



Solid-state NMR: a powerful and versatile method of choice



NMR Centre Workshop

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2015/10/9 —1—




Why solid-state NMR?

2015/10/9 —2—




Solid-state NMR




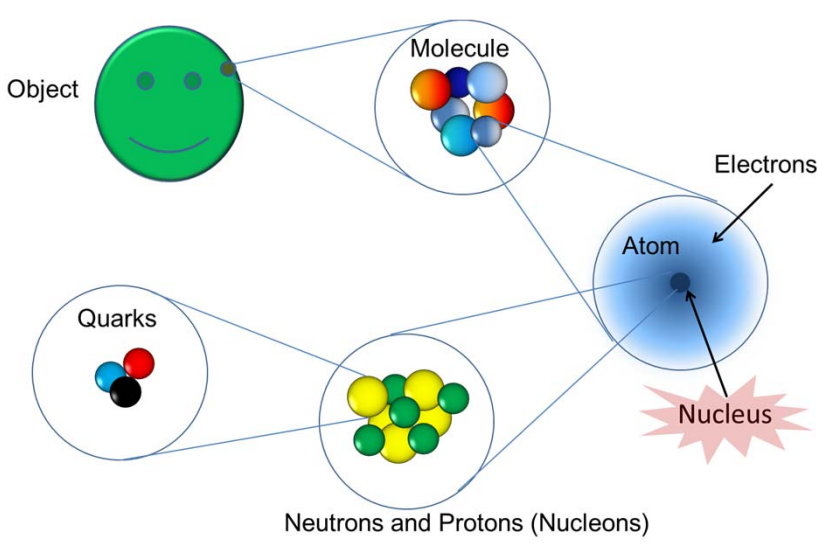
- It can be applied to the vast majority of samples at different levels of complexity;
- Subtle differences in the electronic environment result in different resonance frequencies;
- SSNMR is multinuclear, any element with nuclear spin can be studied;
- Successful on “powder” microcrystalline samples;
- Details about next neighboring atoms (1st and 2nd coordination sphere);
- Can readily distinguish polymorphs;
- Local symmetry and coordination numbers;
- Conformations, bond angles and distances;
- Molecular dynamics – probing molecular motion.

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NMR: where are we?





The diagram illustrates the hierarchical structure of matter relevant to NMR. It starts with an 'Object' (represented by a green smiley face) which is composed of 'Molecule's. A molecule is composed of 'Atom's. An atom consists of a central 'Nucleus' (represented by a red starburst) and 'Electrons' (represented by a blue cloud). The nucleus is composed of 'Neutrons and Protons (Nucleons)', which are further composed of 'Quarks' (represented by small colored spheres).

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SSNMR interactions - summary

In solids there are seven ways for a nuclear spin to communicate with its surroundings.

B_0, B_{rf}

1 = Zeeman Interaction; 2 = direct dipolar Interactions; 3= indirect spin coupling (J) and coupling of nuclear spins with electric field gradients (quadrupolar interaction), nuclear electron-spin coupling (paramagnetic); 4 = direct spin-lattice interactions; 3-5 = indirect spin-lattice interaction; 3-6 = chemical shielding and polarization of nuclear spins by electrons; 4-7 = coupling of nuclear spins to phonons.

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SSNMR Interactions - anisotropic

excitation

chemical shift

J-coupling

chemical environment; molecular mobility; symmetry; polymorphism; asymmetric units; through bond and through space connectivities; internuclear distances;

direct dipolar interaction

relaxation

quadrupolar interaction

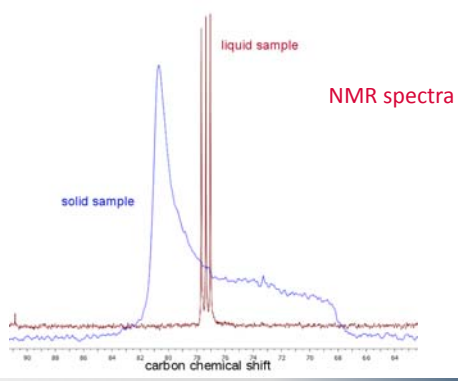
spin > 1/2 only

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Solid State Nuclear Magnetic Resonance

The method is applicable (with some variations in technique) to all types of solids:

Minerals (including aluminosilicates, coal), inorganic samples, wood, polymers, and foodstuffs, pharmaceutical samples, organic and biological samples (not always amenable to investigation by diffraction techniques).

