NMR in Mineralogy

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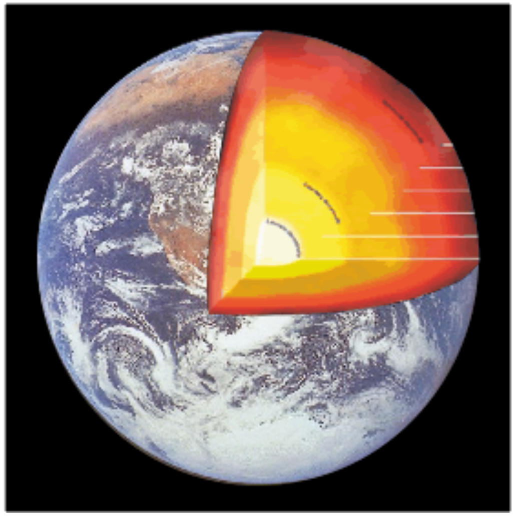
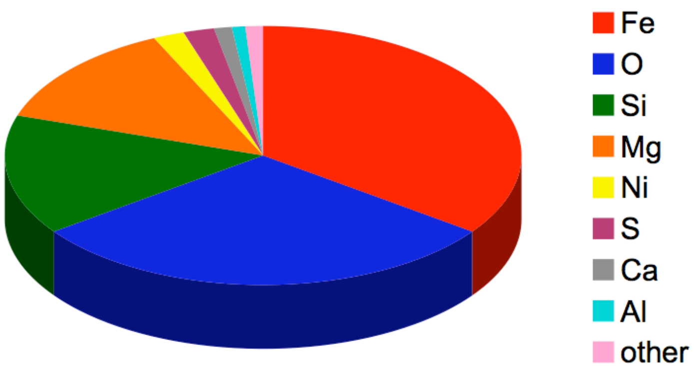
EaStCHEM

Structure of the Earth

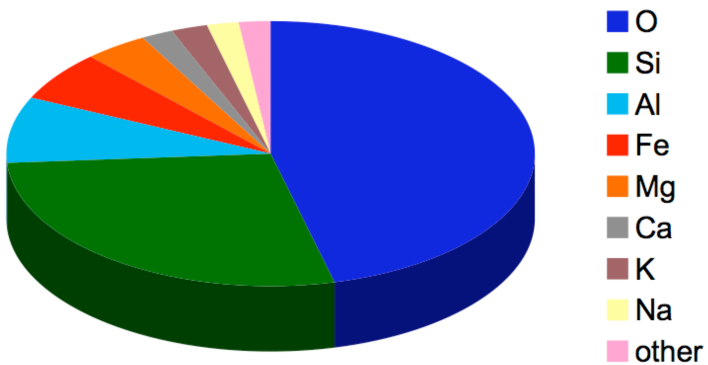


- Study of minerals is important for determining the physical and chemical properties of the Earth
- O and Si are the most abundant elements on Earth
- Strength of the Si-O bond
- Majority of rocks are composed of silicates
- Primarily aluminosilicates in the crust and magnesium silicates in the inner Earth

Whole Earth



Earth's crust



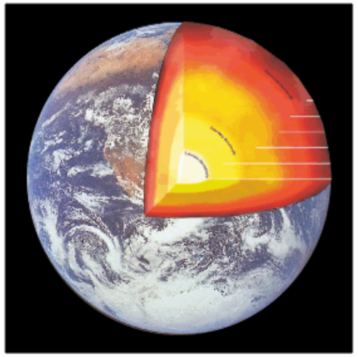
Role of NMR

- NMR provides a probe of the atomic scale environment

- Confirmation of space groups and structures
- Complex structure and phase assemblages in natural materials
- Order/disorder
- Phase transitions
- Reactivity and hydration

Natural vs synthetic?

- Many minerals have achieved their physical state over geological time (millions of years)
- Complicated mixture of phases and compounds
- Extremes of pressures and temperatures in the Earth
- Presence of Fe in many natural minerals
- Exact composition and structure of deep Earth unknown
- Difficulty of obtaining samples with known history
- Cost and difficulty of isotopic enrichment



Role of NMR

- ^{29}Si I = 1/2 4.7% 79.4 MHz (9.4 T)
- Present in all silicate minerals, most widely studied nucleus

- ^{27}Al I = 5/2 100% 104.3 MHz
- Present in aluminosilicates, good chemical shift range, important also in the deep Earth

- ^{17}O I = 5/2 0.037% 54.3 MHz
- Most abundant element on Earth, second-order quadrupolar broadening, cost and ease of isotopic enrichment

- ^{25}Mg I = 5/2 10% 24.5 MHz
- Important in the inner Earth, large second-order quadrupolar broadening, low γ, very costly to enrich

Role of NMR

- ^{31}P I = 1/2 100% 161.3 MHz
- Present in phosphate minerals, large chemical shift range

- ^{43}Ca I = 7/2 0.135% 26.9 MHz
- Present in crustal minerals and minor component in inner Earth, small quadrupolar broadening, low γ

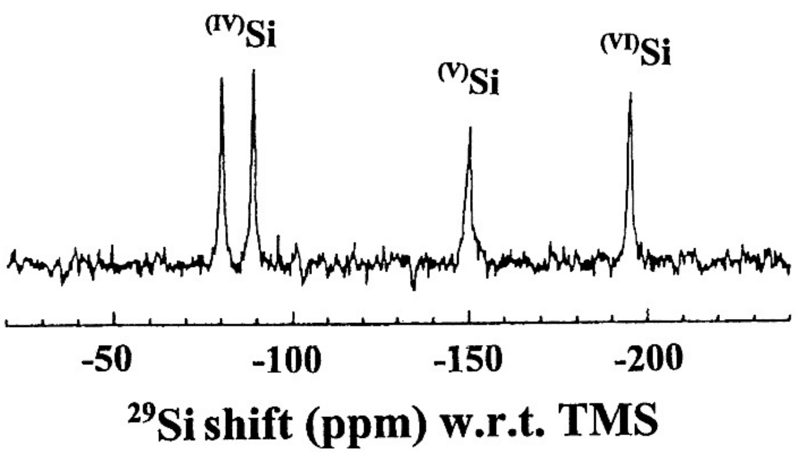
- ^{11}B I = 3/2 80.1% 128.4 MHz
- Present in borate minerals, glasses and melts

- ^{1}H I = 1/2 99.99% 400.13 MHz
- ^{2}H I = 1/2 0.01% 61.4 MHz
- Important in hydration of crustal and deep Earth materials, study of motion

^{29}Si NMR

- ^{29}Si is the most widely studied nucleus of mineralogical interest
- Systematic variation of chemical shift with coordination number

high-pressure $CaSi_2O_5$



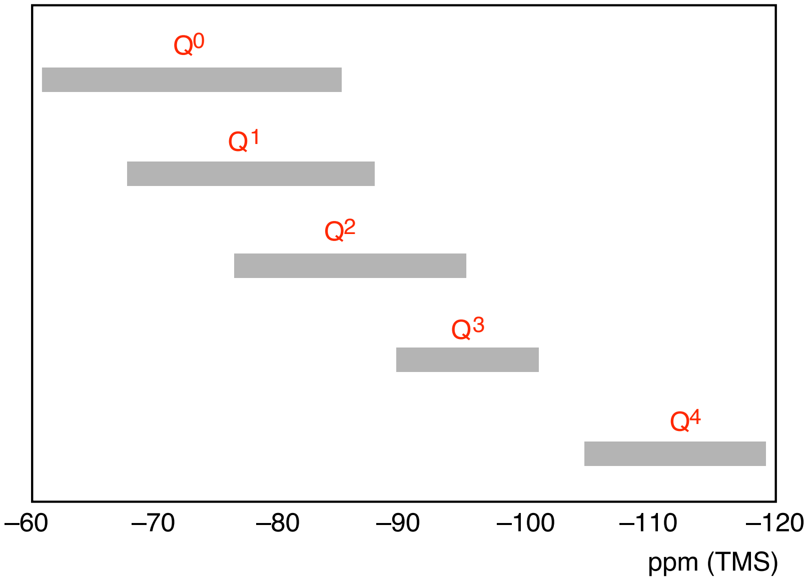
6 CN	–180 to –190 ppm
5 CN	~ –150 ppm
4 CN	–60 to –120 ppm

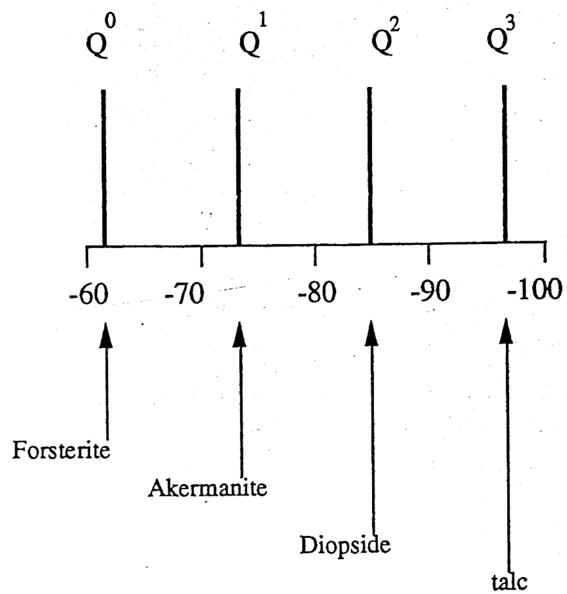
Stebbins et al., Geophys. Res. Lett. ***26****, 2521 (1999)*

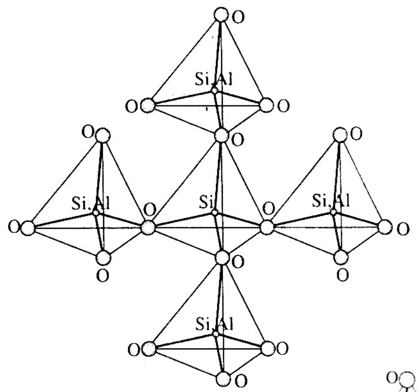
- Four coordinate Si usually preferable at ambient pressure
- Higher coordinations more prevalent in high-pressure phases

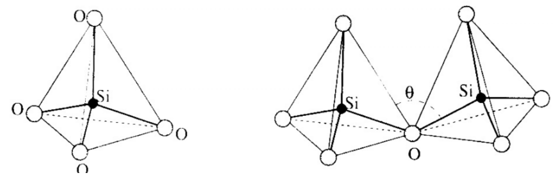
^{29}Si NMR

- Strong correlations of chemical shift with “polymerisation”





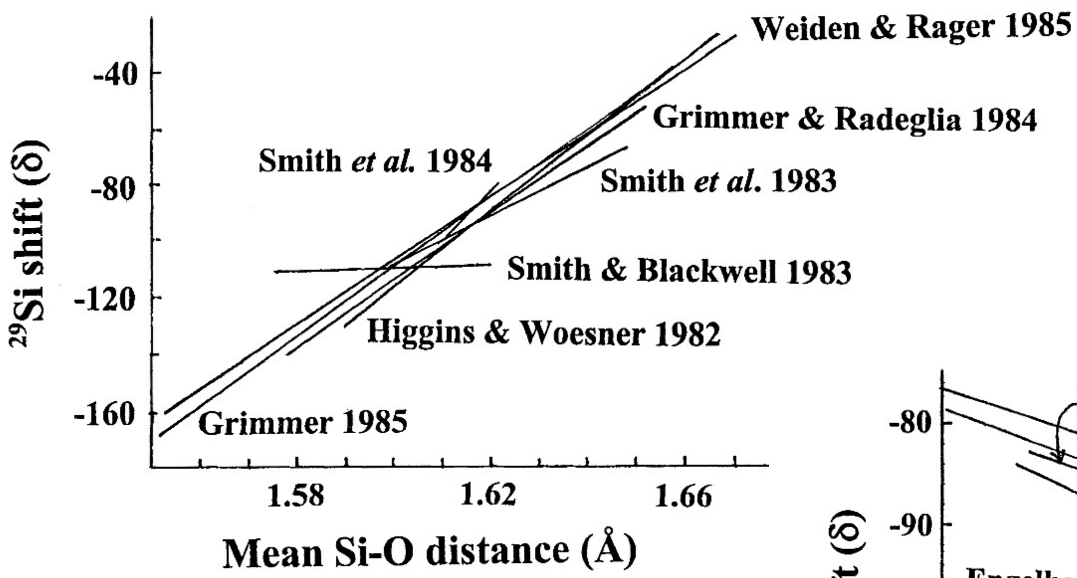


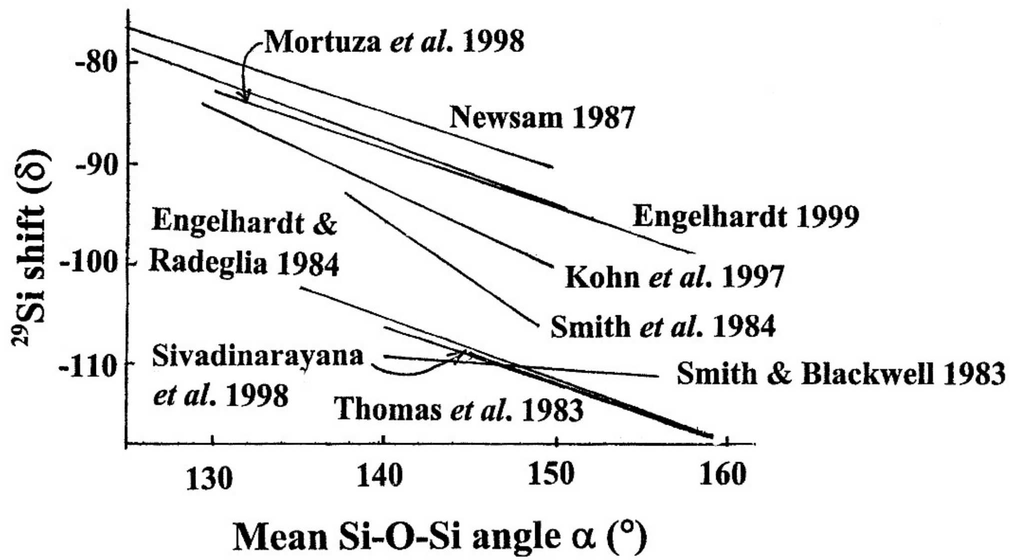


Q^0	ortho or neso silicates
Q^1	di or soro silicates
Q^2	cyclo/chain or ino silicates
Q^3	sheet or phyllo silicates
Q^4	framework or tecto silicates

