University of St Andrews

EaStCHEM

Applications of NMR Calculations

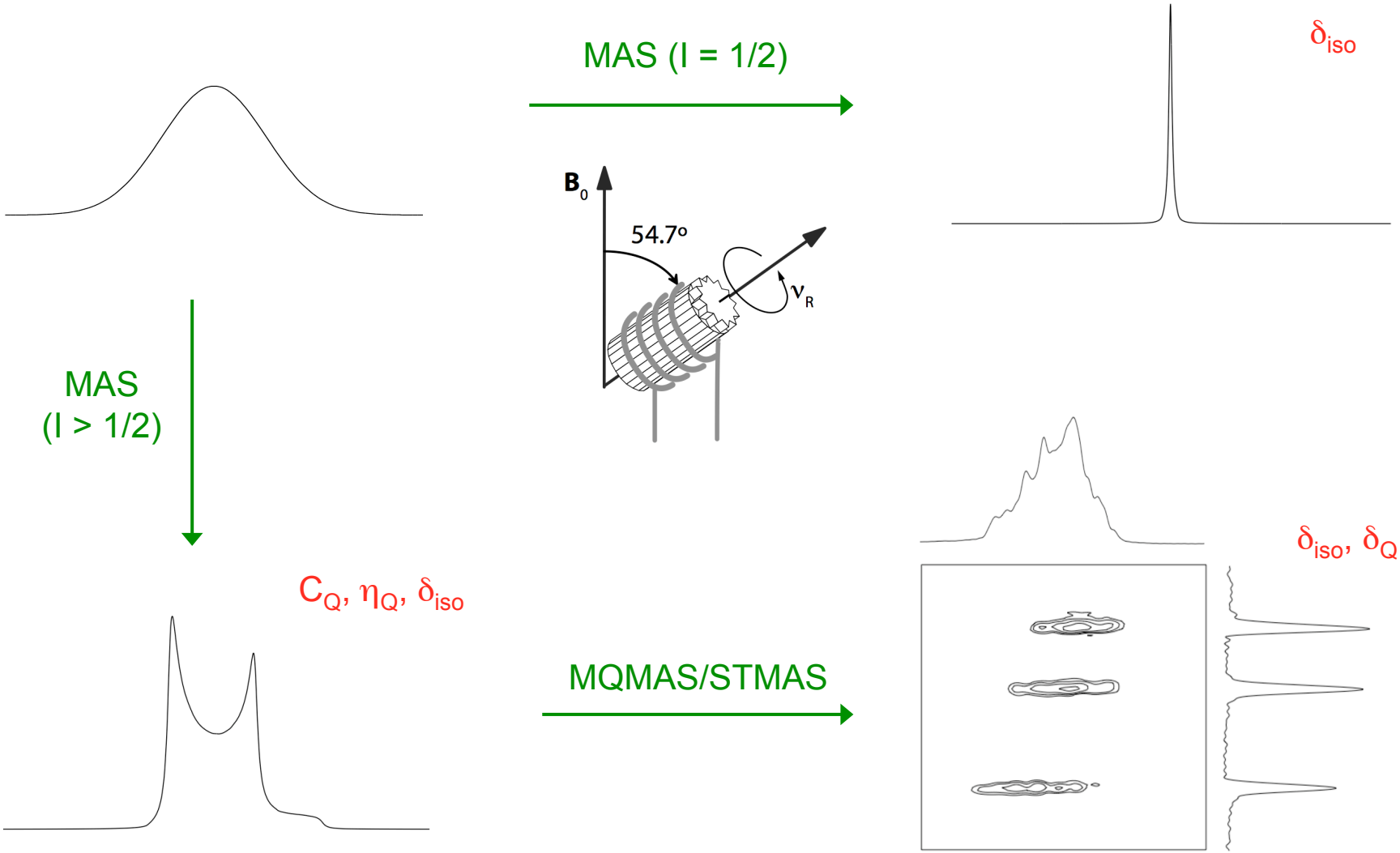
CASTEP Workshop

Oxford, August 2009

Dr Sharon Ashbrook

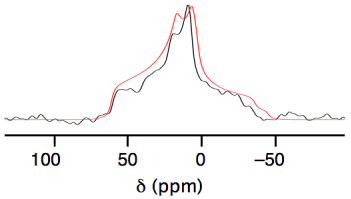
sema@st-andrews.ac.uk

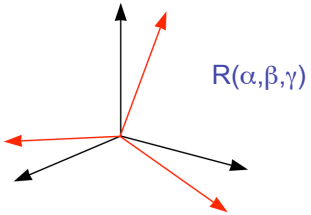
Experimental methods

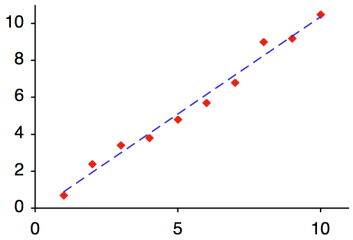


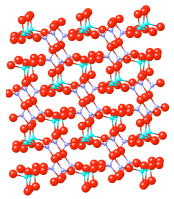
Why calculate NMR parameters?

- Spectral assignment
- Spectral interpretation
- Confirmation of experimental NMR parameters
- Additional information (anisotropy, tensor orientation, etc.,)
- Spectral prediction
- Assessment of experimental feasibility
- Flexible way to study the dependence of NMR parameters upon structure
- Testing of structural models for materials with unknown structure
- More complex properties of solids
  - Disorder
  - Dynamics









??

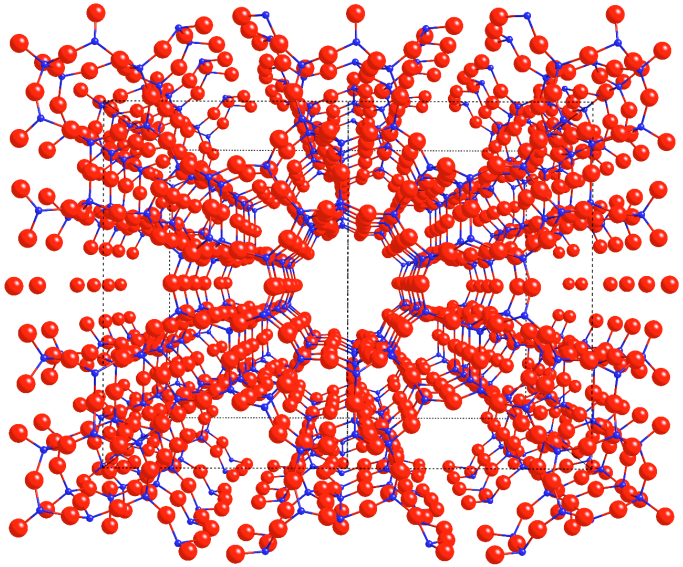
CASTEP NMR calculations

Chemical shielding	δ_{iso}, Δ_{CSA}, η_{CS}, (α, β, γ)
J coupling	J_{iso}, (J_{aniso})
Quadrupolar coupling	C_Q, η_Q, (α', β', γ')

CASTEP parameters

Ultrasoft pseudopotentials
GGA (PBE)
k-point spacing ~0.04 $Å^{-1}$
Energy cut off ~ 60 Ry (~816 eV)

AMD Opteron cluster (2-8 cores) with Infinipath interconnects



Extended frameworks
Typically 12-250 atoms in unit cell

Considerations

How accurate are our calculations?

How accurate do we need them to be - what do we want to know?
How accurate is the experimental data?

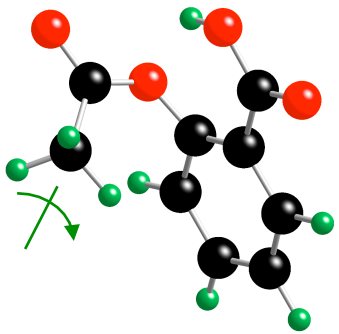
Do we need to optimise the structure?

Structures are of varying quality
^{1}H typically misplaced
Do we vary the unit cell size?
Do we retain the symmetry?

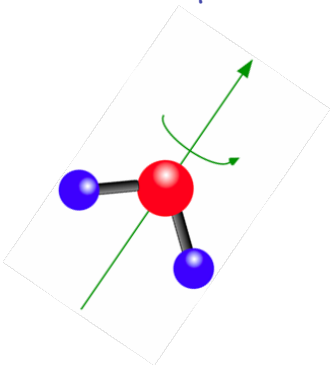
What about dynamics?

Diffraction and NMR are sensitive to different length scales and timescales
Measurements often performed at different temperatures
Significant motion on a range of timescales in the solid state

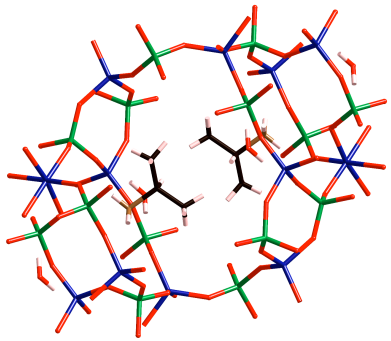
ps-ns



ns-μs



μs-ms



Referencing

- Experiments are referenced to an externally to a reference sample on the same spectrometer on the same day
- How do we reference our calculations?

$$\delta_{iso} = \sigma_{ref} - \sigma_{iso}$$

- 1. Use a simple reference structure (e.g., SiO_2, Al_2O_3, Y_2O_3) to match experiment
- 2. Reference within a calculation if many shifts are present
- 3. Reference calculated from a consideration of many different materials

1. ^{17}O NMR of high-pressure minerals

Experiment

Ashbrook, Berry and Wimperis, Am. Mineral. ***84****, 1191 (1999).*

Ashbrook, Berry and Wimperis, J. Phys. Chem. B ***106****, 773 (2002).*

Ashbrook, Berry, Hibberson, Steuernagel and Wimperis, J. Am. Chem. Soc. ***125****, 11824 (2003).*

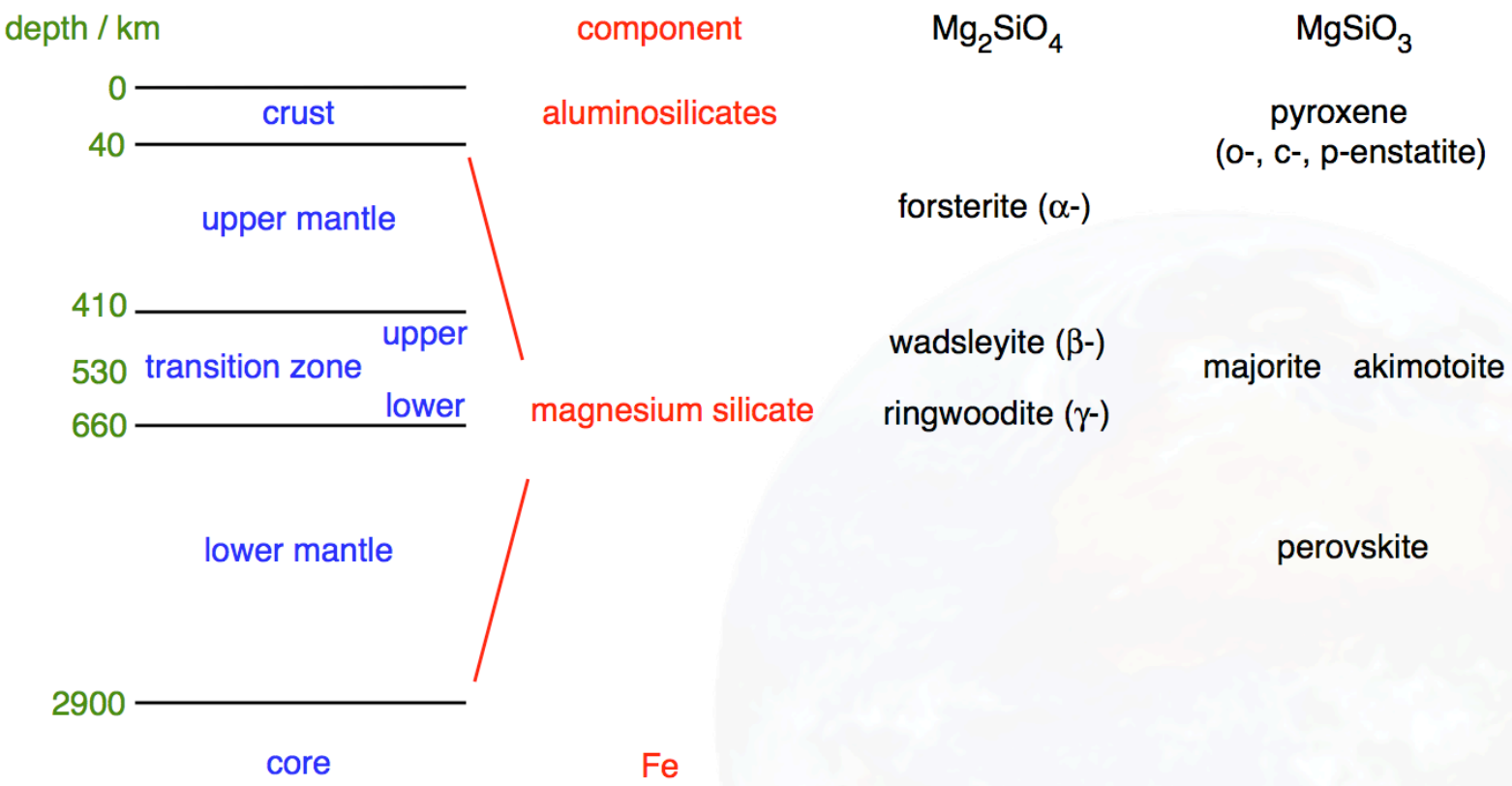
Ashbrook, Berry, Hibberson, Steuernagel and Wimperis, Am. Mineral. ***90****, 1861 (2005).*

Experiment and Calculation

Ashbrook, Le Polles, Berry, Wimperis and Farnan, Phys. Chem. Chem. Phys. ***9****, 1587 (2007).*

Ashbrook, Berry, Frost, Gregorovic, Pickard, Readman and Wimperis., J. Am. Chem. Soc. ***129****, 13213 (2007).*

The deep Earth

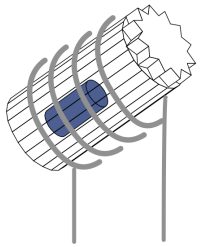


Aims and objectives

- Characterise anhydrous minerals
- Study known hydrated minerals as models for water incorporation
- Position and mechanism of hydration in nominally anhydrous minerals

Experimental challenges

- High-pressure synthesis in a multi-anvil apparatus often produces only small (few mg) amount of material, limiting sensitivity



Samples kept as pellets rather than powders

- ^{17}O, ^{29}Si and ^{25}Mg all have low natural abundance (0.037%, 4.7%, 10%)

Isotopic enrichment (^{17}O (£500-£2000 / g), ^{25}Mg (£10000 / g))

- ^{17}O and ^{25}Mg are quadrupolar (I = 5/2), and spectra are additionally broadened by the quadrupolar interaction

High-resolution approaches (e.g., MQMAS)

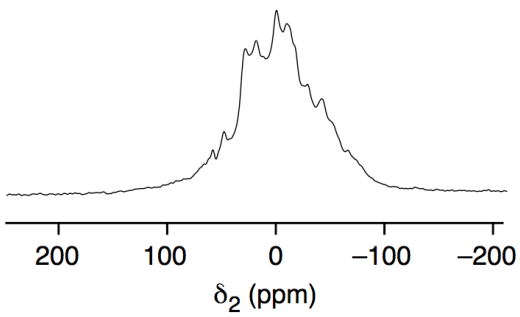
More sensitive (but more technically demanding) experiments (e.g., STMAS)

Spectral prediction and interpretation with DFT

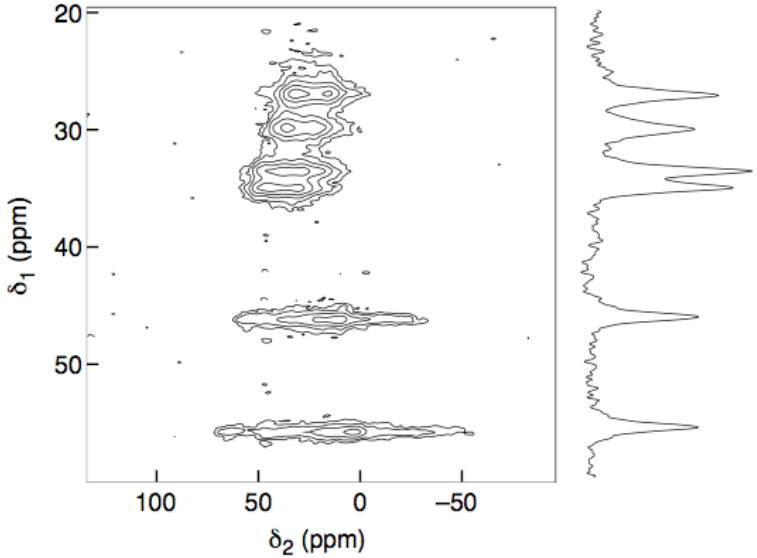
$MgSiO_3$ (150 mg, 75% ^{17}O)
9.4 T (MQMAS, 54 hours)

