University of St Andrews

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Investigating the hydration of inner Earth minerals through *ab initio* random structure searching and solid-state NMR spectroscopy

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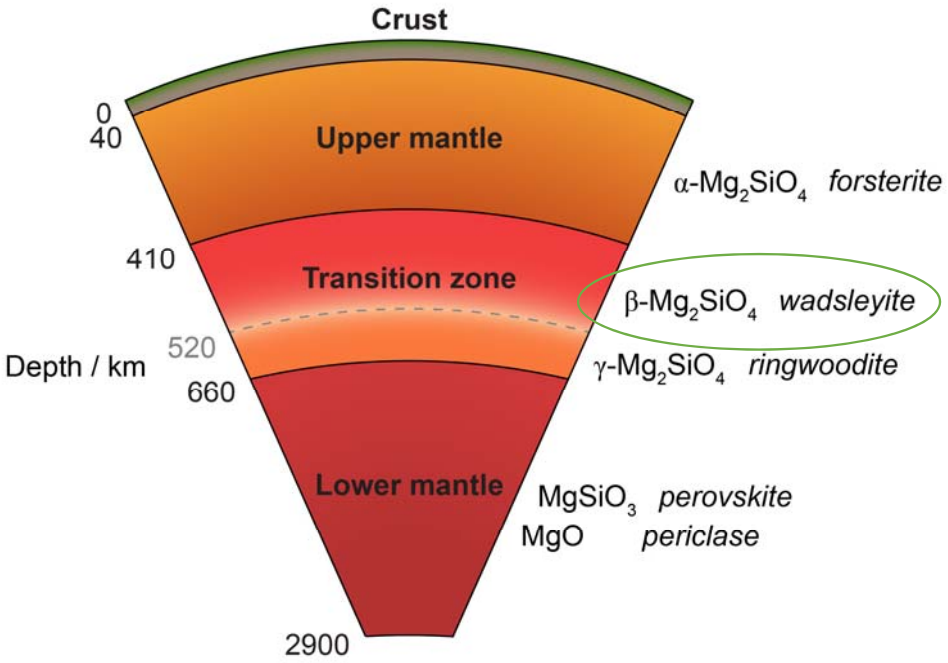
Inner Earth mineral hydration – Fe-free wadsleyite

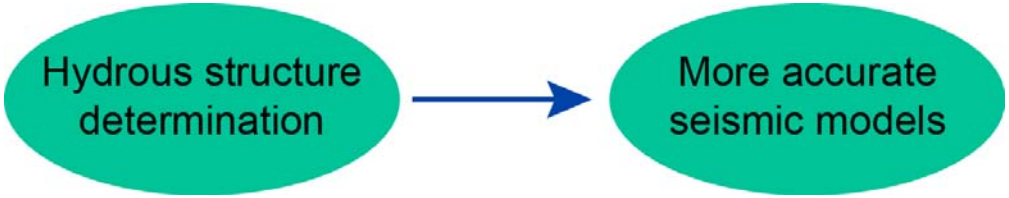
- the Earth's mantle is composed mainly of magnesium silicates known as nominally anhydrous minerals (NAMs)

- phase transitions within the mantle
  - α- to β-Mg_2SiO_4 at ~410 km
  - γ-Mg_2SiO_4 to MgO/$MgSiO_3$ at ~660 km
  - β- to γ-Mg_2SiO_4 at ~520 km

- NAMs can be hydrated at mantle temperature and pressure – the location of the Earth's "missing water"
  - Mg_2SiO_4 1 – 3 wt% H_2O
  - $MgSiO_3$ 0.01 – 0.1 wt% H_2O

- the structures of hydrous NAMs and the effects of hydration on the physical properties of the mantle are not fully understood

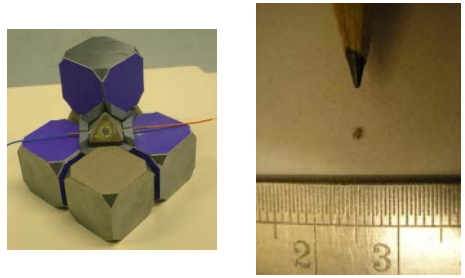


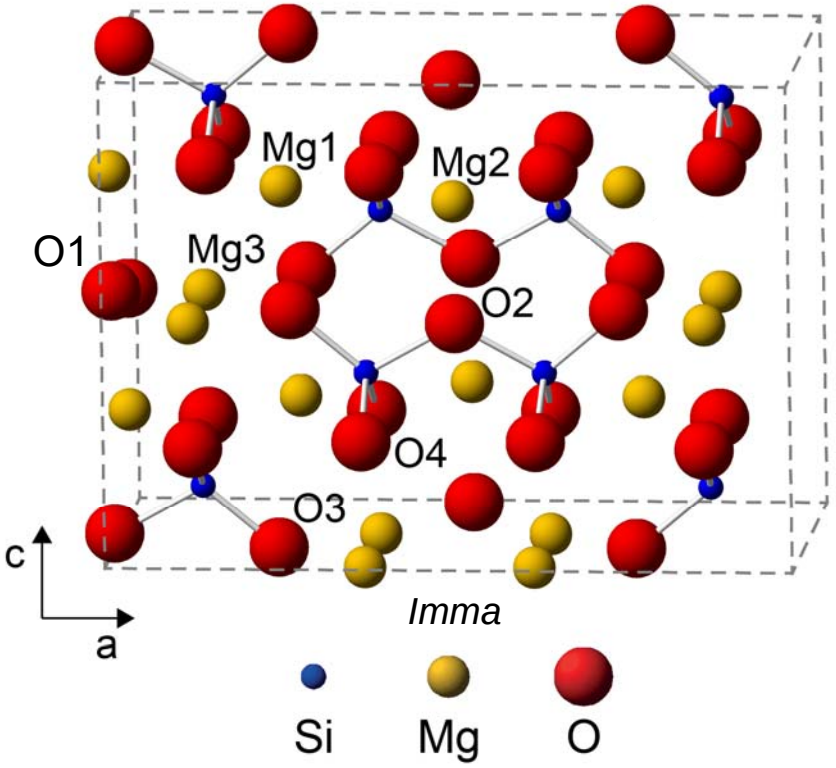


T. Katsura *et al.*, *J. Geophys. Res.*, 1989, **94**, 15663.

Wadsleyite

- 16 Mg^{2+}, 4 $[Si_2O_7]^{6-}$ (pyrosilicate), 4 O^{2-}
- 3 Mg sites, 4 O sites, 1 Si site
- synthesis: 14-15 GPa, 1100-1200 °C, 1-20 mg
- suggested mechanism is loss of Mg^{2+} charge balanced by 2 H^+ giving net hydration
- 1 Mg^{2+} / 2 H^+ = semi-hydrous (1.6 wt% H_2O)
- 2 Mg^{2+} / 4 H^+ = hydrous (3.3 wt% H_2O)
- tentative literature consensus: Mg3 vacancies
- no consensus: location of hydrogen

