Structure of Cement Phases from *ab initio* Modeling

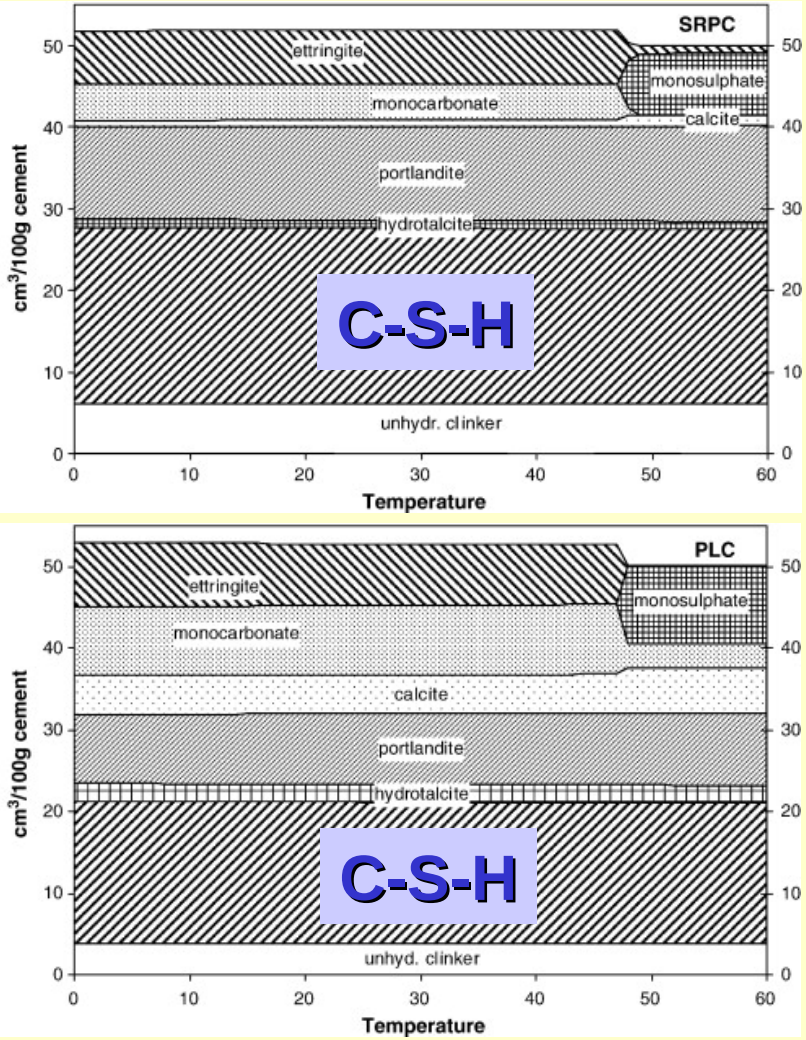
Crystalline C-S-H

Sergey V. Churakov

sergey.churakov@psi.ch

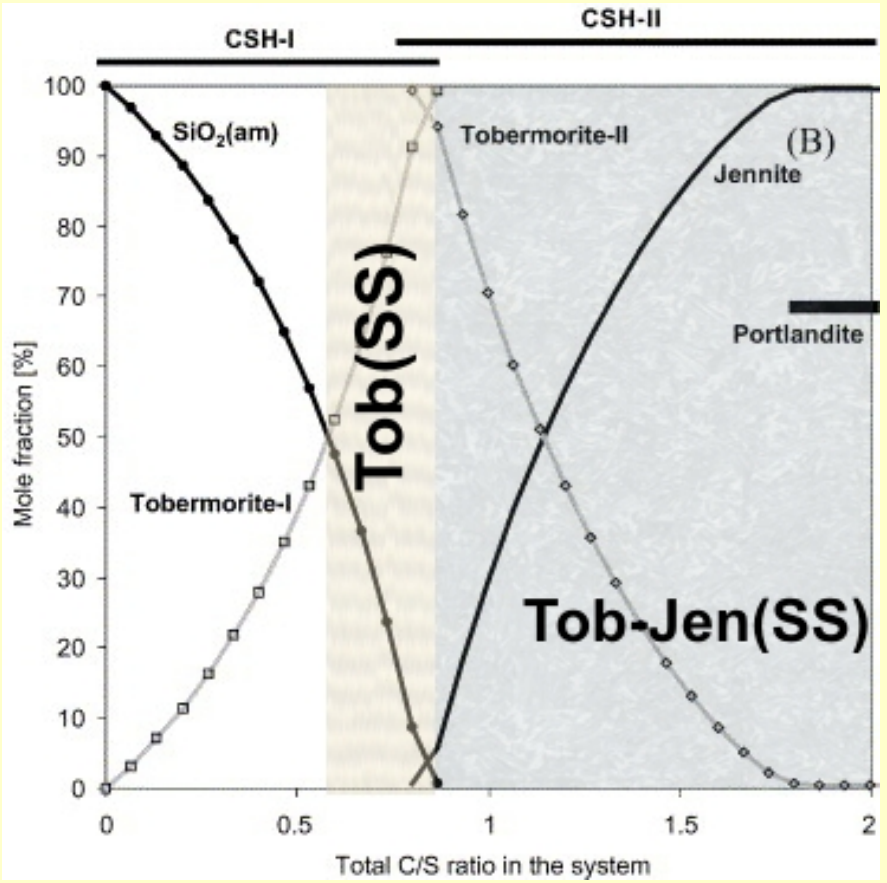
Laboratory for Waste Management
Paul Scherrer Institute
Switzerland

Cement Phase Composition



Lothenbach et al. (2008)

C-S-H Solid Solution Model



Lothenbach &Winnefelf(2006) after Kulik & Kersten (2001)

Possible end-Members for Amorphous C-S-H Solid Solutions

C-S-H (I): Anomalous – Normal Tobermorite Solid Solution

Ca/Si = 0.60 – 0.75

$Ca_4Si_6O_{15}(OH)_2 \times 5H_2O$ – $Ca_{4.5}Si_6O_{16}(OH) \times 5H_2O$

C-S-H (II): Normal Tobermorite – Jennite Solid Solution

Ca/Si = 0.75 – 1.50

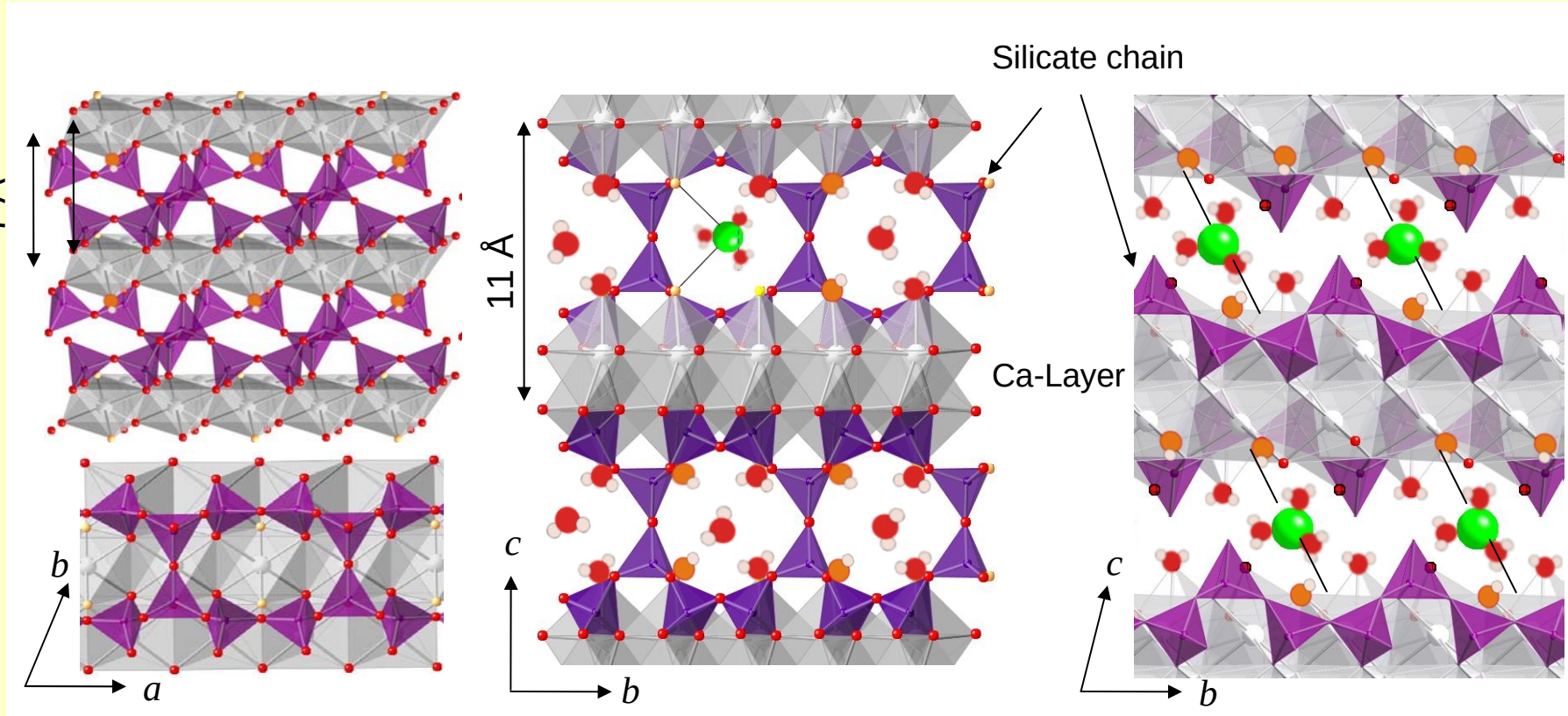
$Ca_{4.5}Si_6O_{16}(OH) \times 5H_2O$ – $Ca_9Si_6O_{18}(OH)_6 \times 8H_2O$

