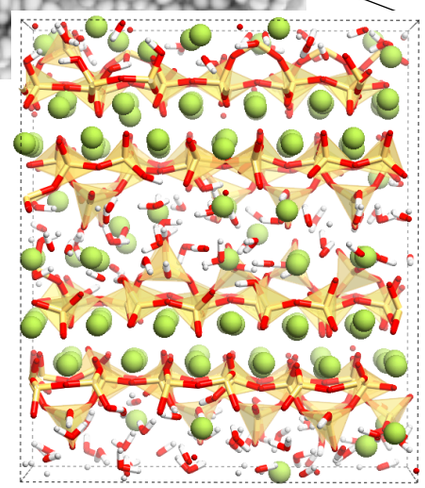

Bulk models

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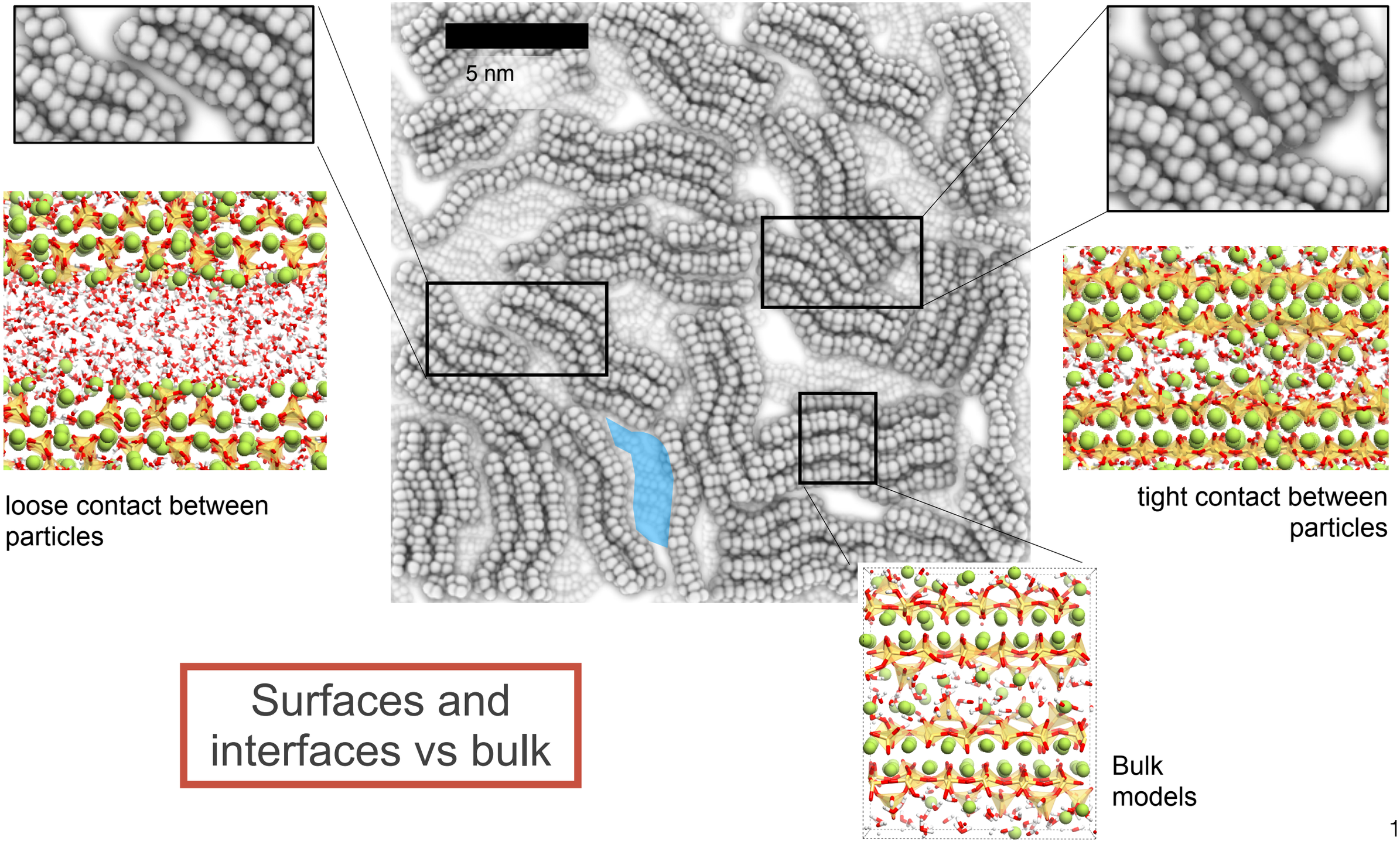

loose contact between particles

tight contact between particles

Surfaces and interfaces vs bulk

Bulk models

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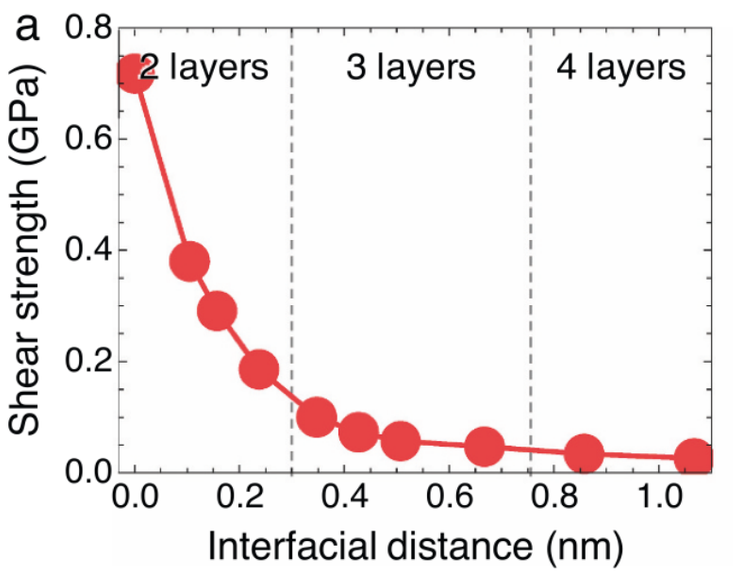

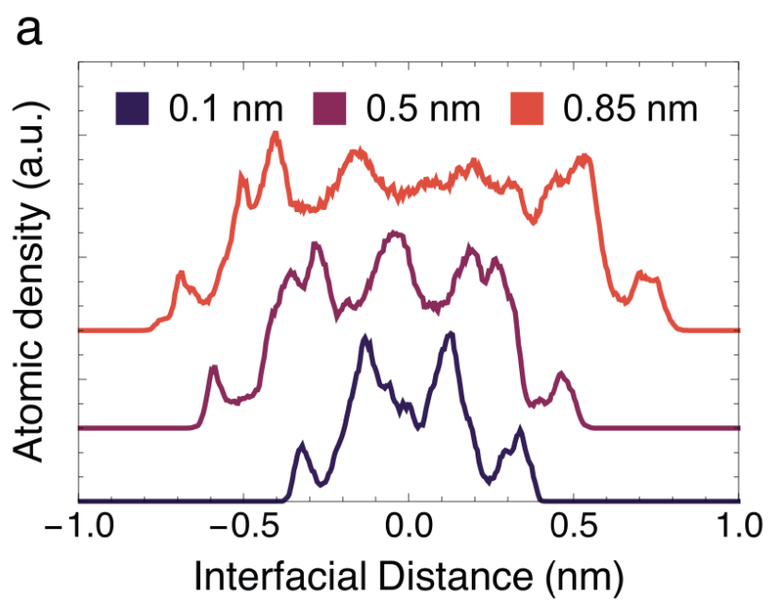

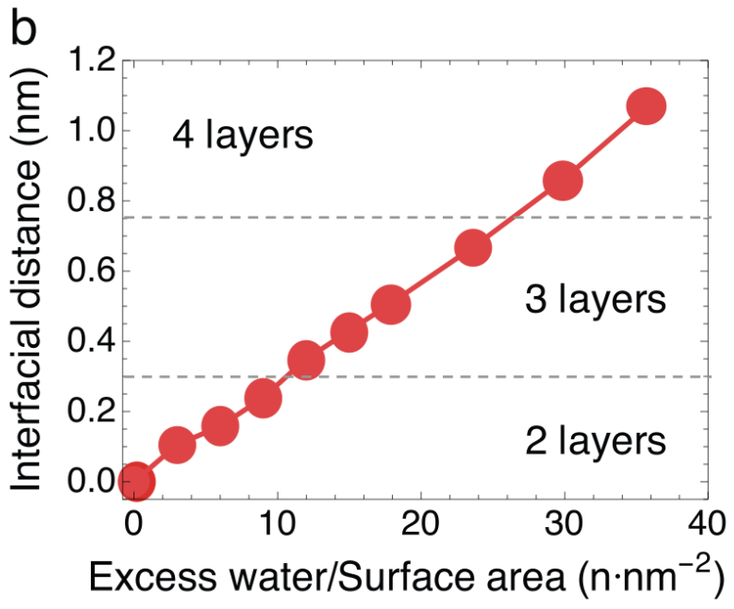

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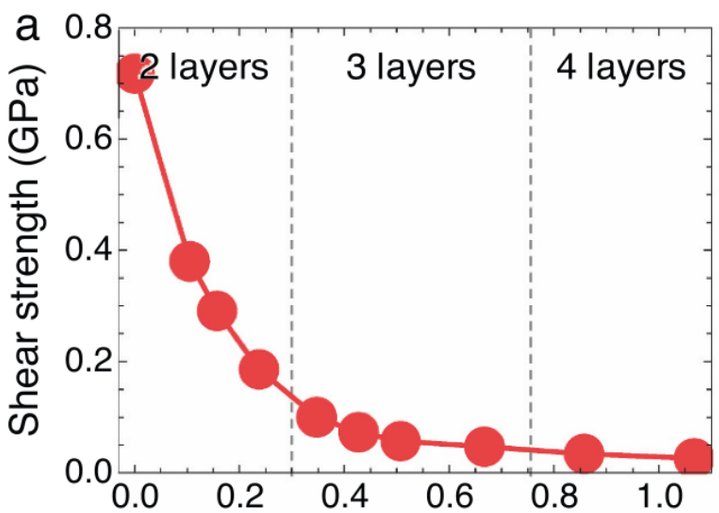

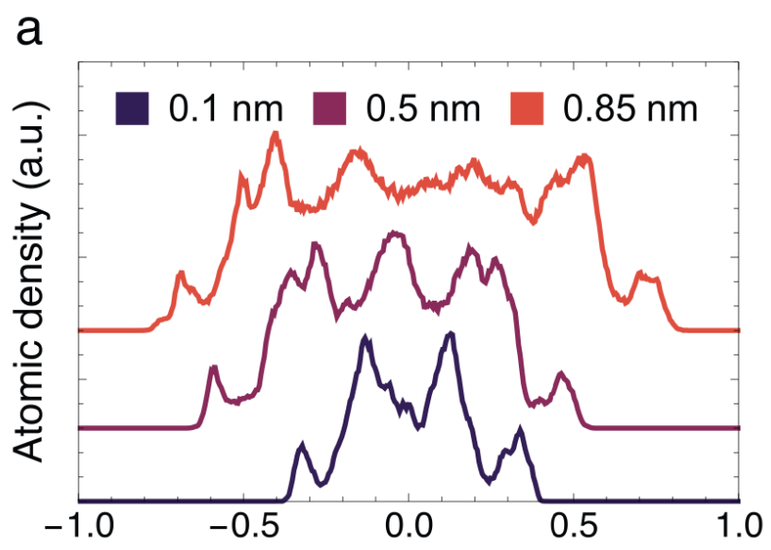

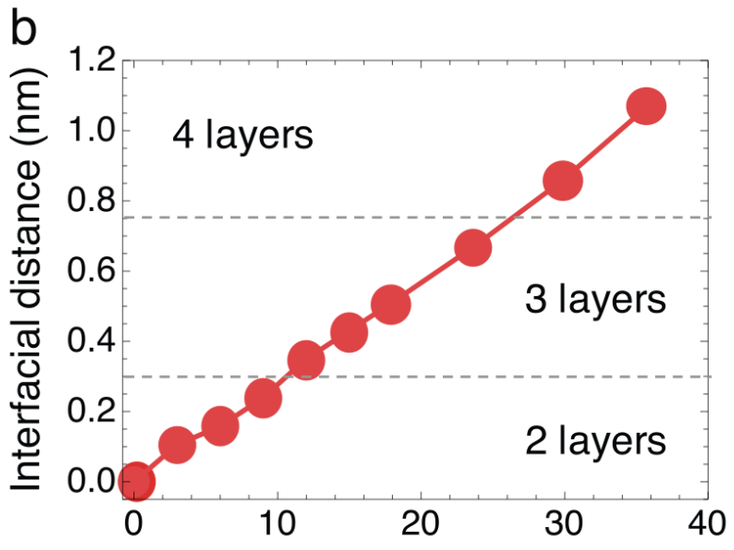

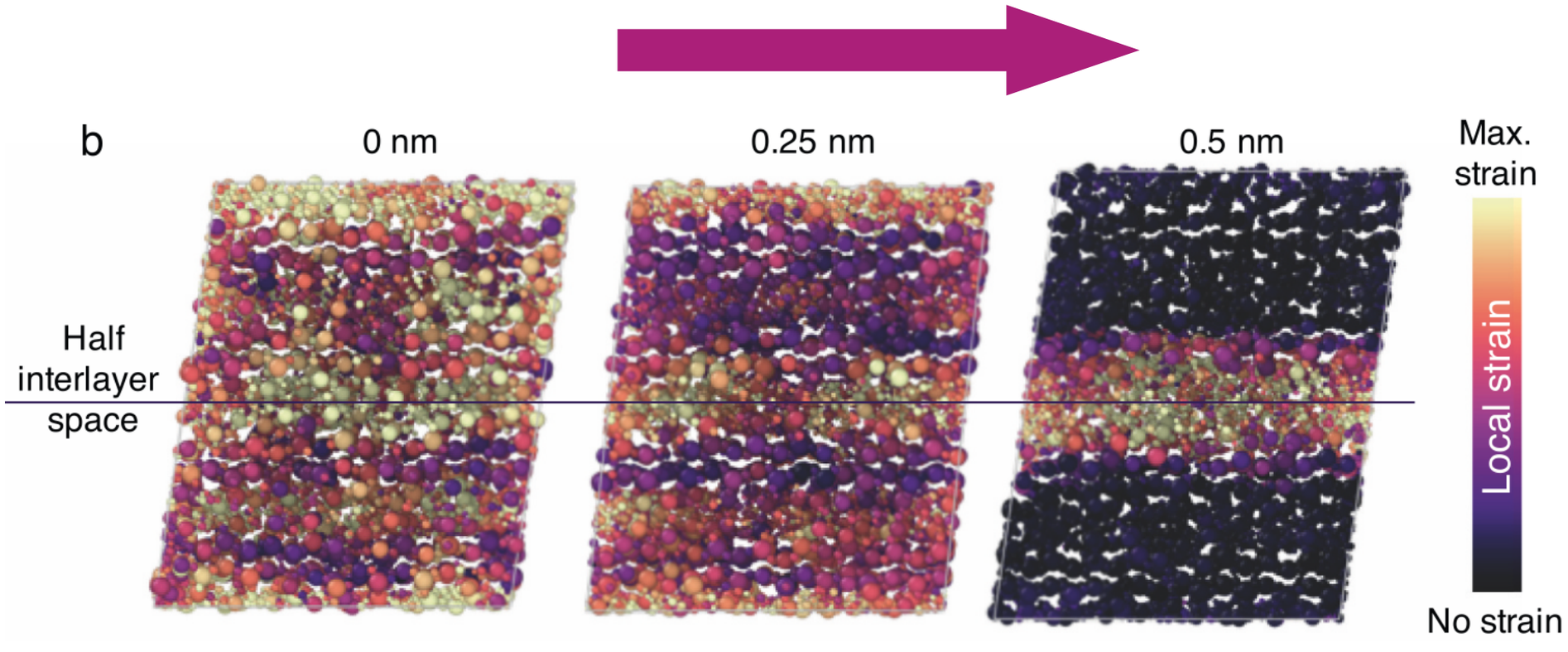

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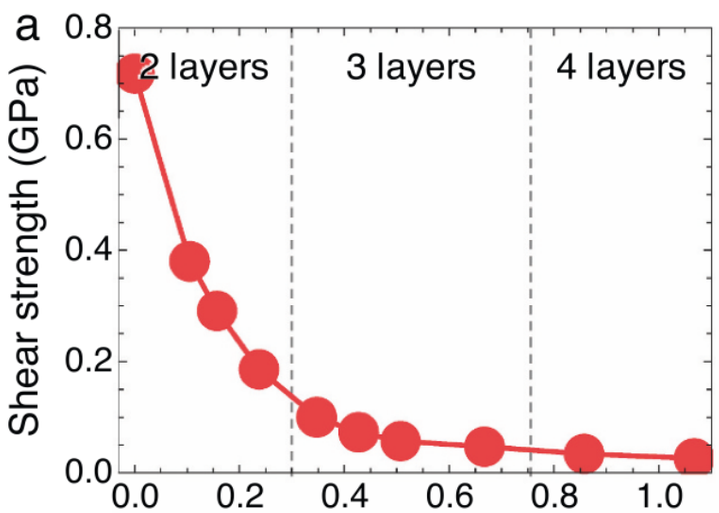
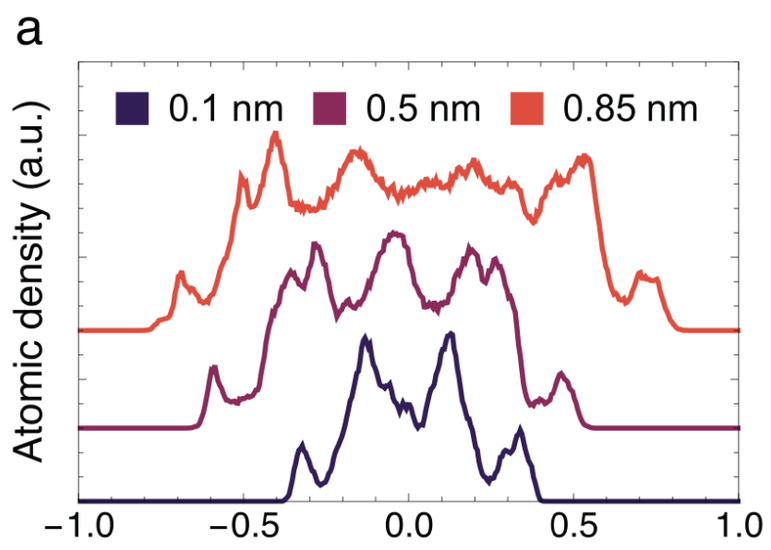
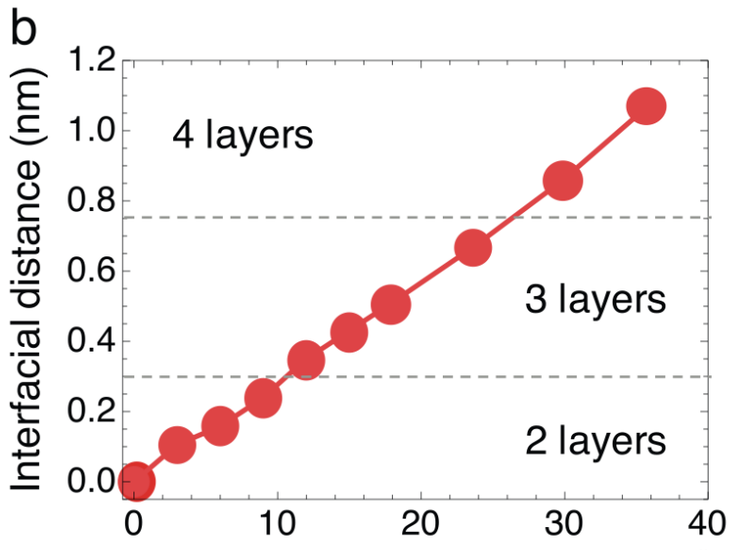
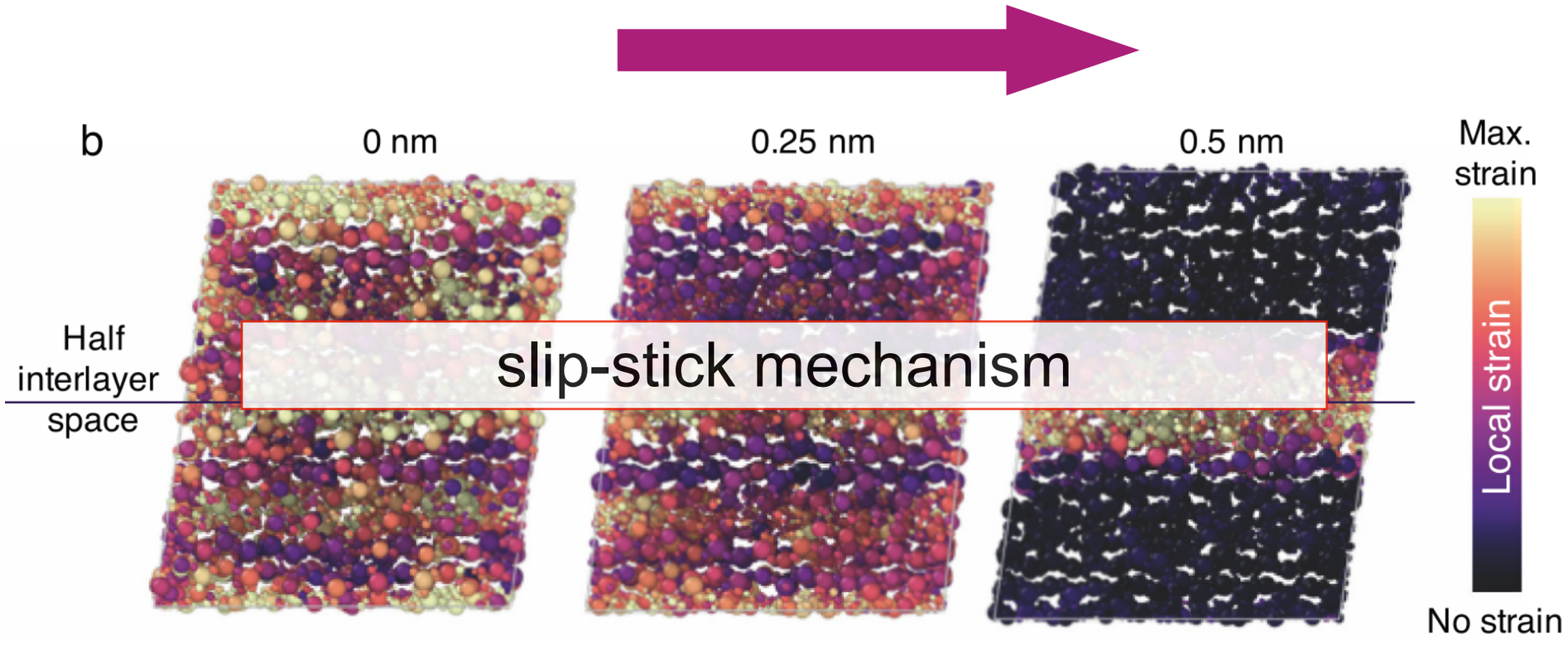