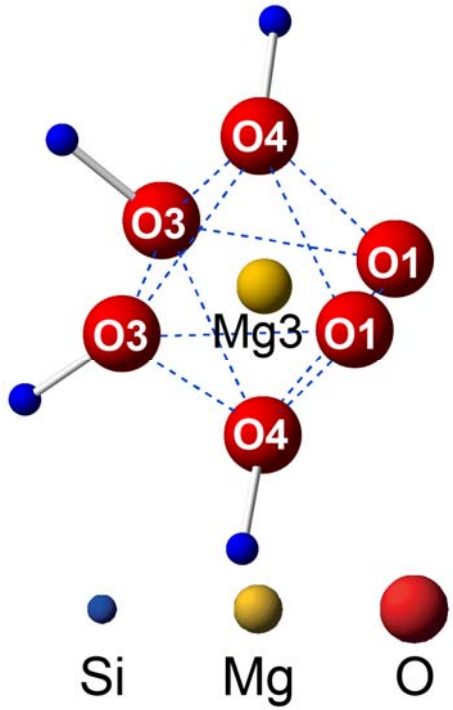




R. Moran, *et al.*, *Phys. Chem. Chem. Phys.*, 2016, **18**, 10173.

Hydrated wadsleyite – diffraction

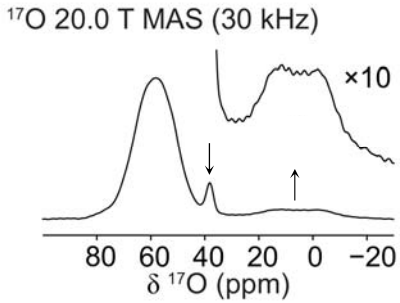
- H location challenging for diffraction
- hydration introduces disordered cation vacancies
- from neutron diffraction (on deuterated sample):
  - Mg3 88 % occupancy (Mg1 99 %; Mg2 100 %)
  - H^+ bound to O1, H-bonding to O4 (O1−H···O4)
  - “We were unable to find evidence of protonation of O2, O3, and O4... Further study is necessary to investigate whether there are the other sites of hydrogen or not.”
- diffraction suggests silanol OH groups *are not* present

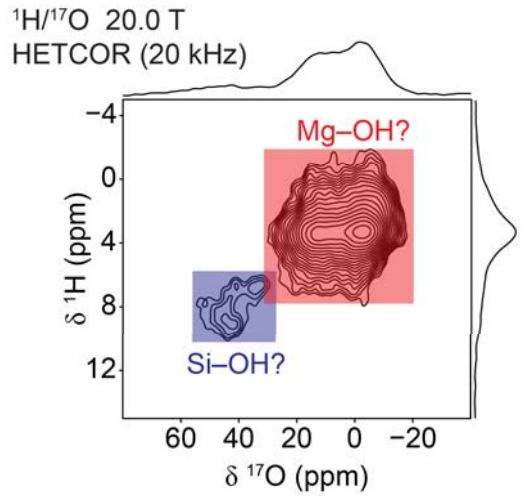


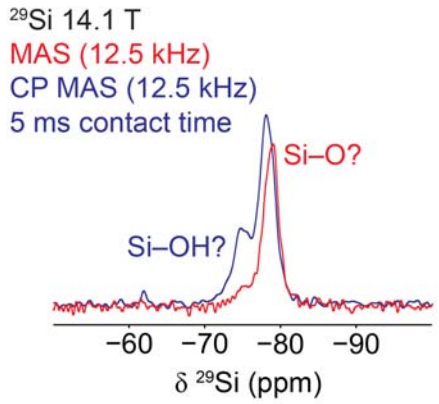
A. Sano-Furukawa *et al.*, *Phys. Earth Planet. Inter.*, 2011, **189**, 56.

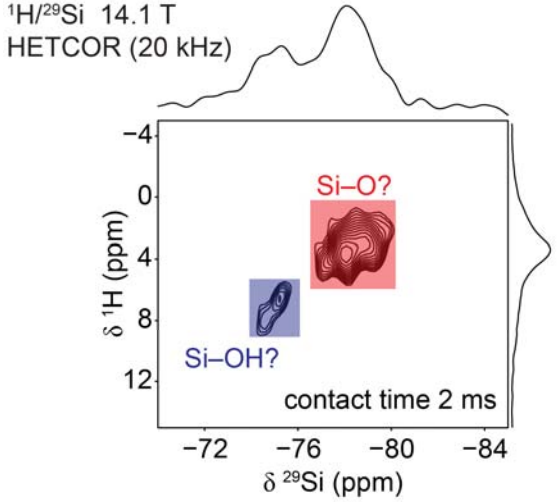
Hydrated wadsleyite – solid-state NMR spectroscopy (~3.3 wt% H_2O)

- not reliant on long-range order
- gives site- and element-specific information
- ^{17}O NMR
  - confirms hydration
  - two distinguishable **^{17}O**–^{1}H environments
- ^{29}Si NMR
  - two types of ^{29}Si environment – one in close proximity to ^{1}H
- NMR suggests silanols *are* present



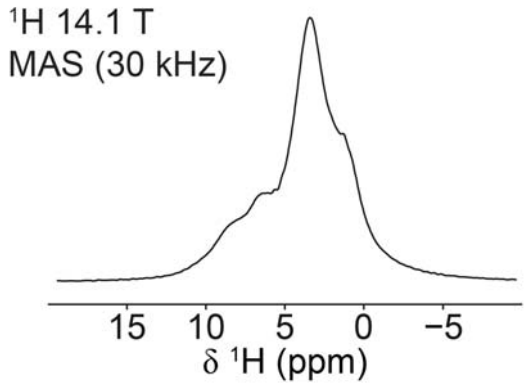




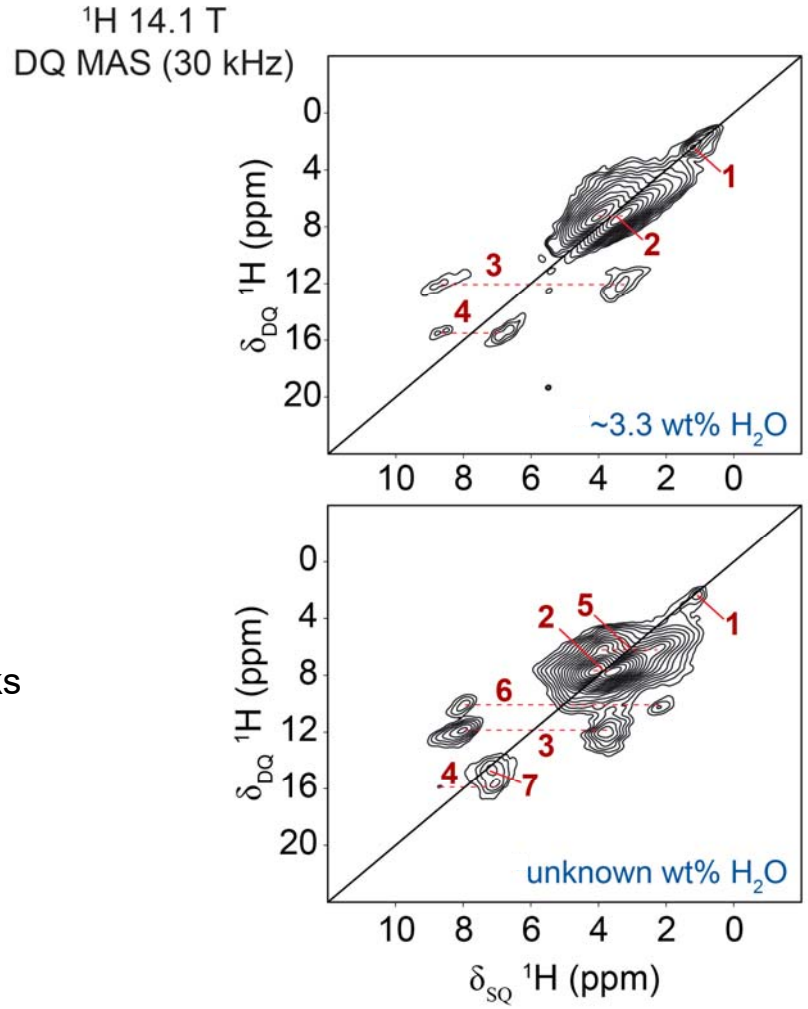


J. M. Griffin *et al.*, *Chem. Sci.*, 2013, **4**, 1523.

Hydrated wadsleyite – solid-state NMR spectroscopy (~3.3 wt% H_2O)



