Limites et Potentiel de la RMN pour la caractérisation structurale de l’environnement des éléments « traces »
Solid State Nuclear Magnetic Resonance (ssNMR) is a powerful spectroscopy to probe the glass structure at the atomic scale. 

Glass structure 

Composition ⇔ Structure ⇔ Properties
The Zeeman Interaction and Larmor Frequency

The NMR spectrum of an isolated nucleus ...

\[ \Delta m = \pm 1 \]

\[ B_0 \neq 0 \]

\[ B_0 = 0 \]

\[ I = \frac{3}{2} \]

\[ E = -\vec{\mu}_N \cdot \vec{B}_0 \]

\[ \nu_0 = -\frac{\gamma_N}{2\pi} B_0 \]

The Larmor frequency and its NMR spectrum.

The Zeeman effect

No information on the chemical surrounding

\[ (\hbar) H = -\hbar \gamma_N \vec{I} \cdot \vec{B}_0 \]
NMR sensitivity and Nuclear Magnetization

Equilibrium Nuclear Magnetization

$\vec{B}_0 \rightarrow \vec{M}_0$

$Larmor Precession at \nu_0$

$\vec{B}_0 \rightarrow \vec{M}(t)$

$\vec{M}_0$: Nuclear Magnetization at Equilibrium is given by the Curie Law

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

$$\chi_0 = N_l \gamma_i^2 \hbar^2 l(l+1) / 3kT B_0$$

$E_{m+1} \rightarrow |m+1\rangle$

$\Delta E \rightarrow \gamma B_0$

$E_m \rightarrow |m\rangle$

- Small polarization $10^{-3}$ to $10^{-6}$
- Signal $\propto N_l$ 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 $\gamma$ (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!

\( M_0: \text{Nuclear Magnetization at Equilibrium} \)

\[
\begin{align*}
\vec{M}(0) &= M_0 \vec{z} \\
\vec{M}(\tau_p) &= M_0 \vec{x} \\
S(t) &= M_0 e^{-i\nu_0 t} e^{-\tau_2^t} \\
S(\nu) &= \int_0^\infty dt \ S(t) e^{-i2\pi\nu t} \approx \sum_{k=0}^{N-1} S(t_k) e^{-i2\pi\nu t_k} = L(\nu - \nu_0)
\end{align*}
\]

Lineshape \( L(\nu) \): Gaussian, Lorentzian ...
**NMR interactions and the local atomic environment**

NMR interactions (without equations . . .)

- One-Spin Interactions
  - Magnetic Shielding / Chemical shift
  - Electif Field Gradient (EFG)
  - Only for \( I > 1/2 \)

- Quadrupolar Interaction
  - Speciation / structural units

- Two-Spins Interactions
  - Dipolar: through Space
  - Connectivities / Proximities (2D)

**Main NMR parameters:**

1. Isotropic chemical shift (position of the line) \( \delta_{iso} \)
2. Quadrupolar coupling constant (width of the line) \( C_Q \)
3. Asymmetry parameter (lineshape) \( \eta \)

\[ \vec{B}_{loc} \]

\[ v_{inter.} \]

\[ v \]

\[ v_0 \]
Rigid lattice (powder)

Tissues - Food

Brownian Motion
Narrow lines

Peak Area = Quantification

NH₂-CH₂-COOH
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

**Static**

* : Spinning sidebands

**Low MAS**

$\nu_{\text{ROT}} = 2$ kHz

**MAS**

$\nu_{\text{ROT}} = 10$ kHz

* : bande de rotation

<table>
<thead>
<tr>
<th>diam. (mm)</th>
<th>Spin rate (kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>15</td>
</tr>
<tr>
<td>3.2</td>
<td>24</td>
</tr>
<tr>
<td>2.5</td>
<td>35</td>
</tr>
<tr>
<td>1.3</td>
<td>67</td>
</tr>
</tbody>
</table>

Thibault Charpentier - USTV – REACH 2013 | 25 Novembre 2013
MAS NMR of $^{29}$Si in binary Na$_2$O-SiO$_2$ glasses

$^{29}$Si MAS NMR

$Q^{(n)}$: Si(OSi)$_n$(O$^-$)$_{4-n}$

(1) Chemical disorder
(2) Geometrical disorder

NMR peaks reflective of a Gaussian distribution of $\delta_{iso}$ ($l=1/2$)

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

\[ \frac{\hbar^2}{2} \sum_i \sum_{j \neq i} \gamma_i \gamma_j \bar{I}_i (D_{ij} + J_{ij}) \bar{I}_j \]

29Si MAS NMR - 59SiO2 - 40Na2O - MoO3

J-MAS-HMQC experiment

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

Topological, Geometric, and Chemical Order in Materials  Massiot et al.

