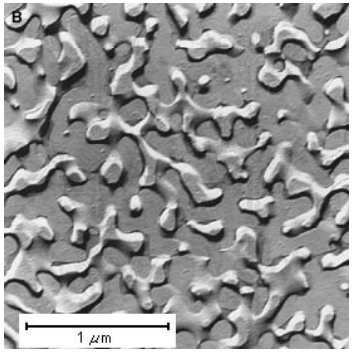
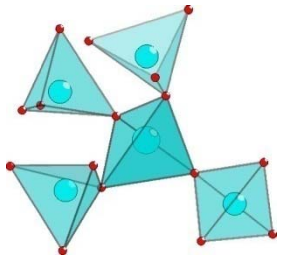
Structure vitreuse à l'échelle subnanométrique : désordre géométrique ou chimique.

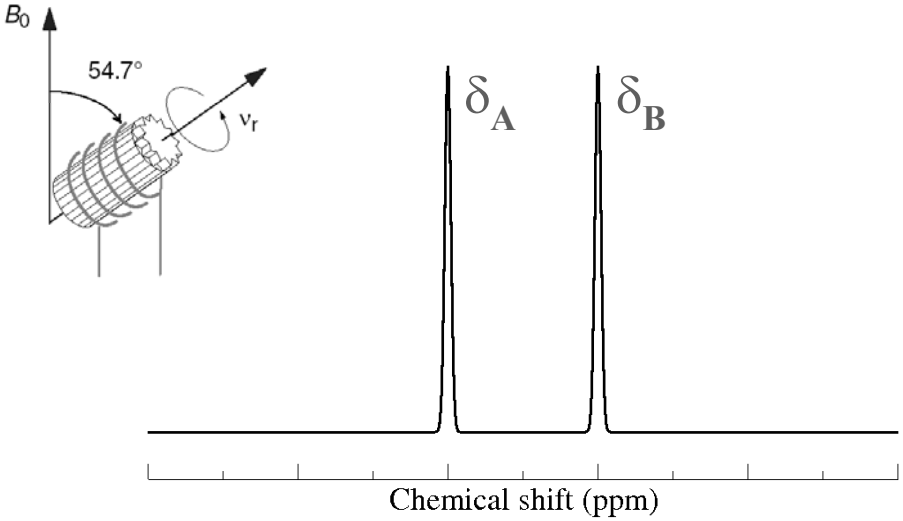
Dominique Massiot,
Franck Fayon, Michael Deschamps, Sylvian Cadars, Valérie Montouillout,
Nadia Pellerin, Emmanuel Véron, Laura Martel, Julien Hiet, Pierre Florian,
Laurent Cormier, Daniel Neuville

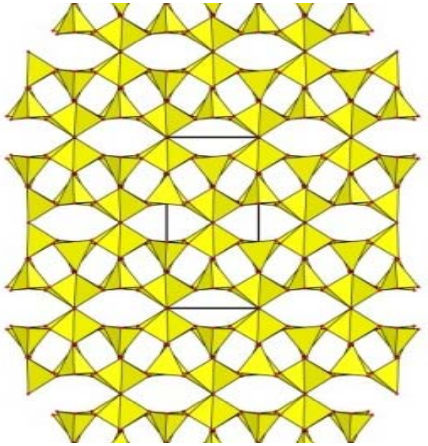
CEMHTI CNRS- UPR 3079 Orléans
http://www.cemhti.cnrs-orleans.fr
dominique.massiot@cnrs-orleans.fr
Google « massiot »

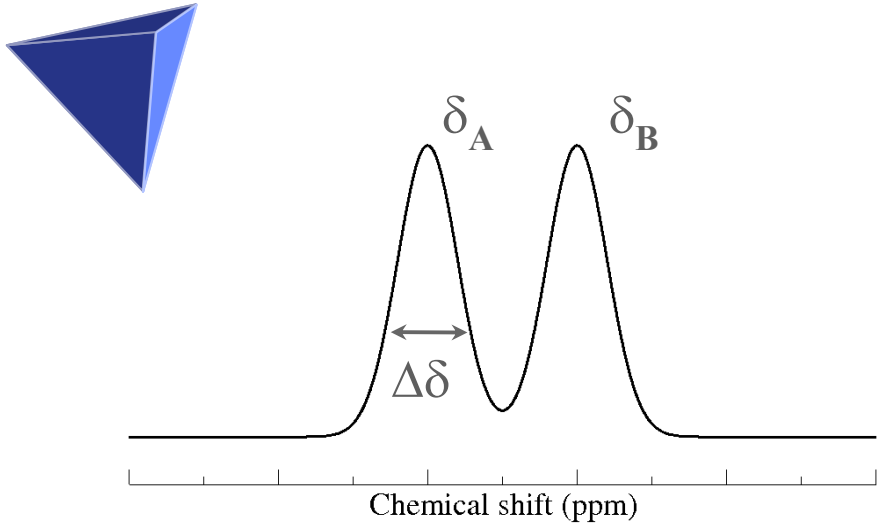


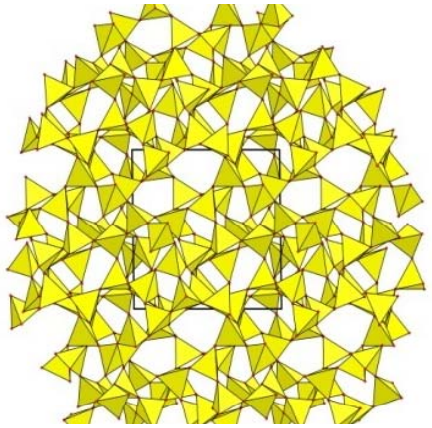


Solid State NMR : Order & Disorder

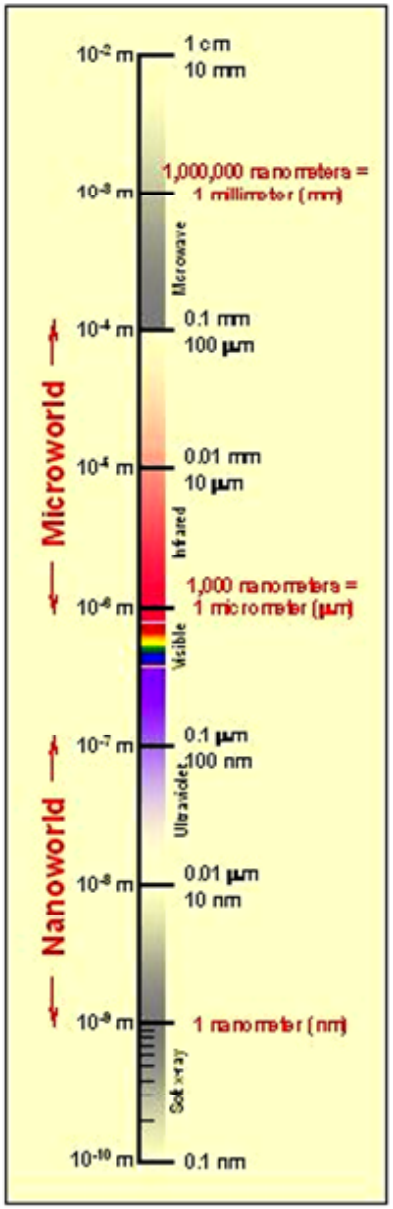






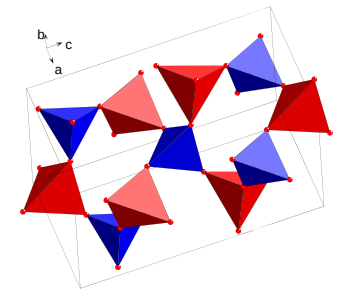


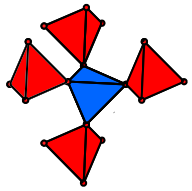
Glasses at different length-scale

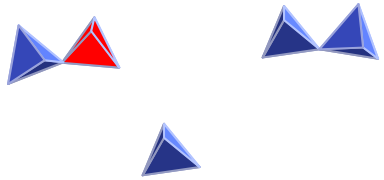


Homogeneous
Isotropic
Disordered

- ✓ Homogeneity
- ✓ Nucleation / Growth
- ✓ Viscosity
- ✓ Configuration
- ✓ Chemistry
- ✓ Glass Transition
- ✓ Modelling





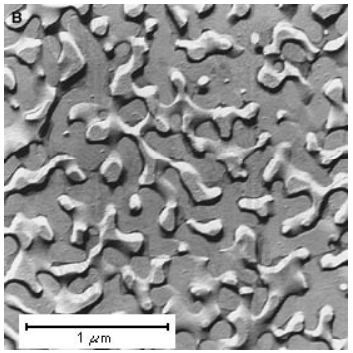


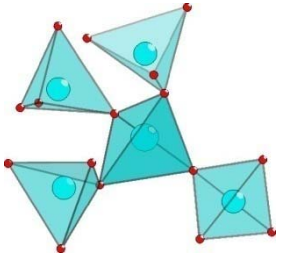
Heterogeneous
Anisotropic
Partly Ordered

nm

Å

Structure vitreuse à l'échelle subnanométrique : désordre géométrique ou chimique.





- **Changements de coordinence**
  - ✓ **RMN 1D : ^{29}Si, ^{11}B, ^{27}Al, ^{17}O**
- **Désordre Chimique / Géométrique**
  - ✓ **Phosphates**
  - ✓ **Chalcogénures PSe**
- **Vers l'échelle sub-nanométrique**
  - ✓ **Anorthite 2SiO2-Al_2O_3-CaO**
  - ✓ **Silicate de Ca $Ca^{29}SiO_3$**
- **Perspectives**

Unexpected coordination state of Si

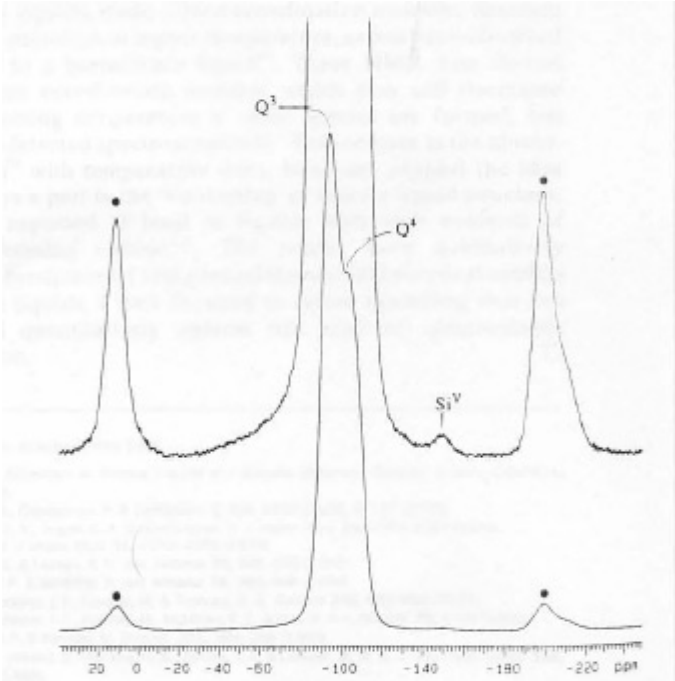
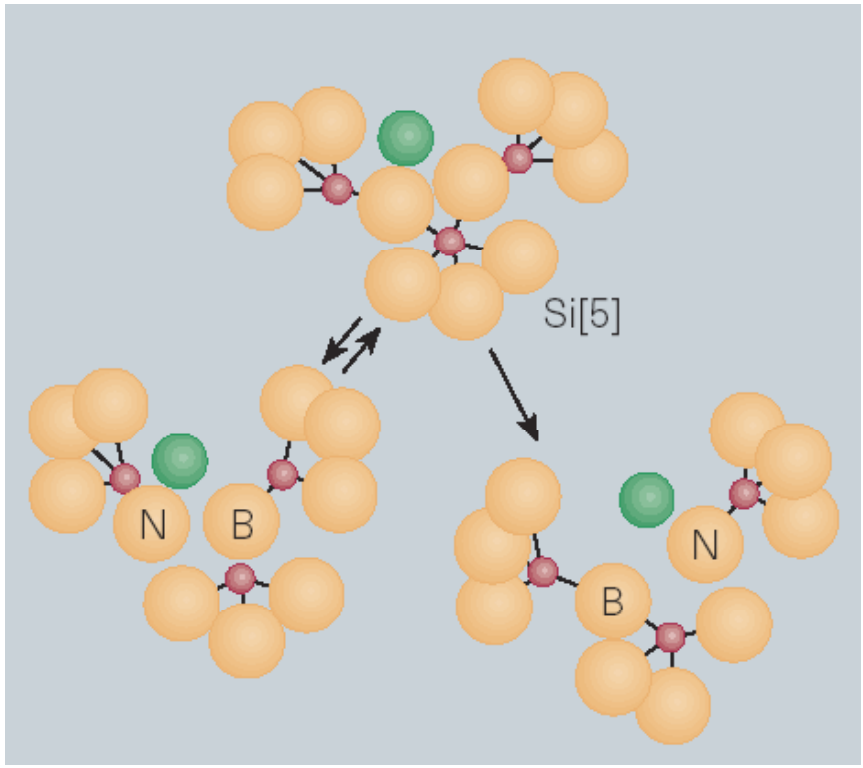


FIG. 1 The ^{29}Si MAS NMR spectrum for fast-quenched $K_2Si_4O_9$ glass. Upper trace is lower trace × 10. Data were collected with a Varian VXR 400 spectrometer at a Larmor frequency of 79.5 MHz, using a high-speed MAS probe (Doty Scientific, Inc.) with a 5-mm rotor. A spin tip angle of 30° and a 1-s delay between pulses were used (using 10 s and 60 s delays produced no significant differences from the 1-s delay in the relative abundance of Si^V sites). Data from ~50,000 pulses were averaged. A 20-Hz exponential line broadening was used to improve the signal-to-noise ratio. Frequency reference was tetramethyl silane. Solid circles mark spinning side bands.

