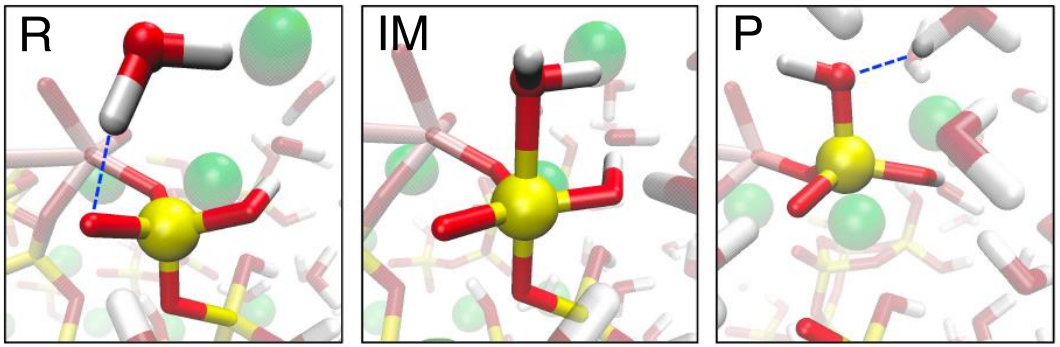
Unraveling the mechanisms of calcium aluminosilicate (CAS) glass dissolution



Luis Ruiz Pestana

Dr. Reza and Georgianna Khatib Endowed Chair
Civil and Architectural Engineering Department

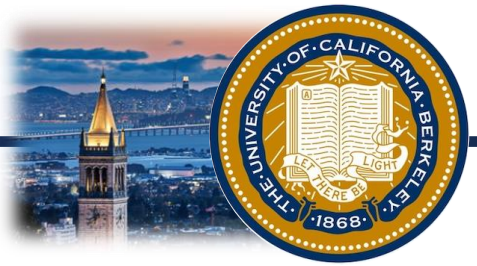
UNIVERSITY OF MIAMI

A bit of background on me

UNIVERSIDAD DE CANTABRIA — ESCUELA DE CAMINOS UNIVERSIDAD DE CANTABRIA

Civil Engineering

Theoretical and Applied Mechanics



Computational Chemistry

EST. 2019

THE COMPUTATIONAL NANOMATERIALS LABORATORY

- Our **goal** is to **understand** and develop physics-based guidelines for the **rational design** of **nanostructured materials**.
- Our **tools** are **multiscale simulation techniques**, **theoretical models**, and **data-driven approaches**.
- Our **guiding principle:**

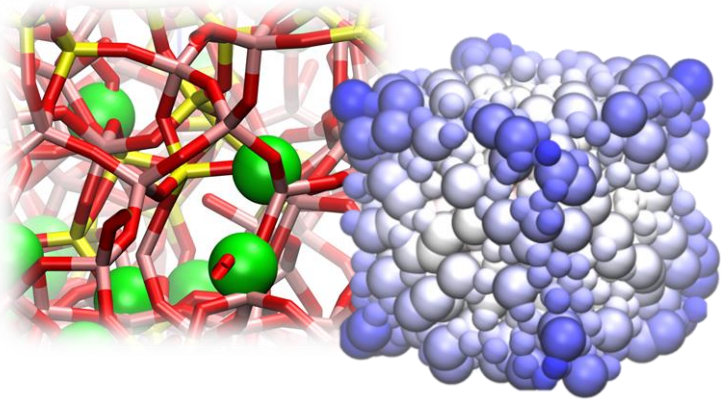
"All models are wrong, but some are useful"

- The **team:**

Messy systems are in focus at the CompNanoLab

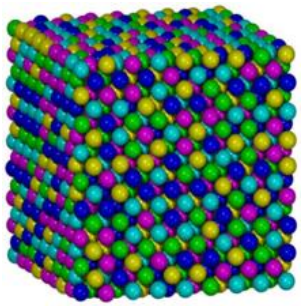
Glasses

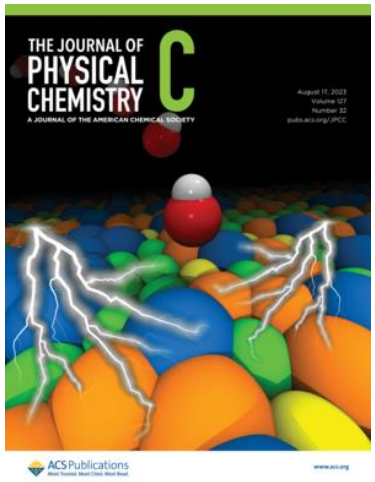
(structural and dynamical disorder)



High Entropy Alloys (HEAs)