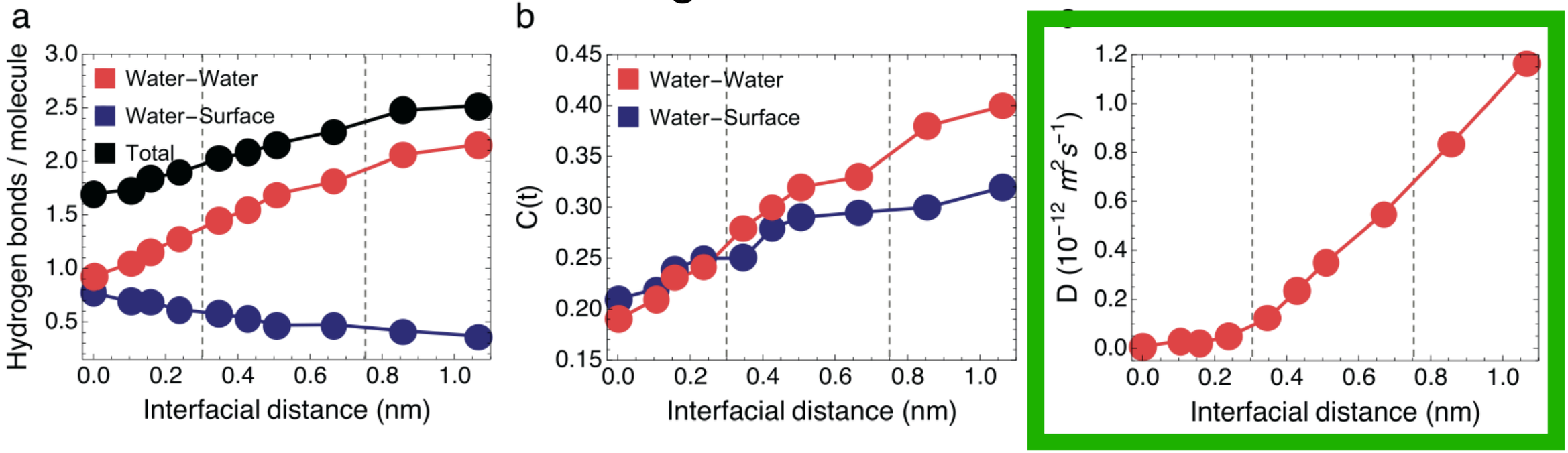






Calcium Silicate Hydrate: interfaces

What changes at the interface?



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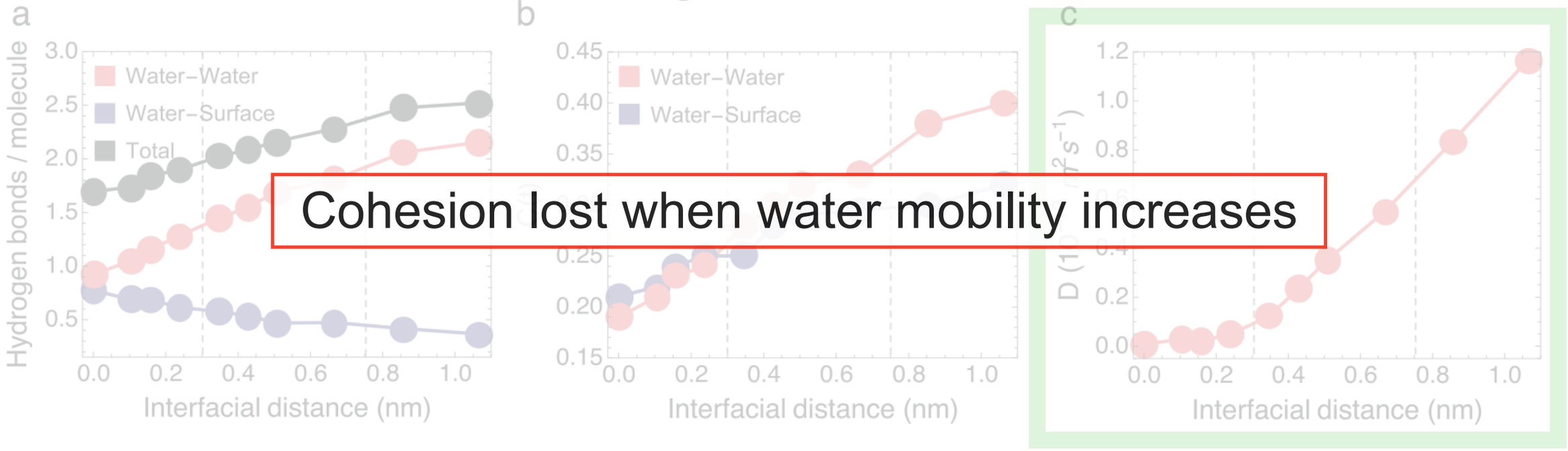


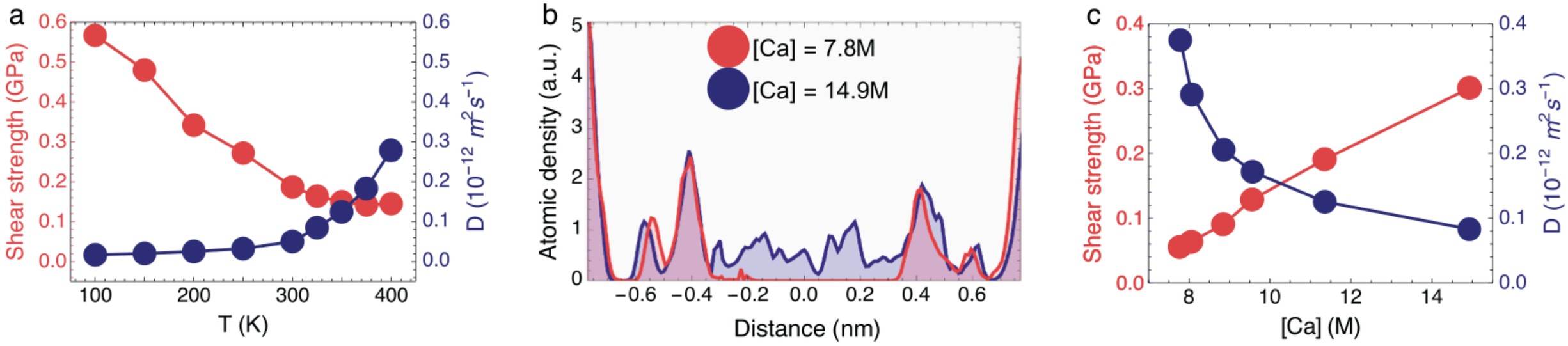
Cohesion lost when water mobility increases

Calcium Silicate Hydrate: interfaces

What changes at the interface?

Cohesion lost when water mobility increases

Control water mobility to test the mechanism



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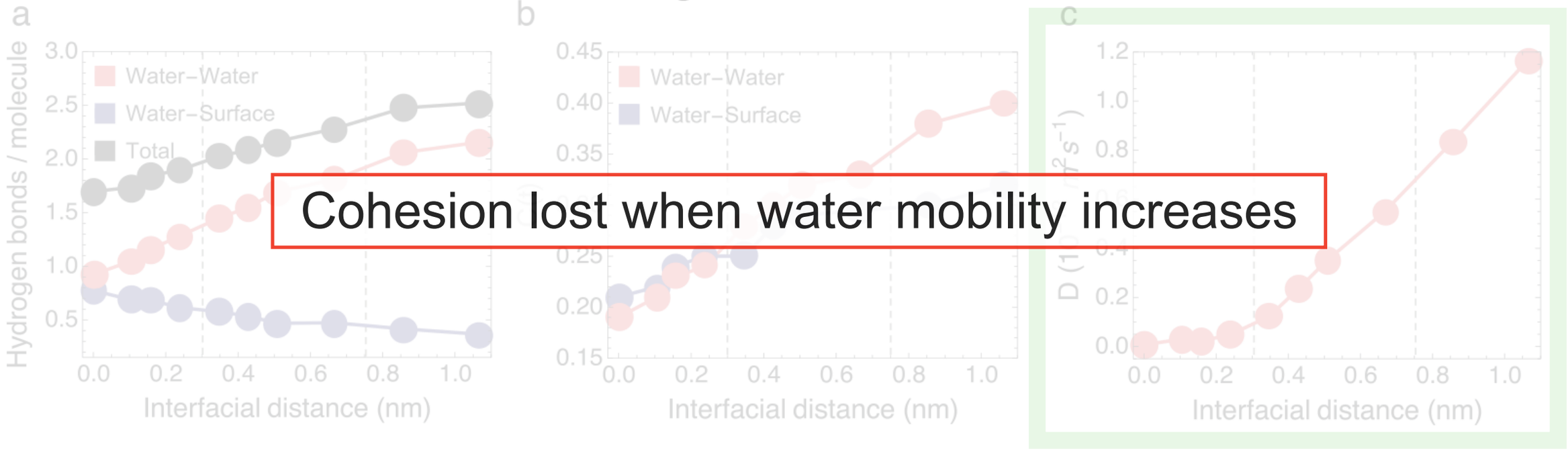

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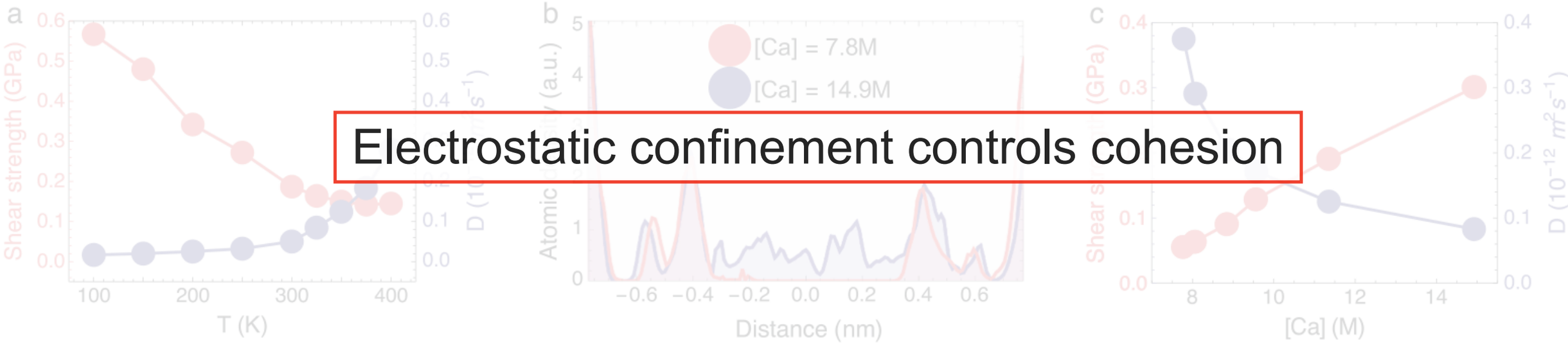
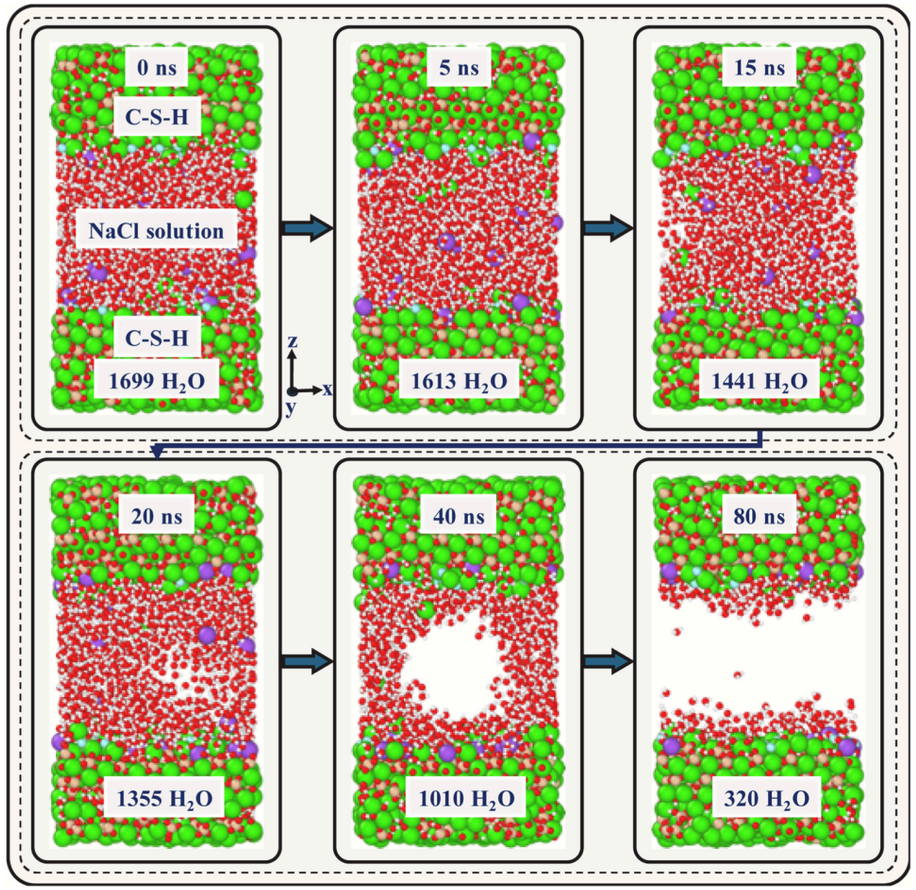


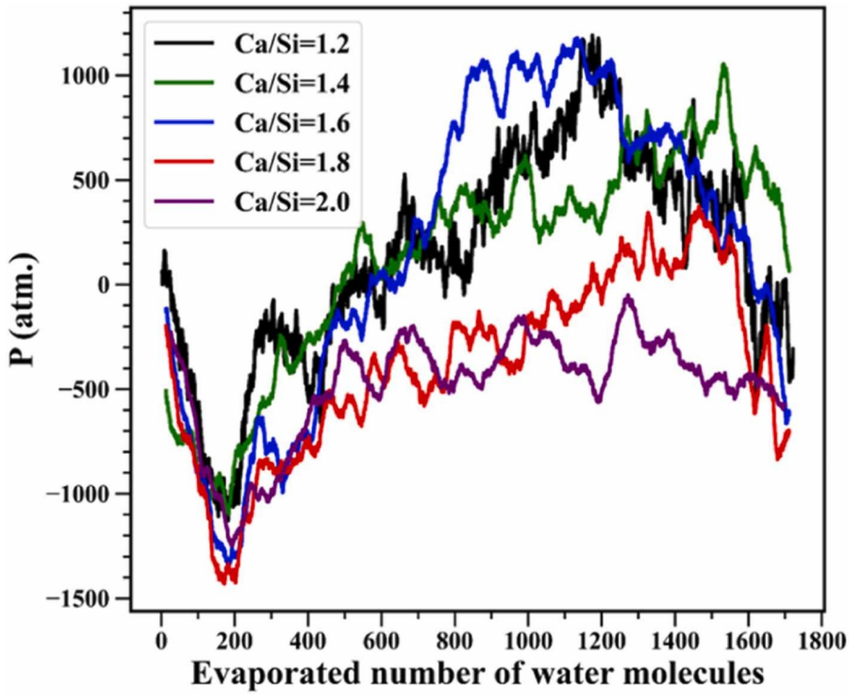
Electrostatic confinement controls cohesion

Calcium Silicate Hydrate: Microstructure

Umar Hayat, Eduardo Duque-Redondo, Ming-Feng Kai, Hegoi Manzano, Muhammad Riaz Ahmad, You Dong, Jian-Guo Dai, Desorption of water from aqueous solution confined in CSH gel pore: A molecular dynamics study Construction and Building Materials 490, 142602



The Ca/Si ratio does not have significant impact



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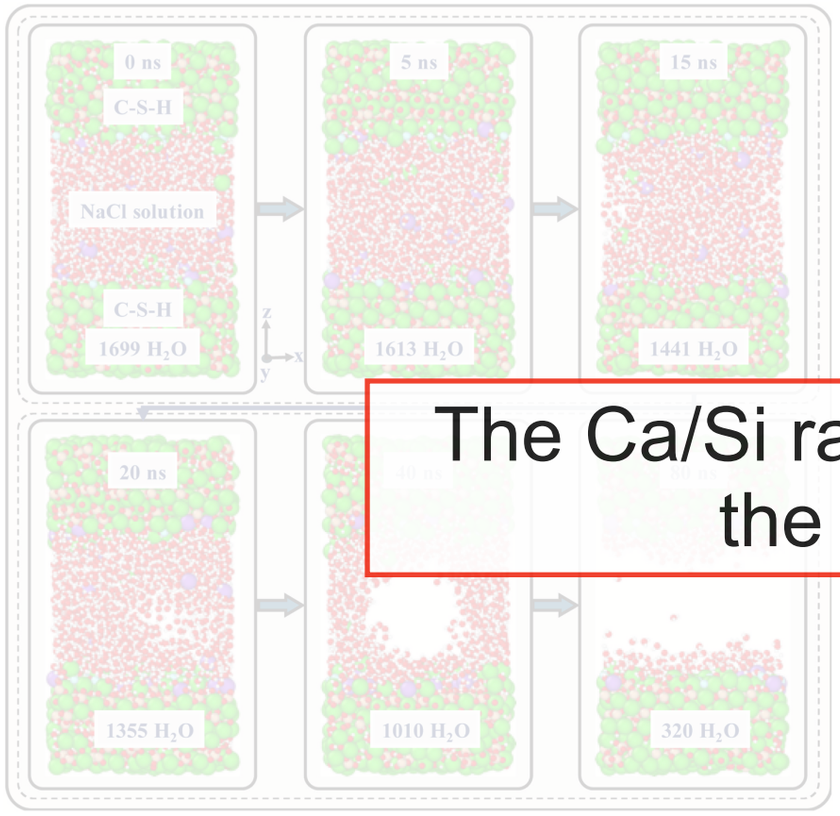