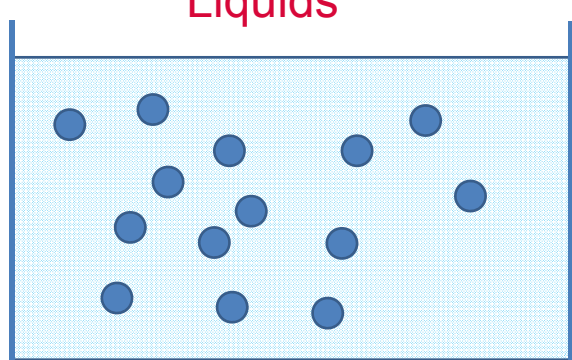


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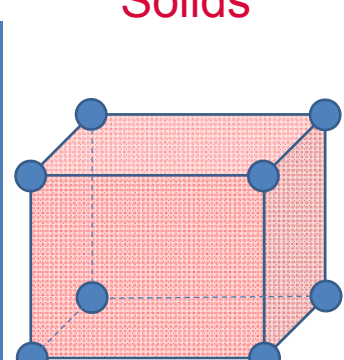
Liquids vs. Solids

Chemical shift anisotropy, direct dipolar coupling, nuclear quadrupole coupling) **are averaged to zero in solution** because of molecular tumbling.

Liquids



Solids



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A basic NMR scheme

The diagram illustrates the basic NMR scheme. It shows the relationship between the magnetic field (B_0), the magnetization vector (M_0), and the resulting signal (free induction decay).

On the left, a graph shows the signal (free induction decay) as a function of acquisition time. The signal is a decaying sinusoidal wave. A vertical bar labeled 90_x indicates the pulse. The y-axis is labeled nX and the x-axis is labeled acquisition time.

In the center, a diagram shows the energy levels of the nuclei. The energy difference is $\Delta E = h\nu$. The magnetic field is $B_0 = 0$ and $B_0 > 0$. The magnetization vector is M_0 .

On the right, a diagram shows the magnetization vector (M_0) and the resulting signal (free induction decay) in the receiver and transmitter coils. The receiver coil is labeled M_y and the transmitter coil is labeled M_x . A 90° pulse is indicated.

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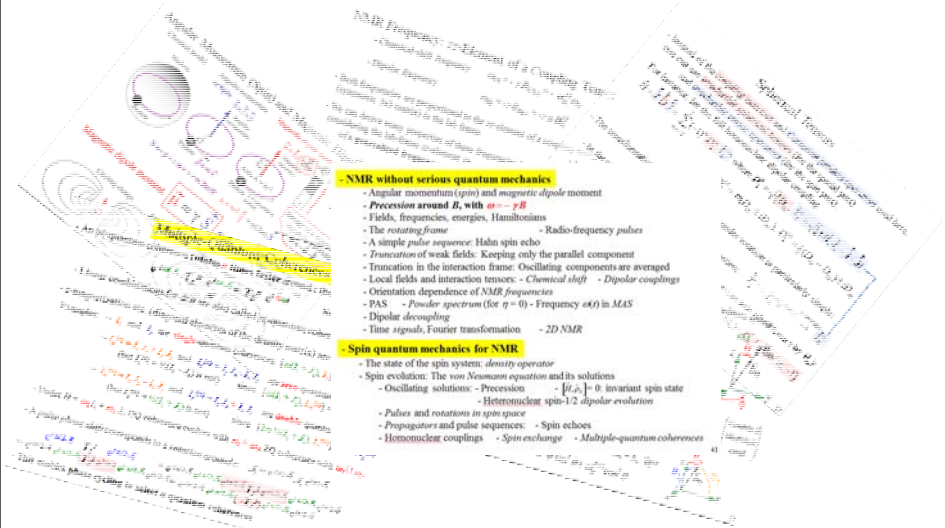

Cross-polarization

Dipolar coupling between the abundant Hs and between ^1H and ^{13}C allows the redistribution and transfer of energy to the ^{13}C nucleus and the signal improvement (4x).

The diagram illustrates cross-polarization. It shows a central ^{13}C nucleus surrounded by several ^1H nuclei. Arrows indicate the transfer of energy from the ^1H nuclei to the ^{13}C nucleus.

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Theoretical background – complicated?

