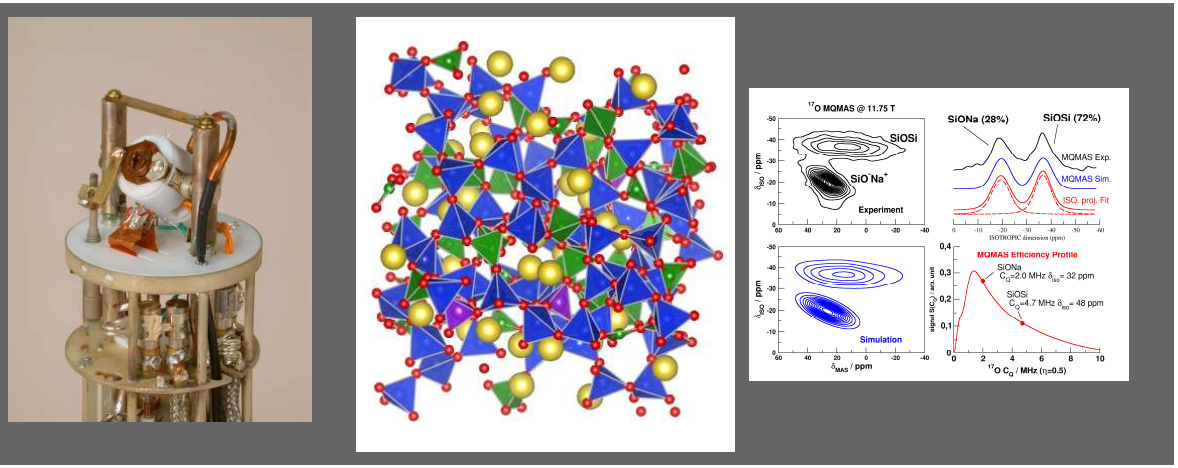
DE LA RECHERCHE À L'INDUSTRIE

cea

UNION
POUR LA SCIENCE
ET LA TECHNOLOGIE
VERRIÈRES

DES LIMITES DE LA CARACTÉRISATION ÉLÉMENTAIRE DANS LES MATÉRIAUX AUX CONTACTS ALIMENTAIRES :
une contrainte scientifique et industrielle (REACH)
25-26 novembre, IPGParis

Limites et Potentiel de la RMN pour la caractérisation structurale de l'environnement des éléments « traces »



USTV - REACH | Thibault Charpentier

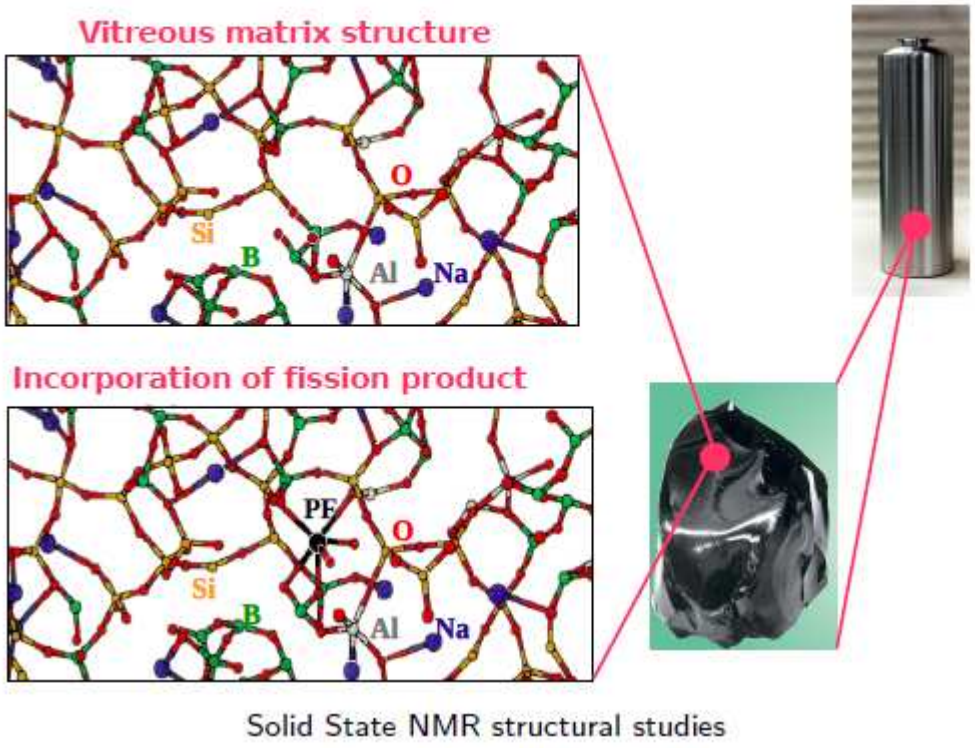
25 Novembre 2013

IRAMIS

NMR of Glasses

Solid State Nuclear Magnetic Resonance (ssNMR) is a powerful spectroscopy to probe the glass structure at the *atomic scale.*

Glass structure



Solid State NMR structural studies

Composition ⇔ Structure ⇔ Properties

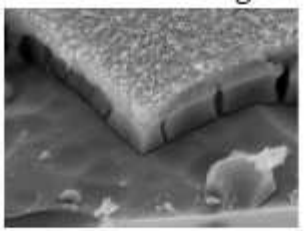
Irradiation effects

Oxygen bubbles under β-irradiation

N. Ollier
CEA/DSM
S. Peuget
CEA/DEN

Glass Leaching

The *alteration gel*



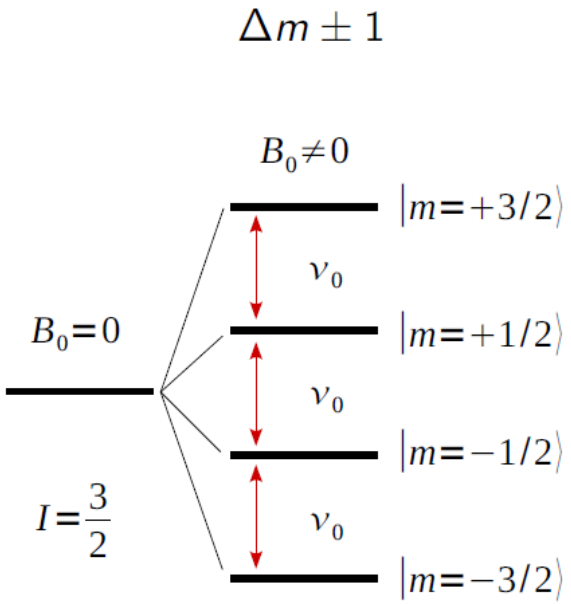
F. Angeli
P. Jollivet
CEA/DEN

Incorporation of low-solubility Elts

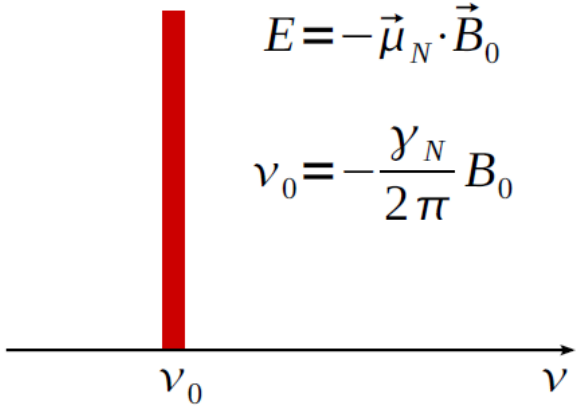
S. Schuller
CEA/DEN

The Zeeman Interaction and Larmor Frequency

The NMR spectrum of an isolated nucleus . . .



The Zeeman effect



The Larmor frequency and its NMR spectrum.

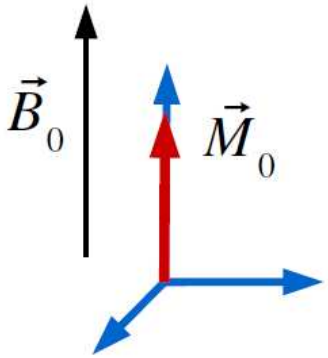
No information on the chemical surrounding

$$(\hbar)\, H = -\hbar \gamma_N \vec{I} \cdot \vec{B}_0$$

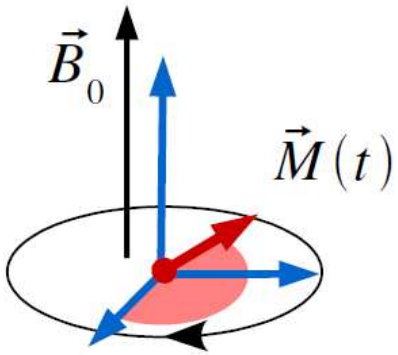
NMR : the polarization

NMR sensitivity and Nuclear Magnetization

Equilibrium Nuclear Magnetization



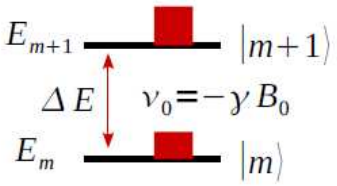
Larmor Precession at ν_0



M_0: Nuclear Magnetization at Equilibrium is given by the Curie Law

$$\vec{M}_0 = \sum_i \vec{\mu}_i = \chi_0 \vec{B}_0 \propto \exp\{-\Delta E/kT\}$$

$$\chi_0 = N_I \frac{\gamma_I^2 \hbar^2 I(I+1)}{3kT} B_0$$



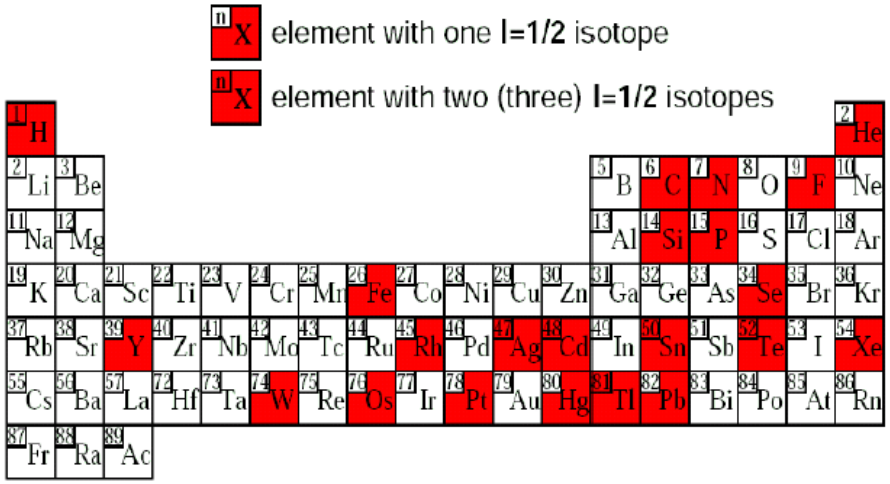
- Small polarization 10^{-3} to 10^{-6}
- Signal $\propto N_I$ Quantitativity
- Signal $\propto B_0$ High Field
- signal $\propto \gamma_I^2$

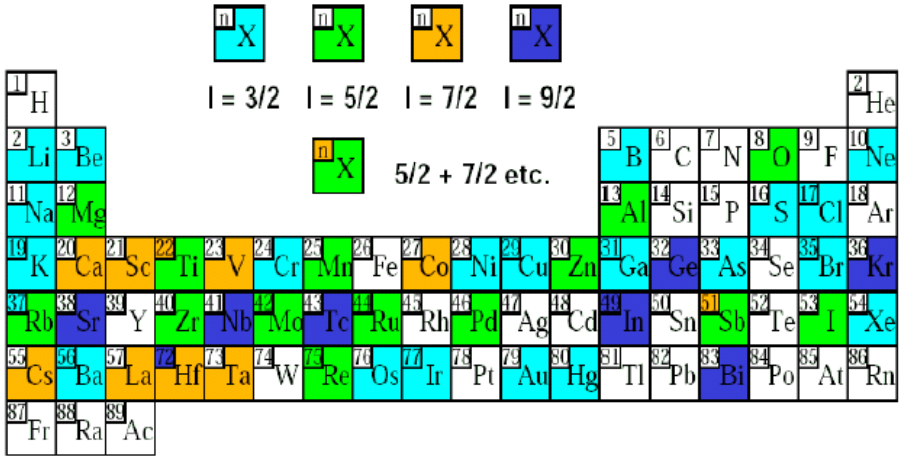
NMR : low frequency (10-1000 MHz)

NMR and the Periodic Table

One-half and *quadrupolar nuclei*

- Isotope, Nuclear Spin
- Natural Abundance
- Gyromagnetic ratio γ (rad/s/T)
  $\omega_0 = 2\pi\nu_0 = -\gamma B_0$
- Quadrupolar Moment Q (see Pyykkö)

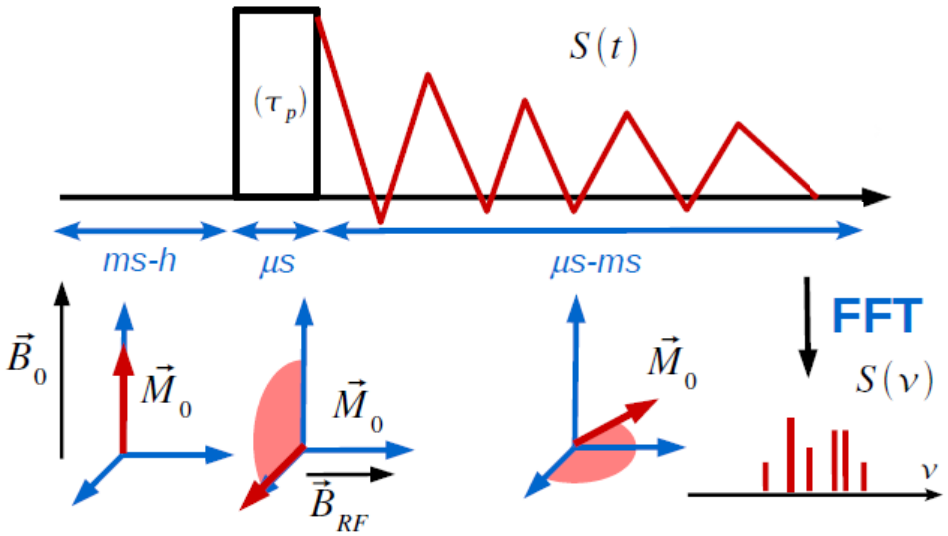


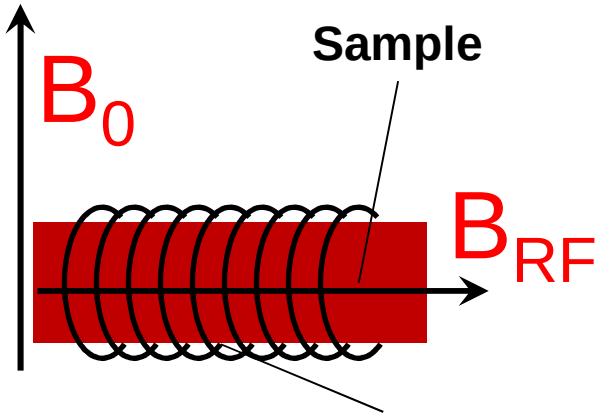


Pulsed NMR

The Basic NMR Experiment . . . One pulse !

M_0: Nuclear Magnetization at Equilibrium





$$\vec{M}(0) = M_0\vec{z}$$
$$\vec{M}(\tau_p) = M_0\vec{x}$$
$$S(t) = M_0 e^{-i\nu_0 t} e^{-\frac{t}{T_2}}$$

$$S(\nu) = \int_0^\infty dt\, S(t) e^{-i2\pi\nu t} \approx \sum_{k=0}^{N-1} S(t_k) e^{-i2\pi\nu t_k} = L(\nu - \nu_0)$$

Lineshape $L(\nu)$: Gaussian, Lorentzian . . .