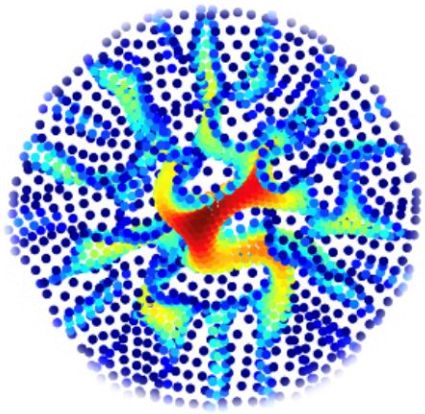
(configurational disorder)

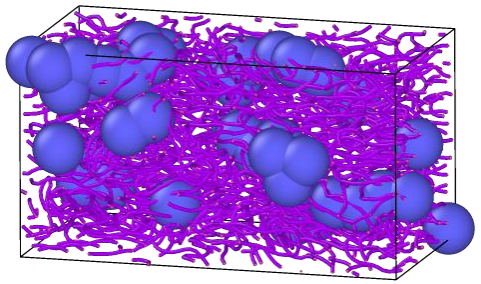




Bacterial Biofilms

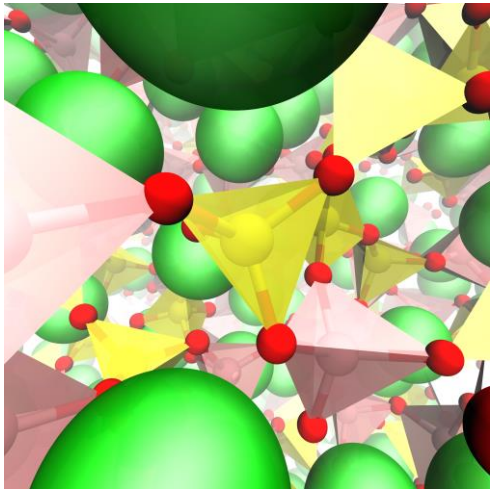
(morphological and phenotypic heterogeneity)



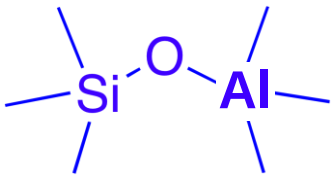


The significance of calcium aluminosilicate (CAS) glasses

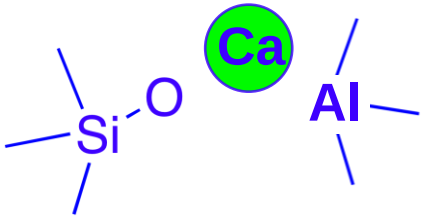
- Substituting **Portland cement** with **supplementary cementitious materials (SCMs)** contributes to the mitigation of carbon emissions.



- The reactive phases of **SCMs** consist primarily of **CAS glasses**.