- NMR without serious quantum mechanics

- Angular momentum (γ) and magnetic dipole moment
- Precession around B_0 with $\omega = \gamma B_0$
- Fields, frequencies, energies, Hamiltonians
- The rotating frame
- A simple pulse sequence: Hahn spin echo
- Truncation of weak fields: Keeping only the parallel component
- Truncation in the interaction frame: Oscillating components are averaged
- Local fields and interaction tensors: - Chemical shift - Dipolar couplings
- Orientation dependence of NMR frequencies
- PAS - Powder spectrum (for $\eta = 0$) - Frequency $\omega(\theta)$ in MAS
- Dipolar decoupling
- Time signals, Fourier transformation - 2D NMR


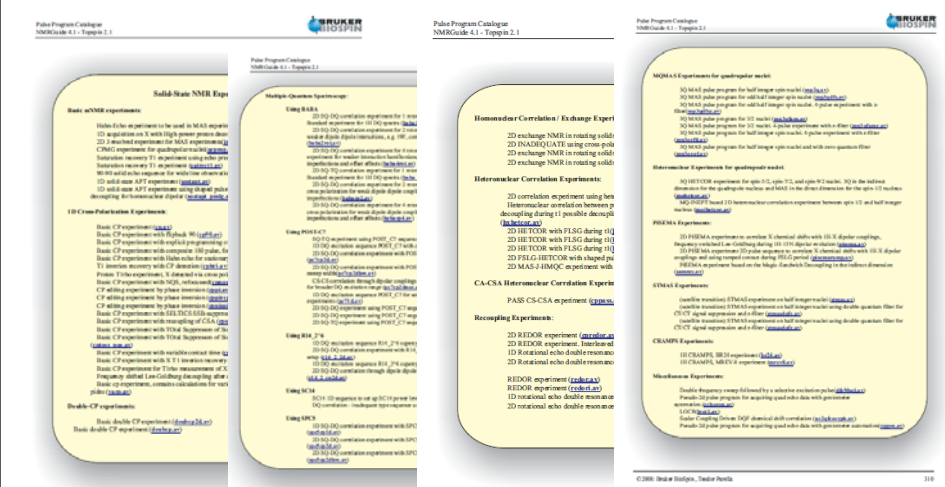

- Spin quantum mechanics for NMR

- The state of the spin system: density operator
- Spin evolution: The von Neumann equation and its solutions
- Oscillating solutions: - Precession - $[\rho, H_0] = 0$: invariant spin state
- Heteronuclear spin-1/2 dipolar evolution
- Pulses and rotations in spin space
- Propagators and pulse sequences: - Spin echoes
- Homonuclear couplings - Spin exchange - Multiple-quantum coherences

Source: Basic Theory of Solid-State NMR Klaus Schmidt-Rohr


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Practical – vast options?






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Choice of SSNMR experiment



Choice of SSNMR experiment

identification

morphology

mobility


structure

homogeneity


polymorphism

What do you want to know?

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Choice of SSNMR experiment



Choice of SSNMR Experiment

^1H

Quadrupole, ^{23}Na , ^{27}Al , ^{17}O

Labeled, ^{15}N , ^{13}C ...



Paramagnetics, unpaired electrons, metals...

amount

heterogeneity



What does the sample contain?

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Applications

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Conducting polymers

Multinuclear approach

2015/10/9 —16—

Polyaniline - from featureless grains to nanostructures

nanotubes
nanofiber(s)
nanospheres

polyaniline

Z.D. Zujovic, Y. Wang, G.A. Bowmaker, R.B. Kaner; *Macromolecules* **44**, 2735-2742 (2011)
 Z.D. Zujovic, C. Laslau, G.A. Bowmaker, P.A. Kilmartin, A.L. Webber, S.P. Brown, et al.; *Macromolecules* **43**, 662-670 (2010)

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SSNMR - spectral assignments

The sequence is composed of the alternating benzenoid diamine and quinoid diimine units the corrected imine/amine ratio should be 1:1

188.5
188.3
187.4
187.5
133.4
113.7

323.9
65.0
31.2

Quinoid diimine
 Benzenoid diamine

carbon chemical shift ppm
 nitrogen chemical shift ppm

Z.D. Zujovic, M.R. Gizdavic-Nikolaidis, P.A. Kilmartin, H. Idriss, S.D. Senanayake, G.A. Bowmaker; *Polymer* **47**, 1166-1171 (2006)

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Nanotubes – the formation mechanism

phenazine PANI chains

walls needle like oligomers

A

ortho para

B

OXIDATION

A concept from Stejskal, J.; Sapurina, I.; Trchová, M.; Konyushenko, E. N.; Holler, P. *Polymer* **47**, 8253 (2006).

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FTIR - early formed structures

T (A.U.)