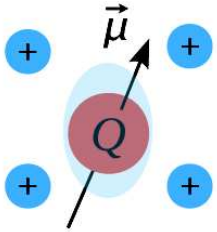
NMR interactions and the local atomic environment

NMR interactions (without equations . . .)

One-Spin Interactions
Magnetic Shielding /
Chemical shift

(1)

Electif Field Gradient (EFG)

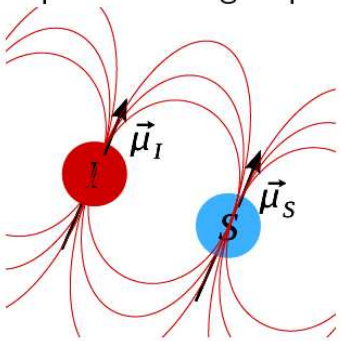


(2)

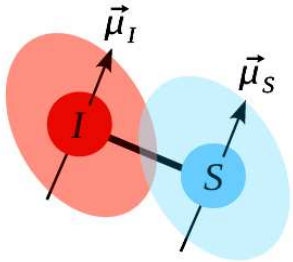
Only for I>1/2 Quadrupolar Interaction

speciation / structural units

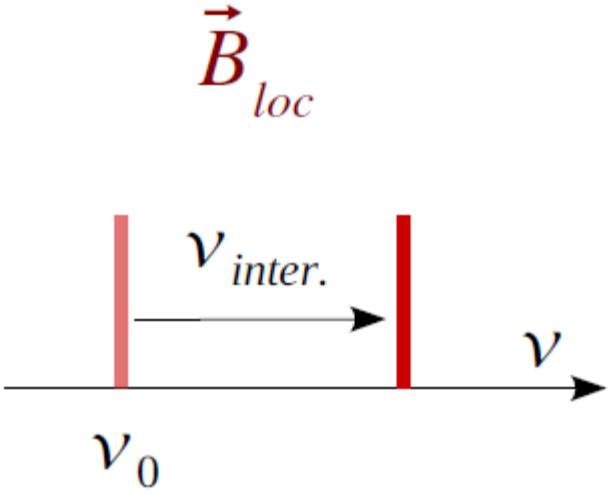
Two-Spins Interactions
Dipolar: through Space



J: through bond



Connectivities Proximities (2D)



Main NMR parameters :

(1) *Isotropic chemical shift (position of the line)* δ_{iso}

(2) *Quadrupolar coupling constant (width of the line)* C_Q

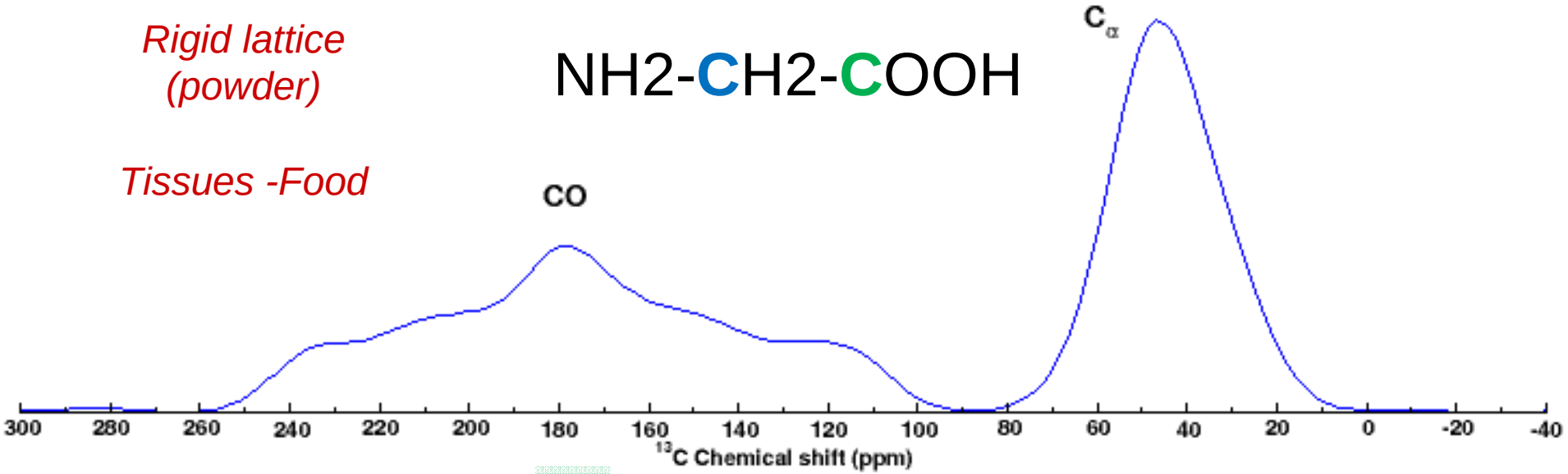
Asymmetry parameter (lineshape) η

NMR : Liquid versus Solid

Rigid lattice (powder)

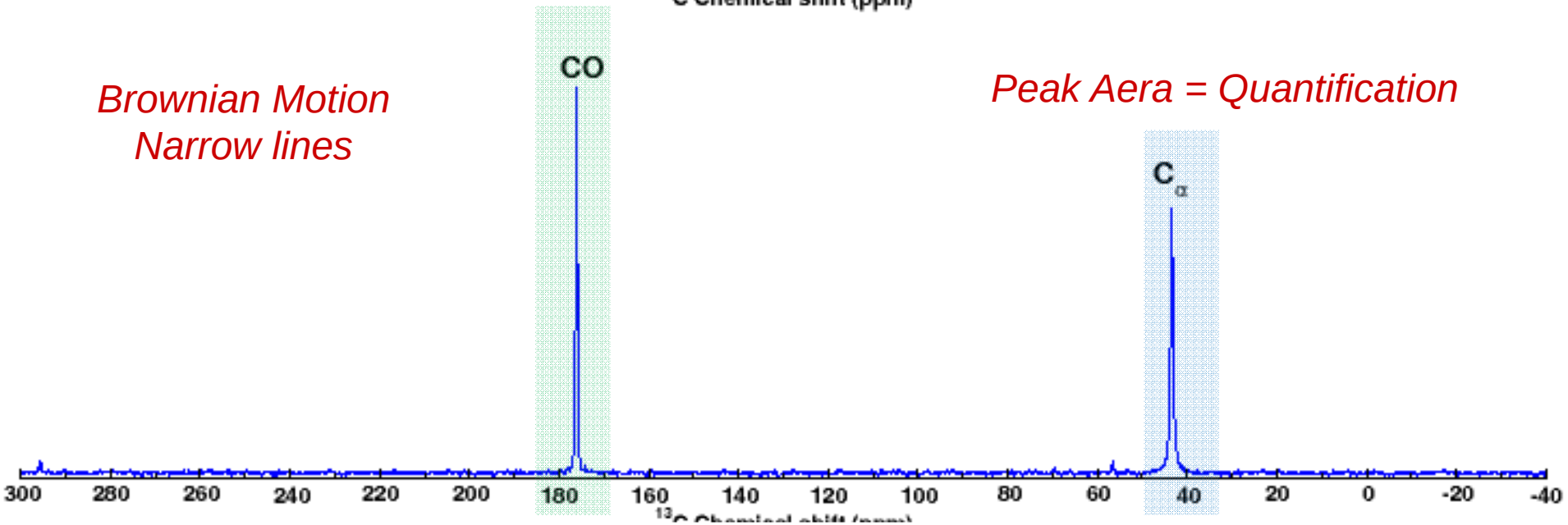
Tissues -Food

NH2-CH2-COOH



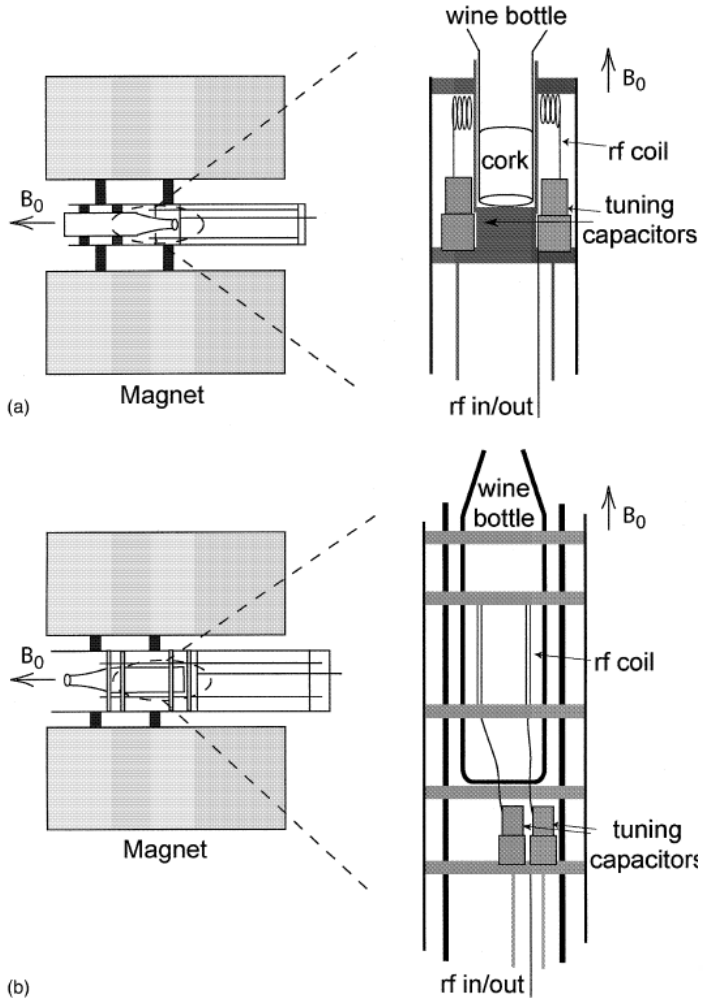
Brownian Motion
Narrow lines

Peak Aera = Quantification

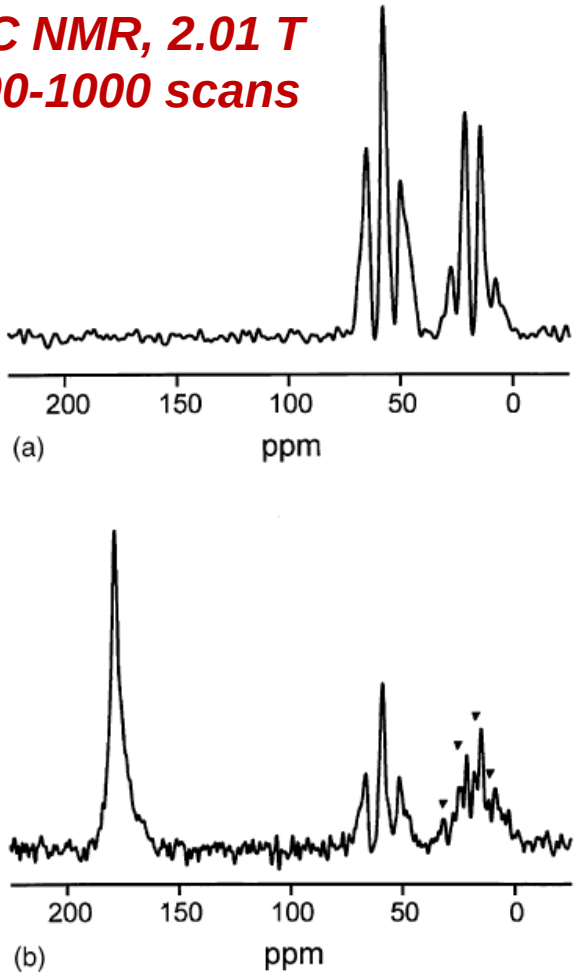


RMN : Une spectroscopie non-destructive

Using NMR to study full intact Wine bottles, A.J. Weekley et al., JMR **161** (2003) 91-98

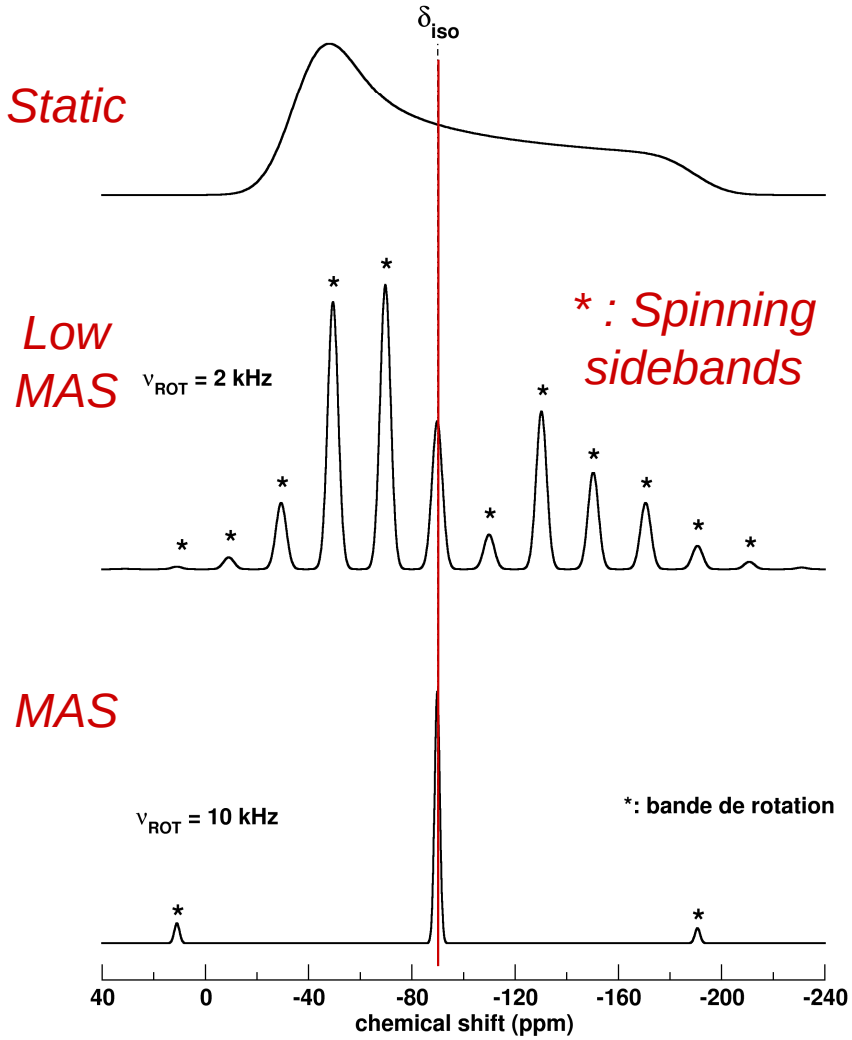


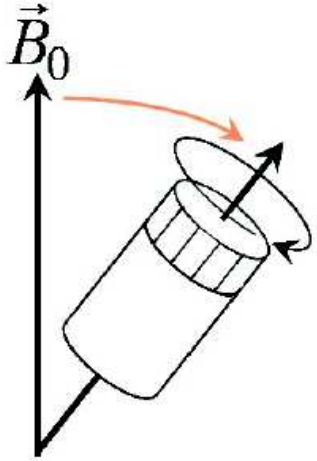
^{13}C NMR, 2.01 T
100-1000 scans

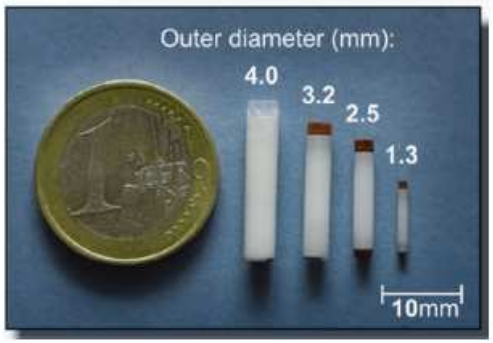


Detection of cocaine (1min, 5mM 1.5g/L) !
(Gambarota et al. 2011) Drug testing and Analysis 3 (2011) 544