^{1}H 1-D spectrum shows 4-6 peaks

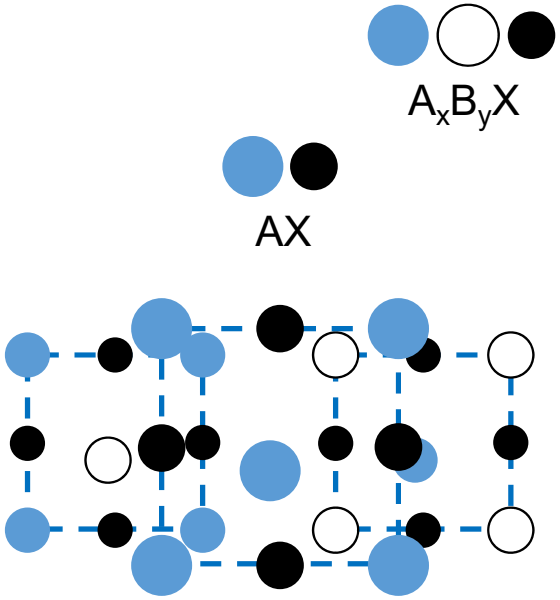


Correlation	δ ^{1}Ha (ppm)	δ ^{1}Hb (ppm)
1	1.1	1.1
2	3.4	3.4
3	3.4	8.6
4	6.7	8.6
5	2.0	3.4
6	2.0	8.6
7	6.7	6.7

- ^{1}H at 1.1 ppm does not couple to different ^{1}H – potential impurity
- (almost) all other ^{1}H species correlate – more later

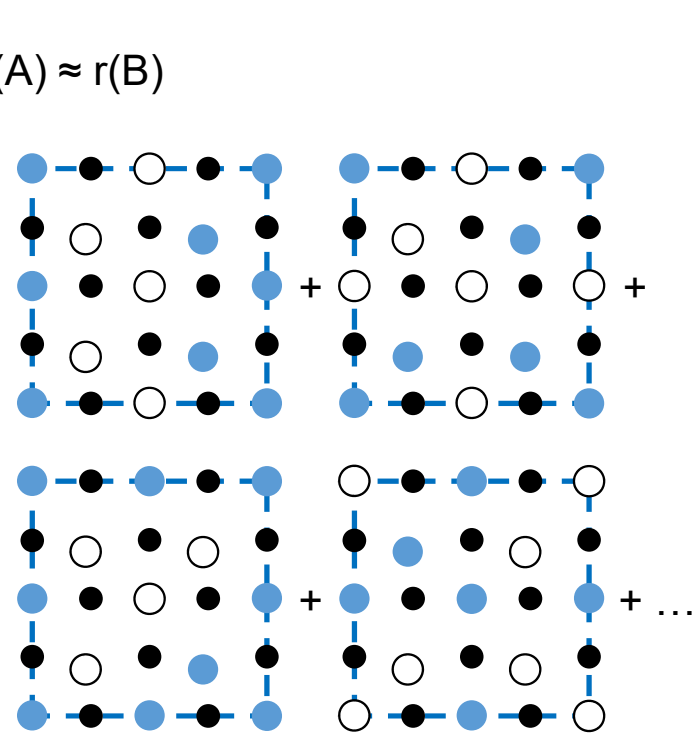
J. M. Griffin *et al.*, *Chem. Sci.*, 2013, **4**, 1523.

Modelling disorder



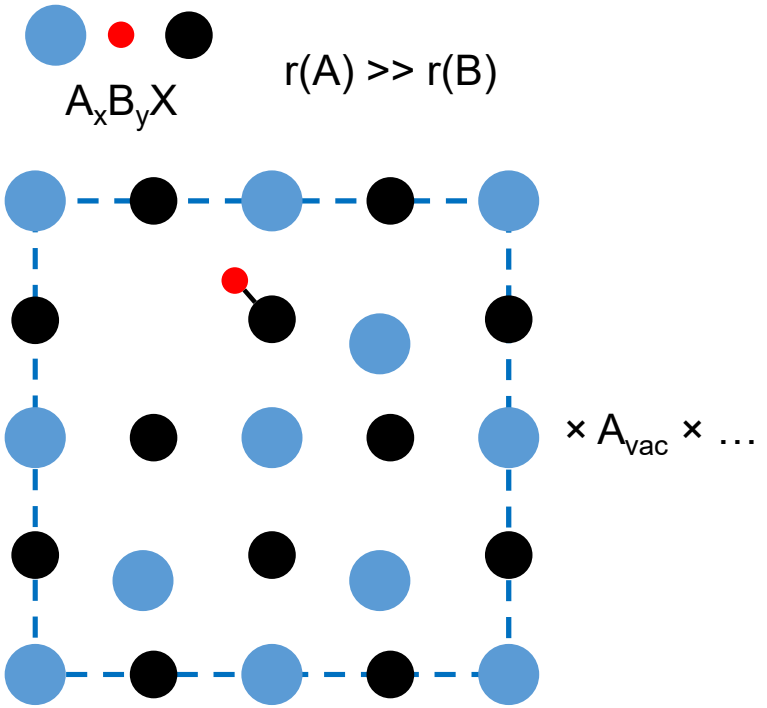
I

simple swapping of atoms
< 10 models
done manually



II

systematic swapping of atoms
10s to 100s of models
manually or automated
consider symmetry

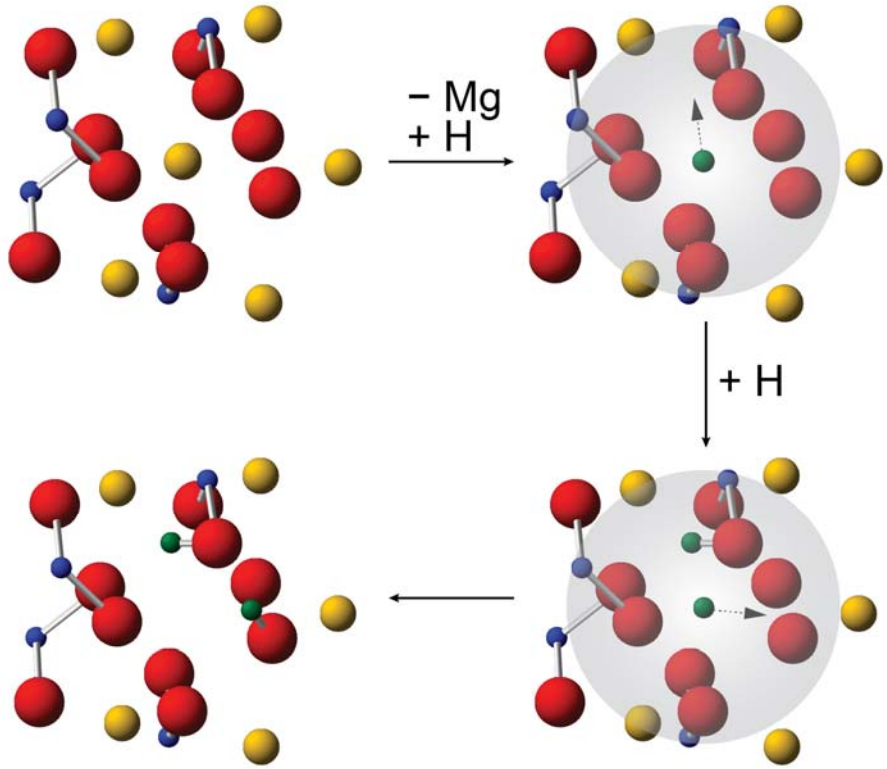


III

simple removal, complex addition
100s to 1000s of models
automated
potentially combinatorial