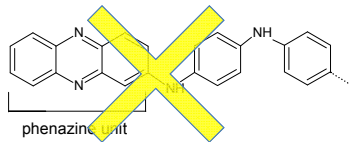
ν (cm⁻¹)

Stejskal, J.; Sapurina, I.; Trchová, M.; Konyushenko, E. N.; Holler, P. *Polymer* **2006**, *47*, 8253

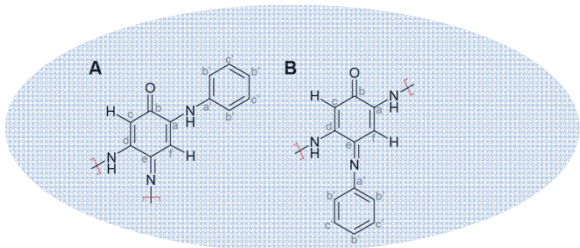
ca. 1620 cm⁻¹ C=O stretching - benzoquinone
ca. 1415, 1450 cm⁻¹ C-C (B) and C=C (Q) stretching Planes et al, *Phys. Chem. Chem. Phys.* **12**, 10584–10593 (2010).

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Summary



phenazine unit



A **B**

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Inorganic materials
Geopolymers

Coordination

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Geopolymers

Geopolymers are inorganic polymers obtained from metakaolin (or other double layered clayed minerals) and commercial sodium silicates.

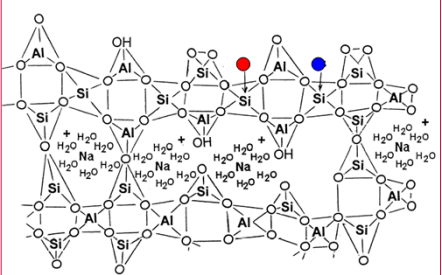
Bonds are bridges through oxygen.

The key attributes of geopolymers:

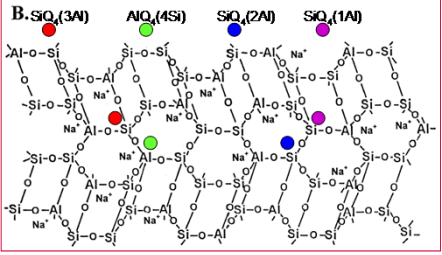
- thermal stability
- chemical stability
- high mechanical strength

Some of possible applications:

- Cement and concrete
- Traditional and high performance ceramics
- Precast and extruded building products
- High temperature automotive parts
- Bio-technologies (materials for medicinal applications)

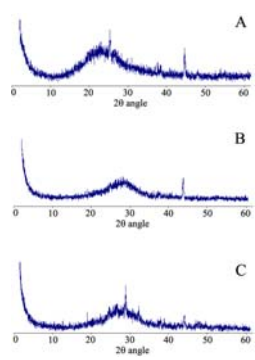


B. SiO₂ (3A) **Al₂O₃ (4Si)** **SiO₂ (2A)** **SiO₂ (1A)**

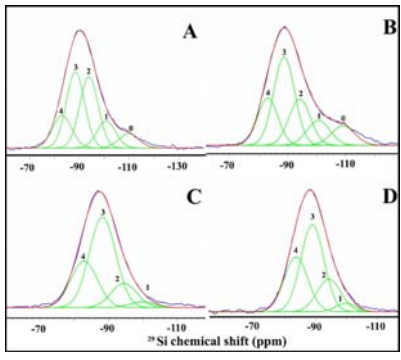


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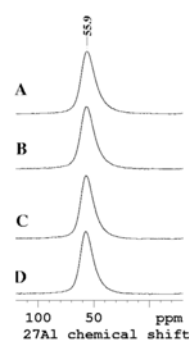
XRD vs. solid-state NMR broad echo vs. resolved resonance



A
B
C



A
B
C
D





A
B
C
D

The XRD diffractograms of Engelhard metakolin (A), and Engelhard-based geopolymers without (B) and with added $(\text{CaOH})_2$ (C).

Deconvoluted ^{29}Si spectra of an Engelhard-based geopolymer powder samples with different concentrations of $\text{Ca}(\text{OH})_2$. Peaks are labelled according to the number of Al neighbouring atoms bridged through oxygen to a tetrahedral Si.

^{27}Al spectra of an Engelhard-based geopolymer powder samples with different concentrations $\text{Ca}(\text{OH})_2$.



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Pharmaceuticals

Amorphous samples Polymorphs

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Difficulties to detect the amorphous form

- Crystalline forms - low aqueous solubilities.
- Conversion of the active compound into an amorphous form.
- Higher dissolution rates and solubilities of an amorphous form.
 - Using solvents (freeze drying, spray drying, co-precipitation).
 - Using heat (melting/quench cooling).
 - Using mechanical activation (milling, cryo-milling).
 - Combination of heat and mechanical activation (melt extrusion).