Magic Angle Sample Spinning (MAS) NMR







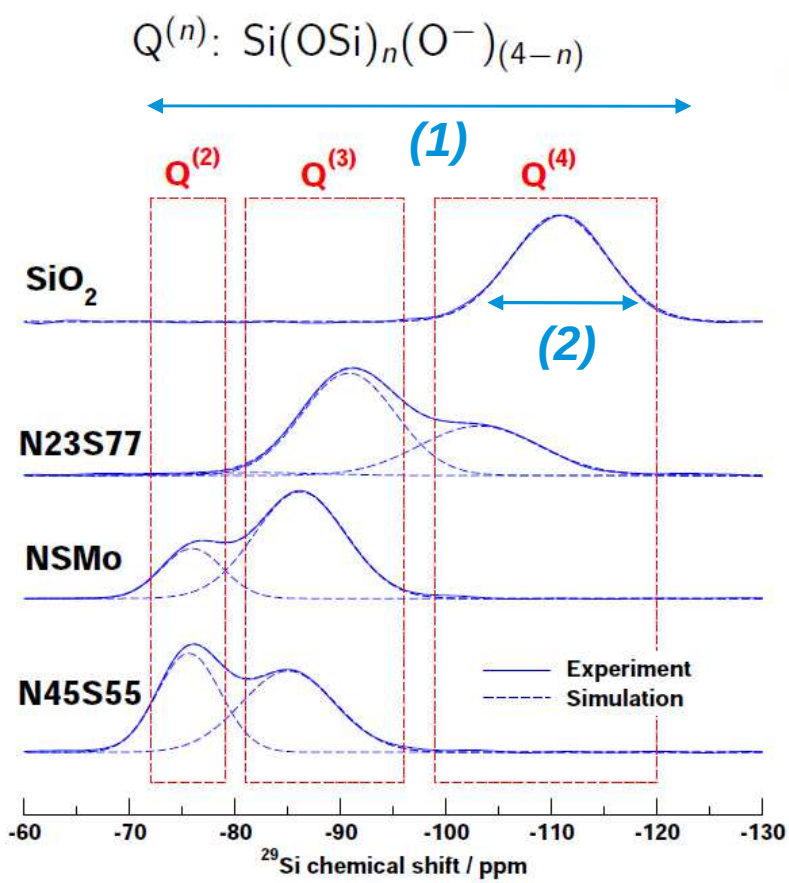
diam. (mm)	Spin rate (kHz)
4	15
3.2	24
2.5	35
1.3	67

MAS NMR of ^{29}Si in binary Na_2O-SiO_2 glasses

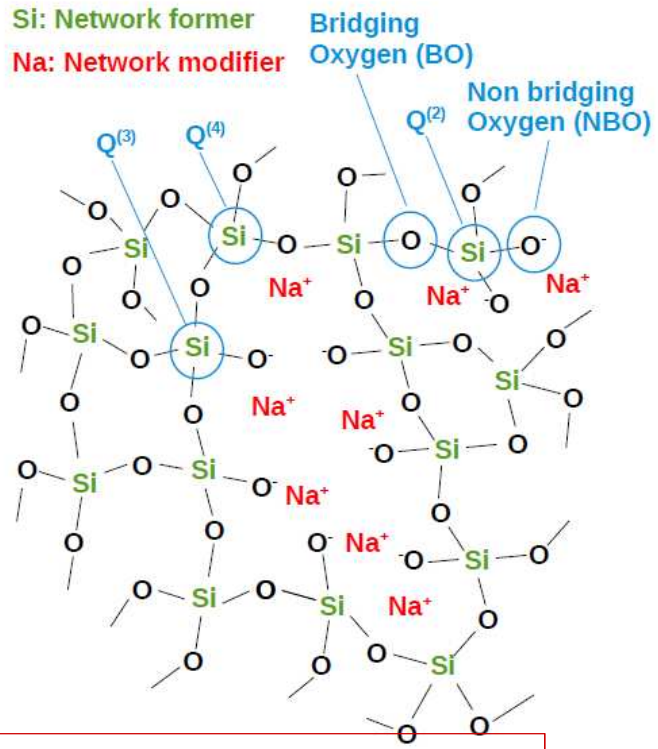
^{29}Si MAS NMR

(1) Chemical disorder

(2) Geometrical disorder



^{29}Si MAS NMR:
Direct access to silicon $Q^{(n)}$ speciation



NMR peaks reflective of a Gaussian distribution of δ_{iso} (I=1/2)

Geochimica et Cosmochimica Acta **75** (2011) 2453

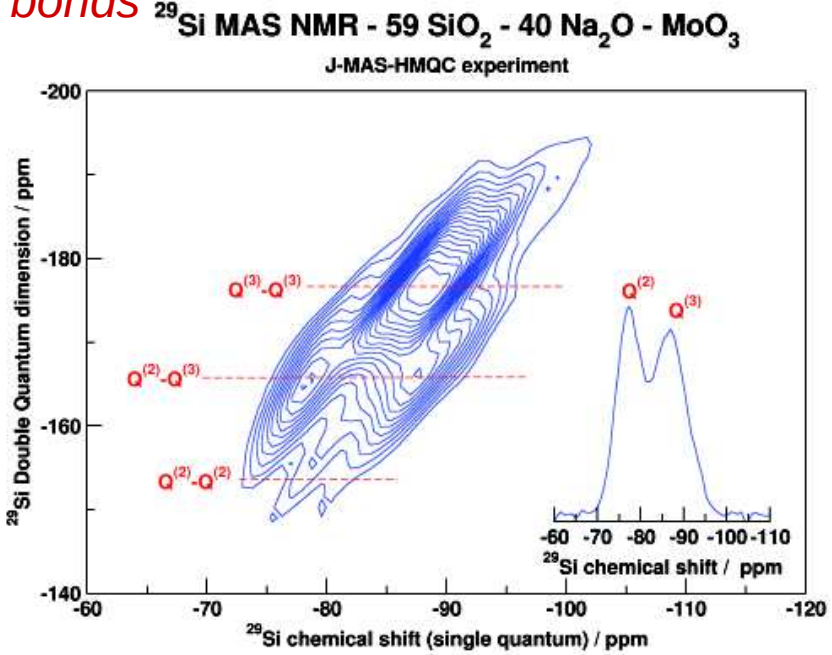
Advanced NMR techniques : two spin interactions

NMR Toolbox: Through-bond (J) correlations

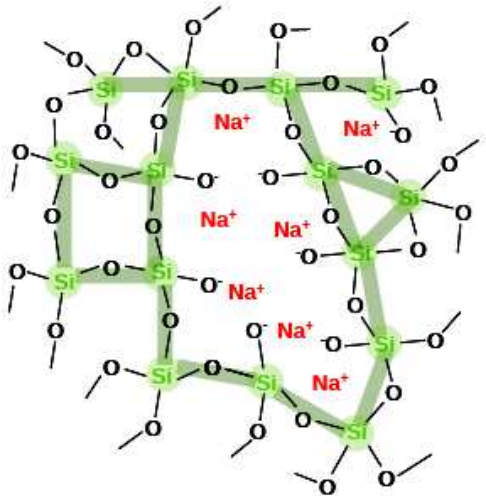
Heteronuclear Multiple Quantum Correlation (HMQC)

Double-Quantum (DQ)
MAS NMR
Probing spin pairs
Through chemical bonds

$$\frac{\hbar^2}{2}\sum_i\sum_{j\neq i}\gamma_i\gamma_j\vec{I}_i\left(\mathbf{D}_{ij}+\mathbf{J}_{ij}\right)\vec{I}_j$$



NMR of bonded nuclear spins (Si-O-Si)



⇒ Structure elucidation from atomic to molecular scale length

Coll. S. Schuller, F. Angeli, CEA/DEN

RMN MAS : résolution de la structure des verres à l'échelle moléculaire

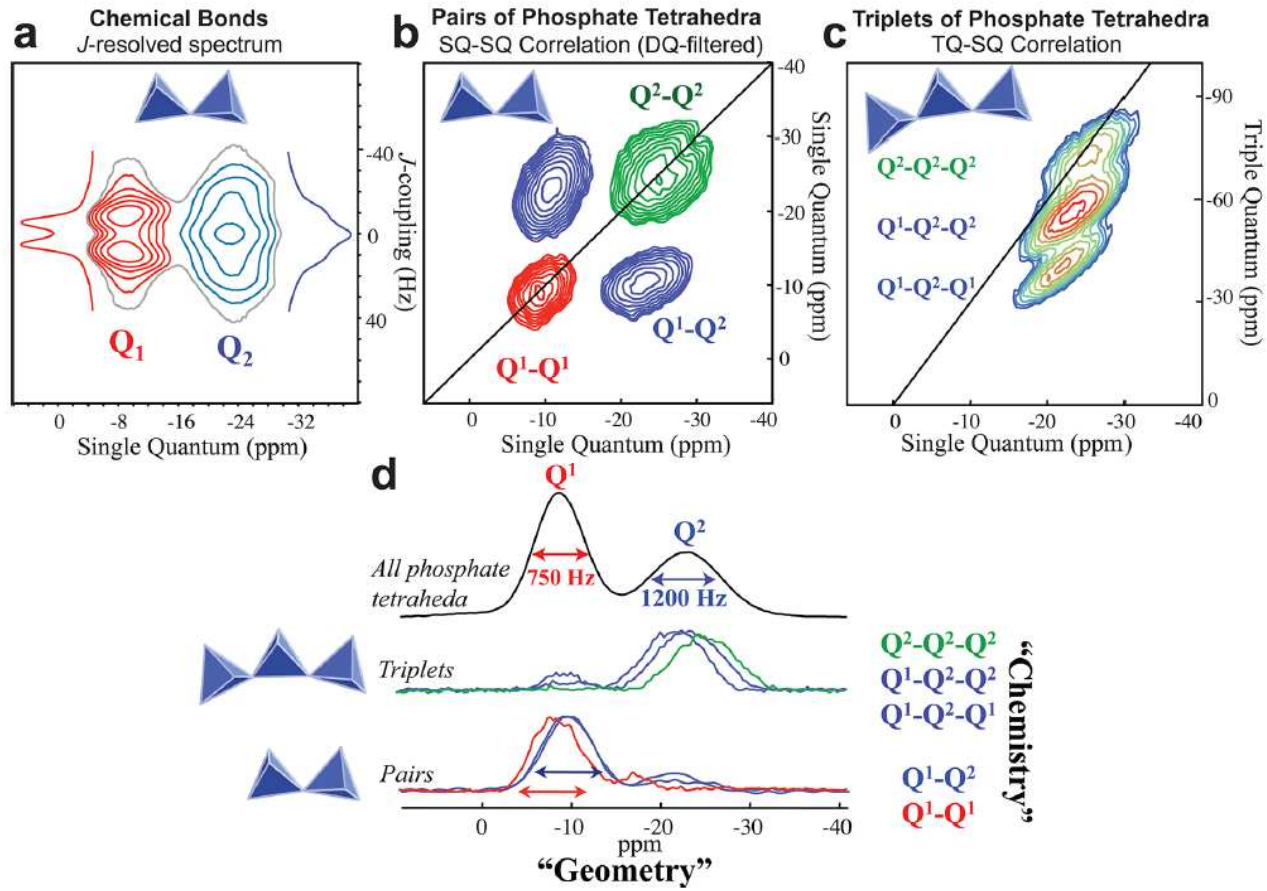
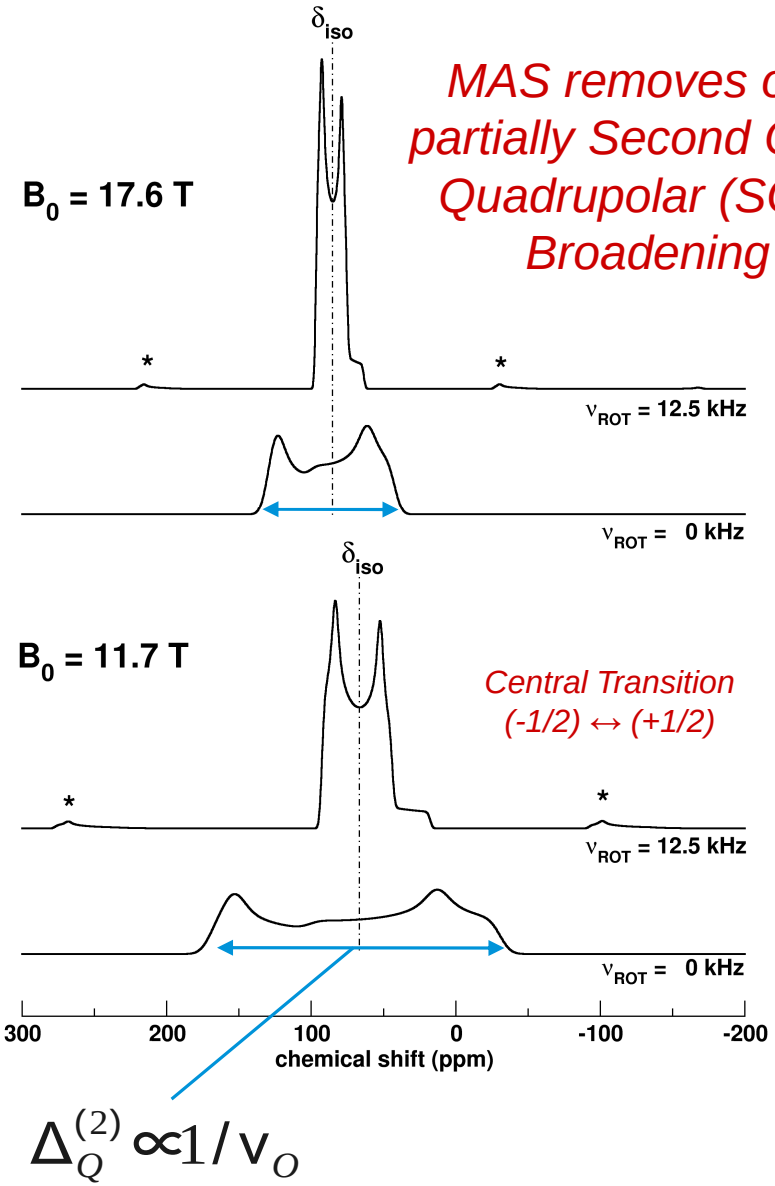


FIGURE 6. ^{31}P NMR characterization of a $(PbO)_{0.61}(P_2O_5)_{0.39}$ glass. (a) Measurements of $^2J_{P-O-P}$ couplings. Two-dimensional correlation spectra that select (b) P–P pairs and (c) P–P–P triplets. (d) One-dimensional spectrum reconstructed with the individual quantitative contributions of the different chemical motifs.[25,26]

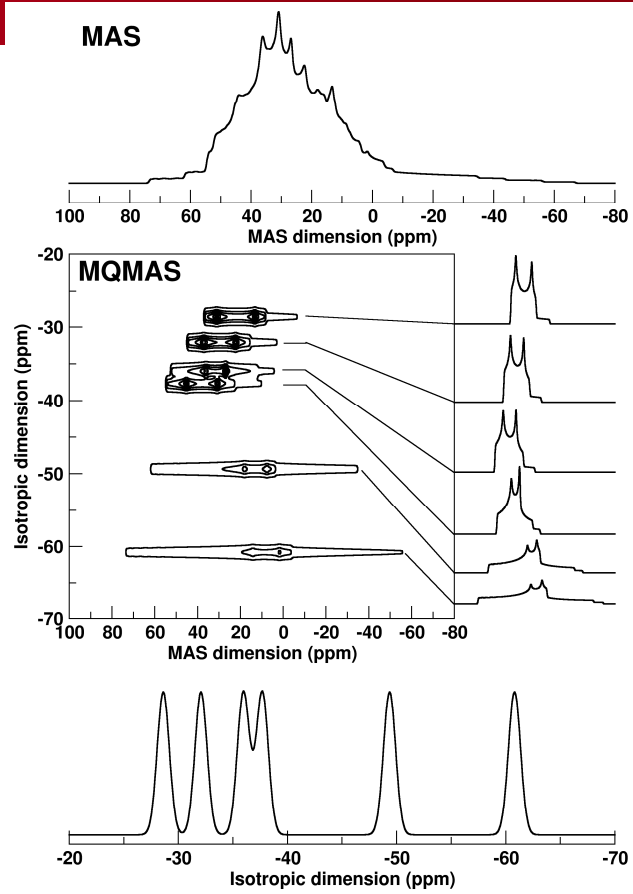
MAS NMR of Quadrupolar Nuclei (I>1/2)