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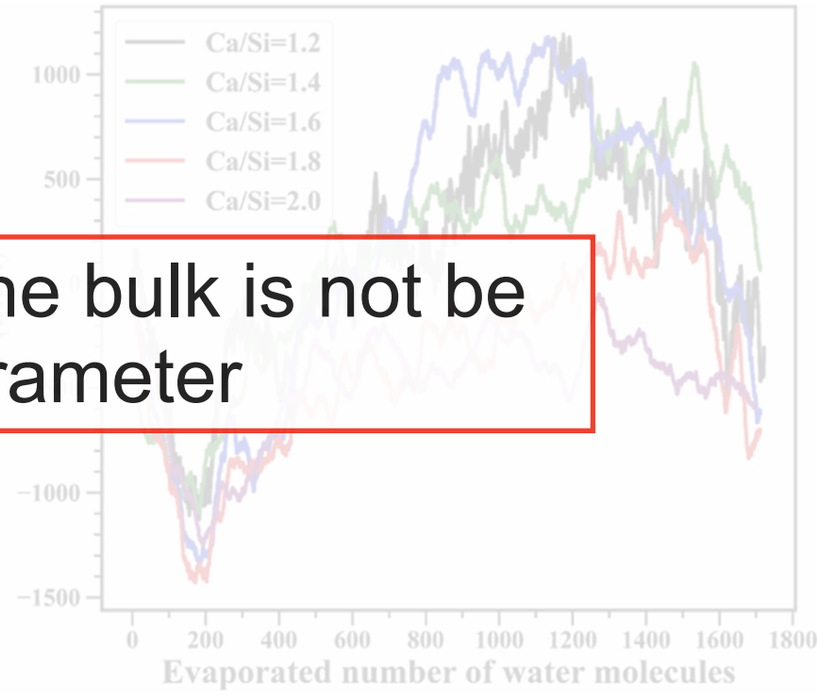
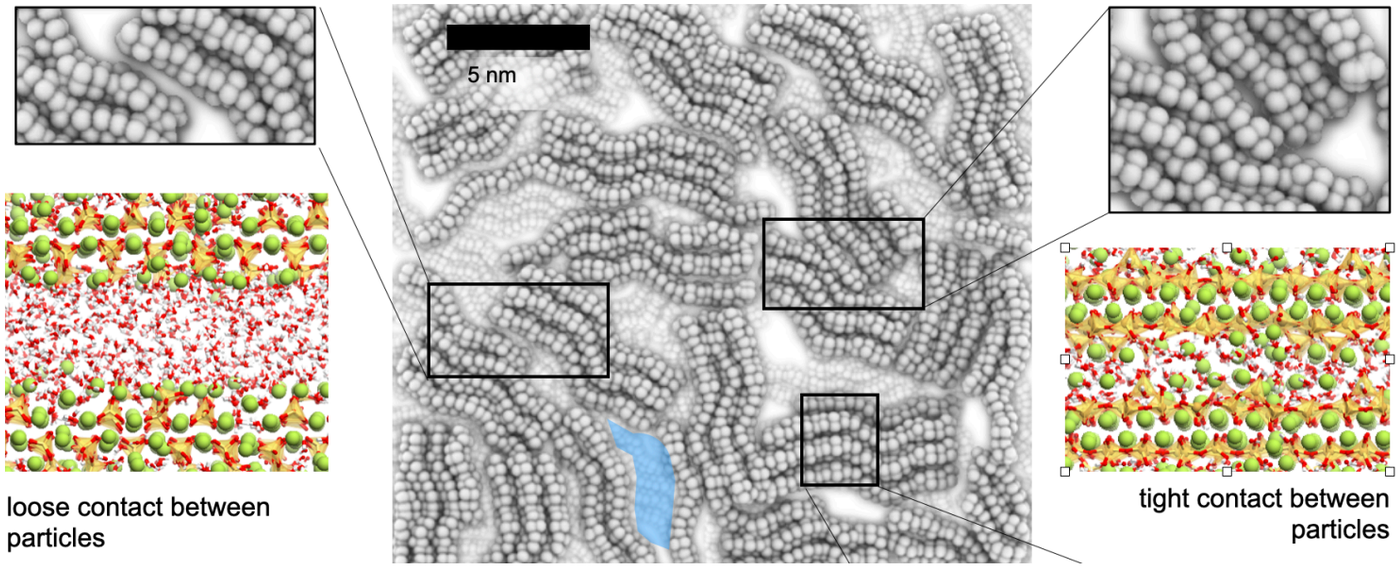


The Ca/Si ratio of the bulk is not be the key parameter



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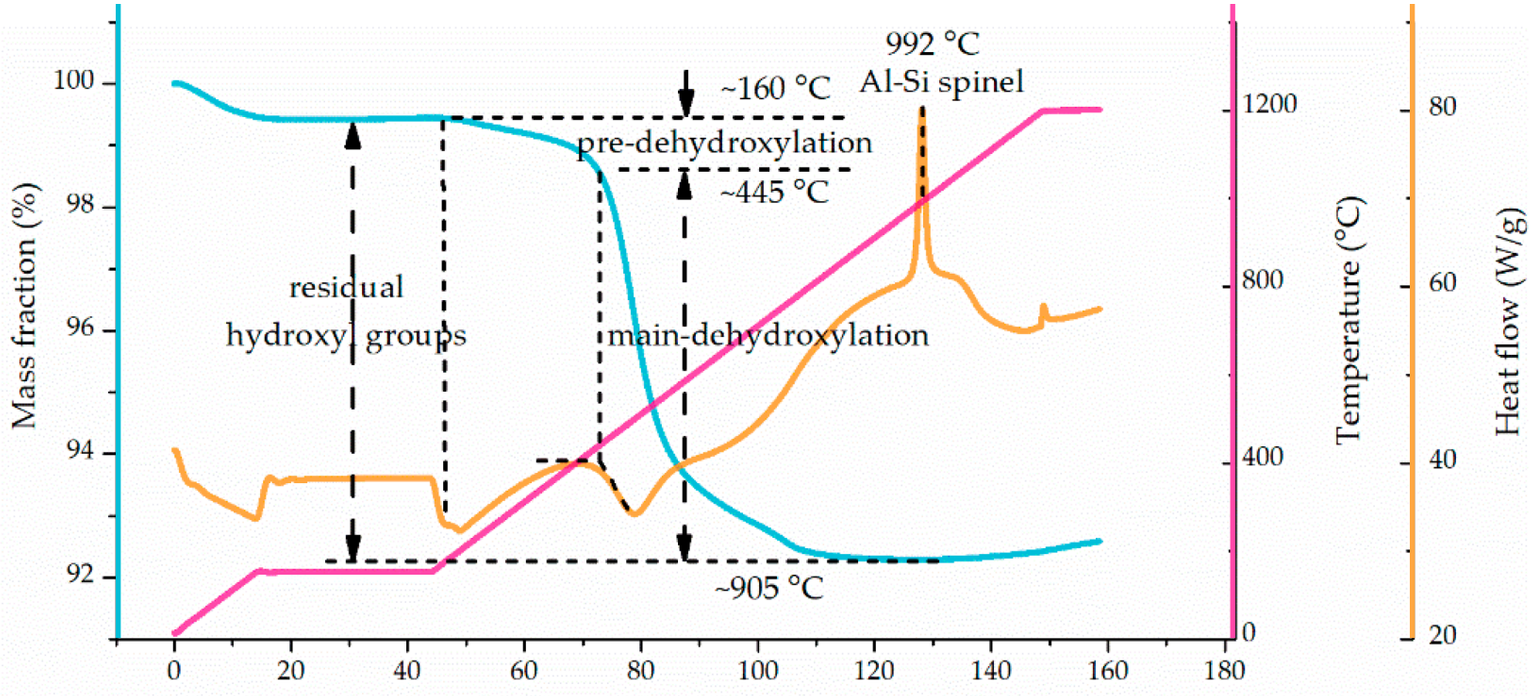
Kaolinite to Metakaolin



Adapted from: Cheng, et al. (2019). Dehydroxylation and structural distortion of kaolinite as a high-temperature sorbent in the furnace. Minerals, 9(10), 587

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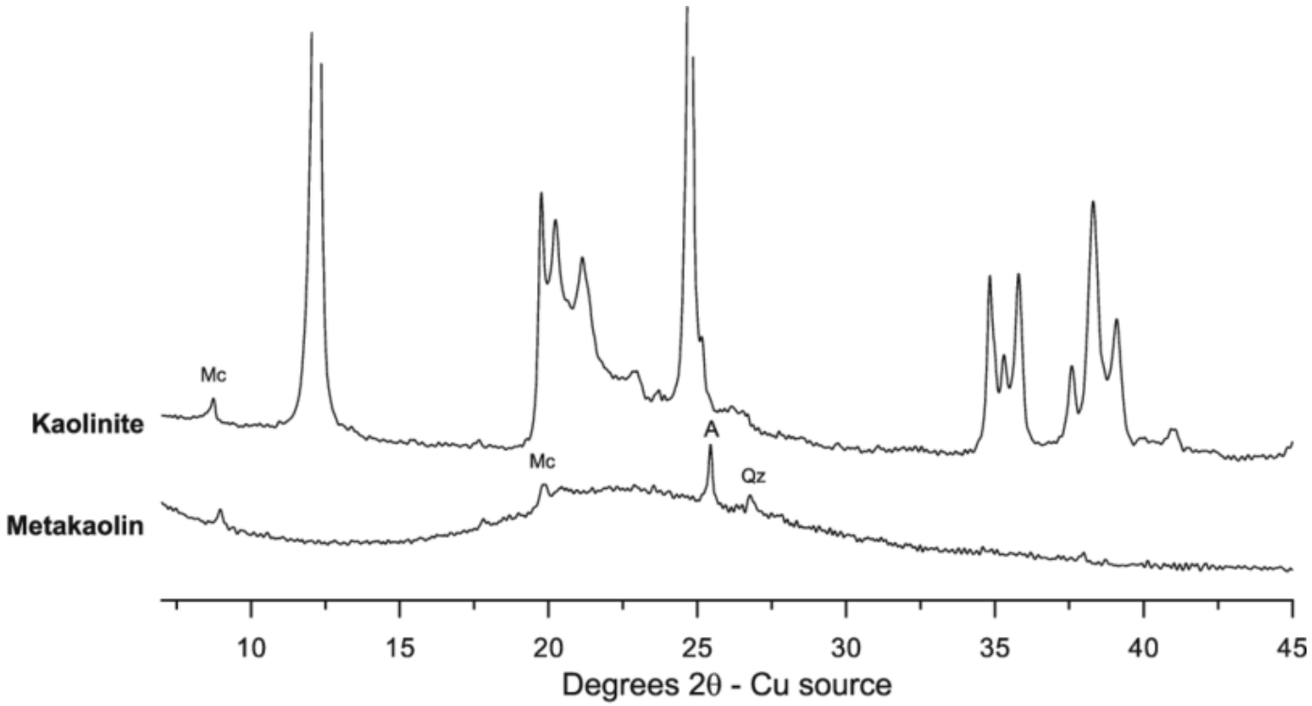

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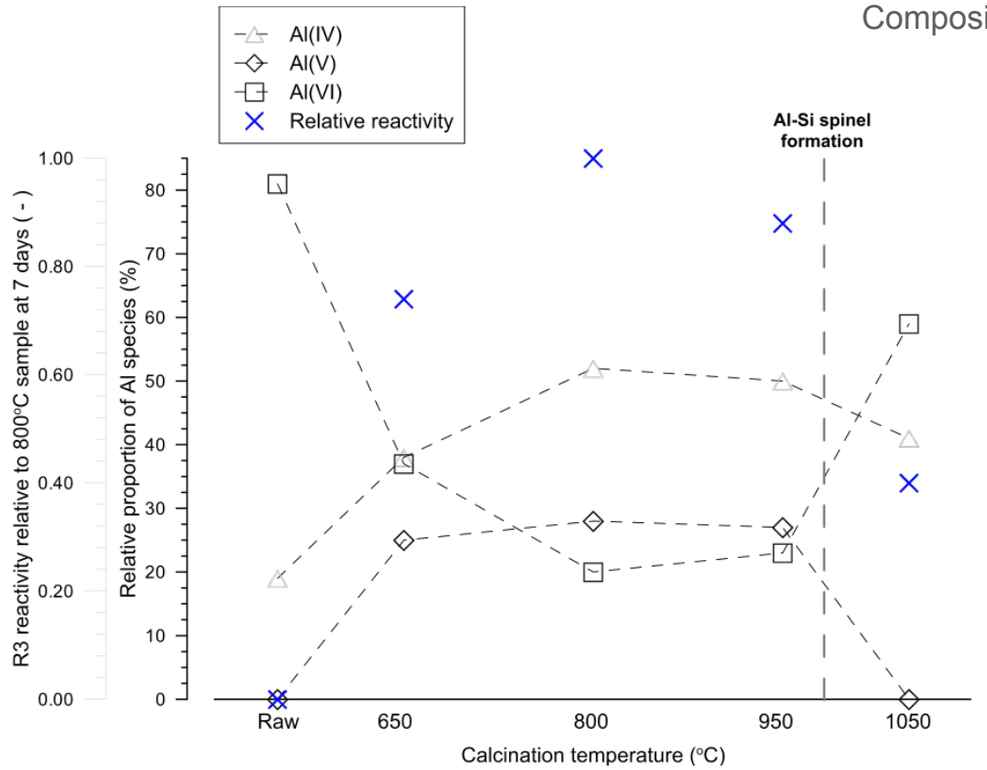

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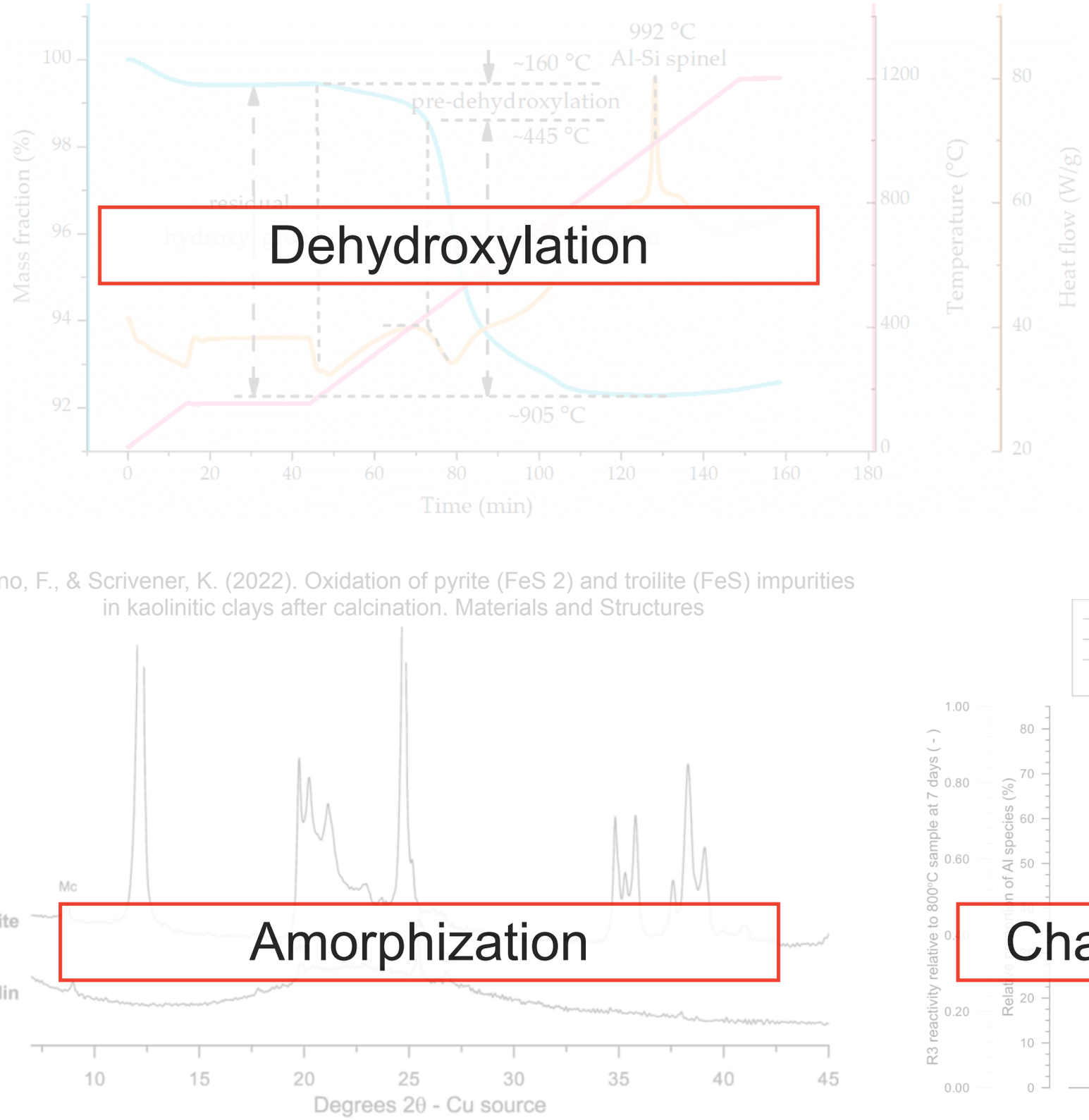

Dehydroxylation

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Amorphization

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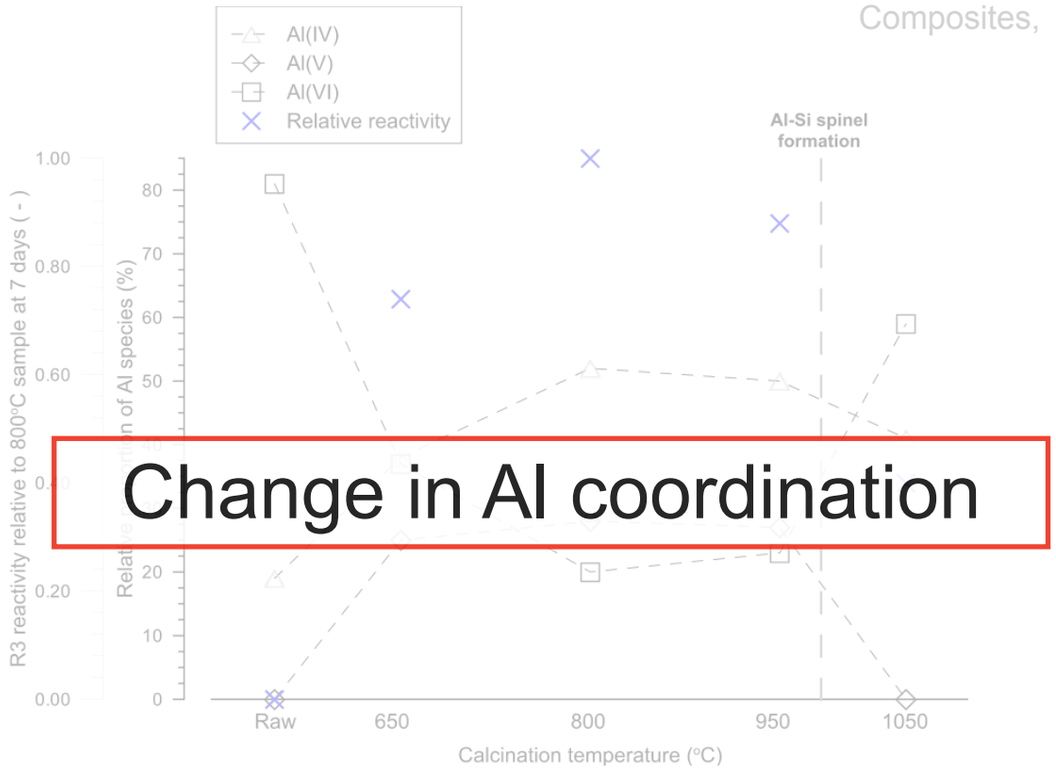
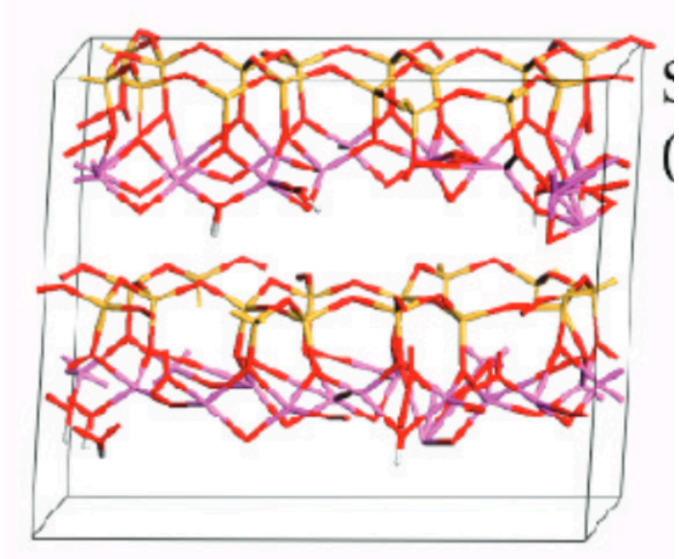