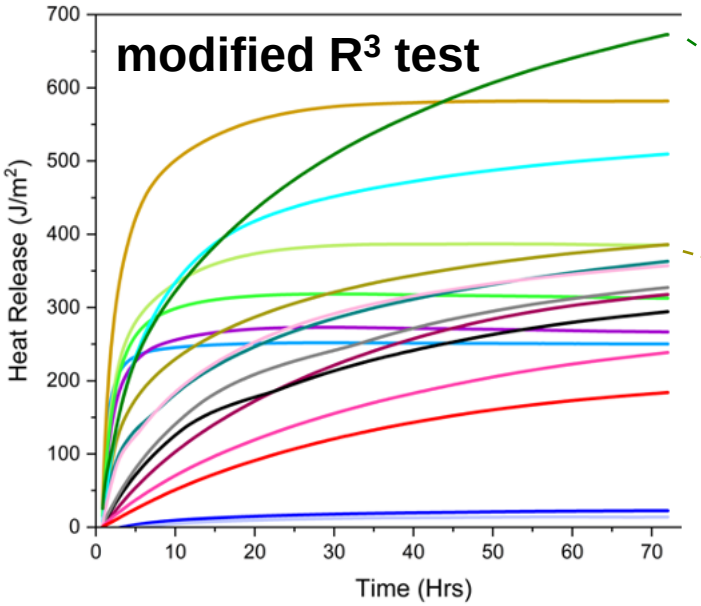
Al, Si - network formers

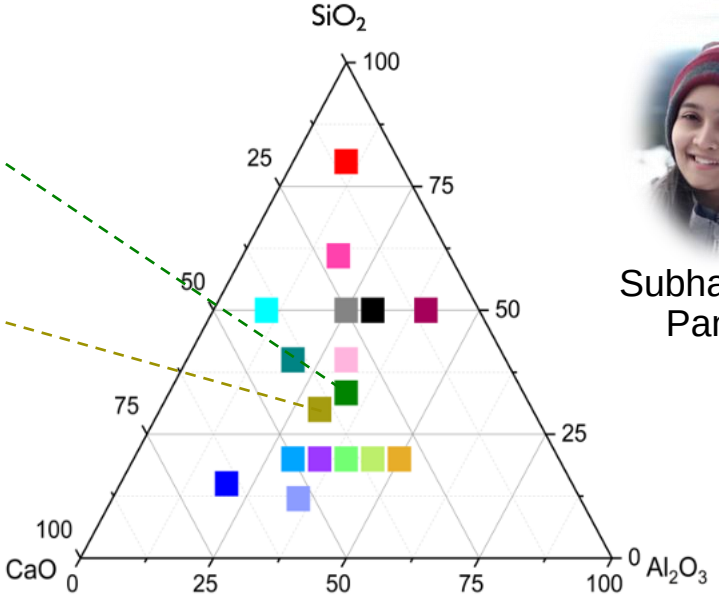


Ca - network modifier

- Understanding the relationships between **composition**, **structure**, and **reactivity** in **CAS glasses** is essential for understanding current **SCMs** and identifying future ones.