Orthoenstatite

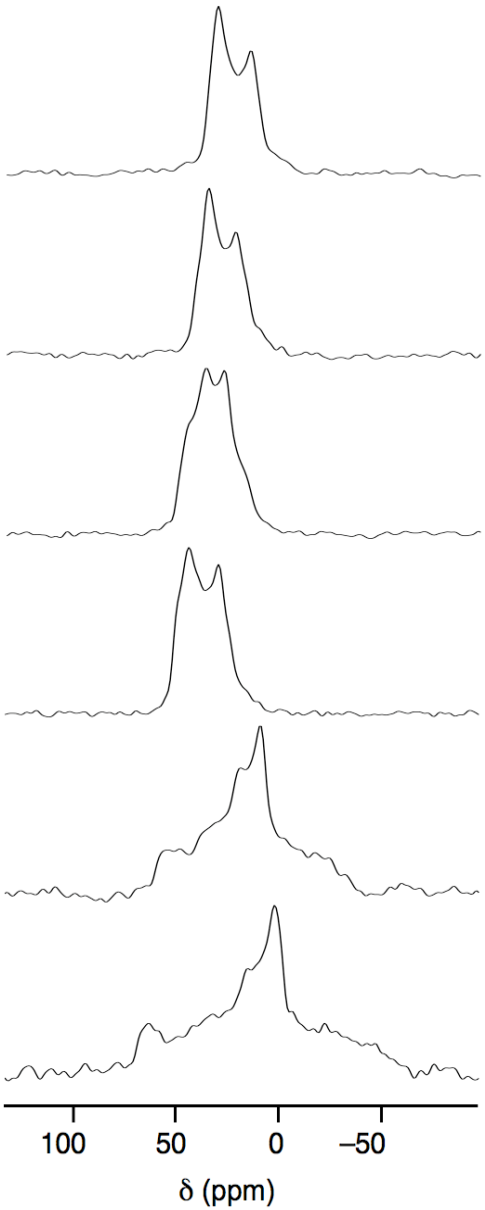
9.4 T MAS



9.4 T MQMAS



6 O

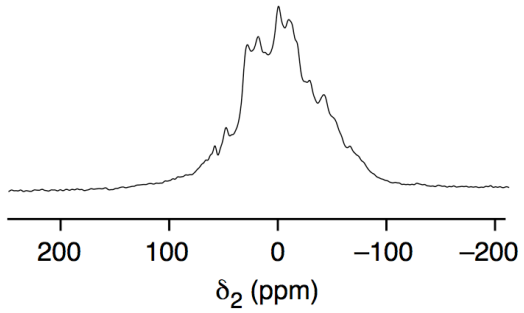


δ_{iso}	$\lvert C_Q \rvert$	η_Q
41 ppm	2.9 MHz	0.19
46 ppm	2.8 MHz	0.29
52 ppm	2.9 MHz	0.53
56 ppm	2.9 MHz	0.29
60 ppm	4.2 MHz	0.78
70 ppm	4.8 MHz	0.80

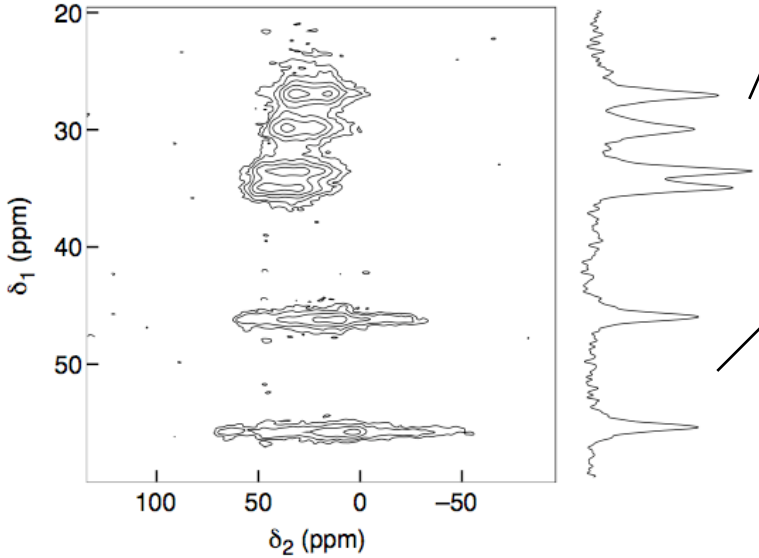
$MgSiO_3$ (150 mg, 75% ^{17}O)
9.4 T (MQMAS, 54 hours)

Orthoenstatite

9.4 T MAS



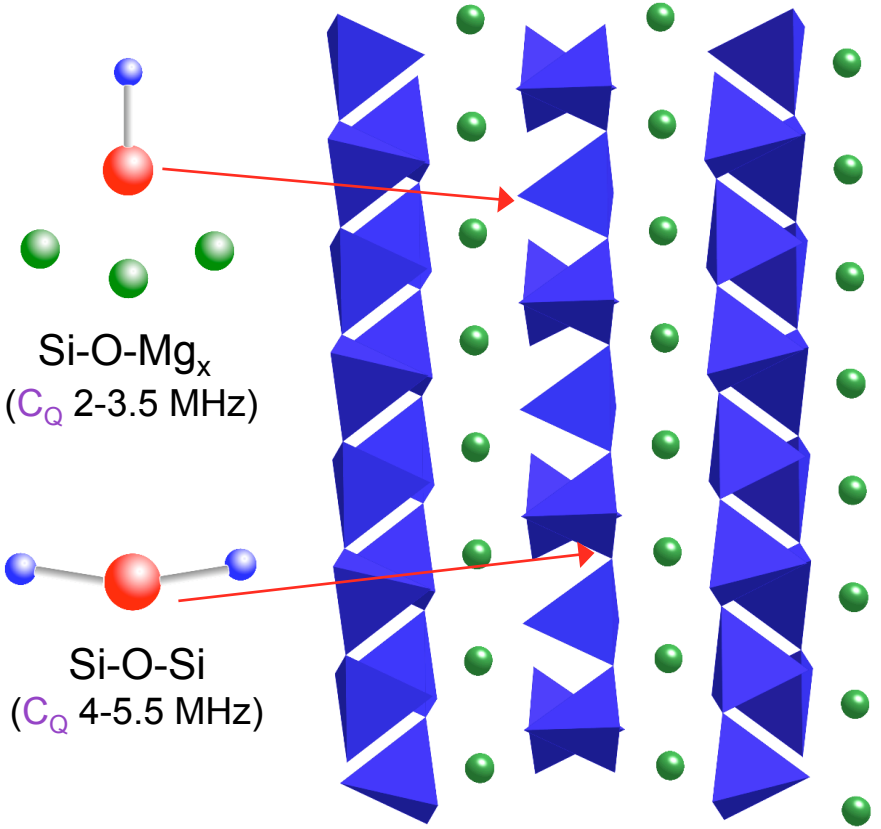
9.4 T MQMAS



6 O

Si-O-Mg_x
(C_Q 2-3.5 MHz)

Si-O-Si
(C_Q 4-5.5 MHz)



Orthoenstatite

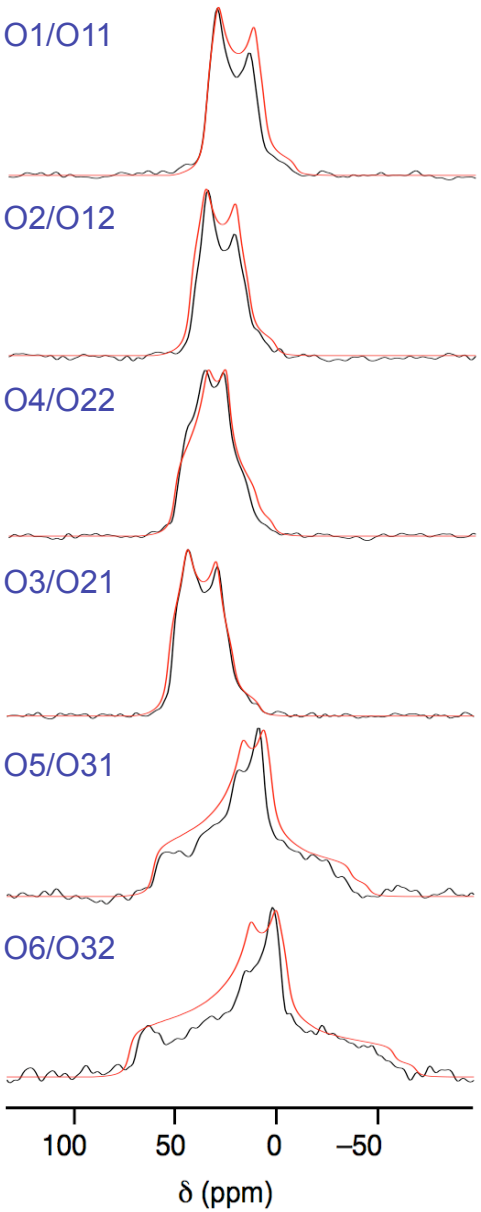
CASTEP

80 atoms in unit cell (16 units of $MgSiO_3$)

GGA/PBE
Ultrasoft pseudopotentials
60 Ry cut-off energy
0.04 $Å^{-1}$ k-point spacing

NMR calculation: 12 processors for 4 days

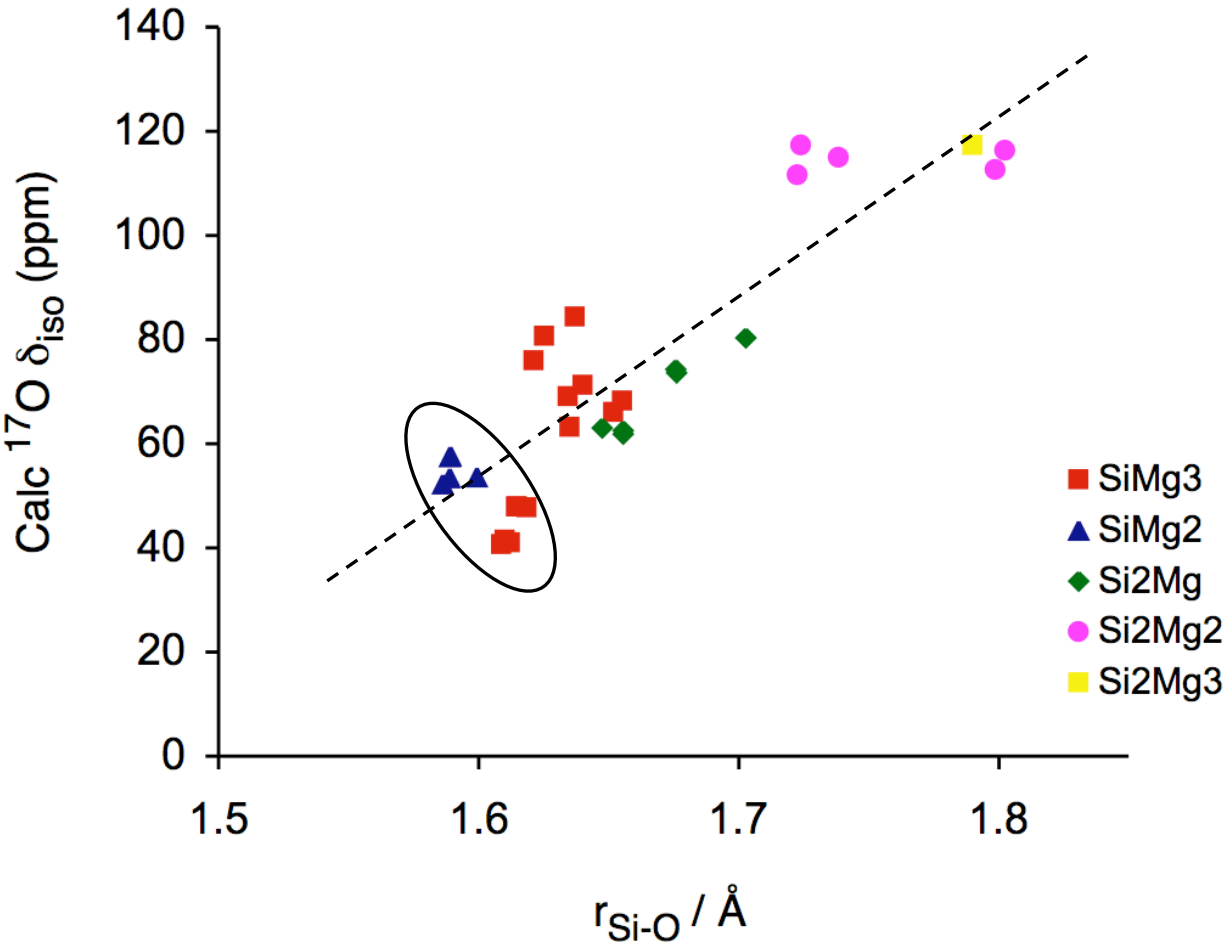
Referenced to forsterite (α-Mg_2SiO_4)



	δ_{iso}	$\lvert C_Q \rvert$	η_Q
O1/O11	41 ppm	2.9 MHz	0.19
	41 ppm	3.06 MHz	0.21
O2/O12	46 ppm	2.8 MHz	0.29
	47 ppm	2.96 MHz	0.29
O4/O22	52 ppm	2.9 MHz	0.53
	53 ppm	3.03 MHz	0.62
O3/O21	56 ppm	2.9 MHz	0.29
	57 ppm	3.03 MHz	0.35
O5/O31	60 ppm	4.2 MHz	0.78
	62 ppm	4.35 MHz	0.78
O6/O32	70 ppm	4.8 MHz	0.80
	73 ppm	5.0 MHz	0.81

Spectral assignment

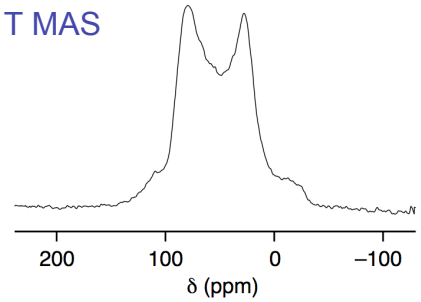
- General linear relationship of ^{17}O δ_{iso} to Si-O bond length
- Dependence upon environment type



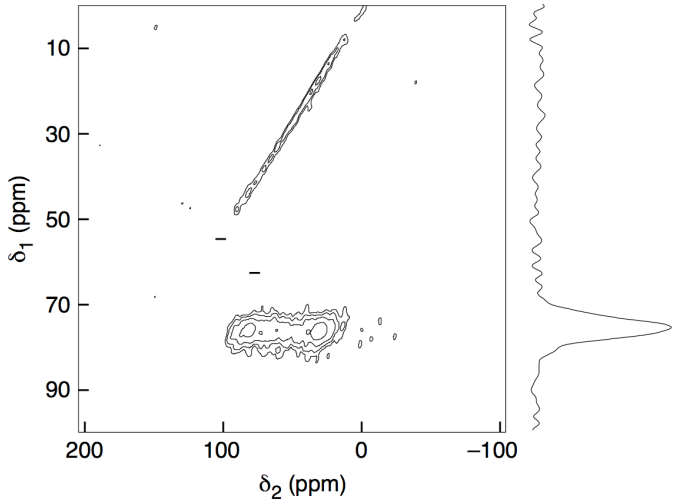
$MgSiO_3$ (~4 mg, 75% ^{17}O)
9.4 T (STMAS, 84 hours)

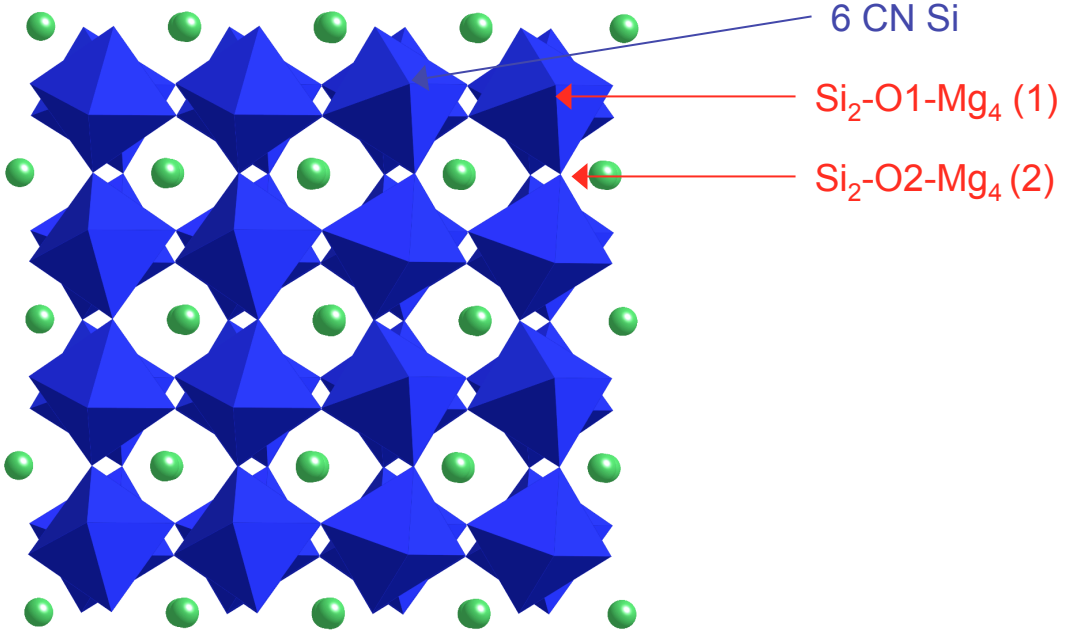
Perovskite

9.4 T MAS



9.4 T STMAS





	Pop^n	Experimental			
		δ_{iso} (ppm)	P_Q / MHz	C_Q / MHz	η
O1	1	109(2)	5.1(2)	5.1(1)	0.1(2)
O2	2				
Si	1	–193(1)			

Only 1 O observed in 1D and 2D spectra?