^{29}Si NMR

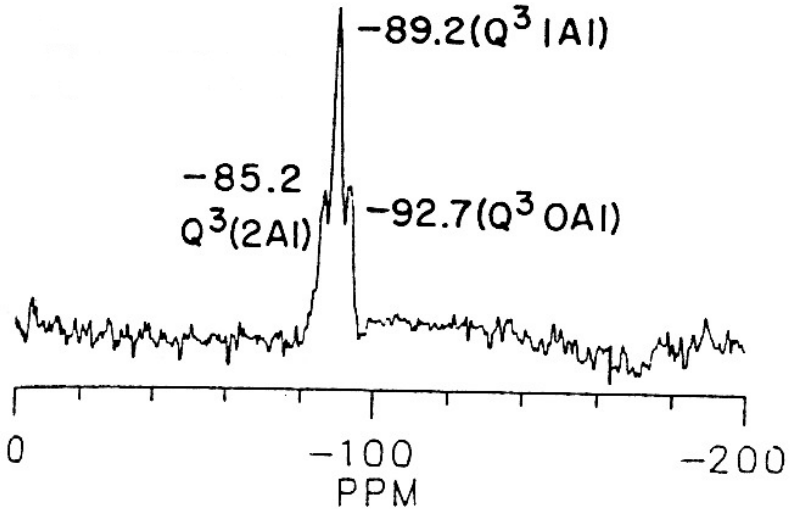
- Much work on "empirical relationships" between structure and NMR parameters





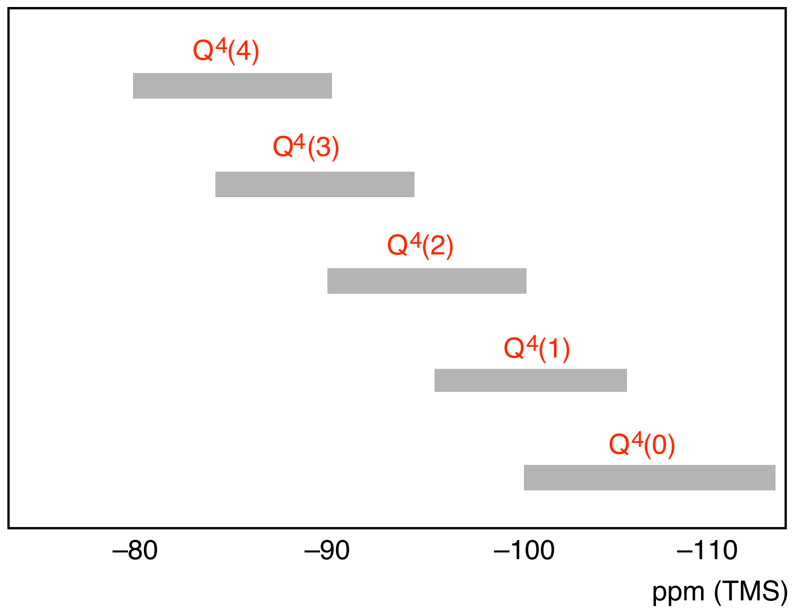
^{29}Si NMR

- As with zeolites, ^{29}Si NMR can be used to study/determine Al/Si ordering in aluminosilicate minerals



^{29}Si MAS NMR of phlogopite

Kirkpatrick, Rev. Mineral. ***18****, 341 (1989)*



- In general, Lowenstein's rule (precluding Al-O-Al linkages) holds for phases formed at low temperatures

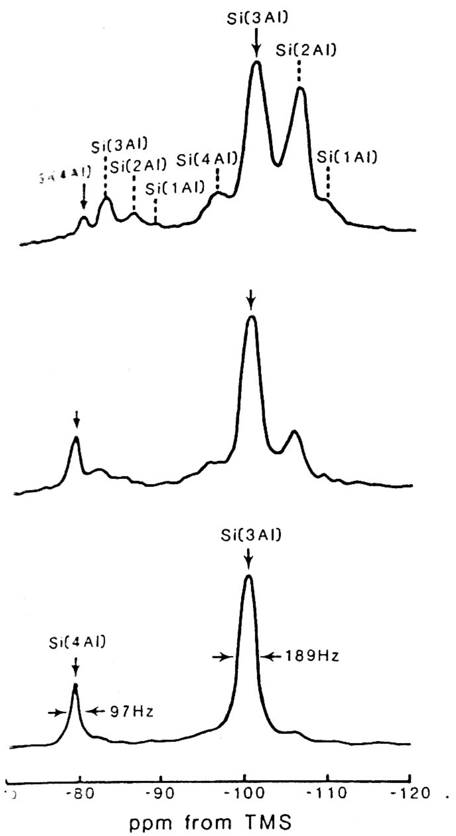
^{29}Si NMR

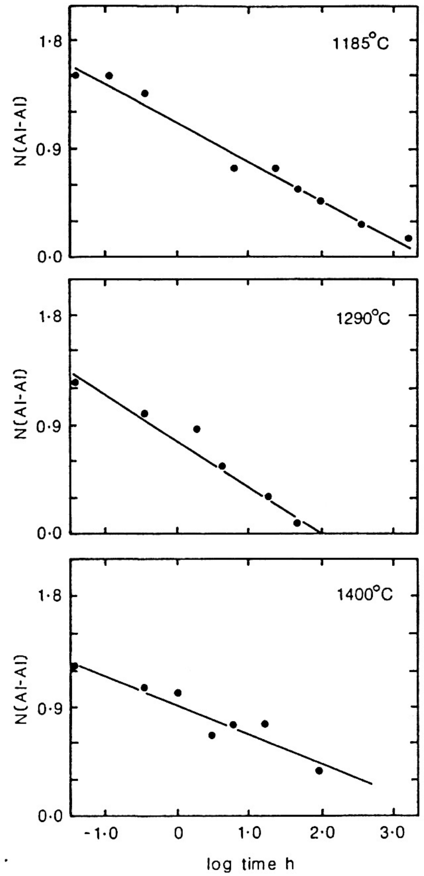
- In contrast to phases formed at low temperatures, phases crystallized directly from melts or glasses have Al/Si distributions which contain Al-O-Al linkages
- The number of these decrease as samples are annealed at high T

^{29}Si MAS NMR of cordierite ($Mg_2Al_4Si_5O_{18}$)

substantial disorder at shorter annealing times

two peaks Q^4(4,3) Al in fully annealed sample



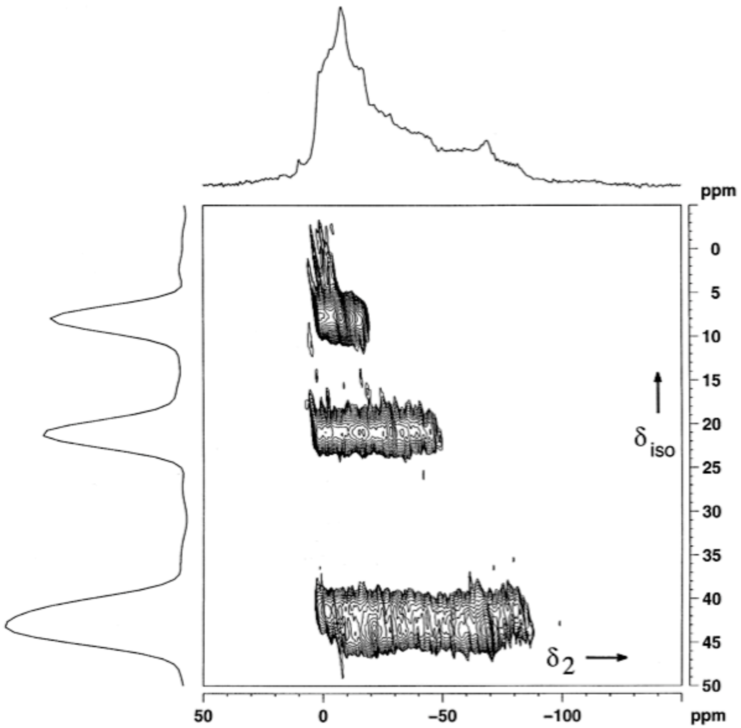


Number of Al-O-Al linkages decreases with annealing time

Putnis et al., Phys. Chem. Mineral. ***12****, 217 (1985)*

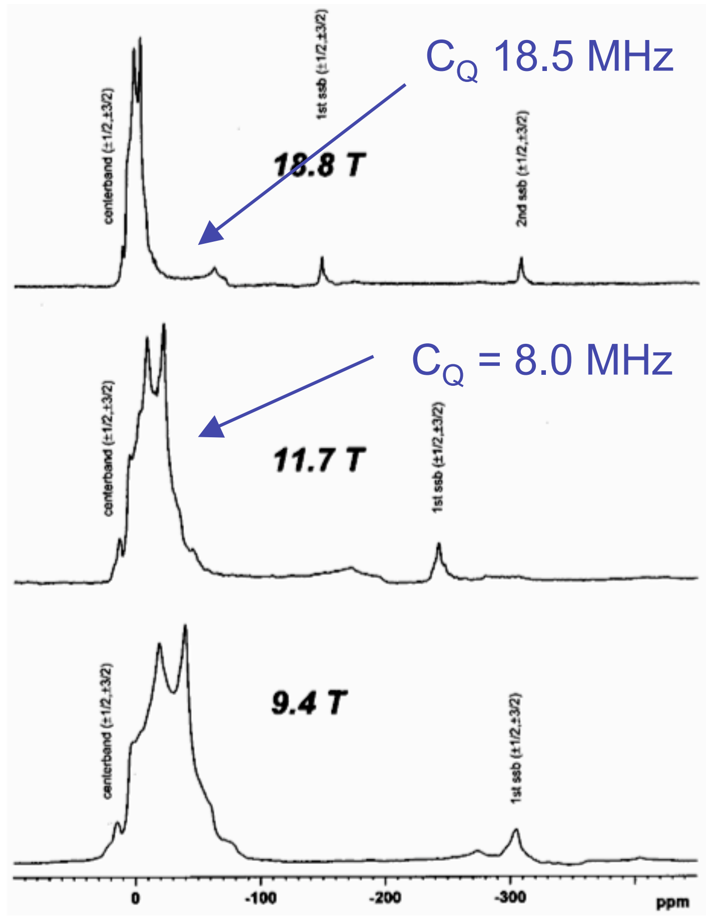
^{27}Al NMR

^{27}Al MAS and MQMAS NMR of kyanite (Al_2SiO_5)



Bodart et al., J. Phys. Chem. Solids ***60****, 223 (1999)*

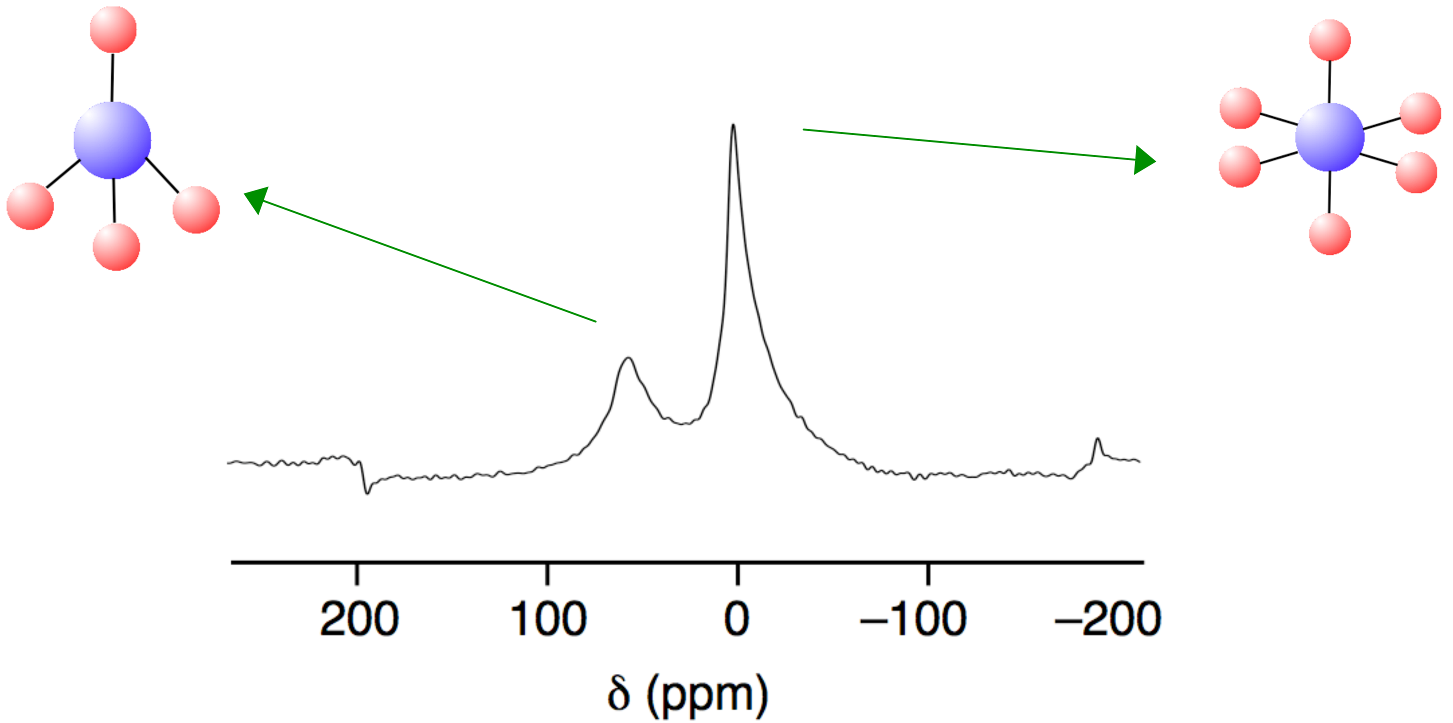
^{27}Al MAS NMR of zoisite ($Ca_2Al_3Si_3O_{12}(OH)$)



Alemany et al., J. Phys. Chem. B ***104****, 11612 (2000)*

^{27}Al NMR

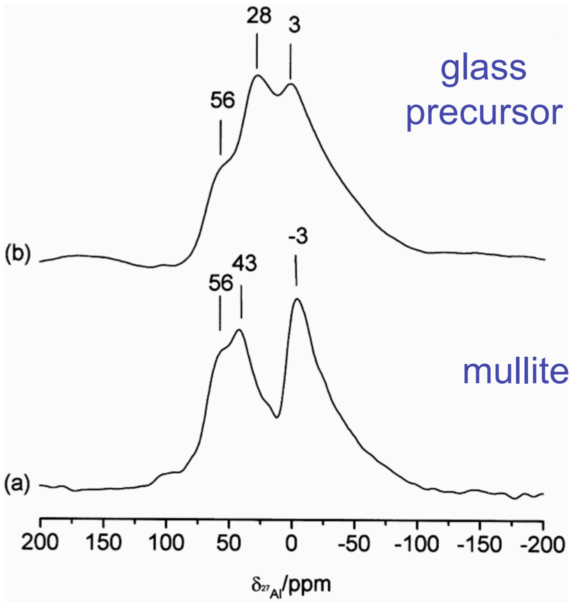
- Substitution of Al into $MgSiO_3$ is important in the inner Earth
- Where does the Al substitute, the six-coordinate Mg site or the four-coordinate Si site?