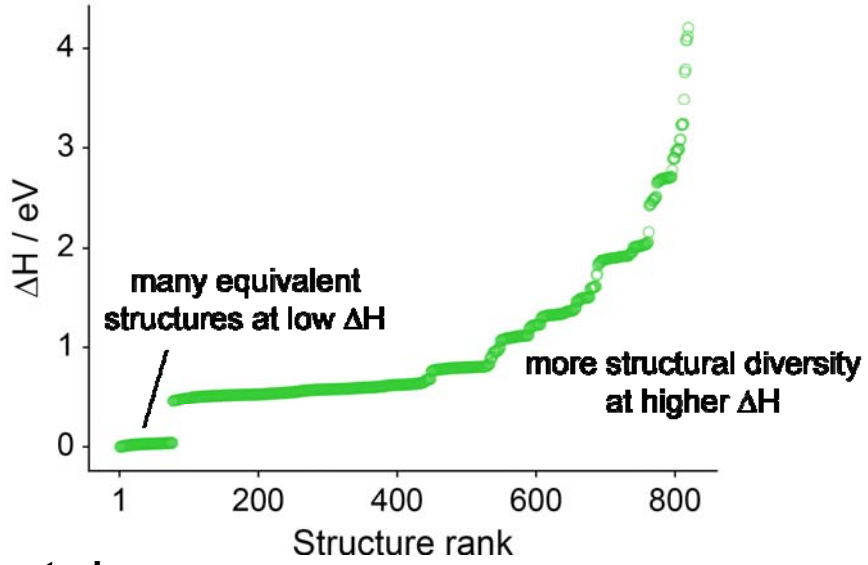
AIRSS approach to hydrous Mg_2SiO_4

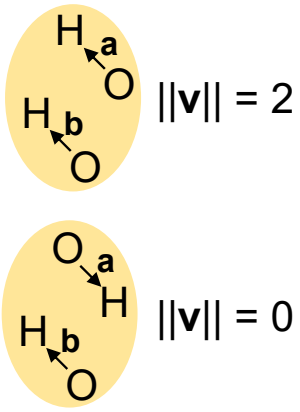
- for each Mg removed, place 2 H
- but H^+ too small to occupy octahedral sites
- use *ab initio* Random Structure Searching (AIRSS) to randomise H positions within a 3 Å radius of Mg vacancy
- repeat ~100-1000 times
- geometry optimise in CASTEP
  - PBE
  - E_{cut} = 25 Ry
  - k-point spacing = 0.1 2π/Å
  - fixed unit cell
  - ~1 structure per node hour

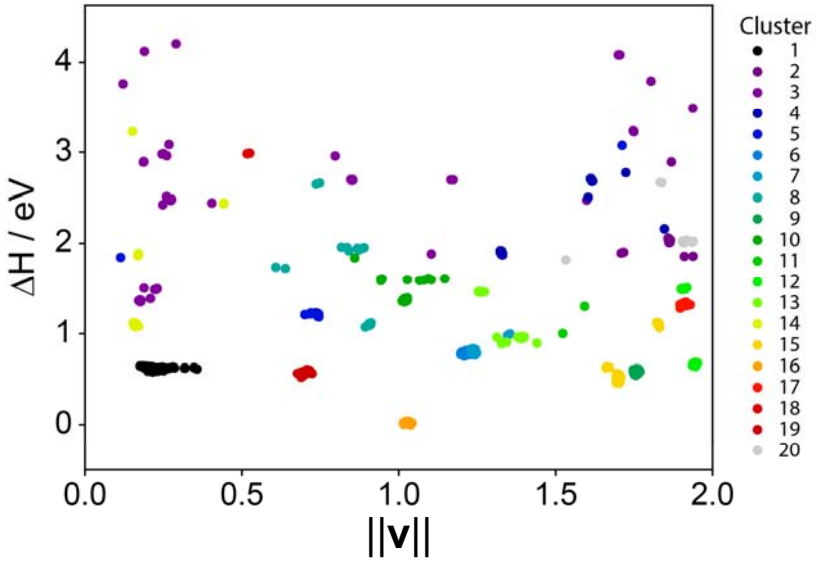


C. J. Pickard and R. J. Needs, *Phys. Rev. Lett.*, 2006, **97**, 045504.
C. J. Pickard and R. J. Needs, *J. Phys.: Condens. Matter*, 2011, **23**, 053201.
R. Moran, *et al.*, *Phys. Chem. Chem. Phys.*, 2016, **18**, 10173.

k-means clustering through Soprano







Clustering

- in-house Python scripts used the Soprano library
- “genes” were built for enthalpy, vac type, hydroxyl O type, combined OH orientation vector, vac···vac dist
- converge against number of clusters, k
- O type gene weighted such that each cluster contained structures with a single O type

Selection

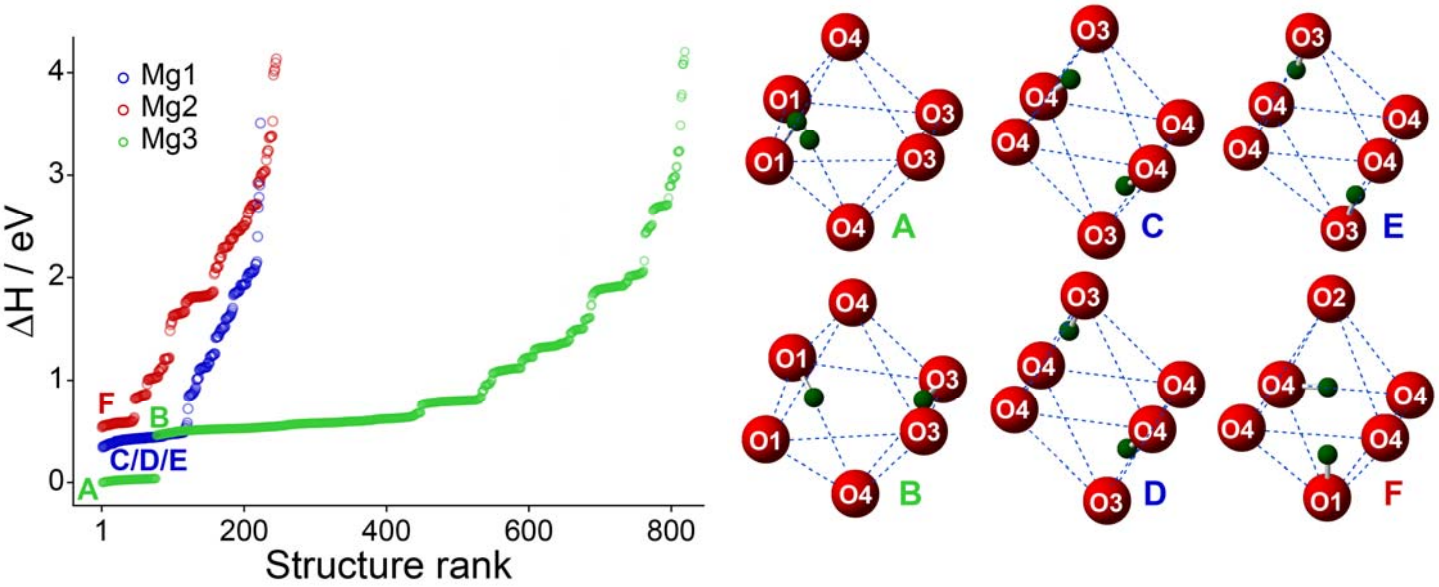
- only consider clusters with a mean $\Delta H < \Delta H_{cut}$ (here, 2 eV)
- always select the most stable structure
- for narrow clusters, select the median ΔH structure
- for broad clusters, include structures at the 5th and 95th percentiles