J.F.Stebbins
'NMR evidence for five-coordinated silicon in a silicate glass at atmospheric pressure.'
Nature **351** *638-639* (1991)



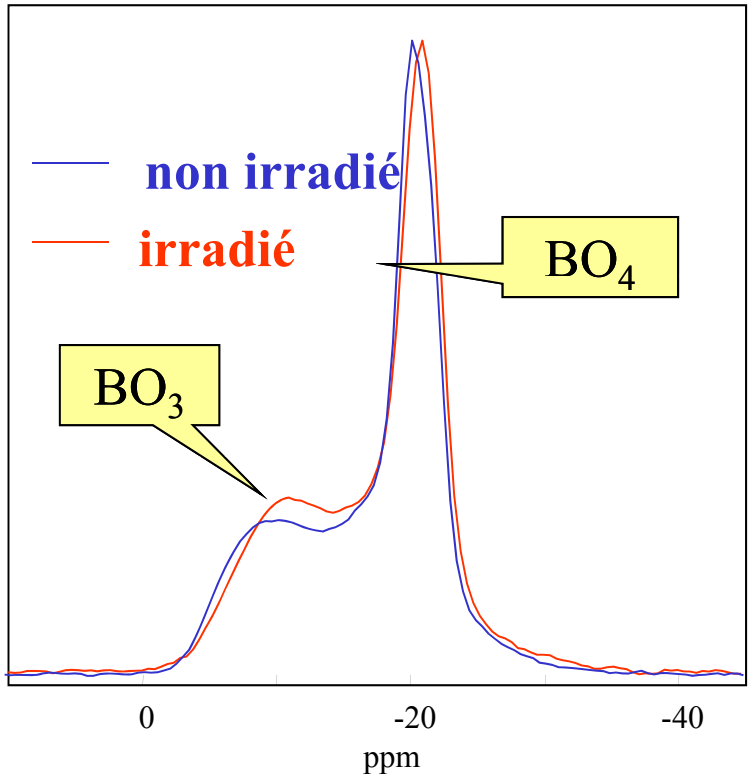
Modèle de mécanisme de viscosité

Si_5 a été identifié expérimentalement dans des verres

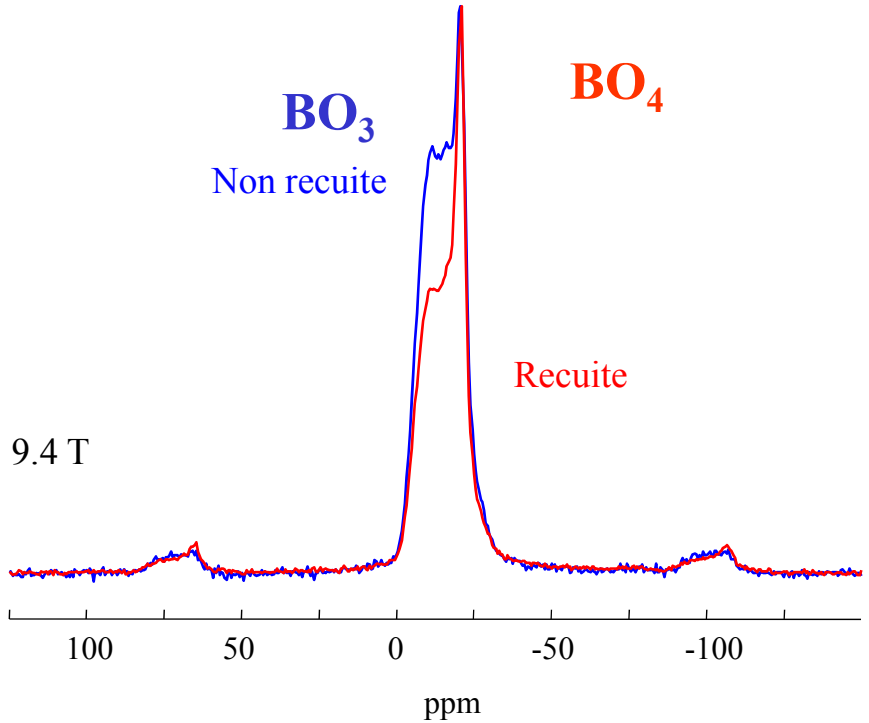
I.Farnan, J.F.Stebbins, "High Temperature 29Si NMR investigation of solid and molten silicates.", J. Am. Chem. Soc., 112 pp32-39 (1990).

différentes coordinences du ^{11}B

Verres Modèles irradiés β
(B. Boizot- LSI)



Fibre de verre E

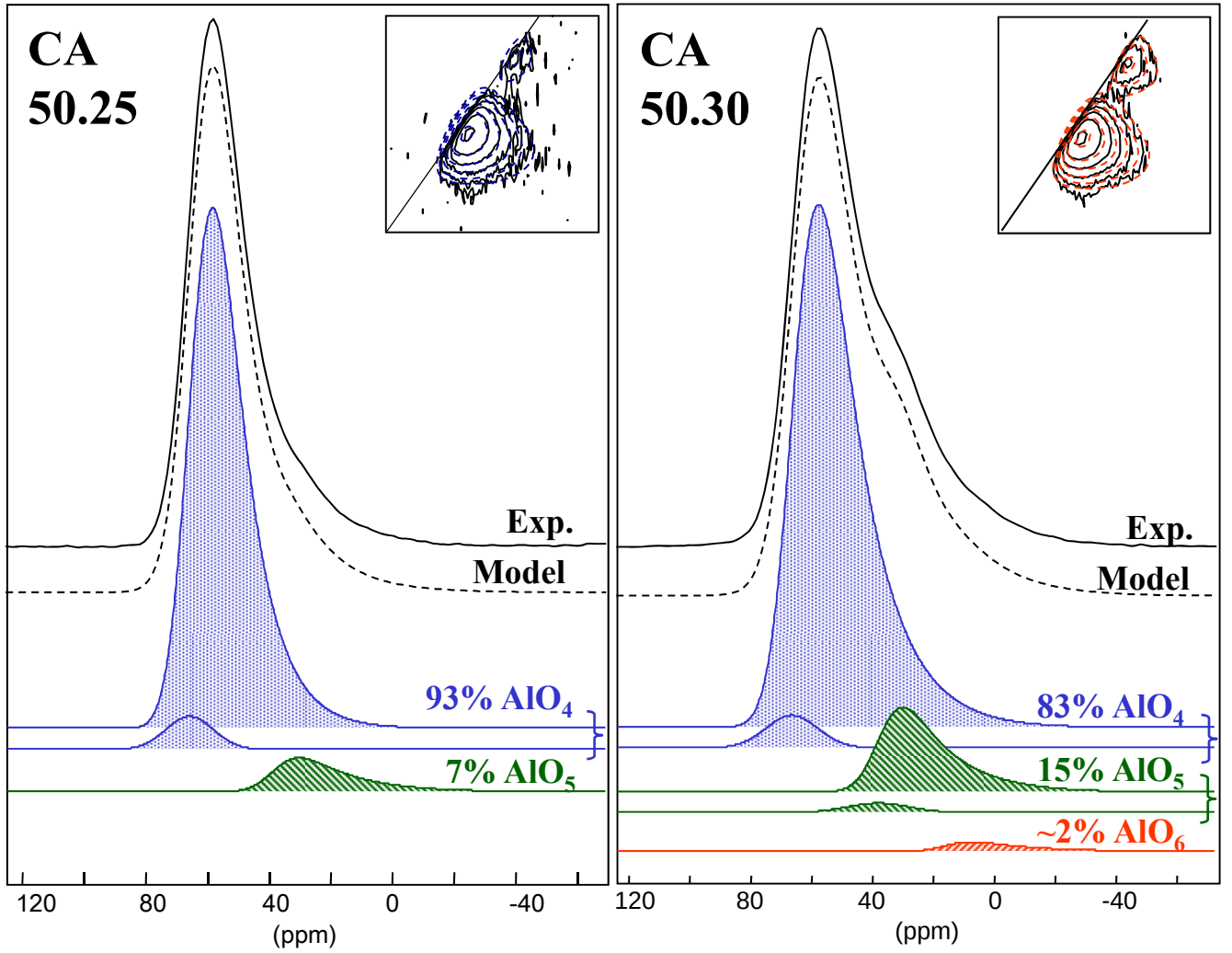


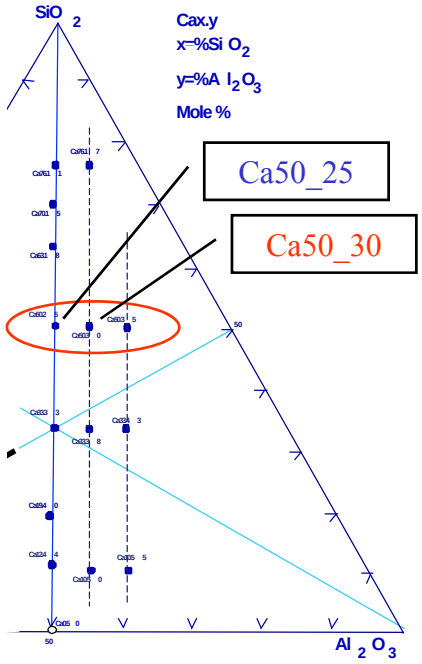
Le rapport B_{III}/ B_{IV} est très sensible : Irradiation, température fictive...

S.Soyer Uzun, S.Sen *A 11B MAS NMR Spectroscopic Study of Structural Relaxation, Ageing and Memory Effect at the Atomic Scale in a Borosilicate Glass*
J. Phys. Chem. B **111** 9758 (2007)

Ca 50_25 / 30 fit 1D 750 MHz

Glass (SiO_2, Al_2O_3,CaO)

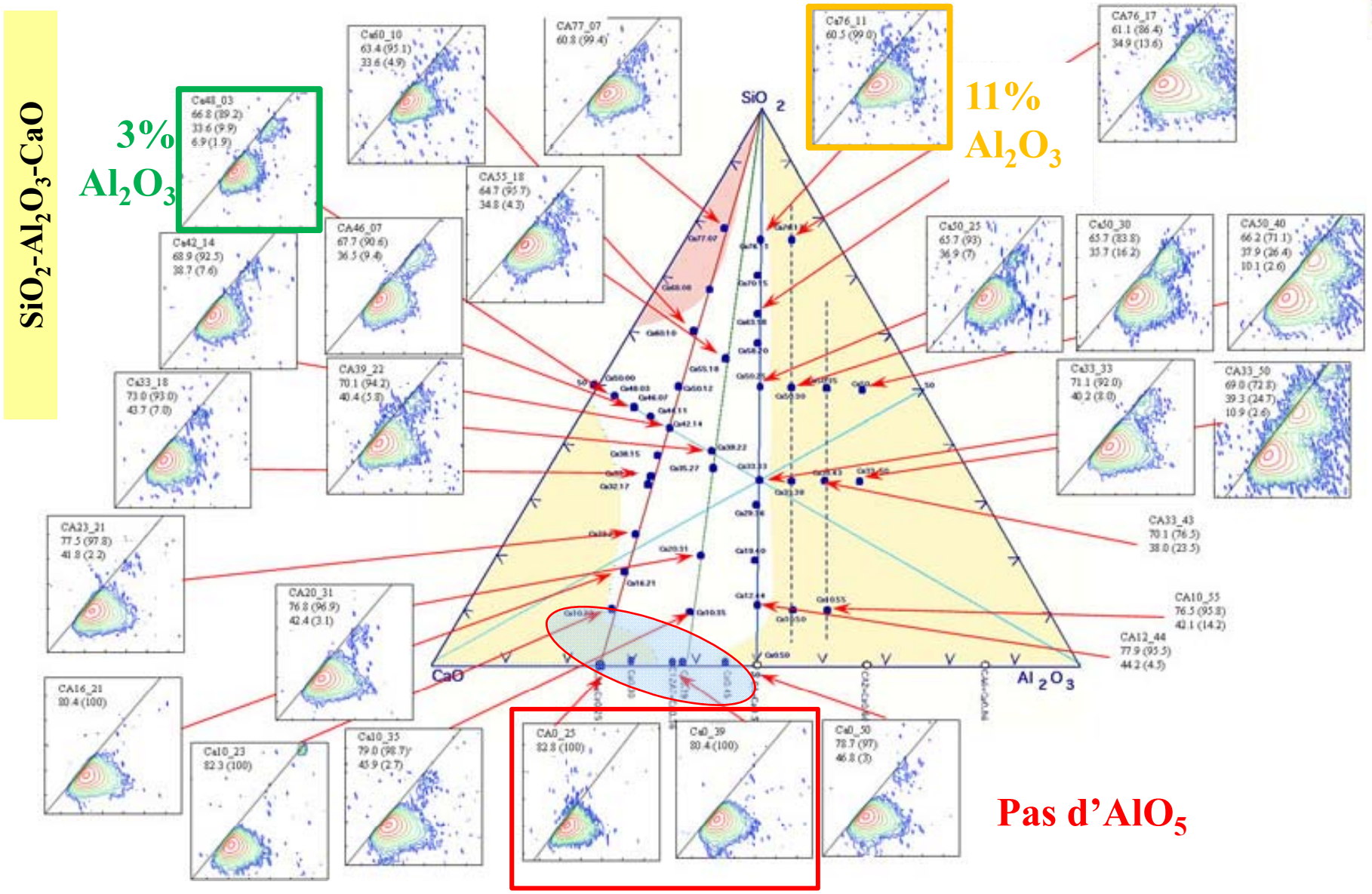




7% AlO_5 pour la composition Ca50_25 – Plagioclase $Si_2Al_2O_8Ca$

D.R. Neuville, L. Cormier, D. Massiot *'Al environment in tectosilicate and peraluminous glasses: a NMR, Raman and XANES investigation'*
Geochim. Cosmochim. Acta **68** 5071-5079 (2004)

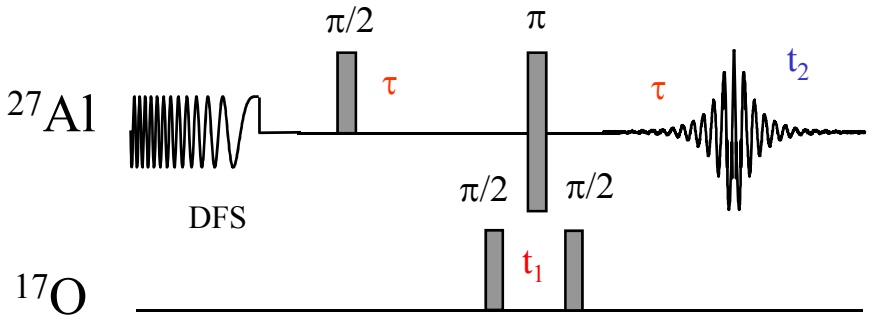
Ternaire SiO_2-Al_2O_3-CaO



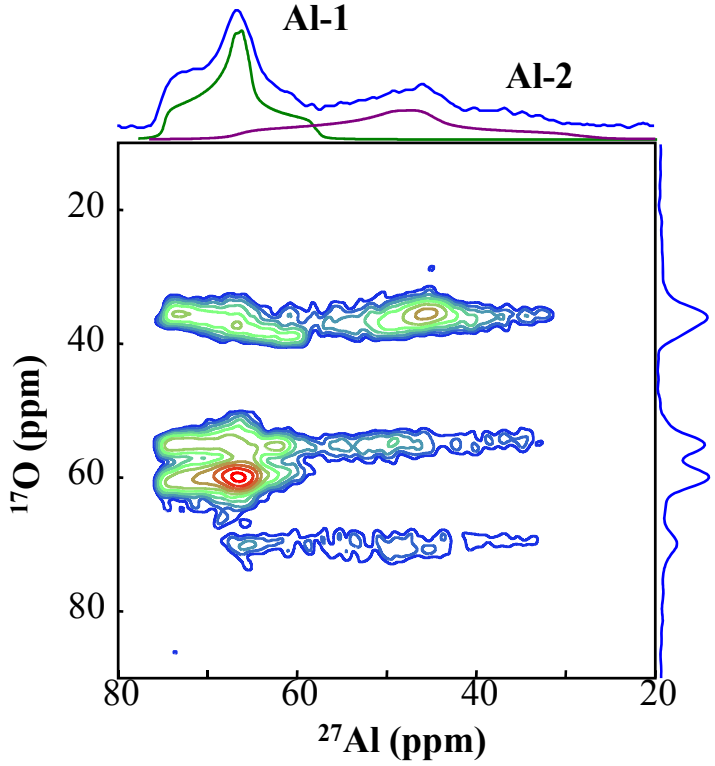
D.R.Neuville, L.Cormier, D.Massiot *'Al coordination and speciation in calcium aluminosilicate glasses : effects of composition determined by 27Al MQ-MAS NMR and Raman spectrocospy'* Chem. Geol. **229** 173-185 (2006)

$CaAl_4O_7$ – CA2

CA2 – $CaAl_4O_7$

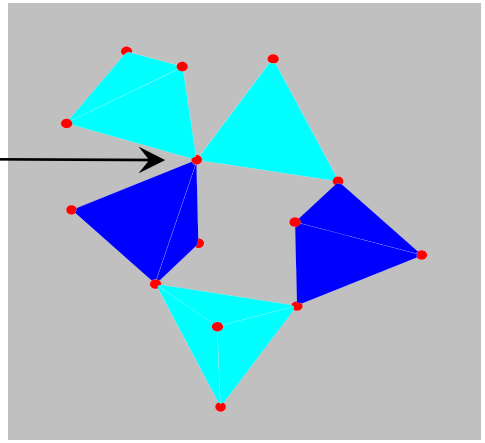


- Quadrupoles with 2nd order broadening
- Gain with B_0^4 in both dimensions
- Lineshape contains the relative orientation of the quadrupolar tensors.