Experimental reactivity of CAS glasses



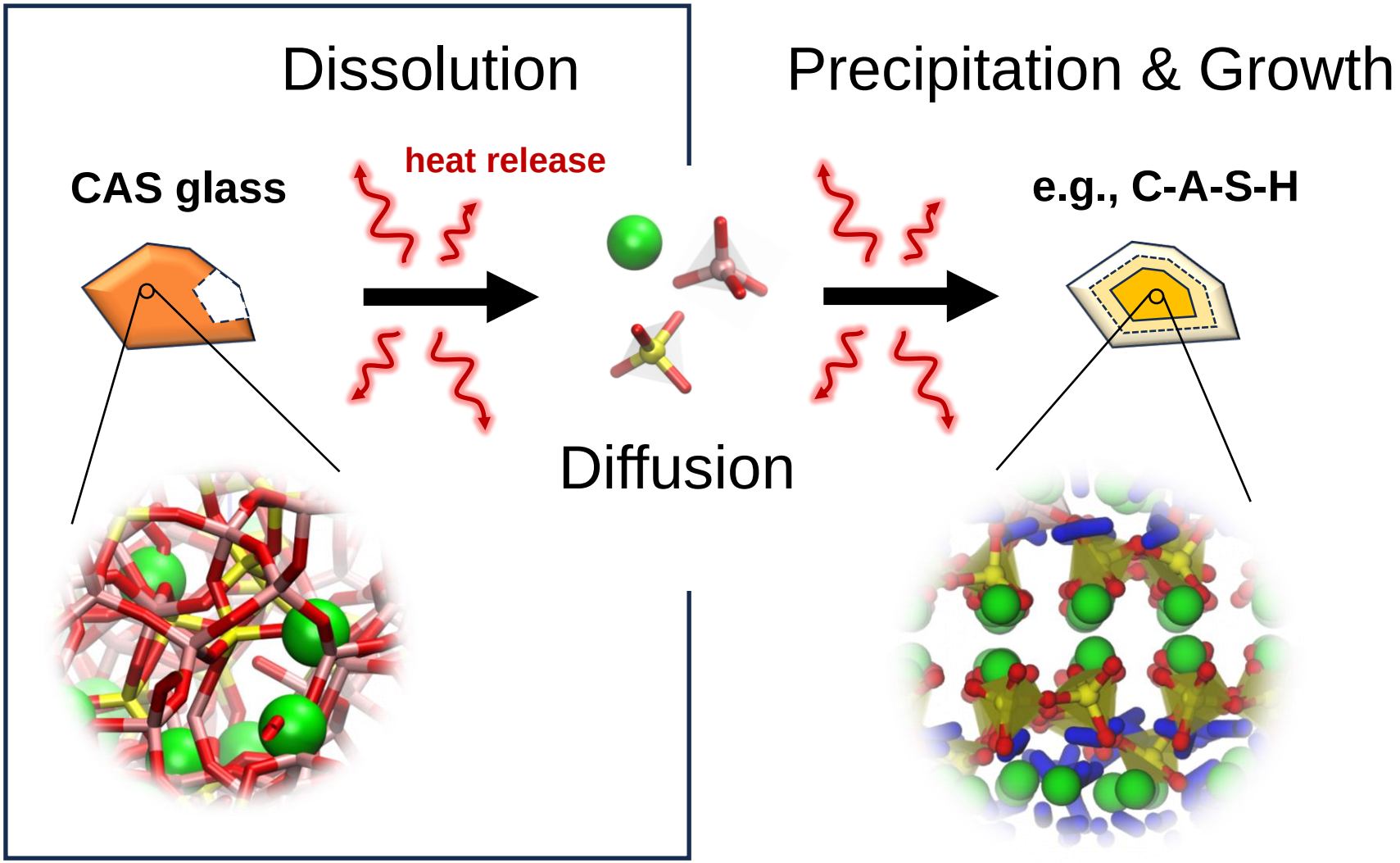


Subhashree Panda

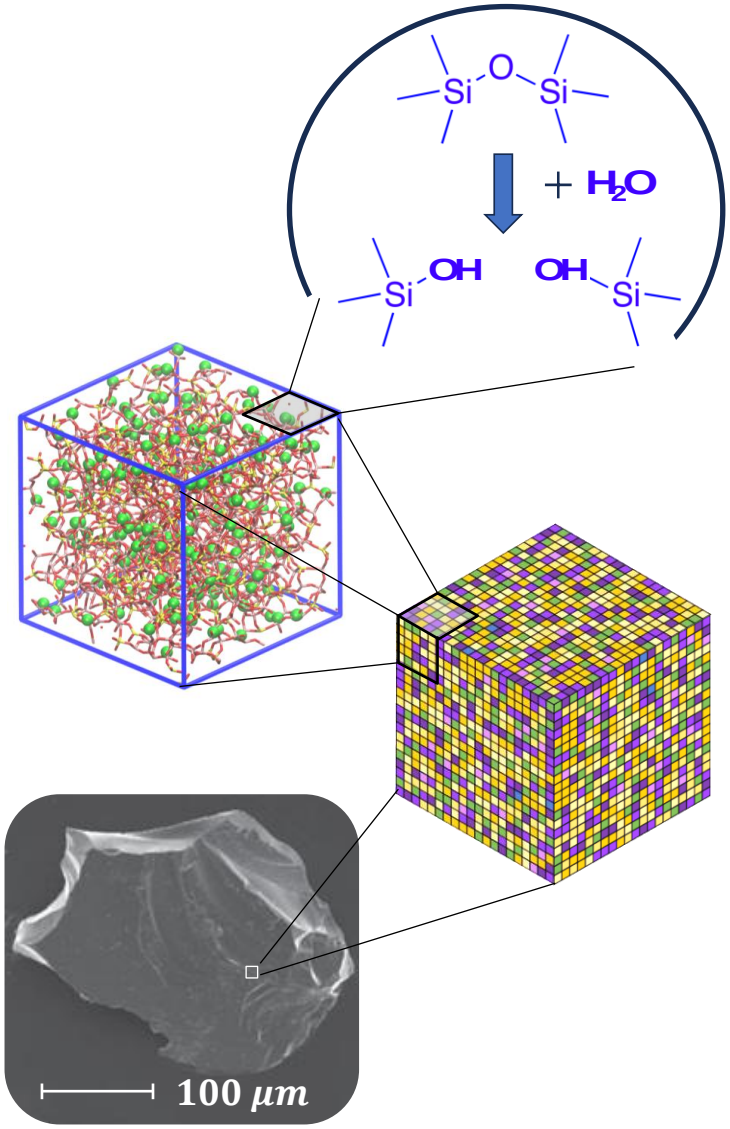
Reactivity — **?** — **Composition**

Stoichiometric descriptors do not fully capture the long-term heat release or the reaction kinetics.