Further relevant C-S-H Phases

Xonotlite: $Ca_6Si_6O_{17}(OH)_2$

Basic Structural Elements of C-S-H Phases

Xonotlite	11 Å Tobermorite	Jennite
$Ca_6Si_6O_{17}(OH)_2$	$Ca_{4+x}Si_6O_{15+2x}(OH)_{2-2x}\times 5H_2O$	$Ca_9Si_6O_{18}(OH)_6\times 8H_2O$



Method

Molecular Dynamics (MD)

Newton Equation

$$M_k \frac{d^2 R_k}{dt^2} = -\frac{\partial U(R)}{\partial R_k}$$

Must be known

$$\Gamma(\{R_k\},\{\dot{R}_k\})$$

Ensemble of position and velocities

Average over Ensemble

Structure:
- Bond distances
- Crystallographic positions
- …

Thermodynamics:
- Energies
- Temperature
- …

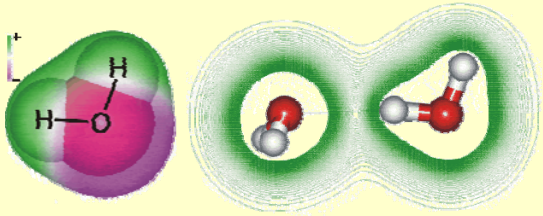
Dynamics:
- IR spectra
- Diffusion
- …

Interaction Potentials

• Ab Initio methods

Solve Schrödinger equation to obtain energy and forces

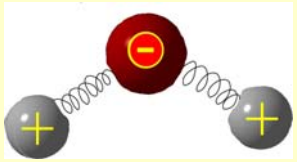
$$-\frac{\hbar^2}{2m}\nabla^2\Psi + U\Psi = E\Psi$$



• Empirical force field methods

intra-molecular: harmonic bond stretching, bending …

inter-molecular: electrostatic and van der Waals interaction



Ab Initio <=> Empirical

☹ *Computationally expensive*
☺ *Valid for any P-T conditions and chemistry*
☺ *Correct description of bond breaking/forming*

☹ *up to ~ n×10 ^{2} atoms*
☹ *up to ~ n×10 ps*

☺ *Fast computation*
☹ *Must be calibrated for the system of interest*
☹ *Fail to describe bond breaking/forming*

☺ *up to ~ n×10 ^{6} atoms*
☺ *up to ~ n×10 ^{2} ns*

Density functional theory

Hohenberg & Kohn, 1964; Kohn & Sham 1965;

Schrödinger Equation

$$H\Psi(R_{3N}) = E\Psi(R_{3N})$$

- *Exact Hamiltonian*
- *3N dimensional problem*

far too complex :-((

Kohn-Sham Equation

$$\begin{cases} H^{KS}\psi_1(r_3) = \varepsilon_1^{KS}\psi_1(r_3) \\ \cdots\cdots\cdots \\ H^{KS}\psi_N(r_3) = \varepsilon_N^{KS}\psi_N(r_3) \end{cases}$$

- *Approximate Hamiltonian*
- *3 dimensional problem*

but can be solved ! :-))

$$H^{KS} = \underbrace{\overbrace{-\frac{1}{2}\nabla^2}^{\text{Kinetic Energy of Electrons}} + \overbrace{\hat{V}_{ext}(R_{nuc})}^{\text{Coulomb Interaction Nuclei – Electrons}} + \overbrace{\hat{V}_{Hartree}[\rho^{el}]}^{\text{Coulomb Interaction Electrons}}}_{\text{Exact}} + \underbrace{\overbrace{\hat{V}_{xc}[\rho^{el}]}^{\text{Quantum effects}}}_{\text{Approximation}}$$

$$\rho^{el}(r) = \sum_i |\psi_i(r)|^2$$

Major uncertainty

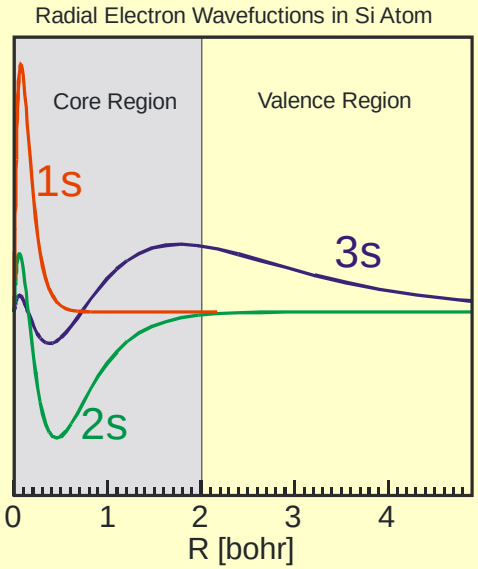
Approximations for Exchange and Correlation functional

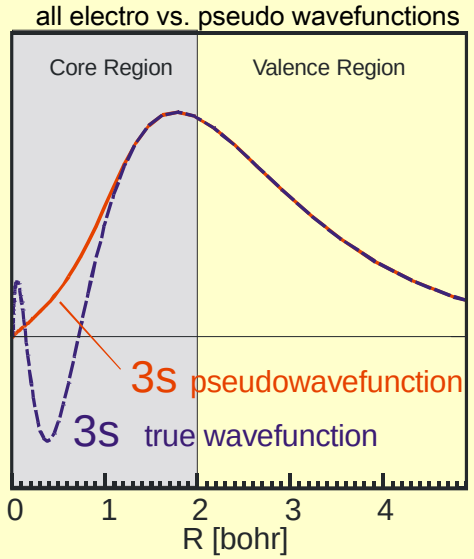
$\hat{V}_{xc}$

- *local density approximation (LDA)* $\hat{V}_{xc}[\rho^{el}(r)]$ *homogeneous electron gas*
- *generalized gradient approximation (BLYP, PBE, ...)* $\hat{V}_{xc}[\rho^{el}(r), \nabla\rho^{el}(r)]$

Pseudopotential approximation

an example for Si atom





Basis set

Plane Waves

$$\psi_i = \sum_{\mathbf{k}} c_{i,\mathbf{k}} e^{-i\mathbf{kr}}$$

Gaussian basis set

$$\psi_i = \sum_{\mu} c_{i,\mu}\varphi_\mu$$

$$\varphi_\mu(\alpha, l, m, n) = Ne^{-\alpha r^2} x^l y^m z^n$$

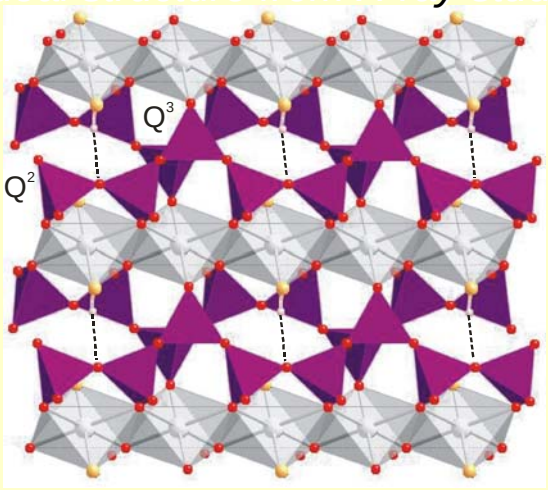
DFT approach used in this work

- CPMD code (used for oblique supercell)
  - Plane Wave basis set
  - 70 Ry cut-off
  - BLYP functional, MT-pseudopotentials
  - Car-Parrinello MD
- CP2K/Quickstep code (used for orthogonal supercell)
  - Gaussian and Plane Wave basis set
  - Triple-ζ basis for O and H, double-ζ for Si and Ca
  - PBE functional, Goedeker - pseudopotentials
  - Born Oppenheimer MD

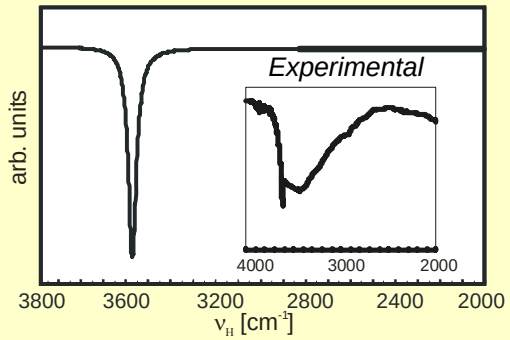
Xonotlite

$Ca_6Si_6O_{17}(OH)_2$

Ideal structure from X-ray studies:



Calculated IR spectra



CPMD, BLYP, MT-PP, 80 Ry

Experimental Observations

NMR:

- Presence of both Q^2, Q^3 and Q^1 sites
- Presence OH with different environment and molecular H_2O

IR and TG/DTA:

- Presence of molecular H_2O

EDS:

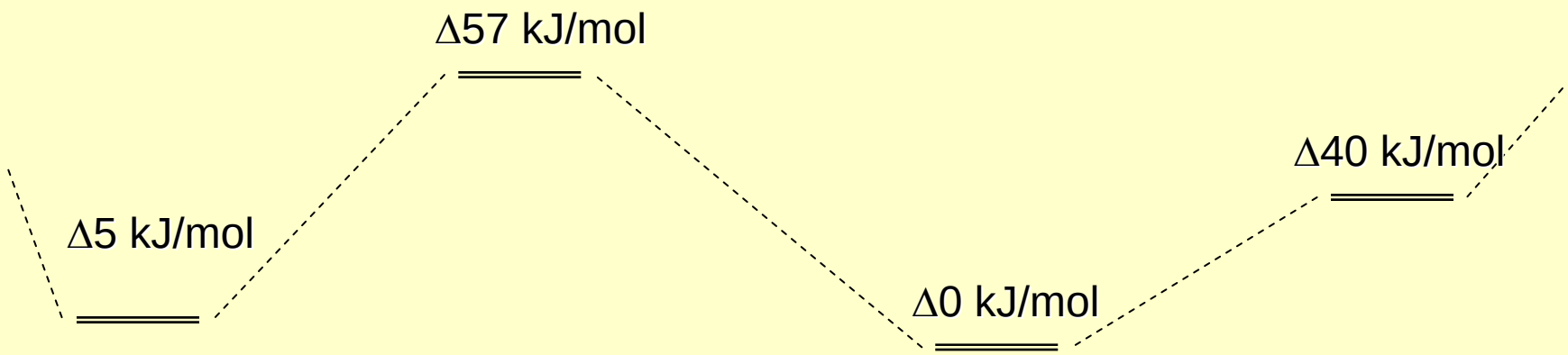
- Ca:Si > 1.0 in disordered samples

Possible defect formation mechanism

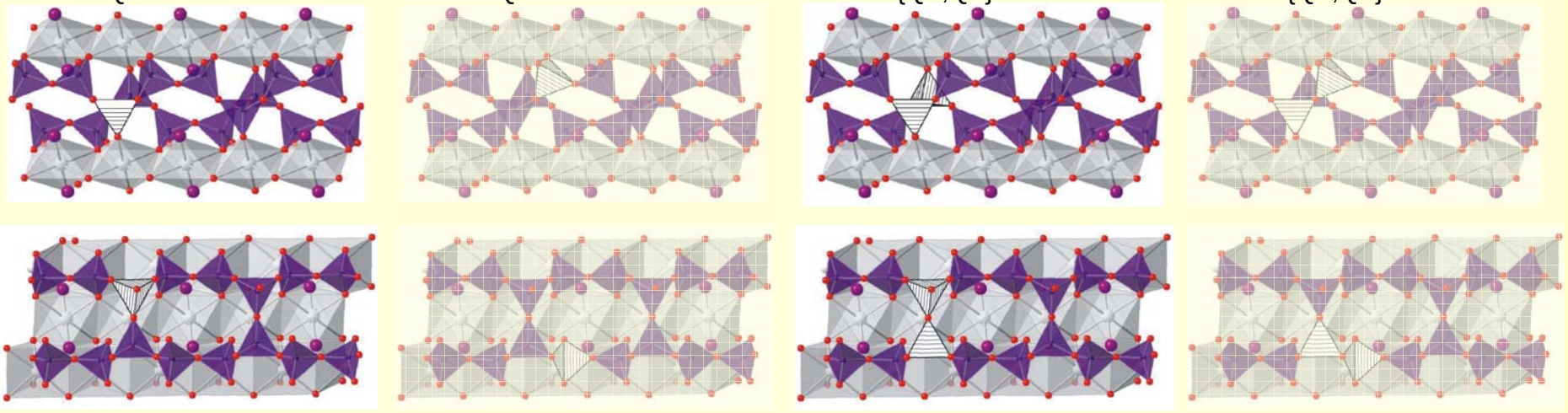
$$\{Si\}^X_{Si} + 2H_2O = \{4H\}^X_{Si} + SiO_2$$

Assumed Defect Formation Mechanism

$$\{Si\}^{X}_{Si} + 2H_2O = \{4H\}^{X}_{Si} + SiO_2$$



$\{4H\}^{x}_{Q3}$ $\{4H\}^{x}_{Q2}$ $\{8H\}^{x}_{\{Q3,Q3\}}$ $\{8H\}^{x}_{\{Q2,Q3\}}$



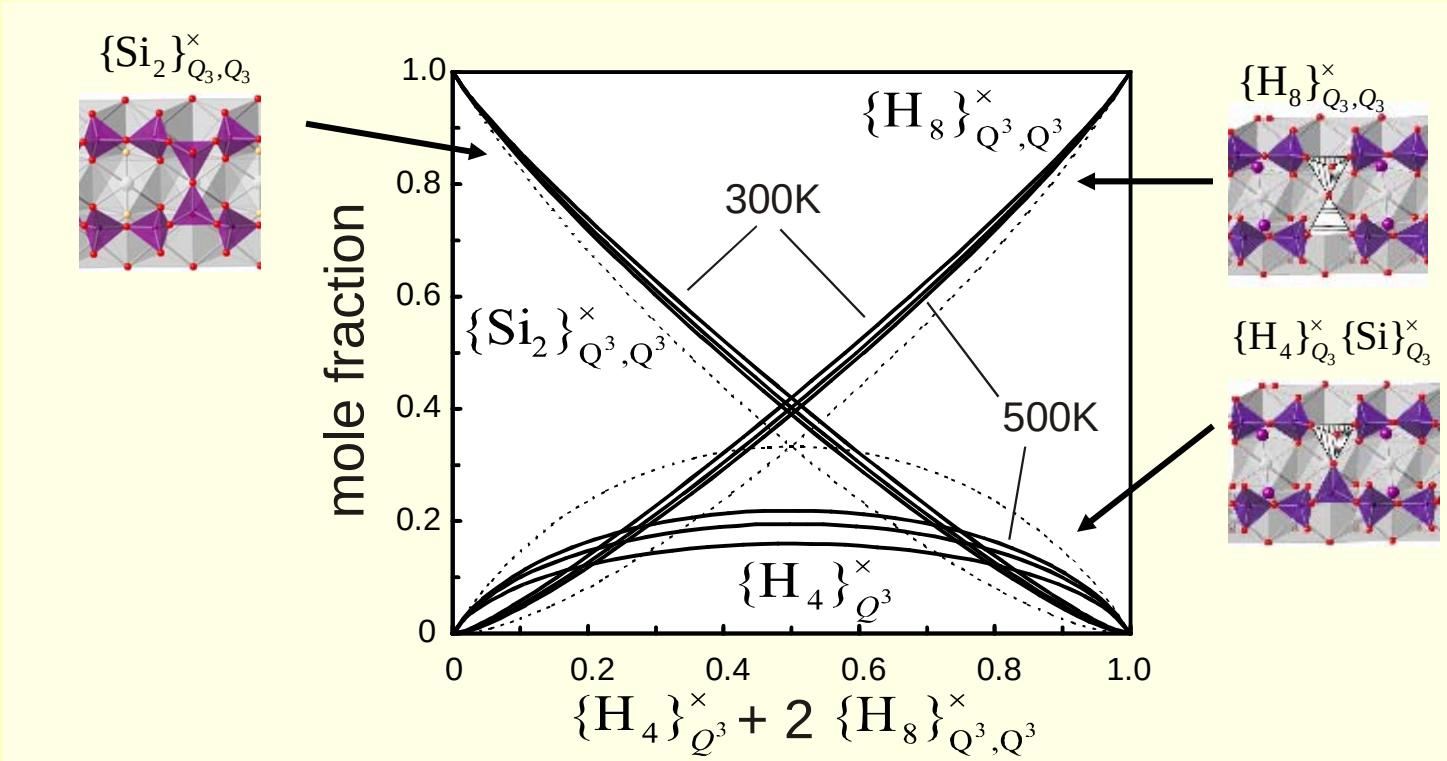
CPMD, BLYP, MT-PP, 80 Ry

Churakov & Mandaliev (2008) CCR

Thermodynamics of Defects in Xonotlite

$$2\{H_4\}^{\times}_{Q_3}\{Si\}^{\times}_{Q_3} = \{Si_2\}^{\times}_{Q_3,Q_3} + \{H_8\}^{\times}_{Q_3,Q_3}$$

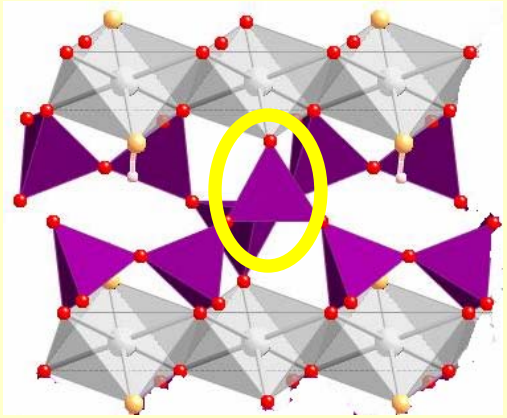
$$\frac{\left[\{Si_2\}^{\times}_{Q^3,Q^3}\right]\left[\{H_8\}^{\times}_{Q^3,Q^3}\right]}{\left[\{H_4\}^{\times}_{Q_3}\{Si\}^{\times}_{Q_3}\right]^2} = \exp\left[-\frac{\Delta E}{RT}\right]$$



