

P1: Water transport simulation in cement paste: the effect of aqueous Calcium in the gel pore.

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A native of France, Serge-Henri Cachia was awarded his MSc in Computation and Physics from the University of Montpellier II, France in 2010. He started work at the University of Surrey Oct 1st, 2011.

Overview

- ¹H Nuclear Magnetic Resonance (NMR) relaxometry has measured water dynamics at three timescales in cement pastes: (i) nanoscale hopping of molecules across pore surfaces, (ii) microsecond residency time for water on pore surfaces and (iii) millisecond exchange of water between C-S-H sheet and gel pores [1,2]. The purpose of this work is to confirm these measurements using Molecular Dynamics (MD) and Monte-Carlo (MC) simulations of C-S-H analogues like Tobermorite.
- Project 1 runs in close collaboration with the Surrey EPSRC funded Nanocem partner project that also uses MD & MC simulations to investigate ¹H dynamics.
- The present poster shows an MD model of a gel pore with modified Tobermorite 14A surfaces and introduces the effects of aqueous calcium in the gel pore on water exchange between surface and bulk sites.

Results

- A MD simulation of modified Tobermorite (removing bridging tetrahedra), with a gel pore, was designed in collaboration with Sergey Churakov (PSI, CH) and André Nonat (Université de Dijon, FR).

- SPC/E and CLAYFF potentials are used.
- Crystal layers are frozen.
- Ca/Si=1.5.
- Generates water dynamics in the bulk and on the pore surface.

- Surface waters are trapped in channels (geometry of the crystal surface)
- Two different simulations are performed: one without Ca in the gel pore (A) and one with Ca populating the gel pore surface (B).