Hydration is a complicated process to simulate from first principles



Multiscale Modeling of Dissolution



scale

Atomistic
~1 nm

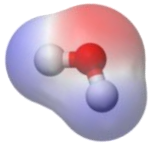
Nano
1 – 100 nm

Meso
100 nm – 1μ

Macro
> 10μ

Ab initio Methods

$$\hat{H}\Psi = E\Psi$$



Molecular Dynamics

$$\mathbf{f} = m\mathbf{a}$$

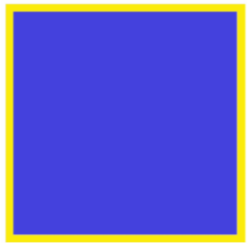
$$\mathbf{f} = -\nabla U(\mathbf{r})$$

Kinetic Monte Carlo

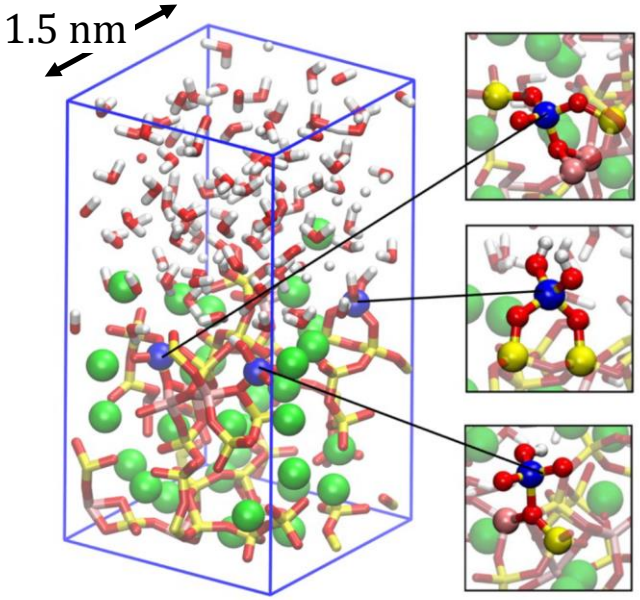
- assign a rate to each possible event

$$r_i = \omega_0 e^{-E_a^i/kT}$$

- realize an event at random



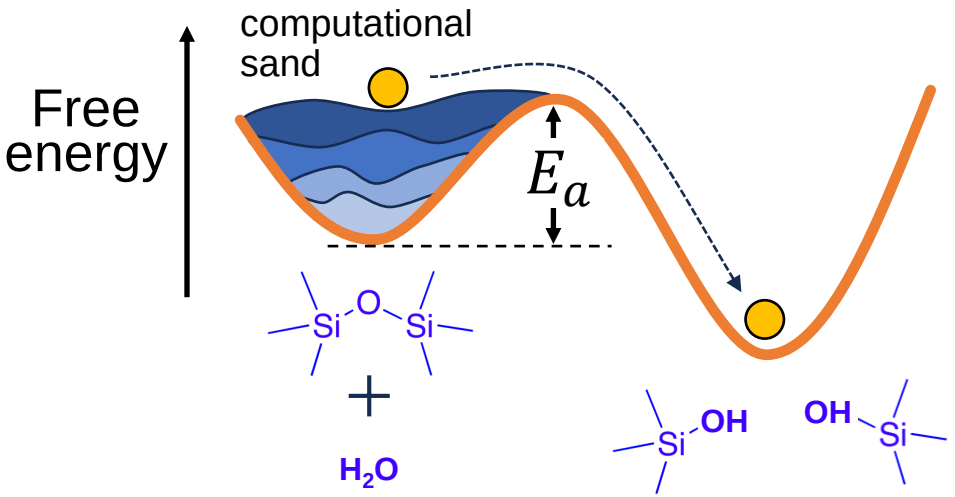
Studying bridge dissociations using AIMD-MetaD simulations



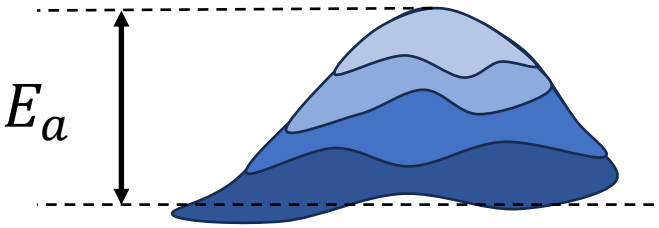
AIMD in a nutshell

$$\mathbf{f} = -\nabla U(\mathbf{r})$$
$$\uparrow$$
$$\hat{H}\Psi = U\Psi$$

Metadynamics in a nutshell



If $E_a \gg k_B\mathrm{T}$ the transition is unlikely to occur during the timespan of a simulation.

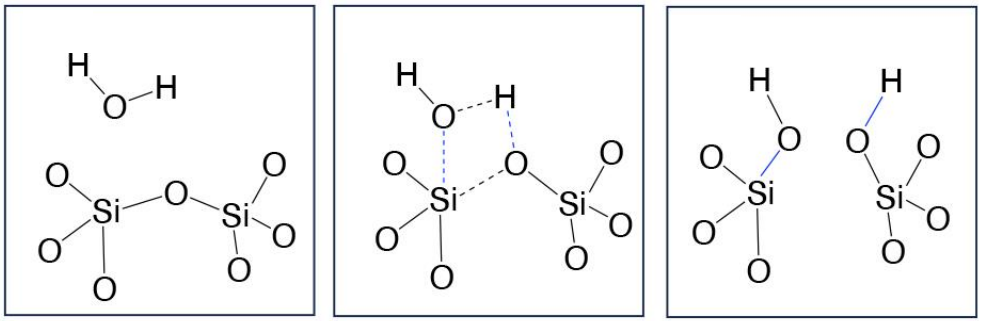


The reaction mechanism of Si-O-X bridge dissociation

Meili Liu

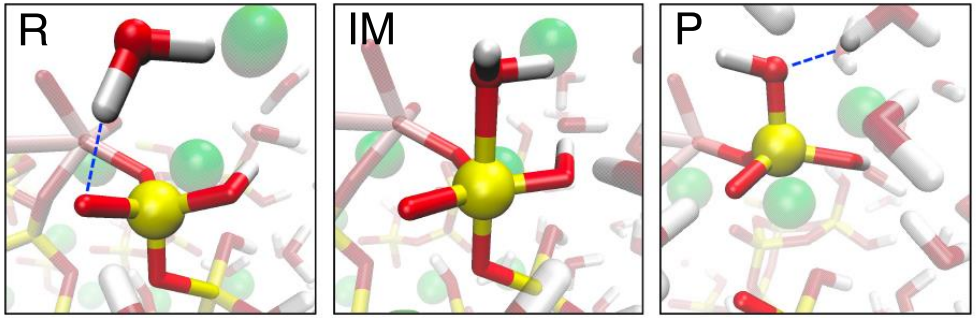
Michalske-Freiman

(hypothesized since 1983)