O4 — μ_3 tricluster O

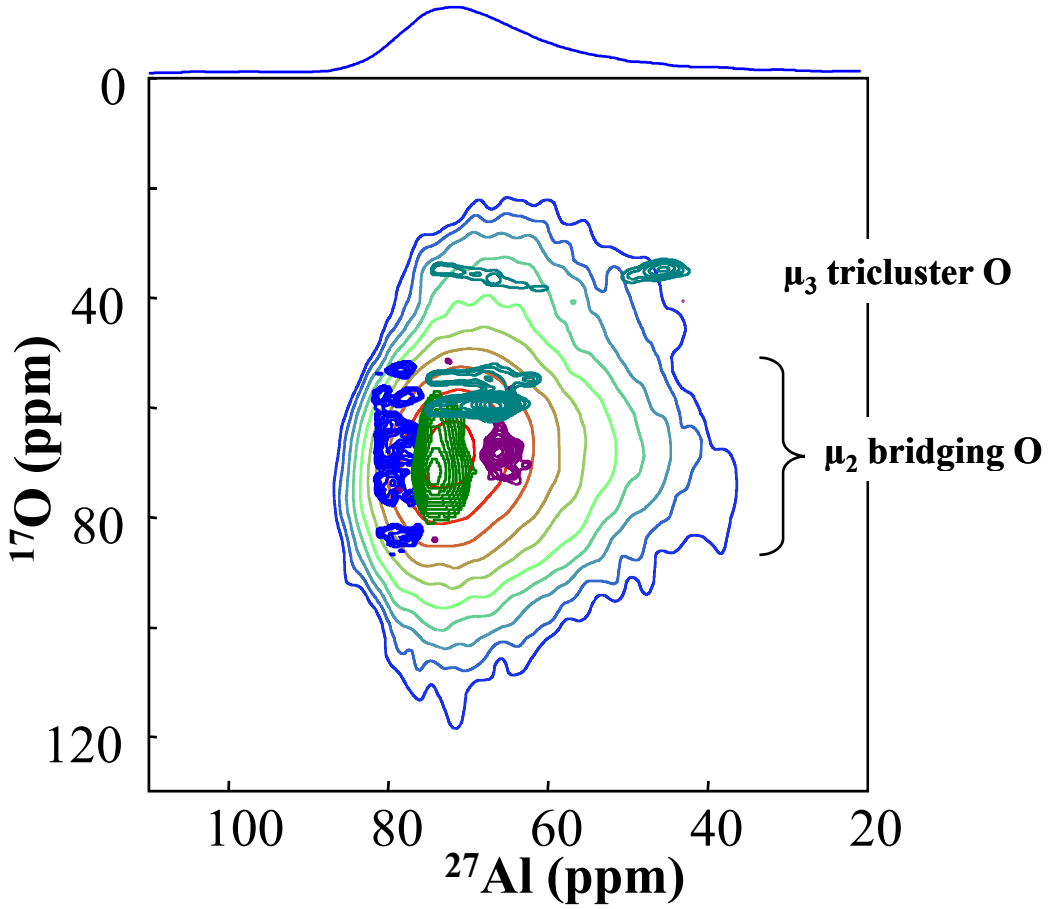
O3, O2, O1 — μ_2 bridging O

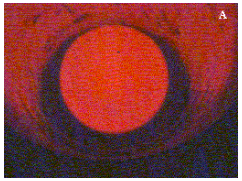


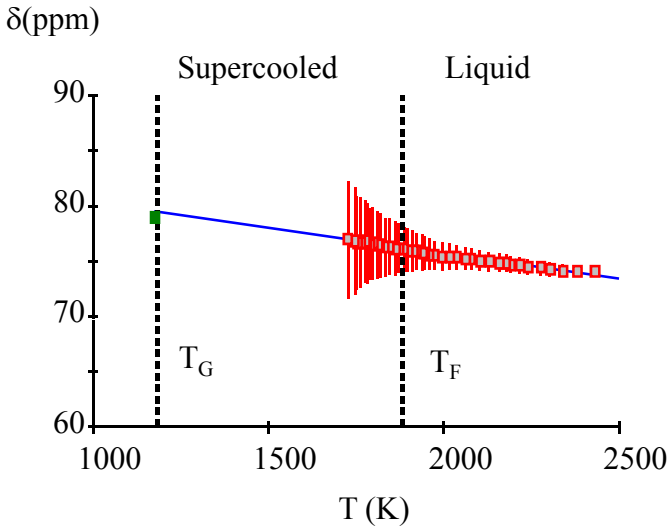
D.Iuga, C.Morais, Z.Gan, D.R.Neuville, L.Cormier, D.Massiot *'NMR Heteronuclear Correlation between Quadrupolar Nuclei in Solids.'* J. Am. Chem. Soc. **127** 11540-11541 (2005)

$CaO\ Al_2O_3$ - Glass

CaO-Al_2O_3 Glass







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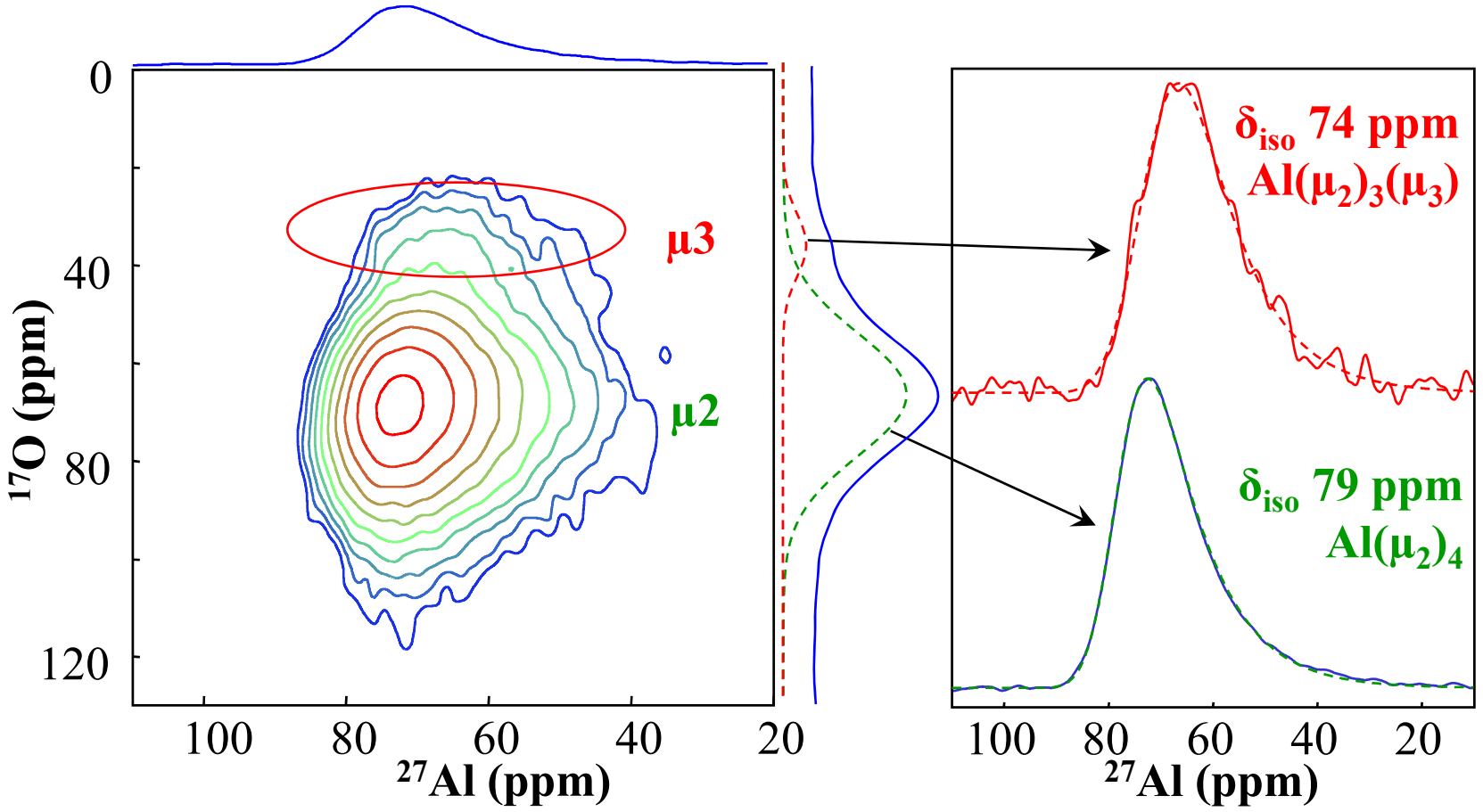
CaO Al_2O_3 - Glass

CaO-Al_2O_3 Glass



Consistent ^{17}O and ^{27}Al signature of Al(μ_2)$_3$(μ_3) structural entities

D.Iuga, C.Morais, Z.Gan, D.R.Neuville, L.Cormier, D.Massiot *'NMR Heteronuclear Correlation between Quadrupolar Nuclei in Solids.'*
J. Am. Chem. Soc. **127** 11540-11541 (2005)

^{17}O Résolution des différents sites Oxygène

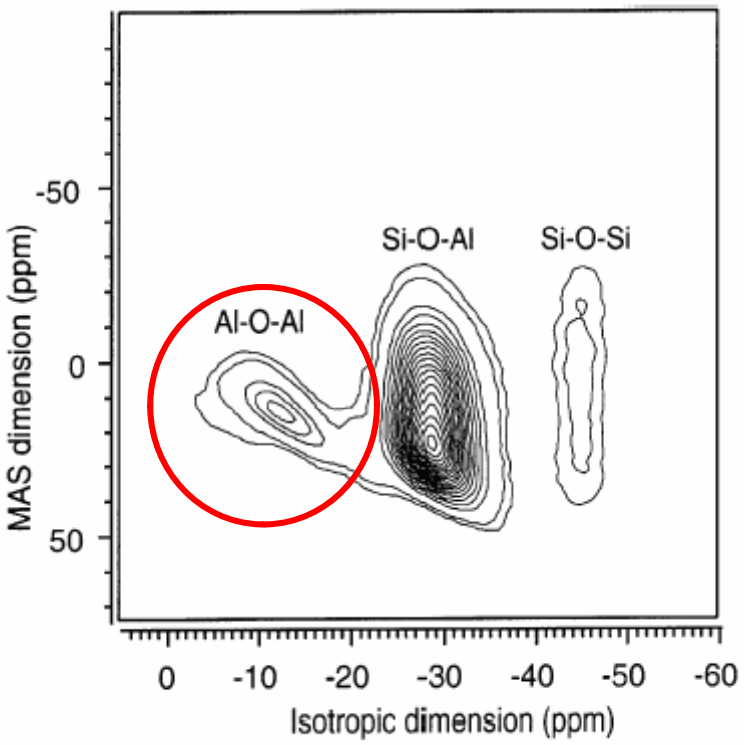


Fig. 5. ^{17}O 3QMAS spectrum collected at 9.4 T for a glass of nominal composition (in mol%) Na_2O, 25; Al_2O_3, 25; SiO_2, 50 [24].

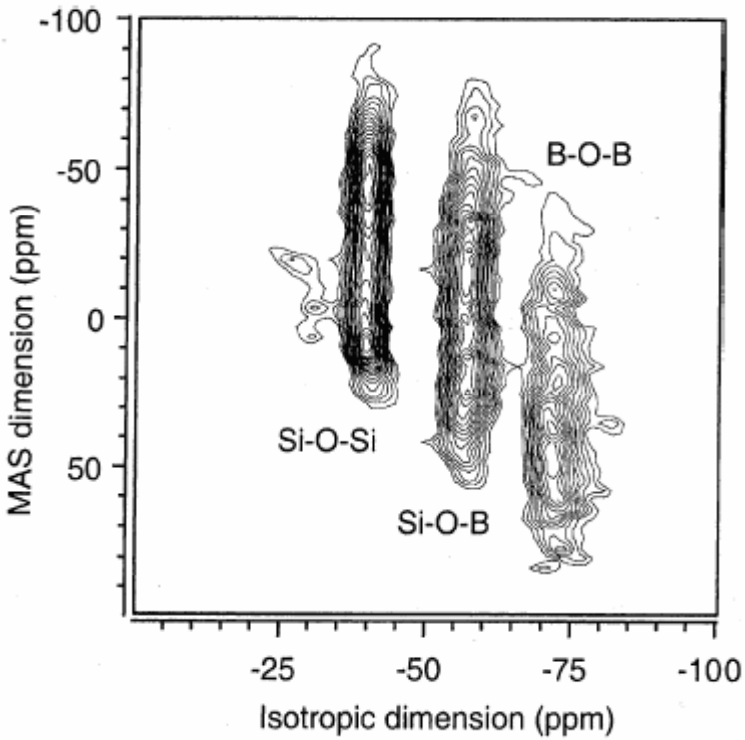
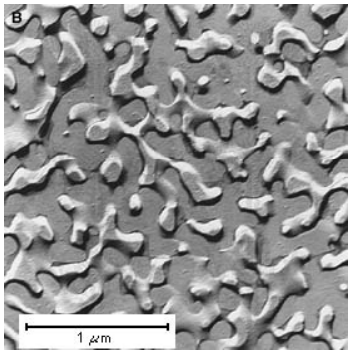


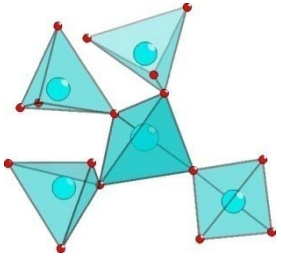
Fig. 4. ^{17}O 3QMAS spectrum collected at 9.4 T for a glass of nominal composition (in mol%) B_2O_3, 40; SiO_2, 60 [21].

Al-O-Al : violation de la règle d'exclusion de Lowenstein Si_3AlO_8Na

J.F.Stebbins, P.Zhao, S.K.Lee, J.V.Oglesby, "Direct observation of multiple oxygen sites in oxide glasses : recent advances from triple-quantum magic-angle spinning nuclear magnetic resonance.", J. Non-Cryst. Solids, 293-295 pp67-73 (2001).

Structure vitreuse à l'échelle subnanométrique : désordre géométrique ou chimique.





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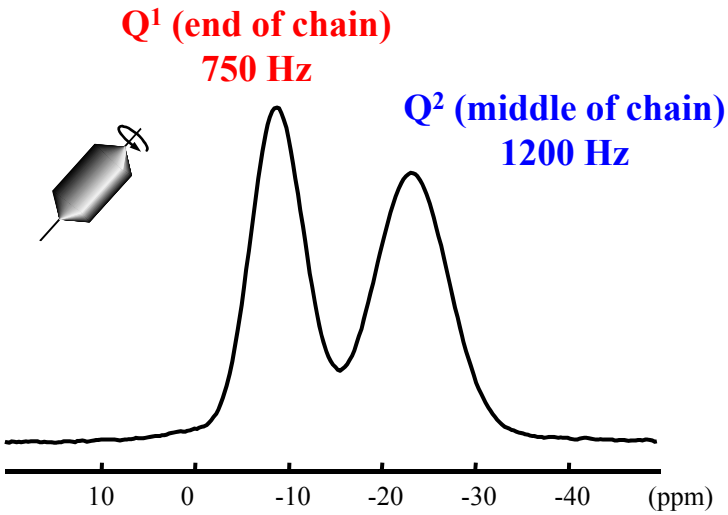
- **Désordre Chimique / Géométrique**
  - ✓ **Phosphates**
  - ✓ **Chalcogénures PSe**
- Vers l'échelle sub-nanométrique
  - ✓ Anorthite $2SiO2\text{-}Al_2O_3\text{-}CaO$
  - ✓ Silicate de Ca $Ca^{29}SiO_3$
- Perspectives

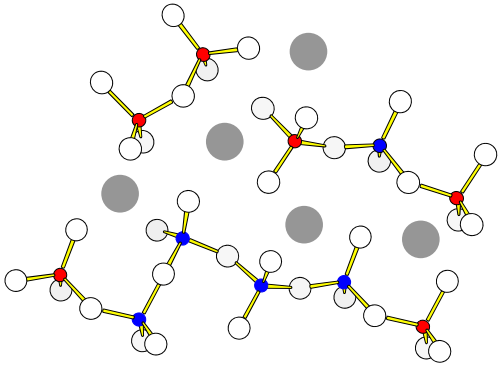
Phosphate Glasses : ^{31}P MAS NMR

$(PbO)_{0.61}(P_2O_5)_{0.39}$ verre

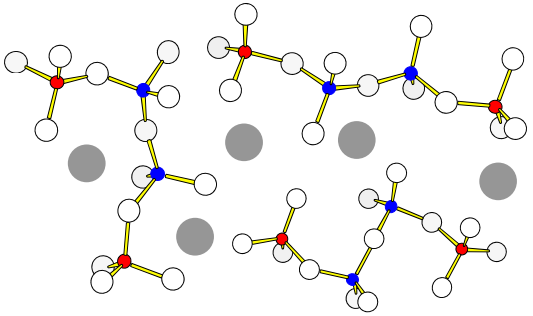


$[Q^1] = [Q^2]$

Average chain length
$N_{av.} \sim 4$



? Nature of disorder at the nanometric scale ?