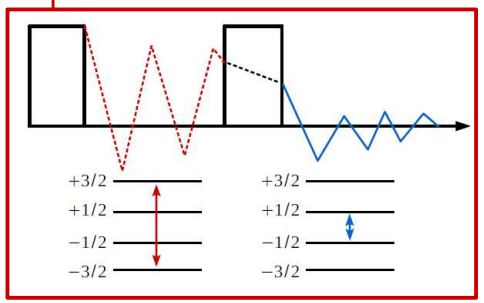


MAS removes only partially Second Order Quadrupolar (SOQ) Broadening

Central Transition (-1/2) ↔ (+1/2)

$$\Delta_Q^{(2)} \propto 1/\nu_O$$





Multiple-Quantum MAS (2D) removes SOQ anisotropy

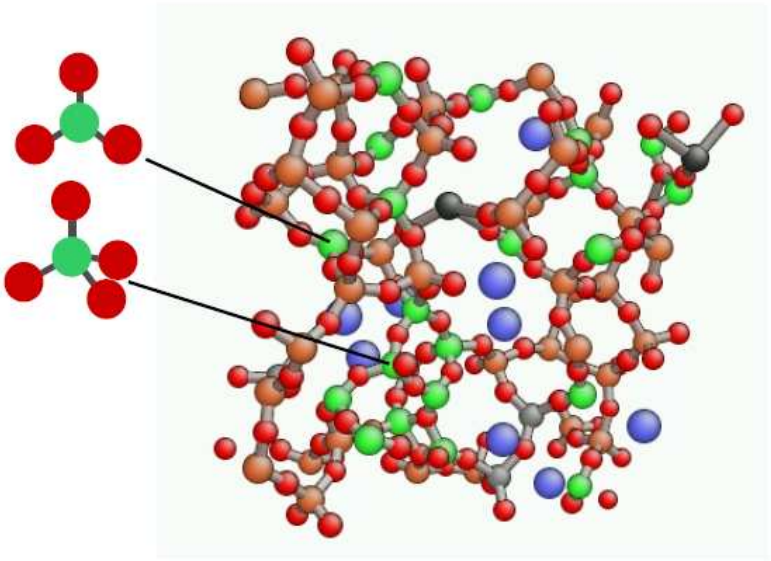
^{11}B MAS NMR in borosilicate glasses

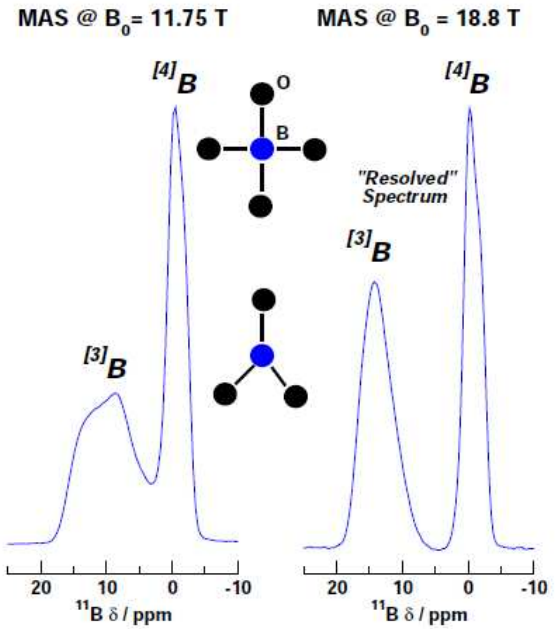
^{11}B MAS NMR in Borosilicate Glasses

1-10%mol Texp~min

Direct access to boron speciation

Detection level
~ 10-100 ppm





Identifying the structural units forming the glass network

High Field MAS NMR: Boron speciation resolved

MD Picture, J.M. Delaye, CEA/DEN

See F. Angeli et al., JACerS 93 (2010)

RMN : Importance de la spéciation des traces

Chemical state of boron in coal fly ash investigated by focused-ion-beam time-of-flight secondary ion mass spectrometry (FIB-TOF-SIMS) and satellite-transition magic angle spinning nuclear magnetic resonance (STMAS NMR)

Shun-ichi Hayashi [a,*], Takafumi Takahashi [a], Koji Kanehashi [a], Naoyoshi Kubota [a], Kaoru Mizuno [b], Shunsuke Kashiwakura [c], Tetsuo Sakamoto [d], Tetsuya Nagasaka [c]

The toxicity of inorganic pollutants largely depends on their chemical state rather than on their concentrations, with the less soluble forms being generally regarded as less toxic. In fact, it has been reported that in CFA, the leaching characteristic of boron varies depending on its chemical state (Iwashita et al., 2005). This result suggests that it may be possible to inhibit the leaching of boron by controlling its chemical state. Thus, the analysis of the chemical state of boron in CFA is essential to propose an effective way to restrain the elution of boron to the environment (Kashiwakura et al., 2009).

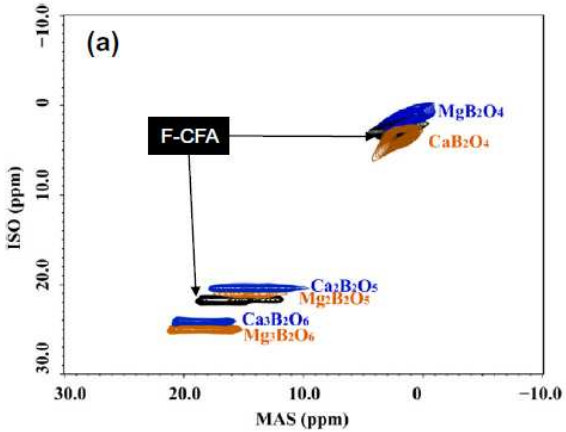
Conventional analytical techniques such as ICP-AES and ICP-MS evaluate the average concentration of trace elements in bulk samples, but do not provide information on their chemical state. Since the concentration of trace elements in CFAs is generally less than 100 mg kg^{-1}, direct and nondestructive detection for some trace

Chemosphere 80 (2010) 881–887

RMN : Importance de la spéciation des traces

SiO_2	63.1	56.1
Al_2O_3	20.5	31.6
Fe_2O_3	3.99	3.66
CaO	5.84	3.99
MgO	1.37	0.95
B (ppm)	1050	540

^{11}B MAS NMR, 16.4 T
100-1000 scans



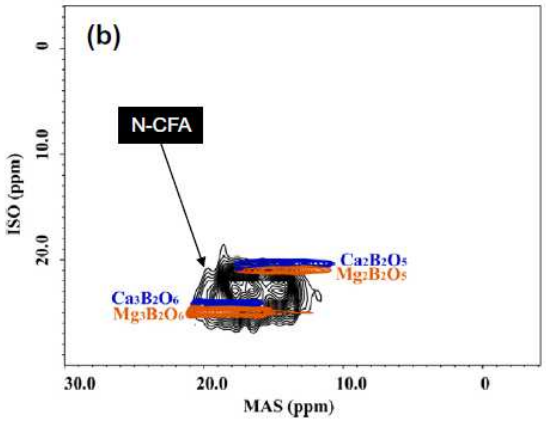


Fig. 3. ^{11}B STMAS spectra for (A) F-CFA and (B) N-CFA.

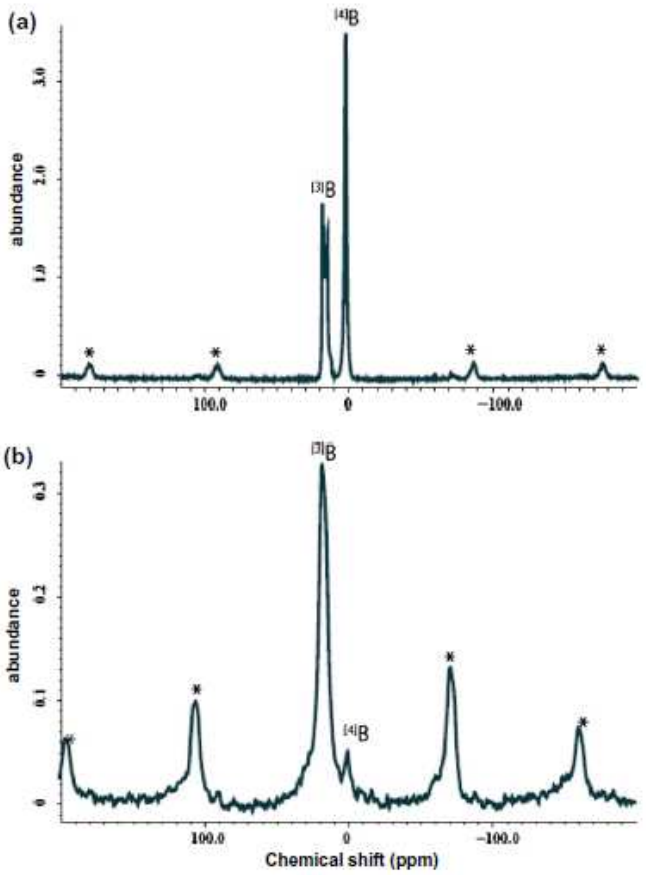


Fig. 2. ^{11}B MAS spectra for (A) F-CFA and (B) N-CFA. An asterisk (*) indicates the spinning side band.

Chemosphere 80 (2010) 881–887

RMN : spéciation de traces

Boron isotopes as pH proxy: A new look at boron speciation in deep-sea corals using ^{11}B MAS NMR and EELS

Claire Rollion-Bard [a,*], Dominique Blamart [b], Julien Trebosc [c], Grégory Tricot [c], Alexandre Mussi [d], Jean-Pierre Cuif [e]

$$pH = pK_B - \log\left(\frac{\delta^{11}B_{sw} - \delta^{11}B_c}{\alpha_{4-3}^{-1} \times \delta^{11}B_c - \delta^{11}B_{sw} + 1000 \times (\alpha_{4-3}^{-1} - 1)}\right) \quad (1)$$

$$^{10}B(OH)_3 + {}^{11}B(OH)_4^- \rightleftharpoons {}^{11}B(OH)_3 + {}^{10}B(OH)_4^-$$

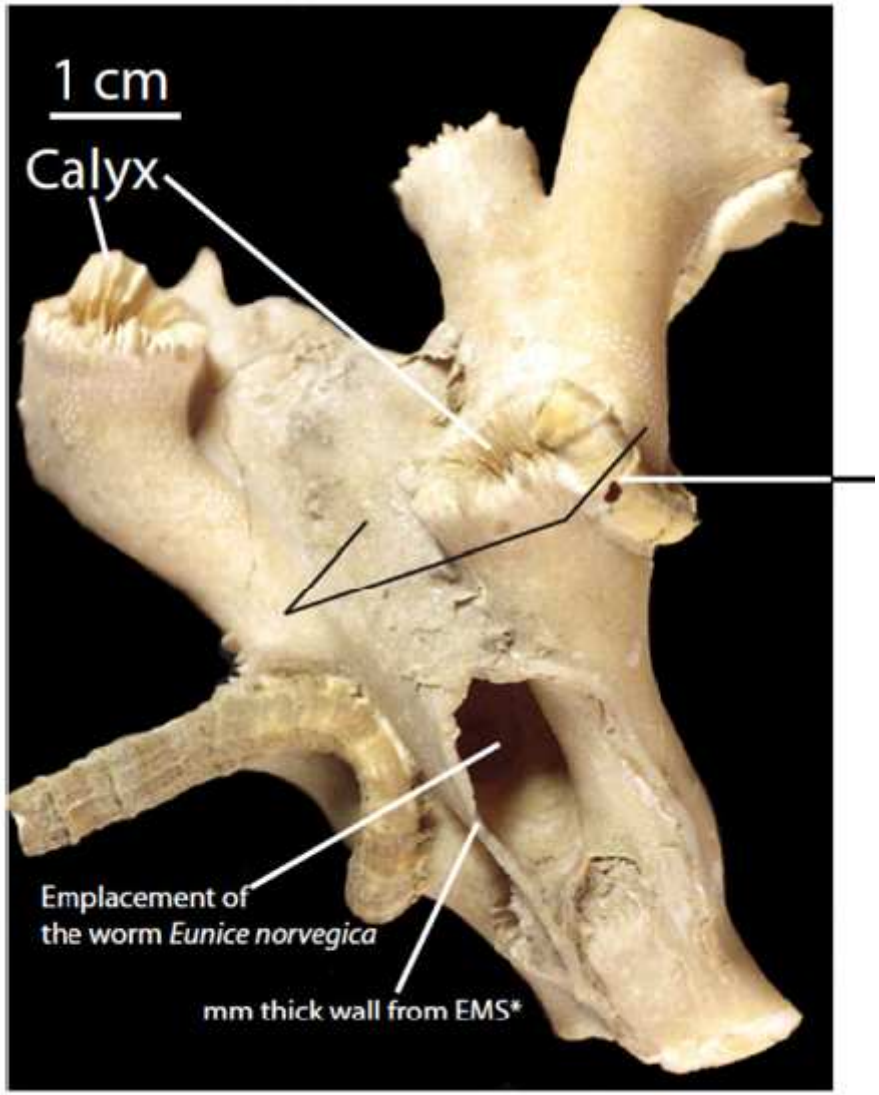
Spéciation du bore = mesure du pH de l'océan (µmol/kg)

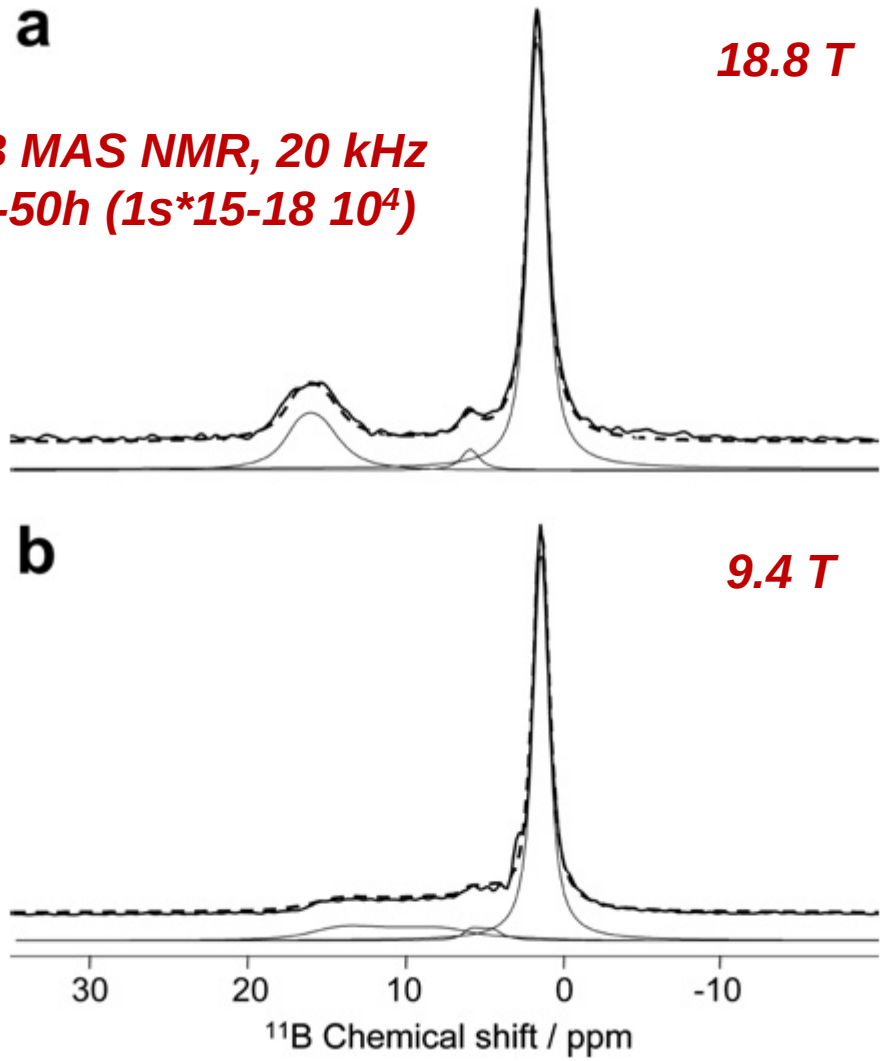
$$B(OH)_3 + 2H_2O \rightleftharpoons B(OH)_4^- + H_3O^+.$$

(that only contains about 100 ppm of boron).