Perovskite

	Pop^n	Experimental				Calculated		
		δ_{iso} (ppm)	P_Q / MHz	C_Q / MHz	η	δ_{iso} (ppm)	C_Q / MHz	η
O1	1	109(2)	5.1(2)	5.1(1)	0.1(2)	116.0	5.31	0.28
O2	2					117.0	5.32	0.12
Si	1	–193(1)				–191.5		

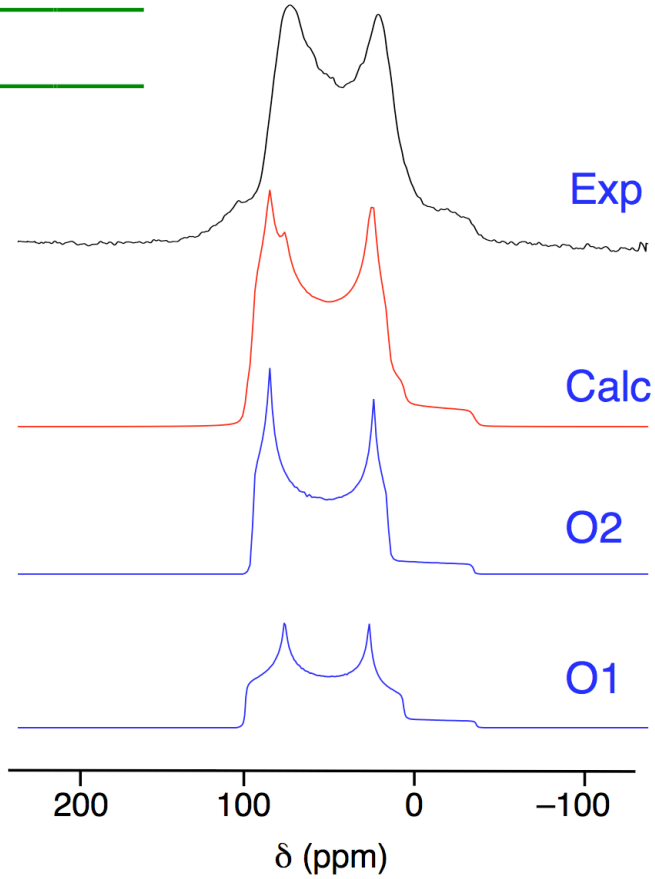
CASTEP

20 atoms in unit cell (4 units of $MgSiO_3$)

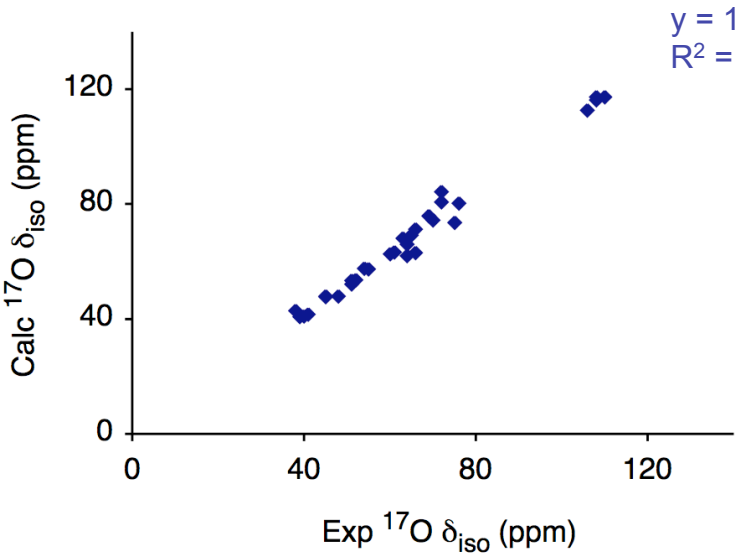
GGA/PBE
Ultrasoft pseudopotentials
60 Ry cut-off energy
0.04 $Å^{-1}$ k-point spacing

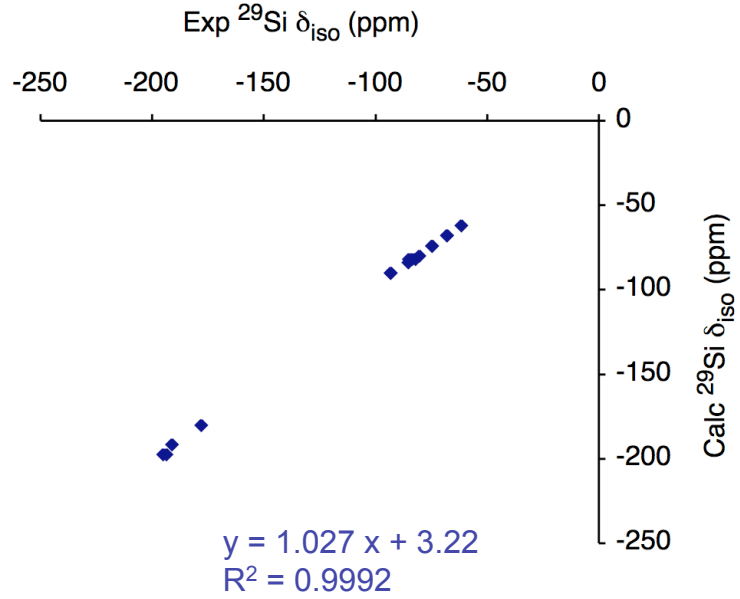
NMR calculation: 12 processors for 4 hours

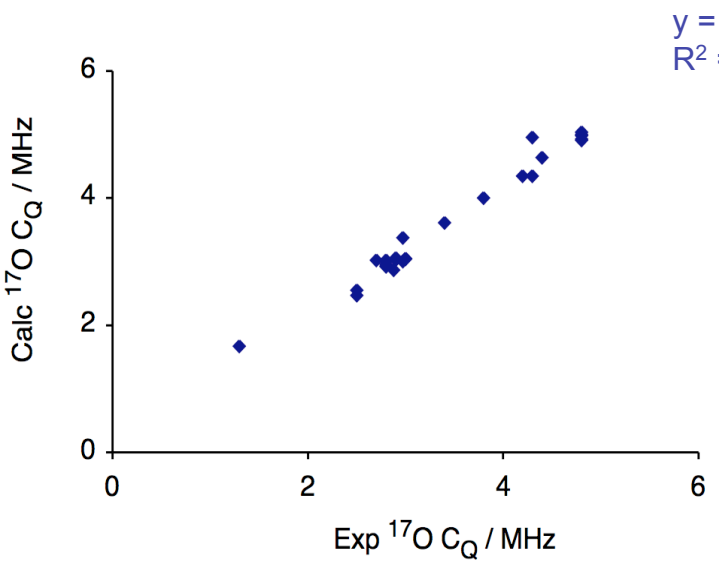
Referenced to forsterite (α-Mg_2SiO_4)



Accuracy of data







- Good agreement between experimental and calculated values
- Use for spectral prediction, assignment and interpretation

2. NMR of microporous materials

Experiment

Antonijevic, Ashbrook, Biedesek, Walton, Wimperis and Yang, J. Am. Chem. Soc. ***128****, 8054 (2006).*

Experiment and Calculation

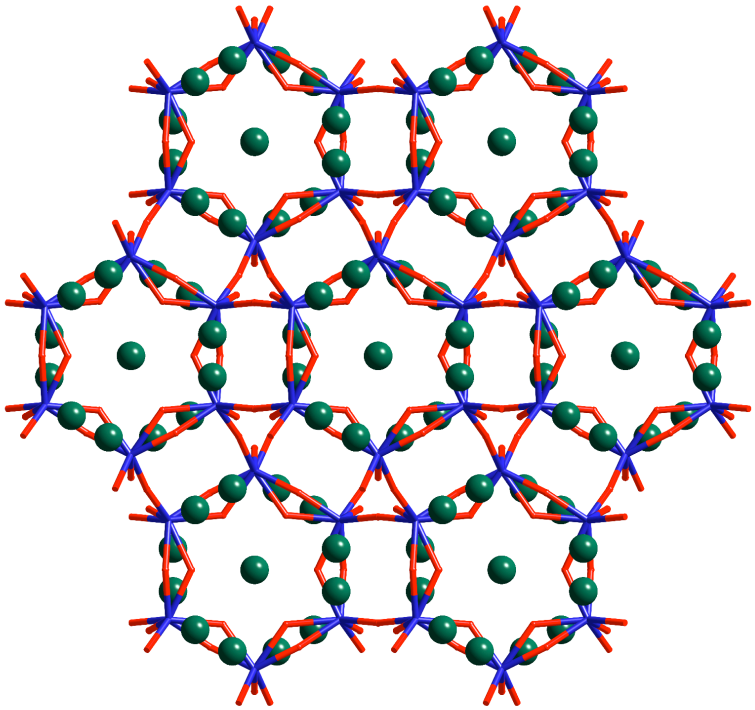
Ashbrook, Cutajar, Pickard, Walton and Wimperis, Phys. Chem. Chem. Phys. ***10****, 5754 (2008).*

Byrne, Warren, Morris and Ashbrook, Solid State Sci. ***11****, 1001 (2009).*

Ashbrook, Cutajar, Griffin, Lethbridge, Walton and Wimperis, J. Phys. Chem. C ***113****, 10780 (2009).*

Microporous materials

- Open framework solids with regular systems of channels and cavities of molecular dimensions
- High surface area
- Typical pore dimensions 4-8 Å



- Industrial uses intimately linked to structure
  - Selective sorption
  - Cation exchange materials
  - Catalysis
  - Gas storage

- Three main types

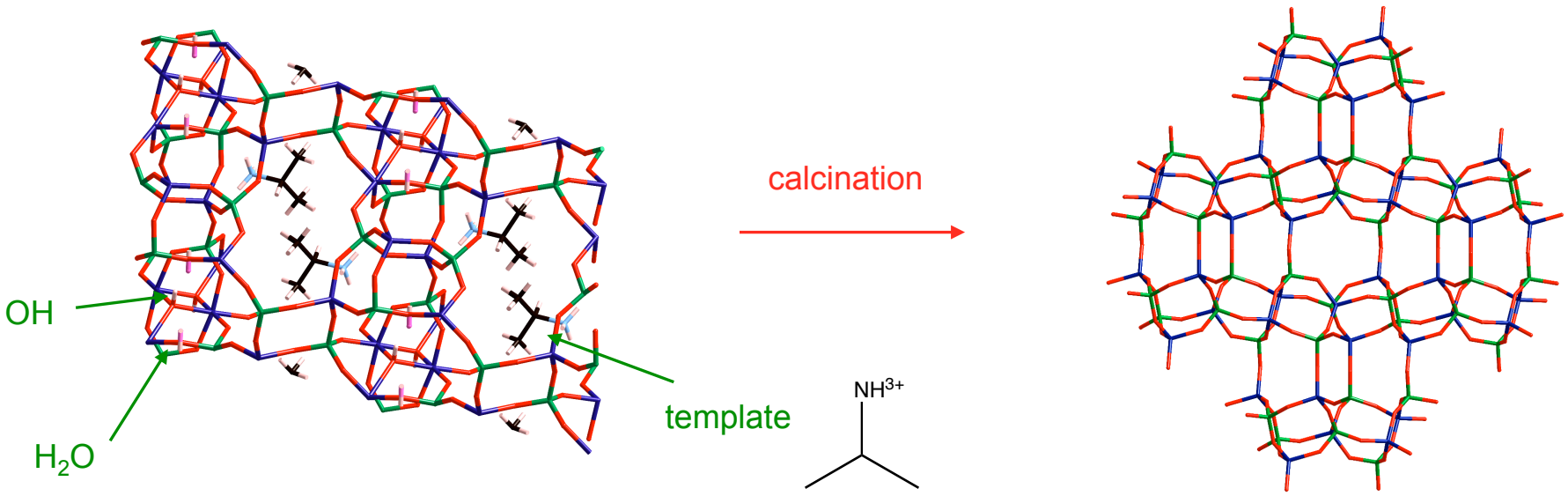
Zeolites	aluminosilicates and Cs, Na, etc., cations
AlPOs	aluminophosphates
MOF	Co, Zn, Sc, Mg, Mn, etc., and organic linkers

Aluminophosphates

- New family of porous solids discovered in 1982, composed of alternating AlO_4 and PO_4 tetrahedra
- Synthesised using a structure directing agent or template (typically an amine base)
- Incorporation of OH^-/F^- into framework to charge balance and water in the pores
- Doping with Si, Ga, Mg, Mn etc., changes the catalytic properties

AlPO-14

- First synthesized in 1982 although initial confusion over the structure as the material can be prepared from a number of templates
- As-synthesized forms contain framework OH, increasing the Al coordination number



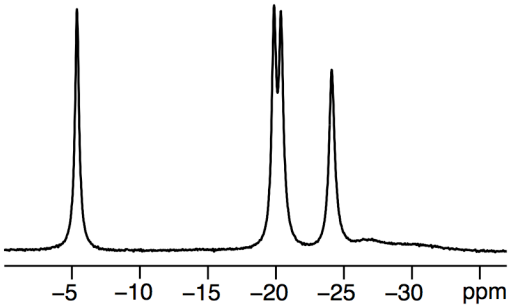
AlPO-14: NMR

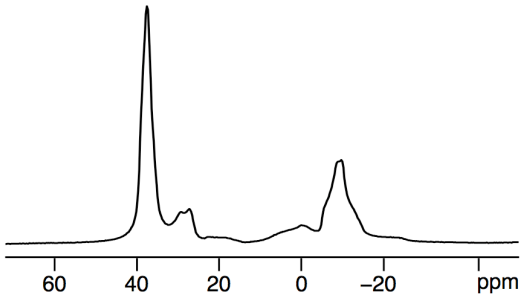
^{31}P MAS

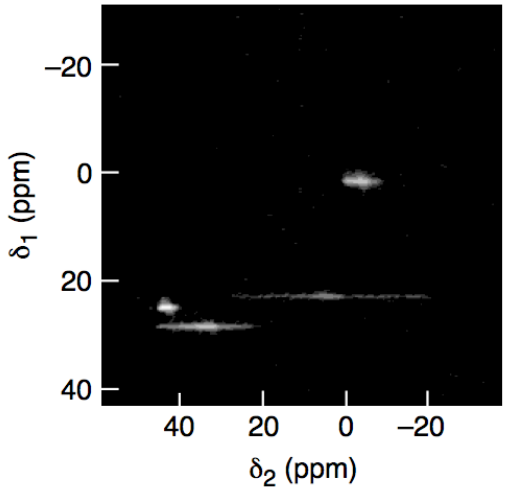
^{27}Al MAS

^{27}Al MQMAS

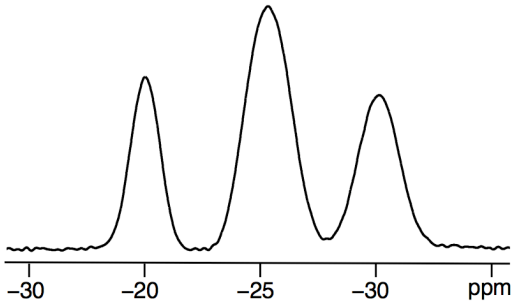
AlPO-14 *ipa*

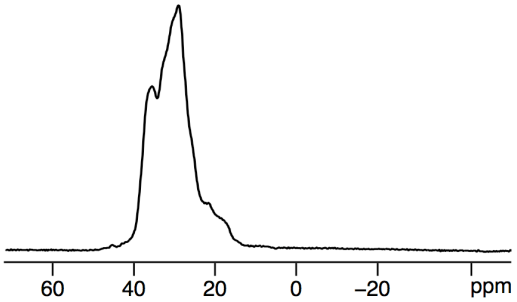


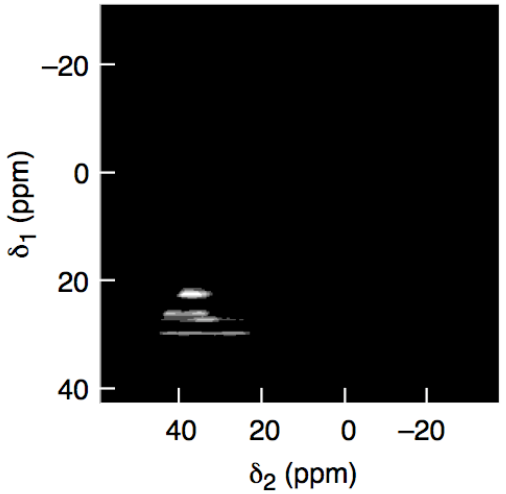




AlPO-14 calcined







AlPO-14 calcined: calculations

Experimental

	δ_{iso} (ppm)	C_Q / MHz	η_Q
Al1	43	4.0	0.8
Al2	43	3.4	0.2
Al3	38	2.5	0.6
Al4	45	4.9	0.3
P1	–21.4		
P2	–26.7		
P3	–31.5		
P4	–26.7		

Calculated

	δ_{iso} (ppm)	C_Q / MHz	η_Q
Al1	38.5	5.30	0.08
Al2	48.6	9.69	0.26
Al3	40.3	5.55	0.74
Al4	55.9	7.04	0.57
P1	–33.5		
P2	–24.0		
P3	–35.7		
P4	–35.8		

CASTEP

48 atoms in unit cell (8 $AlPO_4$)

GGA/PBE
Ultrasoft pseudopotentials
60 Ry cut-off energy
0.04 $Å^{-1}$ k-point spacing

NMR calculation: 12 processors for 2 days

Referenced to berlinite ($AlPO_4$)

Forces up to 4 eV / Å

AlPO-14 calcined: calculations

Experimental

	δ_{iso} (ppm)	C_Q / MHz	η_Q
Al1	43	4.0	0.8
Al2	43	3.4	0.2
Al3	38	2.5	0.6
Al4	45	4.9	0.3
P1	–21.4		
P2	–26.7		
P3	–31.5		
P4	–26.7		

Calculated
optimized (fixed cell)