S. Sturniolo, *Soprano*, https://ccpforge.cse.rl.ac.uk/gf/project/soprano/, 2017

Semi-hydrated wadsleyite

1287 structures with one Mg1, Mg2 or Mg3 vacancy

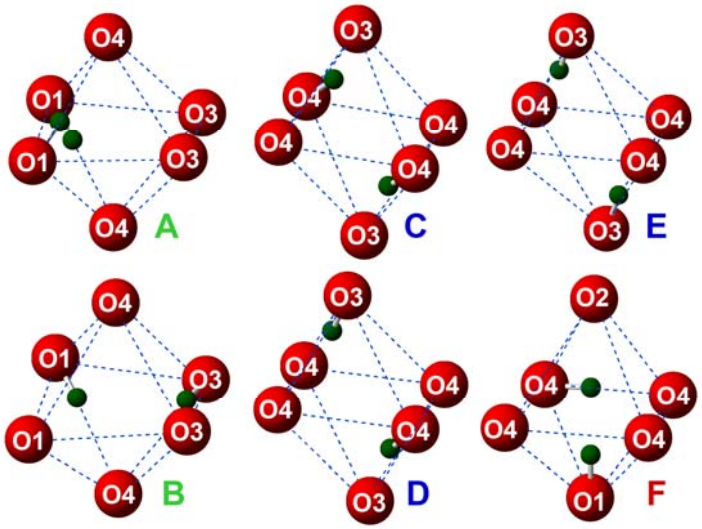
88 structures following k-means clustering



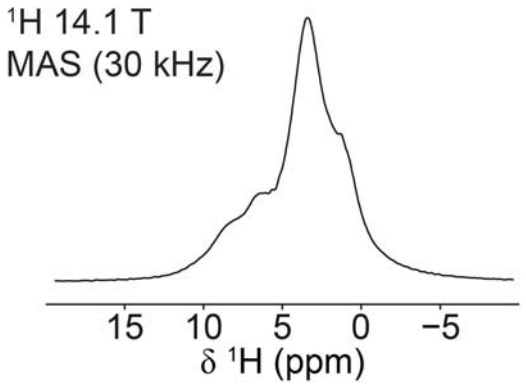
- subset of 88 structures “fully” optimised with PBE, E_{cut} = 60 Ry, k-point spacing = 0.04 2π/Å, TS dispersion correction and variable unit cell

- GIPAW NMR calculations at the same level

Semi-hydrated wadsleyite



Structure	ΔH / eV	^{1}H δ_{iso} (ppm)	O type
A	0.00	3.4 3.4	1 1
B	0.50	2.7 6.4	1 3
C	0.33	8.5 8.7	4 4
D	0.37	10.8 8.9	3 4
E	0.37	10.0 10.0	3 3
F	0.56	2.5 7.7	1 4



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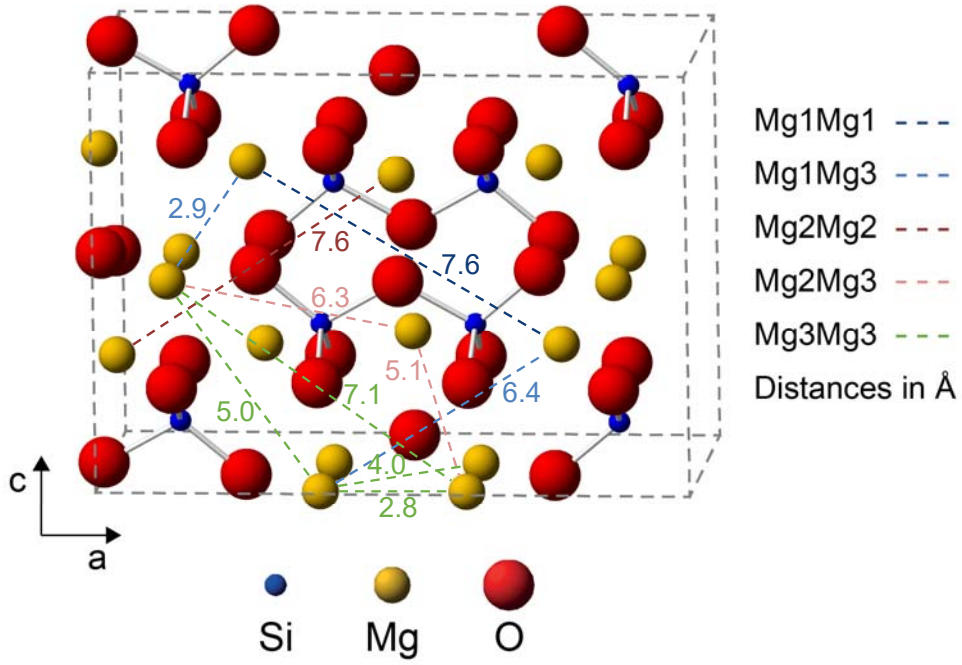
4	6.7	8.6
5	2.0	3.4
6	2.0	8.6
7	6.7	6.7

- shifts of O1−^{1}H species in ground-state structure, A, align with the most intense experimental peak
- Include O1–H hydroxyls and O3−H and O4−H silanol groups, allowing tentative assignment of O1−^{1}H, O3−^{1}H and O4−^{1}H to peaks at 3.4, 6.7 and 8.6 ppm respectively
- however:
  - require high ΔH proton arrangements and disfavoured Mg2 vacancies to explain the 1D spectrum
  - some O3–^{1}H shifts outside of the range seen experimentally
  - features present in 2D spectra cannot be accounted for