Churakov & Mandaliev (2008) CCR

Structure of Defects in Xonotlite

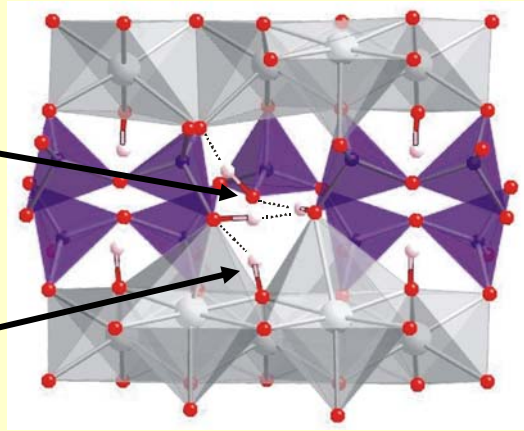
Idealized Structure



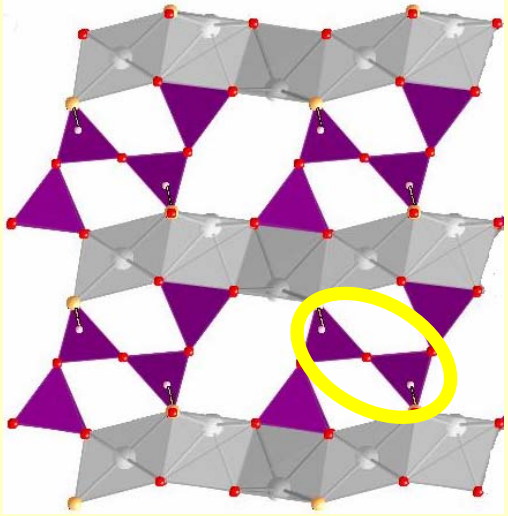
Structure with Defects

Si-OH

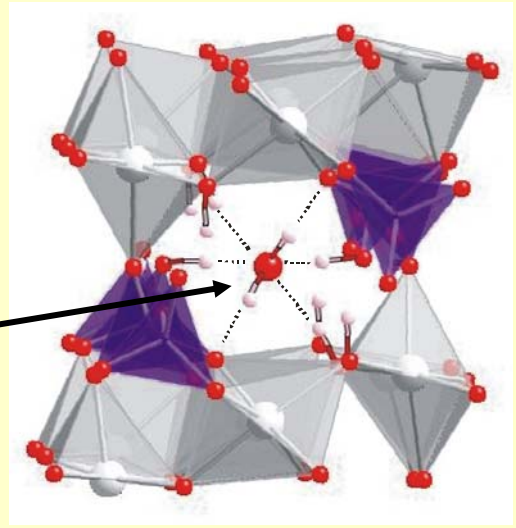
Ca-OH



$\{4H\}^{x}_{Q3}$



H_2O



$\{8H\}^{x}_{\{Q3,Q3\}}$

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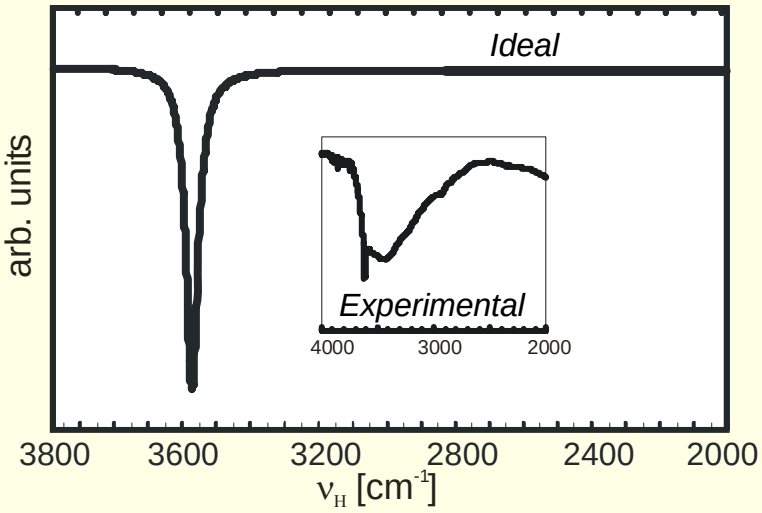
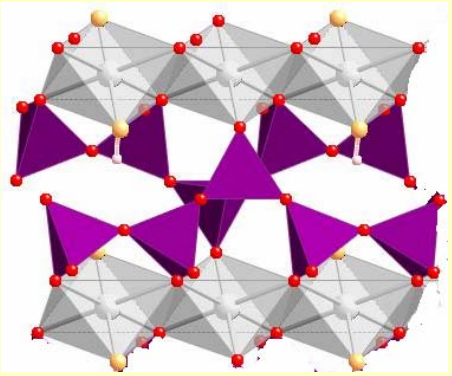
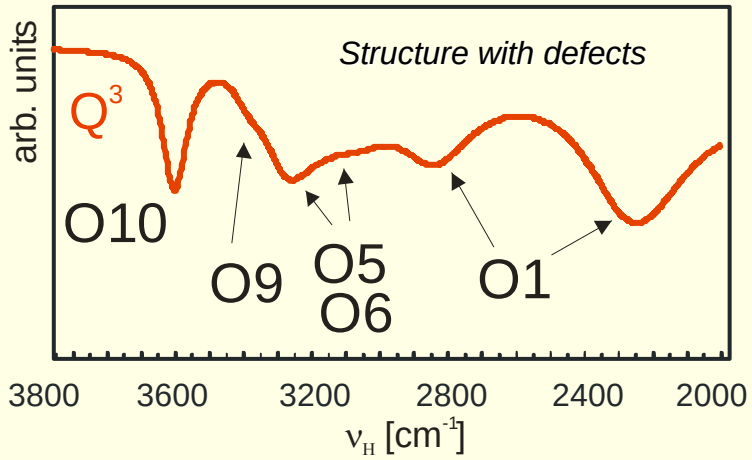
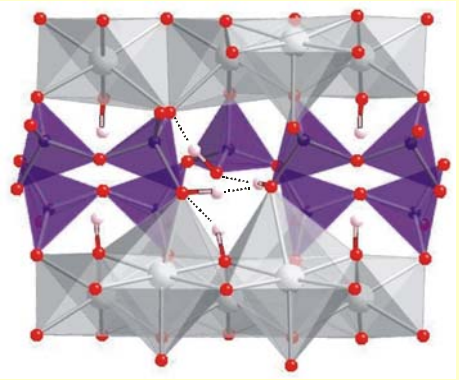
IR spectra