	δ_{iso} (ppm)	C_Q / MHz	η_Q
Al1	46.5	3.72	0.95
Al2	46.8	3.44	0.48
Al3	41.8	2.22	0.37
Al4	48.7	4.5	0.27
P1	–19.3		
P2	–25.6		
P3	–30.3		
P4	–24.5		

Forces up to 0.02 eV / Å

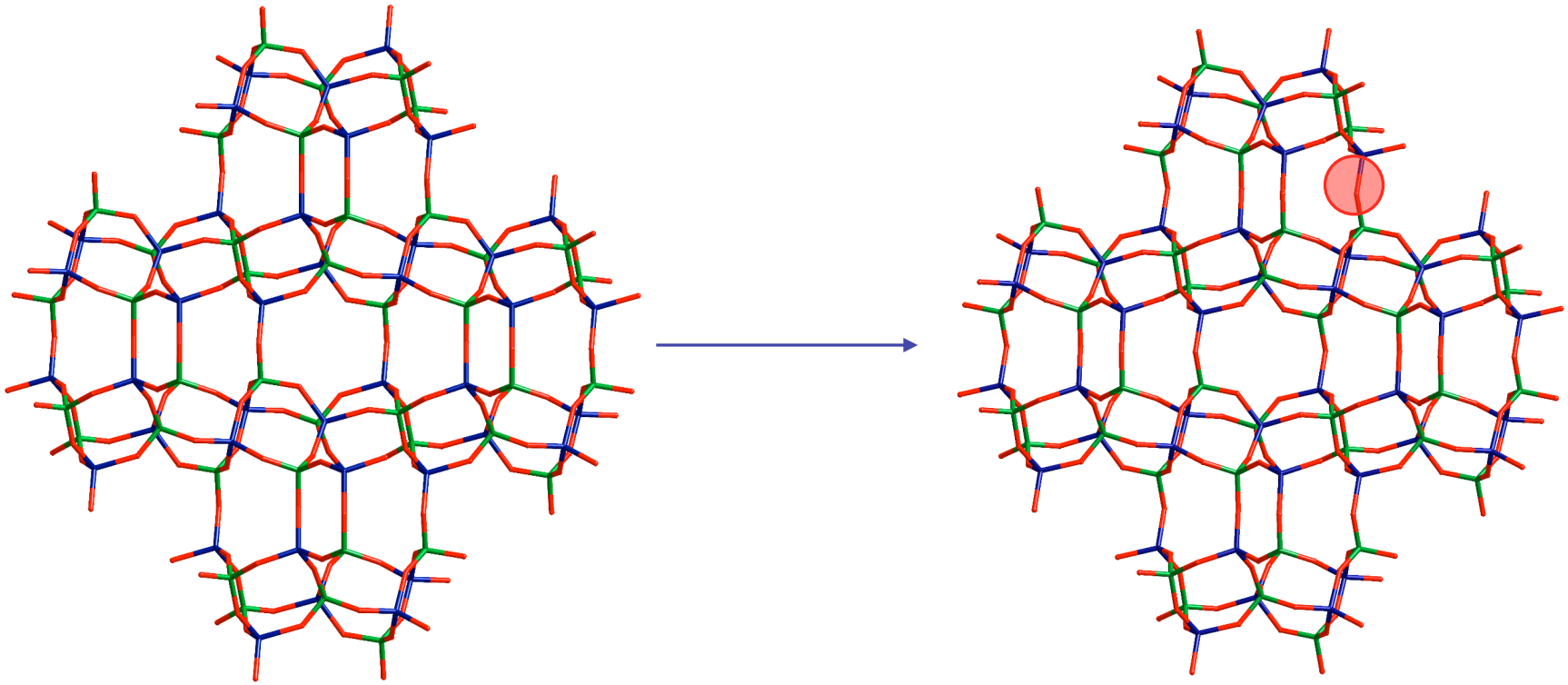
Calculated
optimized

	δ_{iso} (ppm)	C_Q / MHz	η_Q
Al1	43.2	4.54	0.74
Al2	43.8	3.57	0.25
Al3	38.0	2.80	0.71
Al4	46.6	4.96	0.26
P1	–21.4		
P2	–26.6		
P3	–32.9		
P4	–25.3		

Forces up to 0.015 eV / Å

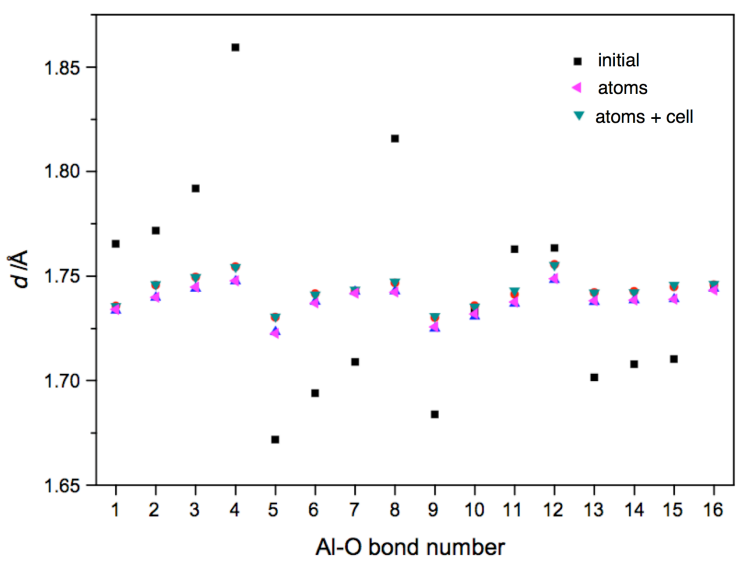
AlPO-14 calcined: calculations

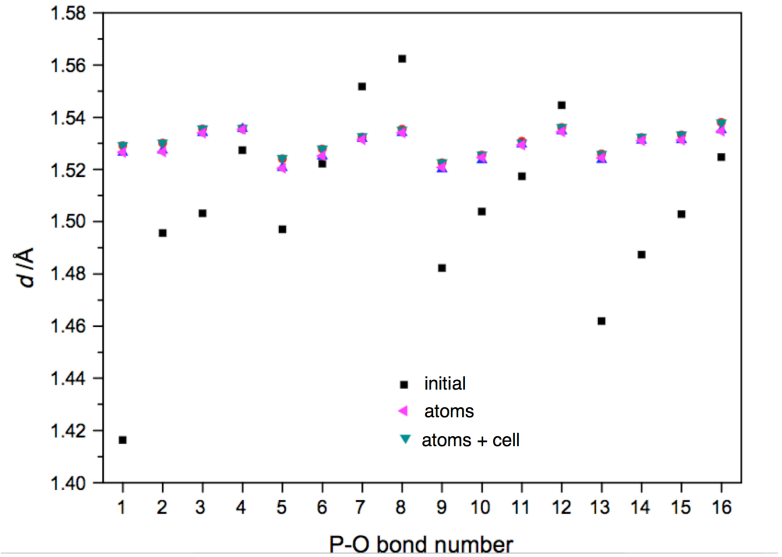
- How much have we changed the structure?

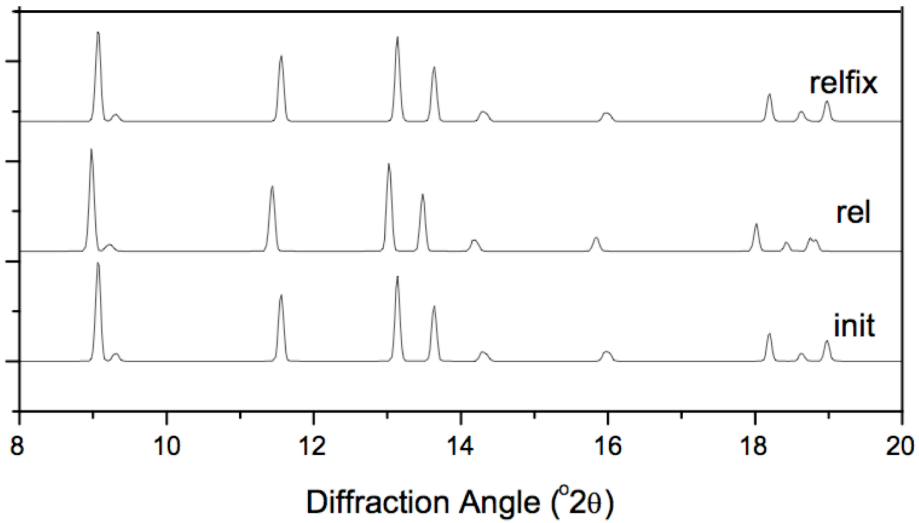


AlPO-14 calcined: calculations

- How much have we changed the structure?







AlPO-14 ipa: calculations

Experimental

	δ_{iso} (ppm)	C_Q / MHz	η_Q
Al1	27	5.6	1.0
Al2	44	4.1	0.8
Al3	43	1.7	0.6
Al4	–1	2.6	0.7
P1	–20.6		
P2	–5.8		
P3	–24.3		
P4	–20.1		

Calculated
^{1}H only optimized

	δ_{iso} (ppm)	C_Q / MHz	η_Q
Al1	35.9	10.5	0.73
Al2	41.6	6.5	0.74
Al3	41.7	3.78	0.59
Al4	6.3	1.98	0.85
P1	–17.5		
P2	3.2		
P3	–19.6		
P4	–16.0		

Forces up to 2.4 eV / Å

Calculated
optimized

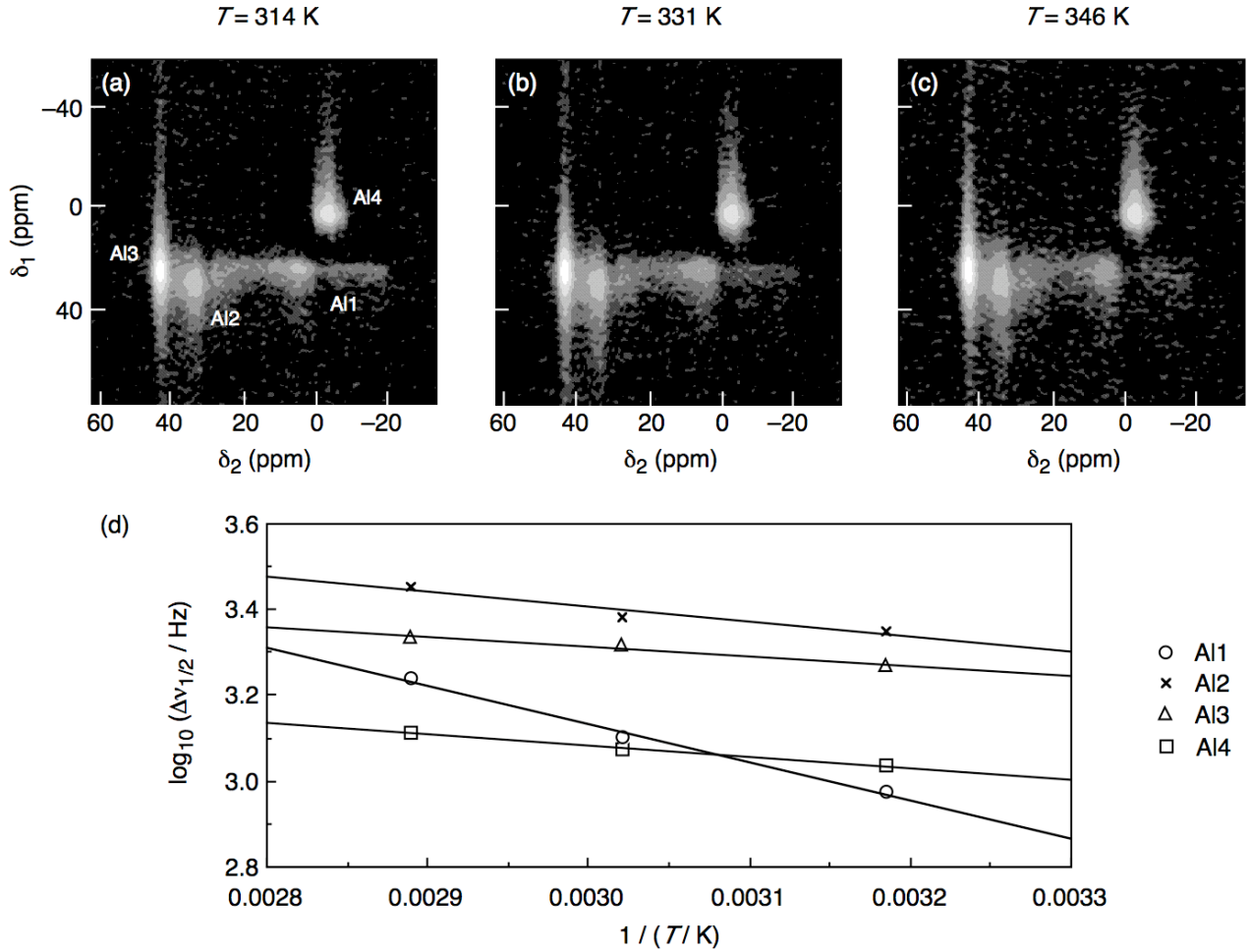
	δ_{iso} (ppm)	C_Q / MHz	η_Q
Al1	29.5	6.01	0.92
Al2	44.8	3.98	0.94
Al3	42.6	2.27	0.98
Al4	1.4	2.42	0.56
P1	–19.9		
P2	–1.1		
P3	–22.3		
P4	–17.0		

Forces up to 0.02 eV / Å

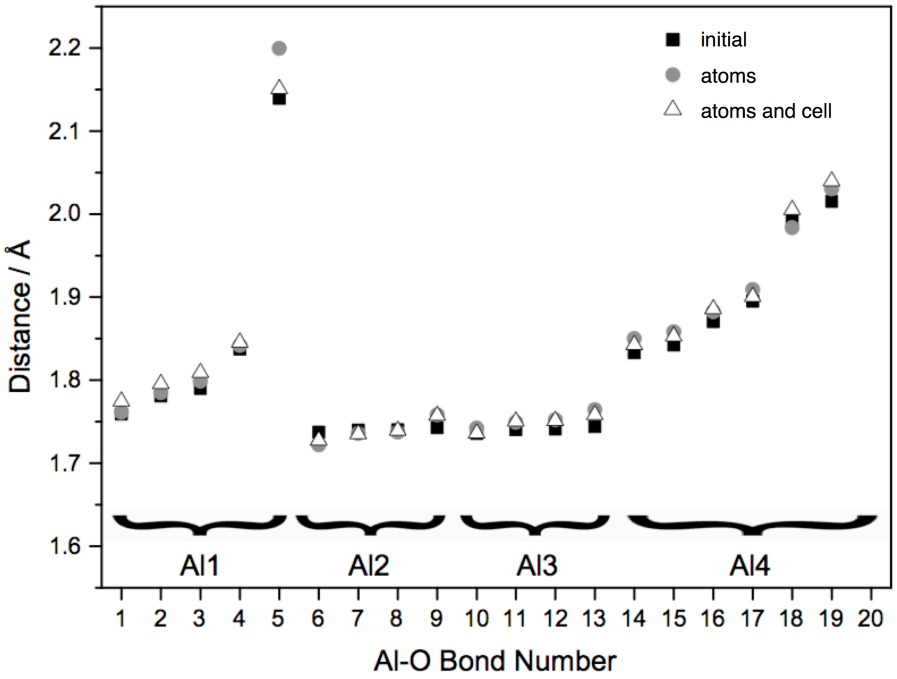
- Additional template, water and hydroxyl groups in structure
- Agreement not as good but assignment possible and in agreement with experiment

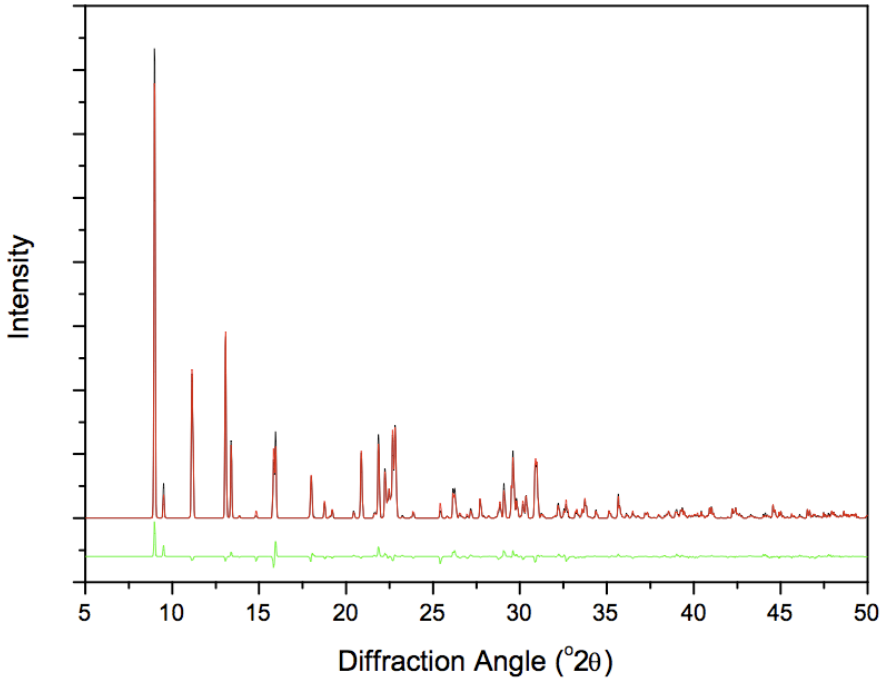
AlPO-14 ipa: motion

- Evidence for dynamics from temperature dependent broadening in STMAS experiment
- Not present in the calcined material