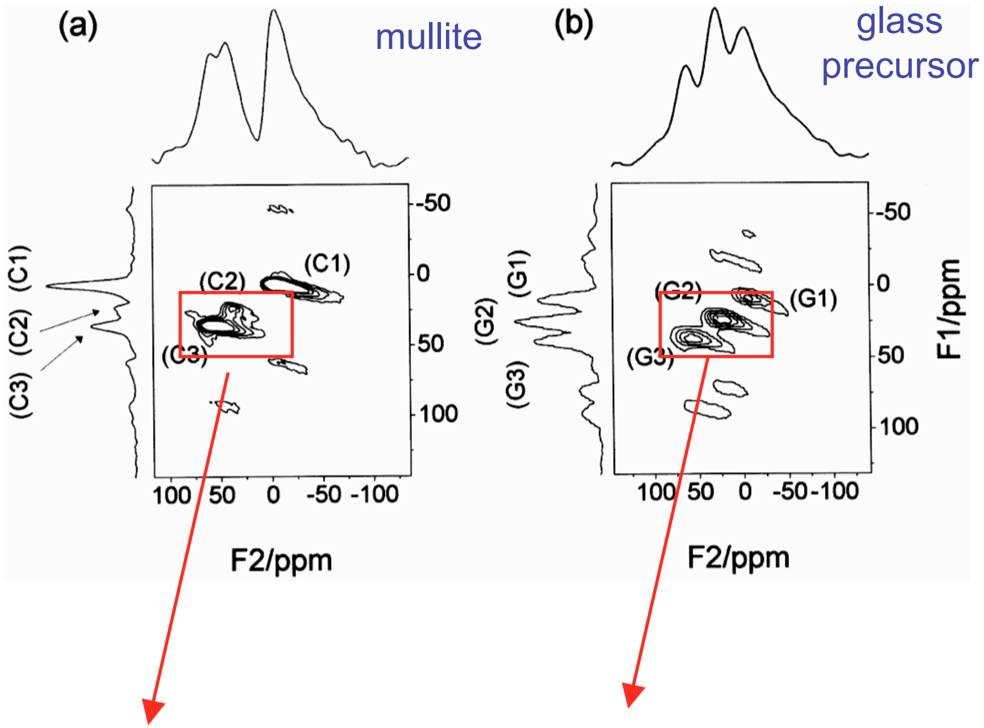


^{27}Al NMR

- Debate over the nature of resonances between 20 and 45 ppm in spectra
- Are these five coordinate Al? Or simply distorted 4 coordinate Al?

^{27}Al MAS NMR





Isotropic chemical shift ranges

6 CN	15 to –20 ppm
5 CN	20 to 40 ppm
4CN	40 to 70 ppm

δ_{iso} of 49 ppm
4 CN

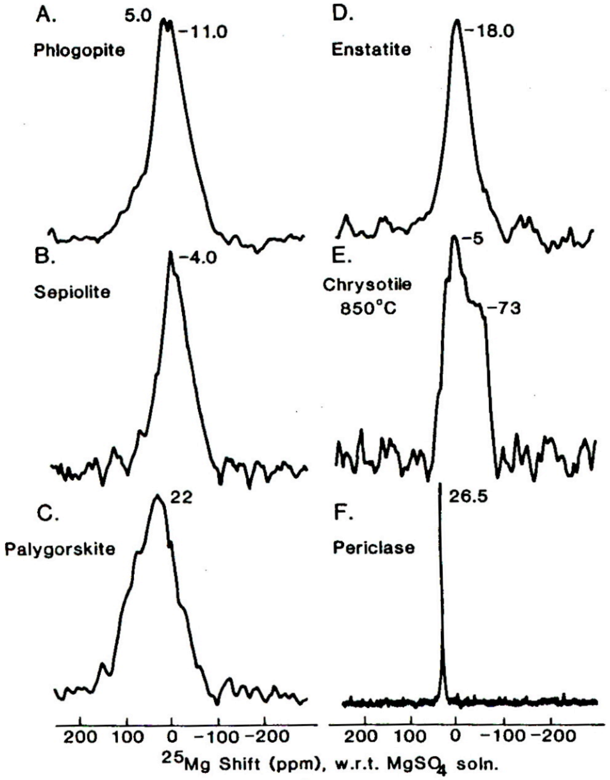
δ_{iso} of 40 ppm
5 CN

Bodart et al., J. Phys. Chem. Solids ***60****, 223 (1999)*

^{25}Mg NMR

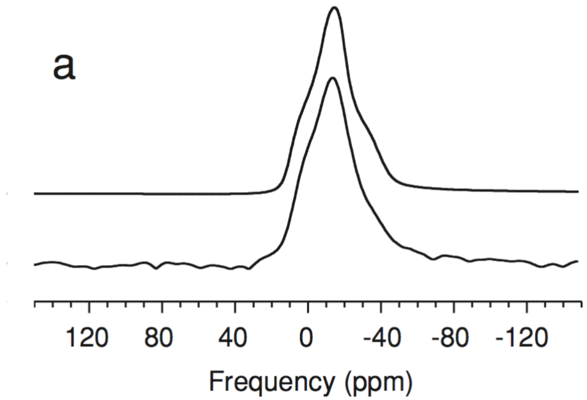
- Low γ, low natural abundance (NA) and large quadrupolar broadening
- Enrichment very costly
- High B_0 fields may be required

^{25}Mg (11.7 T) NMR NA



MacKenzie et al., Am. Mineral. ***79****, 250 (1994)*

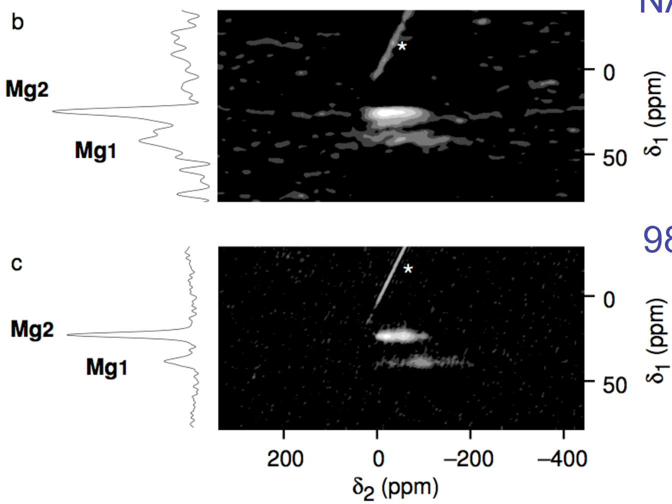
^{25}Mg (14.1 T) NMR of diopside 97%



^{25}Mg (9.4 T) STMAS of talc

NA

98%

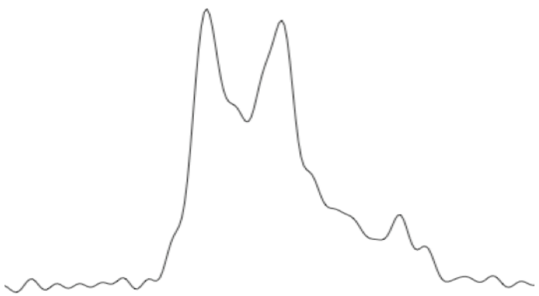


Dowell et al., J. Phys. Chem B ***108****, 13292 (2004)*

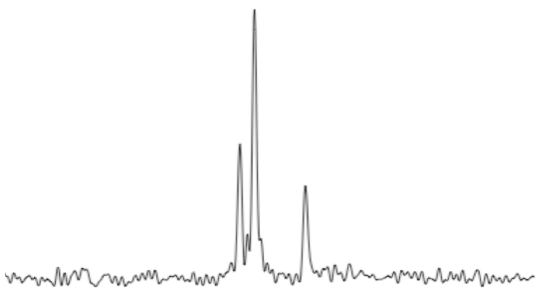
^{17}O NMR

- Low natural abundance often requires isotopic enrichment

9.4 T MAS

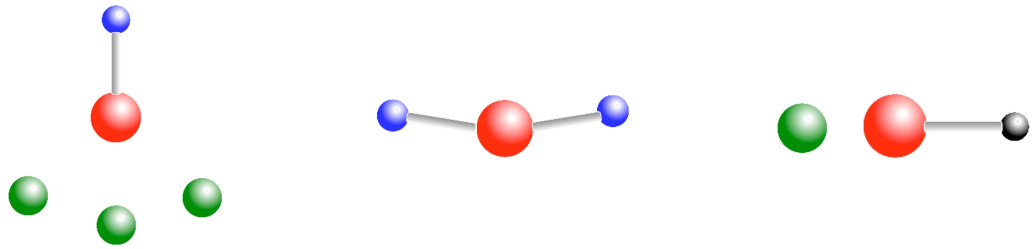


9.4 T MQMAS



α-Mg_2SiO_4

35% enriched ^{17}O



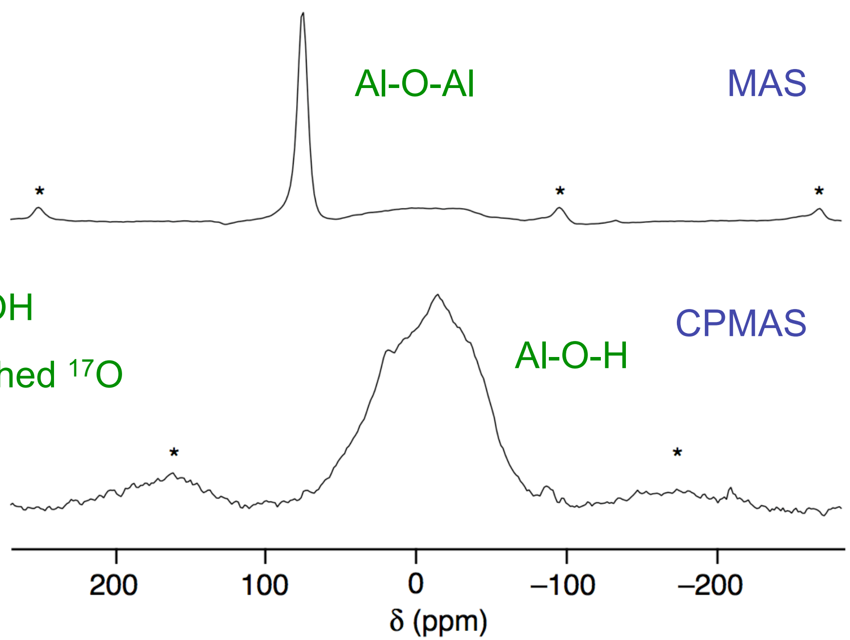
Si-O-Mg_x
2-3 MHz

Si-O-Si
4-5.5 MHz

Mg-O-H
6-8 MHz

AlOOH

35% enriched ^{17}O



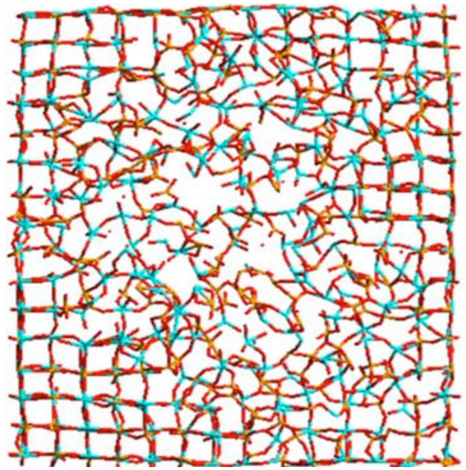
Ashbrook et al., Am. Mineral. ***84****, 1191 (1999)*

Ashbrook et al., J. Magn. Reson. ***147****, 238 (2000)*

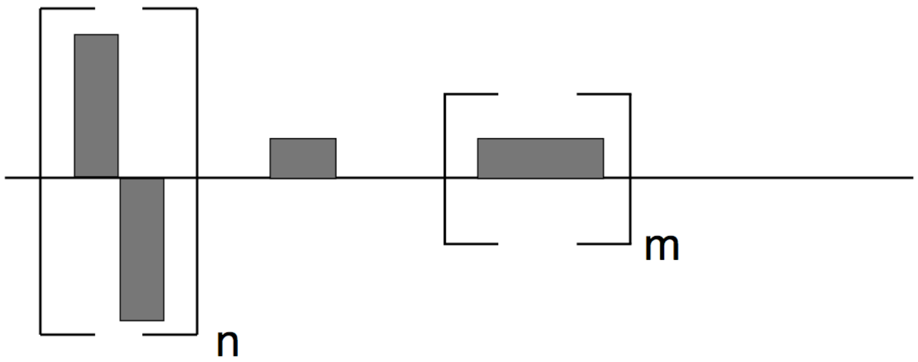
^{17}O NMR

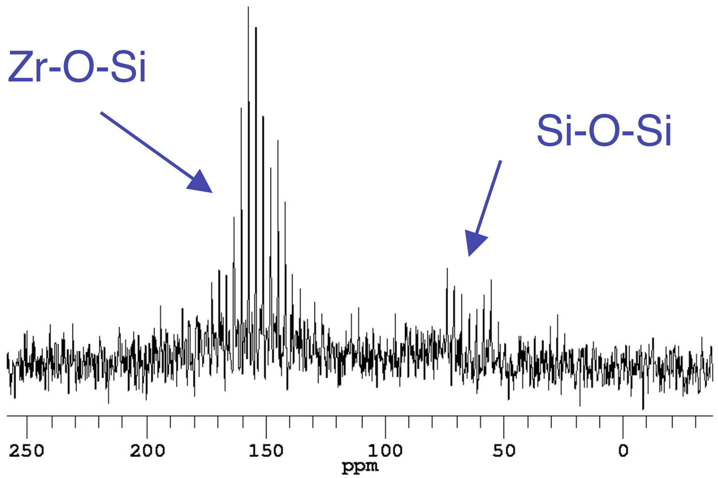
- Natural zircon ($ZrSiO_4$) contains 4000 ppm U/Th
- Radiation damage (alpha decay) over 400 million years