Geochimica et Cosmochimica Acta 75 (2011) 1003–1012

RMN : spéciation de traces





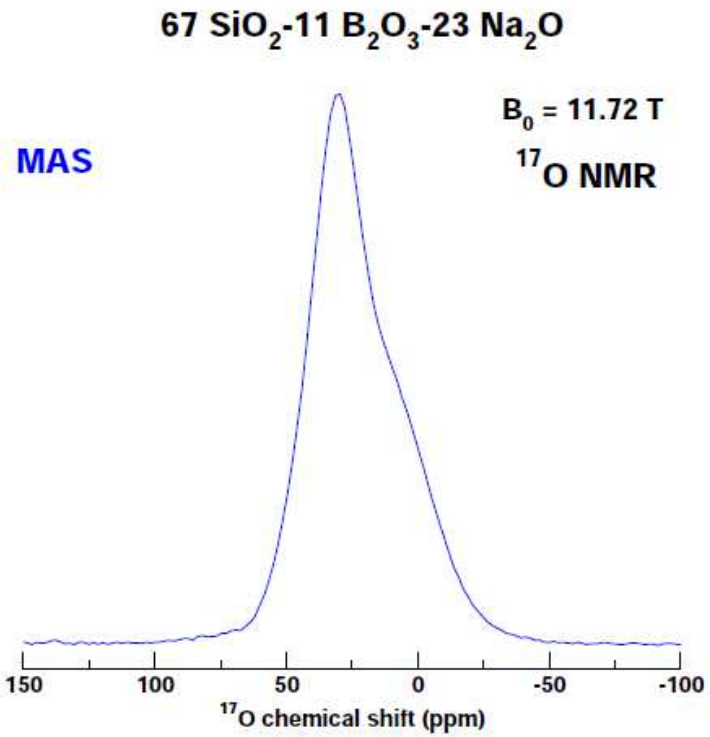
^{11}B MAS NMR, 20 kHz
40-50h (1s*15-18 10^4)

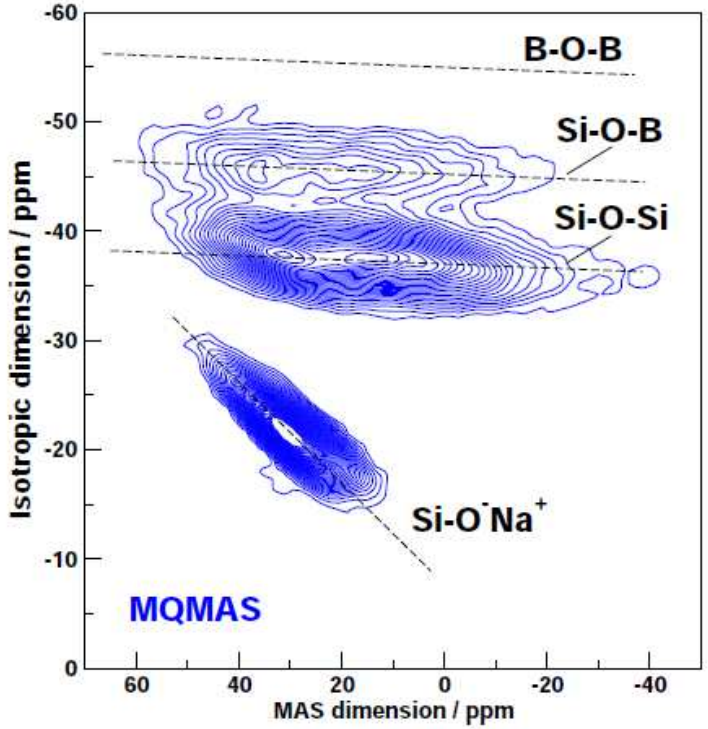
18.8 T

9.4 T

Geochimica et Cosmochimica Acta 75 (2011) 1003–1012

^{17}O MAS & MQMAS NMR





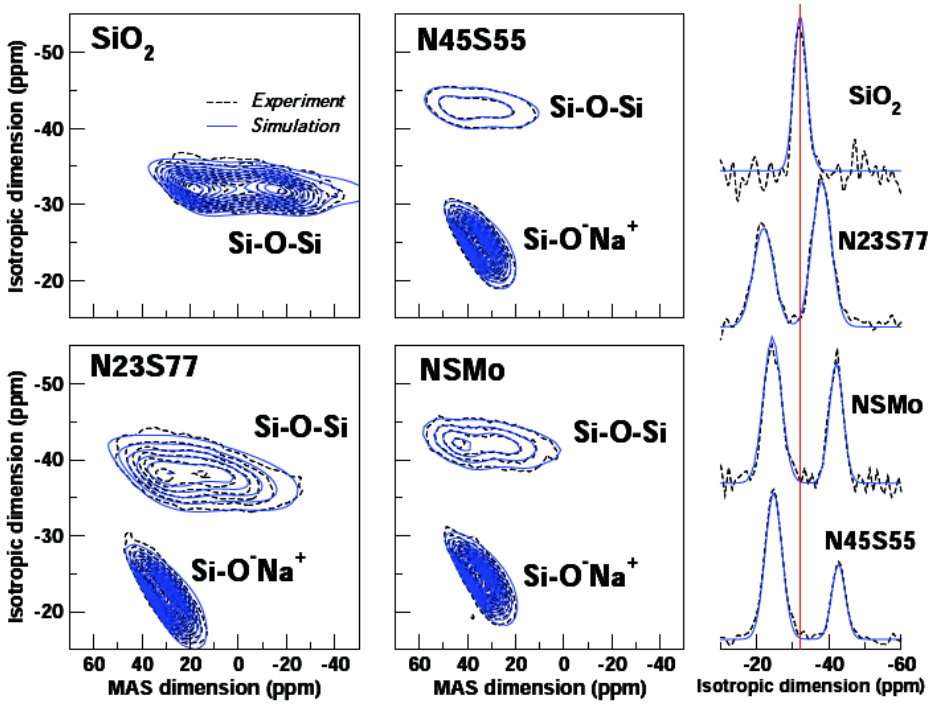
- MAS (1D): Unresolved
- MQMAS (2D): *Direct* reading the glass network structure

See F. Angeli et al., JNCS 354 (2008)

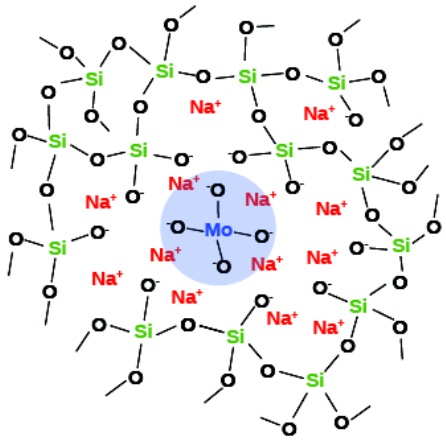
Application to MoO_3 (in low concentation) incorporation in silicates

Modeling and Quantifying ^{17}O MQMAS Spectroscopy

NBO (%)	N45S55	NSMo	N23S77
^{29}Si	56	47	28
^{17}O	58	47	26



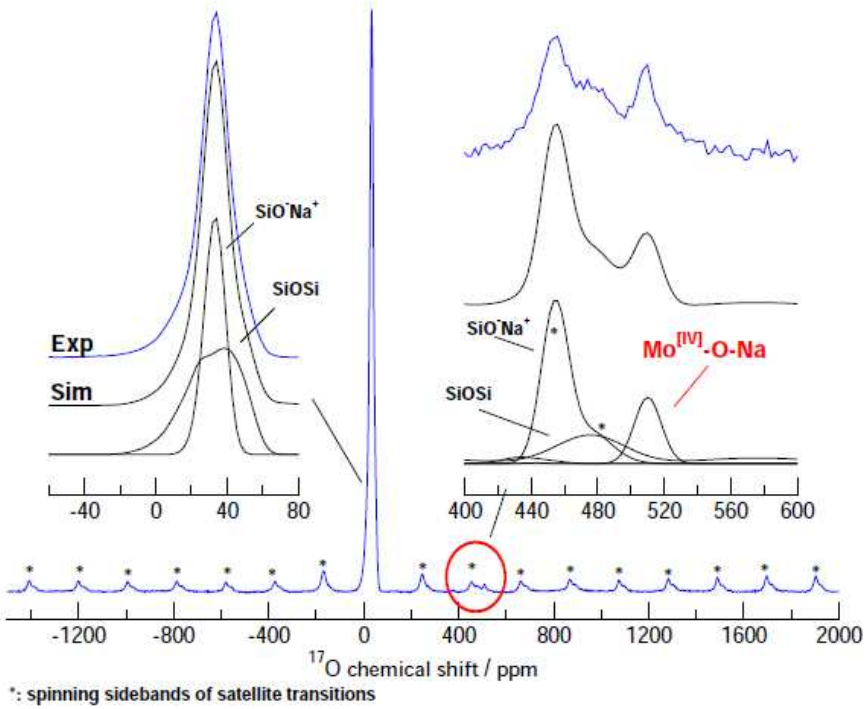
NBO ($Si\text{-}O^{-}Na^{+}$) calculated from ^{17}O agrees with Si $Q^{(n)}$ speciation and glass composition (NBO=Na^{+})

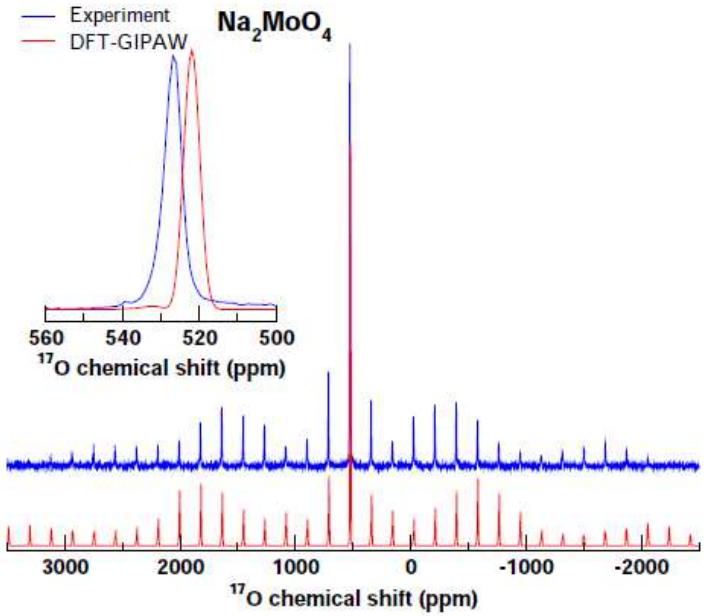


- NMR: formation of $[MoO_4]^{2-}$
- MoO_3 leads to polymerization increase.

Angeli et al. GCA 2011

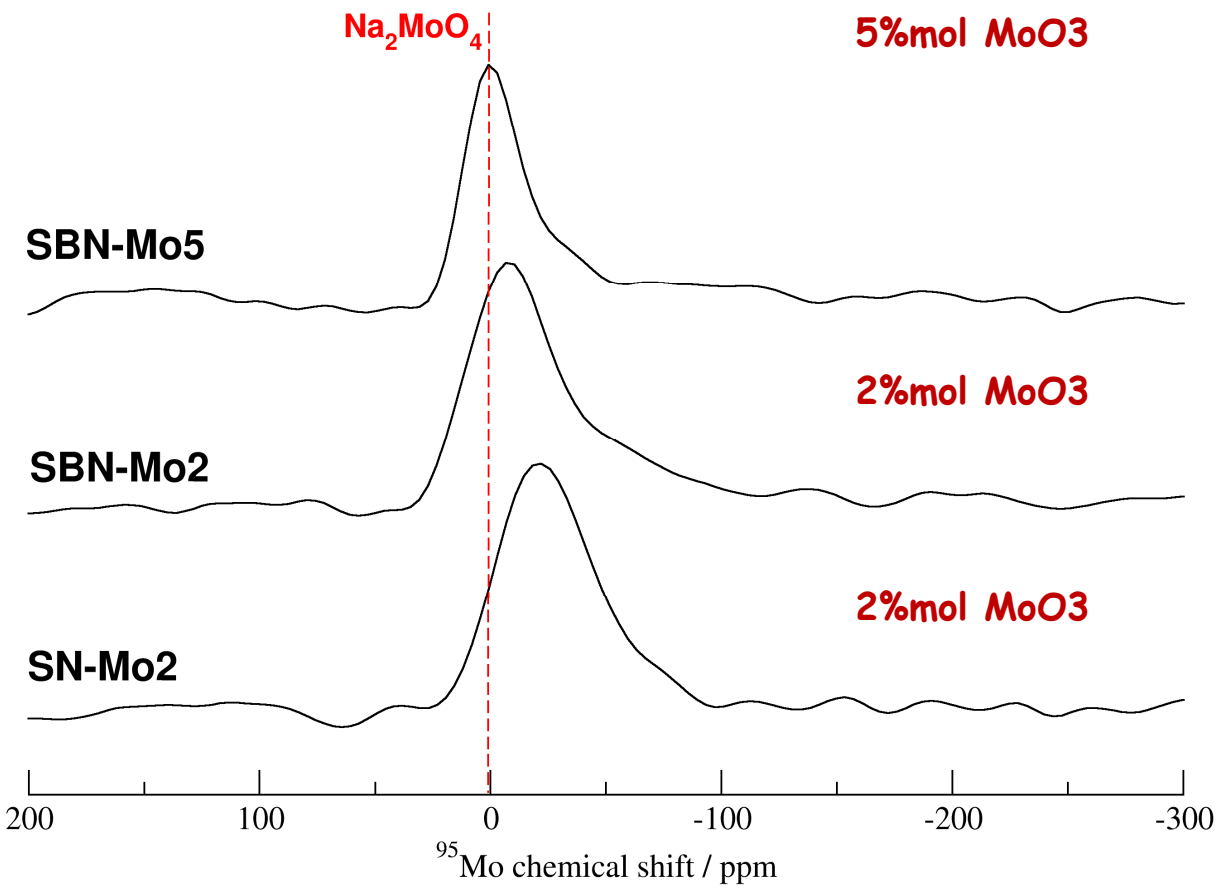
Help of DFT to identify NMR fingerprint





- ^{29}Si, ^{23}Na, and ^{17}O NMR: MoO_3 increases (dramatically) polymerization (also in borosilicate glasses)
- ^{17}O NMR reveals $[MoO_4]^{2-}$ units (only 1% mol. MoO_3 !!)