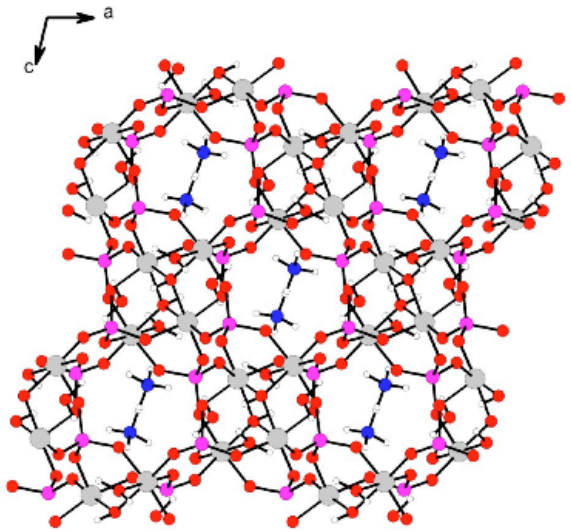


AlPO-14 ipa: calculations





- Much smaller differences in structure than for the calcined material
- NMR parameters very sensitive even to these small changes



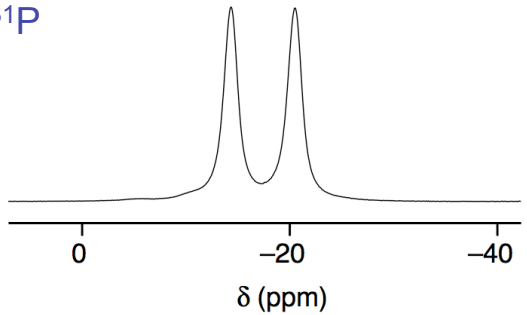
AlPO-15

Structure from synchrotron charge density measurements

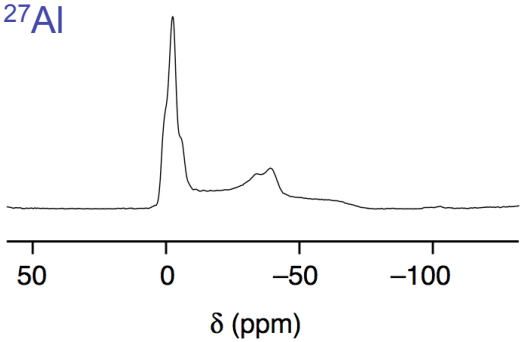
Experimental

	δ_{iso} (ppm)	C_Q / MHz	η_Q
Al1	2.5	3.1	0.8
Al2	−5.0	8.3	0.8
P 1	−14.3		
P 2	−20.5		

^{31}P



^{27}Al



Calculated (^{1}H opt)

	δ_{iso} (ppm)	C_Q / MHz	η_Q
Al1	3.5	−3.2	0.73
Al2	−4.2	8.3	0.87
P 1	−12.6		
P 2	−19.0		

CASTEP

100 atoms in unit cell (8 $AlPO_4$ 4 $(NH_4)^+$ 4 OH^- 8 H_2O)

GGA/PBE

Ultrasoft pseudopotentials

60 Ry cut-off energy

0.04 $Å^{-1}$ k-point spacing

NMR calculation: 12 processors for 3 days

Referenced to berlinite ($AlPO_4$)

Forces up to 0.1 eV / Å

3. ^{89}Y NMR of pyrochlore ceramics

Experiment

Ashbrook, Whittle, Lumpkin and Farnan, J. Phys. Chem. B ***110****, 10358 (2006).*

Experiment and Calculation

Reader, Mitchell, Johnston, Pickard, Whittle and Ashbrook, submitted.

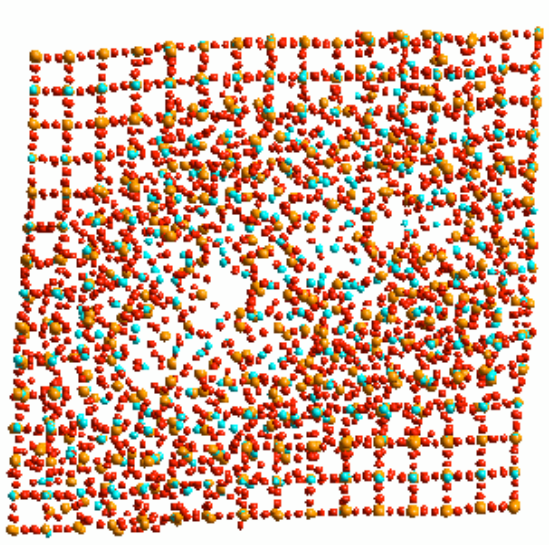
Nuclear waste remediation

- Pyrochlores proposed as host phases for the encapsulation of Ac/Ln nuclear waste

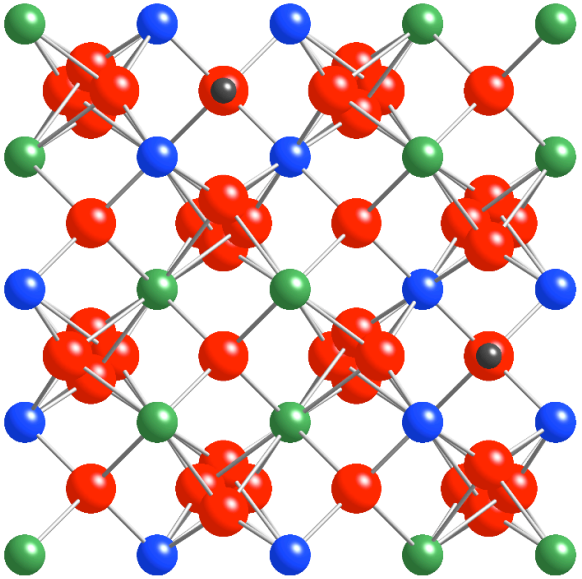
- Over last 50 years 1400 metric tons of Pu produced, and the amount is increasing at 70-80 tons per year
- Long lived isotopes ^{239}Pu (24,100 y), ^{237}Np (2.1 million y) and ^{233}U (160,000 y)

- Good candidate for synthetic wasteforms

High crystal chemical flexibility (> 500 compositions)
Tolerant of defects/substitutions
Variable oxidation states
High waste loading
Low leach rates
Resistant to radiation damage
Natural analogues



Pyrochlores



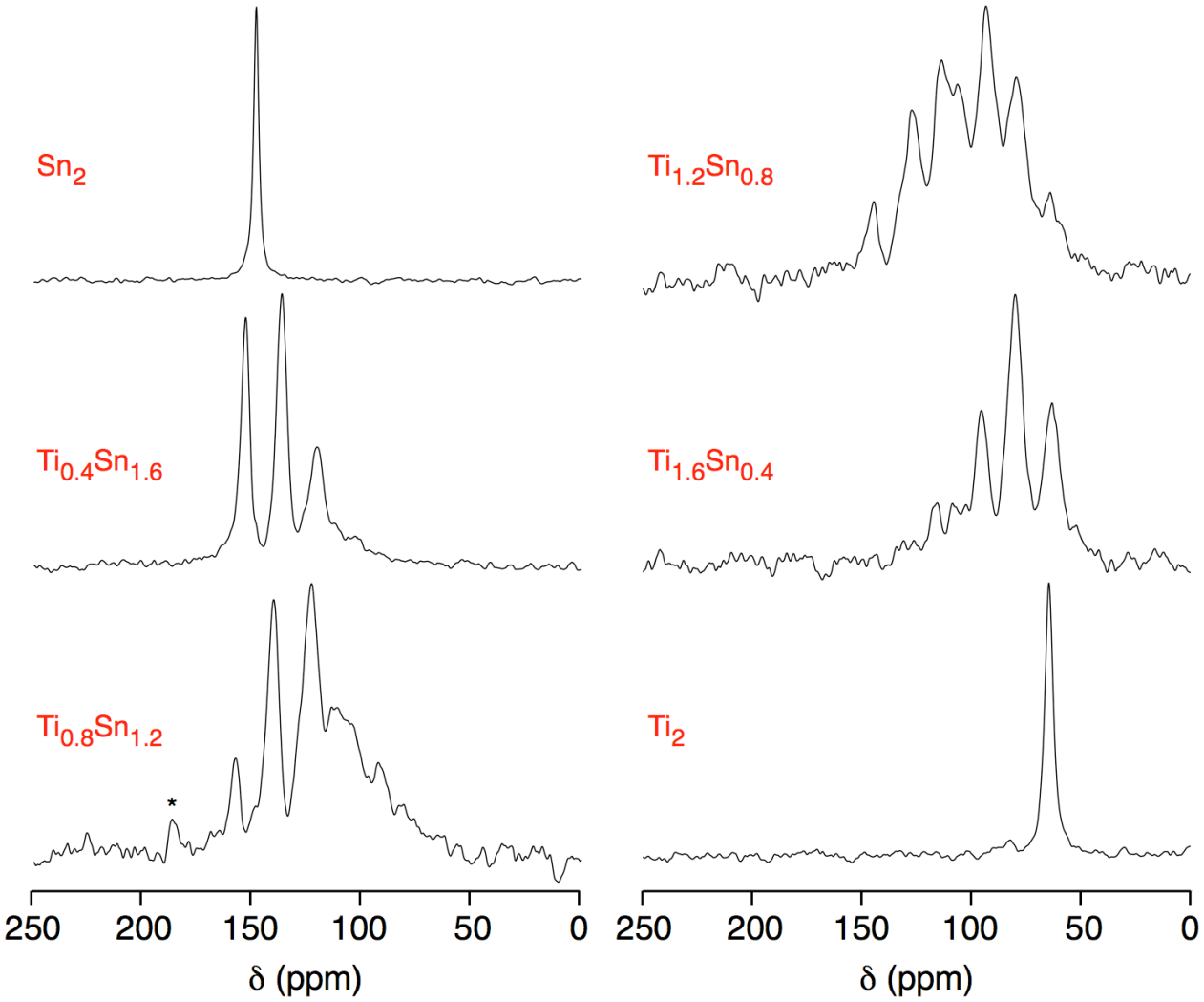
- Pyrochlore: $A_2B_2O_7$
- Ordered superstructure of fluorite with 1/8 O removed in an ordered manner (Fd–3m)
- 2 cation sites
  - ^{VIII}A 2+, 3+
  - ^{VI}B 5+, 4+
- $Y_2(Sn,Ti)_2O_7$ solid solution

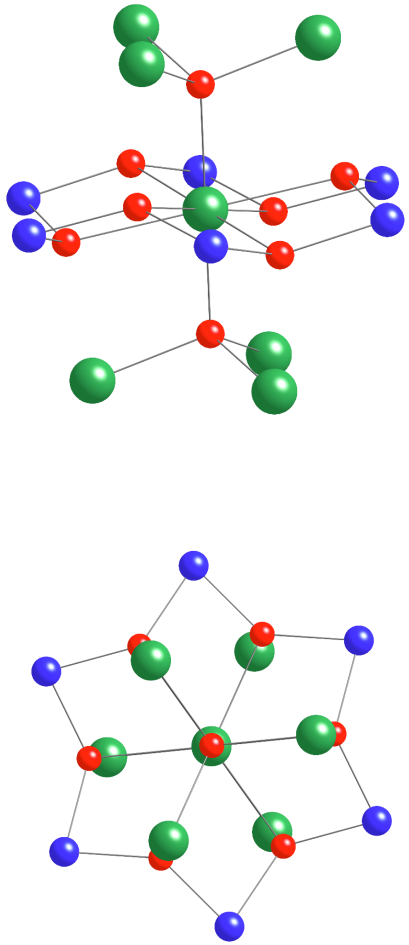
^{89}Y NMR

- Spin quantum number I = 1/2
- 100% natural abundance
- Large chemical shift range

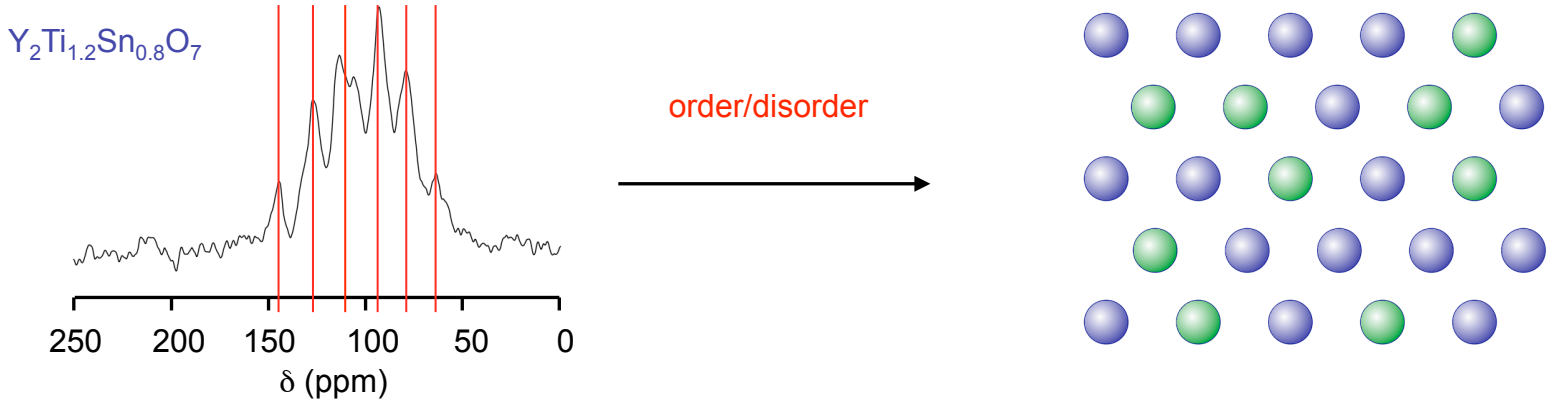
- Low gyromagnetic ratio (1/16th of ^{1}H)
- Long T_1 relaxation times (~1000 s)
- ^{89}Y background in rotor

Pyrochlores: ^{89}Y NMR





Pyrochlores: analysis



- Assume that Y is found only on the ^{VIII}A site

  What would the chemical shift be if Y was on the B site?

- Assume that the chemical shift determined only/primarily by number of Sn/Ti

  How does the shift change as a NNN Sn/Ti is substituted?

- Assume the spatial arrangement has negligible effect on the chemical shift

  Is there a shift difference between the different arrangements?

- Assume that any longer range effects are small/negligible

  For the same NNN arrangement how different can the chemical shift be?

Pyrochlores: calculations

CASTEP

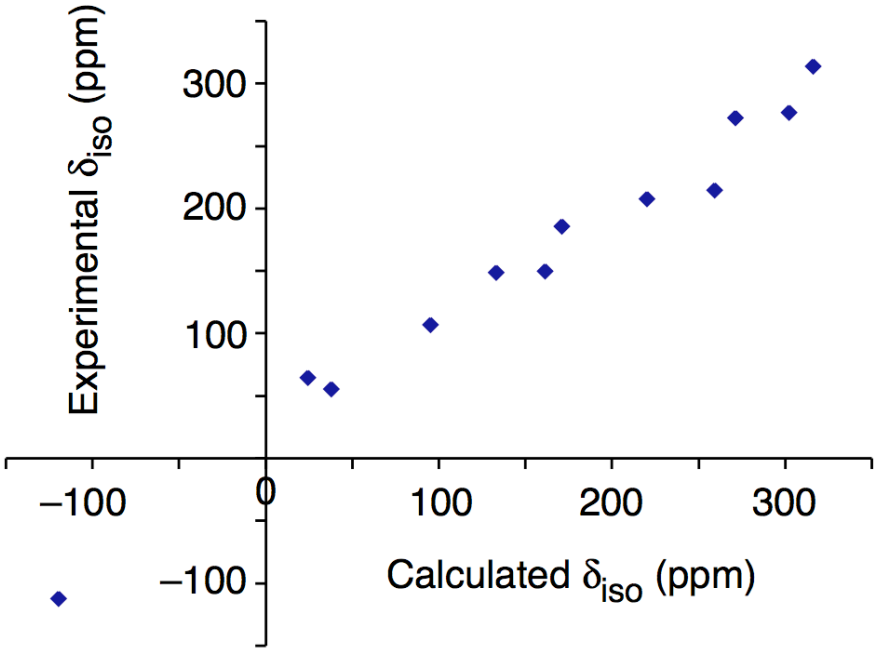
GGA/PBE
Ultrasoft pseudopotentials
50 Ry cut-off energy
0.04 $Å^{-1}$ k-point spacing

Y_2O_3, $Y_2Ti_2O_7$, $Y_2Sn_2O_7$, $YAlO_3$, Y_2O_2S, YF_3, α-$Y_2Si_2O_7$ and β-$Y_2Si_2O_7$

Referenced to Y_2O_3

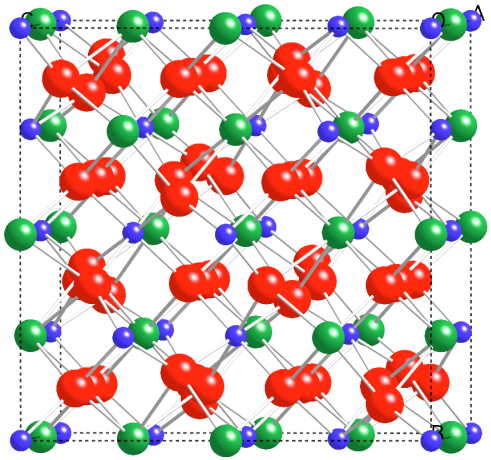
For pyrochlores 88 atoms in unit cell

NMR calculation: 16 processors for 10 hours



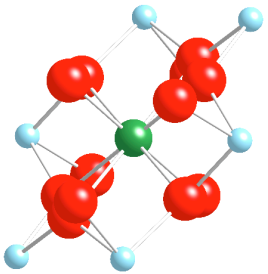
	^{VIII}Y A site	^{VI}Y B site
$Y_2Sn_2O_7$	134 –184 ppm	326 ppm
$Y_2Ti_2O_7$	2-55 ppm	221 ppm