FIGURE 6.  $^{31}$P NMR characterization of a $(\text{PbO})_{0.60}(\text{P}_2\text{O}_5)_{0.39}$ glass. (a) Measurements of $J_{\gamma-P-O-P}$ 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.23,26

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

MAS removes only partially Second Order Quadrupolar (SOQ) Broadening

\[ \Delta Q \propto \frac{1}{\nu_O} \]

Central Transition
(-1/2) \( \leftrightarrow \) (+1/2)

Multiple-Quantum MAS (2D) removes SOQ anisotropy
$^{11}\text{B} \text{ MAS NMR in Borosilicate Glasses}$

Direct access to boron speciation

Identification of the structural units forming the glass network

High Field MAS NMR:
Boron speciation resolved

Detection level
$\sim 10\text{-}100 \text{ ppm}$

$1\text{-}10\% \text{ mol } T_{\text{exp}} \sim \text{ min}$

$\text{See F. Angeli et al., JACerS 93 (2010)}$
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\textsuperscript{a,*}, Taka\textsuperscript{a}, Koji Kanehashi\textsuperscript{a}, Naoyoshi Kubota\textsuperscript{a}, Kaoru Mizuno\textsuperscript{b}, Shunsuke Kashiwakura\textsuperscript{c}, Tetsuo Sakamoto\textsuperscript{d}, Tetsuya Nagasaka\textsuperscript{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\textsuperscript{-1}, direct and nondestructive detection for some trace...
**RMN : Importance de la spéciation des traces**

<table>
<thead>
<tr>
<th>SiO$_2$</th>
<th>63.1</th>
<th>56.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_2$O$_3$</td>
<td>20.5</td>
<td>31.6</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>3.99</td>
<td>3.66</td>
</tr>
<tr>
<td>CaO</td>
<td>5.84</td>
<td>3.99</td>
</tr>
<tr>
<td>MgO</td>
<td>1.37</td>
<td>0.95</td>
</tr>
<tr>
<td>B (ppm)</td>
<td>1050</td>
<td>540</td>
</tr>
</tbody>
</table>

$^{11}$B MAS NMR, 16.4 T
100-1000 scans
Boron isotopes as pH proxy: A new look at boron speciation in deep-sea corals using $^{11}\text{B}$ MAS NMR and EELS

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

$$\text{pH} = pK_B - \log \left( \frac{\delta^{11}\text{B}_{sw} - \delta^{11}\text{B}_c}{\alpha_{4-3}^{-1} \times \delta^{11}\text{B}_c - \delta^{11}\text{B}_{sw} + 1000 \times (\alpha_{4-3}^{-1} - 1)} \right)$$

(1)

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

$\text{B(OH)}_3 + 2\text{H}_2\text{O} = \text{B(OH)}_4^- + \text{H}_3\text{O}^+$.  

(That only contains about 100 ppm of boron).

Geochimica et Cosmochimica Acta 75 (2011) 1003–1012
$^{11}$B MAS NMR, 20 kHz
40-50h (1s$^*_{15-18 \times 10^4}$)

18.8 T

9.4 T
MAS (1D): Unresolved

MQMAS (2D): Direct reading the glass network structure

See F. Angeli et al., JNCS 354 (2008)
Application to MoO₃ (in low concentration) incorporation in silicates

Modeling and Quantifying $^{17}$O MQMAS Spectroscopy

<table>
<thead>
<tr>
<th>NBO (%)</th>
<th>N45S55</th>
<th>NSMo</th>
<th>N23S77</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{29}$Si</td>
<td>56</td>
<td>47</td>
<td>28</td>
</tr>
<tr>
<td>$^{17}$O</td>
<td>58</td>
<td>47</td>
<td>26</td>
</tr>
</tbody>
</table>

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

- NMR: formation of [MoO₄]$^{2−}$
- MoO₃ leads to polymerization increase.
Help of DFT to identify NMR fingerprint

- $^{29}\text{Si}$, $^{23}\text{Na}$, and $^{17}\text{O}$ NMR: MoO$_3$ increases (dramatically) polymerization (also in borosilicate glasses)
- $^{17}\text{O}$ NMR reveals [MoO$_4$]$^{2-}$ units (only 1% mol. MoO$_3$ !!)
95Mo MAS NMR

Na$_2$MoO$_4$, 5%mol MoO$_3$, 2%mol MoO$_3$

SBN-Mo5
SBN-Mo2
SN-Mo2

$^{95}$Mo chemical shift / ppm

11.72 T (500WB)
$T_{\text{exp}} \sim 1-2$ days

Thibault Charpentier - USTV – REACH 2013 | 25 Novembre 2013 | PAGE 23
17O NMR: indirect detection of heavy element?