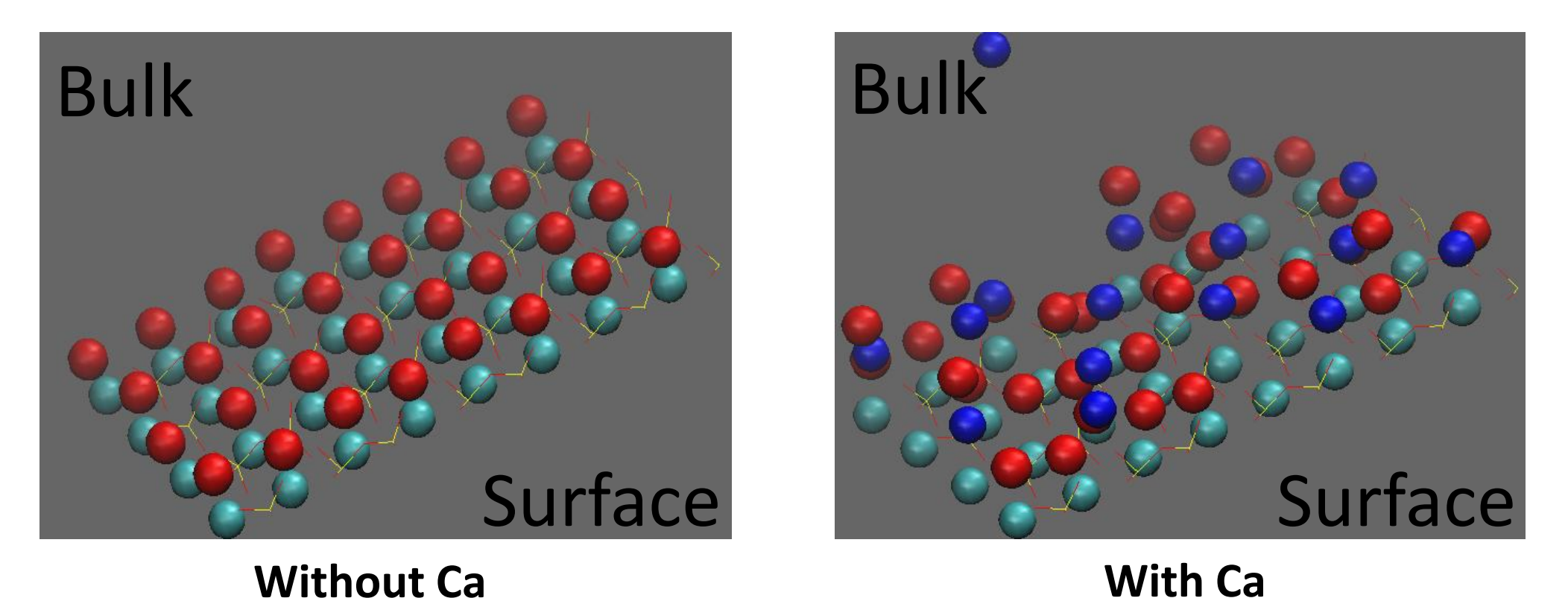
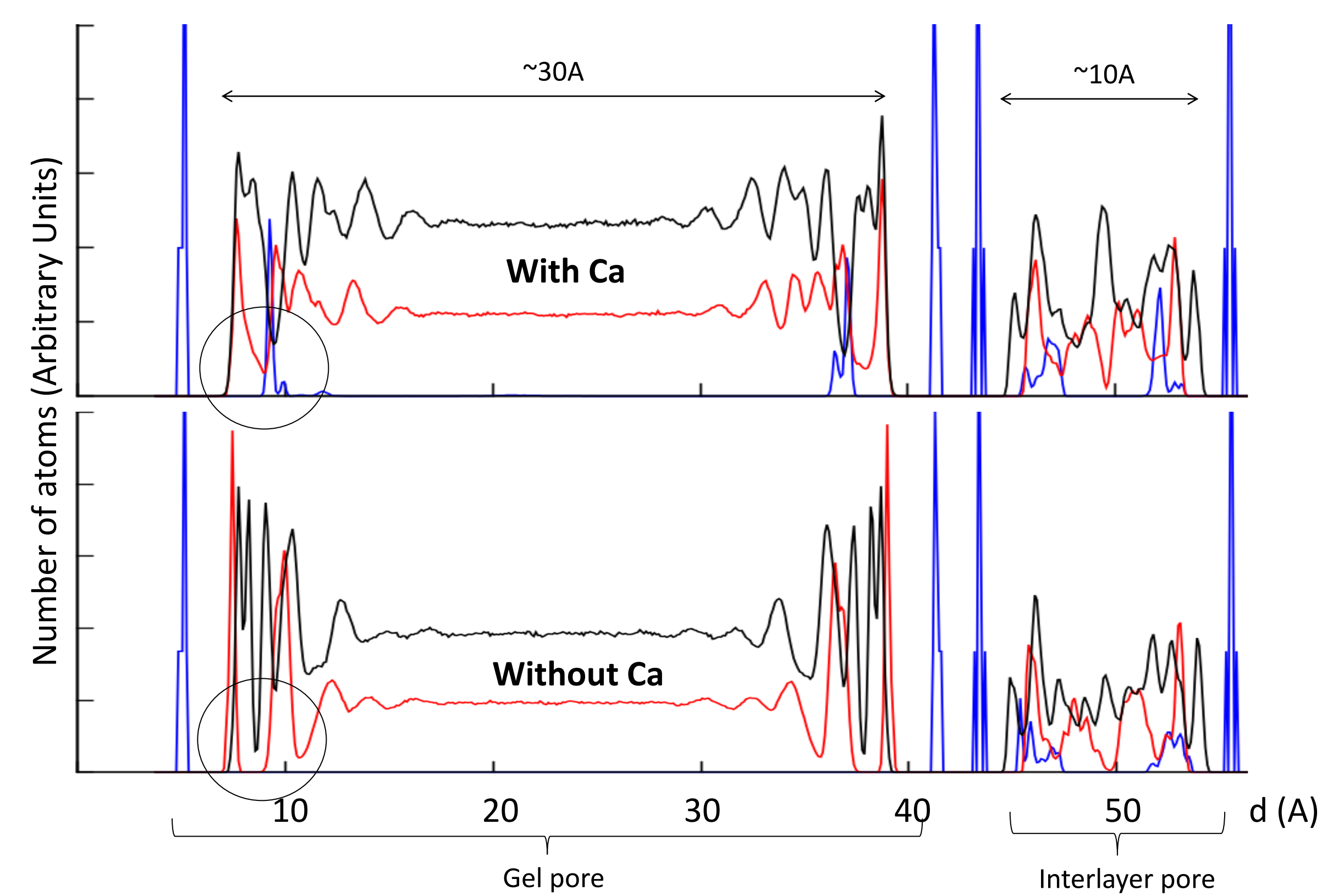
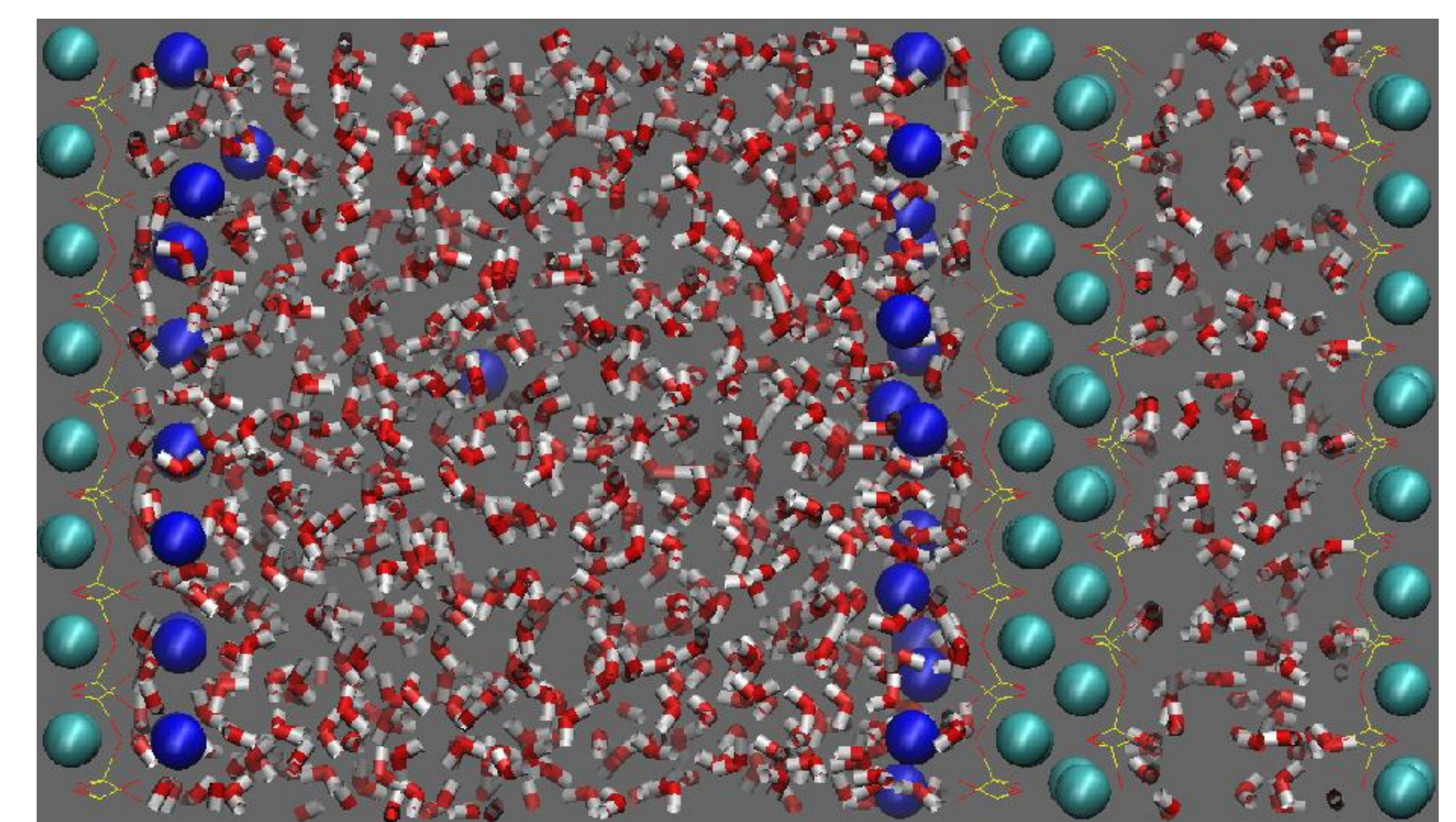
- (A): surface waters are very stable and are not seen to desorb. There is almost no exchange with bulk water.
- (B): Ca atoms tend to align on a regular lattice on the surface replacing former bridging Si tetrahedra. These Ca appear to have a significant role in desorption and diffusion. The water around Ca is structured. Videos show surface water trapped behind Ca rotating around Ca atoms so allowing water to escape from the surface.