- Natural abundance ^{17}O?
- Methods to improve sensitivity
- RAPT (71 sets of +X/–X 1.6 μs pulses) prior to acquisition
- CPMG (20 echoes detected in acquisition)



RAPT/CPMG





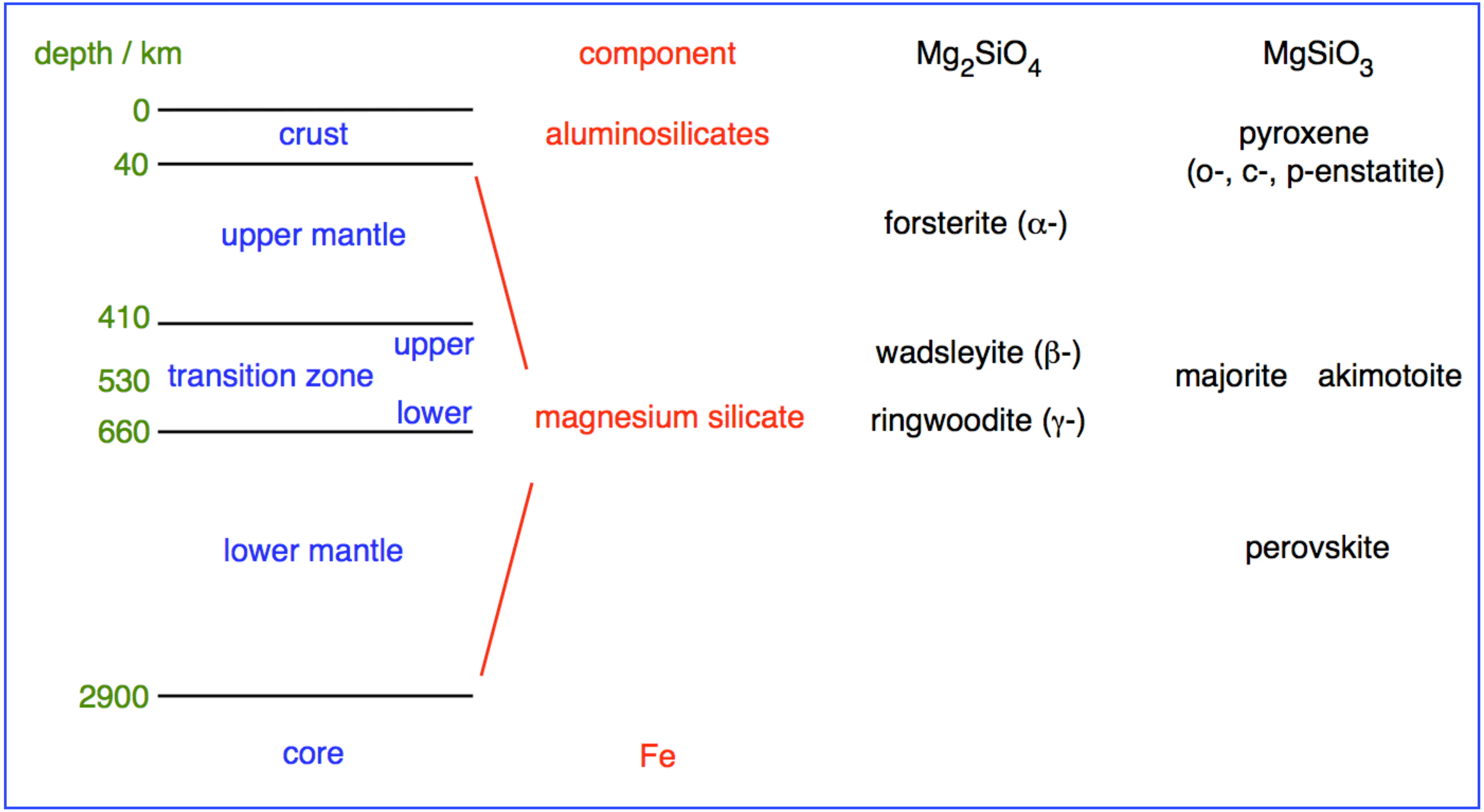
Expt time: 64 hours
(11.7 T)

NMR of High-Pressure Minerals

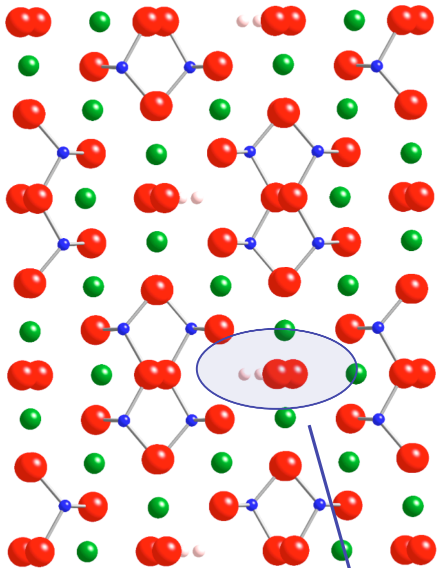
Dr Andrew Berry (Imperial College)
Professor Steve Wimperis (University of Glasgow)
Dr Alan Gregorovic (University of Glasgow)
Dr Chris Pickard (University of St Andrews)
Dr John Griffin (University of St Andrews)
Caroline Pringle (University of St Andrews)

High-pressure minerals

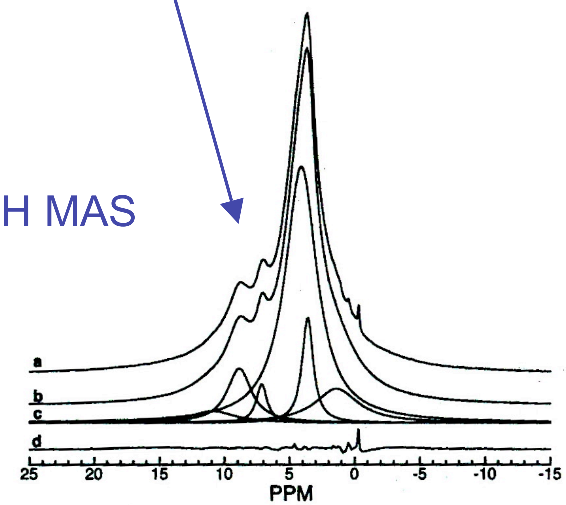
High-pressure minerals



High-pressure minerals



^{1}H MAS



- Water plays a key role in crustal and surface geology but little is known about its role in the Earth's interior
- The mantle is though to contain a vast amount of water
- Thought to be contained within the structure of the nominally anhydrous minerals in the mantle

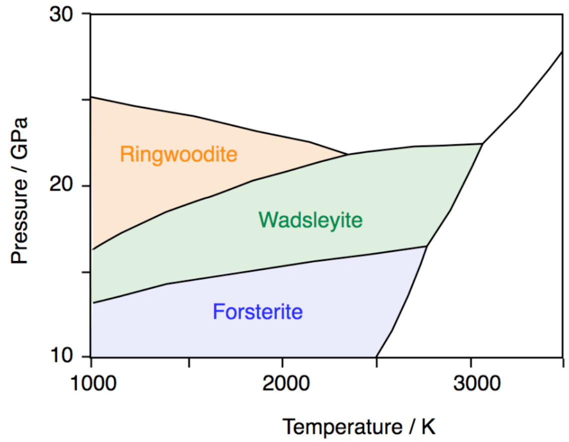
Mg_2SiO_4 0.9-2.4 wt%

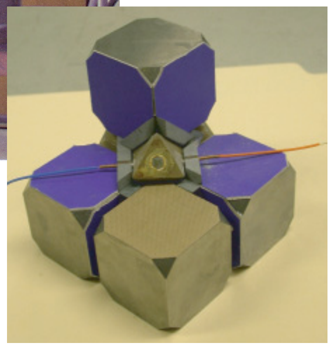
$MgSiO_3$ 100 ppm to 0.1 wt%

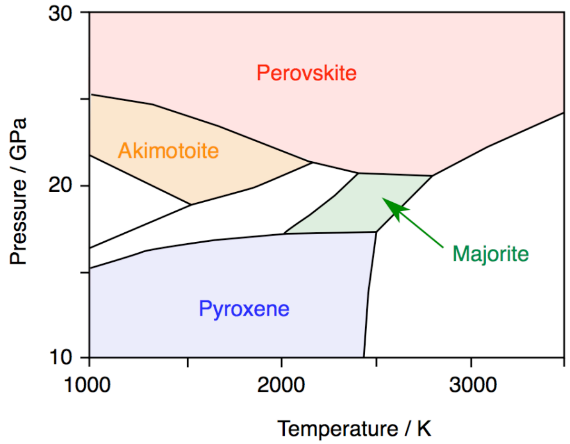
- For β-Mg_2SiO_4 a crystalline hydrated form exists
- For other materials H incorporation is disordered

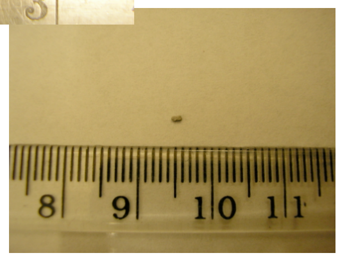
High-pressure minerals

- High temperature (~1500°C) and high pressure (up to 25 GPa) synthesis
- Requires multi anvil apparatus
- Only small (3-10 mg) amounts of material typically produced





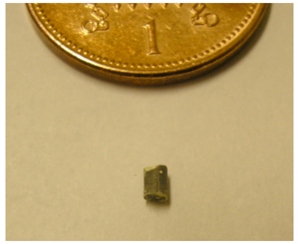


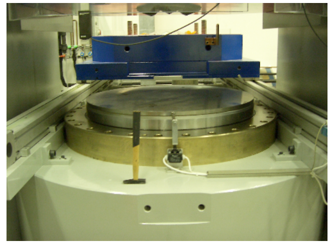


High-pressure minerals

- Significant sensitivity and resolution challenges

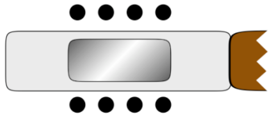
- Small amounts of material





Bigger press (up to 30 mg of material)

Keep sample as pellet



- ^{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

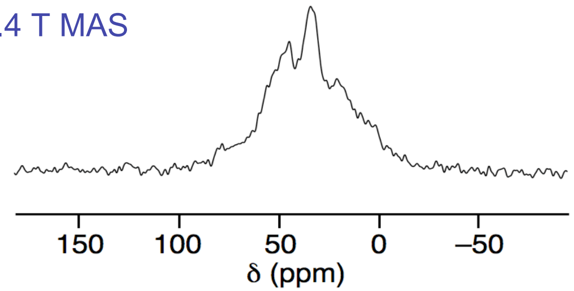
More sensitive high-resolution approaches (e.g., STMAS)

Use of DFT calculations to predict spectra

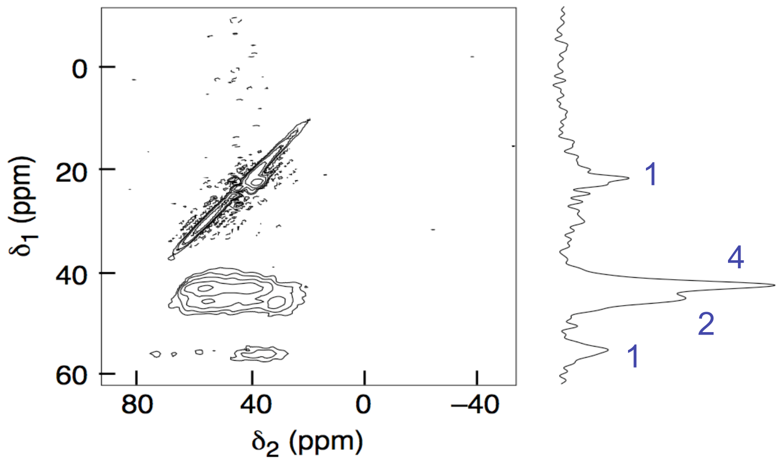
β-Mg_2SiO_4 (10 mg, 35% ^{17}O)
9.4 T (STMAS, 78 hours)

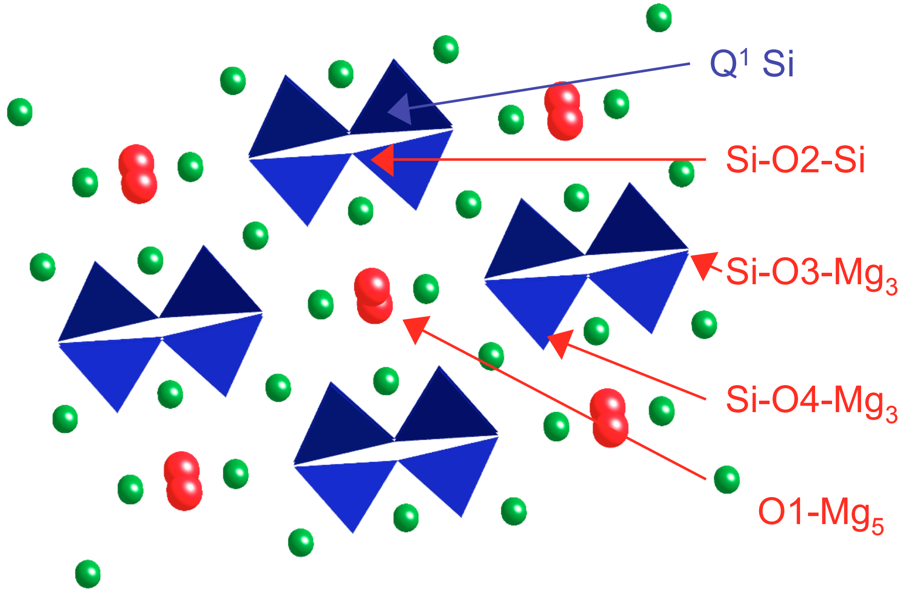
Wadsleyite

9.4 T MAS



9.4 T STMAS





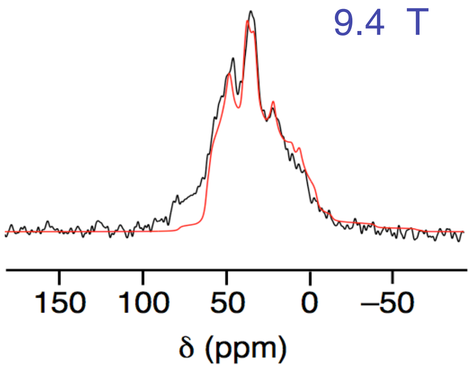
	Pop^n	Experimental		
		δ_{iso} (ppm)	C_Q / MHz	η_Q
O1	1	38(1)		
O2	1	76(1)	4.8(2)	0.9(2)
O3	2	66(1)	4.4(1)	0.2(1)
O4	4	65(1)	3.8(1)	0.3(1)
Si	1	–79(1)		

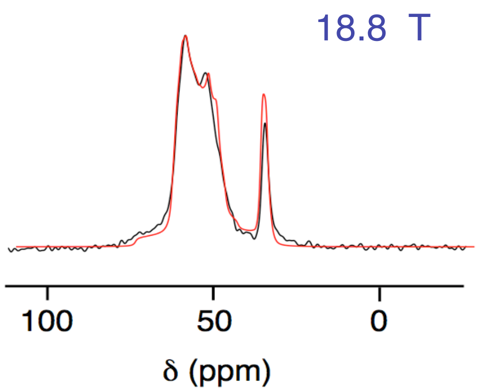
Spectral assignment?
No lineshape for O1
No η_Q for O2
Large C_Q for non-bridging O3/4?