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Indomethacin – different polymorphs

Indomethacin is a nonsteroidal anti-inflammatory drug

XRPD diffractograms of the cryo-milled samples of Indomethacin.

NMR spectra of cryo-milled (a) and quench cooled (b) samples of Indomethacin.

Botker, et al . Assessment of crystalline disorder in cryo-milled samples of indomethacin using atomic pair-wise distribution functions', *International Journal of Pharmaceutics*, 2011 417-112.

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Ranitidine – different polymorphs



Ranitidine is used to treat ulcers

Diffractograms of a form 1 batch milled for various times. Figure inset shows the XRPD halo of the 150 min milled sample.

Solid-state NMR spectra of a form 1 Ranitidine batch milled at various times.

Chieng et al. Effect of milling conditions on the solid-state conversion of ranitidine hydrochloride form 1. *International Journal of Pharmaceutics*, 2006 327-36.

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Natural products

Polysaccharides in the cell walls

Molecular dynamics

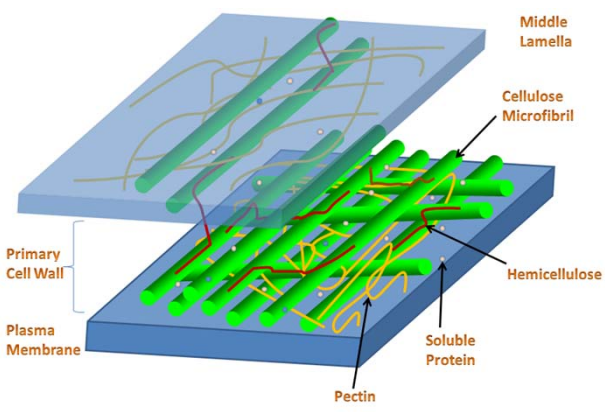
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Cell walls

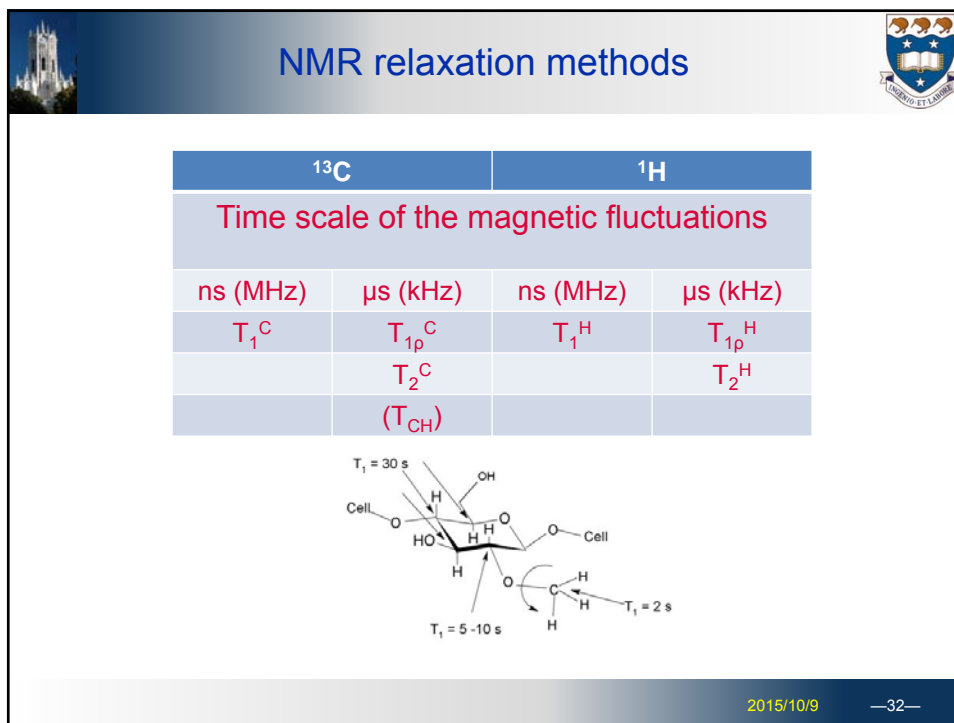
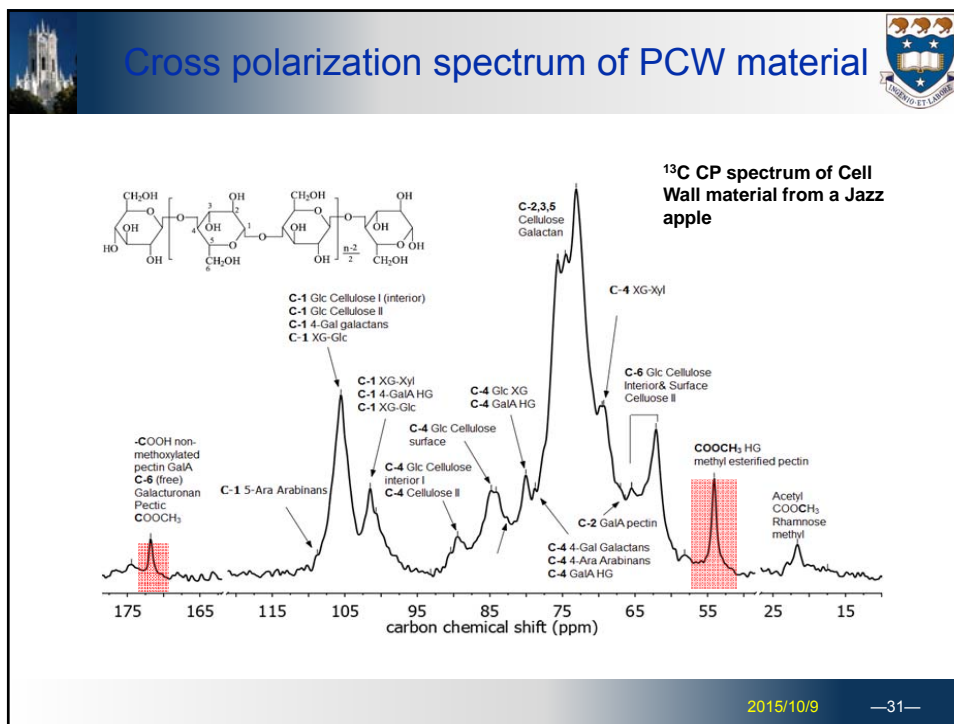
Cell walls mainly consist of:

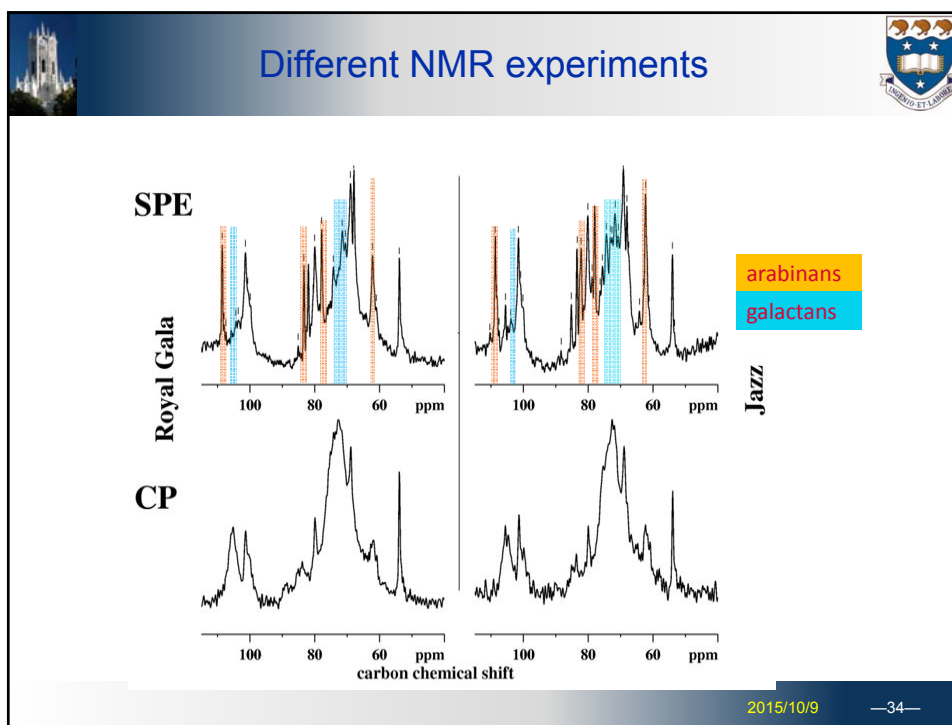
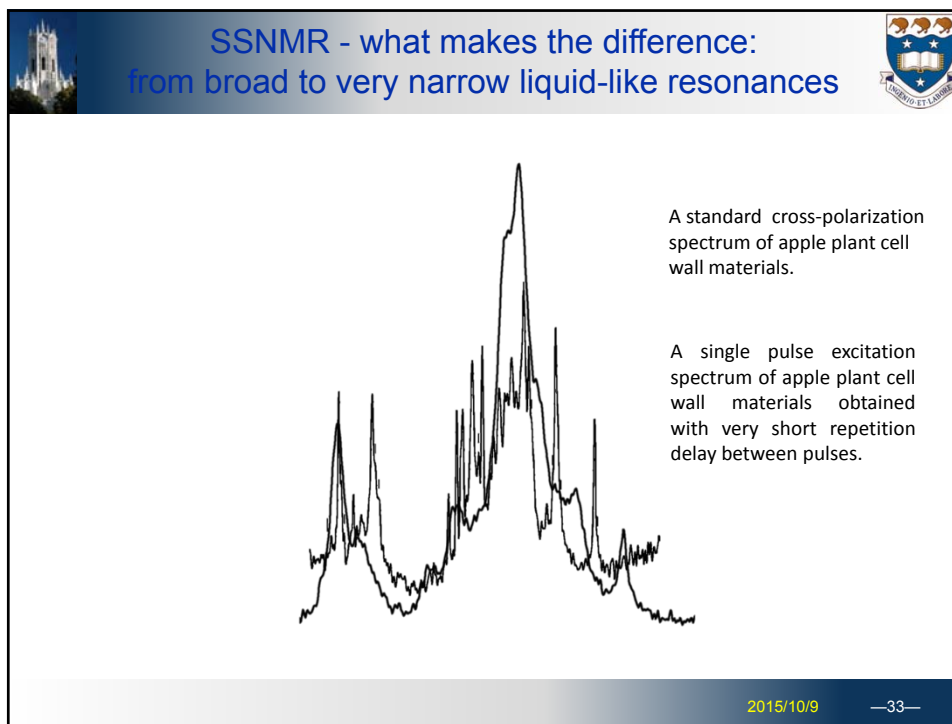
- CELLULOSE ($r = 2-5$ nm)
- HEMICELLULOSE
- PECTIC polysaccharides
- Soluble protein