- Top right picture shows the simulation cell with aqueous Ca. The color code is: red=O, white/black=H, blue=aqueous Ca, blue-grey=crystal Ca, yellow=Si.

- The two next graphs represent density profiles with and without aqueous Ca. Black circles show that aqueous Ca allows water exchange between the surface and the bulk: the oxygen density (red curve) goes to zero without Ca but is positive with Ca.

- The two bottom pictures represent the gel pore surfaces.

- Left: without aqueous Ca, water oxygen align in front of the crystal Ca lattice.
- Right: with aqueous Ca, Ca tends to form a lattice taking the place of removed bridging tetrahedra. Here, they were originally randomly placed and disorder seems to affect water exchange.



What next and outstanding questions?

- Work is already in progress to quantify these qualitative observations by defining surface, second surface, transition zone and bulk water.
- Measure propagators and exchange rates.
- Unfreeze surface oxygen.
- Parameterize MC simulations.
- Calculate directly T_1 and T_2 NMR relaxation times and compare with SiO_2 and Korb model.
- This system is charged: add aqueous hydroxyl groups to charge balance it and analyse the differences (aqueous OH will go to Ca).
- Investigate interlayer pore and analyse exchange between gel pore and interlayer pore.

References

- [1] - L. Monteilhet et al, PhysRevE.74.061404 (2006)
[2] - P. McDonald et al, PhysRevE.72.011409 (2005)