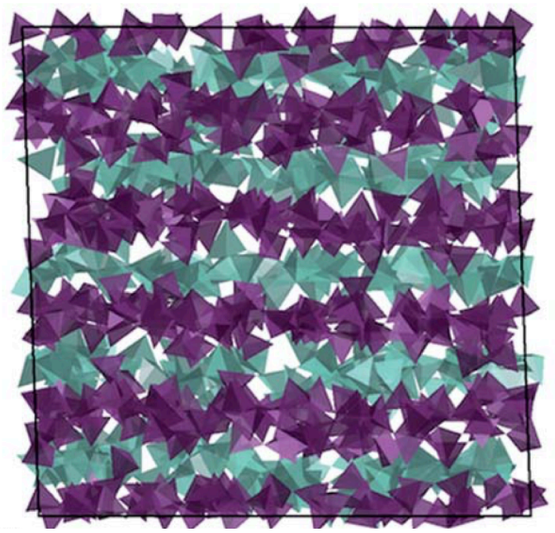
Change in Al coordination

Metakaolin: current models

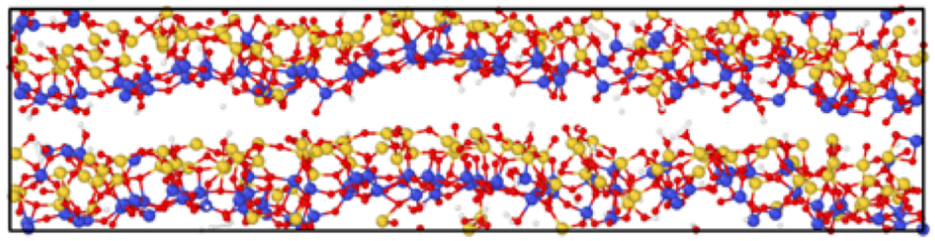
White, C. E., Provis, J. L., et al. (2010). Combining DFT and PDF analysis to solve the structure of metastable materials: the case of metakaolin. PCCP12(13)



Sperinck, S., Raiteri, P., Marks, N., & Wright, K. (2011). Dehydroxylation of kaolinite to metakaolin—a molecular dynamics study. Journal of Materials Chemistry, 21(7)



Muraleedharan, Murali Gopal, et al. "Elucidating thermally induced structural and chemical transformations in kaolinite using reactive molecular dynamics simulations and X-ray scattering measurements." Chemistry of Materials 32.2 (2019):

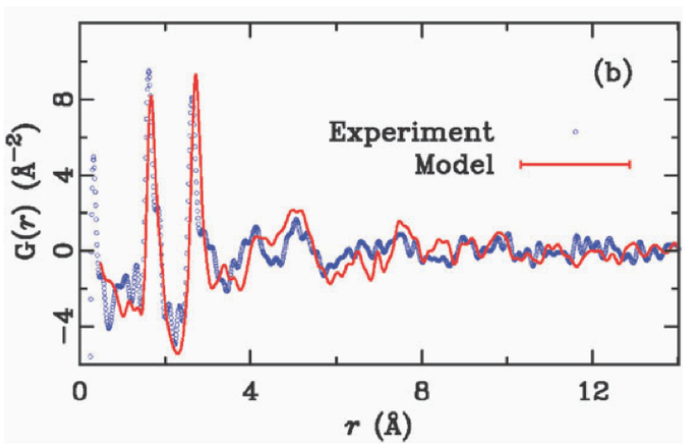


Dehydroxylation: spontaneous with T

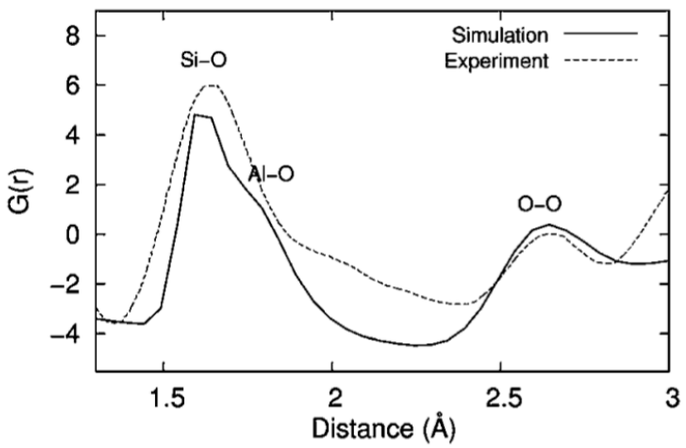
MD from 298L to 1300K, monolayer

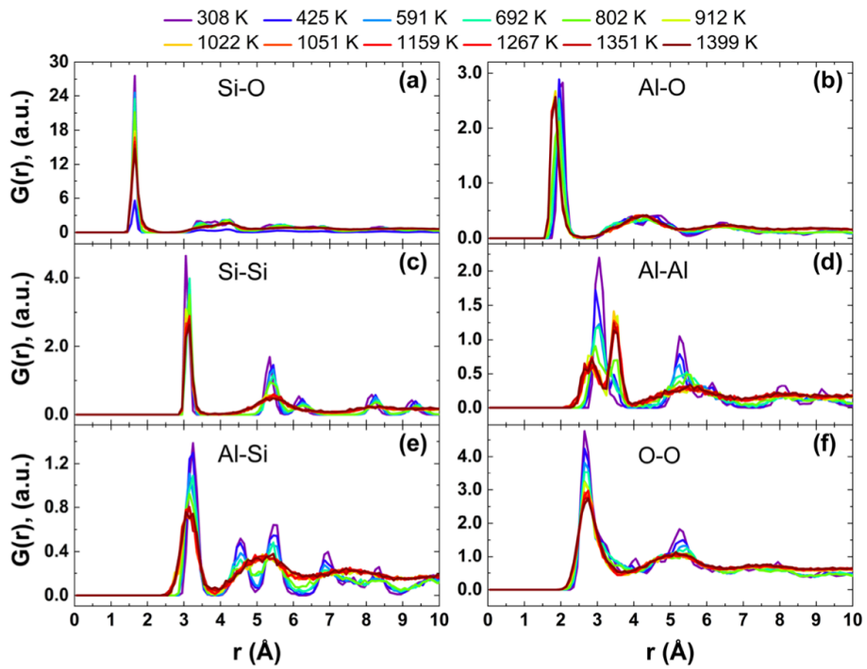
Dehydroxylation: progresive by hand

DFT relaxation (0K)



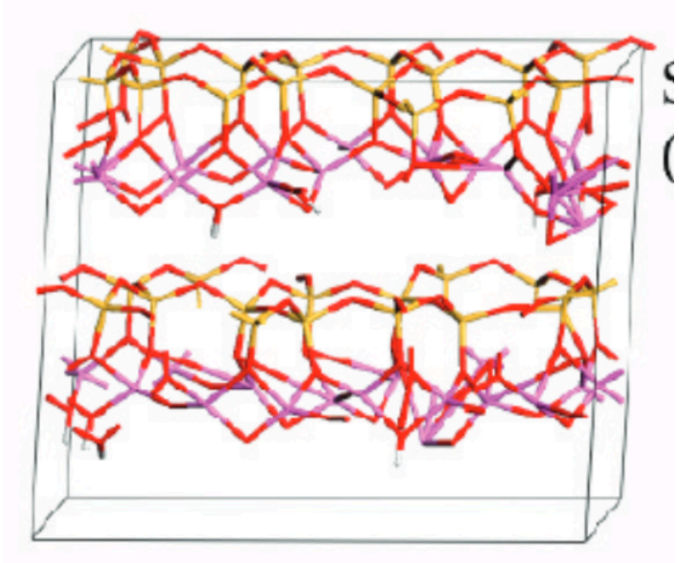
MD 1000K





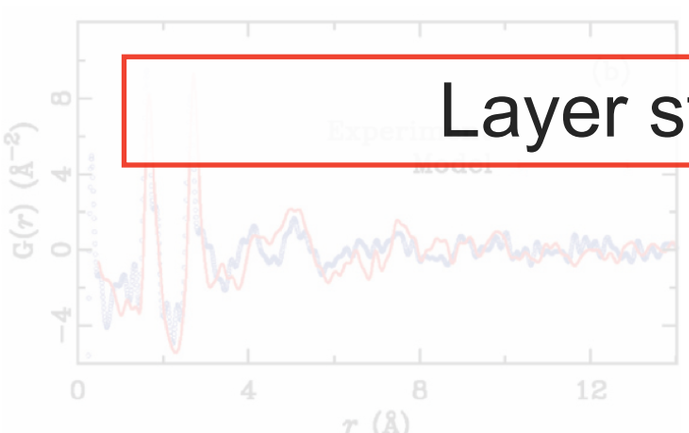
Metakaolin: current models

White, C. E., Provis, J. L., et al. (2010). Combining DFT and PDF analysis to solve the structure of metastable materials: the case of metakaolin. PCCP12(13)

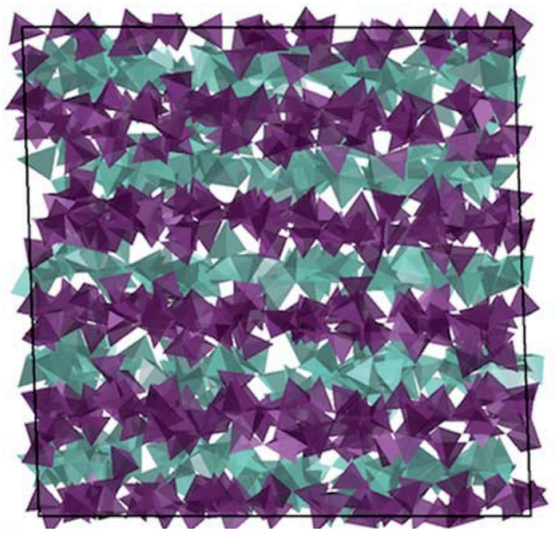


Dehydroxylation: progresive by hand

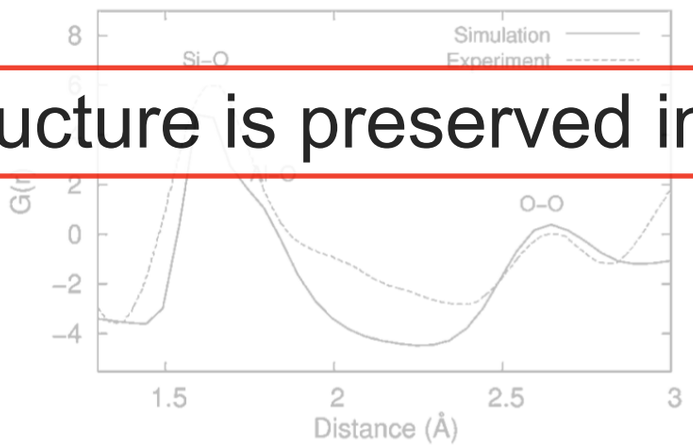
DFT relaxation (0K)



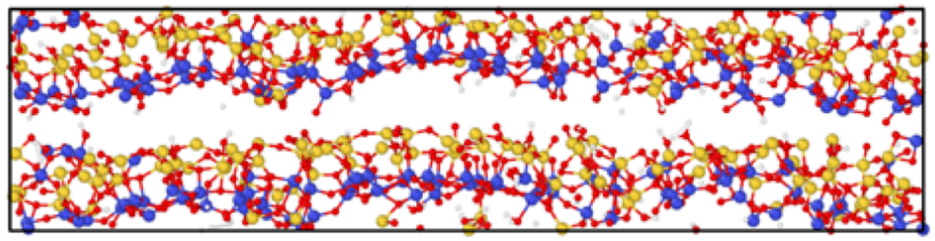
Sperinck, S., Raiteri, P., Marks, N., & Wright, K. (2011). Dehydroxylation of kaolinite to metakaolin—a molecular dynamics study. Journal of Materials Chemistry, 21(7)



MD 1000K

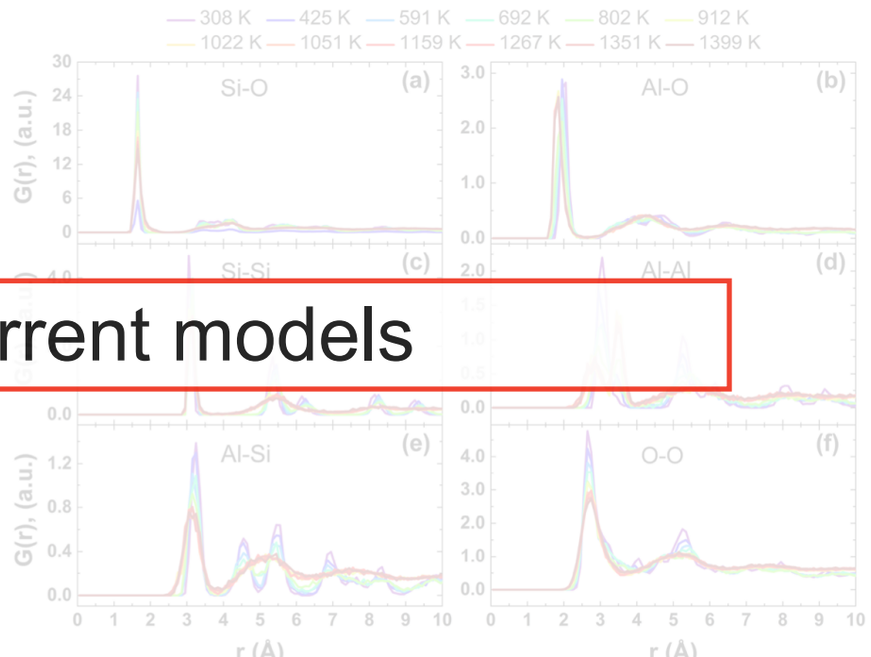


Muraleedharan, Murali Gopal, et al. "Elucidating thermally induced structural and chemical transformations in kaolinite using reactive molecular dynamics simulations and X-ray scattering measurements." Chemistry of Materials 32.2 (2019):



Dehydroxylation: spontaneous with T

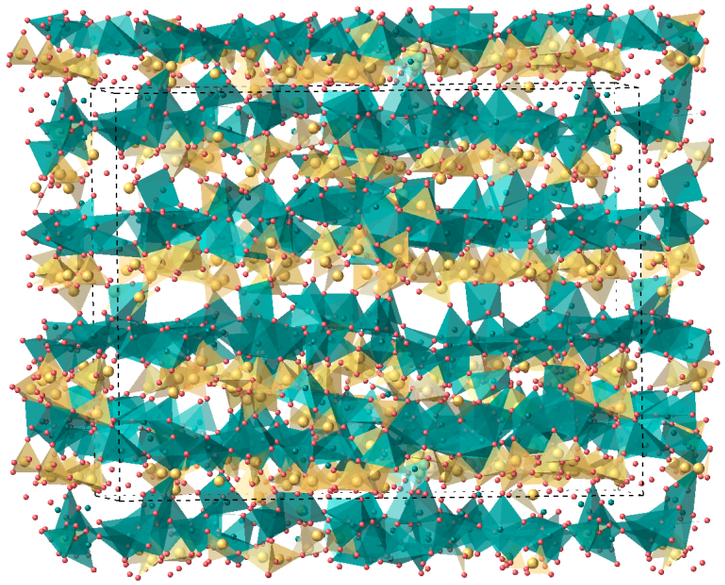
MD from 298L to 1300K, monolayer



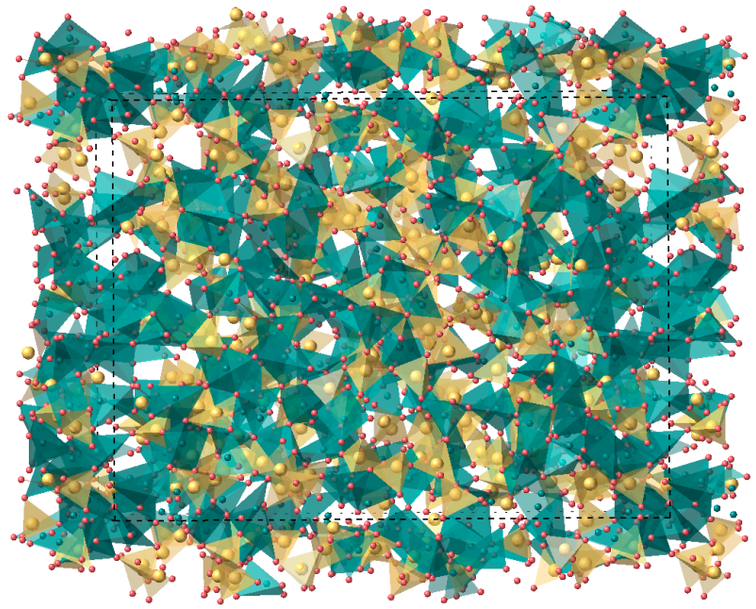
Layer structure is preserved in current models