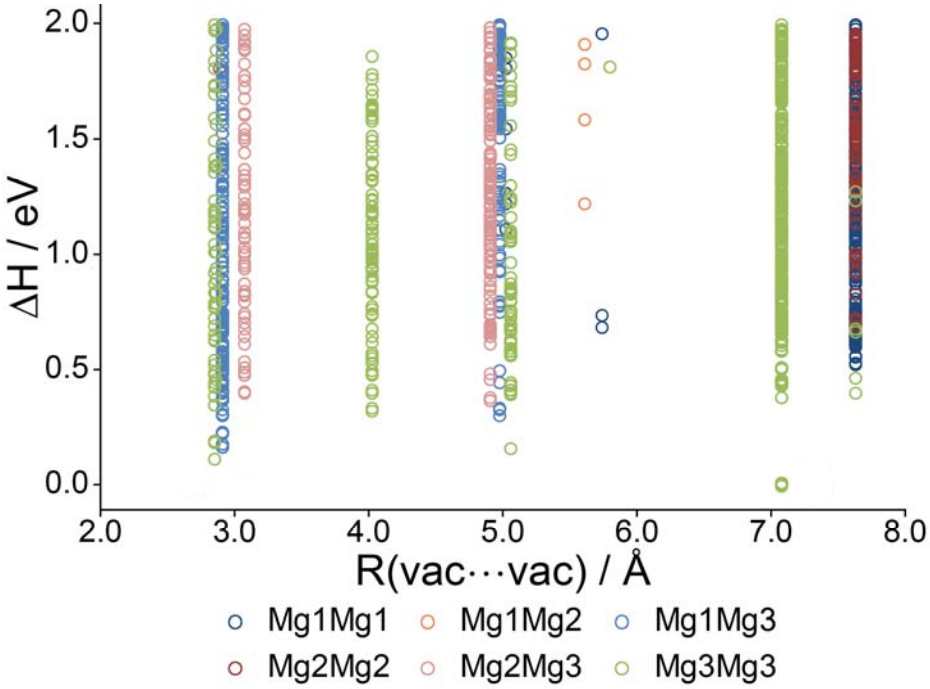
Fully-hydrated wadsleyite

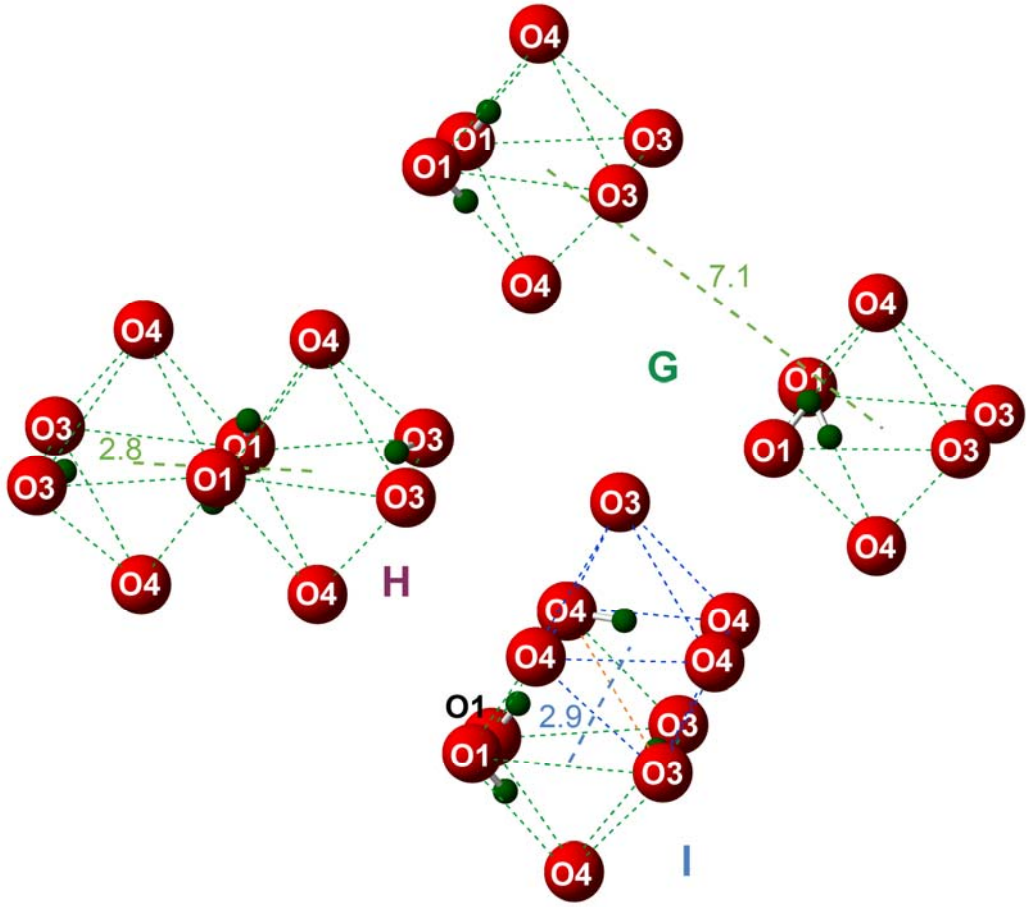


- to model full hydration need to remove two Mg atoms per unit cell
- vacancy combinations were chosen to give a range of vac···vac distances
- should provide information on the likelihood of defect clustering
- subject each vacancy combination to AIRSS-based addition proton of 4 H^+

Fully-hydrated wadsleyite

3150 structures with combinations of two Mg vacancies
198 structures following k-means clustering
showing ΔH ≤ 2.0 eV