Our simulations

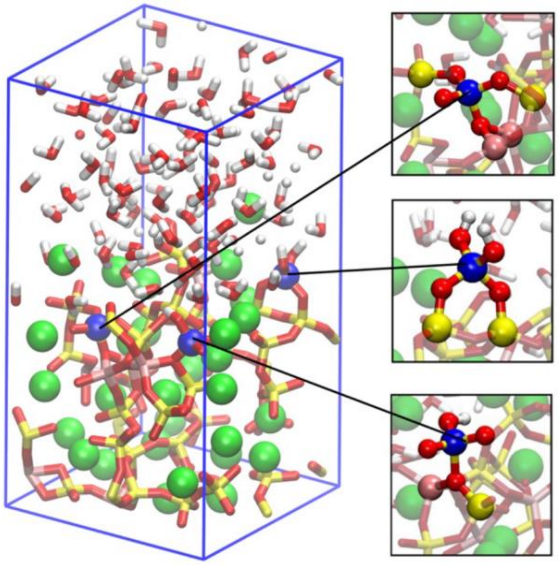
(under review)

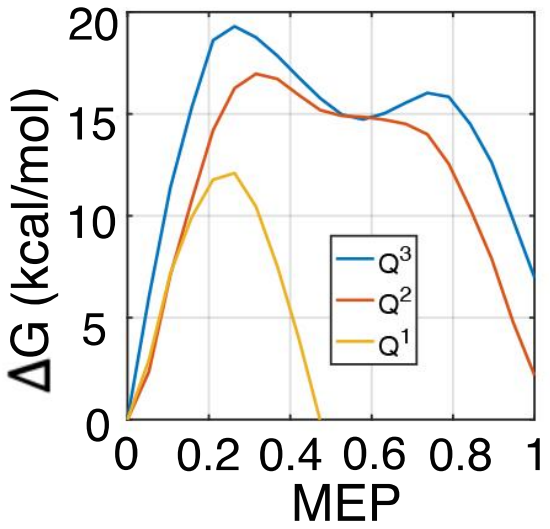


- 5-fold coordinated with a near-trigonal bipyramidal geometry intermediate.
- The bridge opposite to the coordinated nucleophile dissociates.
- The proton from the coordinated nucleophile transfers to bulk water.

nucleophilic substitution reaction

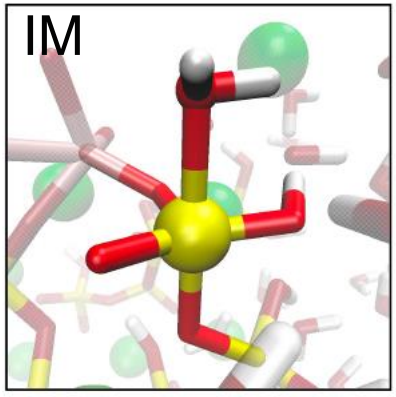
The activation energy depends on the bridge coordination of Si





Si	E_a [kcal/mol]
Q^3	19.3
Q^2	16.9
Q^1	13

Rate limiting step



- The highest the bridge coordination, the higher the energy required to reach the intermediate state.
- For Q^1 and Q^2 the intermediate state becomes the transition state.

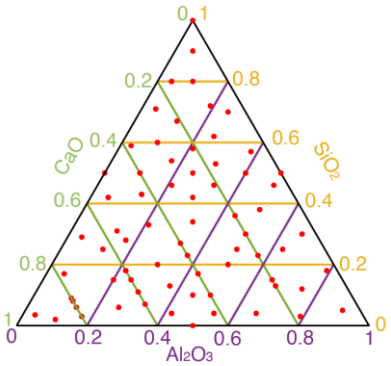
Another part of the puzzle: the chemistry-structure relation