Ashbrook et al., J. Am. Chem. Soc. ***125****, 11824 (2003)*

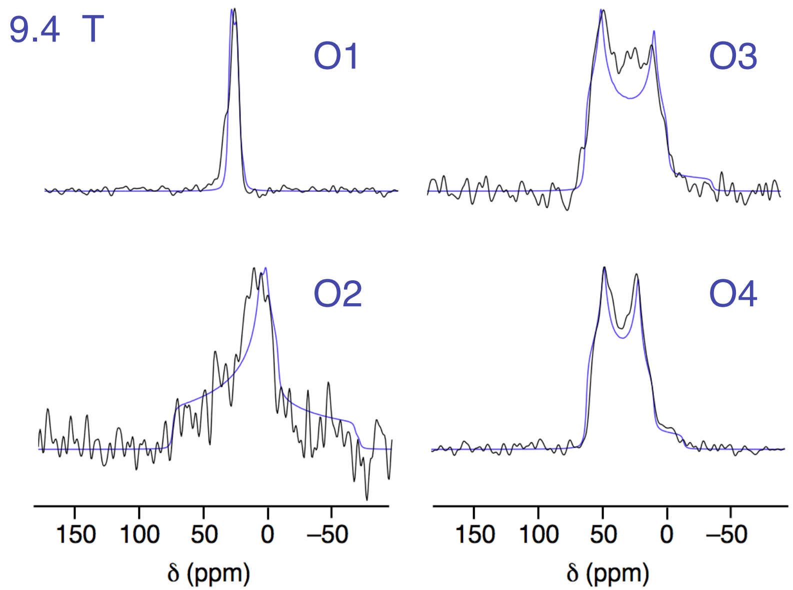
Wadsleyite

96 processors for 6.7 hrs
56 atoms in unit cell
4 4 4 k grid, 50 Ry cut off





	Pop^n	Experimental			Calculated		
		δ_{iso} (ppm)	C_Q / MHz	η_Q	δ_{iso} (ppm)	C_Q / MHz	η_Q
O1	1	38(1)			39.6	1.64	0.31
O2	1	76(1)	4.8(2)	0.9(2)	77.1	5.00	0.94
O3	2	66(1)	4.4(1)	0.2(1)	68.5	4.62	0.20
O4	4	65(1)	3.8(1)	0.3(1)	66.5	3.97	0.30
Si	1	–79(1)			–79.8		

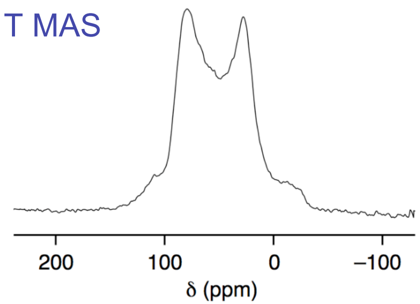


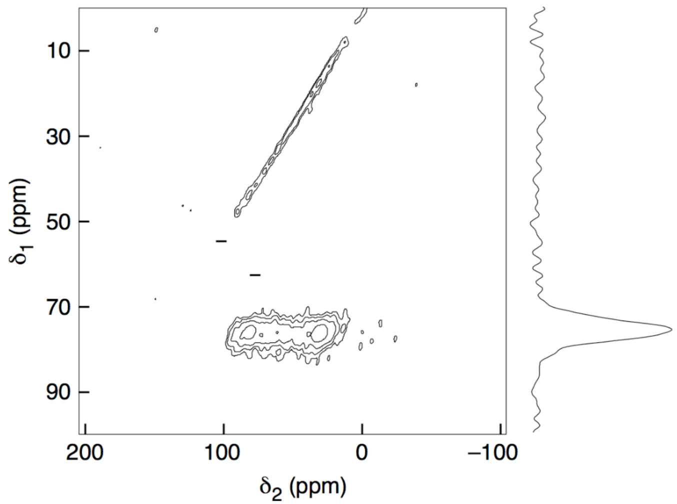
Assignment confirmed
Quadrupolar parameters for O1
O2 η_Q confirmed as ~0.9
Confirms large C_Q for non-bridging O

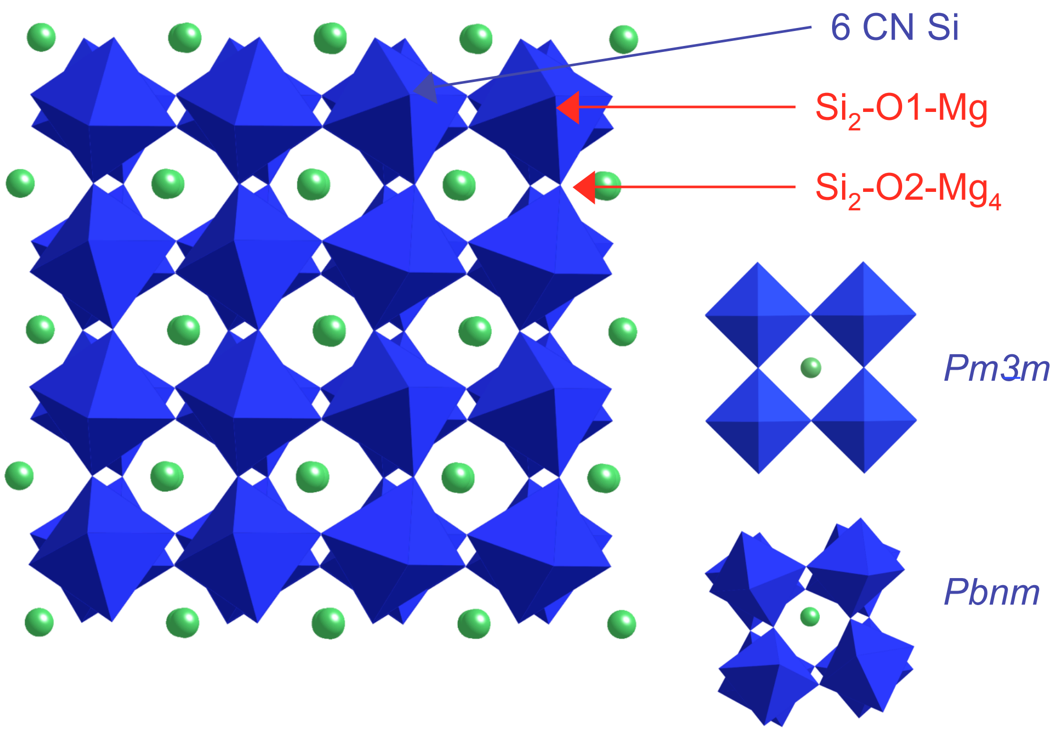
Ashbrook et al., Phys. Chem. Chem. Phys. ***9****, 1587 (2007)*

MgSiO$_3$ (~4 mg, 75% ^{17}O)
9.4 T (STMAS, 84 hours)

Perovskite







	Pop^n	Experimental		
		δ_{iso} (ppm)	C_Q / MHz	η_Q
O	?	109(2)	5.1(1)	0.1(2)
Si	1	–193(1)		

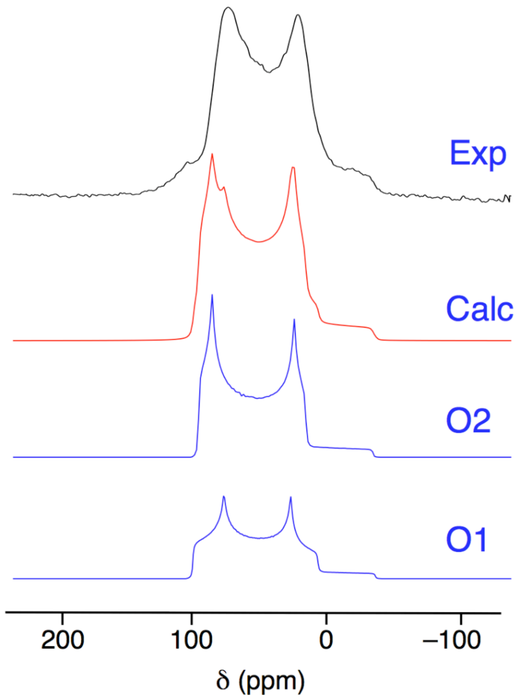
Only 1 O observed by NMR?

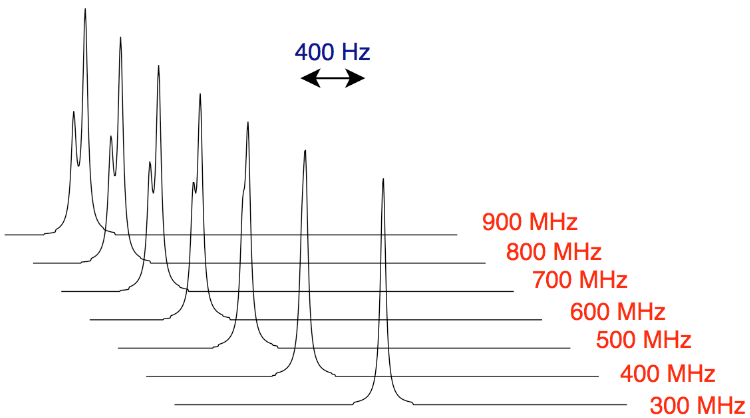
Ashbrook et al., J. Am. Chem. Soc. ***129****, 13213 (2007)*

Perovskite

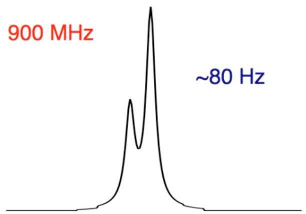
96 processors for 2 hrs
20 atoms in unit cell
4 4 4 k grid, 50 Ry cut off

	Pop[n]	Experimental			Calculated		
		δ_{iso} (ppm)	C_Q / MHz	η_Q	δ_{iso} (ppm)	C_Q / MHz	η_Q
O1	1	109(2)	5.1(1)	0.1(2)	113.2	5.31	0.28
O2	2				114.5	5.33	0.13
Si	1	–193(1)			–190.8		





