Investigating the hydration of inner Earth minerals through \textit{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
  - $\alpha$- to $\beta$-$\text{Mg}_2\text{SiO}_4$ at $\sim$410 km
  - $\gamma$-$\text{Mg}_2\text{SiO}_4$ to $\text{MgO}/\text{MgSiO}_3$ at $\sim$660 km
  - $\beta$- to $\gamma$-$\text{Mg}_2\text{SiO}_4$ at $\sim$520 km

- NAMs can be hydrated at mantle temperature and pressure – the location of the Earth’s “missing water”
  - $\text{Mg}_2\text{SiO}_4$ 1 – 3 wt% $\text{H}_2\text{O}$
  - $\text{MgSiO}_3$ 0.01 – 0.1 wt% $\text{H}_2\text{O}$

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

**Wadsleyite**

- 16 Mg\(^{2+}\), 4 [Si\(_2\)O\(_7\)]\(^{6-}\) (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\(_2\)O)
- 2 Mg\(^{2+}\) / 4 H\(^+\) = hydrous (3.3 wt% H\(_2\)O)
- tentative literature consensus: Mg3 vacancies
- no consensus: location of hydrogen

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
Hydrated wadsleyite – solid-state NMR spectroscopy (~3.3 wt% H₂O)

- 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% H₂O)

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

\[ \text{Correlation} \quad \delta \quad ^1\text{Ha (ppm)} \quad \delta \quad ^1\text{Hb (ppm)} \]

\begin{tabular}{ccc}
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 \\
\end{tabular}

\[ ^1\text{H} 14.1 \text{ T} \]
\[ \text{DQ MAS (30 kHz)} \]

\[ ^1\text{H} \quad \text{1-D spectrum shows 4-6 peaks} \]

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

\[ \text{simple swapping of atoms} \]
\[ < 10 \text{ models} \]
\[ \text{done manually} \]

\[ \text{systematic swapping of atoms} \]
\[ 10s \text{ to } 100s \text{ of models} \]
\[ \text{manually or automated} \]
\[ \text{consider symmetry} \]

\[ \text{simple removal, complex addition} \]
\[ 100s \text{ to } 1000s \text{ of models} \]
\[ \text{automated} \]
\[ \text{potentially combinatorial} \]
AIRSS approach to hydrous Mg$_2$SiO$_4$

- 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
  - $E_{\text{cut}} = 25$ Ry
  - k-point spacing = 0.1 $2\pi$/Å
  - fixed unit cell
  - ~1 structure per node hour

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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 $\Delta H$ 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, \( E_{\text{cut}} = 60 \text{ Ry} \), k-point spacing = 0.04 \( 2\pi/\text{Å} \), TS dispersion correction and variable unit cell

- GIPAW NMR calculations at the same level
Semi-hydrated wadsleyite

- 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 $\Delta H \leq 2.0$ eV
**Fully-hydrated wadsleyite**

<table>
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<th>Structure</th>
<th>$\Delta H$ / eV</th>
<th>vacs</th>
<th>vac...vac / Å$^a$</th>
<th>$^1$H $\delta_{vac}$ (ppm)</th>
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</table>

$^a$ based on initial anhydrous wadsleyite
Fully-hydrated wadsleyite
Fully-hydrated wadsleyite

![Diagram of Fully-hydrated wadsleyite with chemical shifts and molecular structure]
Fully-hydrated wadsleyite
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

• alternative 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:

\[
\text{Mg}_{14}\text{Si}_8\text{O}_{32}\text{H}_4 + \text{Mg}_6\text{Si}_6\text{O}_{18} \rightarrow \text{Mg}_{16}\text{Si}_7\text{O}_{32}\text{H}_4 + \text{Si}_2\text{O}_4 \quad \Delta H = +1.2 \text{ eV}
\]

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- stishovite
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