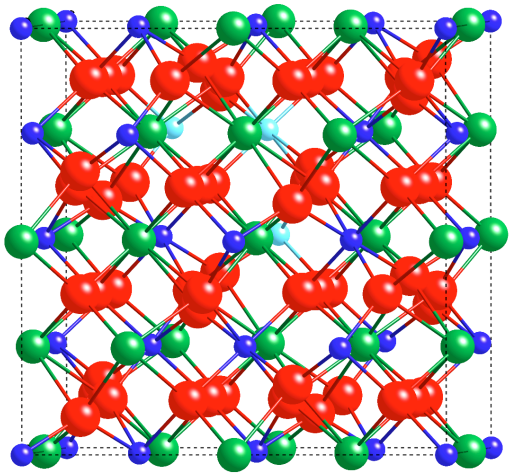
Pyrochlores: approach



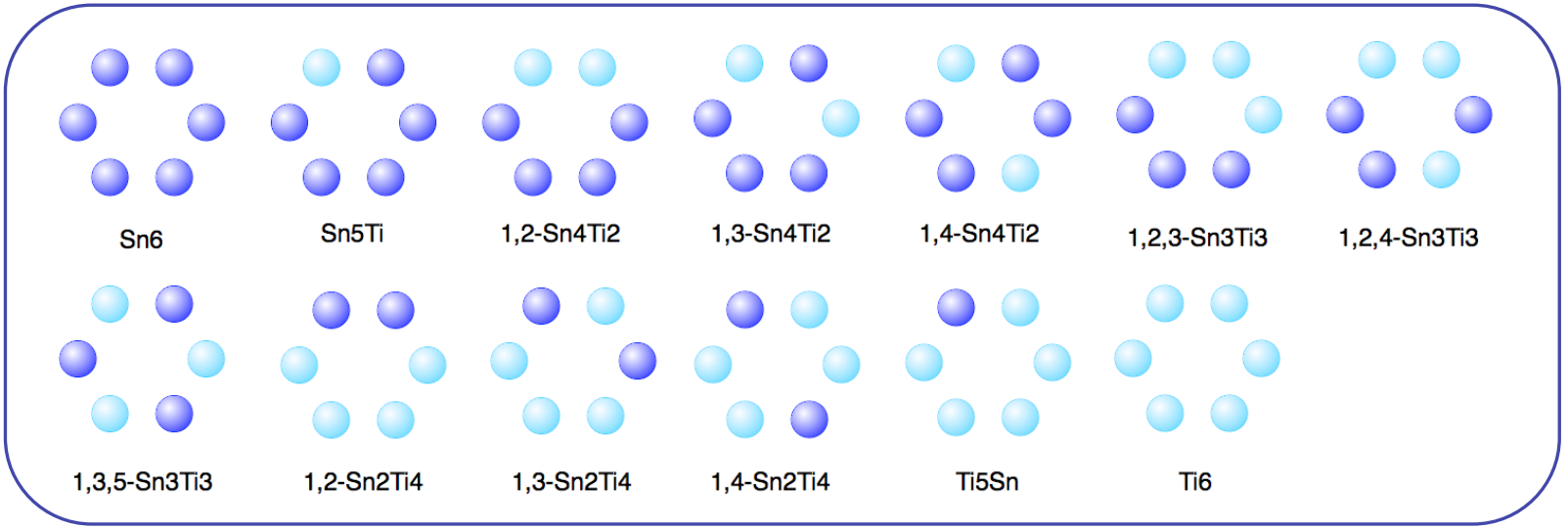
$Y_2Sn_2O_7/Y_2Ti_2O_7$

"embed" cluster into unit cell

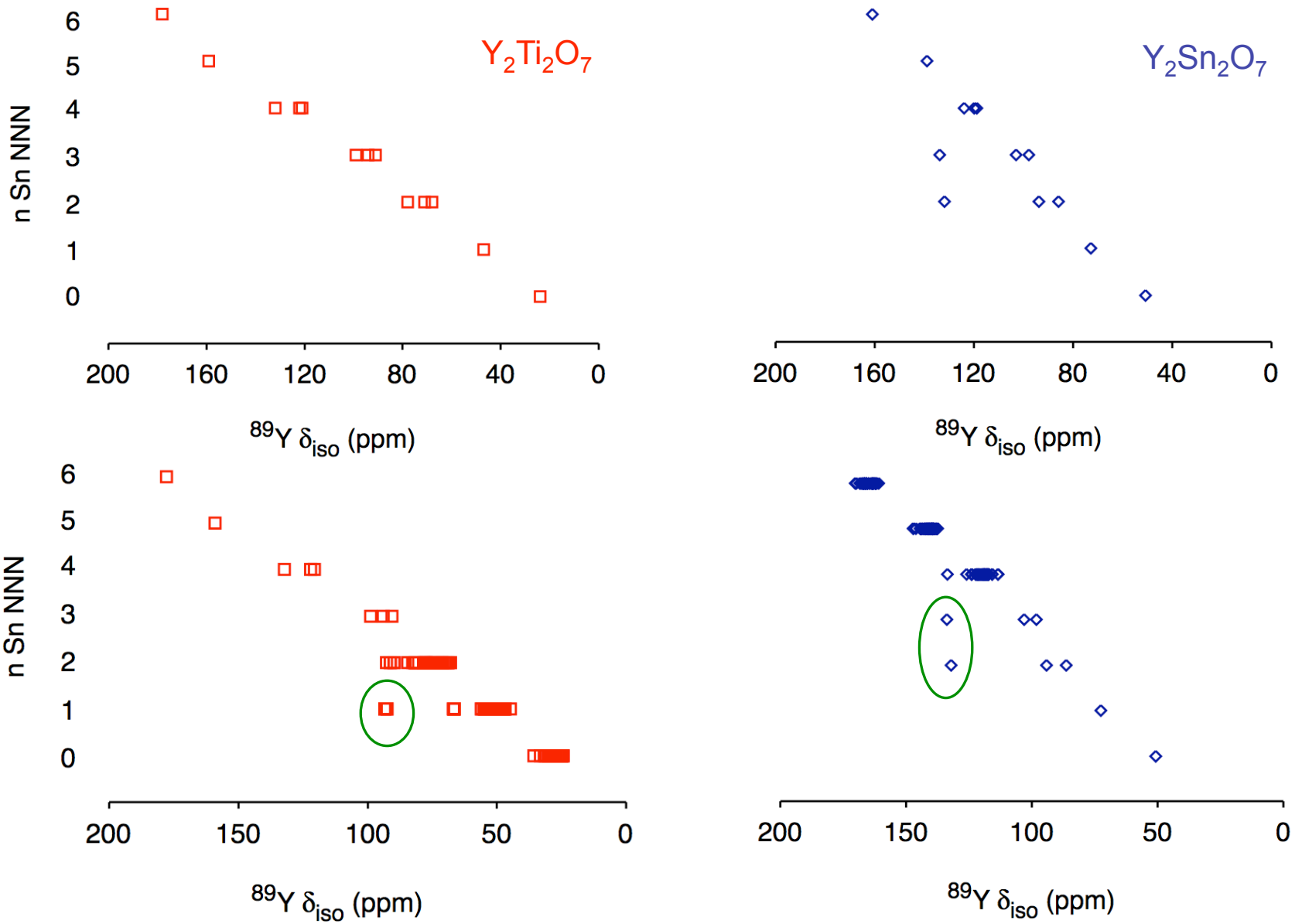




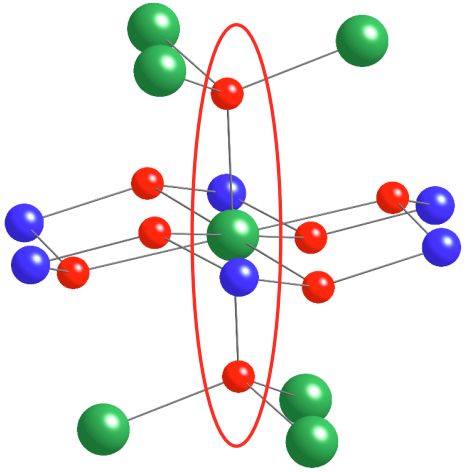
geometry optimisation / NMR



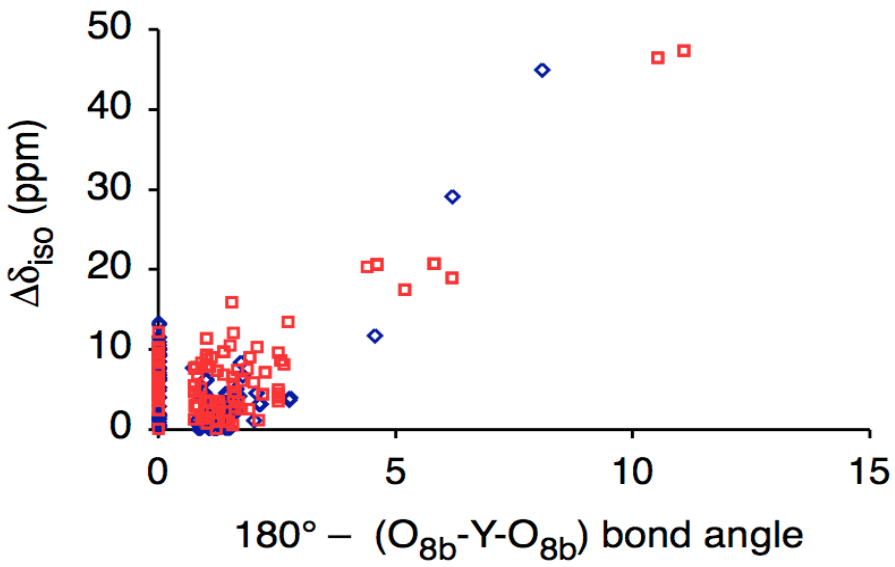
Pyrochlores: results

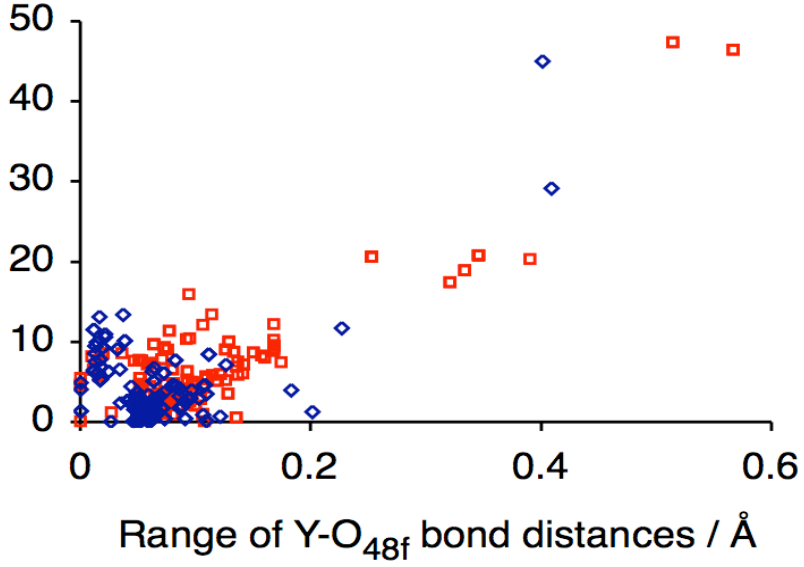


Pyrochlores: results



- Deviation of 6-10° away from linear for O-Y-O bond angle
- Lengthening of a number of the Y-O bonds



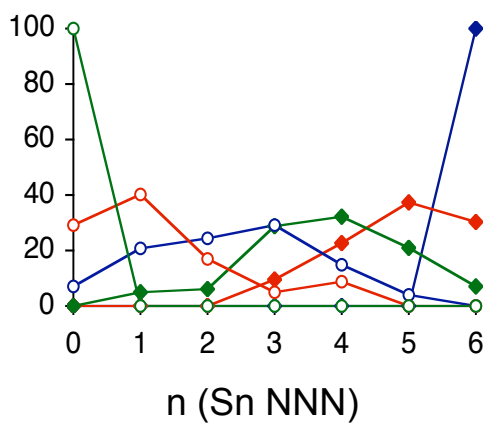


Pyrochlores: results

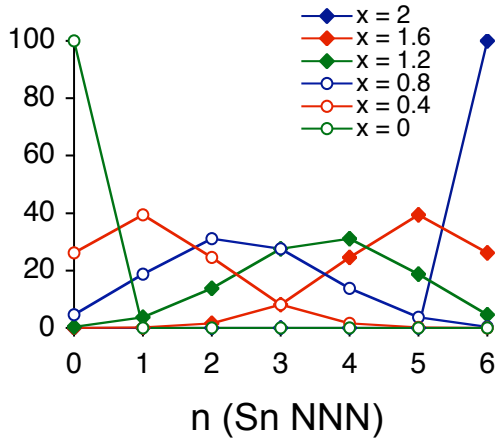
- Why do these distortions occur?
  - *Lattice fixed to be $Y_2Sn_2O_7$ or $Y_2Ti_2O_7$*
  - *Local substitution of different size cations*
  - *Substitutions reproduced periodically - need to try supercells*

- Do the anomalous shifts have any impact upon the experimental analysis?
  - *Over 500 ^{89}Y shifts calculated using both $Y_2Sn_2O_7$ and $Y_2Ti_2O_7$*
  - *Anomalous shifts present in <3% of cases*

Experiment



Theory



$P(n\ Sn\ NNN) = \Omega\ p^6\ (1 - p)^{6-n}$

Random distribution of Sn and Ti on the pyrochlore B sites

4. Disorder and dynamics in humites

Experiment

Ashbrook, Berry and Wimperis, J. Am. Chem. Soc. ***123****, 6360 (2001).*

Ashbrook, Antonijevic, Berry and Wimperis, Chem. Phys. Lett. ***364****, 634 (2002).*

Experiment and Calculation

Griffin, Wimperis, Pickard, Berry and Ashbrook, J. Phys. Chem. C ***113****, 465 (2009).*

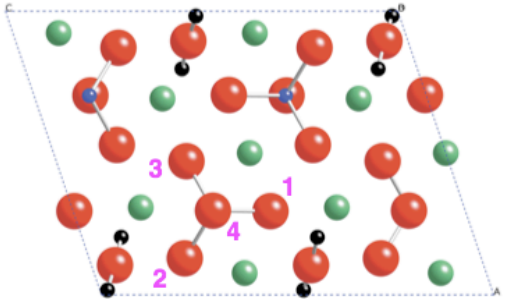
Humite minerals

- Proposed as possible models for defect H incorporation into mantle silicates (e.g., Mg_2SiO_4), but synthesized at relatively low pressure
- Humite minerals have the general formula

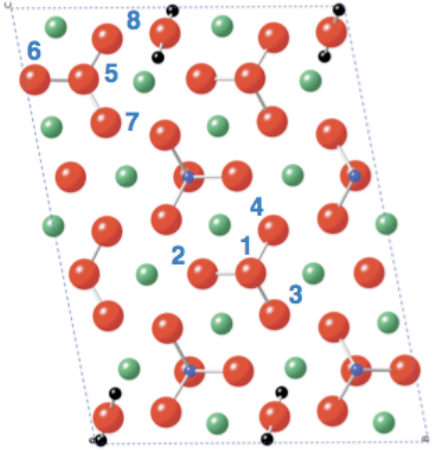
$$nMg_2SiO_4.Mg(OH)_2$$

- where n = 1 (norbergite), 2 (chondrodite), 3 (humite) and 4 (clinohumite)