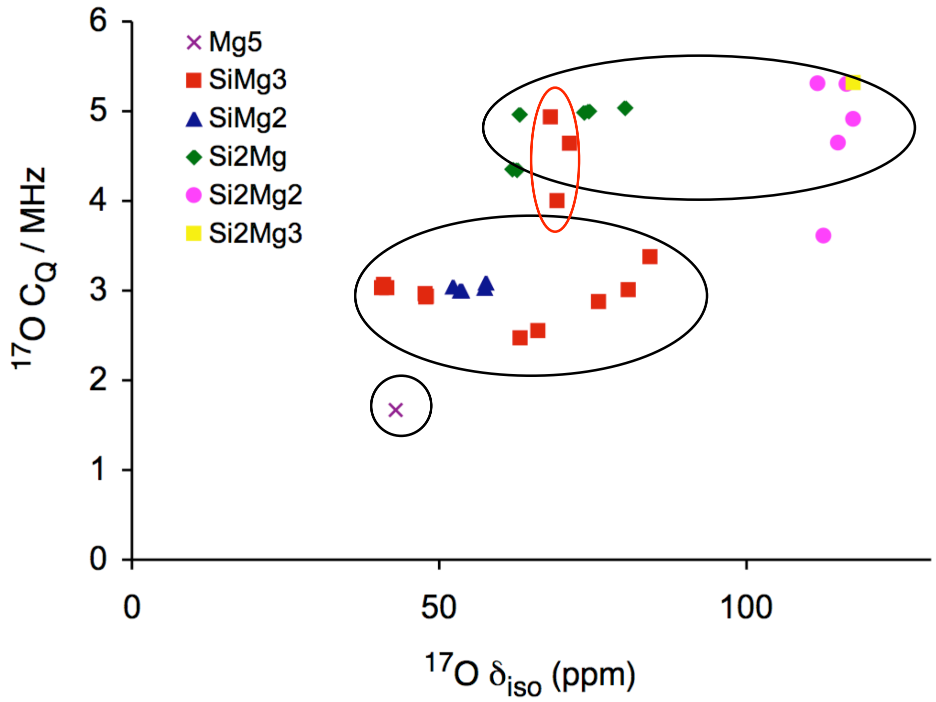
2 O are predicted to be very similar

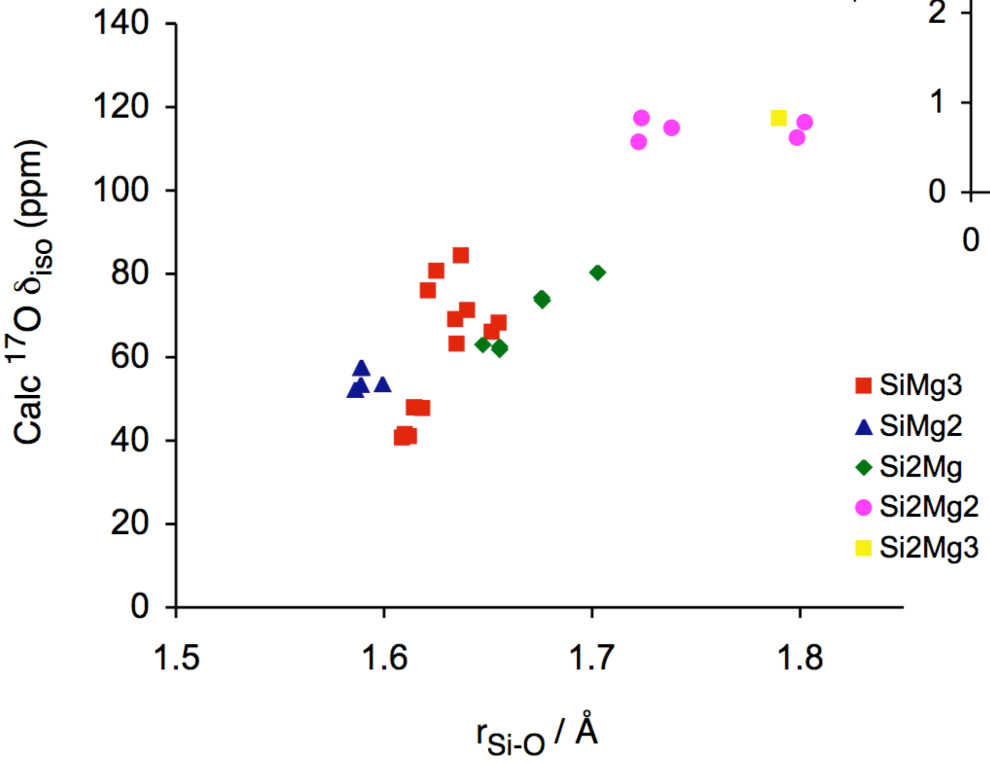


Unresolved by STMAS/MQMAS at 9.4 T
but might be resolvable at higher B_0

Ashbrook et al., J. Am. Chem. Soc. ***129****, 13213 (2007)*

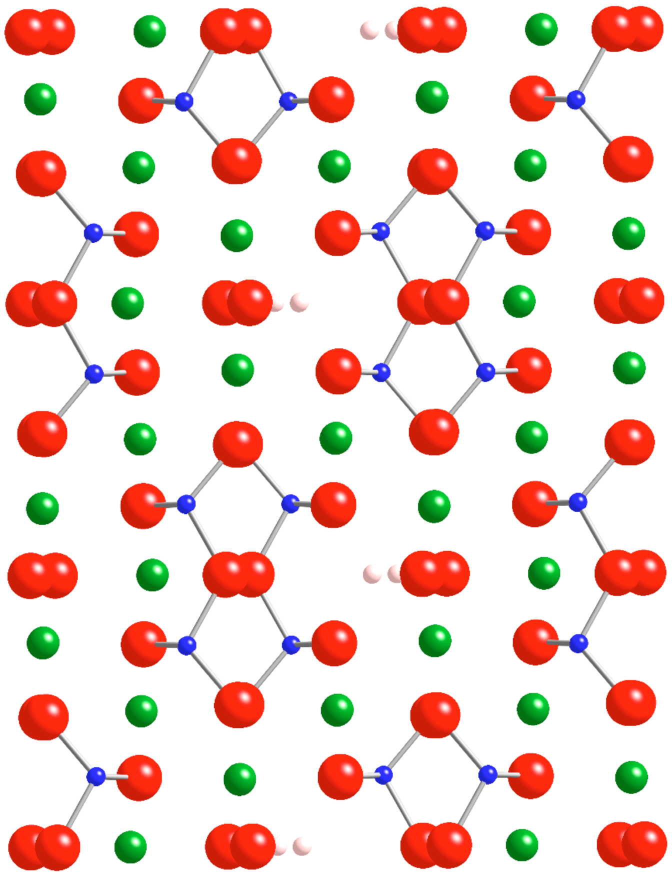
Summary





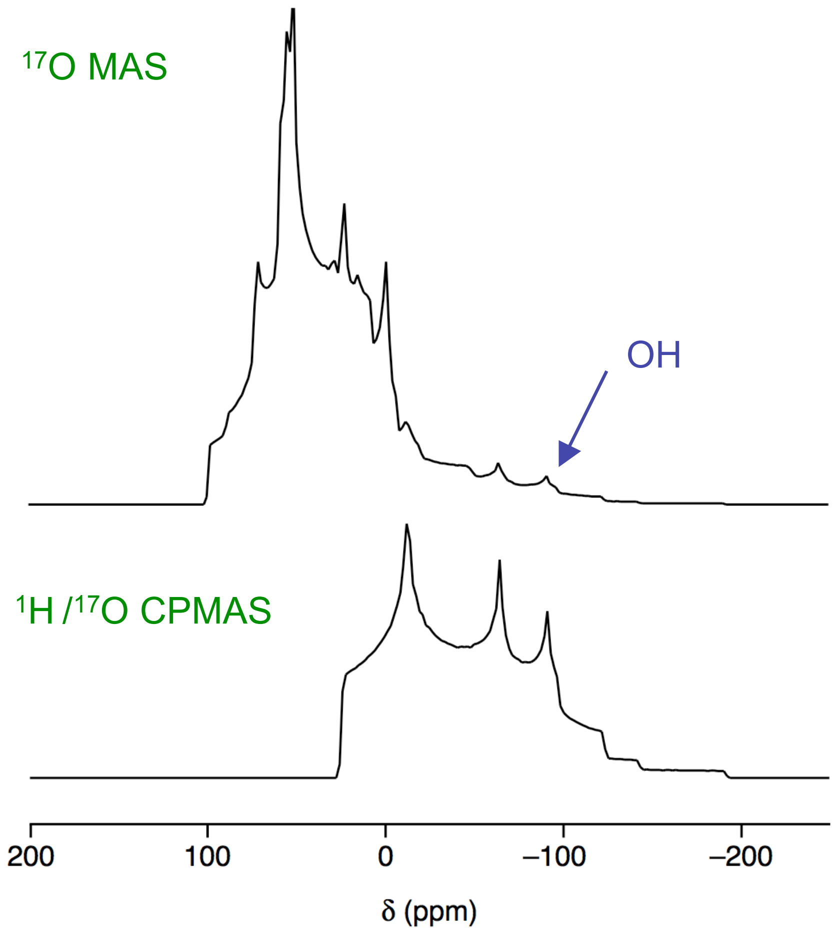
Ashbrook et al., J. Am. Chem. Soc. ***129****, 13213 (2007)*

Nominally anhydrous minerals



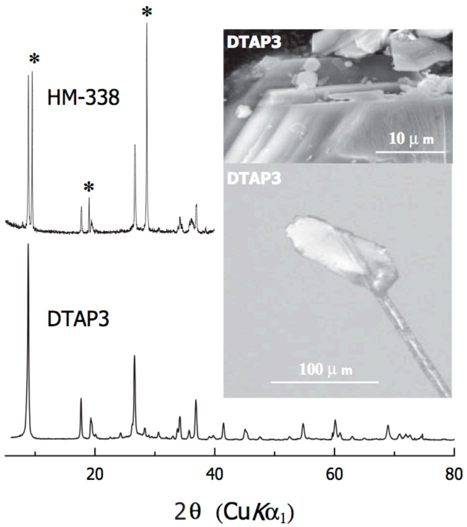
Crystal structure of hydrous wadsleyite

CASTEP calculations



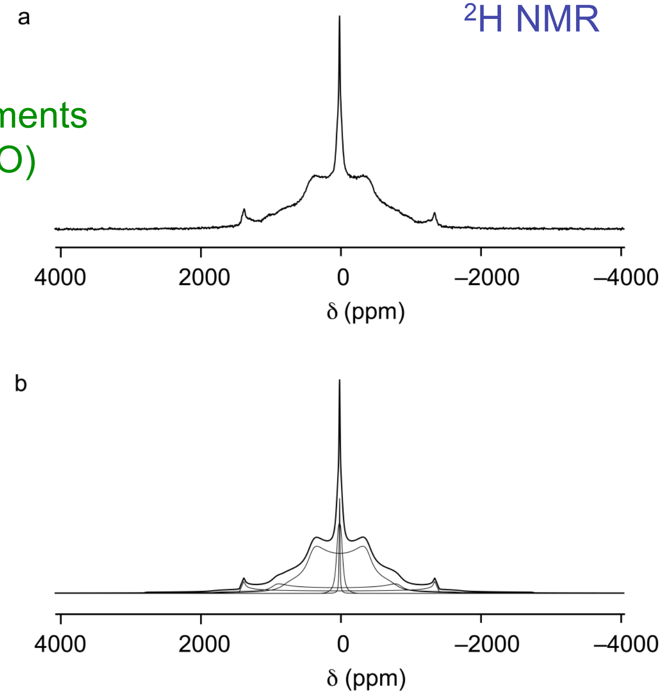
Nominally anhydrous minerals

- The 10 Å phase ($Mg_3Si_4O_{10}(OD)_2.xD_2O$) is a synthetic dense silicate phase proposed as a model for water in high-pressure silicates

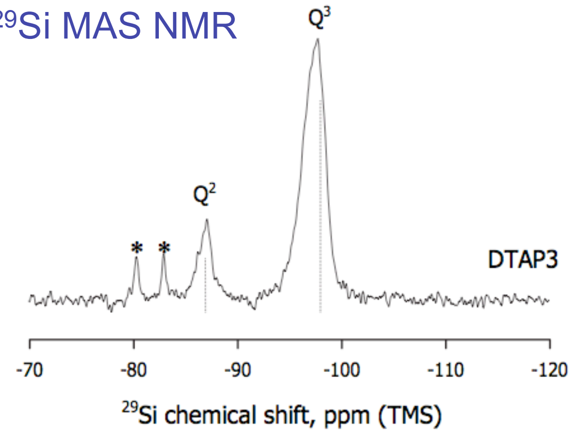


Range of ^2H environments (MgOH, SiOH, H_2O)

^2H NMR



^{29}Si MAS NMR



Observation of enstatite impurity (*) not seen by X-ray

Q^2 peaks suggest isolated Si vacancies (SiO_3OH)

Ratio Q^3:Q^2 5.4:1 suggests 1 in 20 Si vacancies

Welch et al., Am. Miner. ***91****, 1707 (2006)*

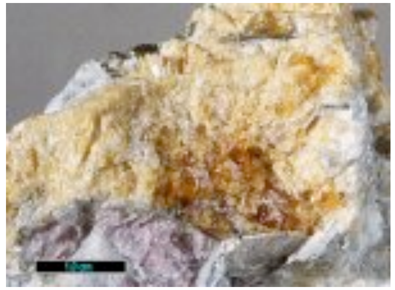
Humite minerals

- Humite minerals have a general formula

$$nMg_2SiO_4.Mg(OH)_2$$

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



- In addition to the hydroxylated (OH-) humite minerals both F- and Ti-substituted minerals exist giving a general formula

$$nMg_2SiO_4.Mg_{1-x}Ti_x(F,OH)_{2-2x}O_{2x}$$

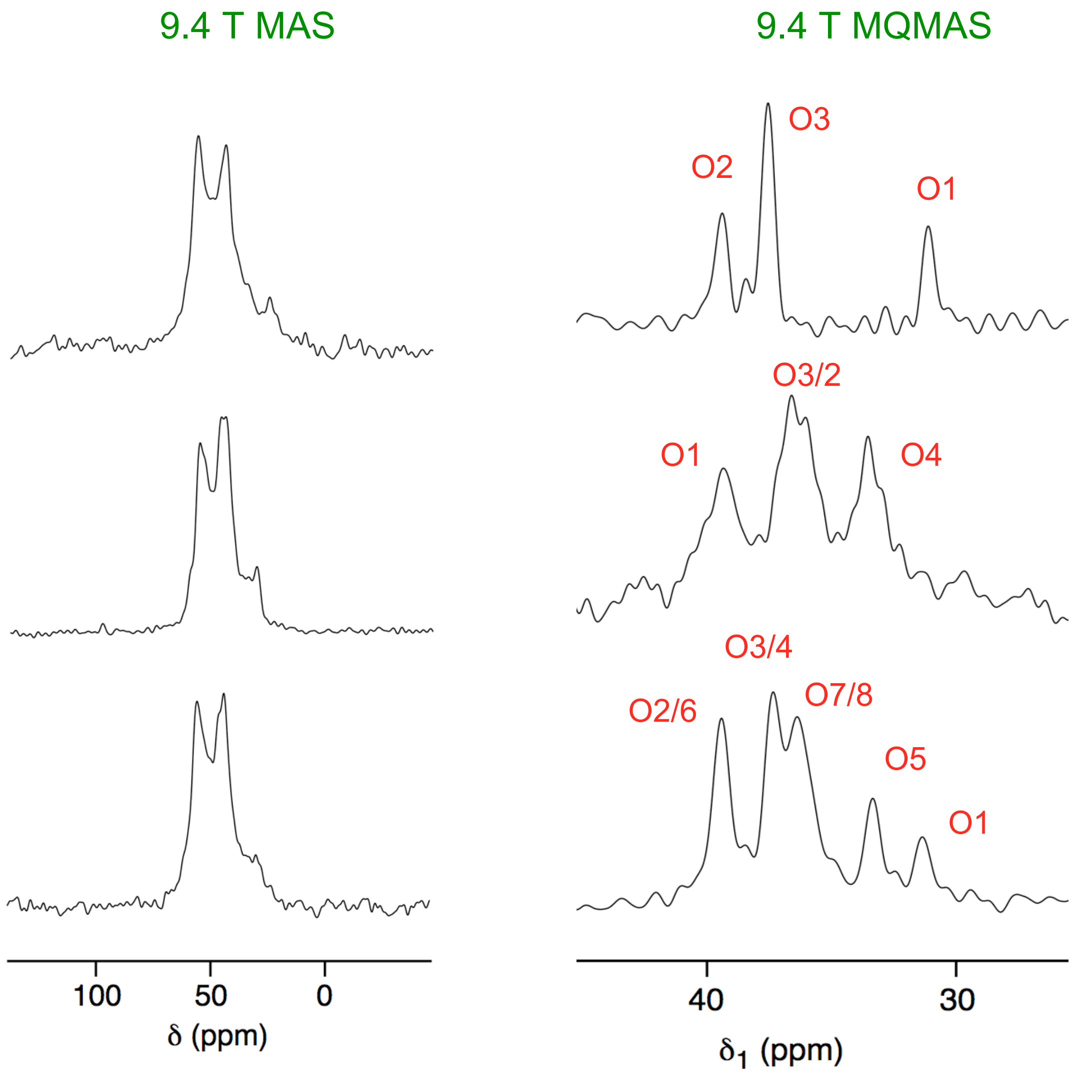
- Proposed as possible models for water incorporation into olivine/forsterite

Humite minerals

Forsterite
(Mg_2SiO_4)