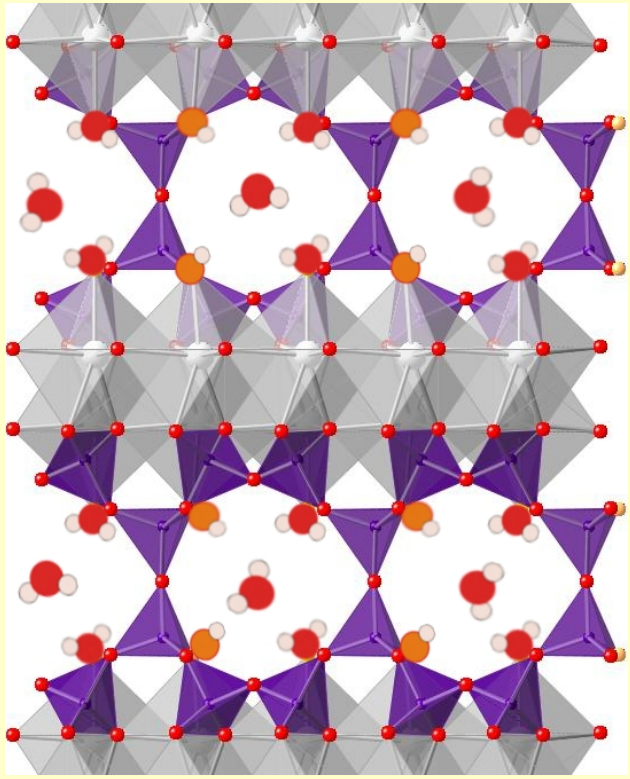


Churakov & Mandaliev (2008) CCR

Structure of 11 Å Tobermorite

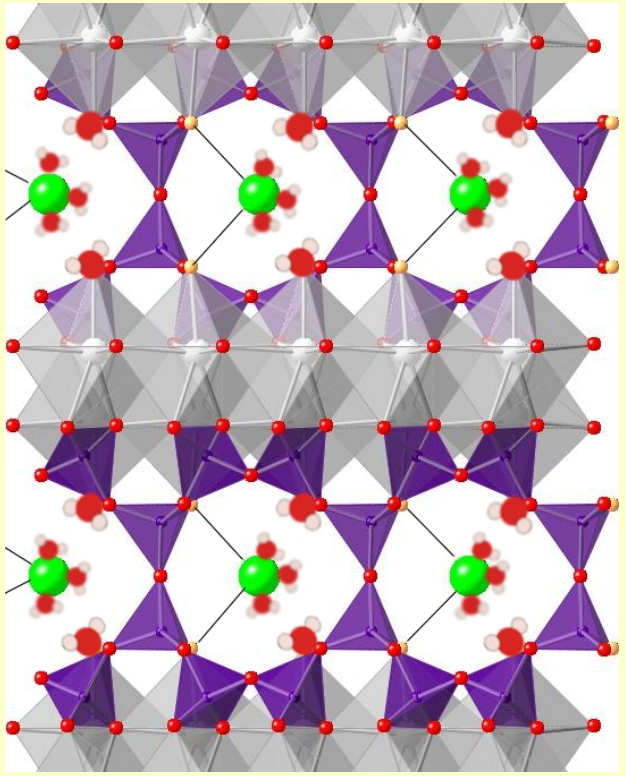
Anomalous Tobermorite

$Ca_4Si_6O_{15}(OH)_2 \times 5H_2O$



Normal Tobermorite

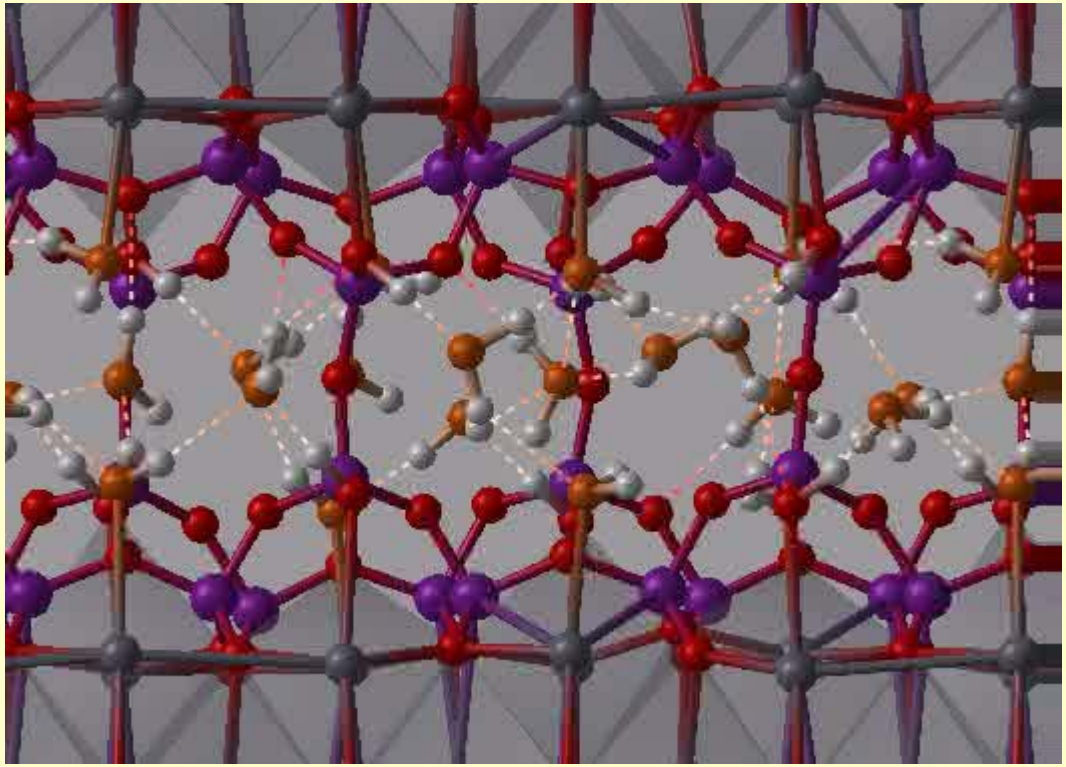
$Ca_{4.5}Si_6O_{16}(OH) \times 5H_2O$



Anomalous 11 Å Tobermorite

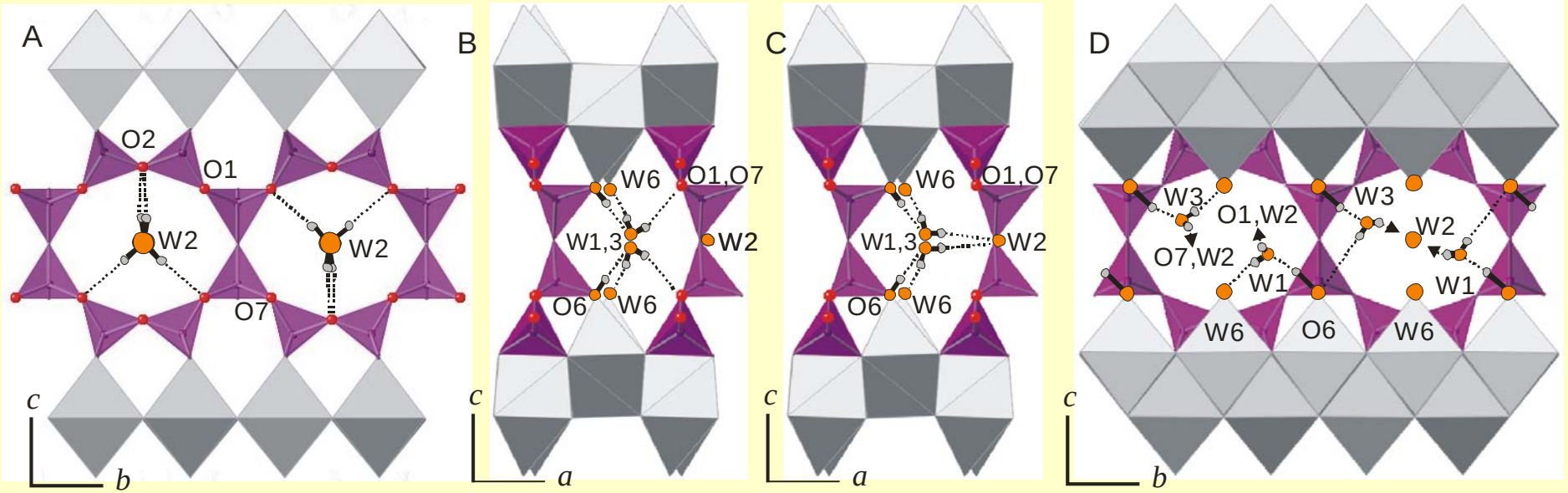
$Ca_4Si_6O_{15}(OH)_2 \times 5H_2O$

20 ps NVE ab initio MD trajectory T~ 310 K



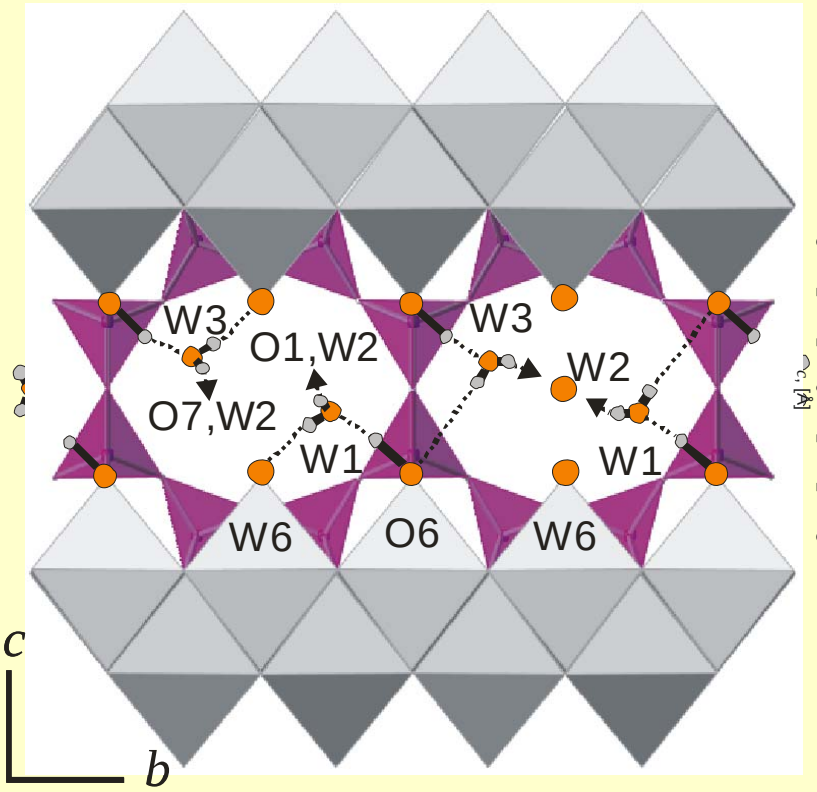
cp2k/QuickStep/GPW, PBE, DZP(Ca,Si), TZ2P(O,H)

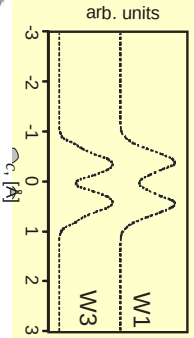
Preserential orientation of water molecules in anomalous 11 Å Tobermorite

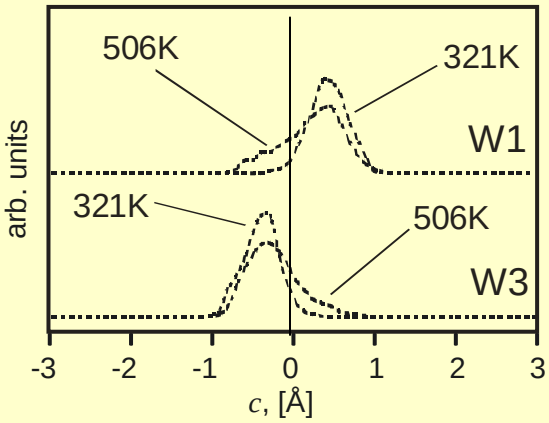


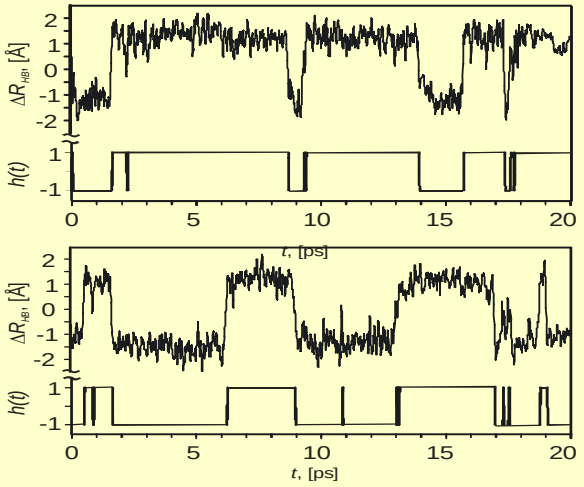
Churakov (2009) Amer. Miner.