Metakaolin: work in progress

Dehydroxylation protocols

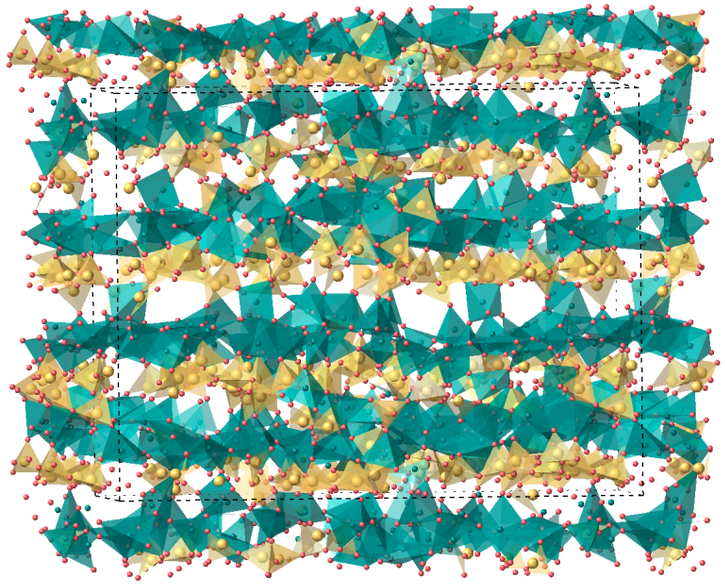


Melting - quenching

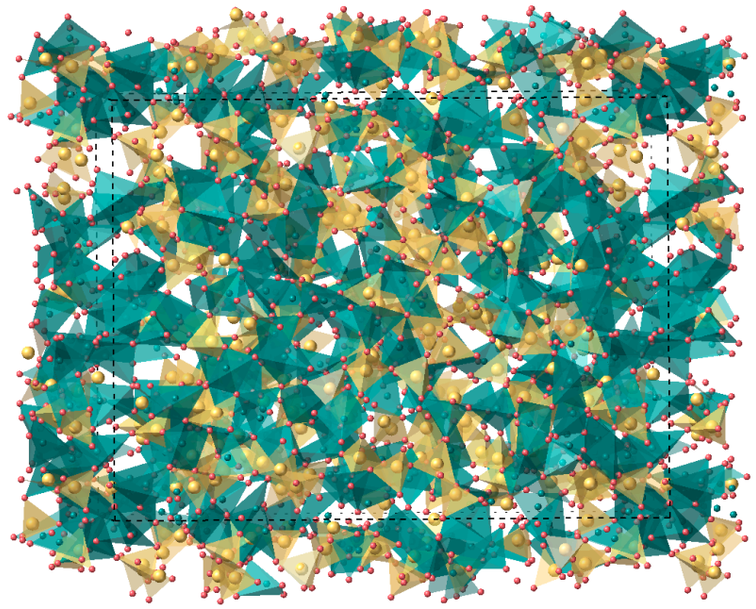


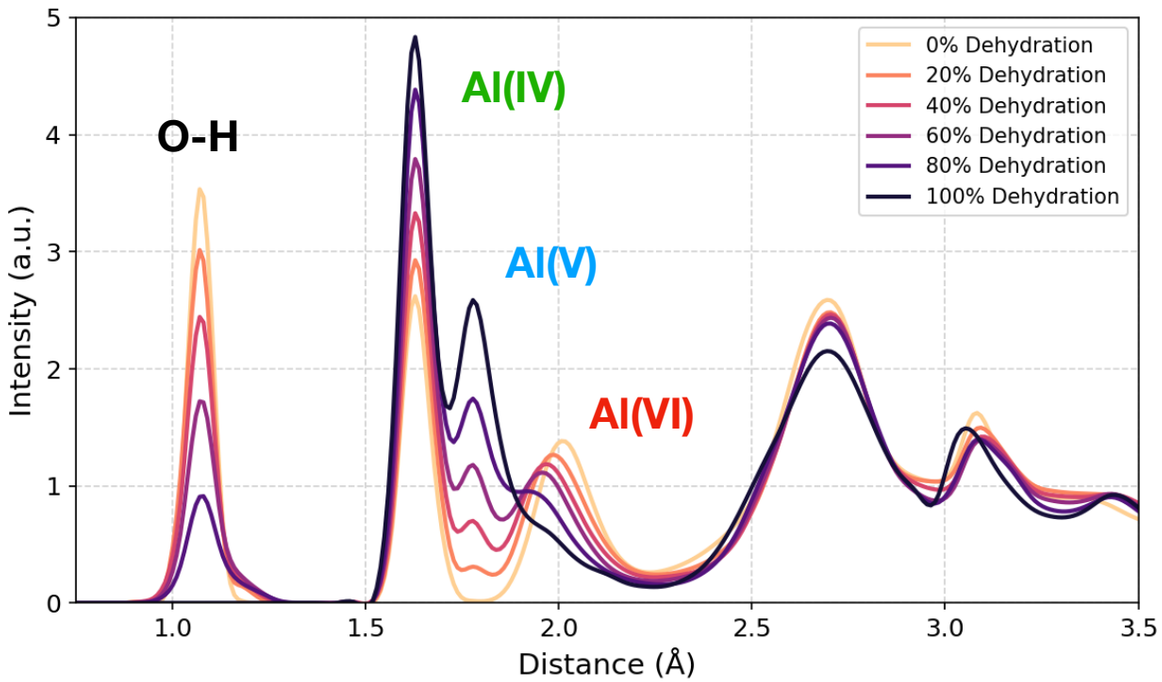
Metakaolin: work in progress

Dehydroxylation protocols



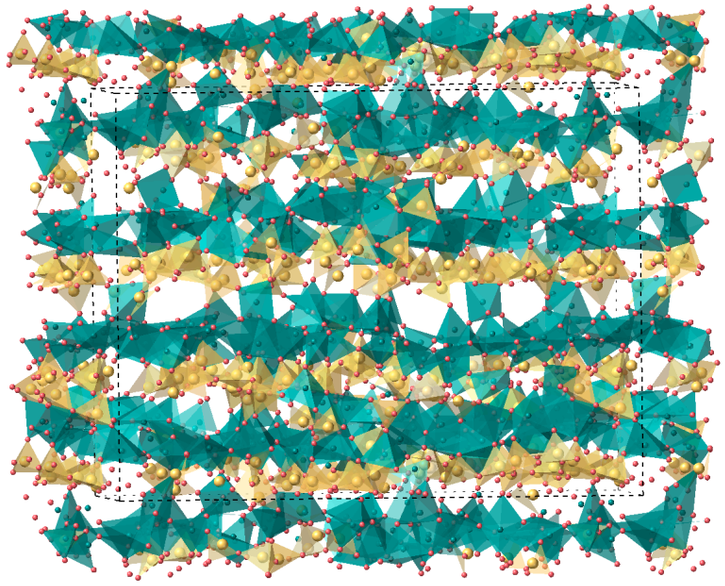
Melting - quenching



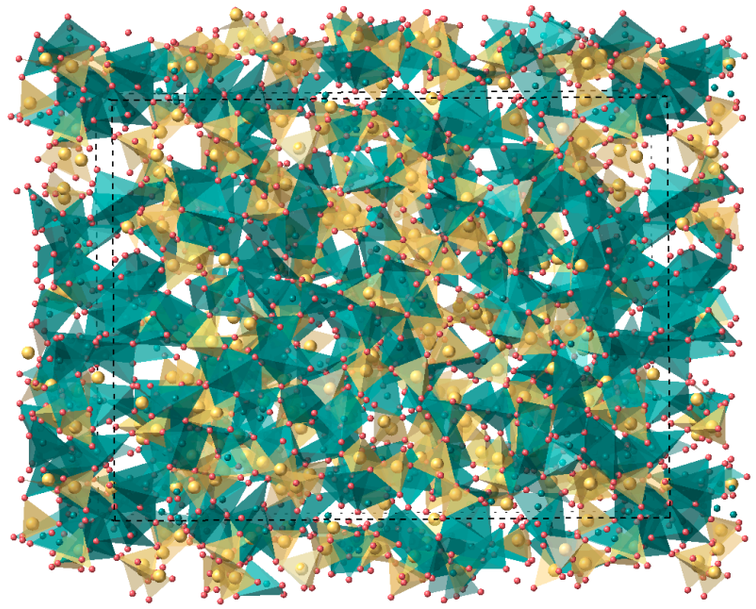


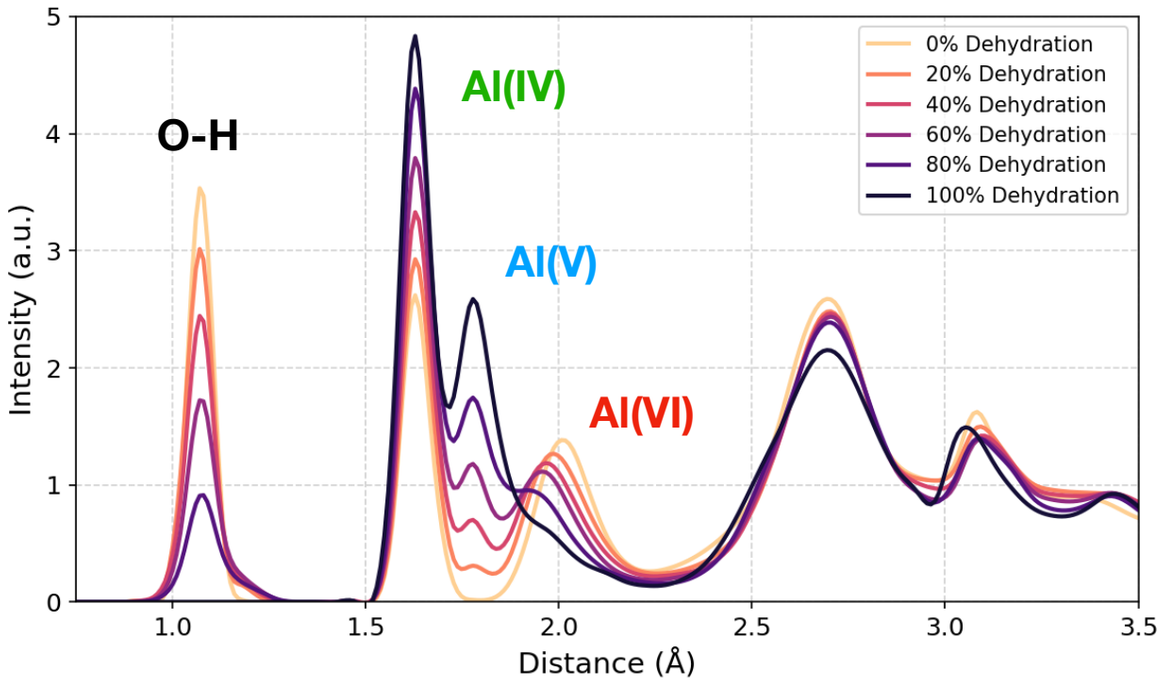
Metakaolin: work in progress

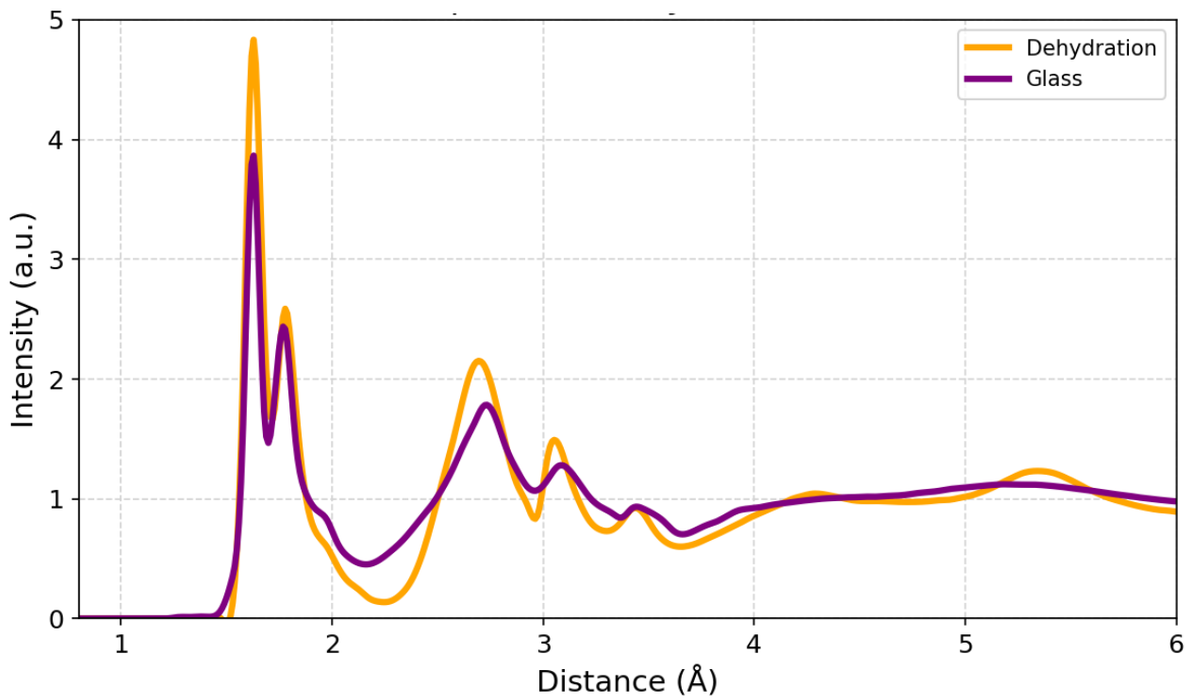
Dehydroxylation protocols



Melting - quenching

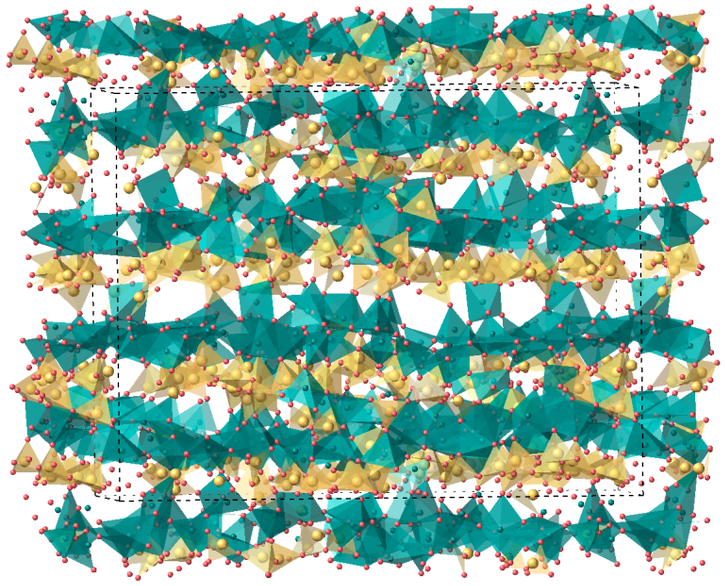




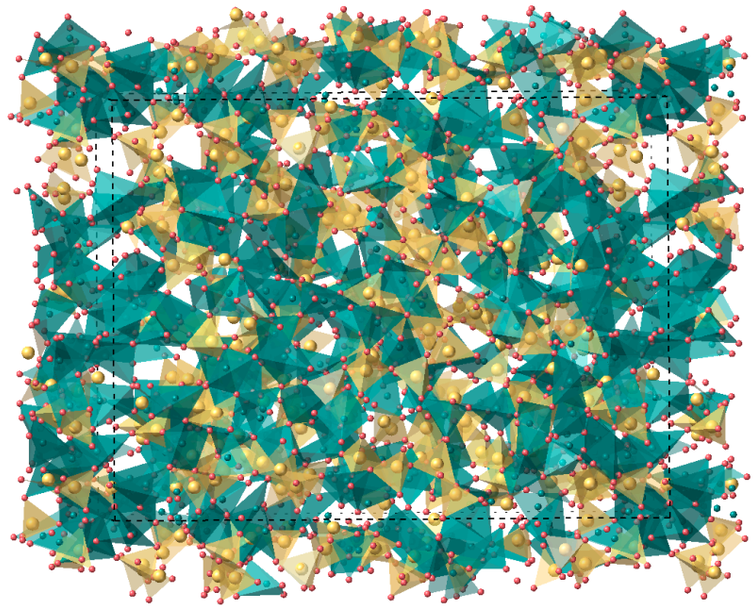


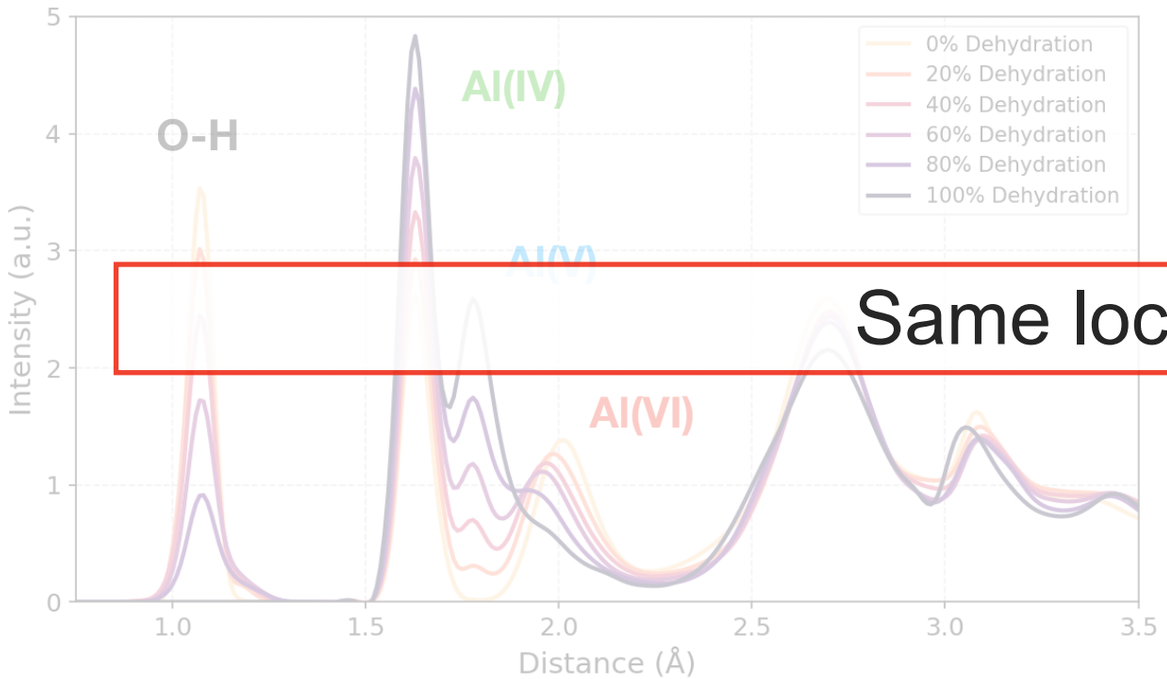
Metakaolin: work in progress

Dehydroxylation protocols

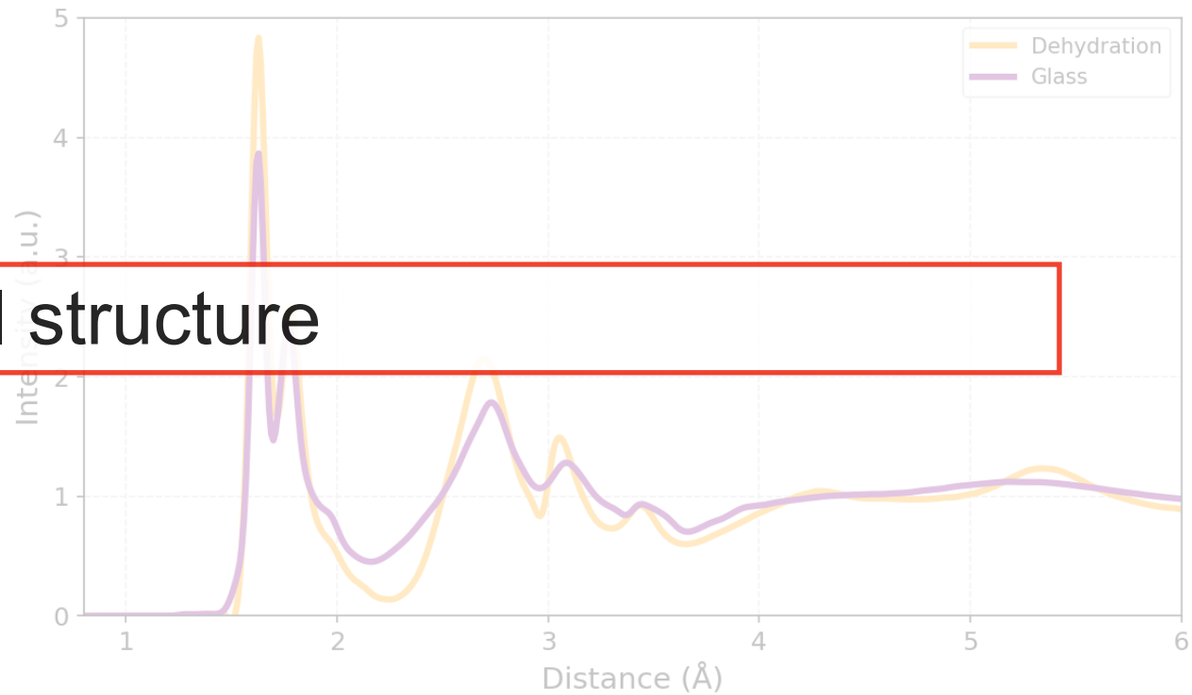


Melting - quenching



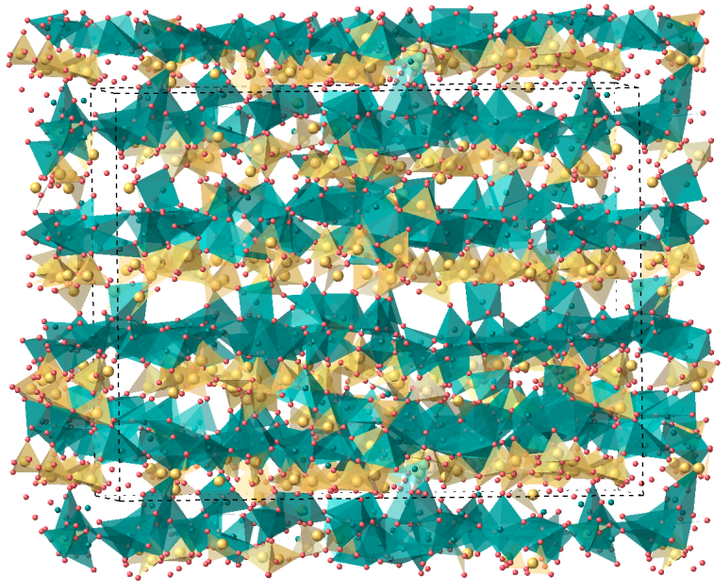


Same local structure

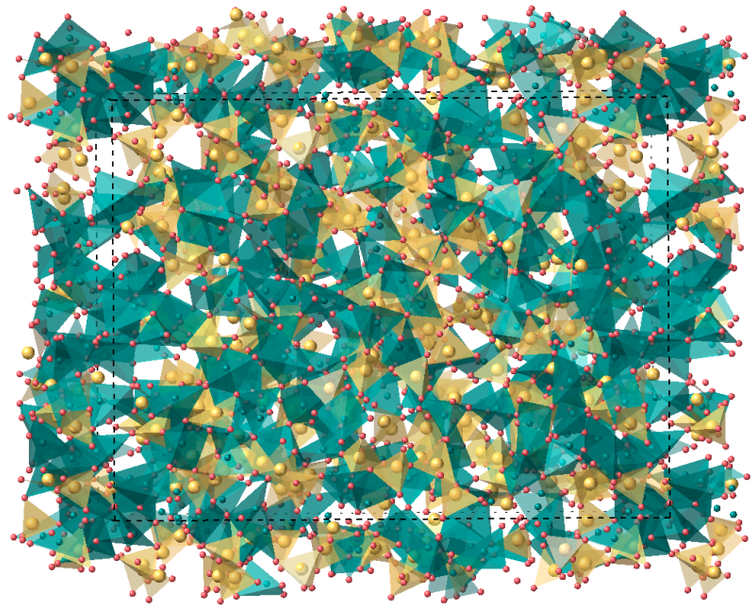


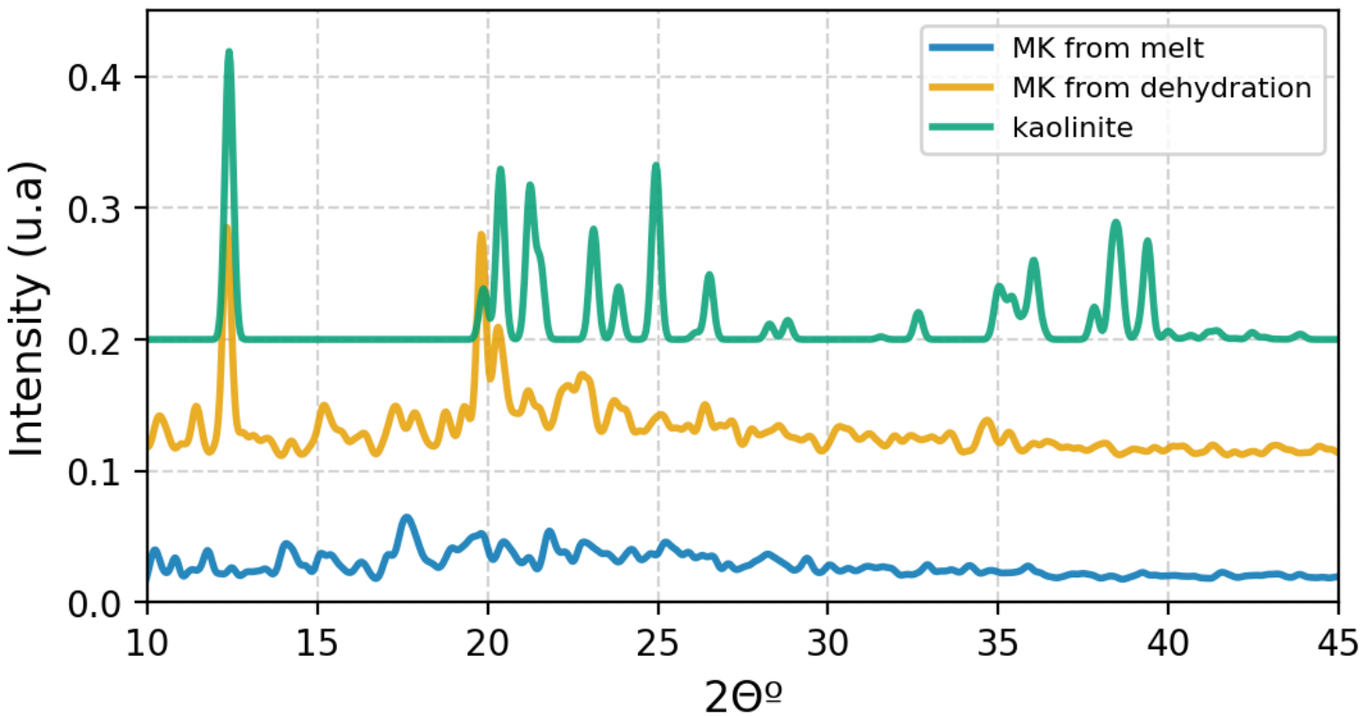
Metakaolin: work in progress

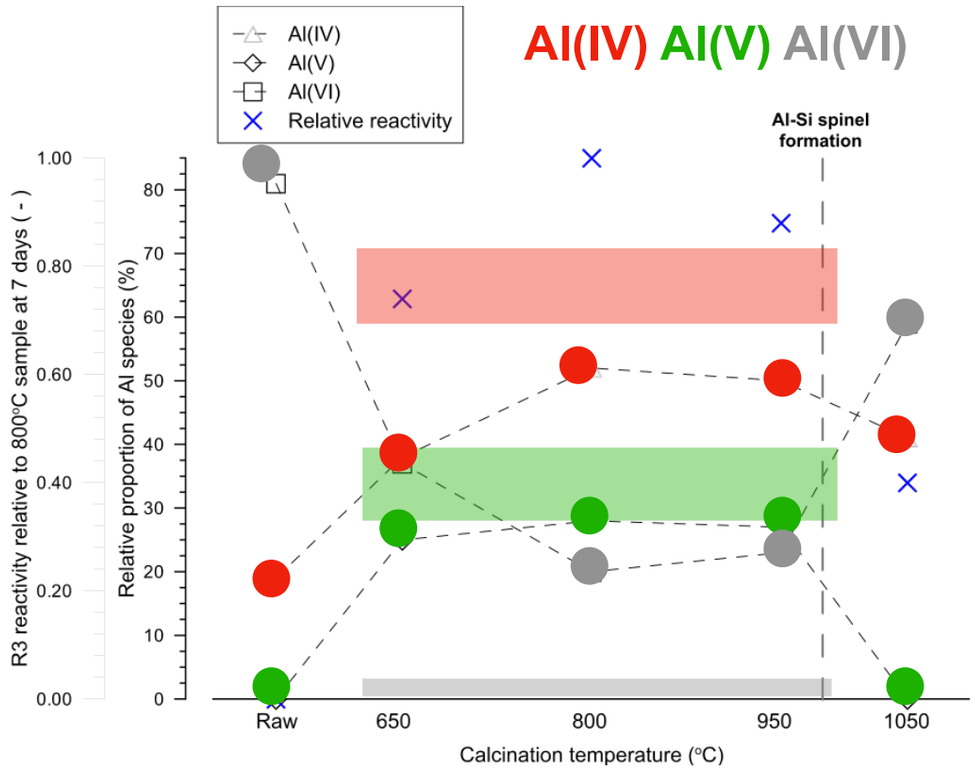