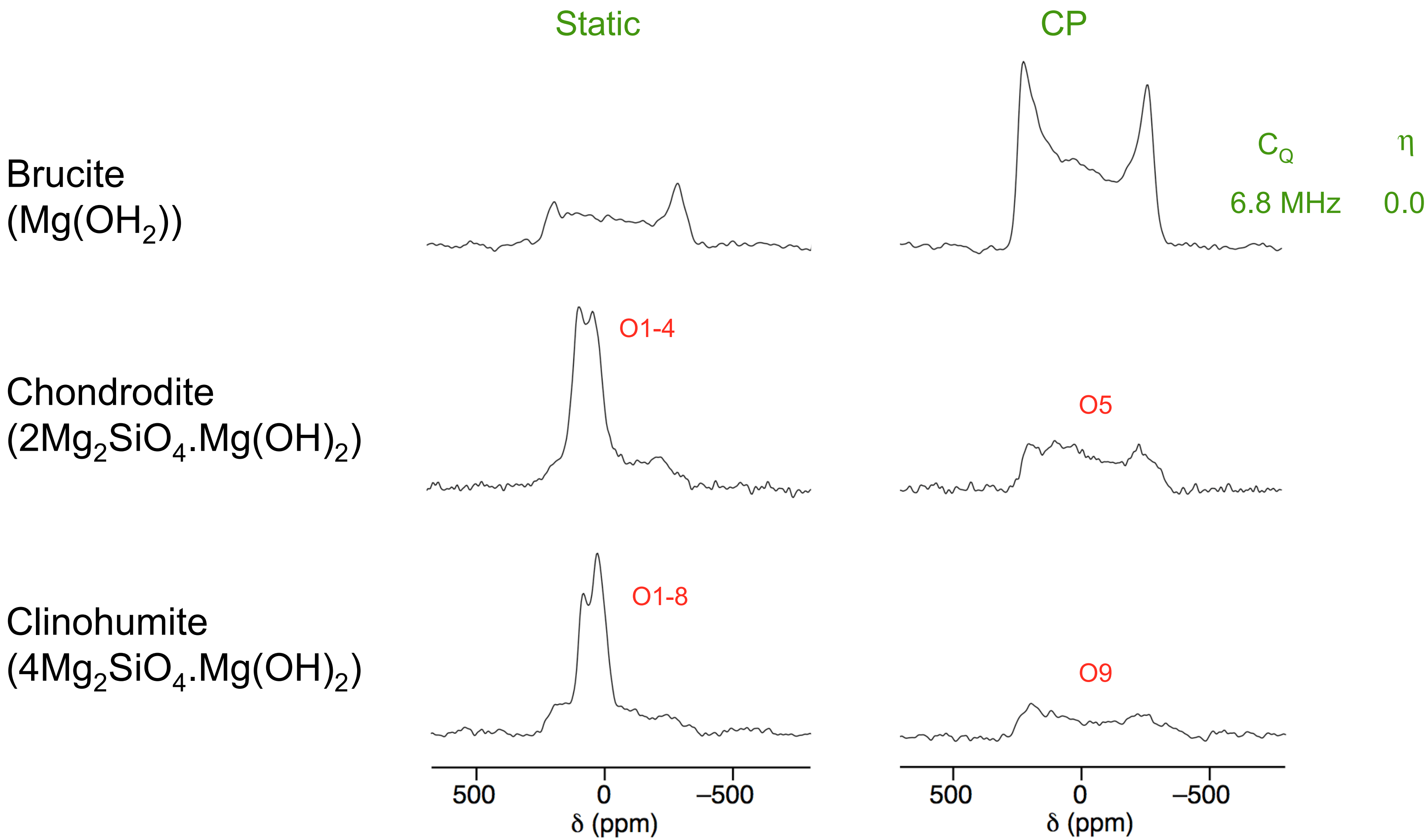
Chondrodite
($2Mg_2SiO_4.Mg(OH)_2$)

Clinohumite
($4Mg_2SiO_4.Mg(OH)_2$)



Ashbrook et al., J. Am. Chem. Soc. ***123****, 6360 (2001)*

Humite minerals

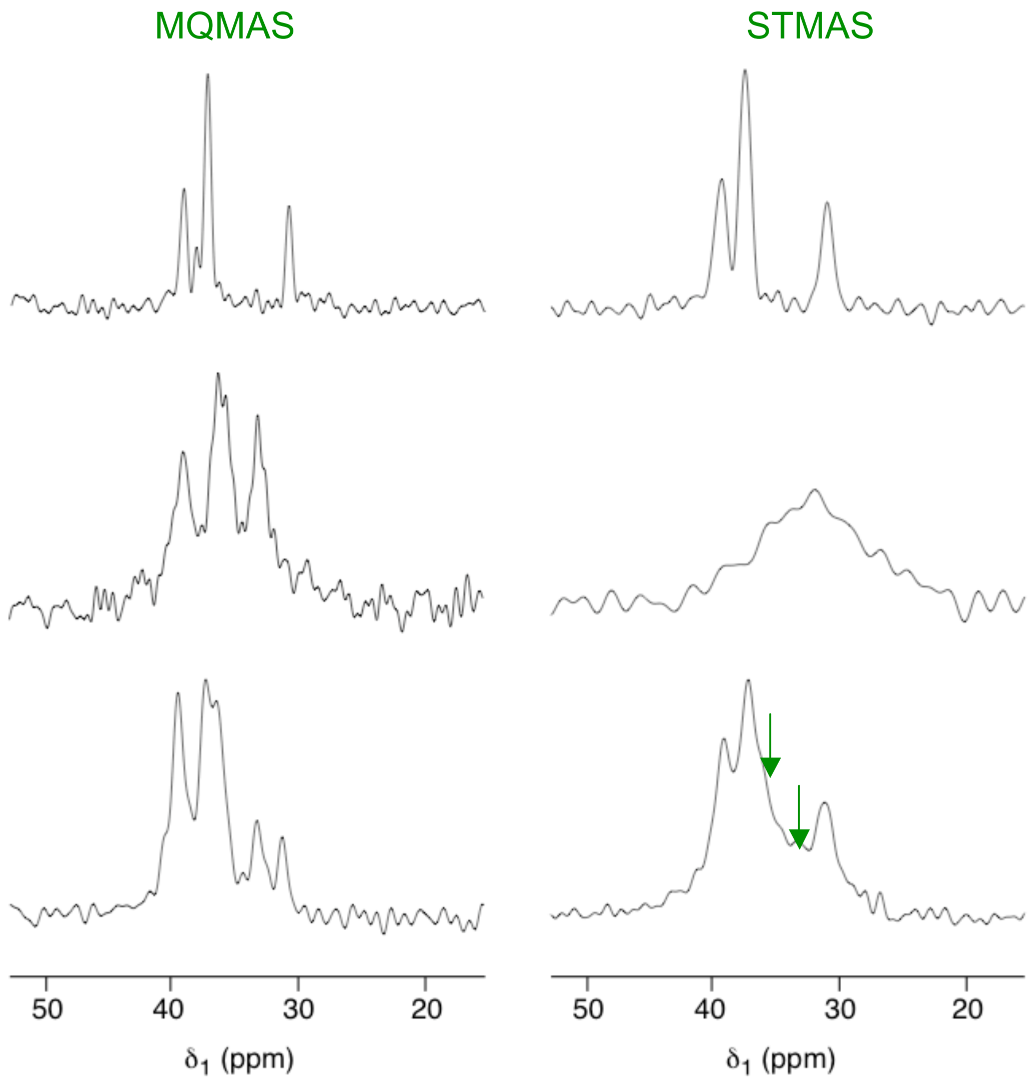


Ashbrook et al., J. Am. Chem. Soc. ***123****, 6360 (2001)*

Humite minerals

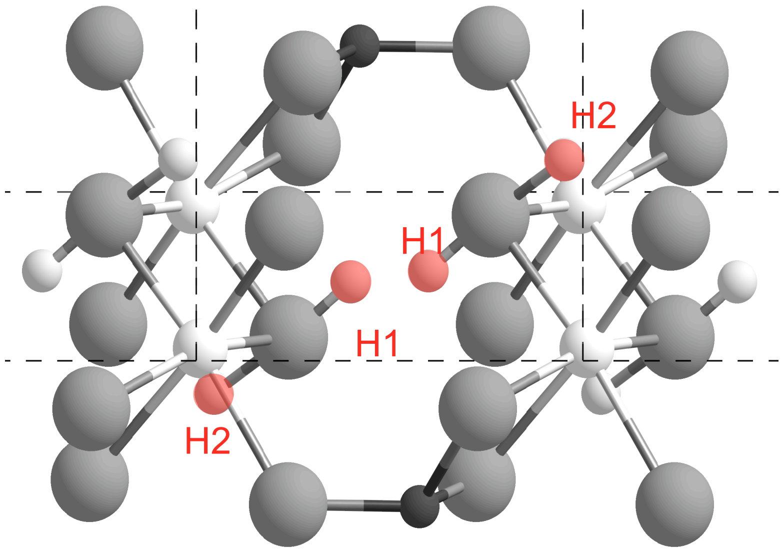
- Spectra for forsterite (α-Mg_2SiO_4) almost identical
- Single broad resonance observed for chondrodite ($2Mg_2SiO_4.Mg(OH)_2$)
- Only 3 out of 5 sharp peaks in clinohumite ($4Mg_2SiO_4.Mg(OH)_2$)

Satellite transitions are sensitive to molecular motion



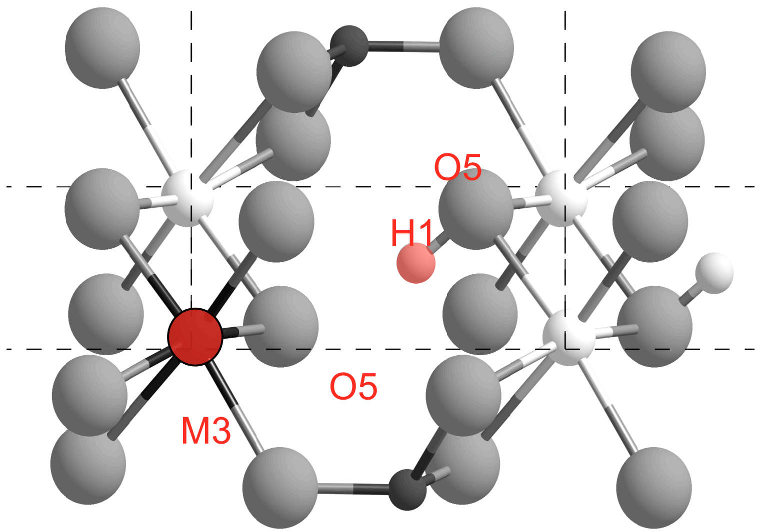
Ashbrook et al., Chem. Phys. Lett. ***364****, 634 (2002)*

Humite minerals



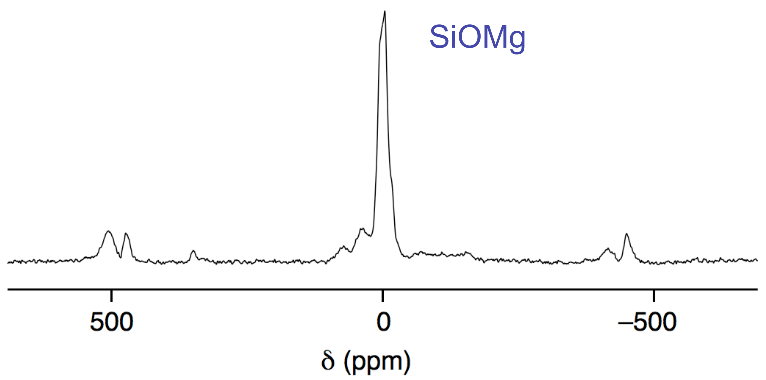
- Two [1]H species by neutron diffraction each 50% occupied
- If H1 is occupied nearest neighbour is H2
- Two sites have similar energy and exchange between them is possible

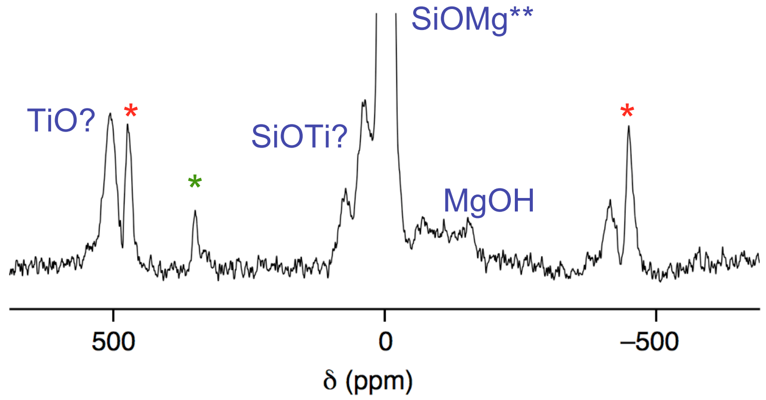
- Use of Ti-substituted materials
- Ti substitutes for Mg on the M3 (4e) site
- Stabilized by H bonding O5-H1-O5
- Results in only one possible H