$60\text{SiO}_2 - 35\text{Na}_2\text{O} - 5\text{La}_2\text{O}_3$

$B_0=11.7\ T$

$B_0=7.1\ T$

La contribution

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

$\sim1\text{-}0.1\%\text{mol La}_2\text{O}_3$ can be resolved if resolution is achieved (and fingerprint known)

$\Rightarrow$ enables to refine the quantifications

Thibault Charpentier - USTV – REACH 2013 | 25 Novembre 2013 | PAGE 24
Agreement with experiment considering La-Na mixing: 3.3 Na\(^+\) for 1 La\(^{3+}\)

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

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

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

F. Angeli et al., JNCS (2013)
29Si and 207Pb 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. 3. Experimentally determined J distribution in lead silicate glasses as a function of the lead content (lines are guides for the eye).
Pb-207 NMR spectroscopy reveals that Pb(II) coordinates with glutathione (GSH) and tris cysteine zinc finger proteins in a PbS$_3$ coordination environment.

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

![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.](image)

![Scheme 1. Proposed structure of Pb(II)-bound glutathione at physiological pH.](image)

*Journal of Inorganic Biochemistry 105 (2011) 1030–1034*
NMR Sensitivity is (still) an issue!

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

\(\gamma_e\) : Excited Spin, \(\gamma_d\) : Detected Spin

\(T_s\) : Sample temperature, \(B_0\) : Magnetic field

\(T_c\) : 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 area is proportional to the number of spins (Quantitativity)

\[\text{NMR sensitivity} = \text{Polarisation} \times \text{Detection} \times \text{Resolution}\]
NMR at Low and Ultralow Temperatures

ROBERT TYCKO

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

(a)  
(b)  

acetate CH₃  
glycerol  

25K  
40K  
79K  

\[ ^{13}C \text{ NMR frequency (ppm)} \]

Vol. 46, No. 9 = 2013 = 1923–1932 = ACCOUNTS OF CHEMICAL RESEARCH = 1923
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 N₂ 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)

μNMR detector

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

Whole Organism

Cell

Biopsy
High Frequency Dynamic Nuclear Polarization

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

**Equilibrium**

**Positive \( \varepsilon \)**

\[ |++\rangle + q |++\rangle \]

\[ |++\rangle - q |+-\rangle \]

**Negative \( \varepsilon \)**

\[ |--\rangle - q |--\rangle \]

\[ |--\rangle + q |+-\rangle \]

**Coupling**
Dynamic Nuclear Polarization Surface Enhanced NMR Spectroscopy

AARON J. ROSSINI,† ALEXANDRE ZAGDOUN,† MORENO LELLI,† ANNE LESAGE,‡ CHRISTOPHE COPERET,‡ AND LYNDON EMSLEY*,†
RMN MAS : DNP et surface

(A) 

\( e^- \)  

\( \text{CW MW on / off} \)  

\( \pi/2 \)  

\( \text{H Decoupling} \)  

\( \text{CP} \)  

\( X \)

(B) 

\( 4.5 \text{ nm} \)  

\( \sim 1 \text{ nm} \)  

\( 9 \text{ nm} \)

(D) 

MW On  
\( \varepsilon_{\text{Si CP}} = 21 \)  

MW Off

100  50  0  -50  -100  -150  -200  -250  -300  
\( ^{29}\text{Si chemical shift (ppm)} \)

\( Q_3 \)  

\( Q_2 \)  

\( Q_1 \)

\( \gamma\text{-alumina, with } \varepsilon_{\text{Al CP}} \sim 20. \)

(E) 

MW On  
\( \varepsilon_{\text{Al CP}} \sim 20 \)  

MW Off  

\( ^{27}\text{Al chemical shift (ppm)} \)

\( \text{Al(IV)} \)  

\( \text{Al(VI)} \)
Dynamic Nuclear Polarization Enhanced Natural Abundance $^{17}$O Spectroscopy

Frédéric Blanc,$^a$²,³ Luke Sperrin,$^b$ David A. Jefferson,$^b$ Shane Pawsey,$^b$ Melanie Rosay,$^b$ and Clare P. Grey$^b$"
Optical Pumping

Angular momenta of photons \[ 
\begin{align*}
2P_{1/2} & \quad +1/2 \\
2S_{1/2} & \quad +1/2
\end{align*}
\]

Electron spin

Lifetime of Xenon polarization \(~\text{hours}!\)
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 $^{27}\text{Al}$)

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

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

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 ($^{129}\text{Xe}$)

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