Dehydroxylation protocols



Melting - quenching

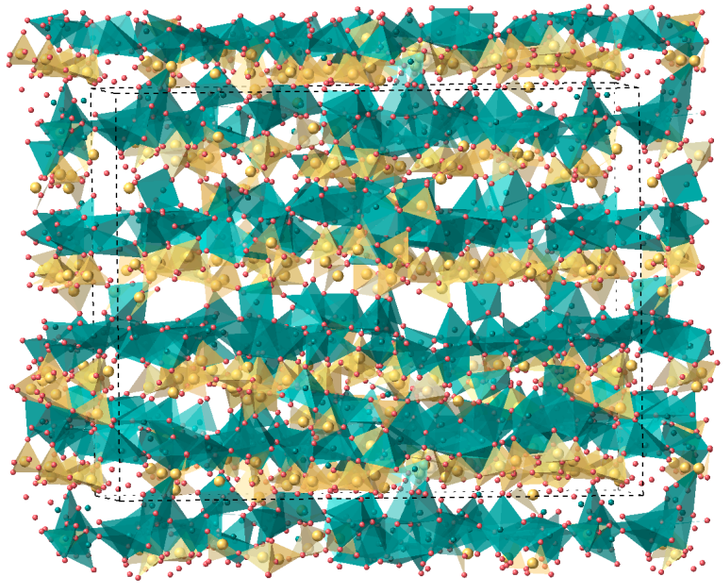




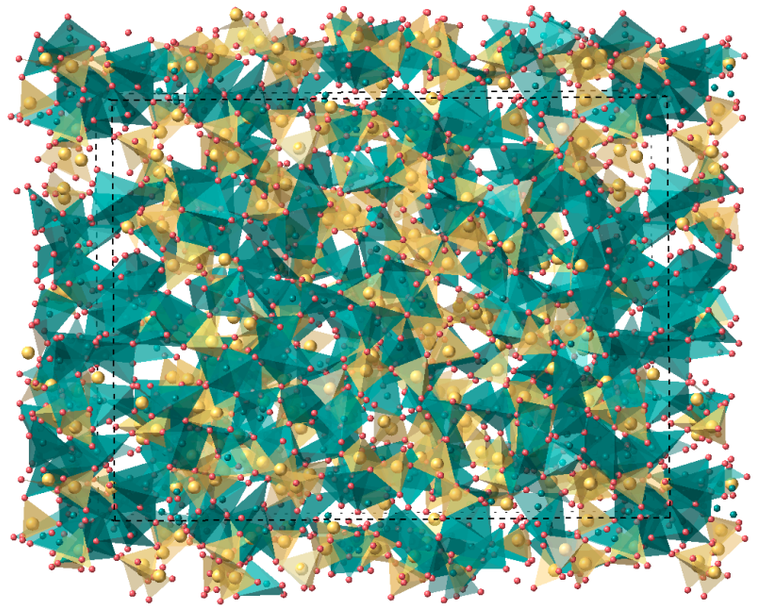


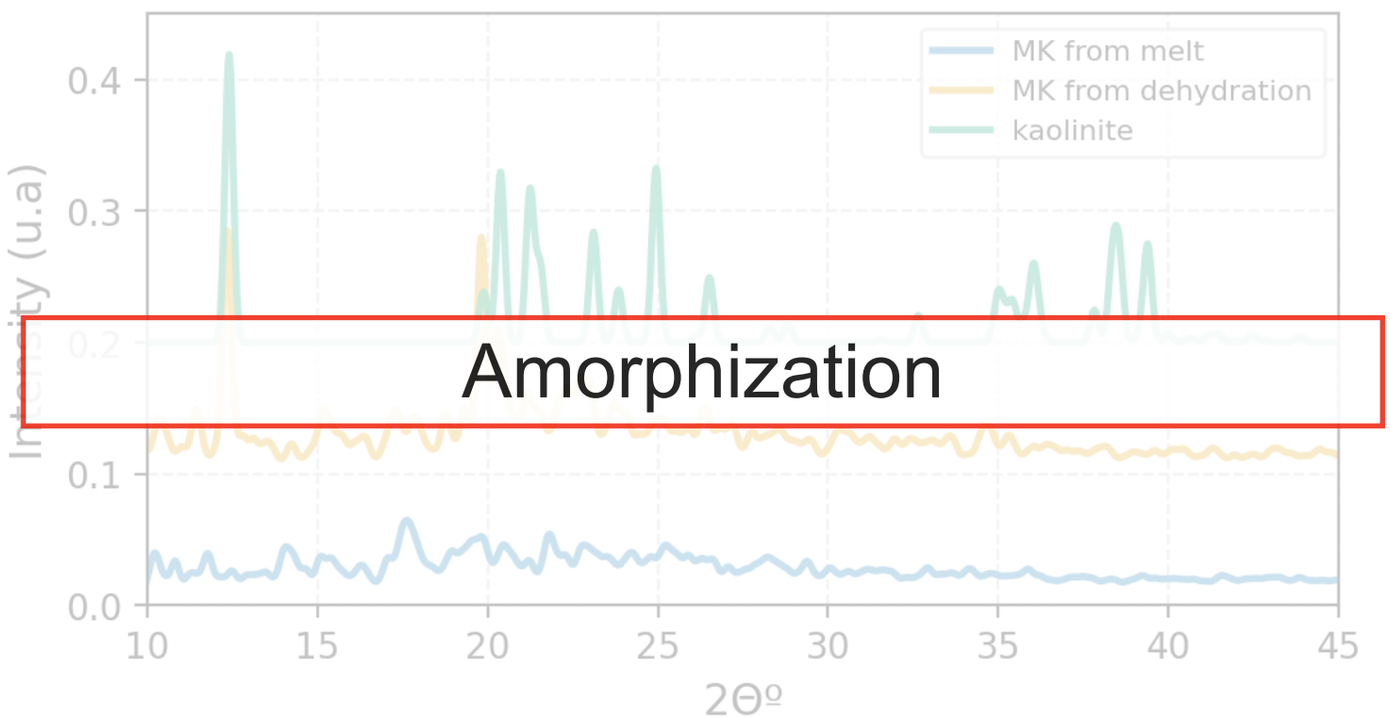
Metakaolin: work in progress

Dehydroxylation protocols

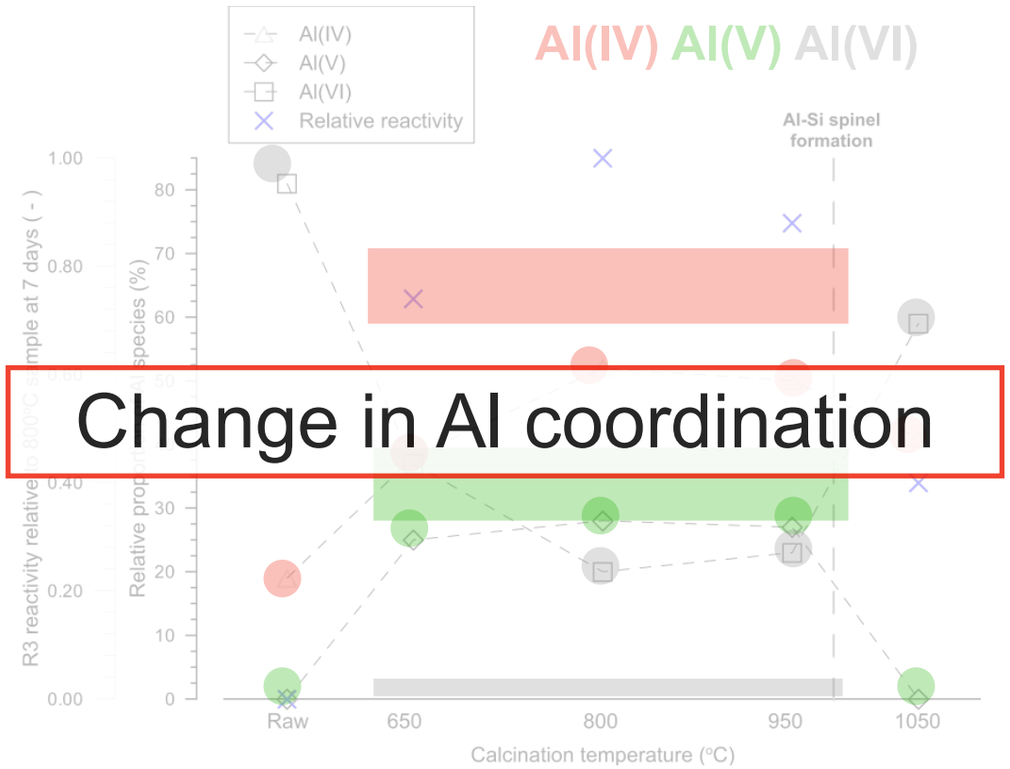


Melting - quenching





Amorphization



Change in Al coordination

The present of atomistic simulations in cement

My 2005 self

“We can go beyond laboratory limitations, do thousands of simulations to test materials and calculate properties, and design cement from electrons to buildings”

20 years later

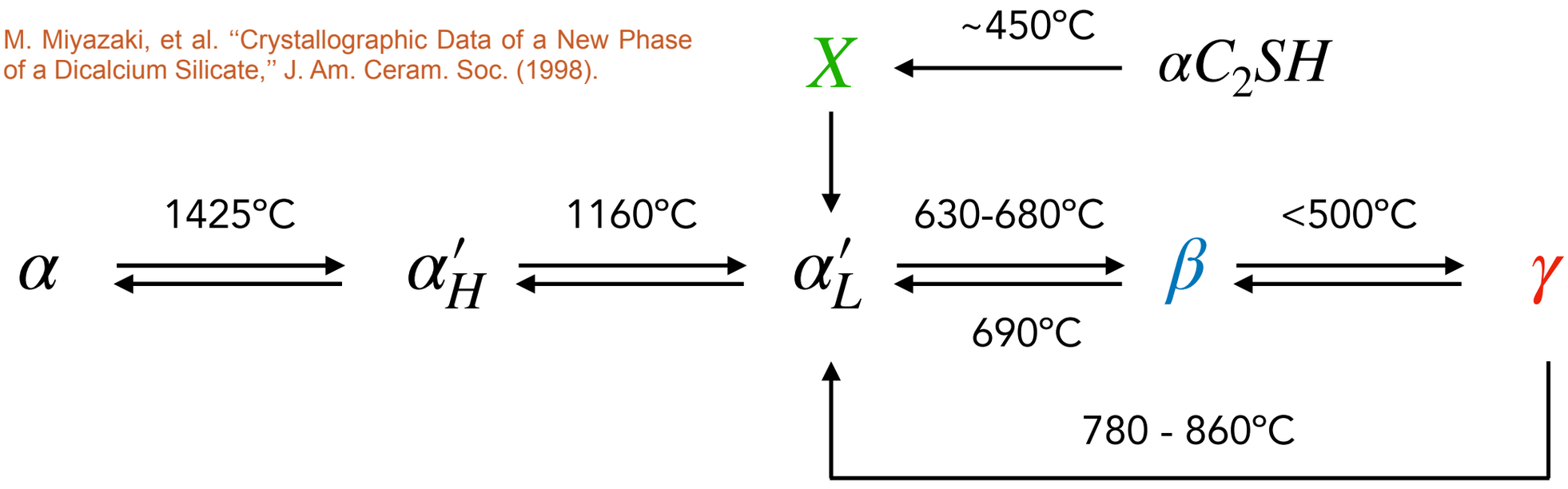
“In practice, the number of atomistic simulation studies that truly imply a practical advance or guide the design of cement towards enhanced performance is limited”

Duque-Redondo, E., de Souza, F. B., Geng, G., & Manzano, H. (2026). A critical review and perspectives on atomistic models of non-crystalline cementitious materials. Cement and Concrete Research, 199, 108067.