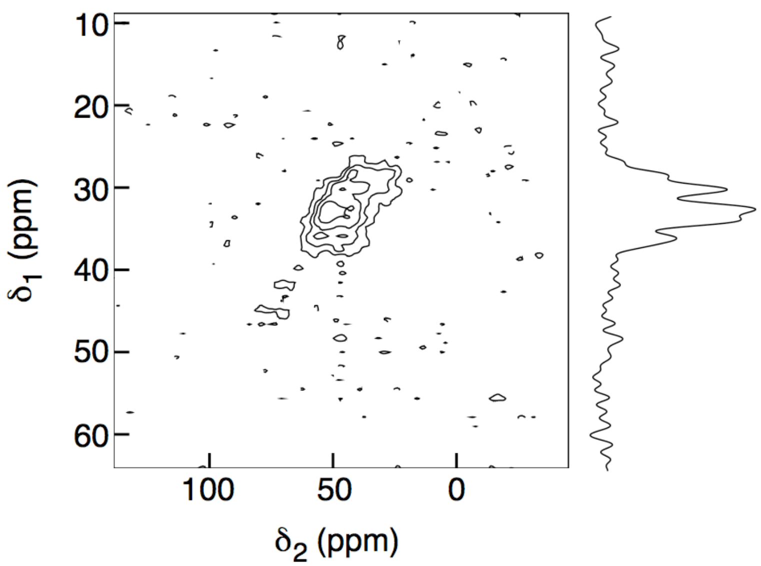
Humite minerals

9.4 T MAS

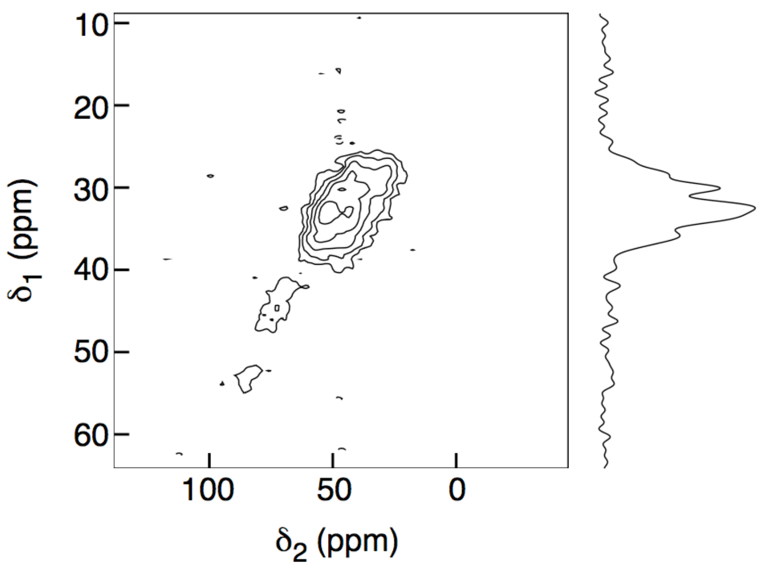




MQMAS

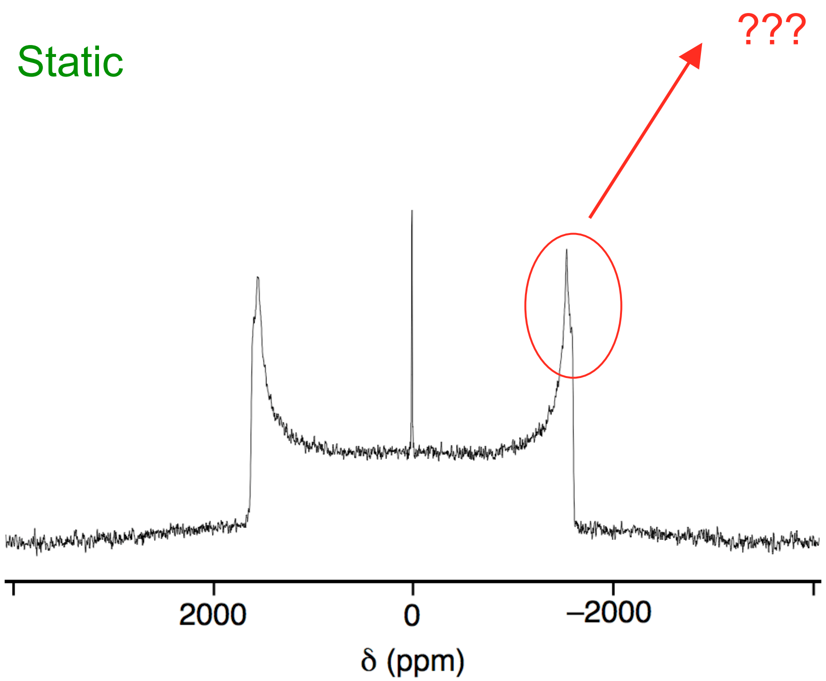


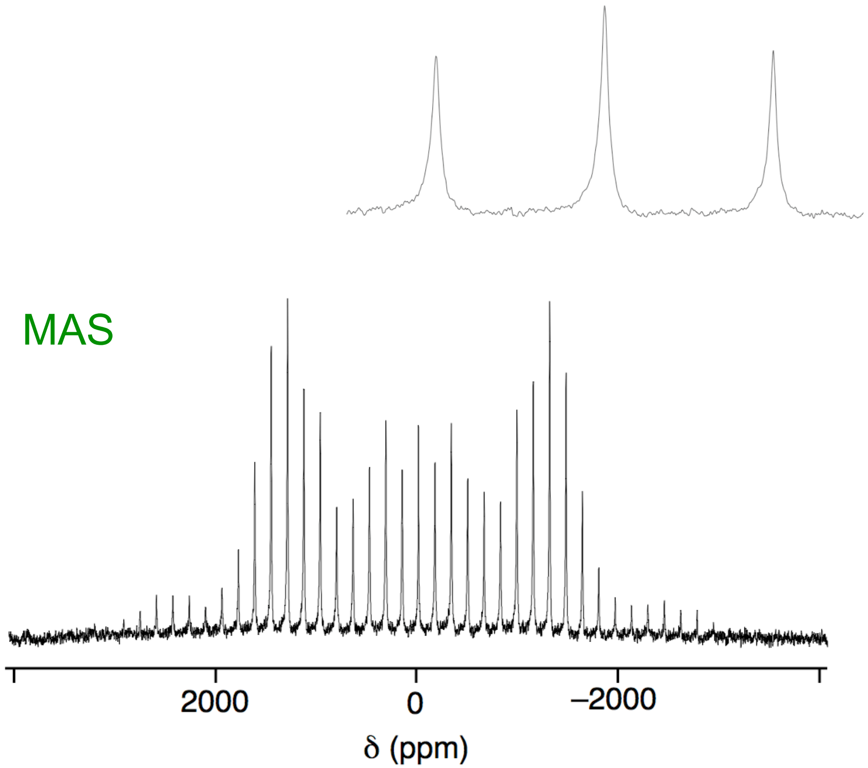
STMAS



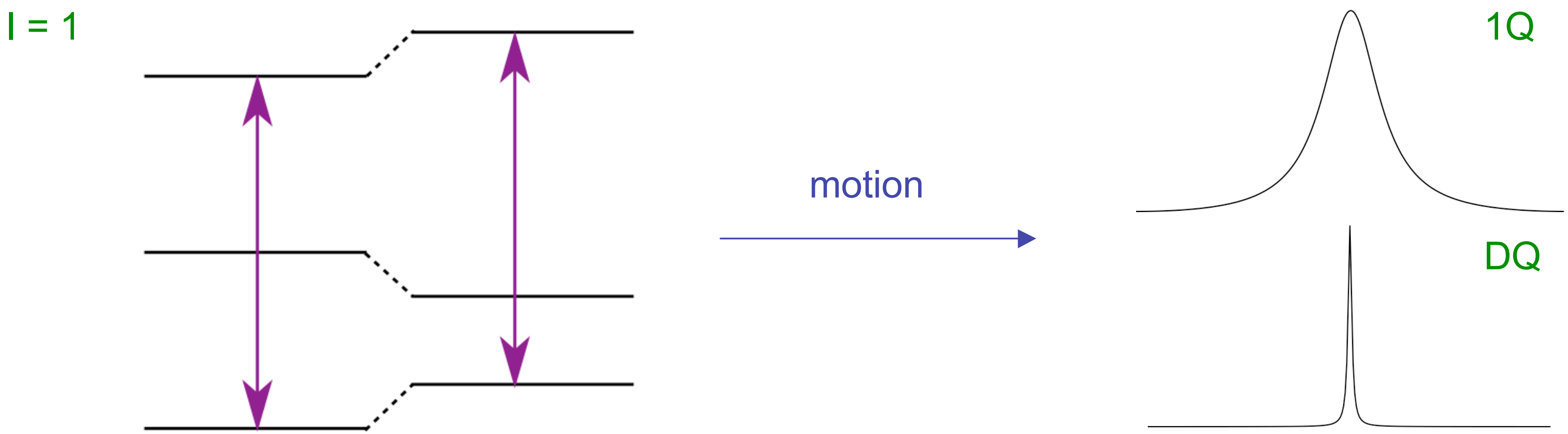
Humite minerals

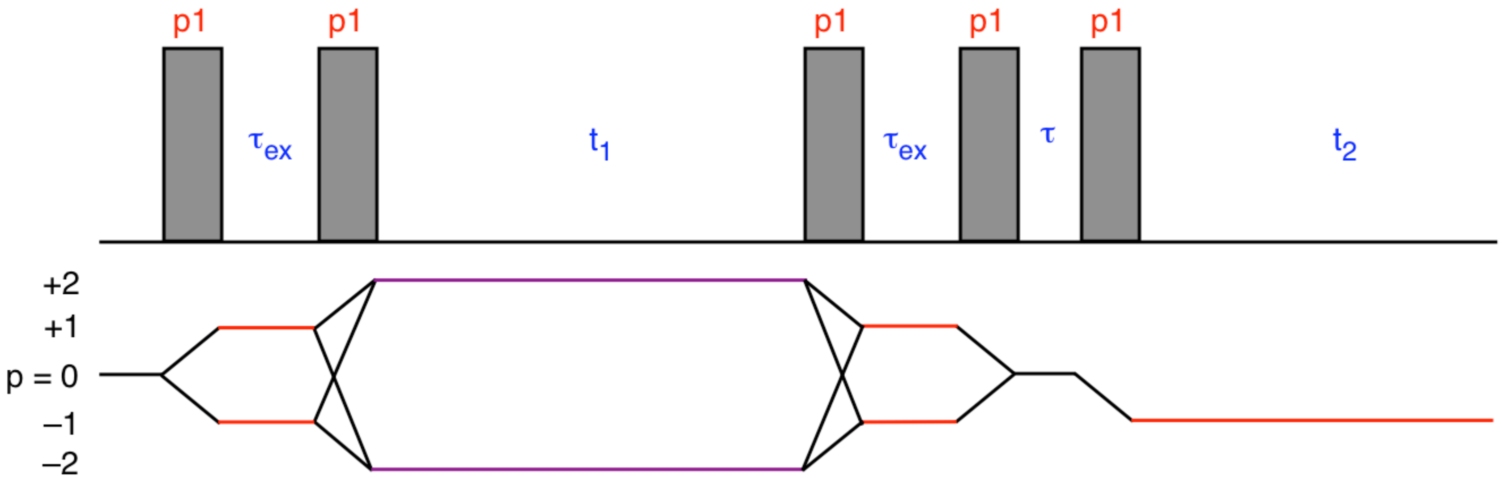
- Is there any evidence for two ^2H species?
- Is there any evidence for dynamics?





DQ NMR

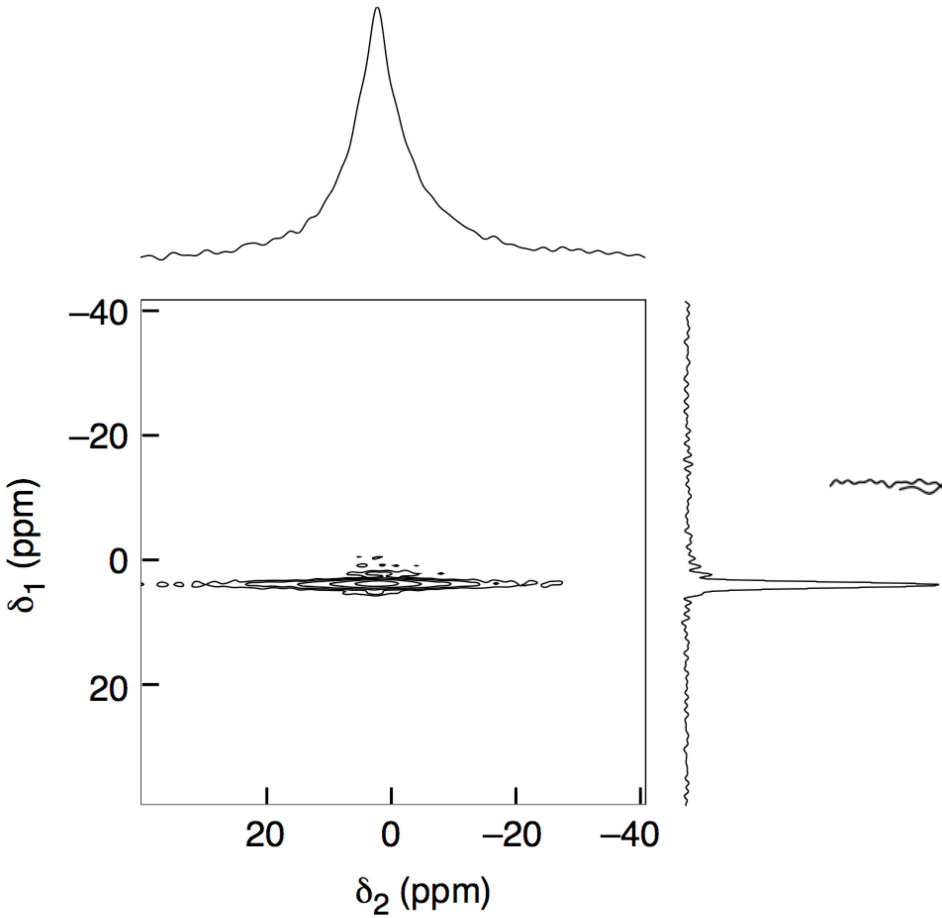


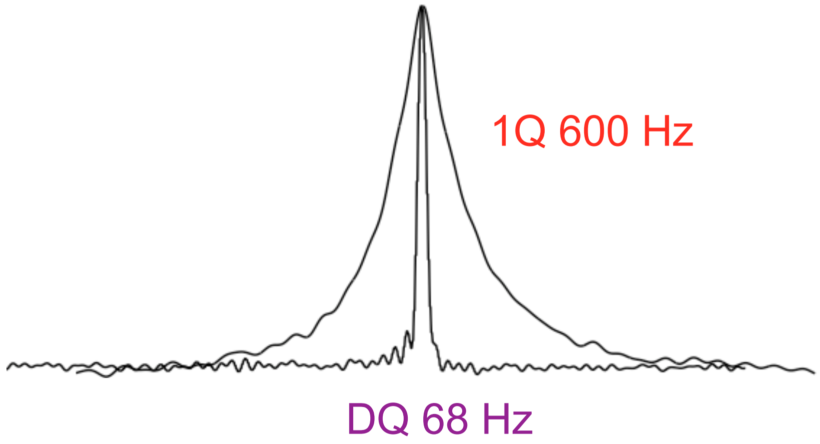


Cutajar et al., Chem. Phys. Lett. ***423****, 278 (2006)*

DQ NMR of humites

^2H DQ MAS of clinohumite ($4Mg_2SiO_4.Mg(OD)_2$)





Conclusions

- Study of high-pressure silicate minerals by NMR can be difficult owing to sensitivity limitations
- Eased through preparation of larger samples, higher enrichment levels and two-dimensional high-resolution experiments
- Use of first-principles calculations aids spectral assignment and interpretation
- Allows insight into the correlation of NMR parameters and the structural environment
- Use of STMAS and DQMAS experiments to probe dynamics in hydrous silicates