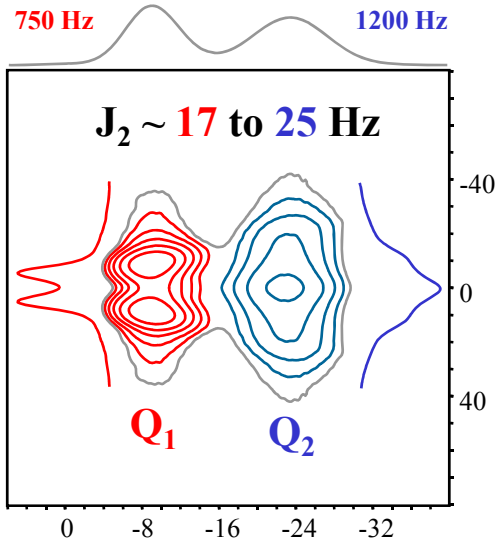


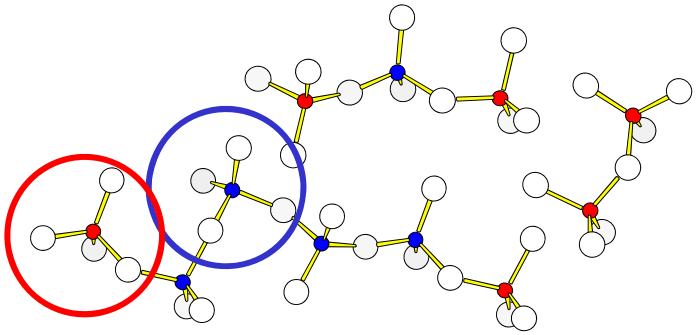
Chain length distribution?
Chemical disorder

Chain geometries?
Geometrical disorder

1 to 3 tetraedra – ^{31}P

$(PbO)_{0.61}(P_2O_5)_{0.39}$ glass





F. Fayon, I.J. King, R.K. Harris, J.S.O. Evans, D. Massiot Comptes Rendus de Chimie 7 351-361 (2004)
F.Fayon, C.Roiland, L.Emsley, D.Massiot, Journal of Magnetic Resonance 179 50-58 (2006)

1 to 3 tetraedra – ^{31}P

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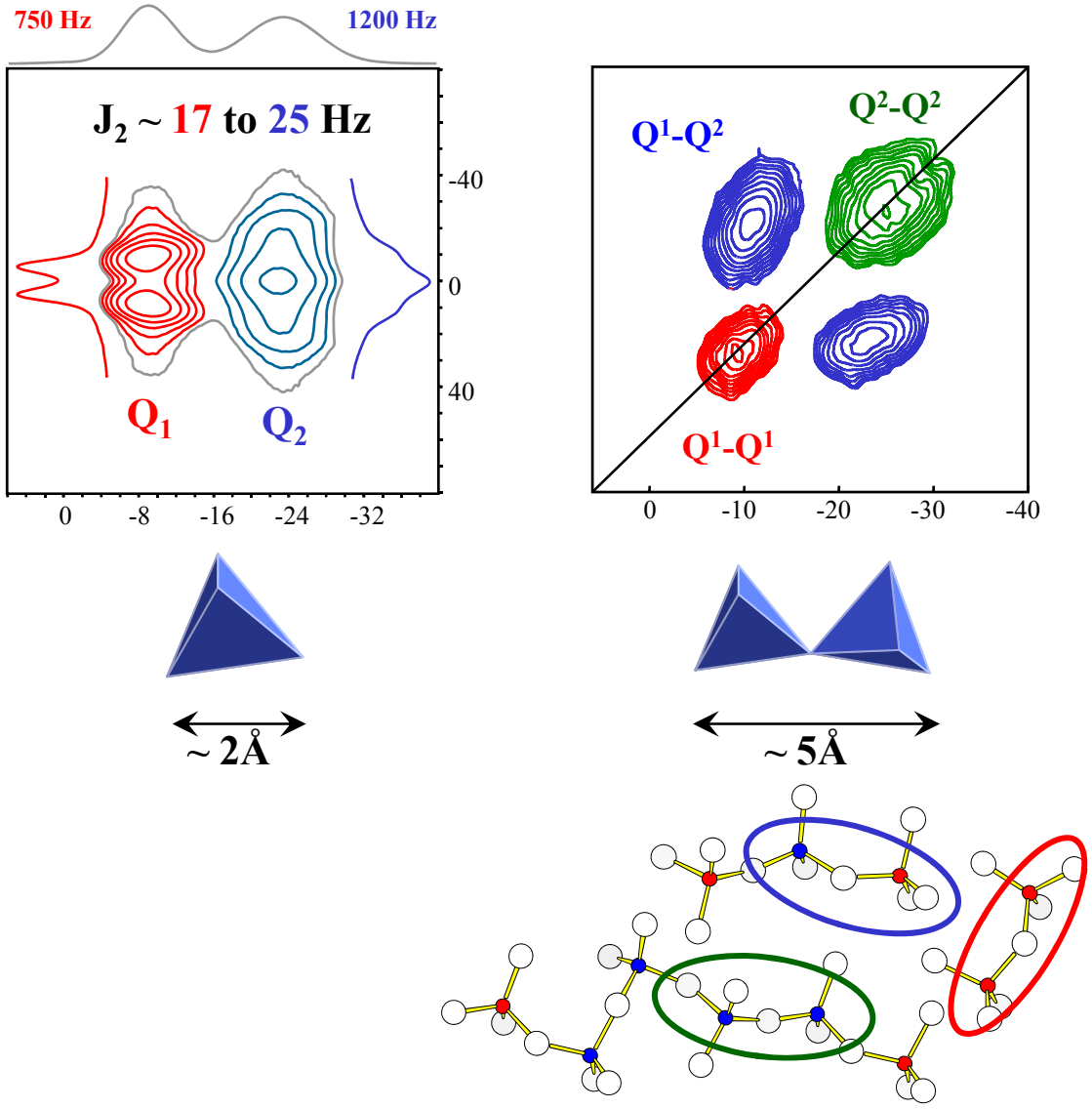

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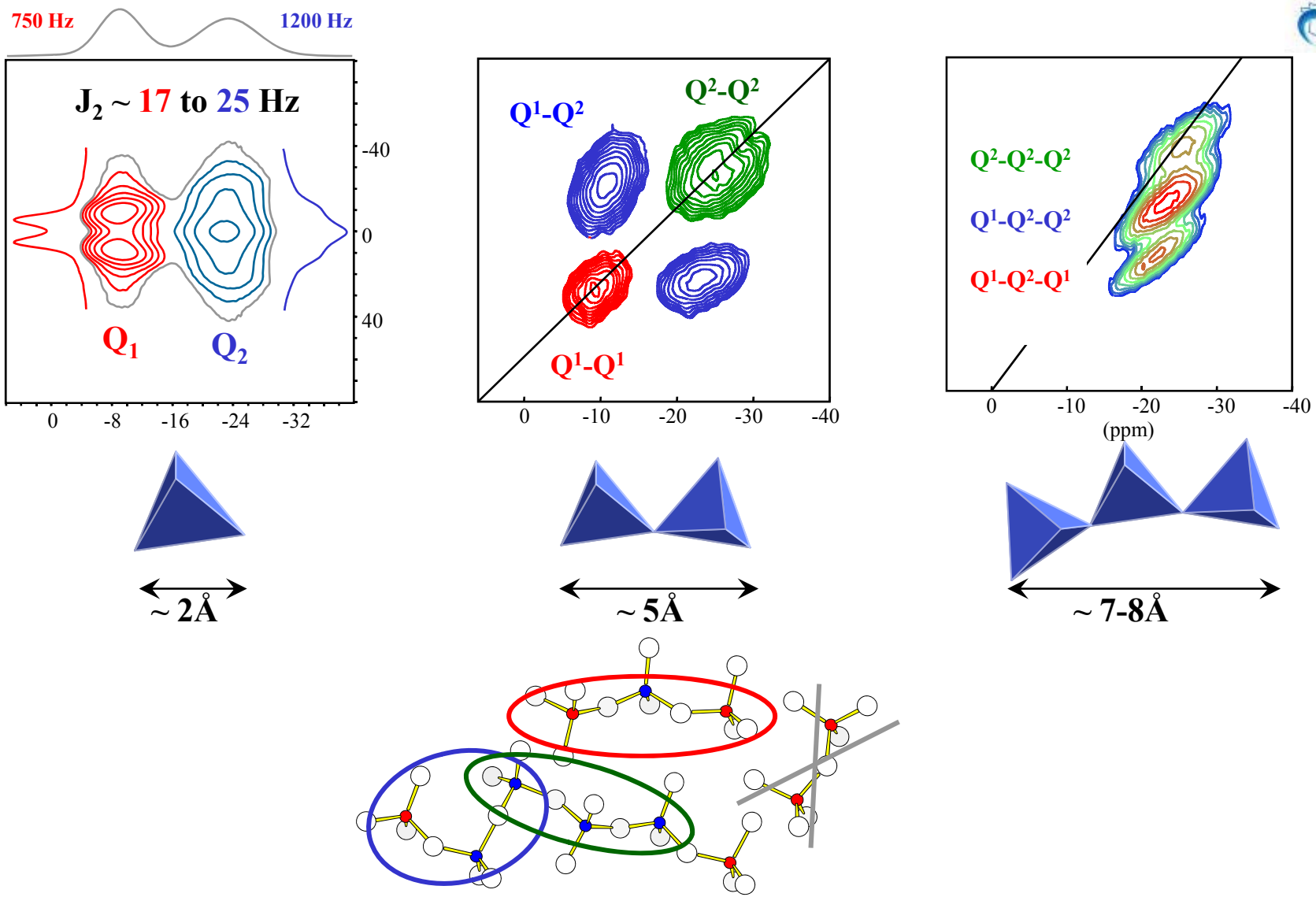

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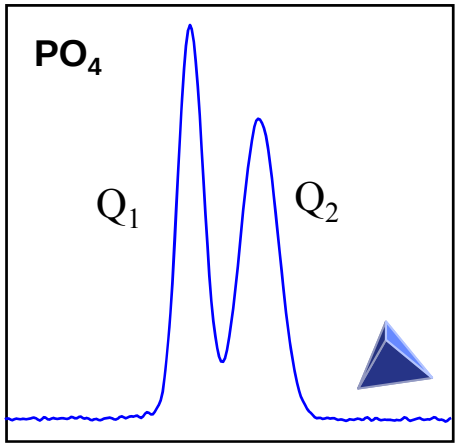
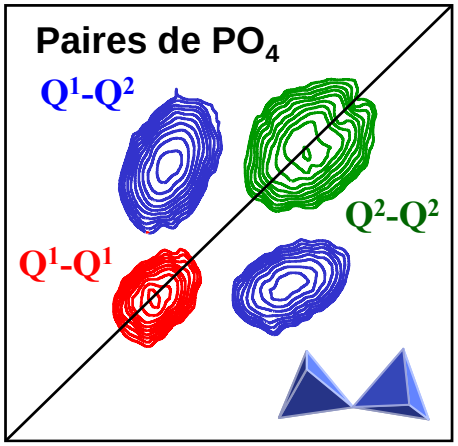
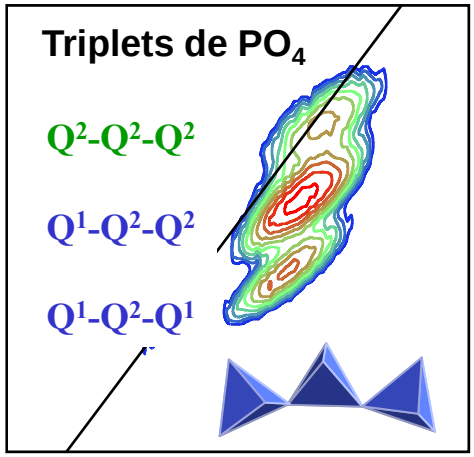
Désordre géométrique et Chimique



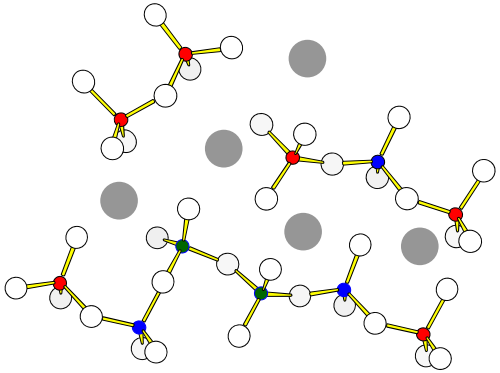
~ 2Å



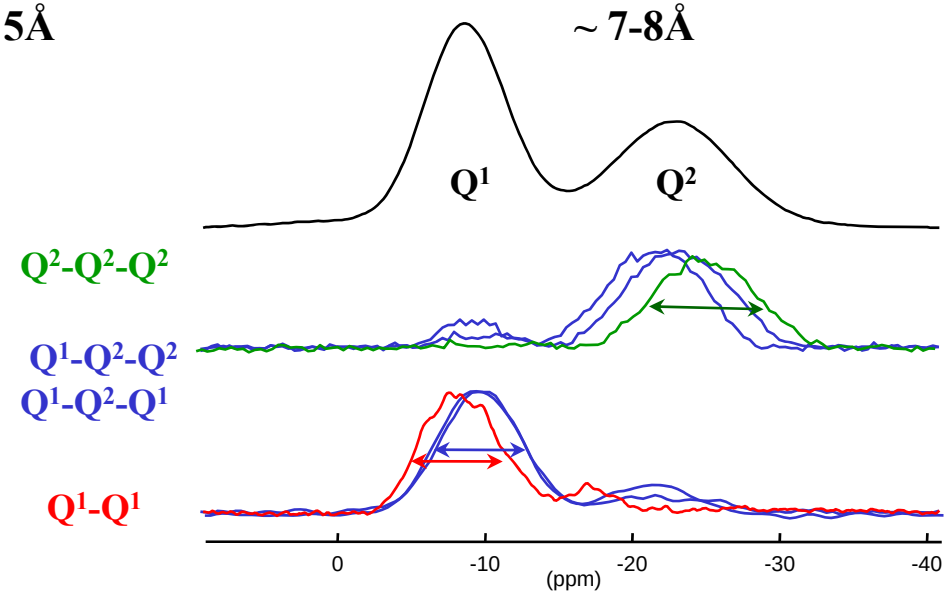
~ 5Å



~ 7-8Å



Distribution Chimique et Géométrique



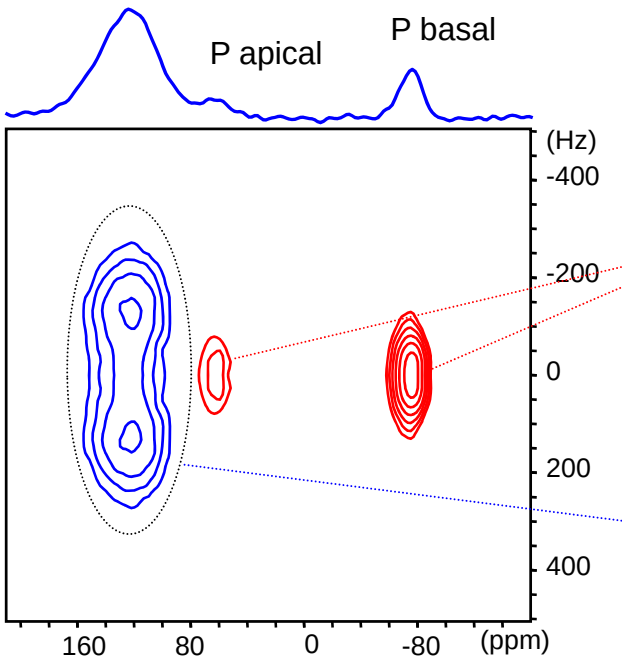
⟷ Geométrie

F. Fayon, I.J. King, R.K. Harris, J.S.O. Evans, D. Massiot Comptes Rendus de Chimie 7 351-361 (2004)
F.Fayon, C.Roiland, L.Emsley, D.Massiot, Journal of Magnetic Resonance 179 50-58 (2006)