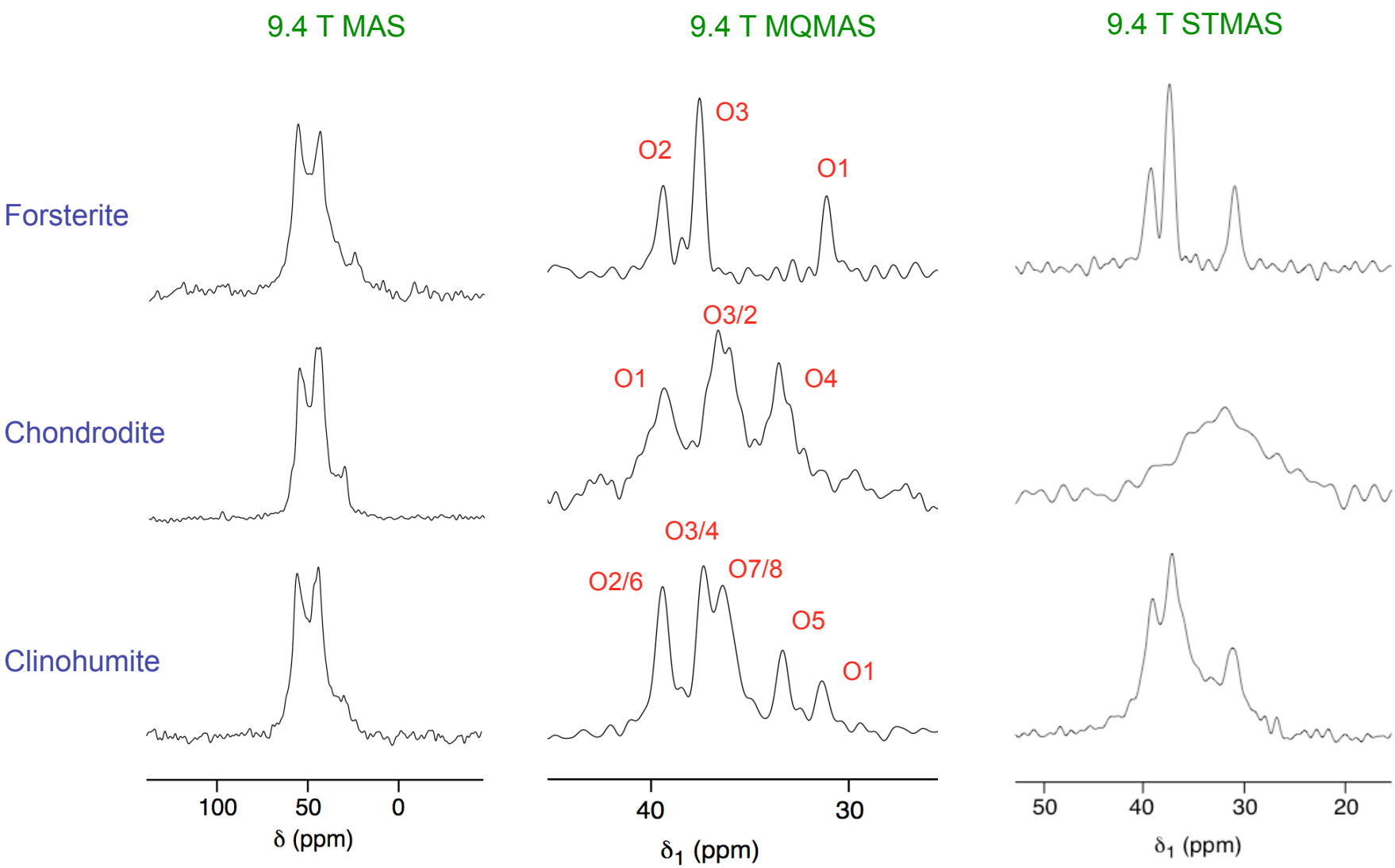
Chondrodite



Clinohumite

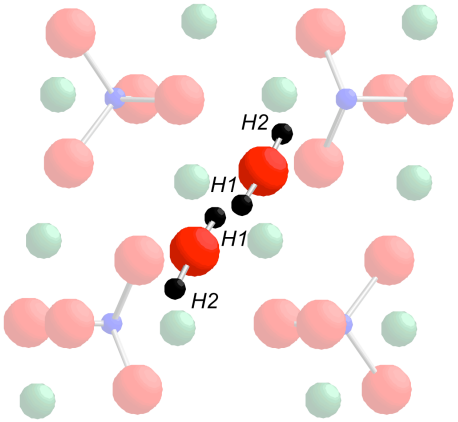


Humite minerals: ^{17}O NMR



Humite minerals: approach

- Two ^{1}H sites H1 and H2 which are 50% occupied by diffraction
- Two nearby H1 cannot be occupied simultaneously



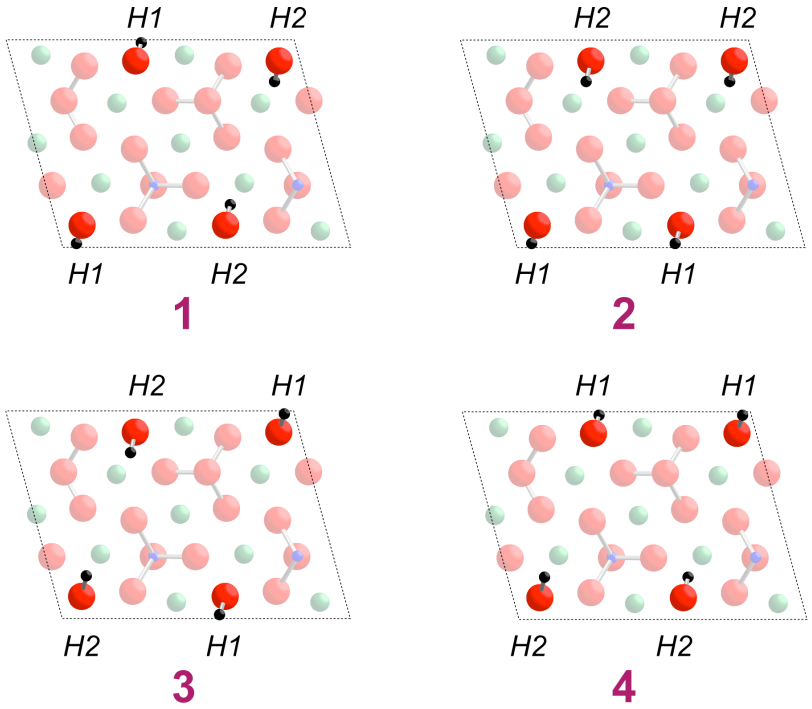
CASTEP

38/66 atoms in unit cell

GGA/PBE
Ultrasoft pseudopotentials
50 Ry cut-off energy
0.05 $Å^{-1}$ k-point spacing

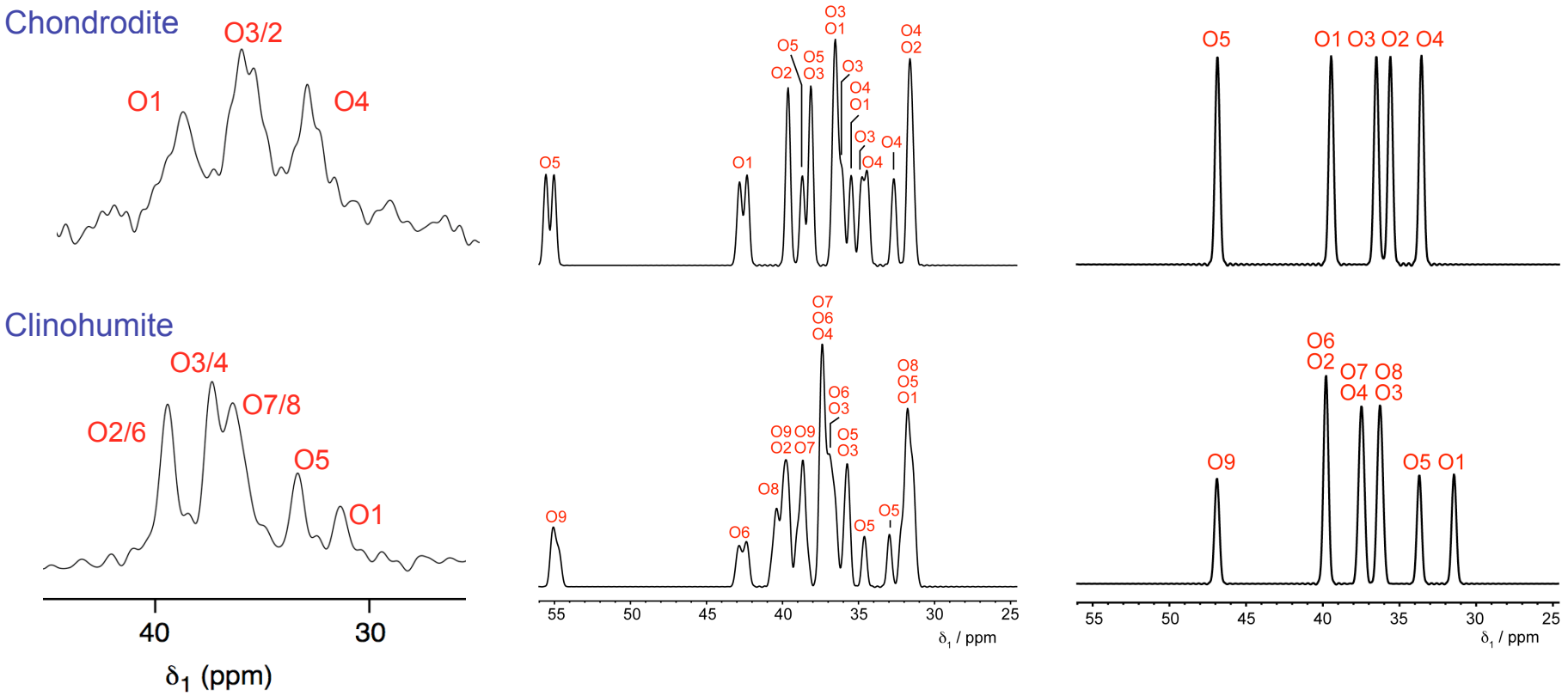
NMR calculation: 16 processors for up to 1 day

Referenced to forsterite



Humite minerals: calculations

9.4 T MQMAS

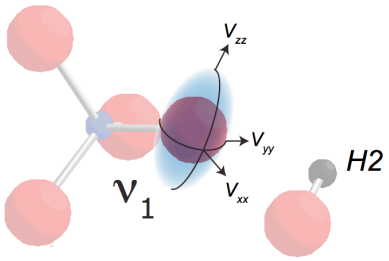


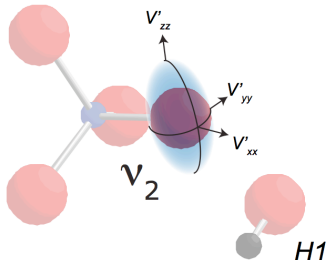
Humite minerals: calculations

- ^{1}H dynamics cause a change in the magnitude/orientation of nearby ^{17}O quadrupolar tensors
- This will cause a change in the quadrupolar splitting for any one crystallite, $\Delta\nu^{J}$

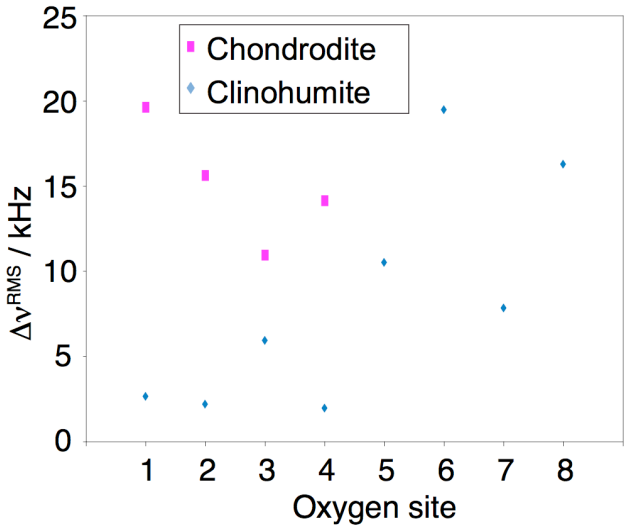
$$\nu_1 = \frac{\nu_Q^{PAS}}{2}\left(3\cos^2\beta_1 - 1 + \eta_Q \sin^2\beta_1 \cos 2\gamma_1\right)$$

$$\nu_2 = \frac{\nu'^{PAS}_Q}{2}\left(3\cos^2\beta_2 - 1 + \eta'_Q \sin^2\beta_2 \cos 2\gamma_2\right)$$

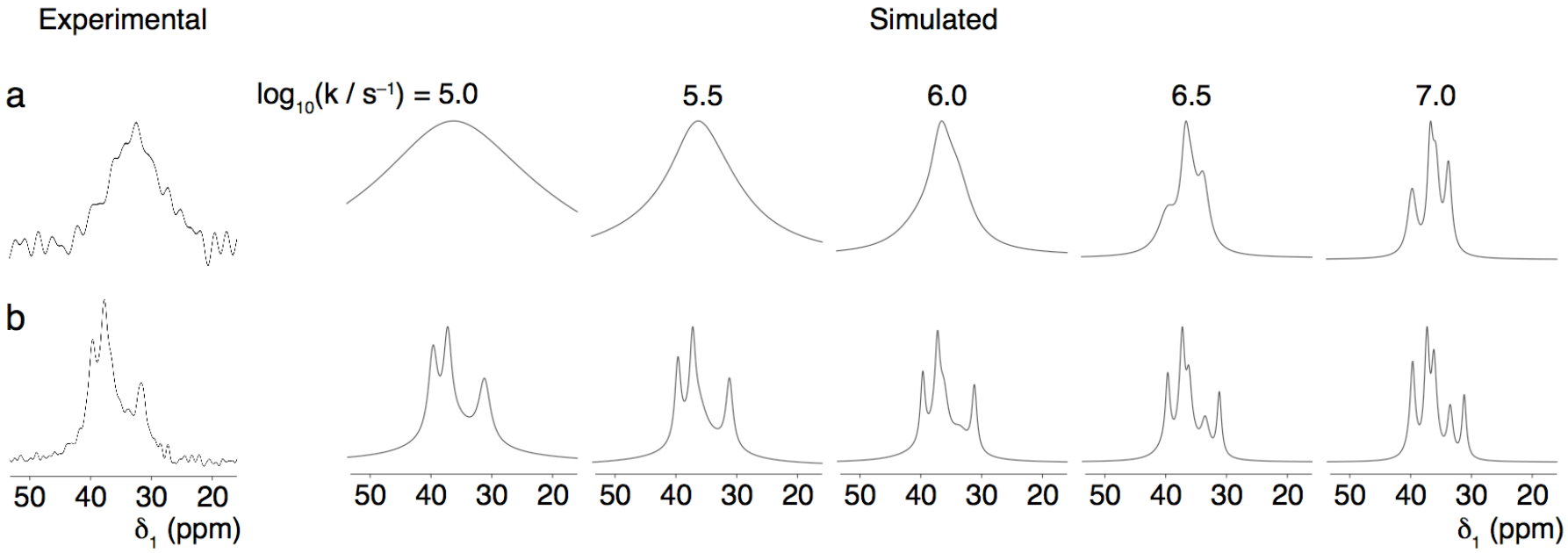




- If the rate constant is comparable to $\Delta\nu^{J}$ this will cause motional broadening in any experiment affected by the first-order quadrupolar interaction
- Broadening of STMAS not MQMAS spectra



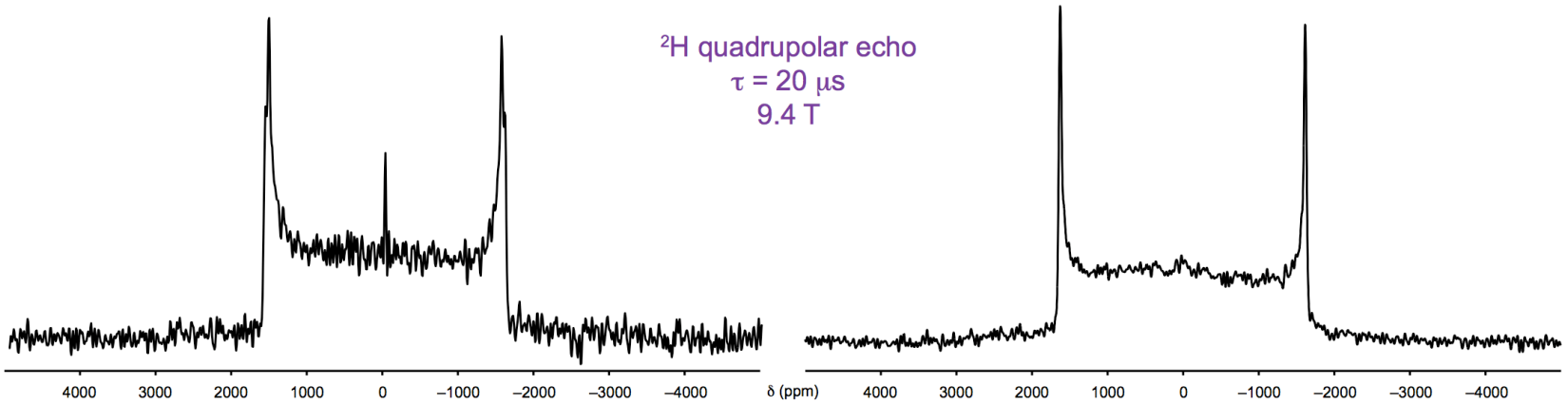
Humite minerals: calculations



- Good agreement when $\log_{10}(k / s^{-1}) \sim 5.5$
- Estimate rate constant for H1 - H2 interchange $k \sim 3.2 \times 10^5\ s^{-1}$

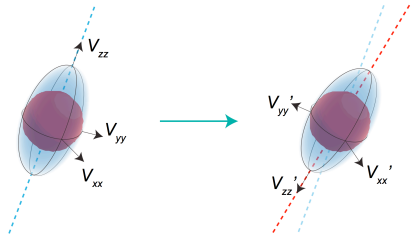
Humite minerals: ^{2}H NMR

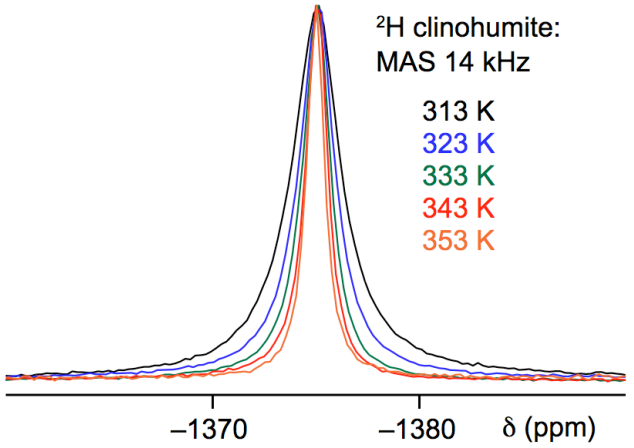
^{2}H NMR of clinohumite (9.4 T)



CASTEP

	δ_{iso} (ppm)	Δ_{CSA} (ppm)	η_{CS}	C_Q / kHz	η_Q
H1	2.1	11.85	0.110	276.3	0.027
H2	1.4	9.66	0.162	272.3	0.048