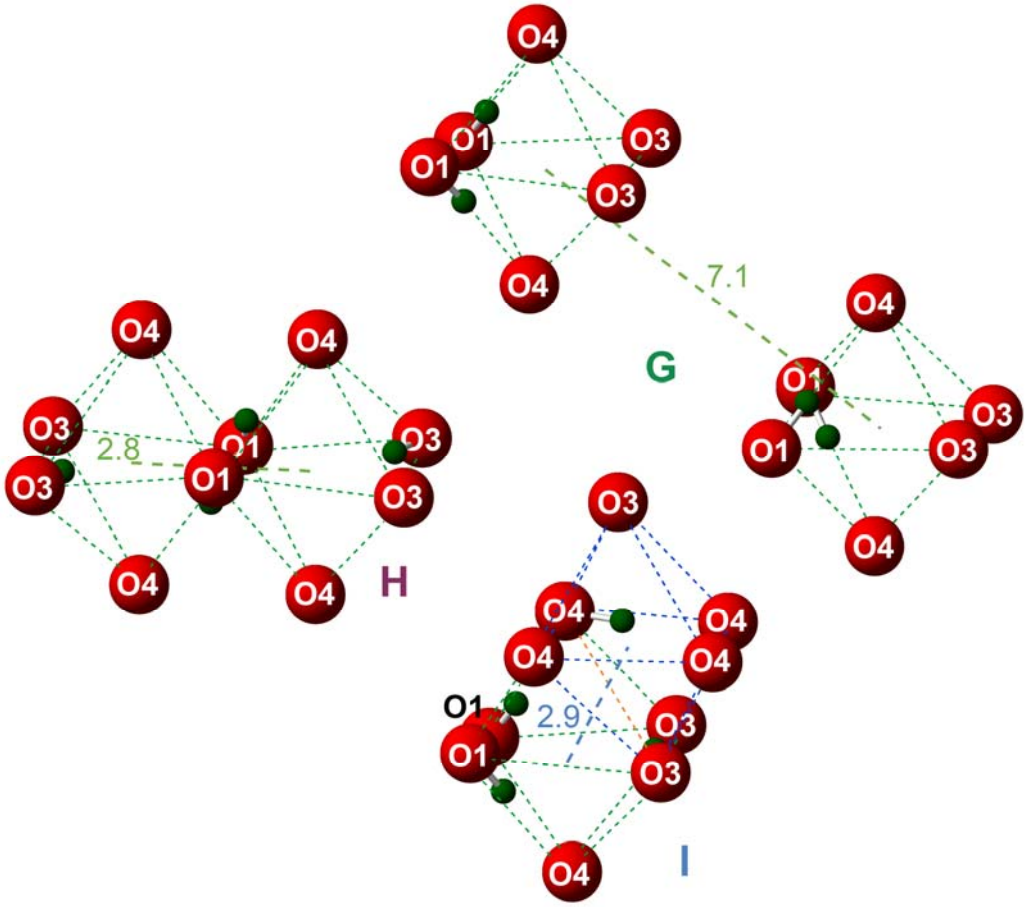




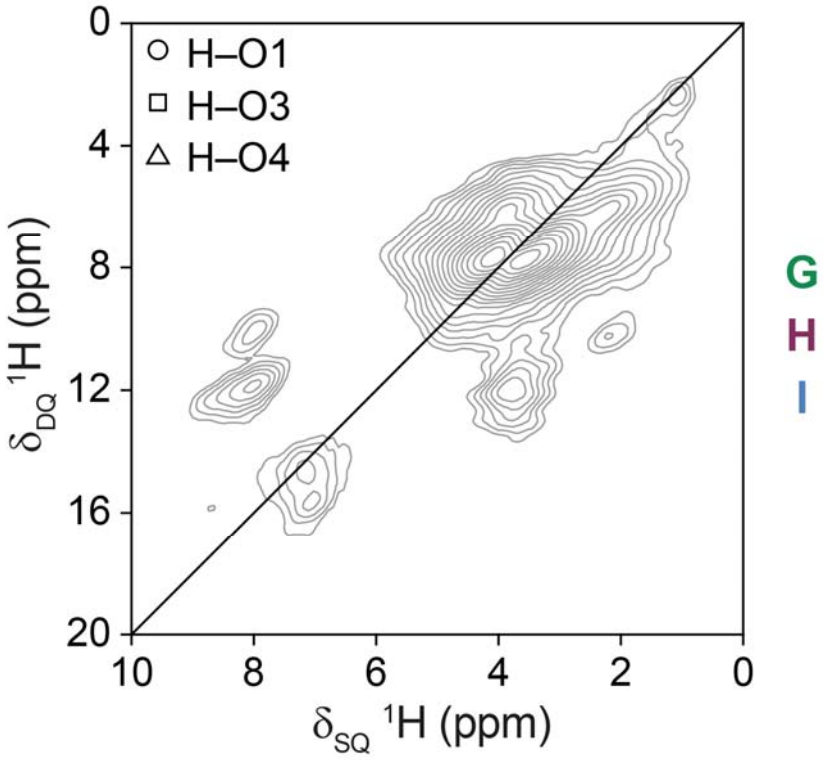
Fully-hydrated wadsleyite

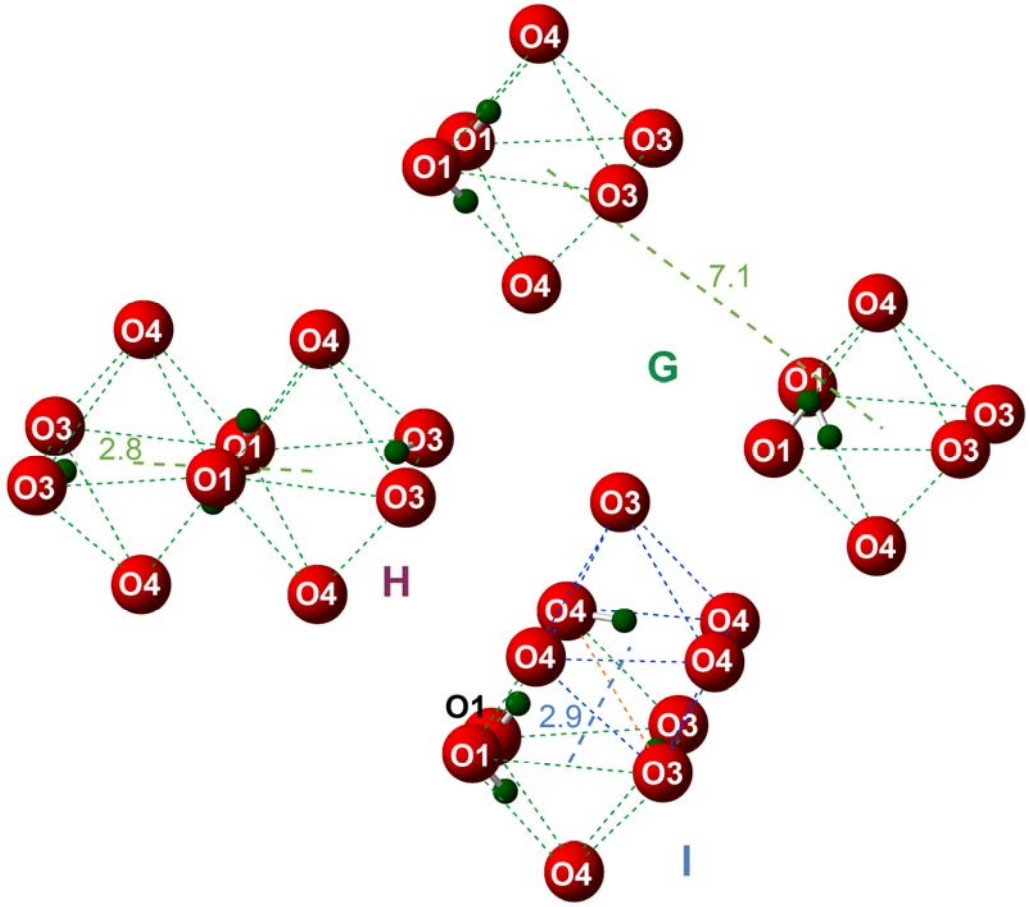
Structure	ΔH / eV	vacs	vac···vac / Å[a]	^{1}H δ_{iso} (ppm)	O type
G	0.00	Mg3 Mg3	7.1	3.3 3.5 3.5 3.3	1 1 1 1
H	0.22	Mg3 Mg3	2.8	1.9 6.8 6.8 1.9	1 3 3 1
I	0.37	Mg1 Mg3	2.9	6.8 8.6 2.2 3.8	3 4 1 1

[a] based on initial anhydrous wadsleyite



Fully-hydrated wadsleyite





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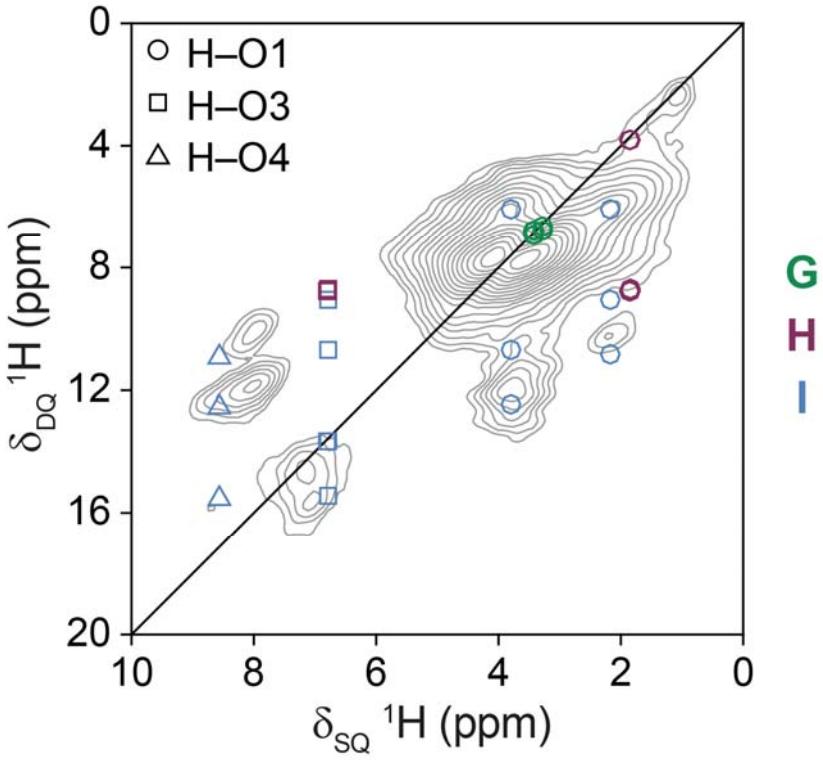