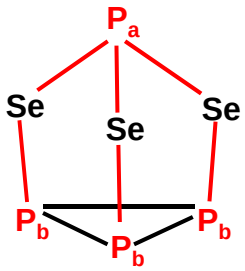
$P_{50}Se_{50}$ glass

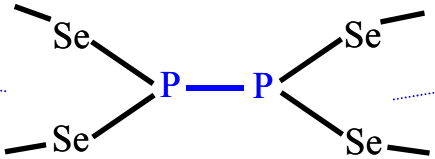
Chemical Bond

Correlation

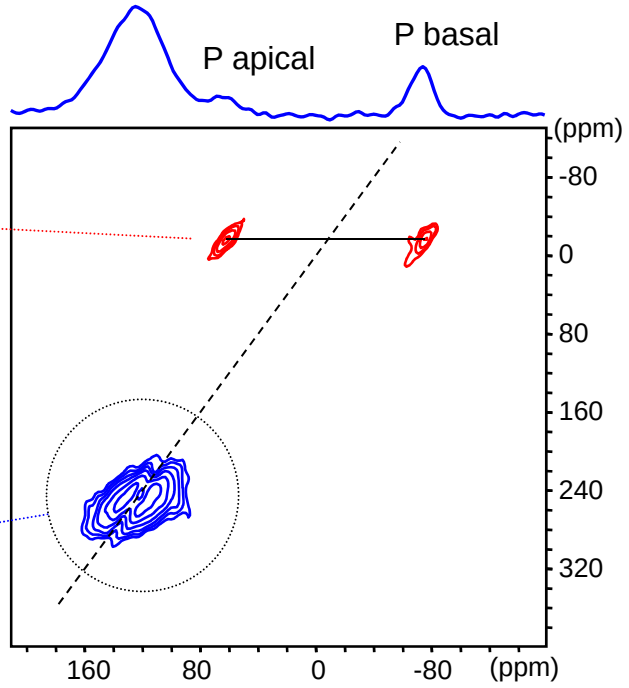


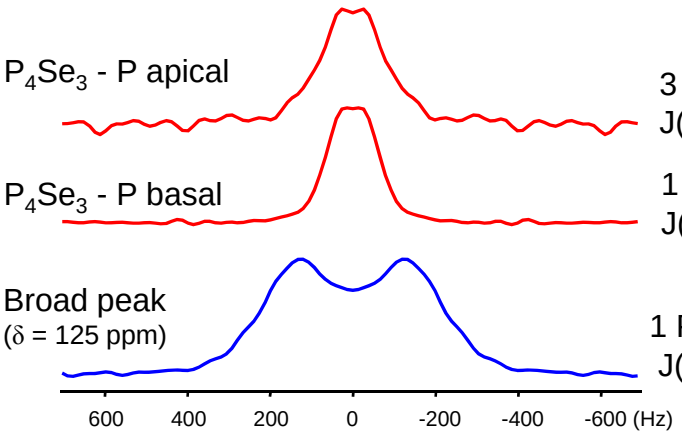
Heteronuclear





Homonuclear





3 P-Se-P bonds
J(P-Se-P) = 64 Hz

1 P-Se-P bond
J(P-Se-P)= 64 Hz

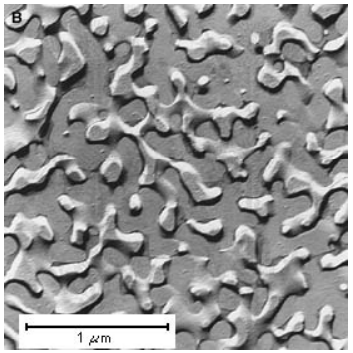
1 P-P bond
J(P-P)= 260 Hz

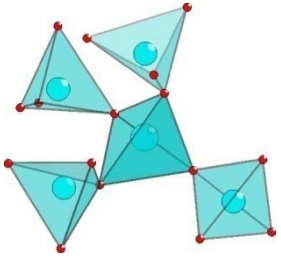
- Cross-correlation peaks between Papical and Pbasal
- One broad auto-correlation peak

⇒ **P_4Se_3 molecules and $Se_{2/2}P\text{-}PSe_{2/2}$ units forming a polymeric network**

(in agreement with the structural model proposed by H. Eckert and coworkers)

Structure vitreuse à l'échelle subnanométrique : désordre géométrique ou chimique.

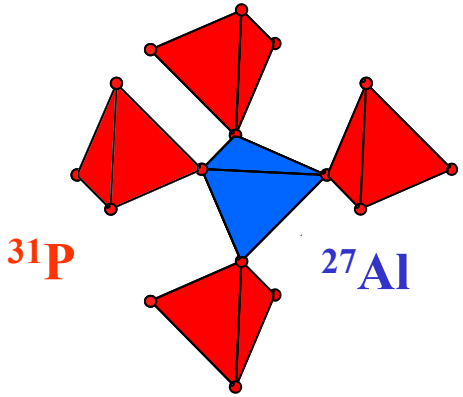




- Changements de coordinence
  - ✓ RMN 1D : ^{29}Si, ^{11}B, ^{27}Al, ^{17}O
- Désordre Chimique / Géométrique
  - ✓ Phosphates
  - ✓ Chalcogénures PSe
- **Vers l'échelle sub-nanométrique**
  - ✓ **Anorthite 2SiO2-Al_2O_3-CaO**
  - ✓ **Silicate de Ca $Ca^{29}SiO_3$**
- Perspectives

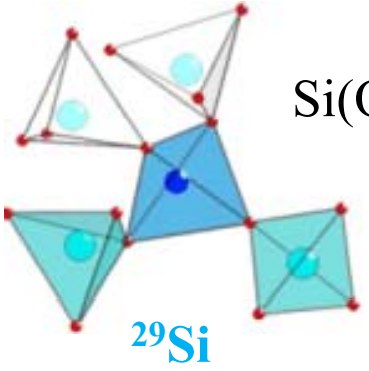
New Possibilities

Heteronuclear Counting



$Al(OP)_{n\geq?}$

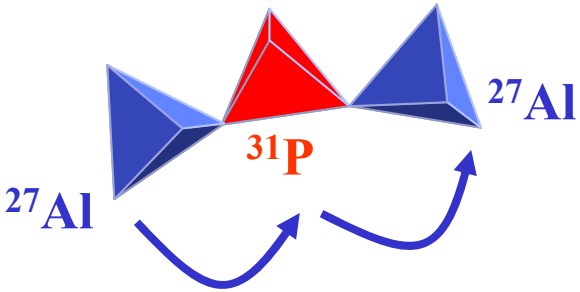
nm

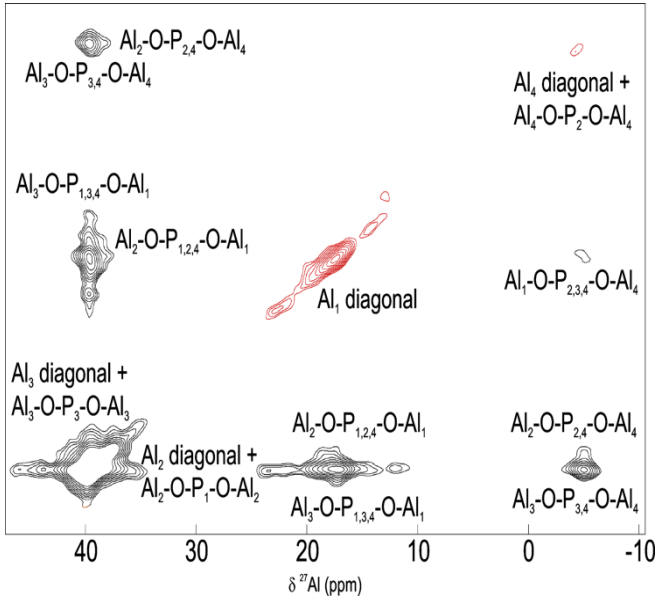


$Si(OSi)_{n\geq?}$

Homonuclear Counting

Relayed Transfer





{^{71}Ga/^{31}P} {^{27}Al/^{31}P} {^{27}Al/^{29}Si} {^{27}Al/^{17}O} {^{29}Si/^{31}P} {^{19}F/^{207}Pb} {^{17}O/^{31}P} …

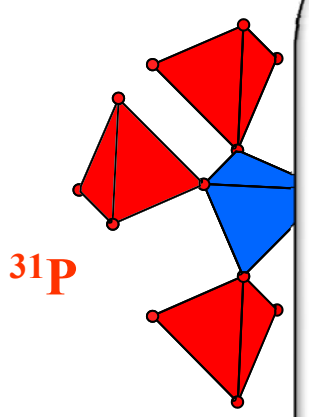
New Possibilities

Heteronuclear Counti

Relayed Transfer

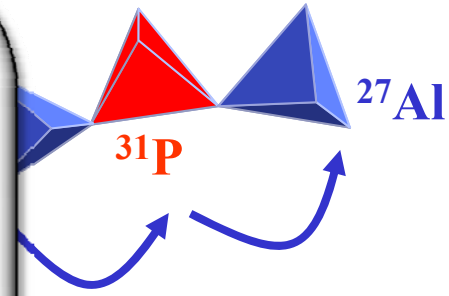
- **Identification of neighbors**
- **Counting neighbors**
- **Chemical bond / Distance**
- **From Å to nm**

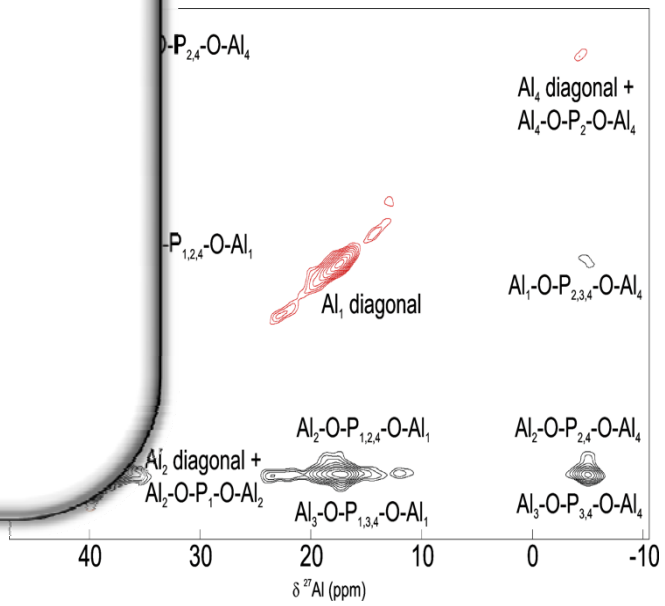
- ✓ **Glass**
- ✓ **Ceramics**
- ✓ **Molecular Sieves**
- ✓ **Meso-porous**
- ✓ **Catalysts Zeolites**
- ✓ **Biomaterials**
- ✓ **…**



Al(OP)$_n$

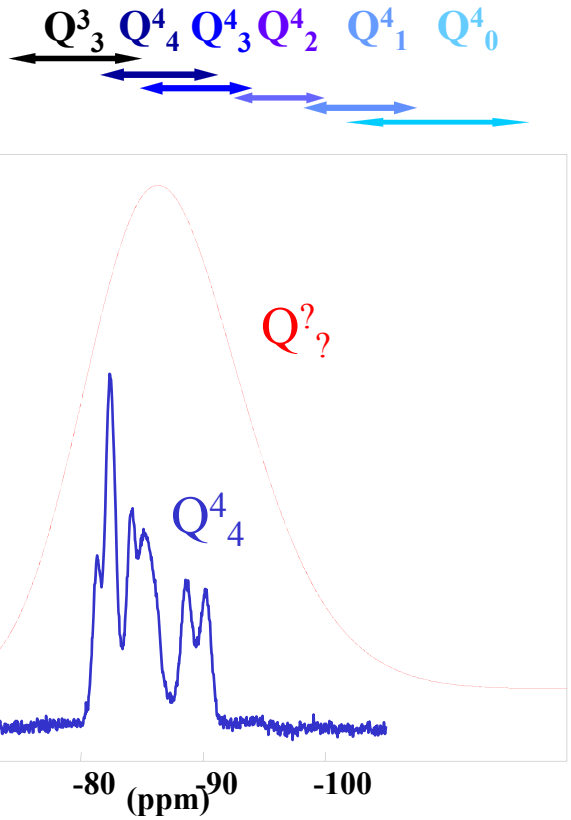
nm



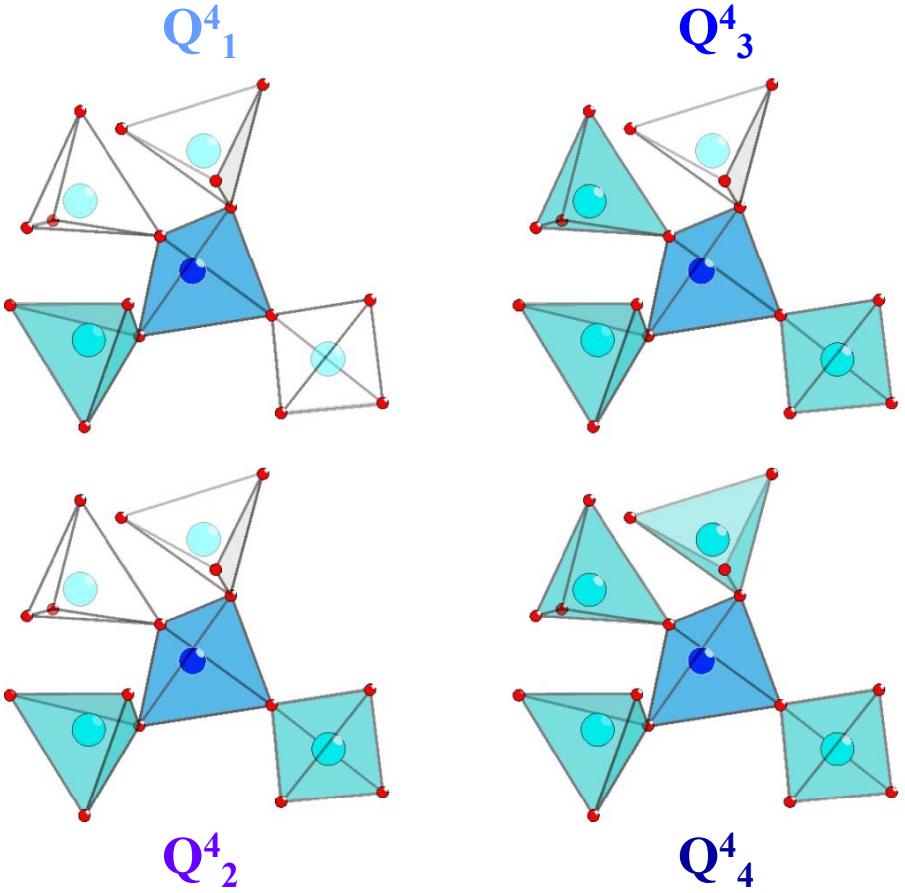


{^{71}Ga/^{31}P} {^{27}Al/^{31}P} {^{27}Al/^{29}Si} {^{27}Al/^{17}O} {^{29}Si/^{31}P} {^{19}F/^{207}Pb} {^{17}O/^{31}P} …

Anorthite Glass $Si_2Al_2O_8Ca$



NMR^{29}Si
Anorthite
Crystalline & Glass



J.Hiet, M.Deschamps, N.Pellerin, F.Fayon, D.Massiot
"*Probing chemical disorder in glasses using silicon-29 NMR spectral editing*" *Phys. Chem. Chem. Phys.* 11 6935–6940 ***2009***