The diagram illustrates the hierarchical structure of a plant cell wall. It shows a cross-section with several layers. The outermost layer is the Middle Lamella, followed by the Primary Cell Wall. The Primary Cell Wall is composed of Cellulose Microfibrils (represented by thick green cylinders), Hemicellulose (represented by yellow wavy lines), and Pectin (represented by red wavy lines). Below the Primary Cell Wall is the Plasma Membrane. Soluble proteins are also shown within the cell wall structure.

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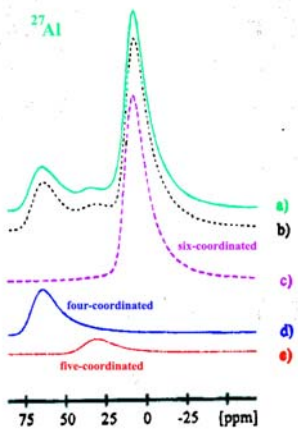
Alumina (Al_2O_3) samples

Quadrupolar NMR Coordination

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Alumina (Al_2O_3) - ^{27}Al NMR spectrum

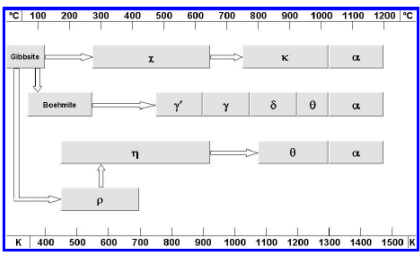


^{27}Al

a) experimental spectrum
b) six-coordinated
c) four-coordinated
d) four-coordinated
e) five-coordinated

75 50 25 0 -25 [ppm]