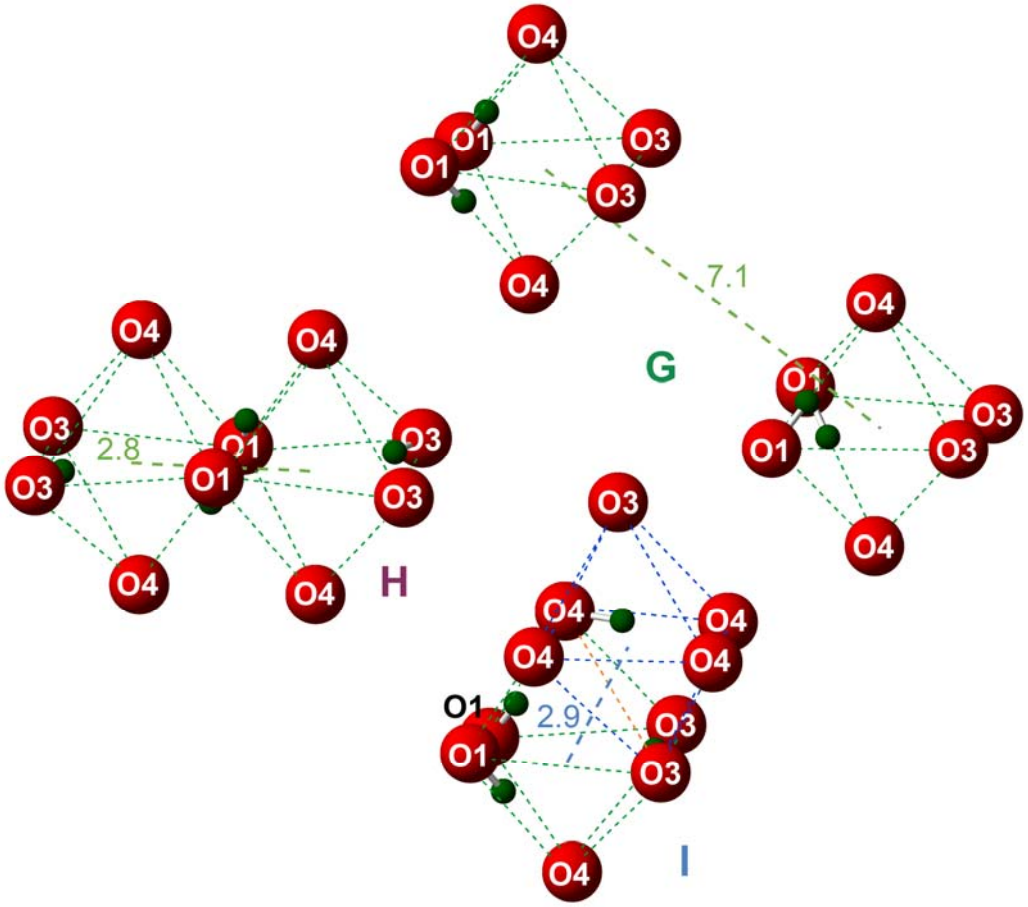

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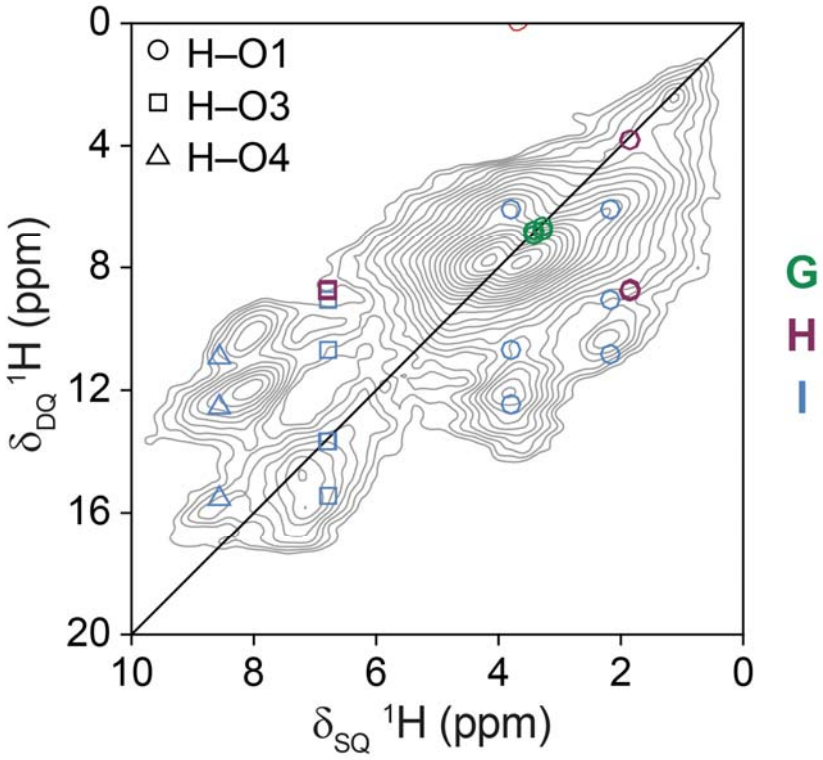

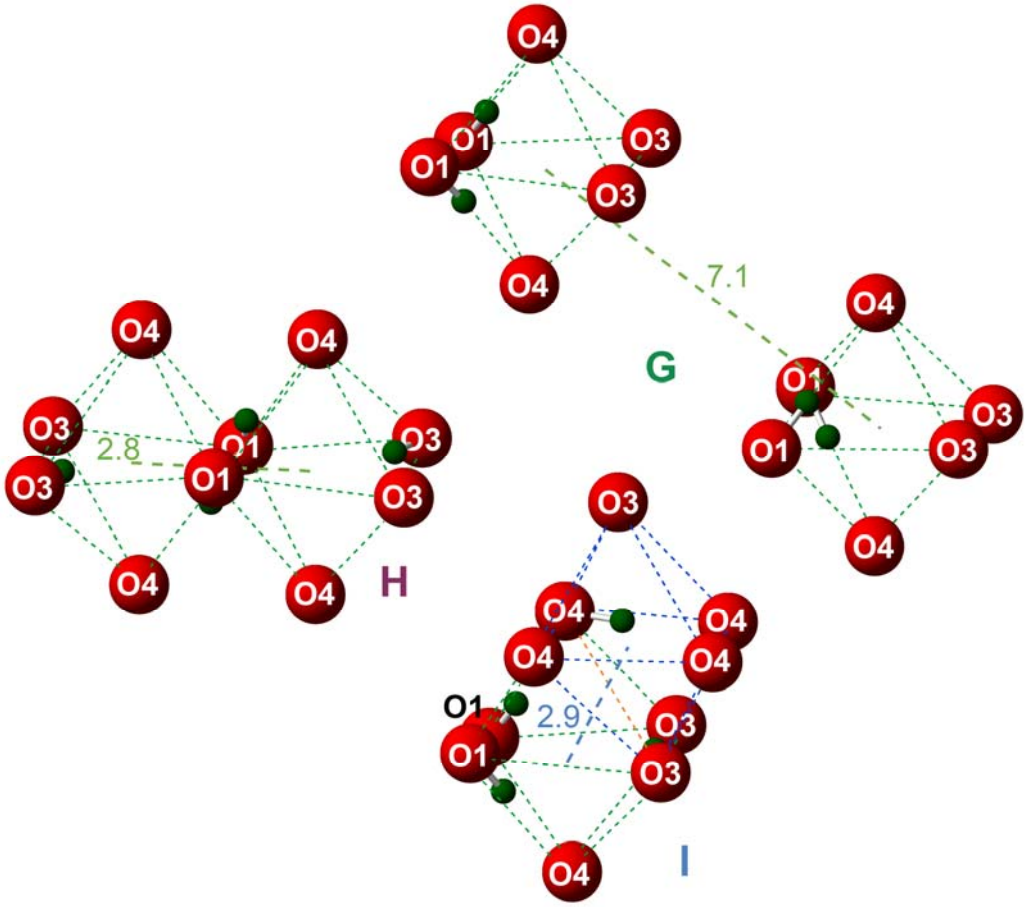

Summary

- the ground-state structure of semi- or fully-hydrated wadsleyite results from Mg3 vacancies, charge balanced by protons, which bind to O1
- NMR experiments provide evidence of protonation of the pyrosilicate oxygens
- fully-hydrated structures allow full spectral assignment, showing O3 and O4 are protonated to form silanols
- calculations provide evidence for defect clustering
- O2 sites are not found to be protonated in any low enthalpy structure, its bridging position likely reducing its proton affinity
- alterative Si vacancies (not in the talk!) are discounted on enthalpy grounds (below) and due to excess Si used in synthesis to mimic the natural environment:

$$Mg_{14}Si_8O_{32}H_4 + \underset{\text{akimotoite}}{Mg_6Si_6O_{18}} \longrightarrow Mg_{16}Si_7O_{32}H_4 + \underset{\text{stishovite}}{Si_2O_4} \qquad \Delta H = +1.2 \text{ eV}$$

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