Preferential orientation of water molecules in anomalous 11 Å Tobermorite





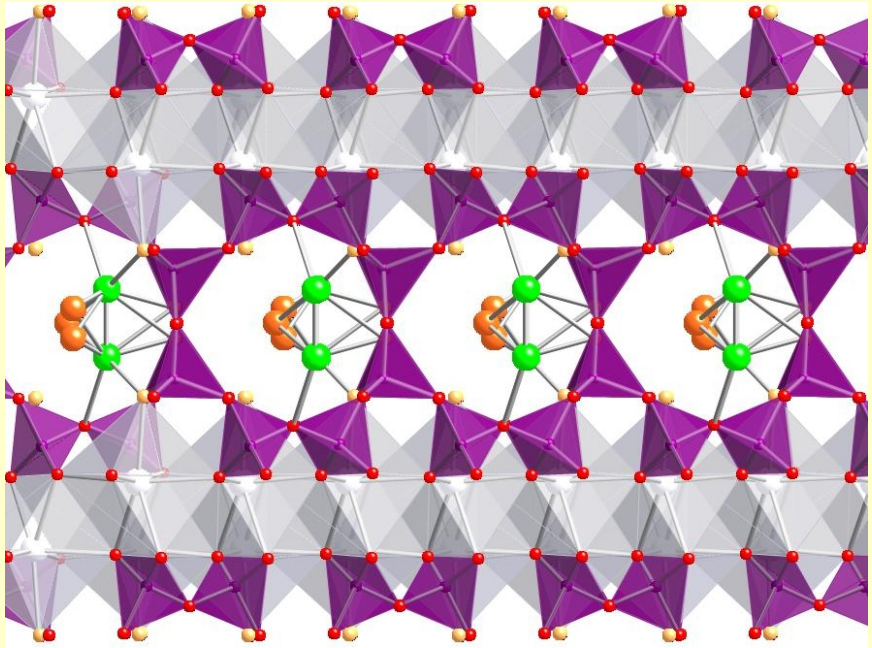




Churakov (2009) Amer. Miner.