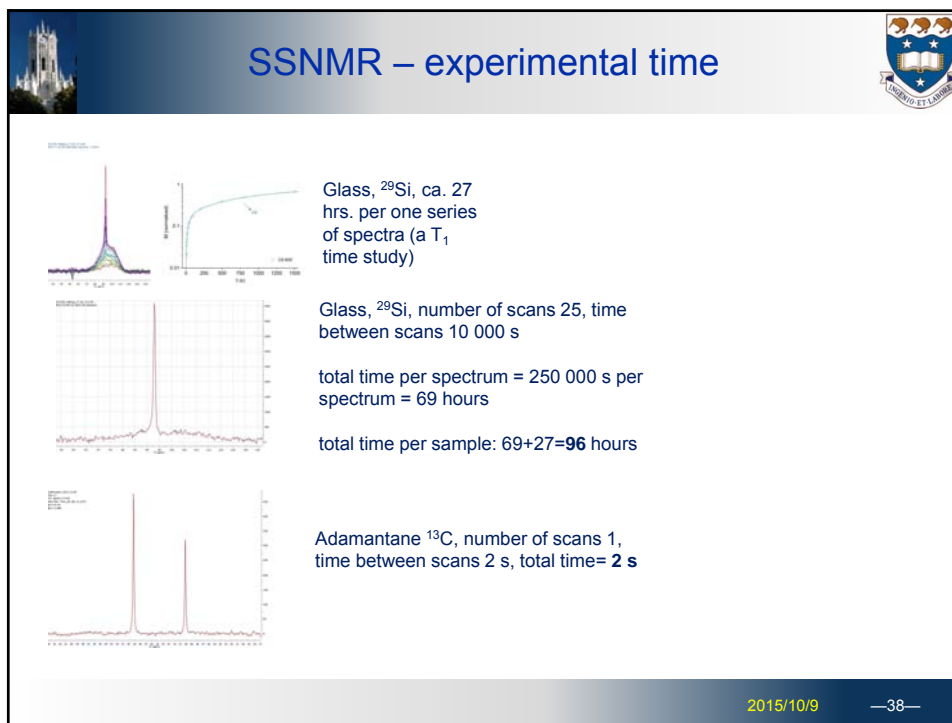
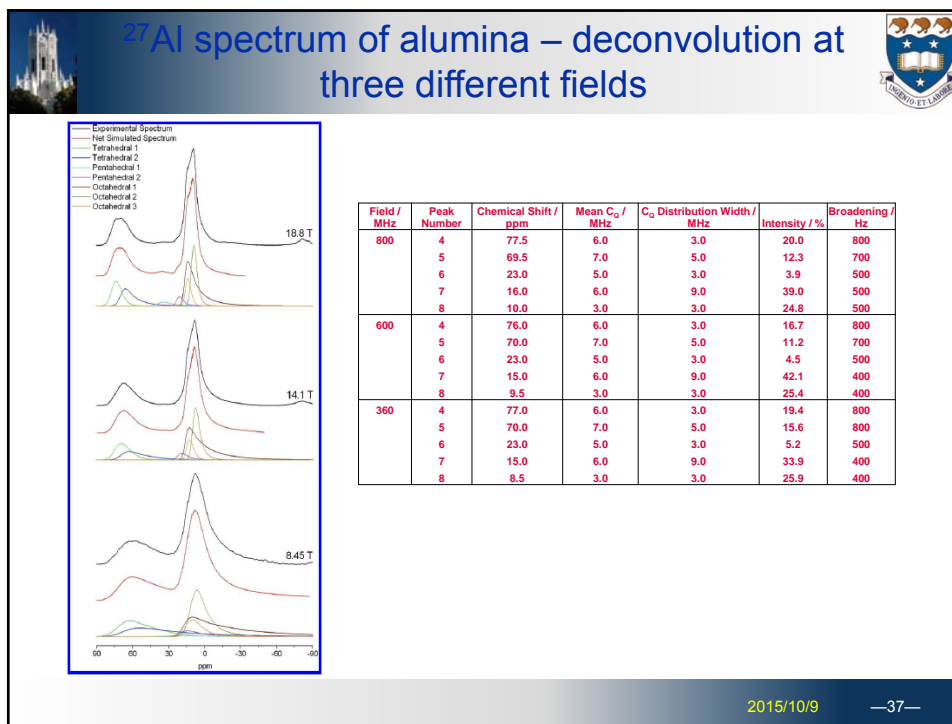
^{27}Al spectrum of an alumina sample, experimental a) and deconvoluted b) along with its components c), d), e).



Gibbsite ($\gamma\text{-Al}(\text{OH})_3$)
Boehmite ($\gamma\text{-AlOOH}$)

Purification
Filler for plastics
Abrasive
Catalysis
Composite fibre
Paint









2015/10/9 —36—








Thank you!



Graham A Bowmaker - NZ
 Jadranka Travas-Sejdic - NZ
 Laurie Melton - NZ
 James Metson - NZ
 Marija Gizdavic-Nikolaidis_ NZ
 Paul Kilmartin - NZ
 Amy Webber- UK
 Steven P. Brown - UK
 Mark Smith - UK
 Richard Kaner - USA
 Yue Wang - USA
 Conrad Perera- NZ
 Peter Swedlund- NZ
 Bronwen Smith - NZ
 Thomas Rades – NZ, Denmark
 Christian Mayer - Germany
 Dragomir Stanisavljev- Serbia
 Rosie Schroeder - NZ
 Elise Champeil- USA
 Jaroslav Stejskal – Czech Republic
 Miroslava Trchova- Czech Republic
 Ajit Sarmah – NZ
 Luitgard Schwendenmann - NZ

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Thank you for your attention!

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