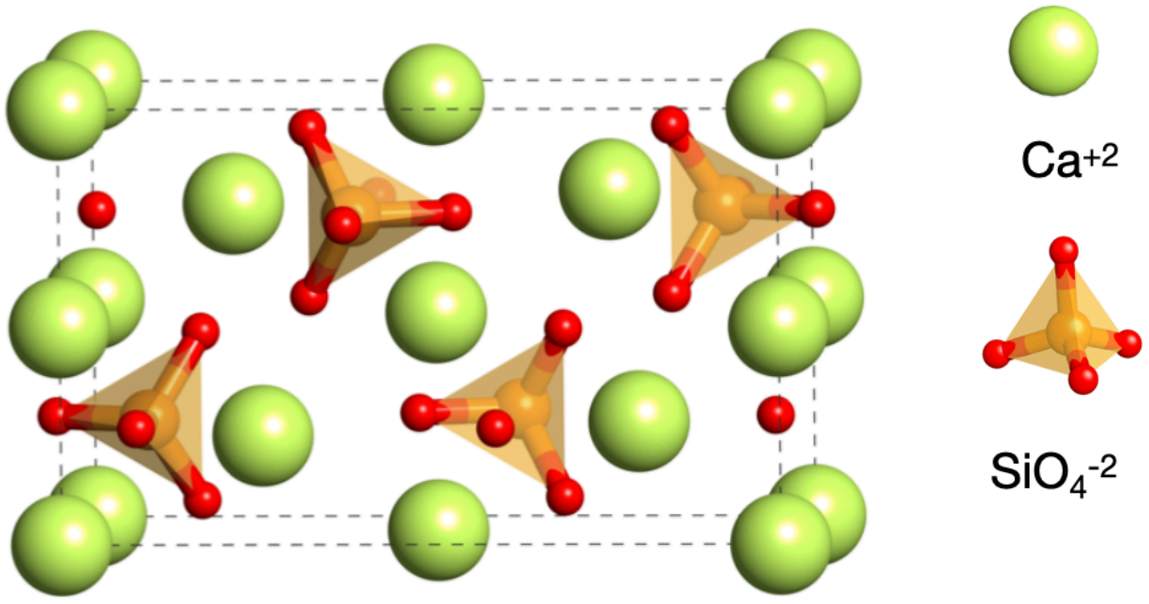
Intrinsic scale limitations, lack of contextualization, incomplete models, lack of experimental focus,…

Case of study: belitic cements

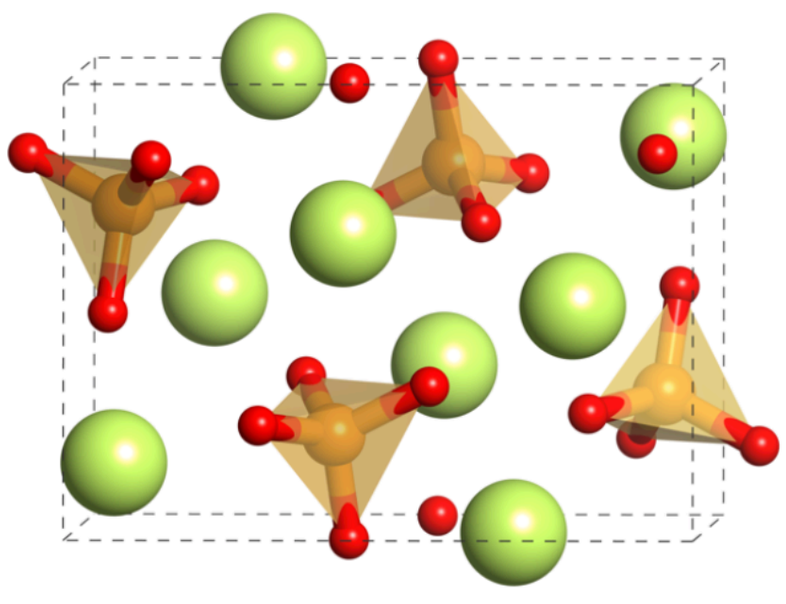
M. Miyazaki, et al. "Crystallographic Data of a New Phase of a Dicalcium Silicate," J. Am. Ceram. Soc. (1998).



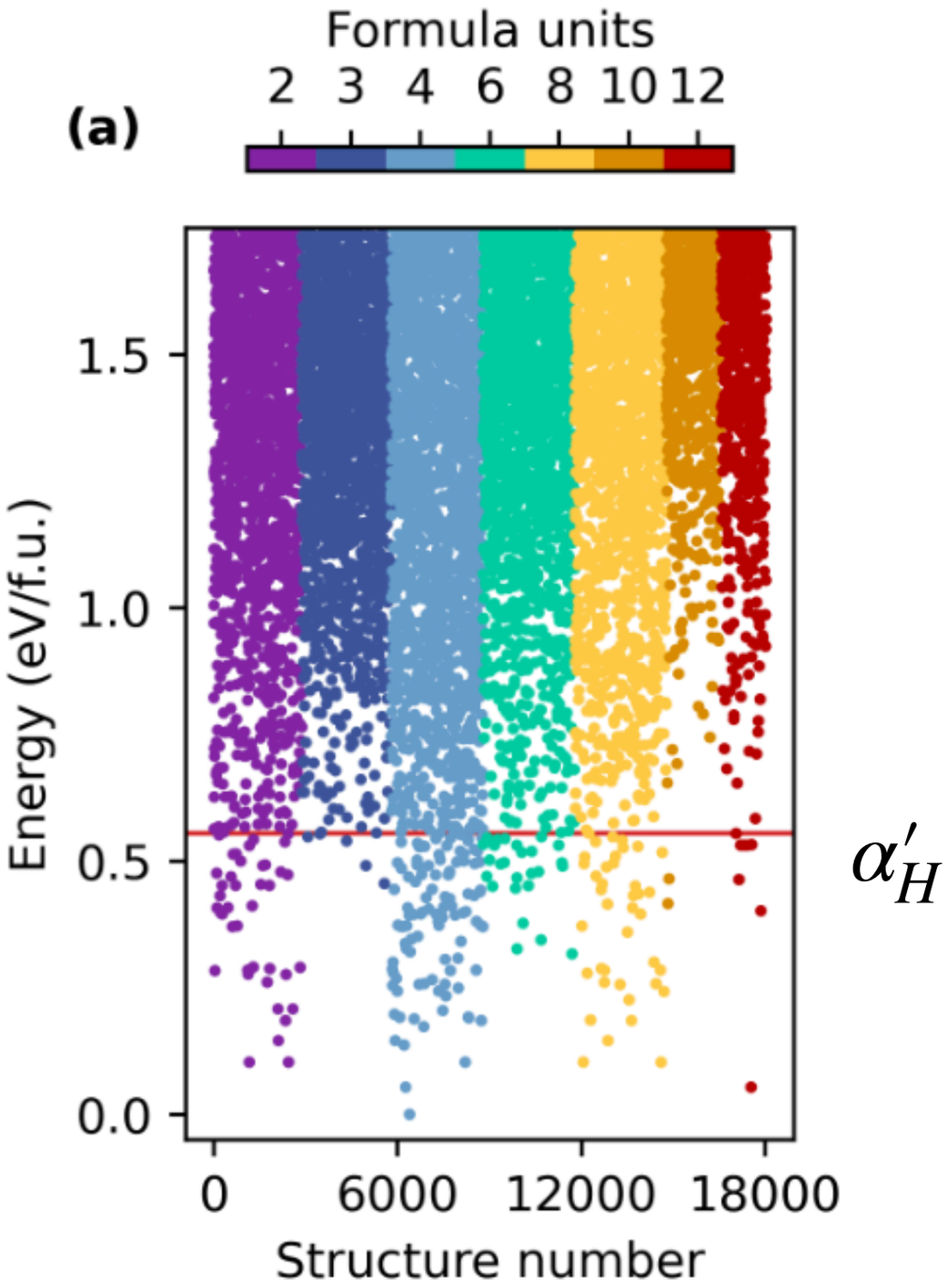
β C_2S (r_{diss} = 18 µmol m^{-2} s^{-1})



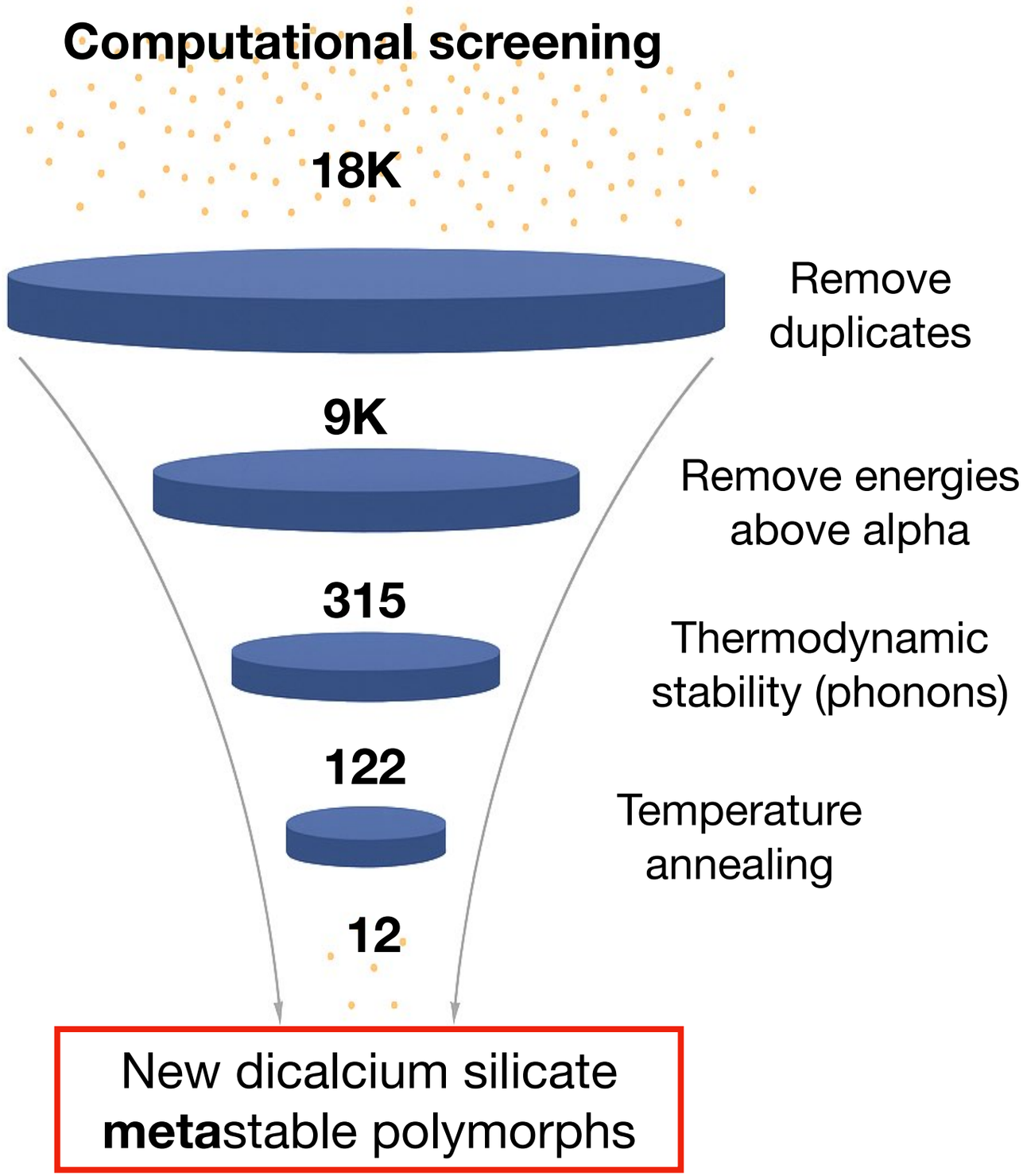
γ C_2S (r_{diss} = 3x10^{-4} µmol m^{-2} s^{-1})



Dicalcium Silicate: searching for new polymorphs

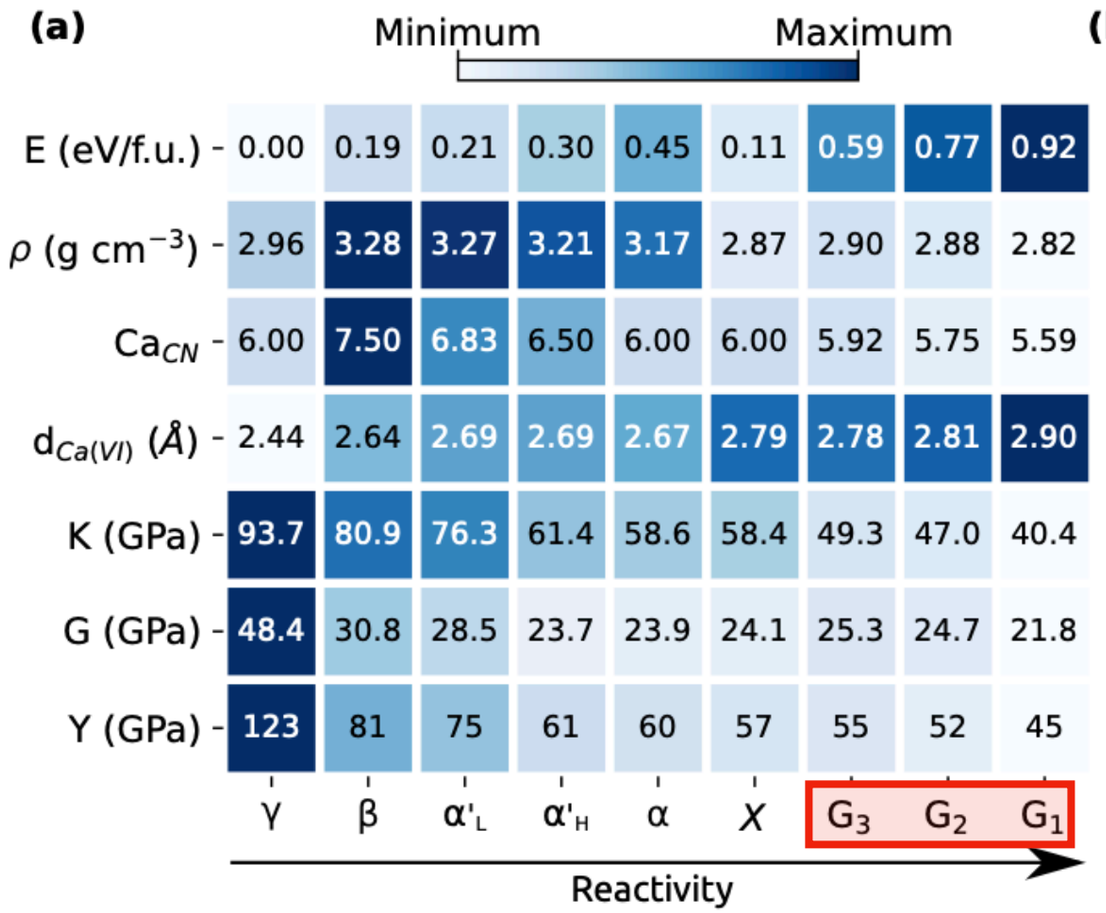


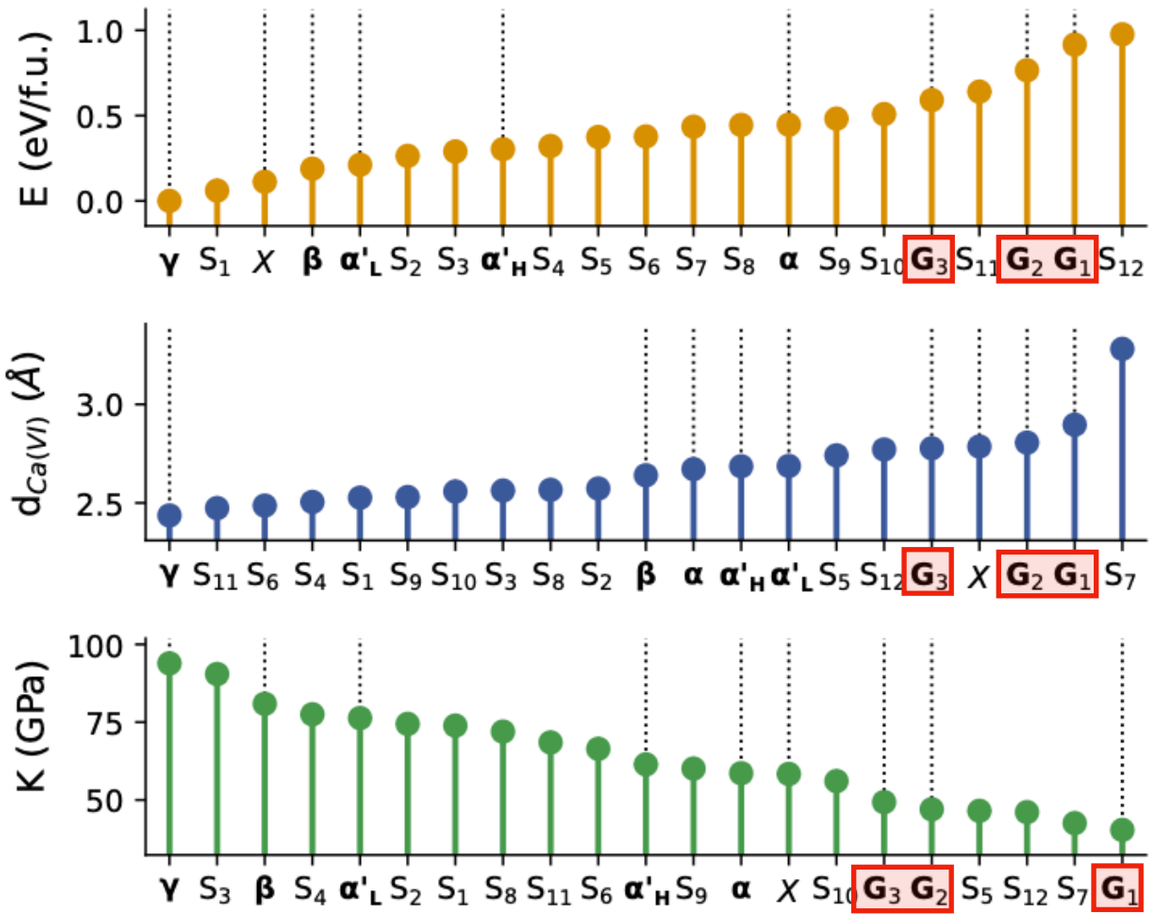
α'_H



López-Zorrilla, J., Aretxabaleta, X. M., & Manzano, H. (2024). Exploring the polymorphism of dicalcium silicates using transfer learning enhanced machine learning atomic potentials.

Dicalcium Silicate: searching for new polymorphs



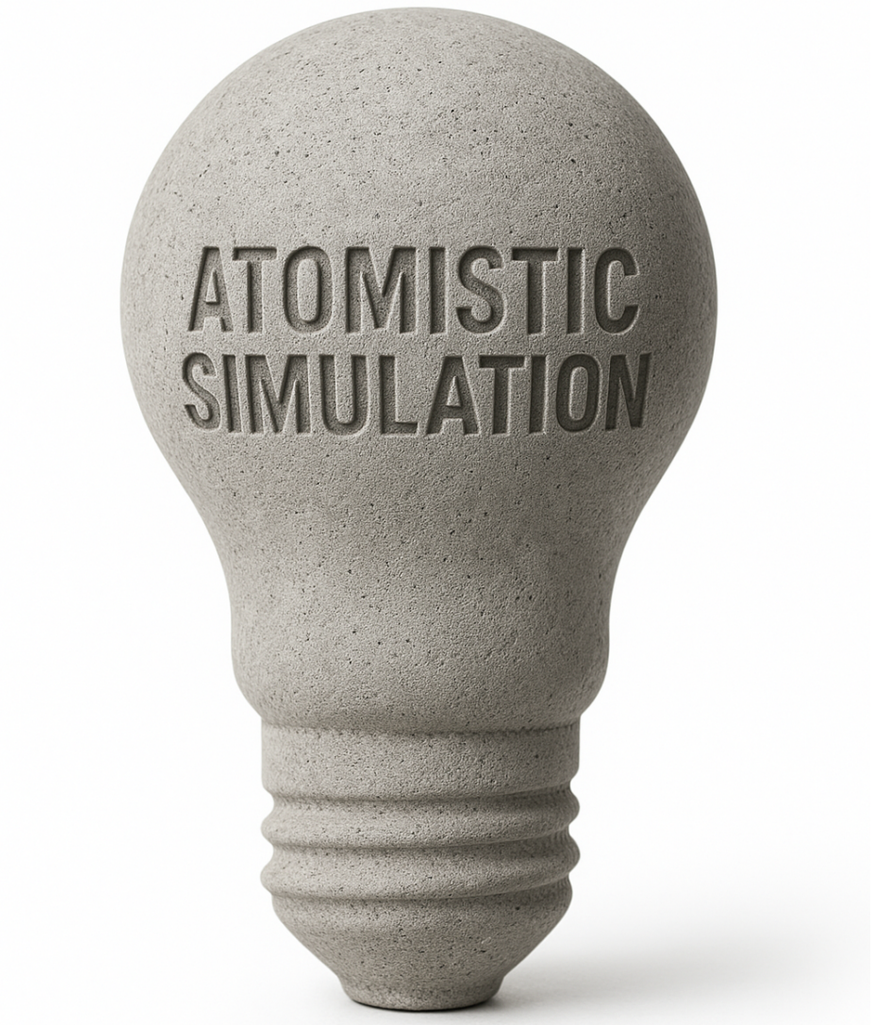


(c)

The amorphous phases are likely to be the reactive ones

López-Zorrilla, J., Aretxabaleta, X. M., & Manzano, H. (2024). Exploring the polymorphism of dicalcium silicates using transfer learning enhanced machine learning atomic potentials.