Normal 11 Å Tobermorite

$Ca_{4.5}Si_6O_{16}(OH)\times 5H_2O$

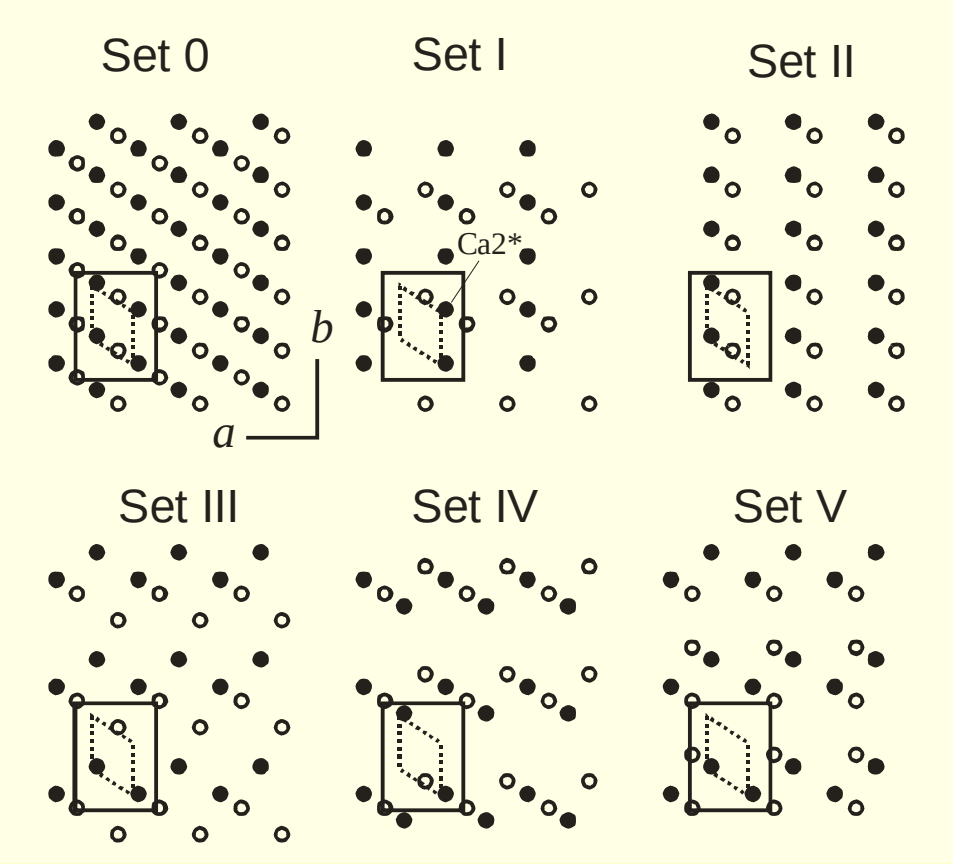


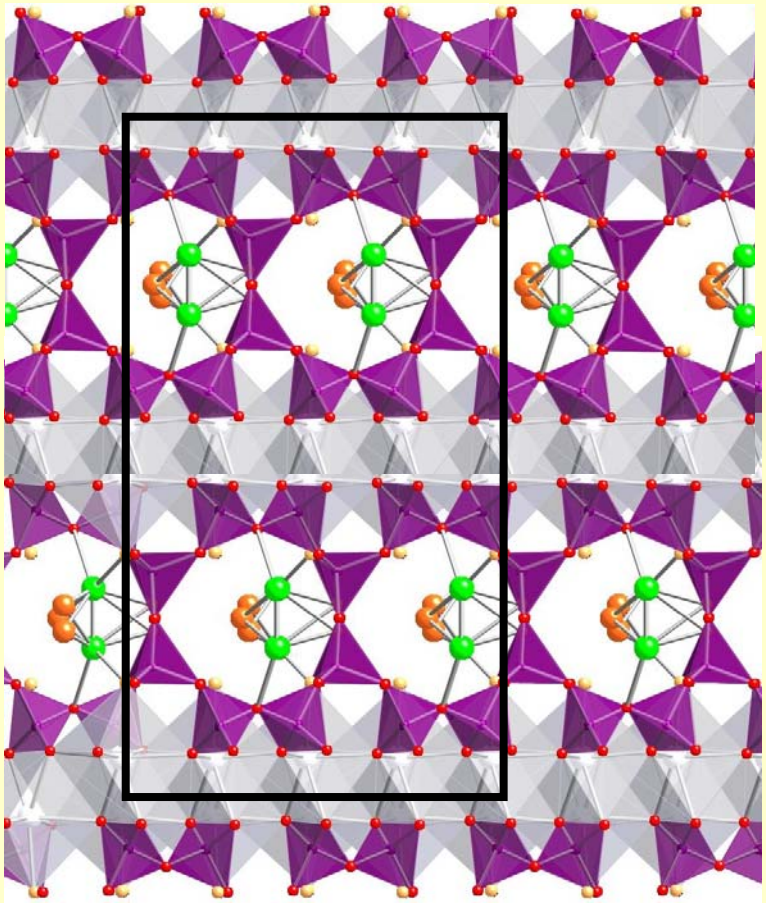
Merlino et al. (2001) X-ray diffraction

Normal 11 Å Tobermorite

$Ca_{4.5}Si_6O_{16}(OH)\times 5H_2O$

Supercell setup





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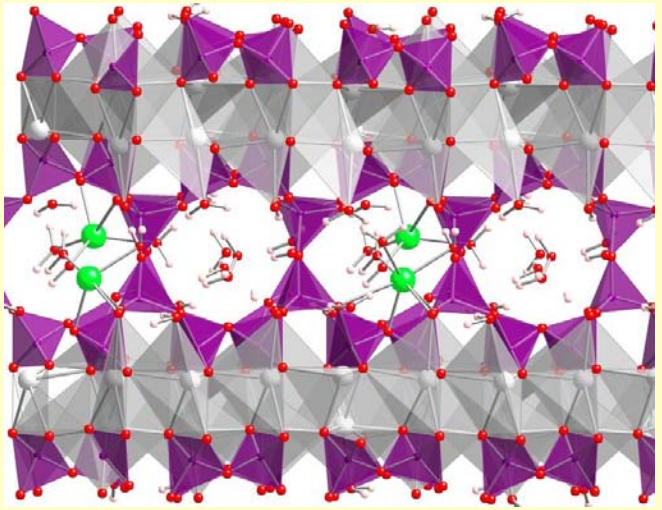
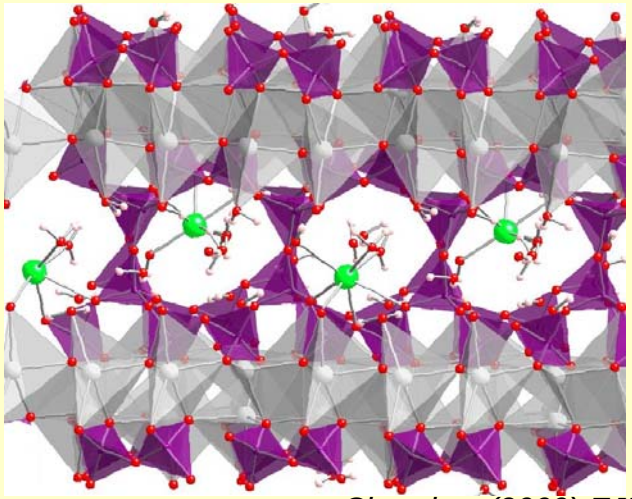
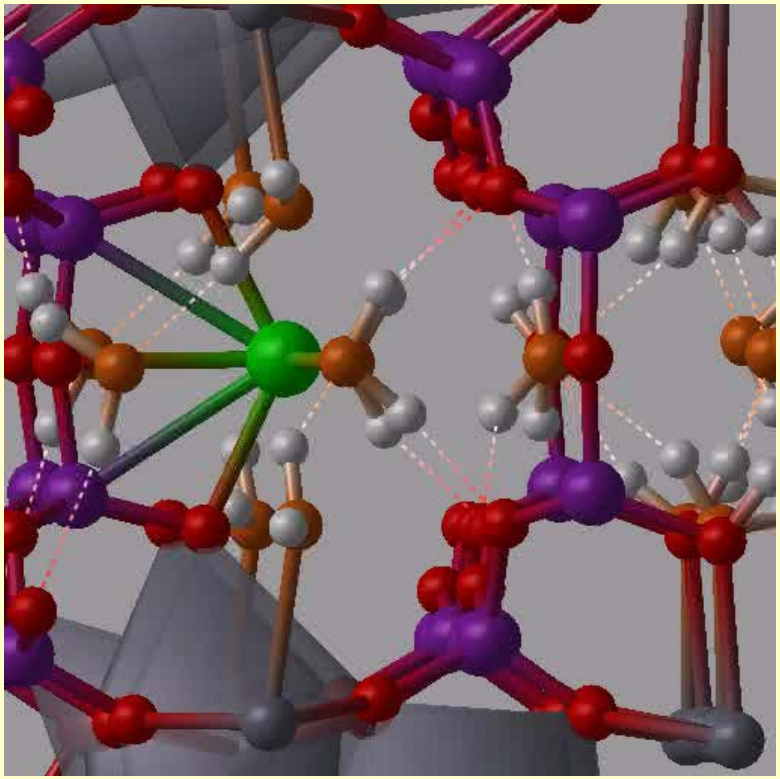
$Ca_{4.5}Si_6O_{16}(OH)\times 5H_2O$

Snapshot form ab initio MD





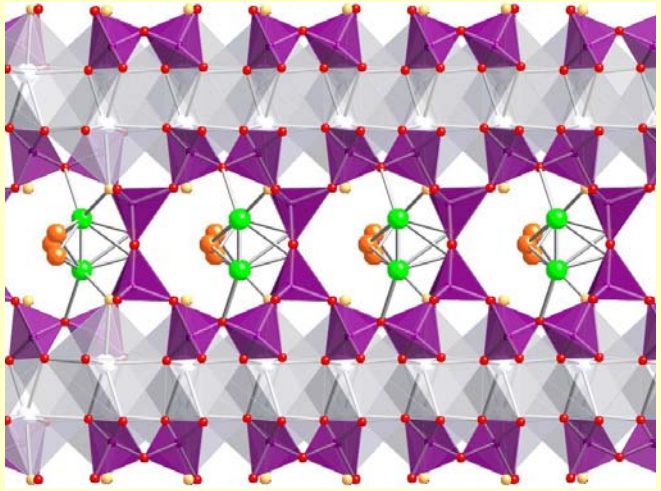


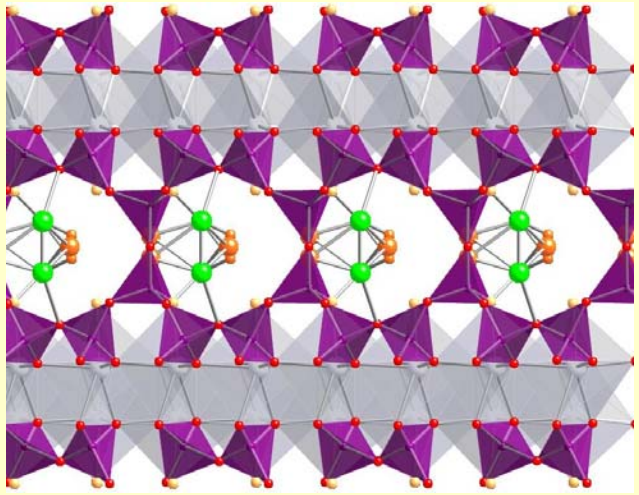
AI MD, PBE, cp2k/QuickStep/GPW, 310 K

Churakov (2009) EJM

Normal Tobermorite

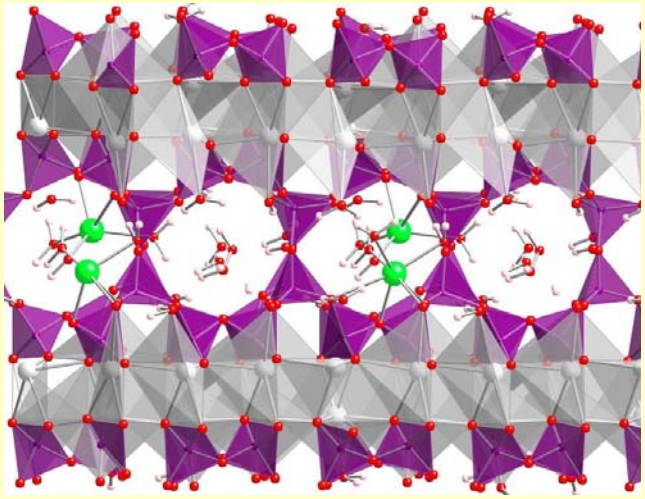
X-ray diffraction

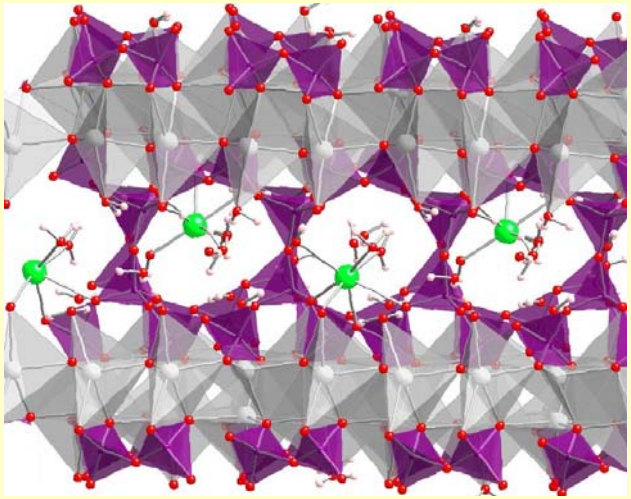




Merlino et al. (2001)

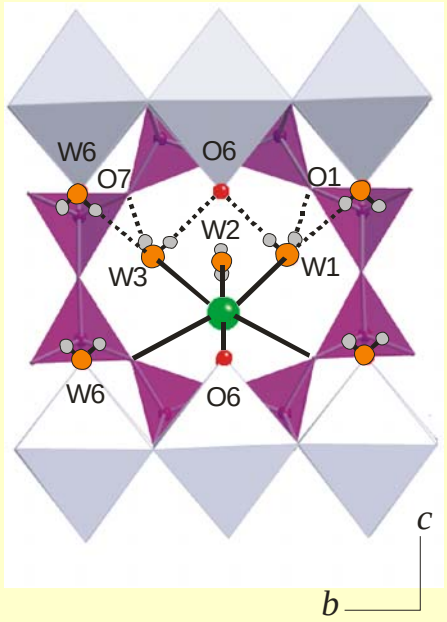
Snapshot form ab initio MD

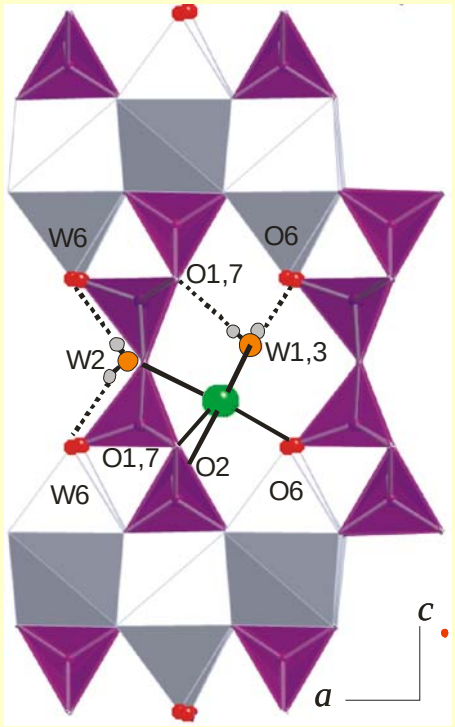




cp2k/QuickStep/GPW, PBE, 310 K

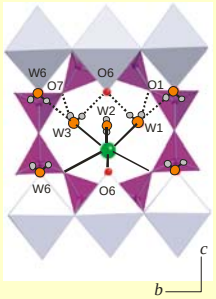
Structure of interlayer Ca ion in Normal Tobermorite