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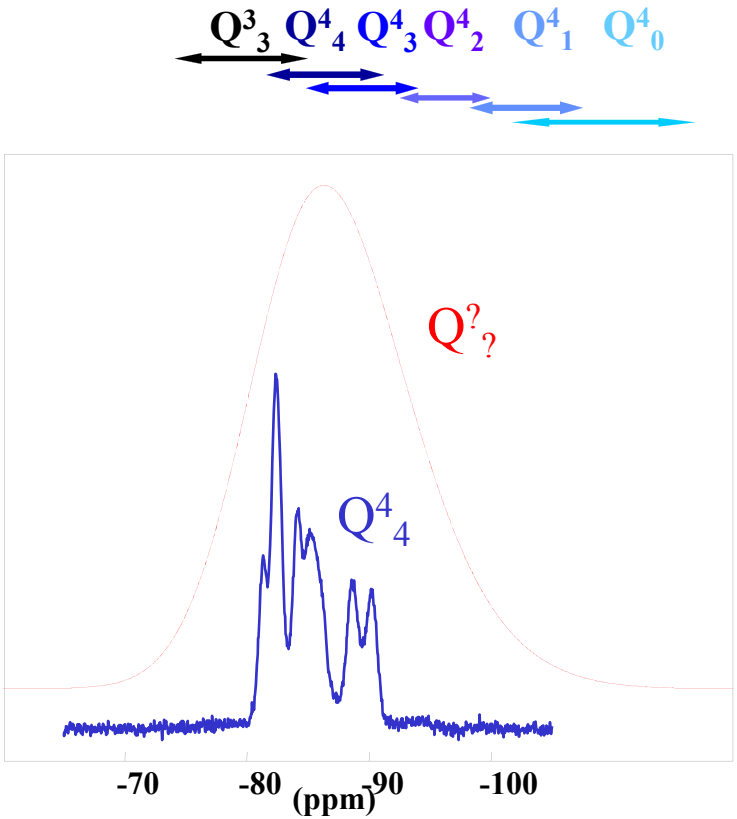
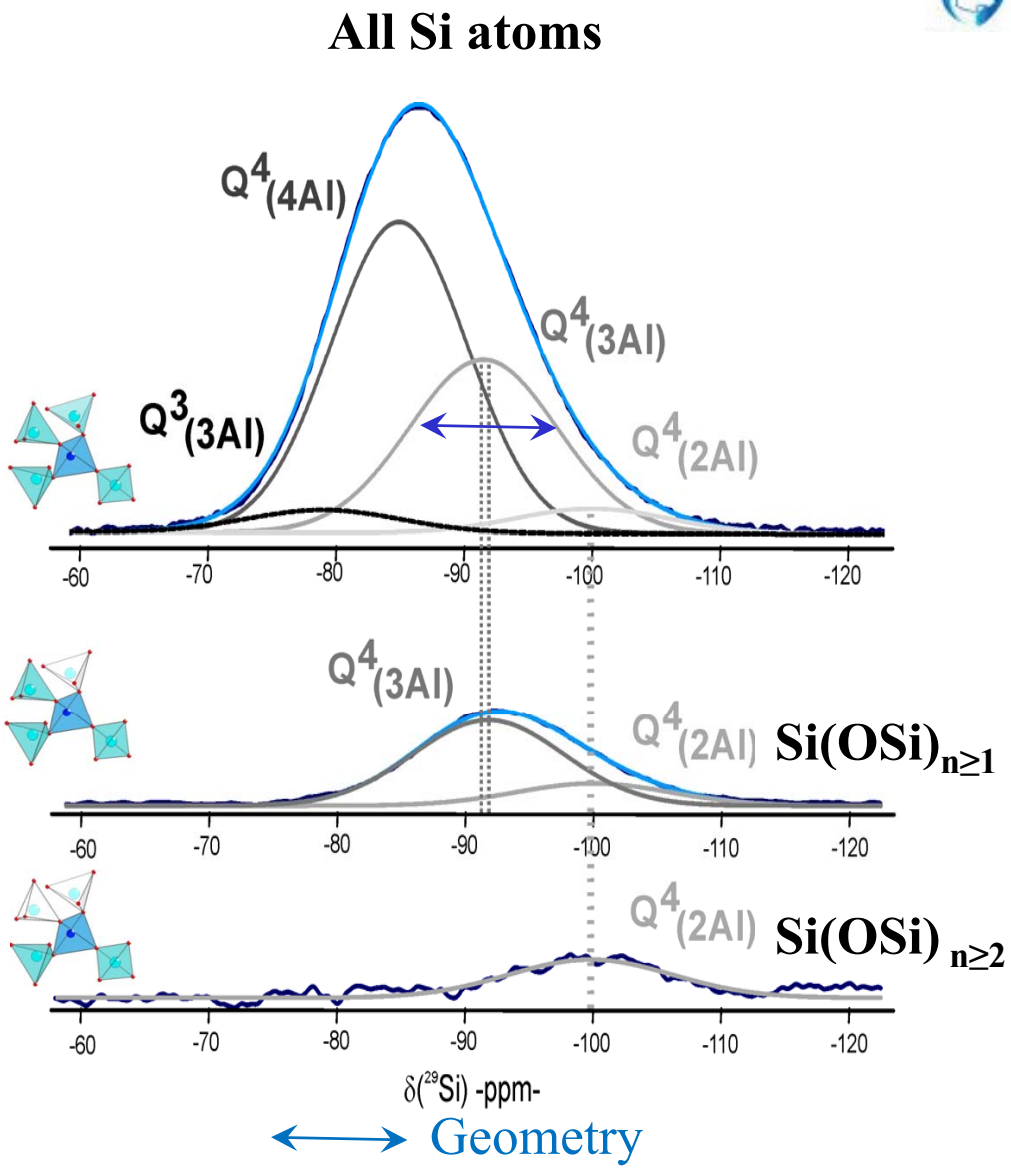


NMR^{29}Si
Anorthite
Crystalline & Glass



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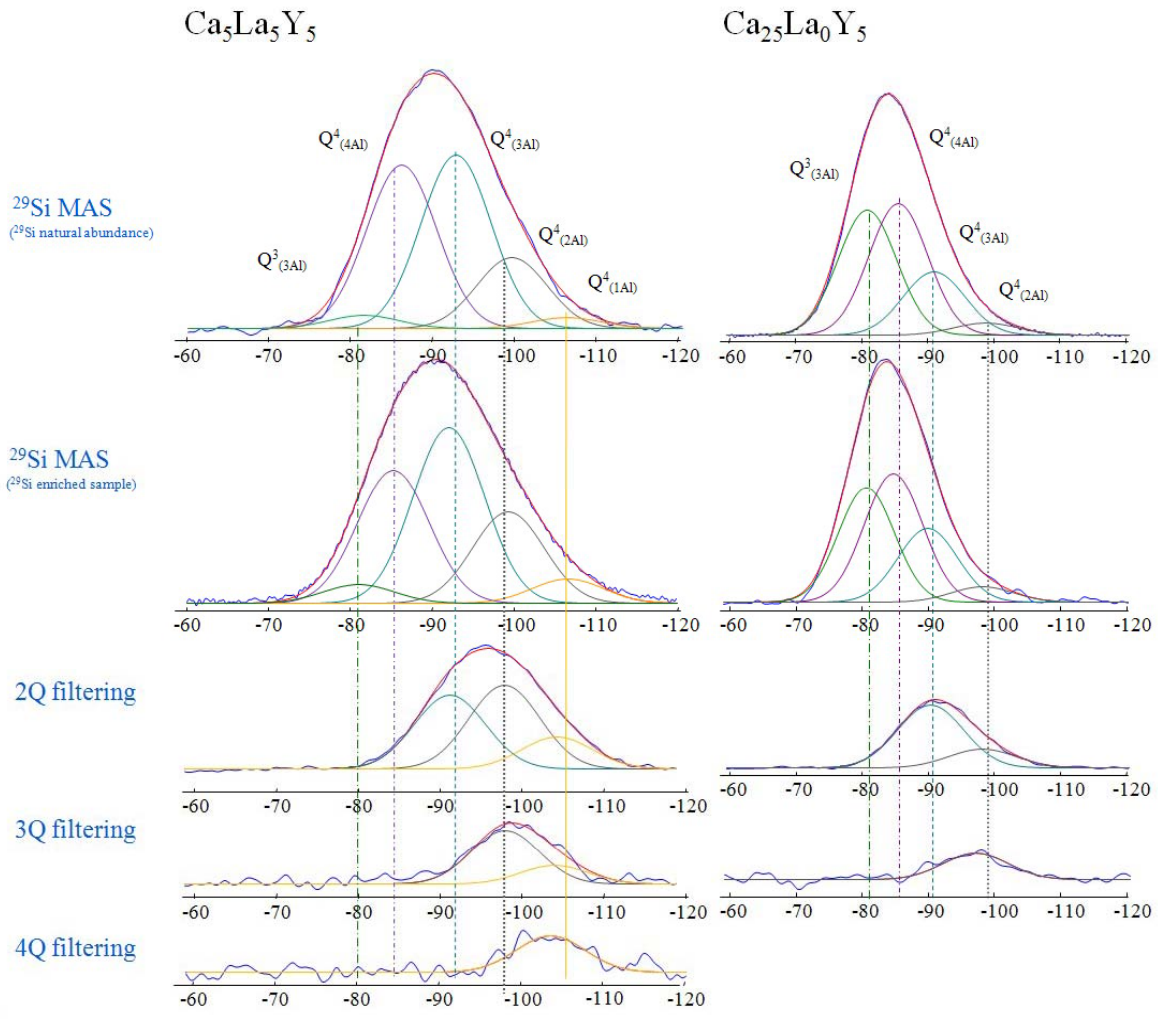
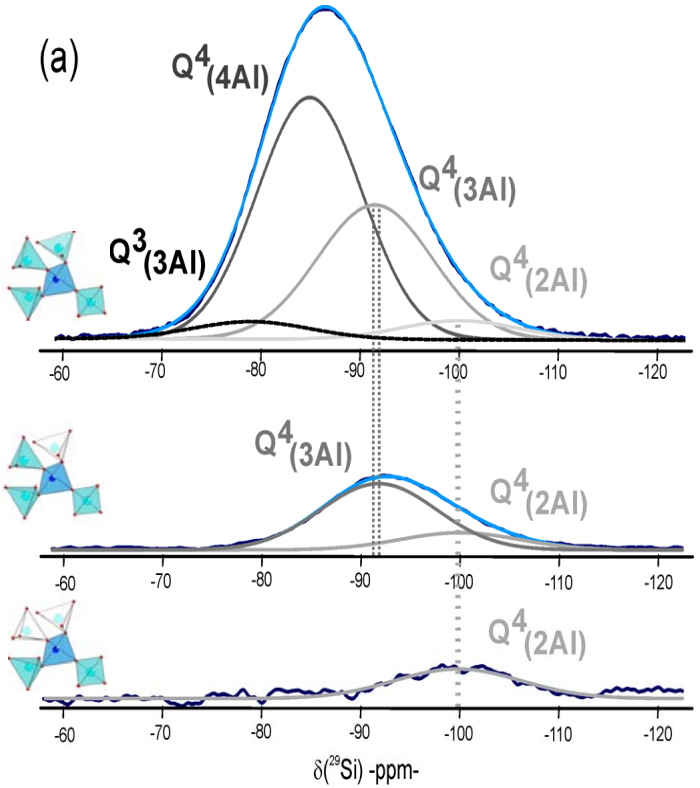
"*Probing chemical disorder in glasses using silicon-29 NMR spectral editing*" *Phys. Chem. Chem. Phys.* 11 6935–6940 ***2009***

(Y/La) Complex Glasses

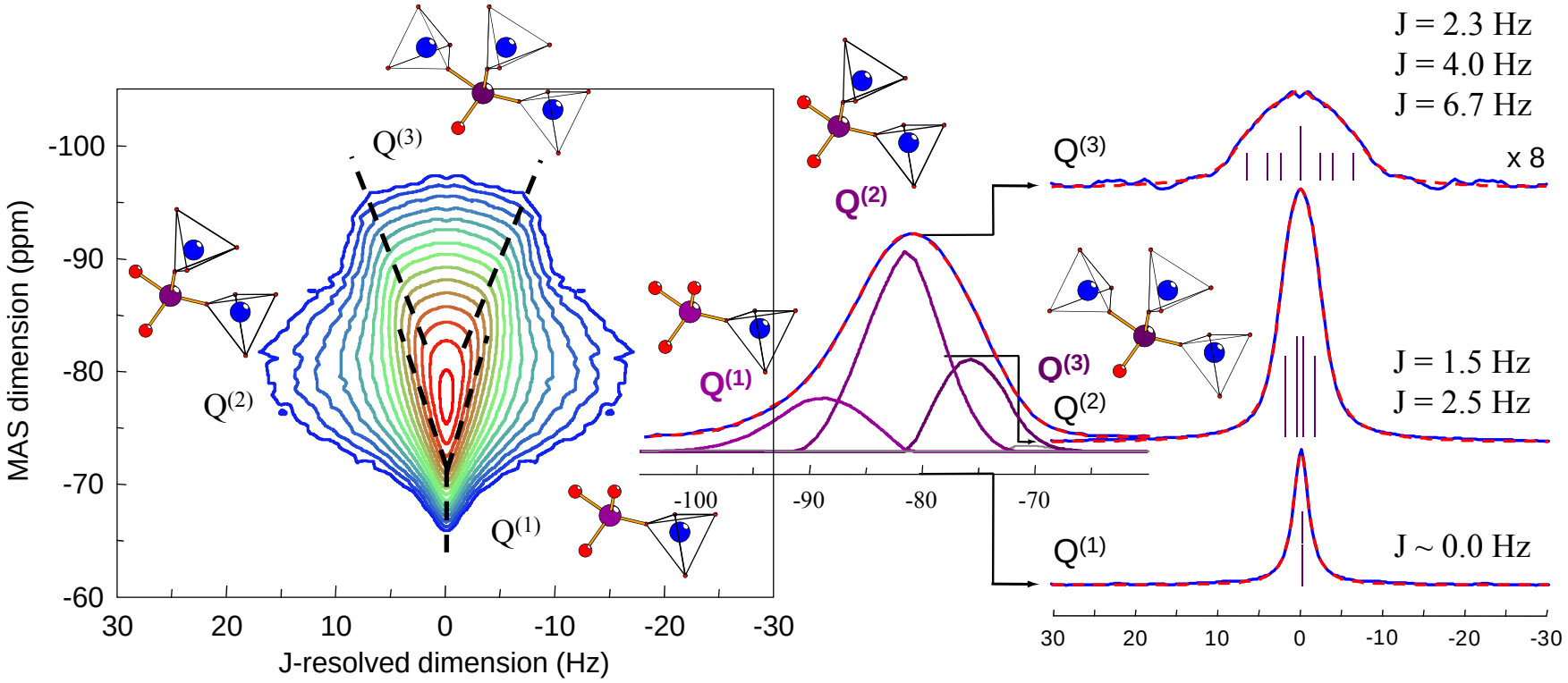




Anorthite Glass
$Si_2Al_2O_8Ca$

J.Hiet, M.Deschamps, N.Pellerin, F.Fayon, D.Massiot
"*Probing chemical disorder in glasses using silicon-29 NMR spectral editing*" *Phys. Chem. Chem. Phys* ***accepted***

J-resolved experiment in $Ca^{29}SiO_3$ glass



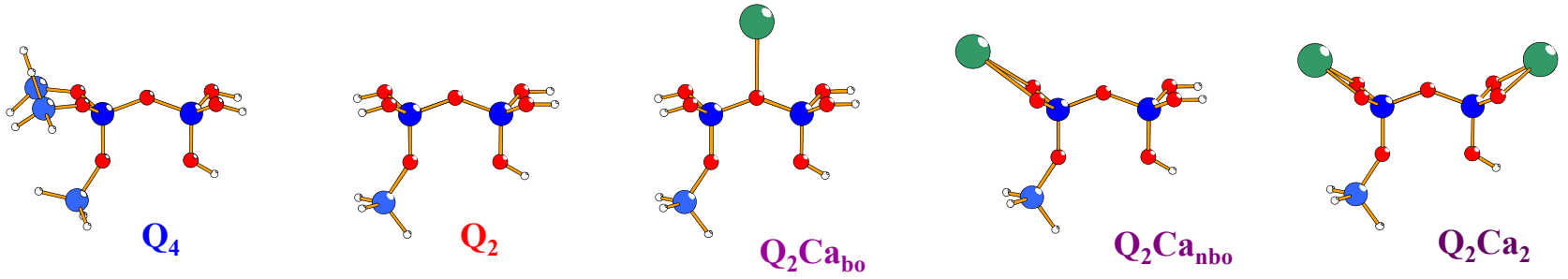
Uncertainty < ± 0.5 Hz

- Discontinuities not resolved but ^2J(Si,Si) measurable

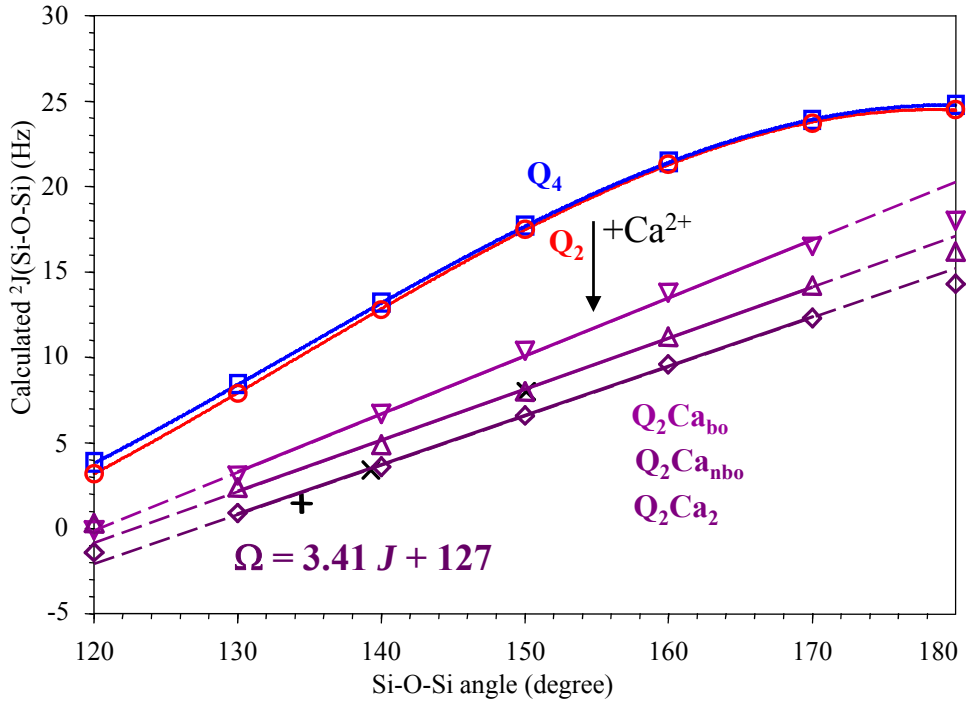
Experimental decomposition of glass spectra with MAF:
Zhang *et al.*, J. Phys. Chem. B 1997, 101, 4004-4008