A bright future ahead!



Better models

Better methods

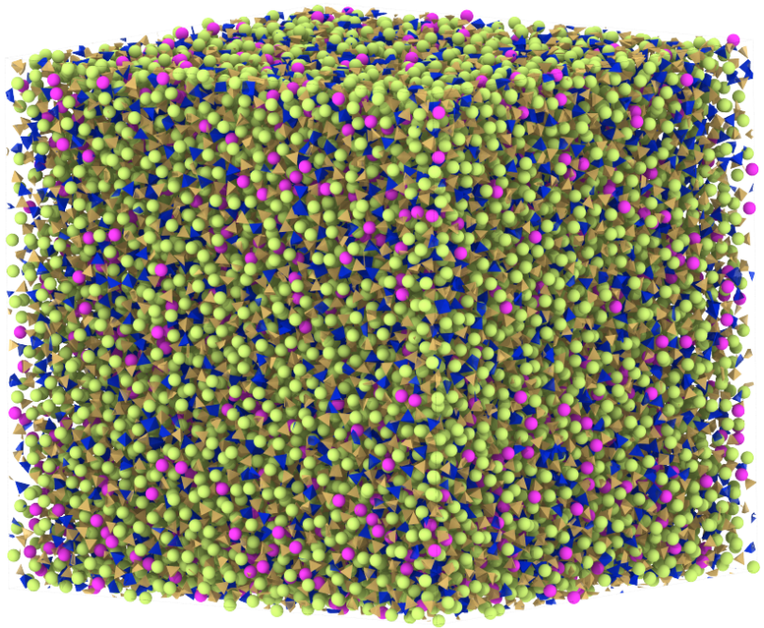
Focused studies

Increasing contextualization and interaction with experiments

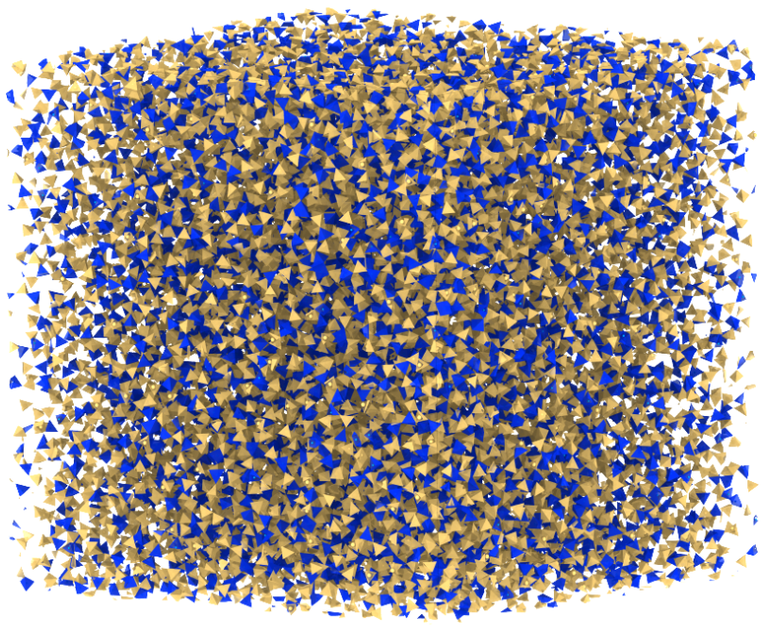
Fly ashes and slags: current models

Qi Zhai, Macro Bertani, Hegoi Manzano, Takayasu Ito, Koji Ohara, Kiyofumi Kurumisawa, The changes in the reactivity of synthetic aluminate silicate-based slag in alkaline environment induced by **minor** components, under review

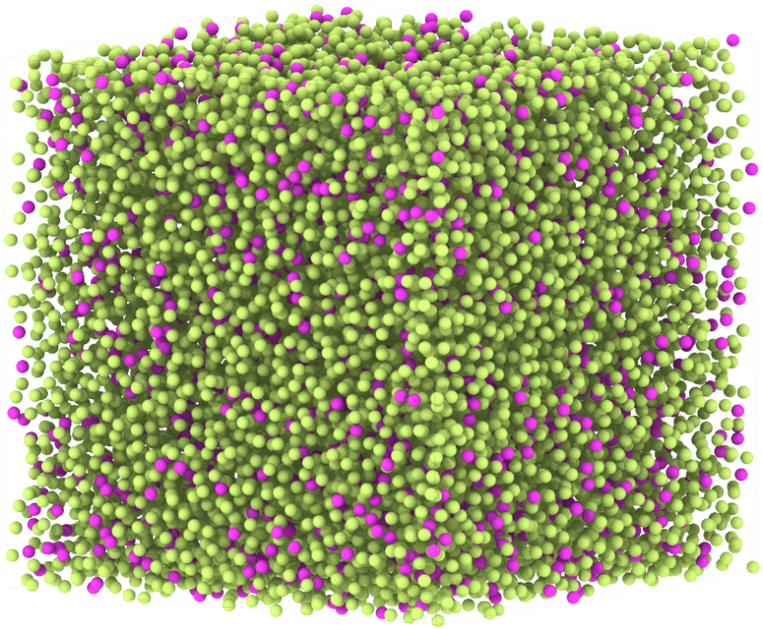
Full slag model



Al/Si T-O-T network



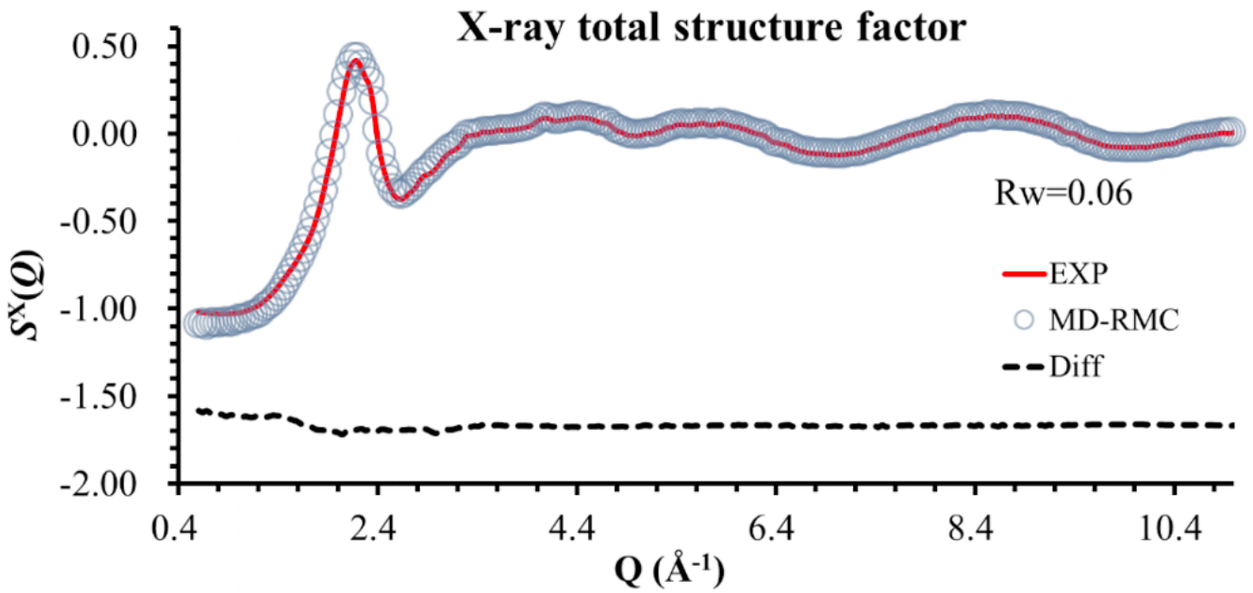
Ca-Mg network modifiers



~70,000 atoms!

70 substitions!

Molecular Dynamics + Reverse Monte Carlo



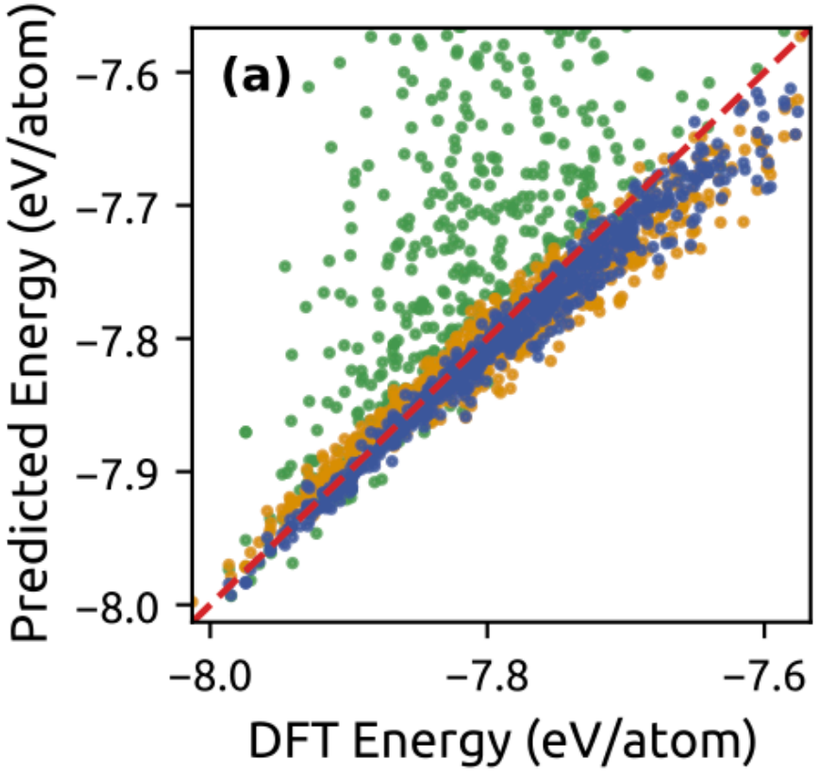
Machine Learning potentials

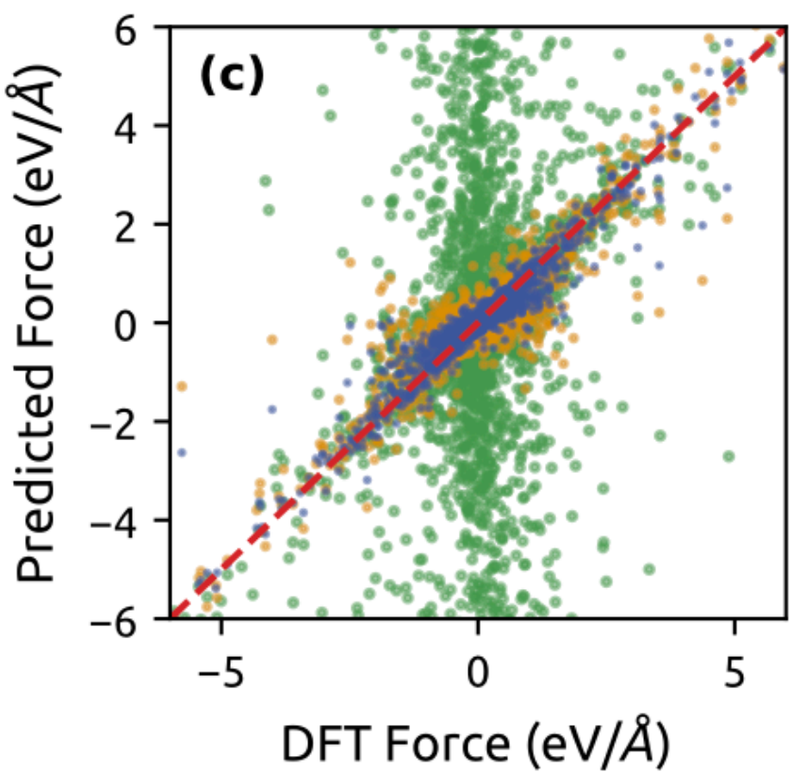
20K calculations; DFT @ 10h ~ 23 years CPU time

20K calculations; MLP @ 10’ ~ 0.4 years CPU time

Transfer Learning
of **ænet MLP**

	C_1S	C_2S	C_3S	SiO_2	CaO	Dimers
ReaxFF	4000	14000	4000	2000	1000	-
DFT	1291	5662	1447	750	300	500



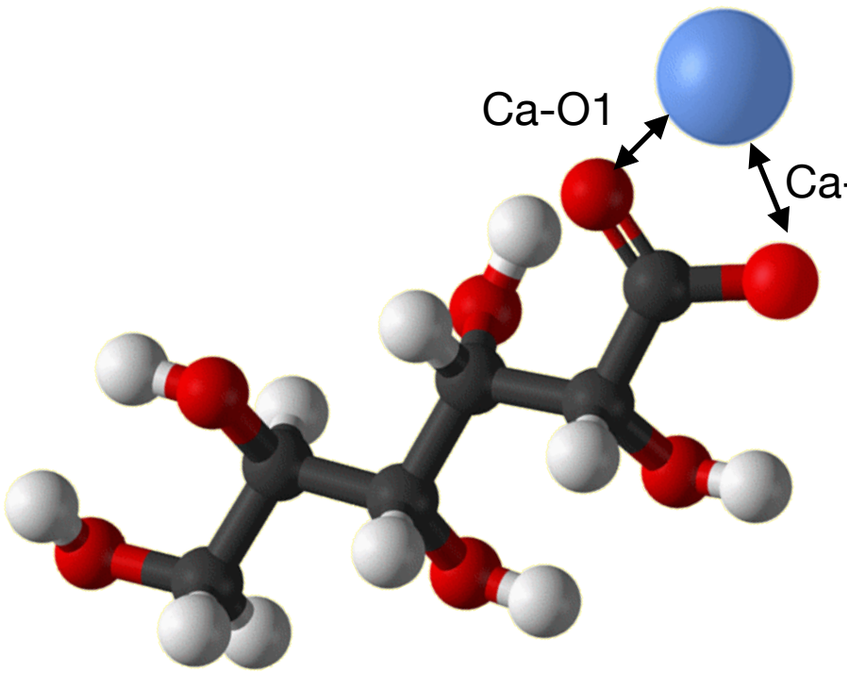


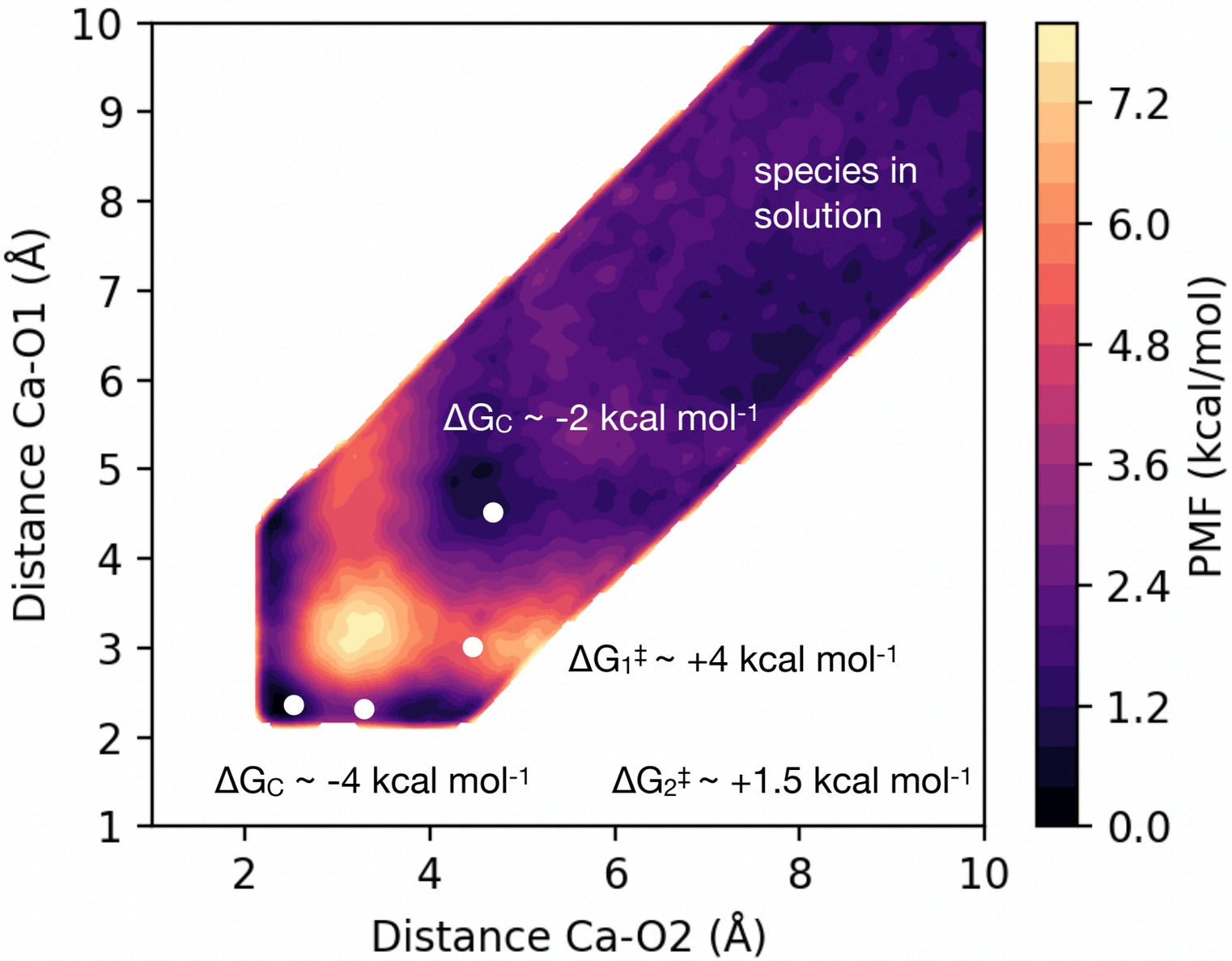
MLP - direct
MLP -transfer
ReaxFF

López-Zorrilla, J., Aretxabaleta, X. M., & Manzano, H. (2024). Exploring the polymorphism of dicalcium silicates using transfer learning enhanced machine learning atomic potentials.

Chemical admixtures

Complexation of ions by chemical admixtures
Adsorption of chemical admixtures on surfaces





Jiale Huang, Hegoi Manzano et al. Ongoing work

Zhai, Q., Kurumisawa, K., Manzano, H., Moon, J., & Hwang, I. H. (2024). New insights in the adsorption behavior of triethanolamine on OPC by experimental and theoretical study. Cement and Concrete Research, 184, 107610.

Duque-Redondo, E., de Souza, F. B., Geng, G., & Manzano, H. (**2026**). A critical review and perspectives on atomistic models of non-crystalline cementitious materials. Cement and Concrete Research, 199, 108067.

Duque-Redondo, E., Masoero, E., & Manzano, H. (**2022**). Nanoscale shear cohesion between cement hydrates: The role of water diffusivity under structural and electrostatic confinement. *Cement and Concrete Research*, *154*, 106716.

López-Zorrilla, J., Aretxabaleta, X. M., & Manzano, H. (**2024**). Exploring the polymorphism of dicalcium silicates using transfer learning enhanced machine learning atomic potentials.

López-Zorrilla, J., Duque-Redondo, … & Manzano, H. (**2025**). Mechanistic insights into calcium-silicate-hydrate nucleation from molecular dynamics simulations. *Cement and Concrete Research*, *198*

Aretxabaleta, X. M., López-Zorrilla, J., Etxebarria, I., & Manzano, H. (**2023**).
Multi-step nucleation pathway of CSH during cement hydration from atomistic simulations. Nature Communications, 14(1)

Manzano, H., A. Ayuela, and J. S. Dolado. (**2007**) "On the formation of cementitious C–S–H nanoparticles." *Journal of computer-aided materials design* 14(1)

Qi Zhai, Macro Bertani, Hegoi Manzano, Takayasu Ito, Koji Ohara, Kiyofumi Kurumisawa, The changes in the reactivity of synthetic aluminate silicate-based slag in alkaline environment induced by minor components, under review

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