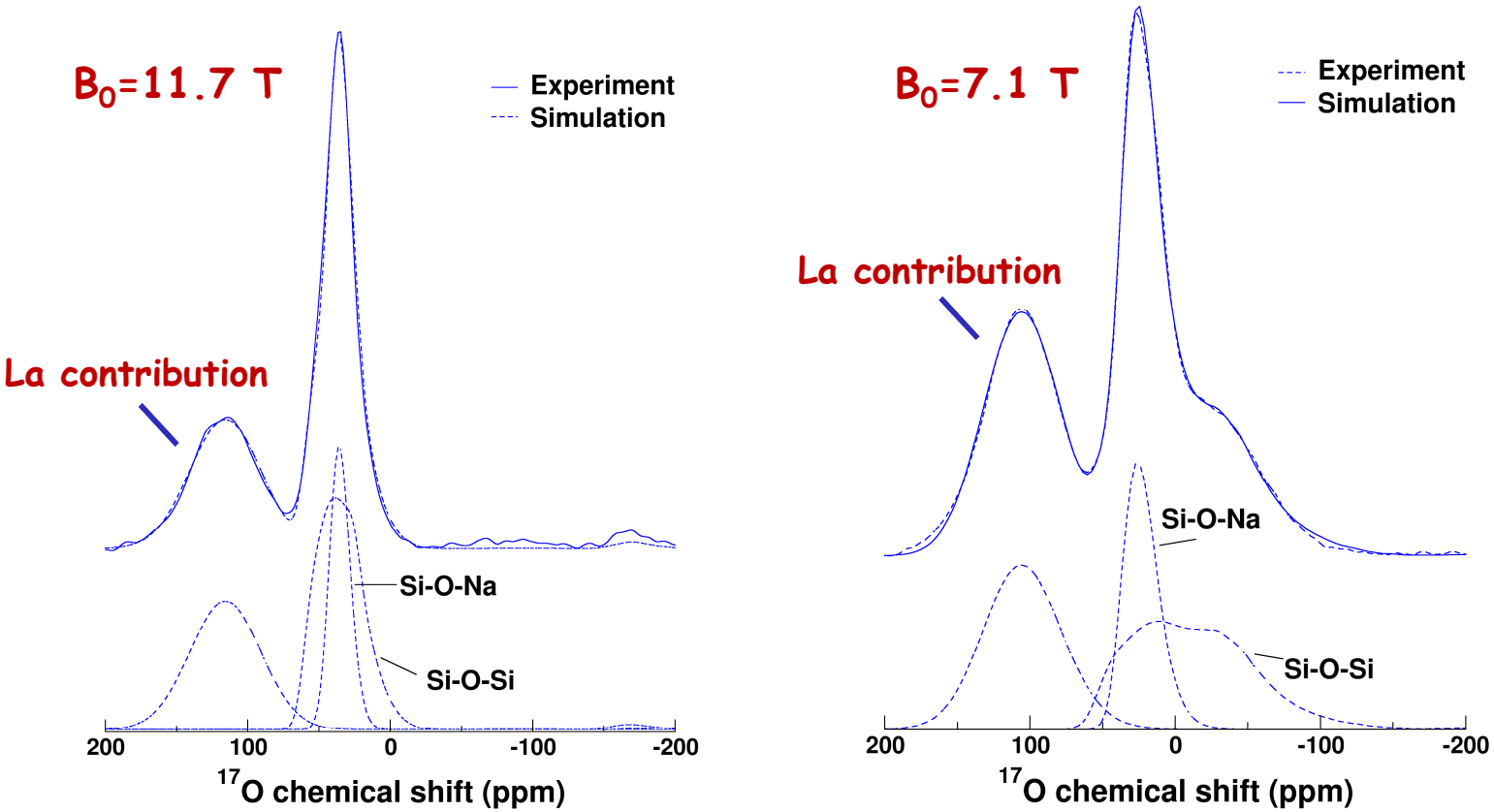
95Mo MAS NMR



11.72 T (500WB)
Texp ~ 1-2 days

17O NMR : indirect detection of heavy element ?

$60SiO_2 - 35Na_2O - 5La_2O_3$



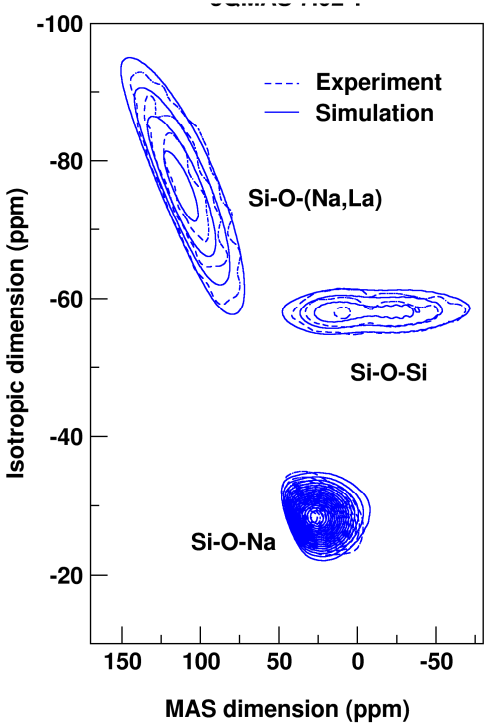
~1-0.1%mol La2O3 can be resolved if resolution is achieved (and fingerprint known)

Separation between Si-O-Na/Si-O-Si is enhanced at lower magnetic field

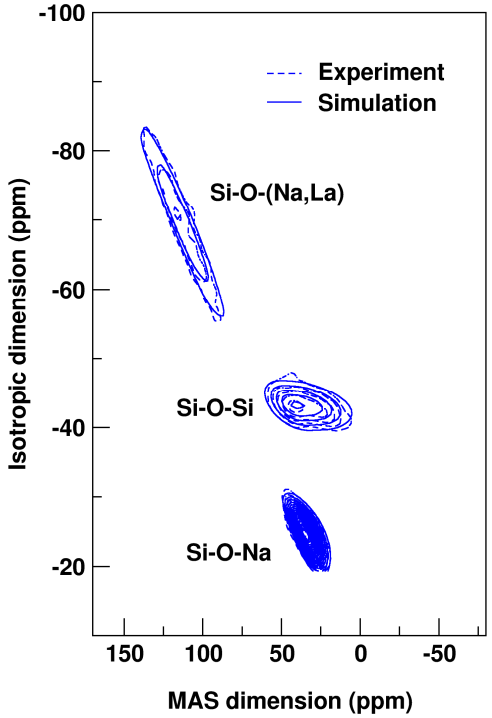
(-> enables to refine the quantifications)

17O MAS / MQMAS NMR

B_0=11.7 T



B_0=7.1 T



$$Si-O-Na = \frac{2(Na_2O - {}^{[4]}B * B_2O_3 - x_{Na}La_2O_3)}{\sum O}$$

$$Si-O-(Na,La) = \frac{2(3La_2O_3 + x_{Na}La_2O_3)}{\sum O}$$

- Agreement with experiment considering La-Na mixing:
  3.3 Na^+ for 1 La^{3+}

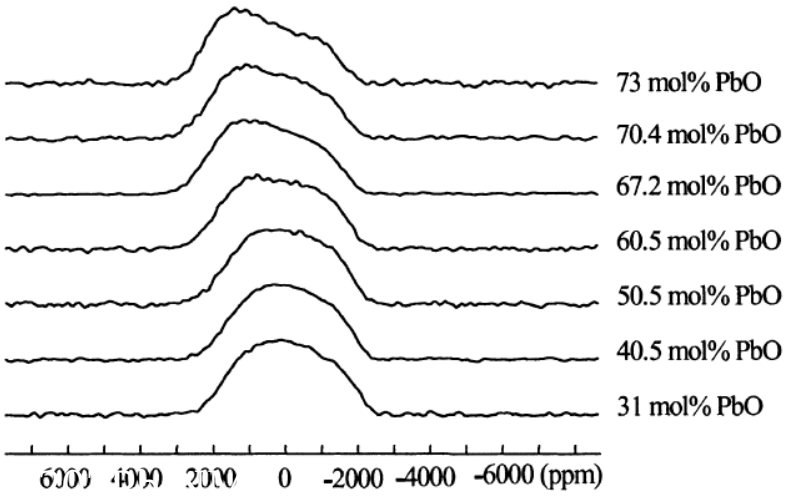
La-Na mixing: 6.3 positive charge
- requires the same NBOs
- La coordination ~ 6

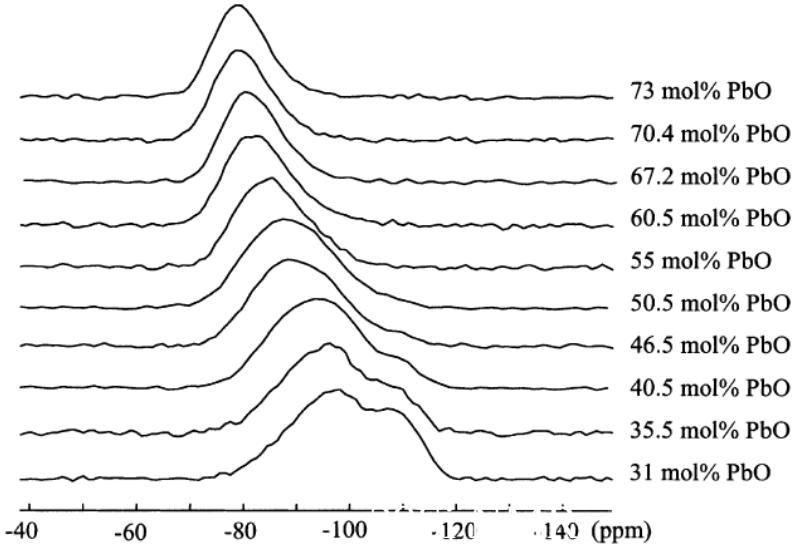
F. Angeli et al., JNCS (2013)

RMN de métaux lourd dans des verres

^{29}Si and ^{207}Pb NMR study of local order in lead silicate glasses

F. Fayon [a,*], C. Bessada [a], D. Massiot [a], I. Farnan [b], J.P. Coutures [a]





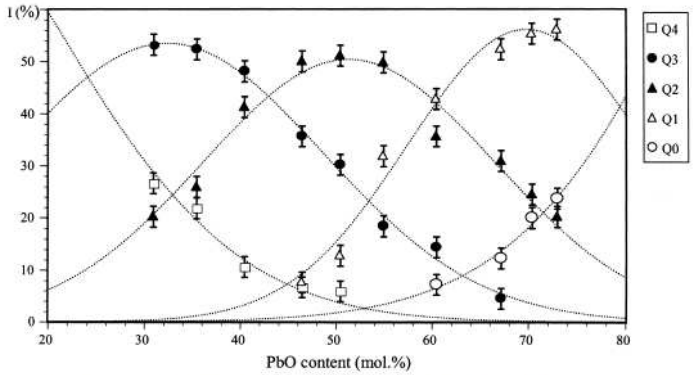


Fig. 5. Experimentally determined Q_n distribution in lead silicate glasses as a function of the lead content (lines are guides for the eye).

Journal of Non-Crystalline Solids 232–234 (1998) 403–408

RMN des métaux lourds en solution (*RMN liquide*)

Pb-207 NMR spectroscopy reveals that Pb(II) coordinates with glutathione (GSH) and tris cysteine zinc finger proteins in a PbS_3 coordination environment

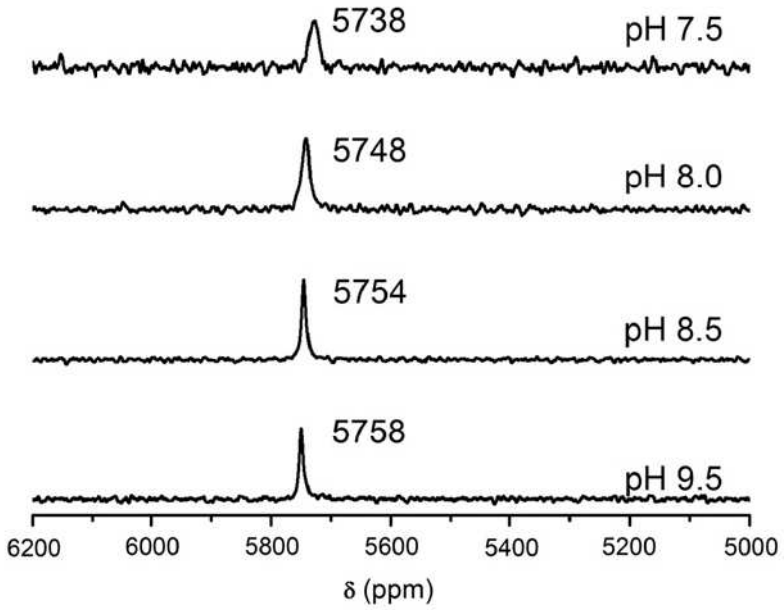
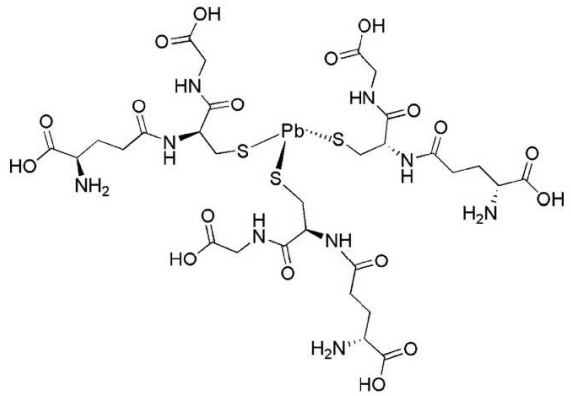


Fig. 2. ^{207}Pb NMR spectra of Pb(II)-bound reduced glutathione (GSH) in a molar ratio of 1:3 (5 mM Pb(II): 15 mM GSH) at different pHs. All spectra were recorded for 2 h using enriched $^{207}Pb(NO_3)_2$ (^{207}Pb = 92.4%) at 25 °C.

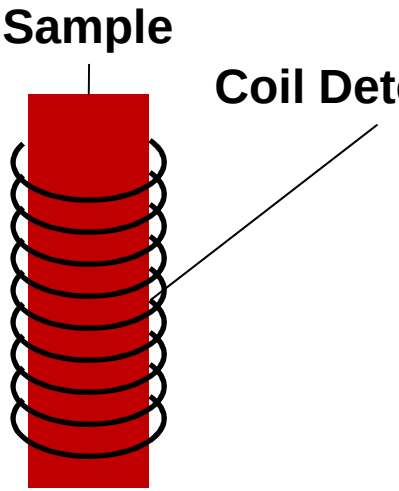
Heavy metal ions can target thiol rich molecules such as glutathione and zinc fingers in cells. We studied the interaction of glutathione and zinc finger peptides with Pb(II) by using ^{207}Pb NMR spectroscopy. The study shows that glutathione is preferentially bound in a PbS_3 coordination environment in the pH range from 7.0 to 9.5. We were



Scheme 1. Proposed structure of Pb(II) bound glutathione at physiological pH.

Journal of Inorganic Biochemistry 105 (2011) 1030–1034

NMR Sensitivity is (still) an issue !