P.Florian, F.Fayon, D.Massiot
"2J Si-O-Si scalar spin-spin coupling in the solid-state: the case of crystalline and glassy wollastonite CaSiO3" ***J. Phys. Chem. C*** **113** 2562-2572 **2009**

G03W *ab-initio* calculations of ^{2}J(Si-O-Si)



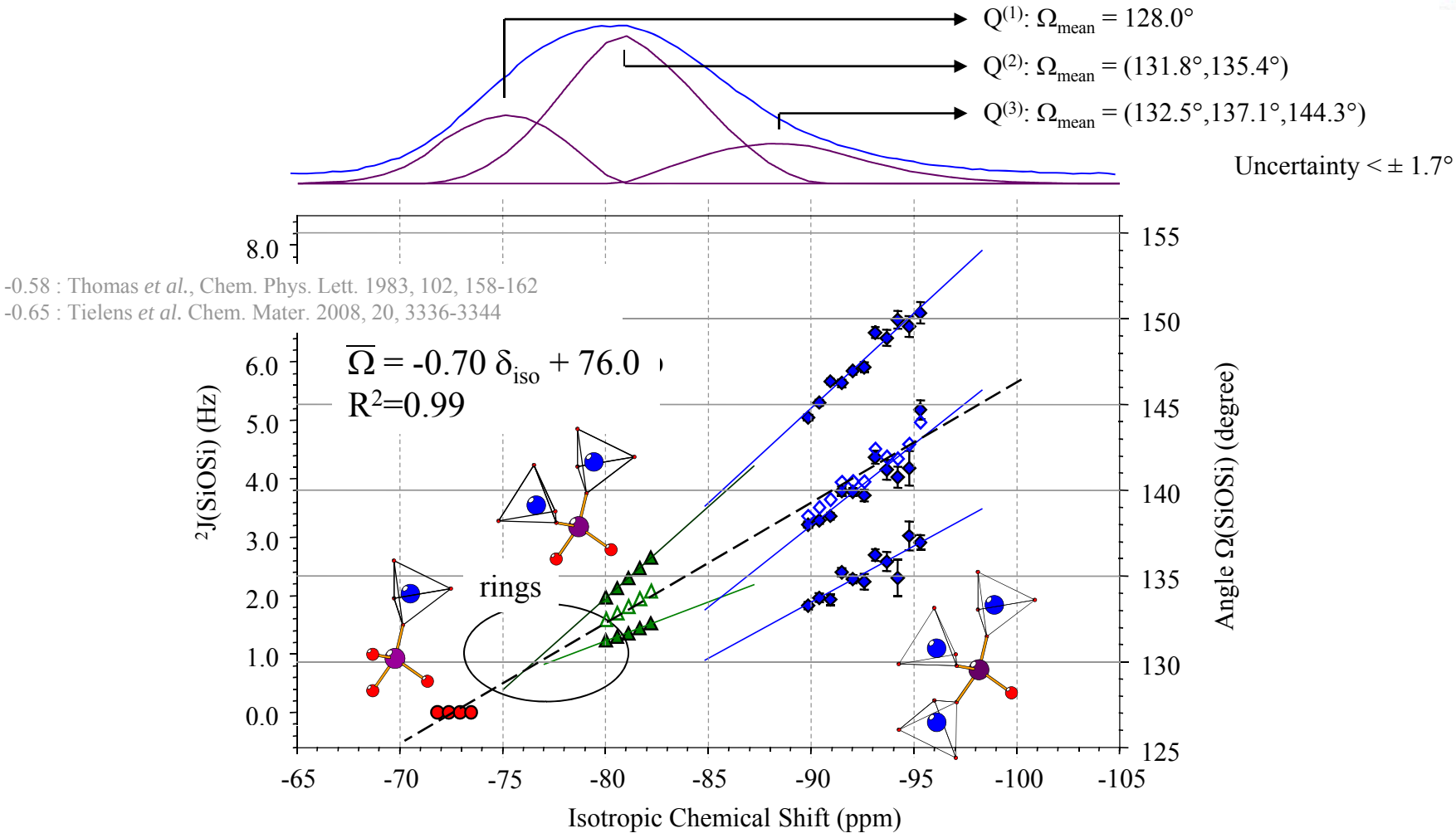
Opt: RHF/6-31G
NMR: B3LYP/pc-J2
(Ca: 3-21G)



- ^{2}J(Si,Si) is a function of <SiOSi

P.Florian, F.Fayon, D.Massiot
"2J Si-O-Si scalar spin-spin coupling in the solid-state: the case of crystalline and glassy wollastonite CaSiO3" ***J. Phys. Chem. C*** **113** 2562-2572 **2009**

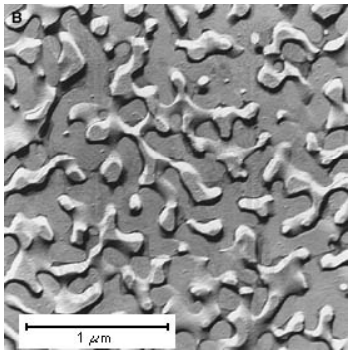
Evolution of $^2J_{SiOSi}$ as a function of δ_{iso}

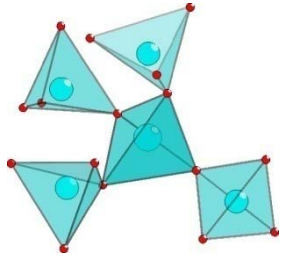


- Angles within a $Q^{(n)}$ unit are strongly correlated !

P.Florian, F.Fayon, D.Massiot
"2J Si-O-Si scalar spin-spin coupling in the solid-state: the case of crystalline and glassy wollastonite CaSiO3" ***J. Phys. Chem. C*** **113** 2562-2572 **2009**

Structure vitreuse à l'échelle subnanométrique : désordre géométrique ou chimique.





- Changements de coordinence
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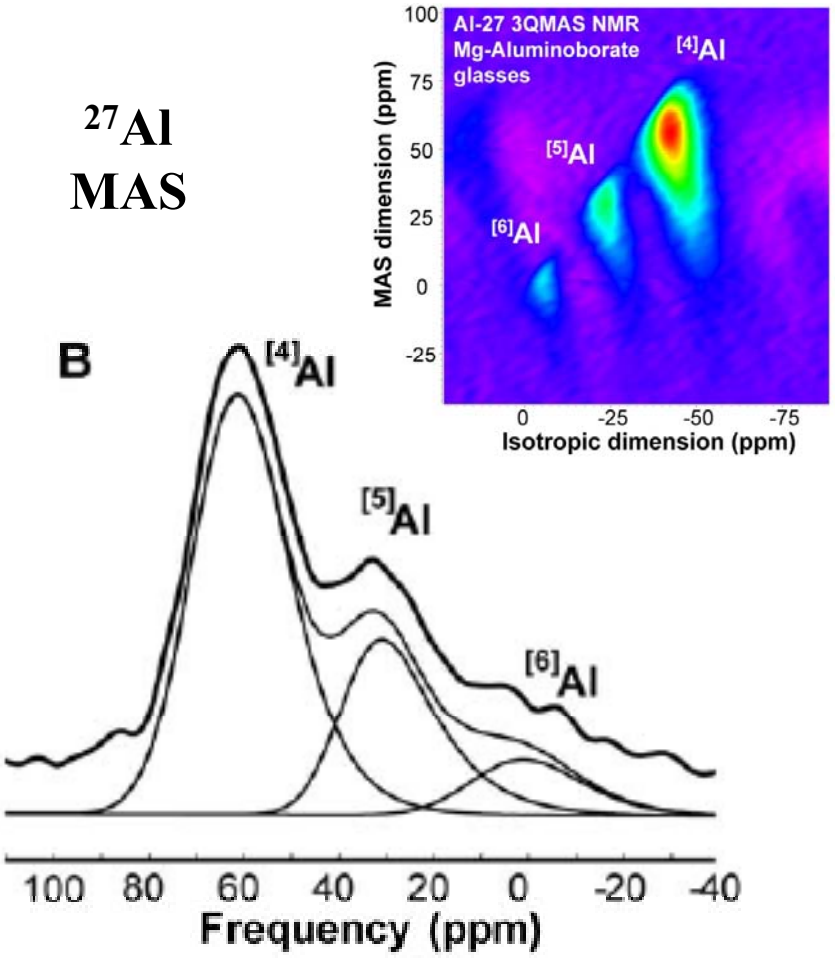
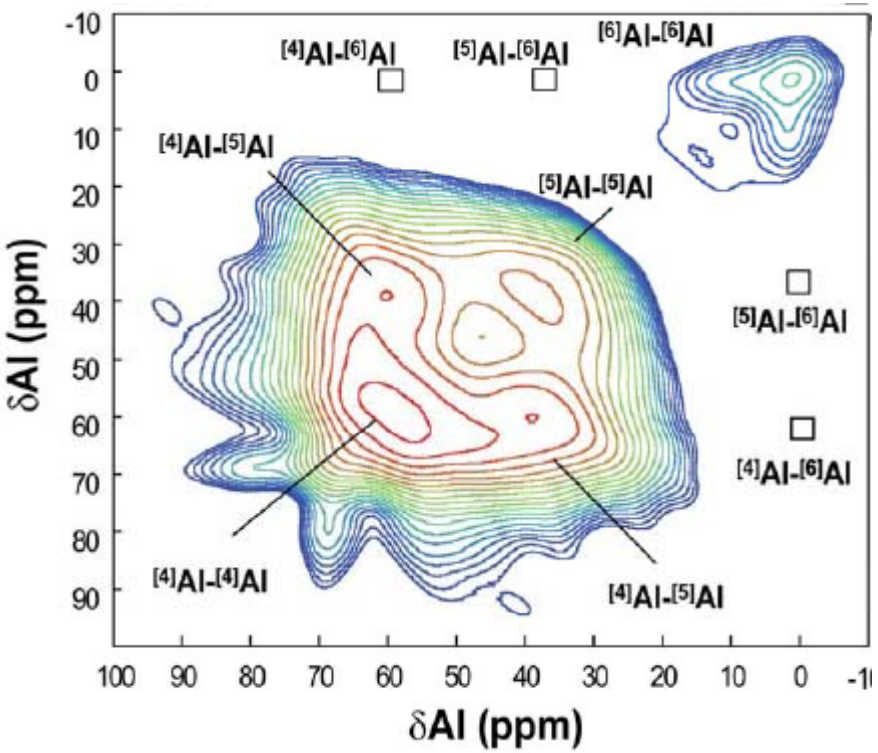
- Désordre Chimique / Géométrique
  - ✓ Phosphates
  - ✓ Chalcogénures PSe
- Vers l'échelle sub-nanométrique
  - ✓ Anorthite $2SiO2\text{-}Al_2O_3\text{-}CaO$
  - ✓ Silicate de Ca $Ca^{29}SiO_3$
- **Perspectives**

Clusters AlO_6

^{27}Al MAS



Paires de ^{27}Al



750MHz

Verre d'aluminoborate de magnesium

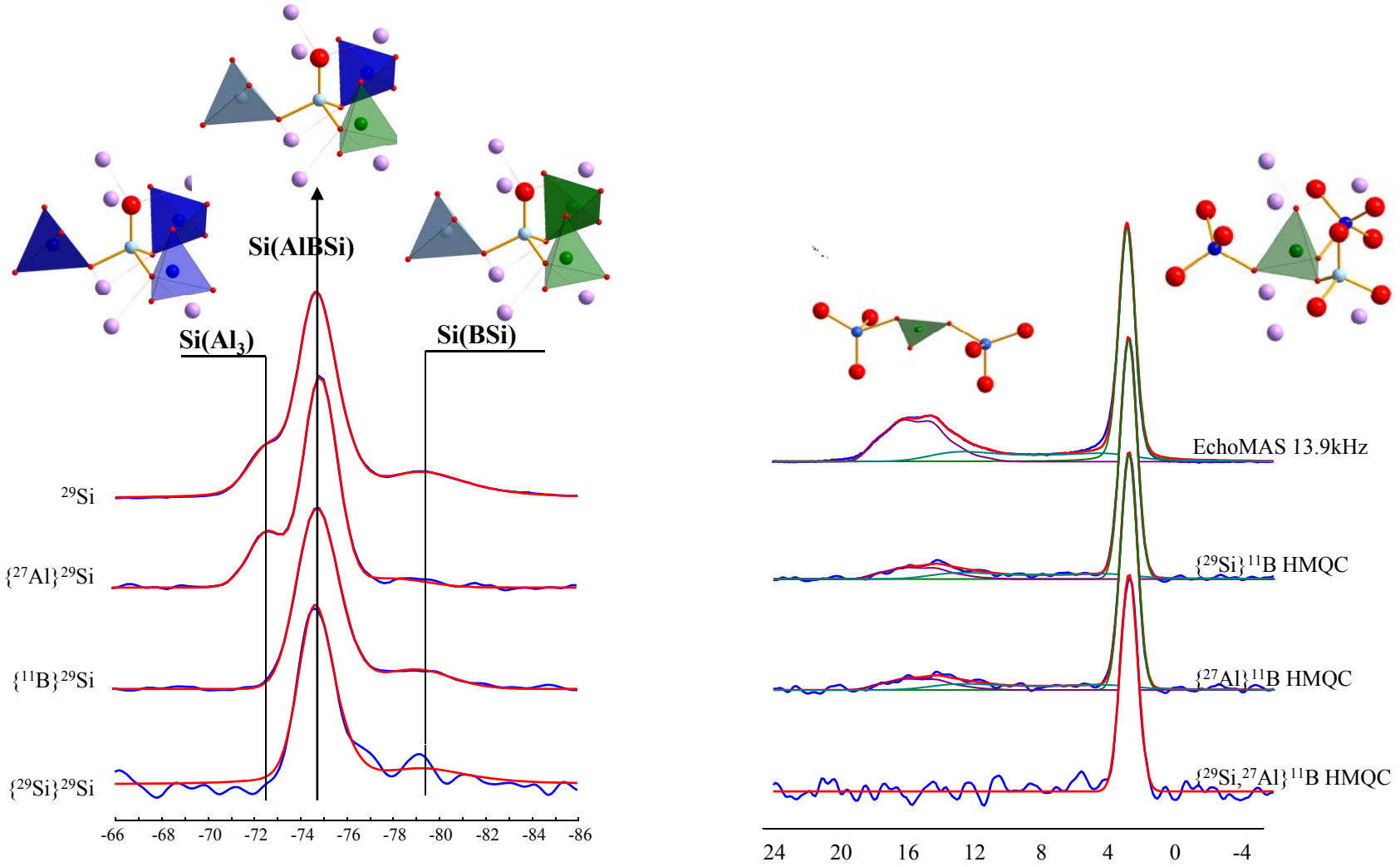
$2\ MgO / Al_2O_3 / 2\ B_2O_3$

S.K.Lee, M.Deschamps, J.Hiet, D.Massiot, S.Y.Park

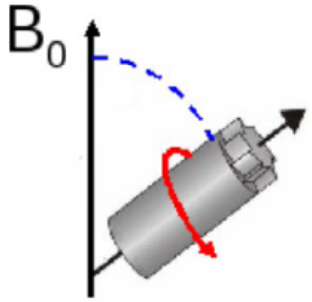
"*Connectivity and proximity between quadrupolar nuclides in oxide glasses: Insights from through-bond and through-space correlations in solid-state NMR*"