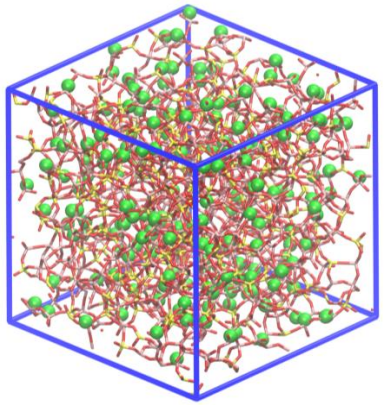
ELSEVIER

Journal of Non-Crystalline Solids
Volume 618, 15 October 2023, 122545

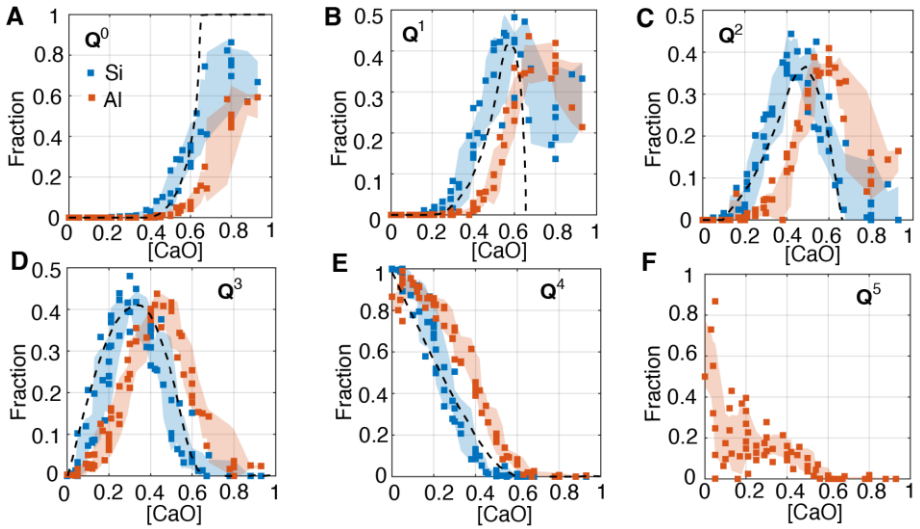
Insights from molecular dynamics into the chemistry-structure relationships of calcium aluminosilicate glasses

Meili Liu, Subhashree Panda, Prannoy Suraneni, Luis Ruiz Pestana

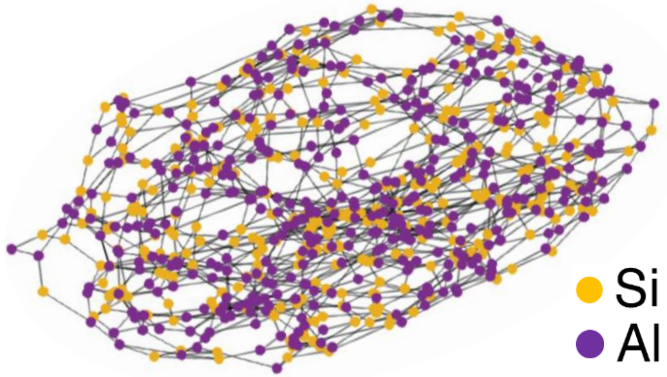




- Access to ALL structural information:

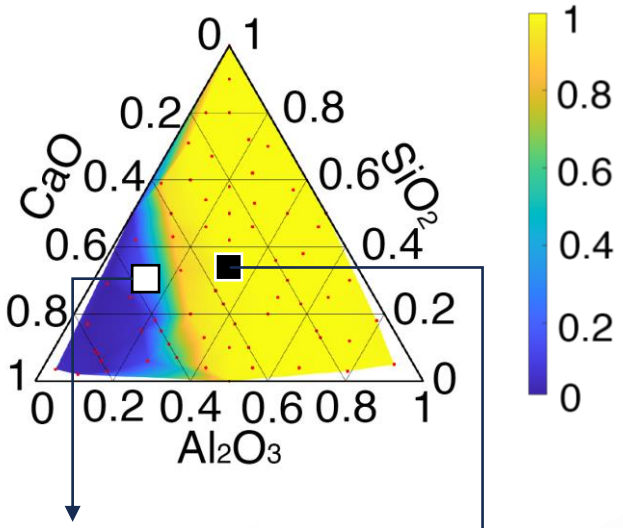


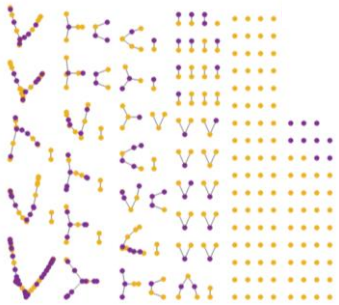
- We can represent the atomistic structures as graphs:

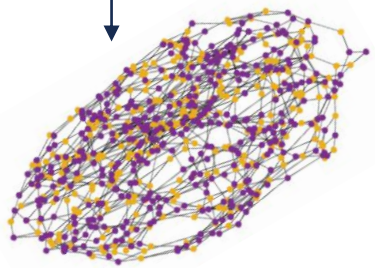


Small compositional changes can have drastic effects on the glass structure

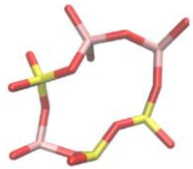
Fraction of nodes in largest cluster

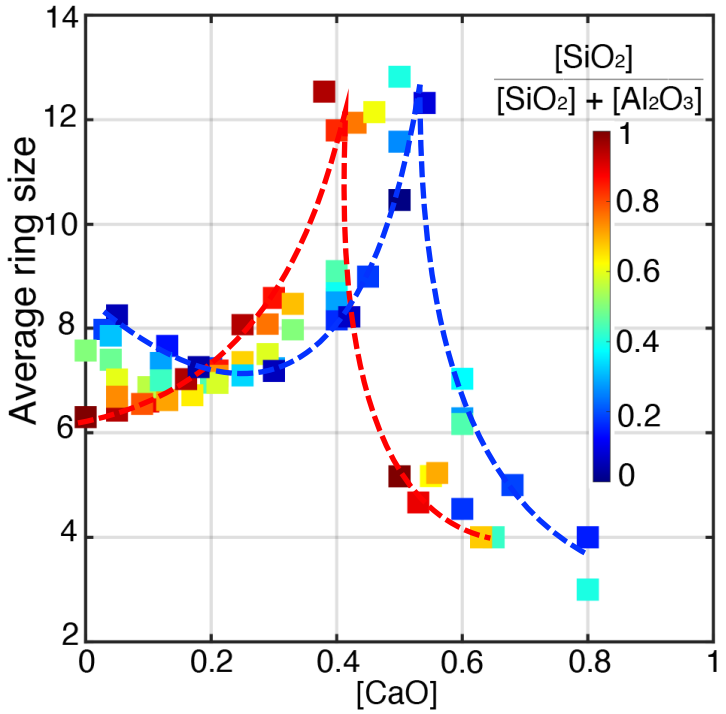






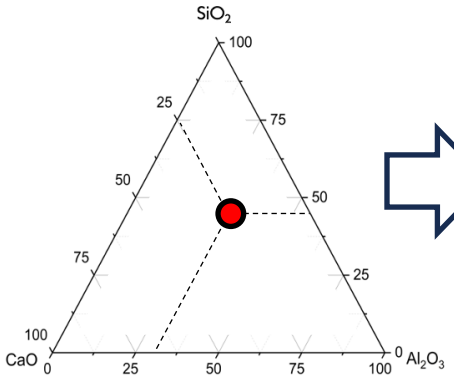
Ring Size Analysis





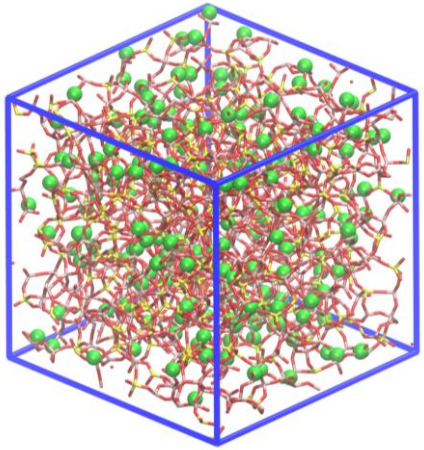
Wrapping up: connecting simulations to experiments

Composition

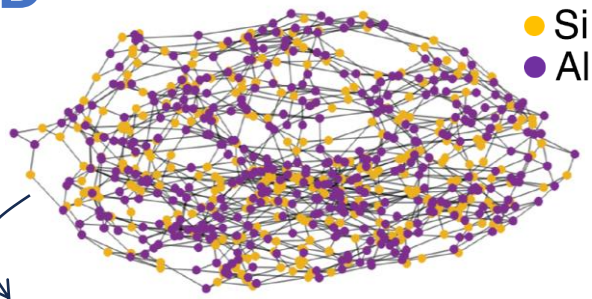


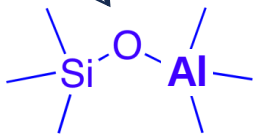
Atomistic structure

MD



=

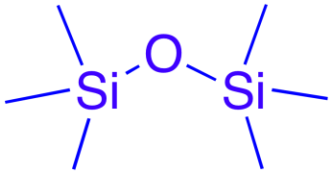




Graph Representation

+

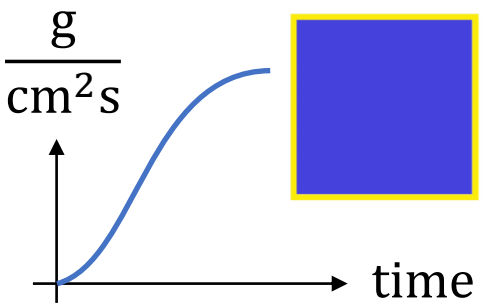
Activation energies of bridge dissociation



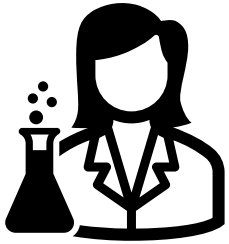
AIMD + MetaD

Dissolution Kinetics

KMC



vs.



experimental validation

~~Pitting~~ Playing to the strengths of simulations and experiments

EXPERIMENTS

- Excel at capturing the **full complexity** of a system.
- Effortlessly cover **macroscopic** time and length scales.
- Experiments excel in providing **quantitative** assessments, revealing *how much*.

SIMULATIONS (bottom-up)

- Offer the advantage of **decoupling effects**, as the system and its environment can be precisely controlled.
- Readily provide **atomistic** and **molecular** resolution.
- Simulations shine in elucidating **underlying mechanisms**, addressing *how* things happen.

Acknowledgements

CMMI - 2101961

Prannoy Suraneni

Subhashree Panda

Meili Liu

ACCESS LAB

Thank you!

And remember…

"A computer lets you make more mistakes faster than any invention in human history – with the possible exceptions of handguns and tequila."

Mitch Ratliffe