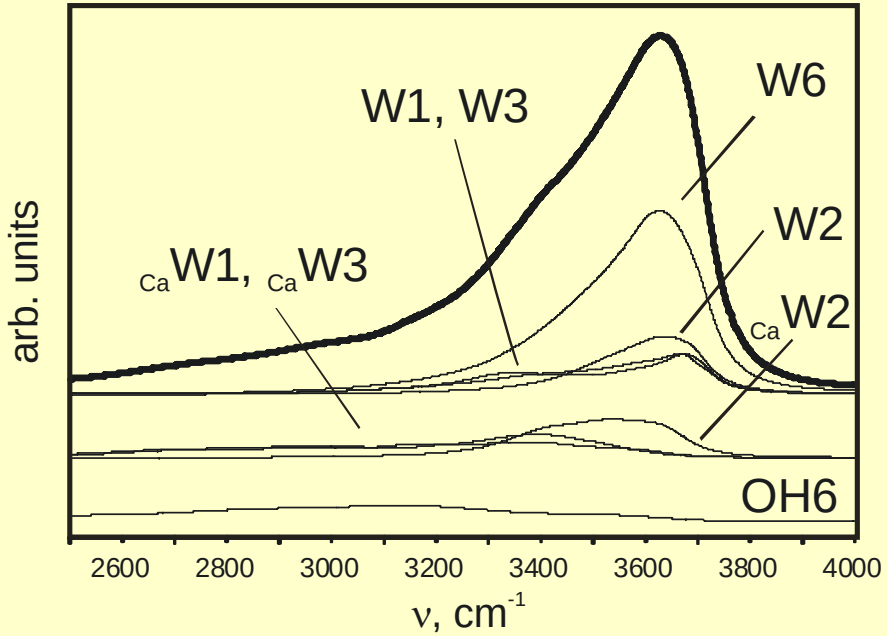


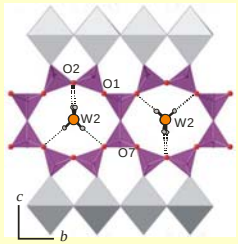


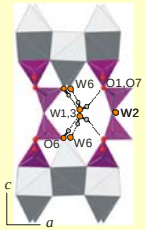
Churakov (2009) EJM

Calculated vibrational density of state
Normal 11 Å Tobermorite

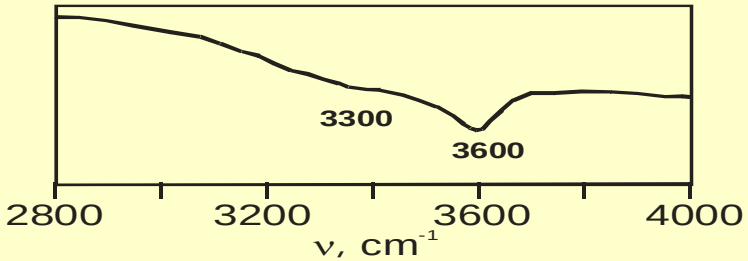








Measured IR spectra

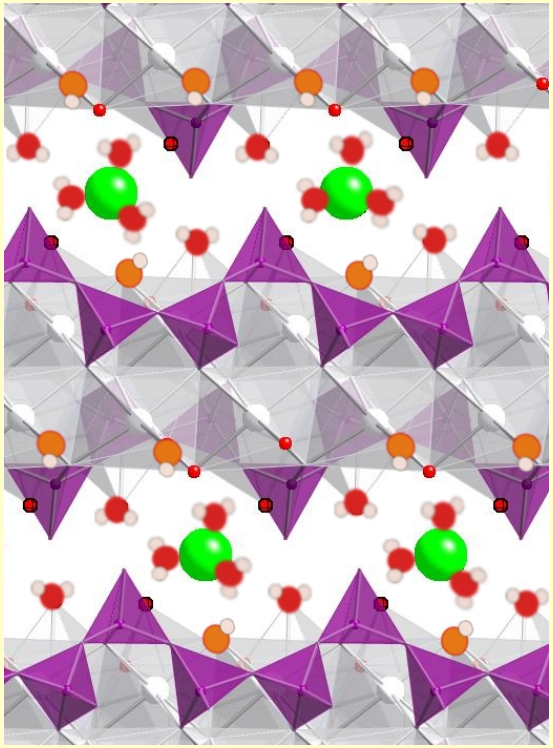


Yu et al. (1999)

Churakov (2009) EJM

Jennite

$Ca_9Si_6O_{18}(OH)_6 \times 8H_2O$



Bonaccorsi et al. (2004)

Experimental Observations

XRD:

- Presence of both Q^2 sites only
- Presence >Ca-OH linkage only

NMR:

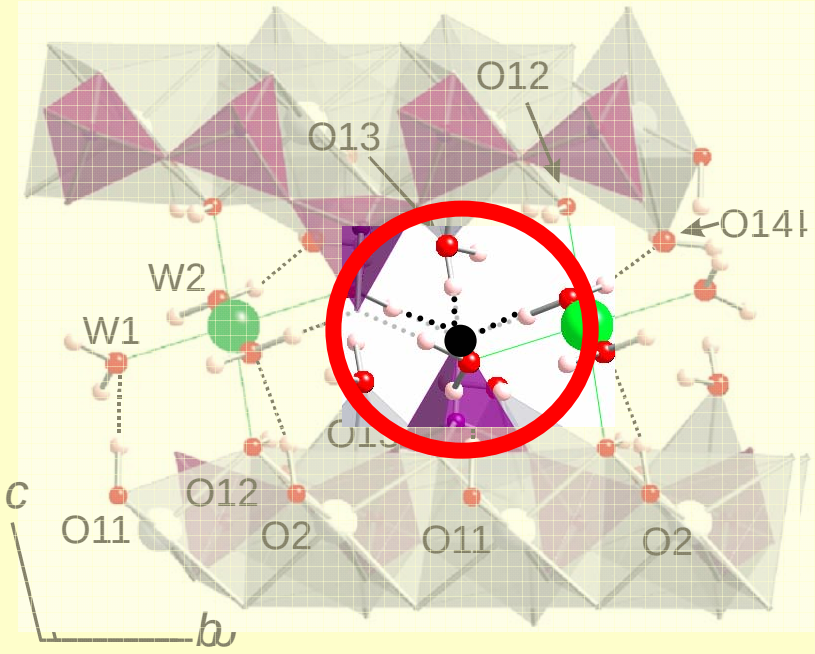
- Presence of both Q^2, and Q^1 sites
- Presence both >Si-OH and >Ca-OH linkage

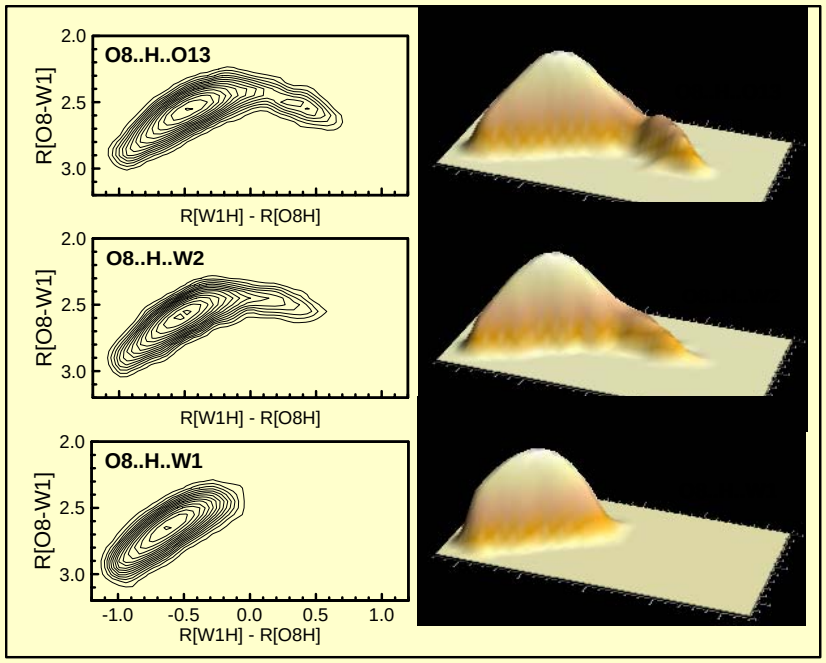
Jennite

$Ca_9Si_6O_{18}(OH)_6 \times 8H_2O$

Dynamic Proton Distribution

$$\log(\rho_H(r)) \sim -\Delta E/kT$$





ΔE = 10-15 kJ mol^{-1}

310 K MD CPMD, BLYP, MT-PP, 70 Ry

Churakov (2008) CNR

Summary
structure of C-S-H phase
Xonotlite, Tobermorite and Jennite

- Distribution of water and cations in the interlayer of tobermorite and jennite
- IR and NMR spectra are interpreted on the basis of calculation
- Preferential formations of defects in Q^3 sites in xonotlite
- Preferential stability of defects in bridging tetrahedra of CSH phases
- Dangling O-sites on the bridging Si tetrahedra of jennite are de-protonated
- The dangling de-protonated sites are likely sorption sites

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