J. Phys. Chem. B 113 5162-5167 ***2009***

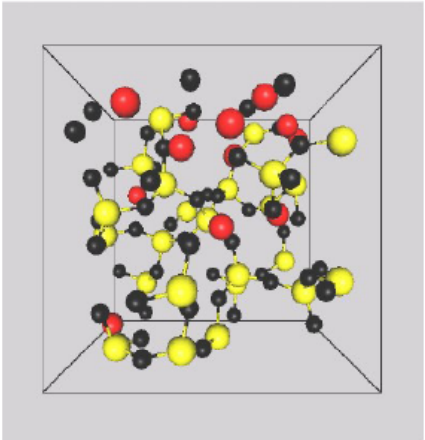
Triple Resonance Si/Al/B

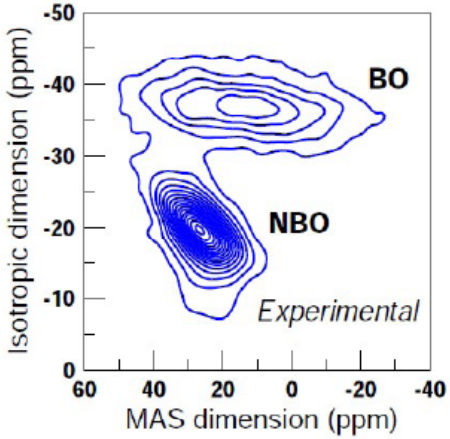


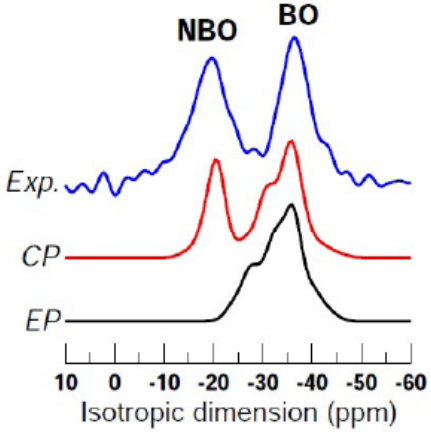
A New Methodology : The First Principles NMR Approach or In Silico NMR

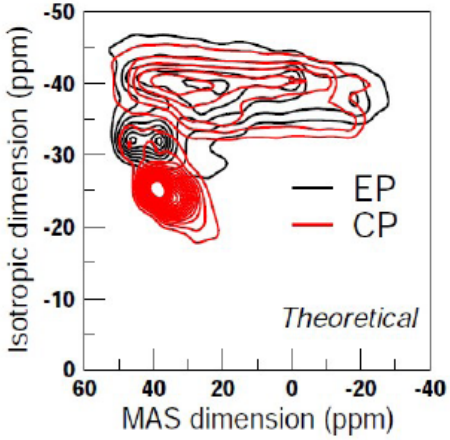


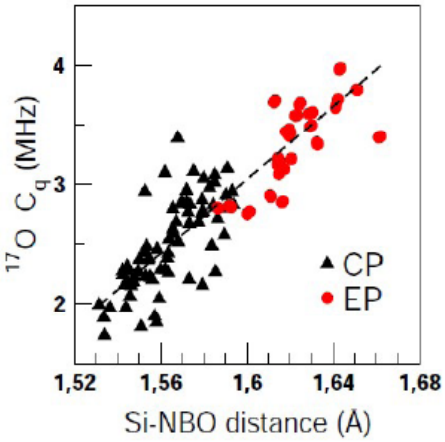
RMN MAS
(magic angle spinning)





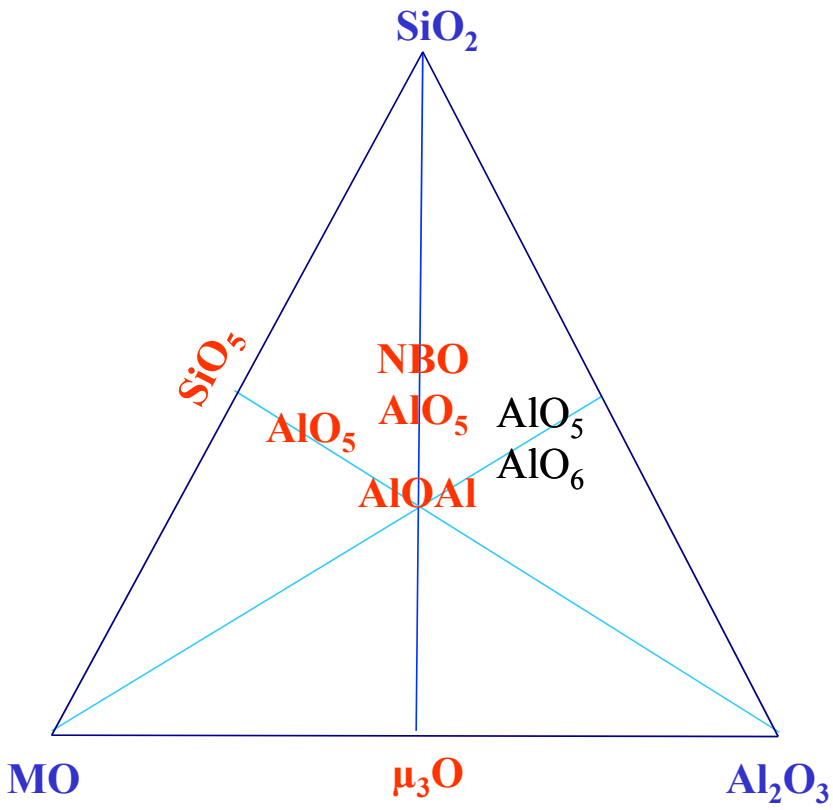






T.Charpentier, P.Kroll, F.Mauri *First-Principles Nuclear Magnetic Resonance Structural Analysis of Vitreous Silica J. Phys. Chem. C* **113** 7917-7929 (2009)
G.Ferlat, T.Charpentier, A.P.Seitsonen, A.Takada, M.Lazzeri, L.Cormier, G.Calas, F.Mauri "*Boroxol Rings in Liquid and Vitreous B2O3 from First Principles*" *PRL* 101 065504 ***2008***

Sorting the different nature of disorder



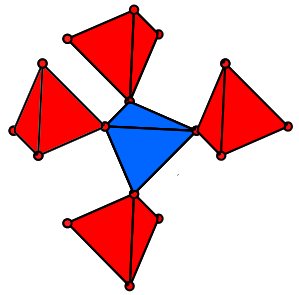
Molecular Motifs

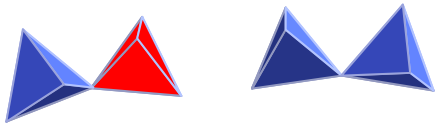
$^{27}Al(-O-Si_?)$

$^{29}Si(-O-Si_?)$

$^{27}Al(-O-Al_?)$

$^{27}Al(-O-B_?)\ (-O-Si_?)$





Coordination

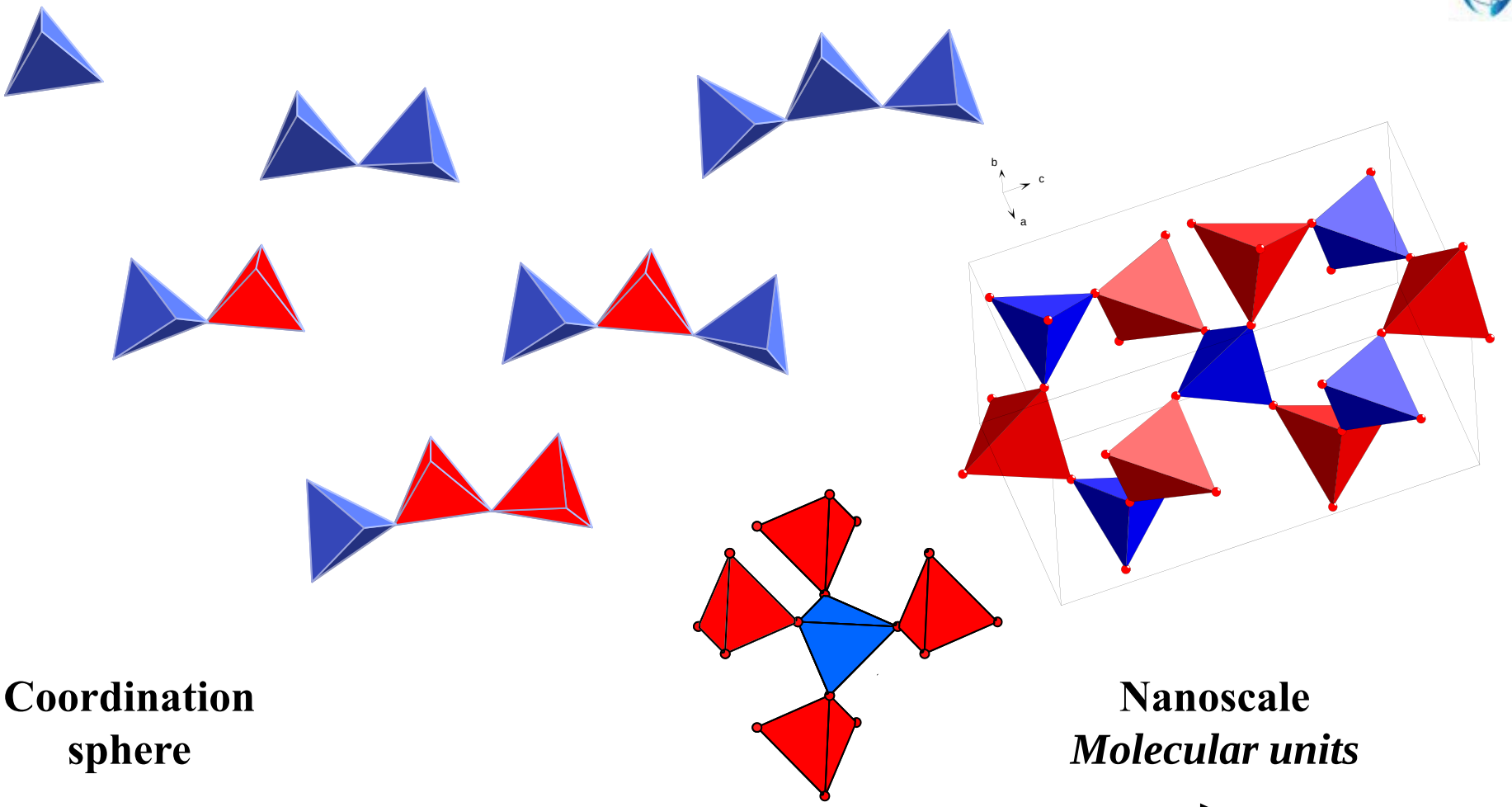
$^{27}AlO_4\ AlO_5\ AlO_6$

$^{29}Si\ Q_n$

^{17}O μ2 Si-O-Si Si-O-Al Al-O-Al

μ3

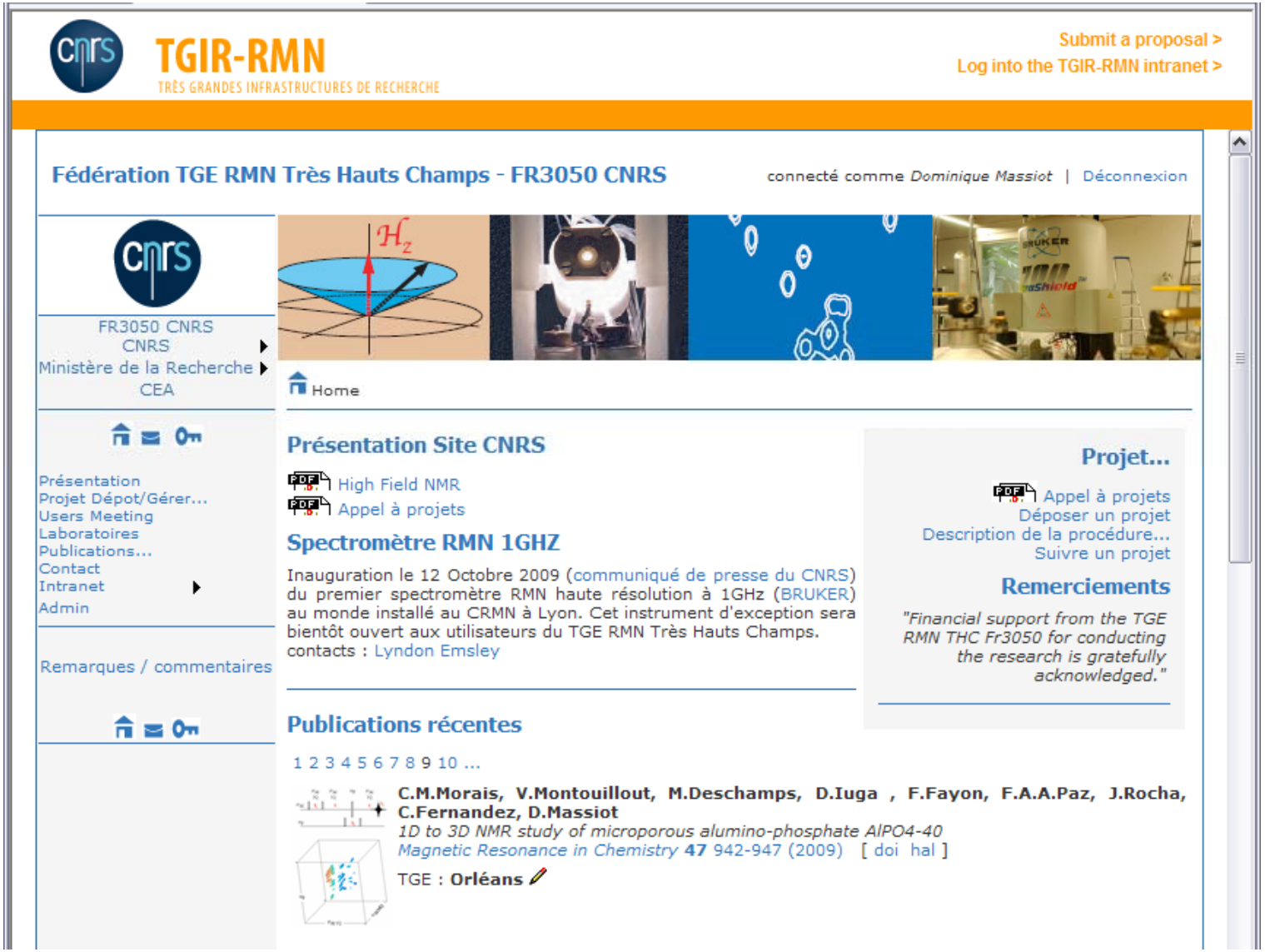
NBO



Coordination sphere

Nanoscale *Molecular units*

Increasing size of molecular units



http://www.tgir-rmn.org/ ou google "tgir-rmn"

RMN Solide à Hauts Champs : Orléans et Lille

Remerciements

CRMHT – Orléans
Julien Hiet
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Université de Lille
Jean Paul Amoureux
Julien Trebosc

LCMC Paris
Clément Sanchez
Florence Babonneau
Christian Bonhomme
Christel Gervais
Thierry Azaïs
Laurence Rozes…

IPG LMCP
Daniel Neuville
Laurent Cormier

Seoul Corée
Seung Kun Lee

NHMFL USA
Zhehong Gan
Tim Cross

ENS – Lyon
Lyndon Emsley
Anne Lesage

Southampton – UK
Malcom Levitt

Warwick – UK
Steven Brown

Durham – UK
Ian J. King
Robin K. Harris
John S.O. Evans

Accès RMN à Haut Champ (750 MHz)
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Dominique Massiot massiot@cnrs-orleans.fr
CEMHTI – CNRS UPR 3079, Orléans, France
http://www.cemhti.cnrs-orleans.fr