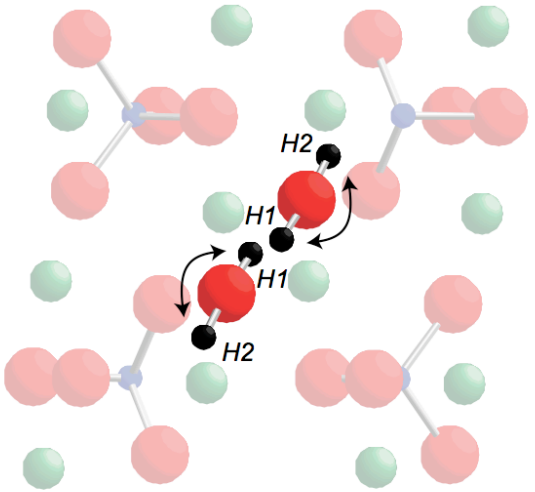




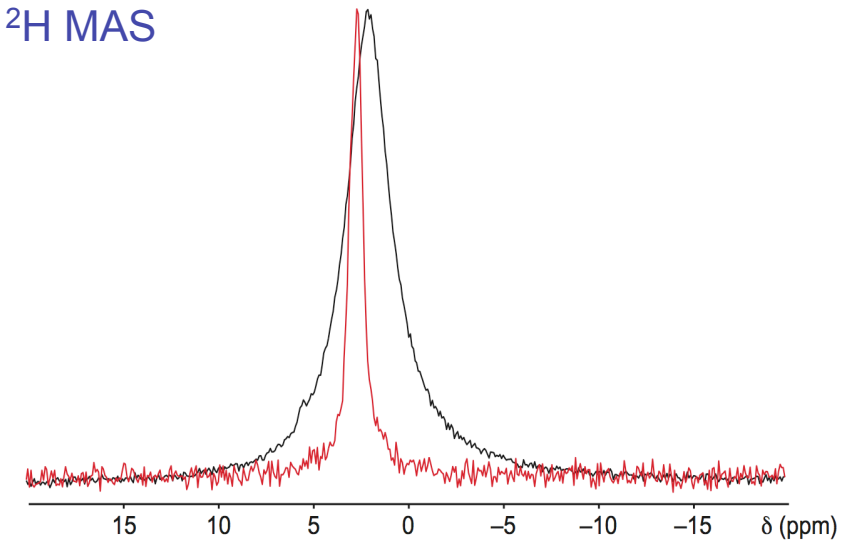
- Plot of ln ($\Delta\nu_{1/2}$) against 1/T gives activation energy of ~26 kJ mol^{-1}

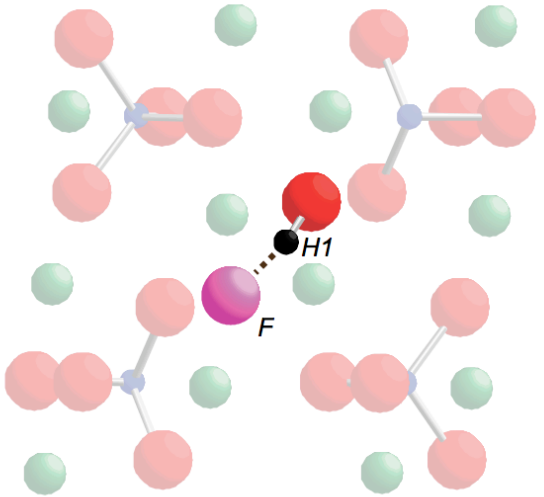
Humite minerals: substitutions

- In nature, humite minerals can have substantial amounts of F or Ti incorporated
- By diffraction, only a single ^{1}H species is observed in substituted humites
- Hydrogen bonding restricts ^{1}H to the H1 site



^{2}H MAS





Humite minerals: ^{19}F NMR

^{19}F MAS (30 kHz) NMR of clinohumite (14.1 T)

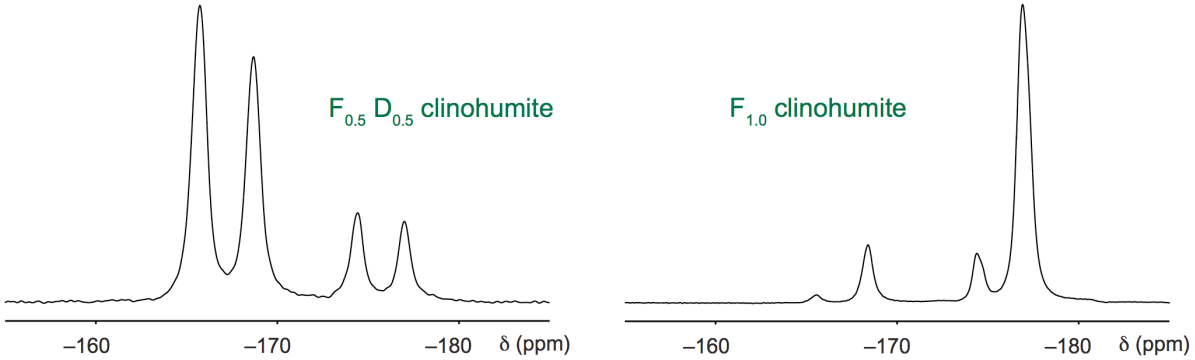
CASTEP

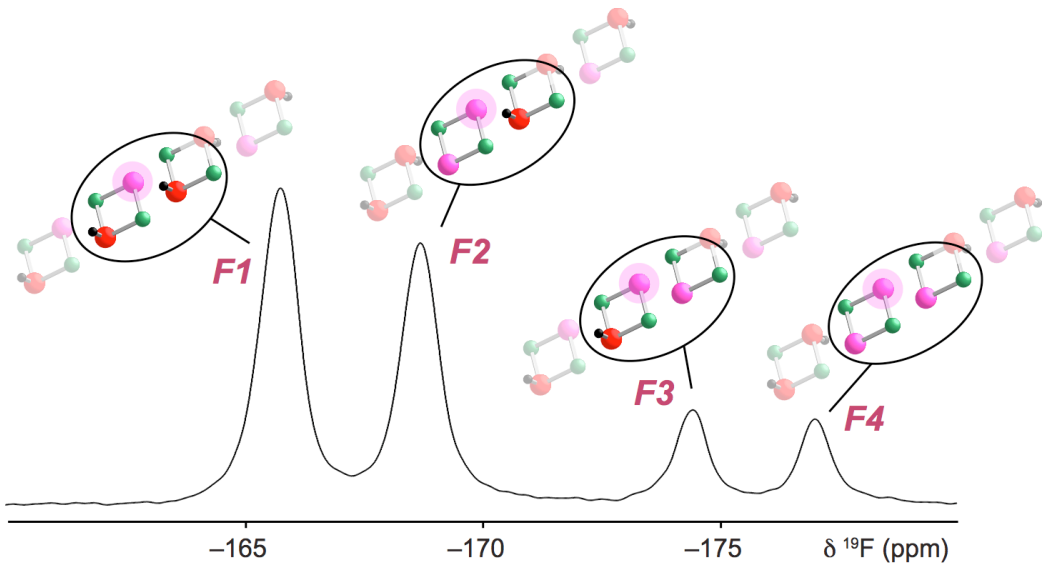
Up to 128 atoms in unit cell

GGA/PBE
Ultrasoft pseudopotentials
50 Ry cut-off energy
0.04 Å^{-1} k-point spacing

NMR calculation: 16 processors for up to 3 days

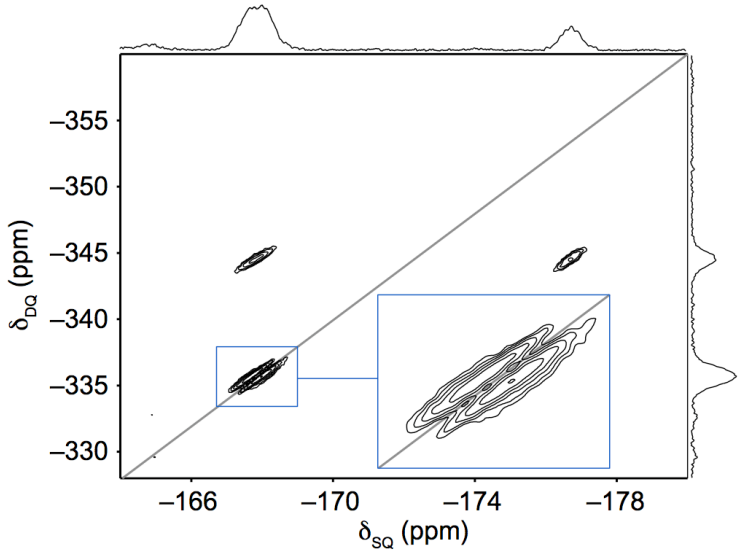
Referenced to set of simple inorganic fluorides





Humite minerals: ^{19}F NMR

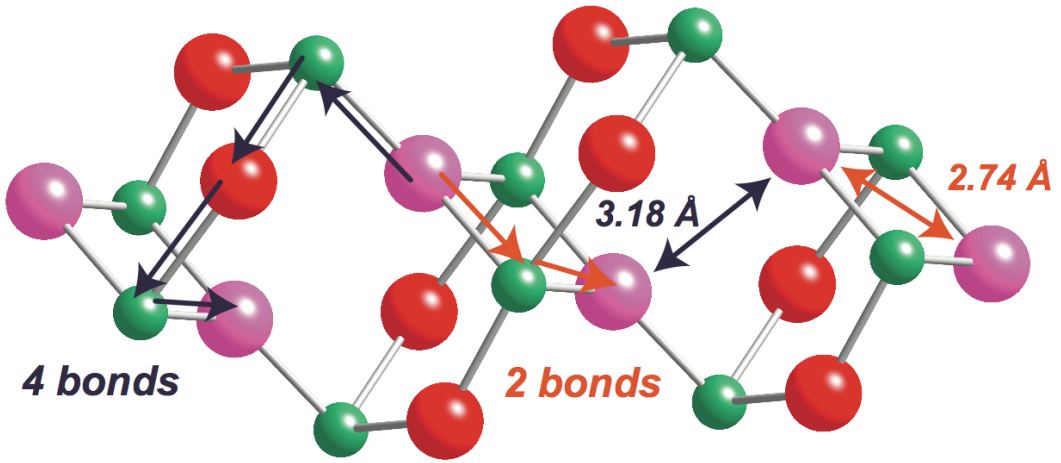
^{19}F refocussed INADEQUATE MAS (30 kHz) spectrum of clinohumite (14.1 T)



Use two-dimensional correlation experiments to attempt to support assignment

Indicates a through-bond interaction

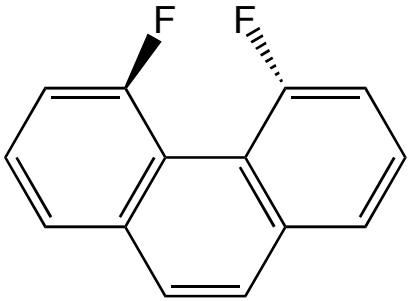
- Is the “INADEQUATE” transfer via the J coupling?



Humite minerals: ^{19}F NMR

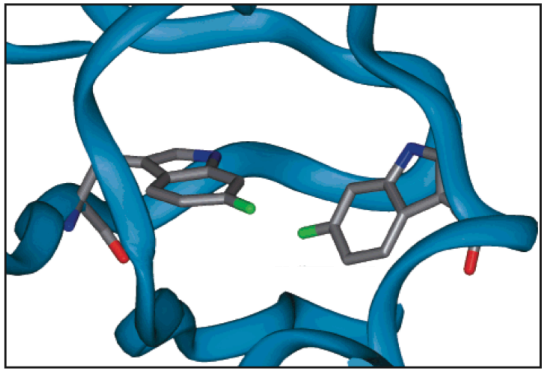
- Is the “INADEQUATE” transfer via the J coupling?

“Through space” J couplings known in the literature



~170 Hz interaction observed in solution between two ^{19}F in phenanthrene derivatives which are 5 bonds apart
*(Mallory et al. J. Am. Chem. Soc. **122**, 4108 (2000))*

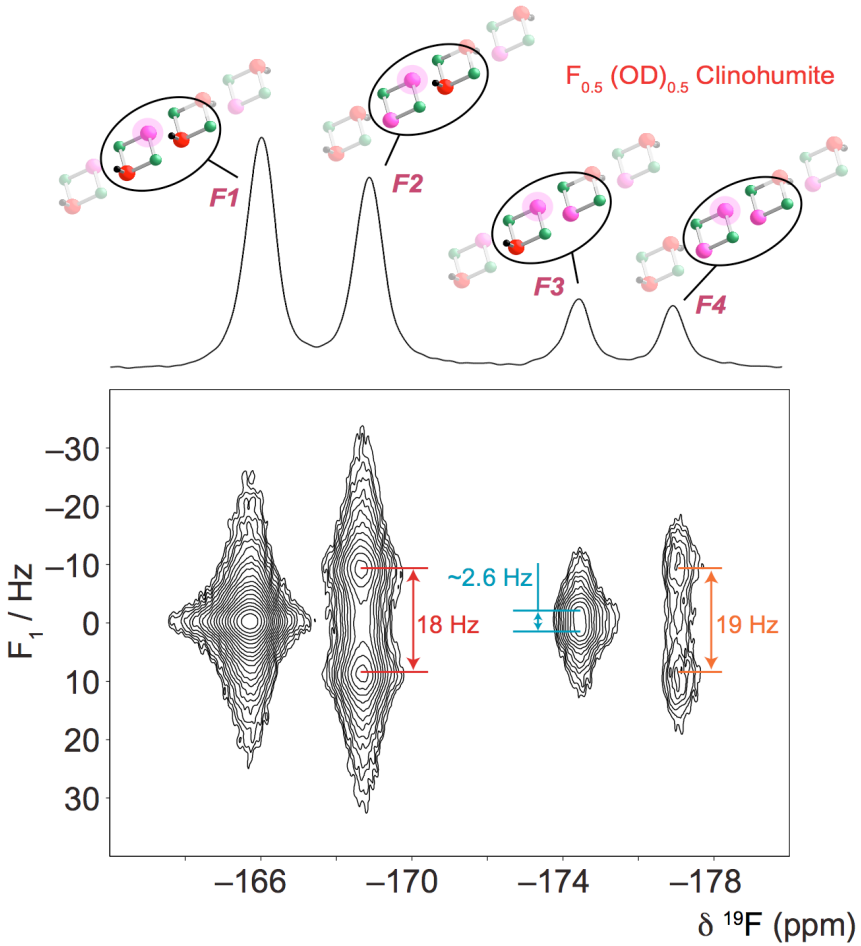
17 Hz interaction observed between two ^{19}F in reductase complex which are 398 bonds apart
*(Arnold et al. J. Am. Chem. Soc. **122**, 12164 (2000))*



Involves direct overlap of the F lone pairs - ab initio calculations
*(Bryce and Wasylishen, J. Molec. Struc. **602-603**, 463 (2002))*

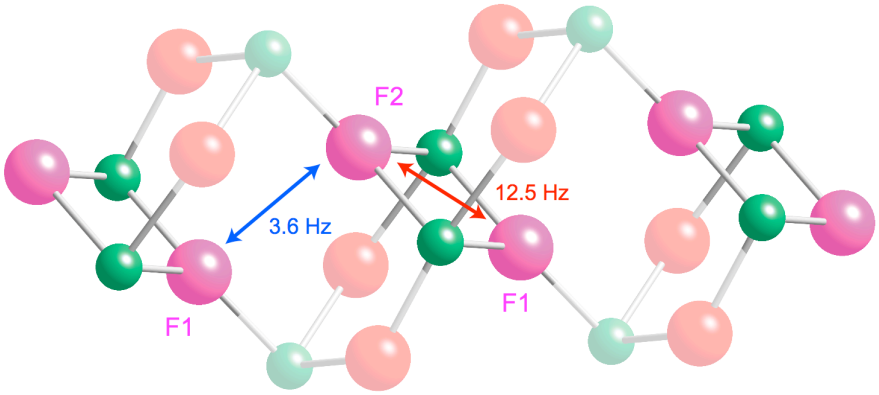
Humite minerals: ^{19}F NMR

^{19}F J-resolved experiment (14.1 T, 30 kHz)



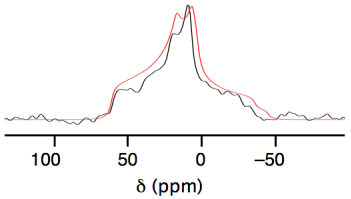
Preliminary CASTEP calculations using a 3 × 1 × 1 supercell produced values of 12.5 and 3.6 Hz

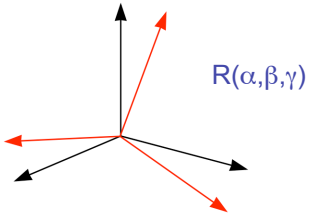
Note large J anisotropy predicted (~225 and 41 Hz)

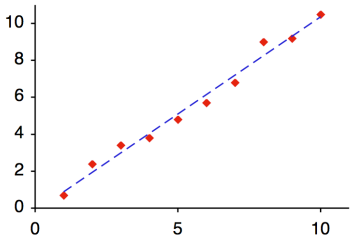


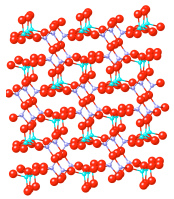
Why calculate NMR parameters?

- Spectral assignment
- Spectral interpretation
- Confirmation of experimental NMR parameters
- Additional information (anisotropy, tensor orientation, etc.,)
- Spectral prediction
- Assessment of experimental feasibility
- Flexible way to study the dependence of NMR parameters upon structure
- Testing of structural models for materials with unknown structure
- More complex properties of solids
  - Disorder
  - Dynamics









??