Filling factor

$$\frac{S}{N} = N_d \frac{\gamma_e \gamma_d^{3/2}}{\sqrt{T_c T_s}} B_0^{3/2} \sqrt{N_s}$$

γ_e : Excited Spin , γ_d : Detected Spin

Ts : Sample temperature , B_0 : Magnetic field

Tc : Circuit (Coil) temperature (CryoMAS, CryoNMR)

N_s : Number of scans (accumulation = $\sqrt{time}$)

N_d : Number of detected spins

+ Higher Resolution : higher sensitivity

NMR peak aera is proportional to the number of spins (Quantitativity)

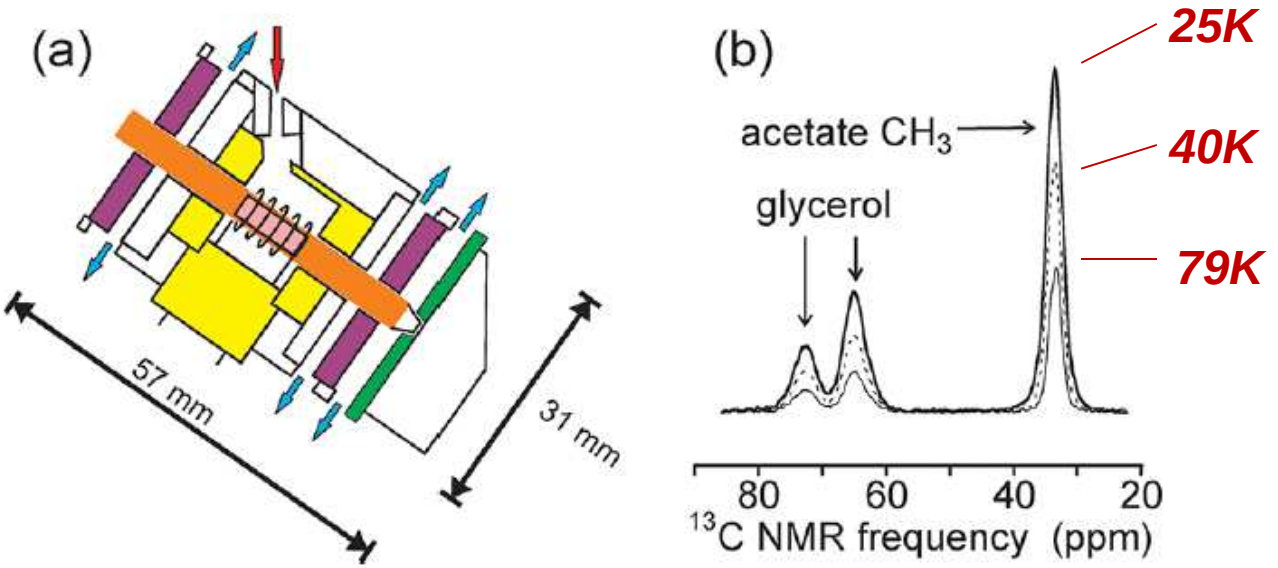
NMR sensitivity = Polarisation x Detection x Resolution

Low temperature MAS-NMR

$$\frac{S}{N} = N_d \frac{\gamma_e \gamma_d^{3/2}}{\sqrt{T_c T_s}} B_0^{3/2} \sqrt{N_s}$$

NMR at Low and Ultralow Temperatures

ROBERT TYCKO*



Vol. 46, No. 9 ■ 2013 ■ 1923–1932 ■ ACCOUNTS OF CHEMICAL RESEARCH ■ 1923

RMN MAS : CryoMAS

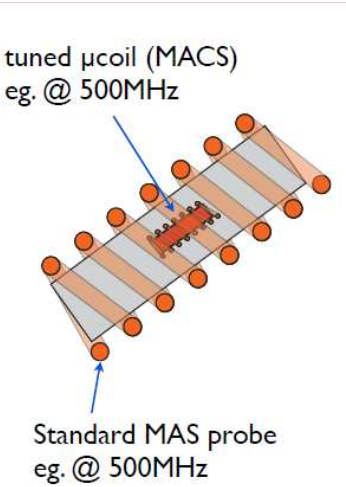
$$\frac{S}{N} = N_d \frac{\gamma_e \gamma_d^{3/2}}{\sqrt{T_c T_s}} B_0^{3/2} \sqrt{N_s}$$

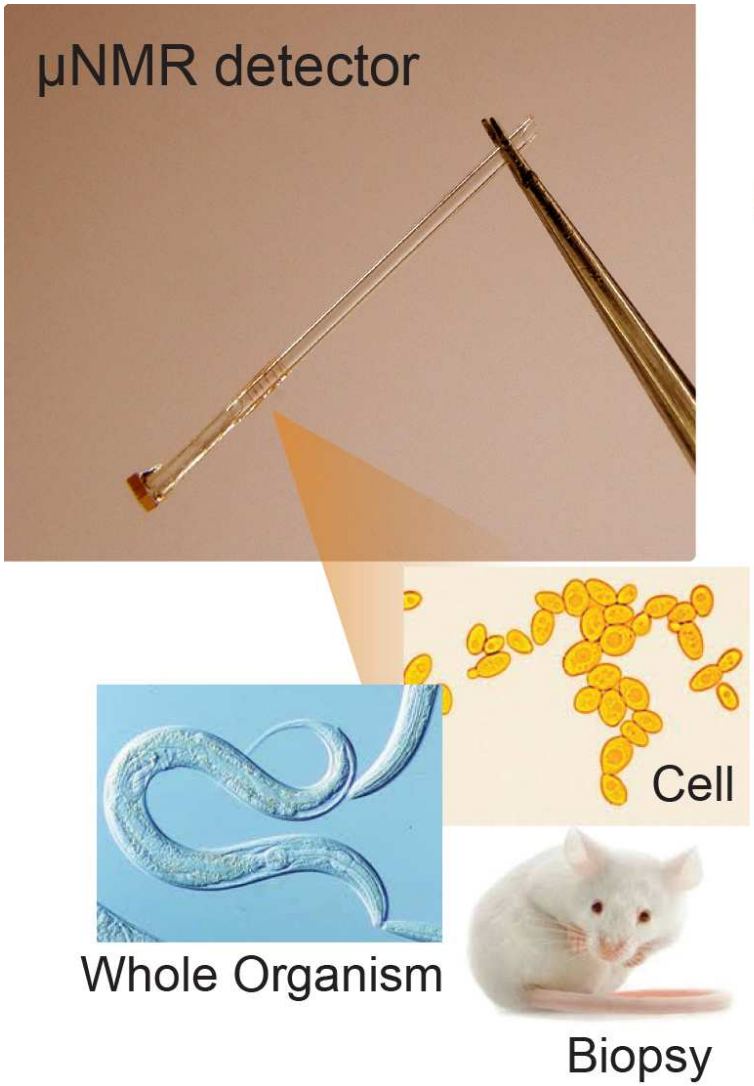
Doty CryoMAS - The Cryo Probe for Solids

- **Factor of 5 increase in S/N in an MAS solids Probe by cryogenically cooling the rf coil to 25 K, and cooling the rf circuit, and preamps**
- 3 mm spinner for MAS up to 20 kHz
- H/C/N triple resonance tuning
- Independent control of sample temperature from -140°C to +80°C with N_2 spinning gas
- Automatic sample eject
- Cryogen-free operation with closed-loop GM cryo-coolers
- For wide-bore magnets up to 750 MHz

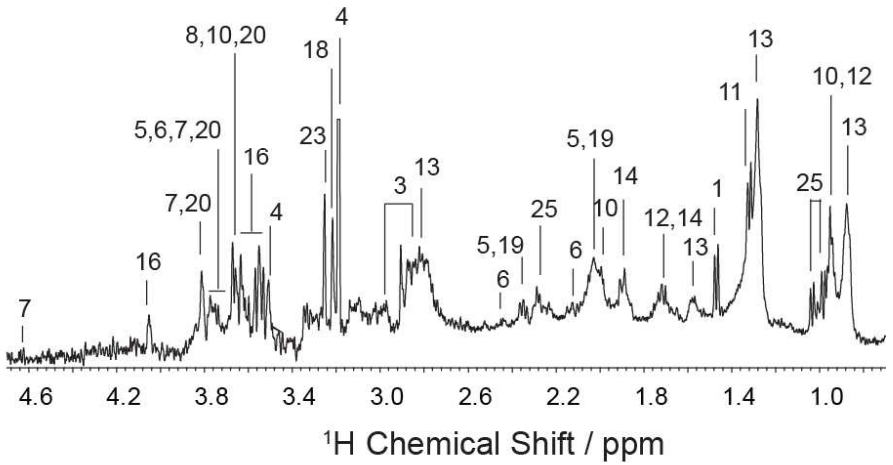
http://www.dotynmr.com/solids/sol_cryocoilpg.htm

HR-MACS-NMR : RMN miniaturisée (A. Wong, D. Sakellariou, LSDRM)





250nL NMR Detection of Rabbit Kidney
(22 metabolites indentified)

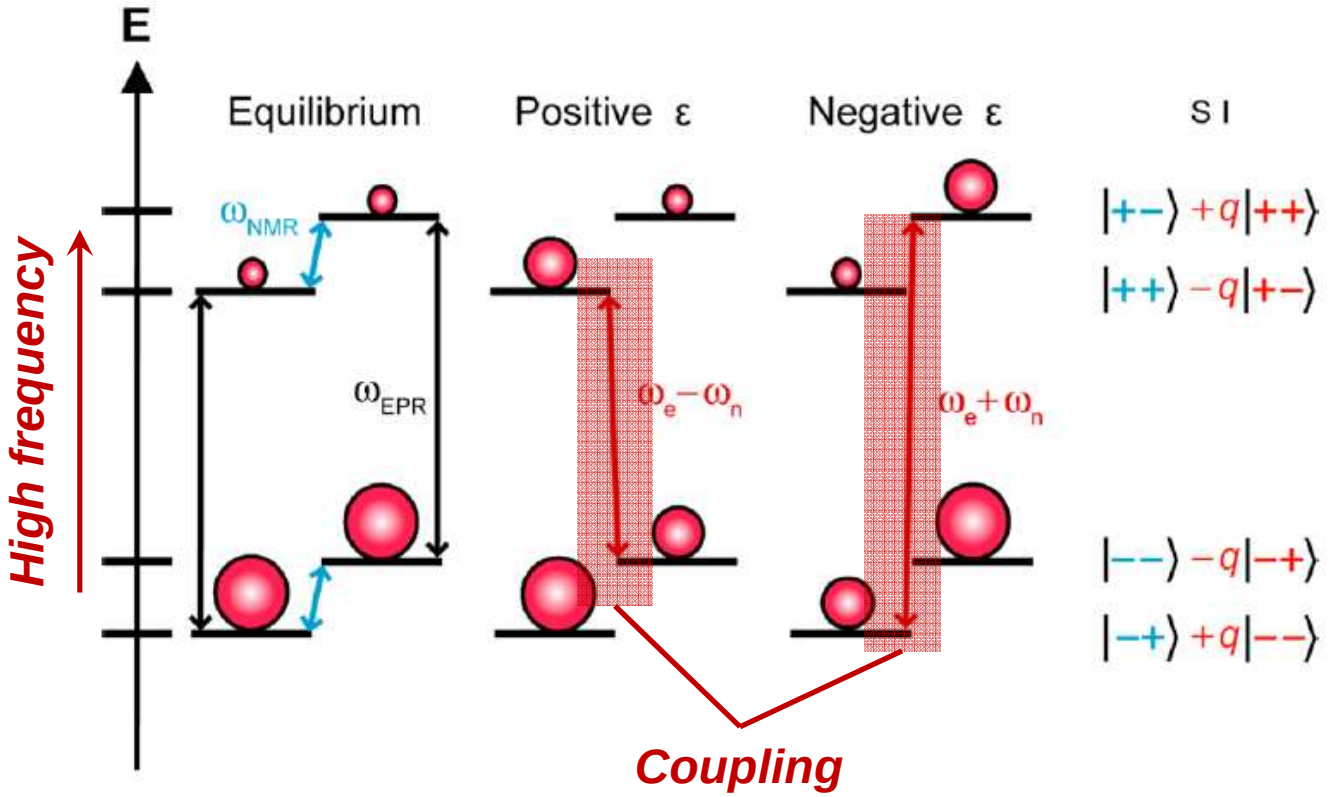


DNP MAS NMR : use high frequency polarization

High Frequency Dynamic Nuclear Polarization

QING ZHE NI,[†,‡] EUGENIO DAVISO,[†,‡,∥] THACH V. CAN,[†,‡]
EVGENY MARKHASIN,[†,‡] SUDHEER K. JAWLA,[§]
TIMOTHY M. SWAGER,[‡] RICHARD J. TEMKIN,[§]
JUDITH HERZFELD,[∥] AND ROBERT G. GRIFFIN[*,†,‡]

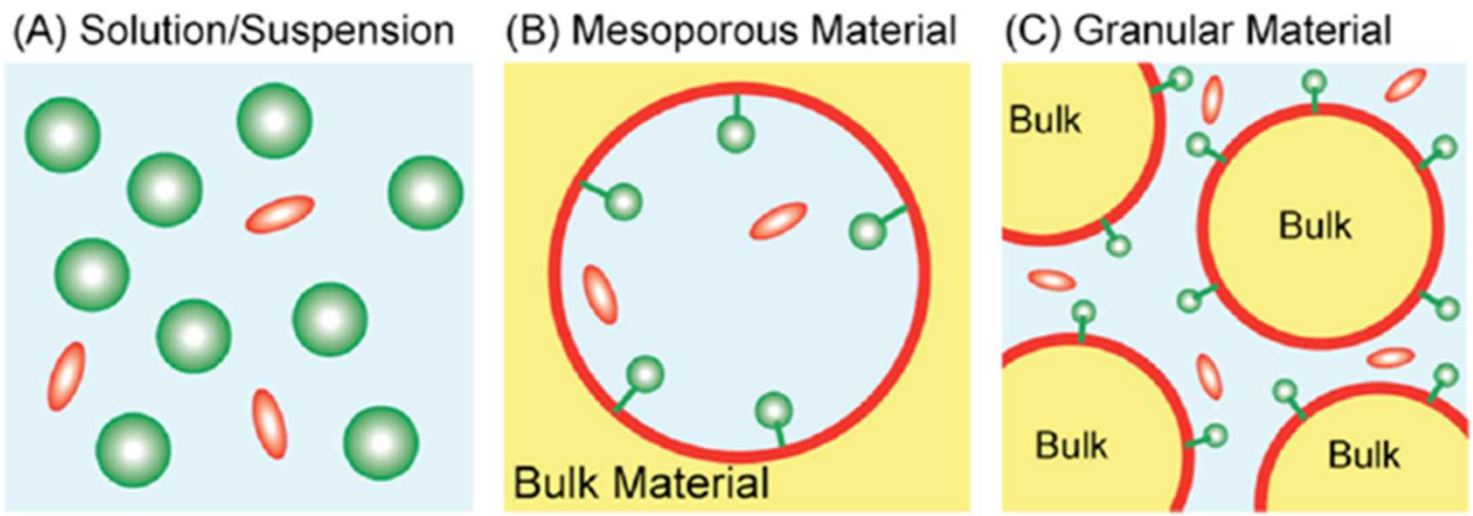
$$\frac{S}{N} = N_d \frac{\gamma_e \gamma_d^{3/2}}{\sqrt{T_c T_s}} B_0^{3/2} \sqrt{N_s}$$



RMN MAS : DNP et surface

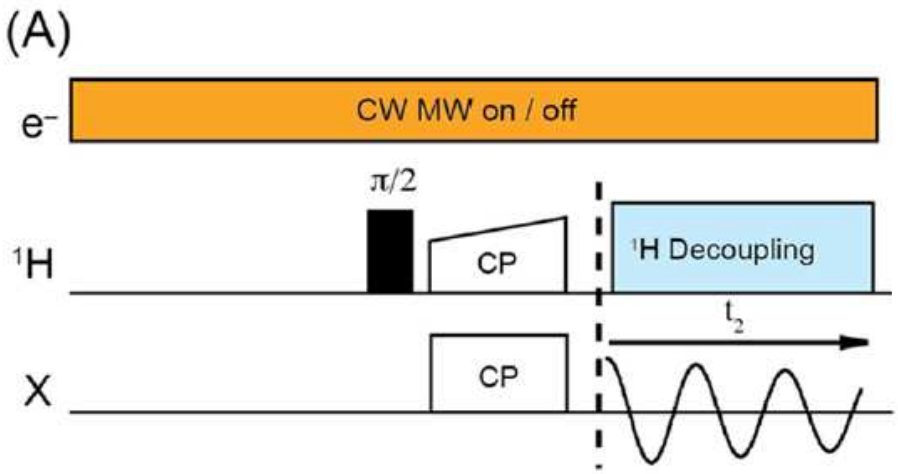
Dynamic Nuclear Polarization Surface Enhanced NMR Spectroscopy

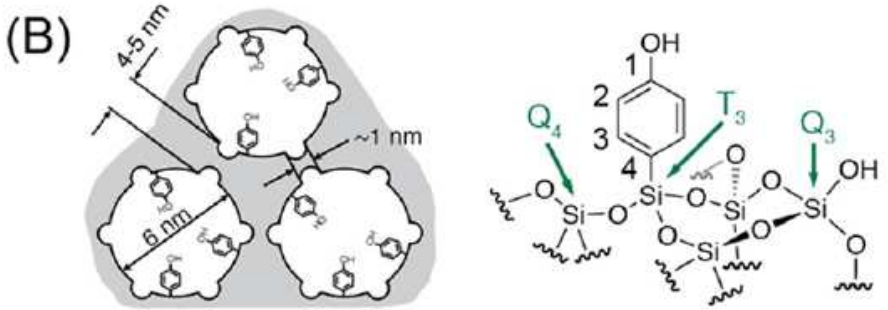
AARON J. ROSSINI,[†] ALEXANDRE ZAGDOUN,[†] MORENO LELLI,[†]
ANNE LESAGE,[†] CHRISTOPHE COPÉRET,[‡] AND
LYNDON EMSLEY*,[†]

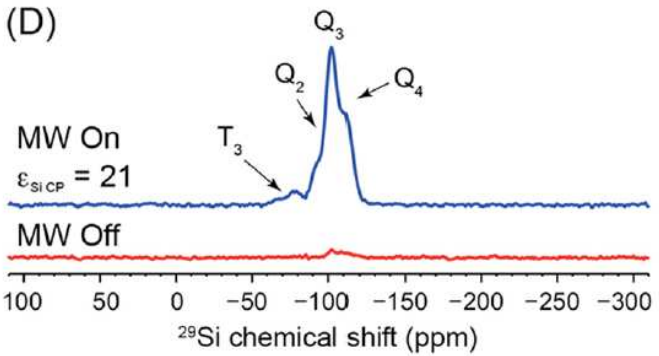


1942 ■ ACCOUNTS OF CHEMICAL RESEARCH ■ 1942–1951 ■ 2013 ■ Vol. 46, No. 9

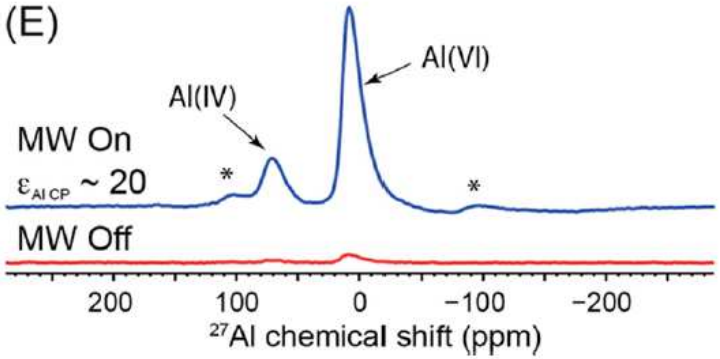
RMN MAS : DNP et surface





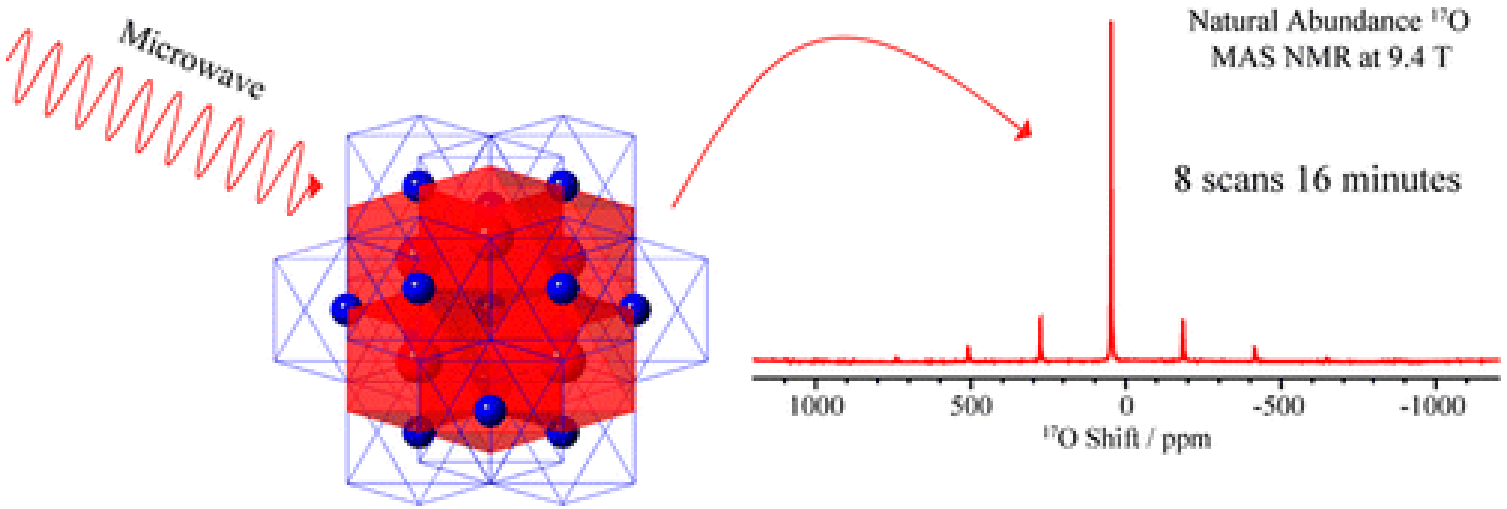


γ-alumina, with $\varepsilon_{Al\ CP} \sim 20$.



RMN MAS : Dynamic Nuclear Polarization - DNP (Hyperpolarisation)

!!! Nat. Abund. 17O excited near or on the surface !!!



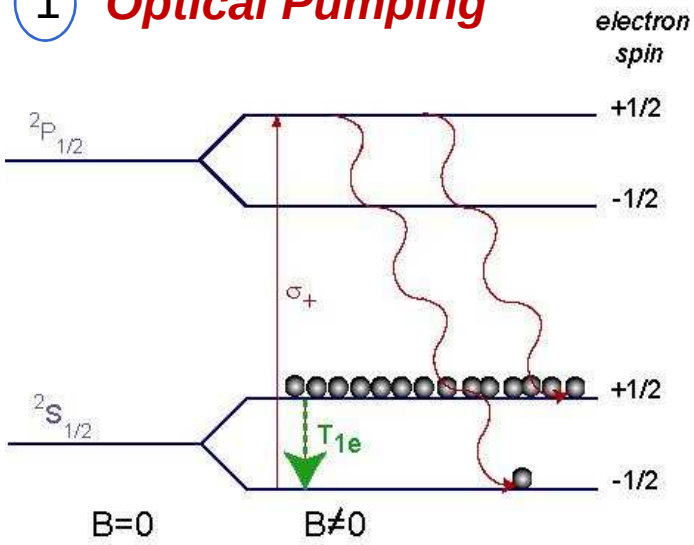
Dynamic Nuclear Polarization Enhanced Natural Abundance ^{17}O Spectroscopy

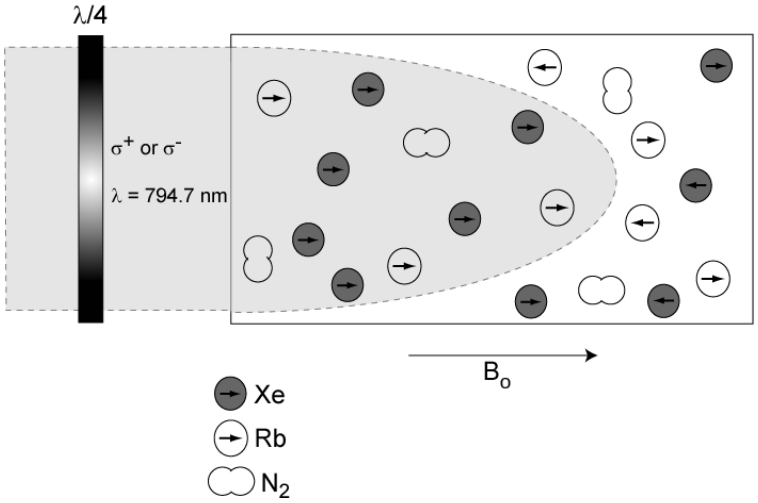
Frédéric Blanc,*[,†,‡] Luke Sperrin,[†] David A. Jefferson,[†] Shane Pawsey,[§] Melanie Rosay,[§] and Clare P. Grey[†,⊥]

dx.doi.org/10.1021/ja4004377 | *J. Am. Chem. Soc.* 2013, 135, 2975−2978

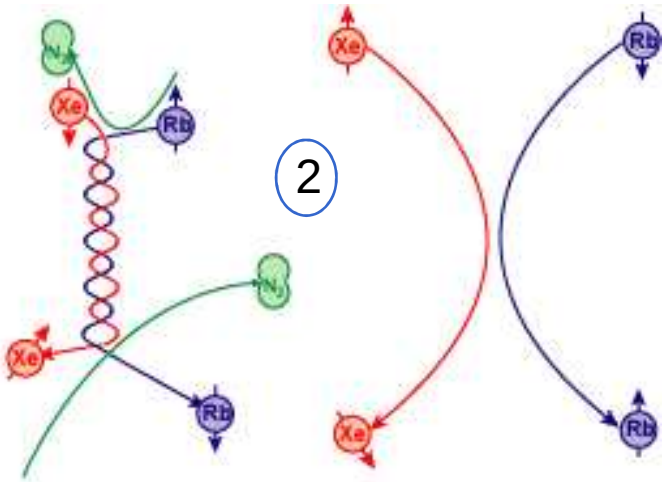
^{129}Xe NMR : Hyperpolarization (LSDRM)

1 *Optical Pumping*



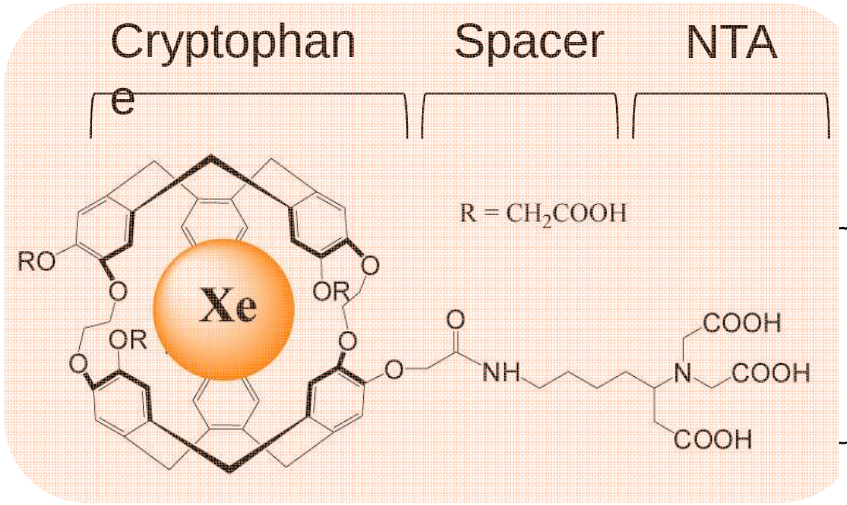


Angular momenta of photons → (1) → *Electron spins of an alkali-metal* → (2) → *Nuclear spins of a noble gas*



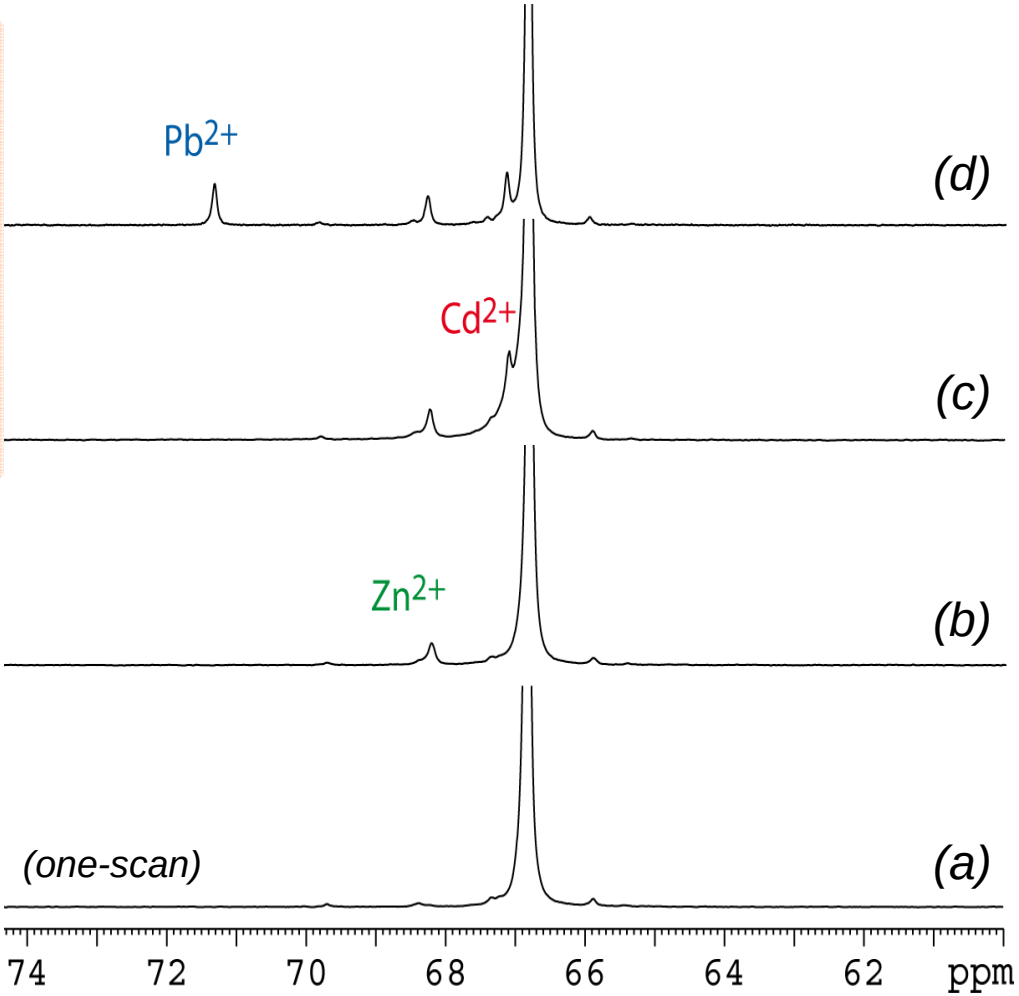
Lifetime of Xenon polarization ~hours !!

^{129}Xe NMR: detecting trace elements in solution (LSDRM)



✓ *Specific chemical shift effect to Zn^{2+} (Pb^{2+}, Cd^{2+}, …)*

✓ *Towards nM detection !*



P. Berthault et al. , LSDRM

Conclusion

NMR provides valuable information on *chemical environment* in crystalline and amorphous materials (High-Resolution) (and in solution)

Standard Sensitivity 1-100 mg . 0.1 (-0.01%mol) (0.1%weight ^{27}Al)

^{27}Al, ^{11}B, ^{7}Li, ^{31}P, ^{23}Na … min @1% mol (but background signal)

^{113}Cd (I=1/2), ^{207}Pb (I=1/2), ^{205}Tl (I=1/2), ^{199}Hg (I=1/2) ? (~1 days)

NMR sensitivity is « still » an issue by *Hyper-NMR* is coming (x100)

Hyper-Polarisation (DNP, Xenon, Parahydrogen , …)

Hyper-Dectection (Optical detection, …)

Effective Methodologies for surface studies now exists !

Sensitive (indirect) probe of trace elements exist with *Hyper Resolution* (^{129}Xe)

NMR is also a tool for Food profiling (^{1}H, ^{13}C, ^{23}Na)