DE LA RECHERCHE À L'INDUSTRIE

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March 27th-31st 2017,

Cargese (France)

Structural Role of Elements in Glasses from Classical Concept to a Reflexion over Broad Composition Range

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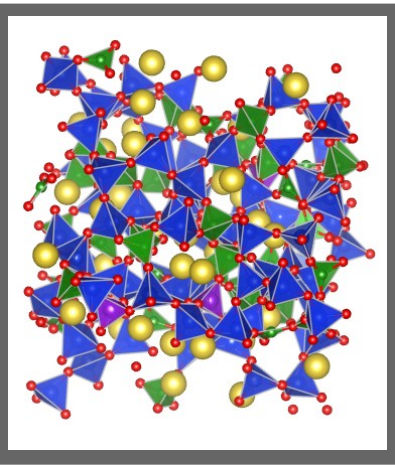
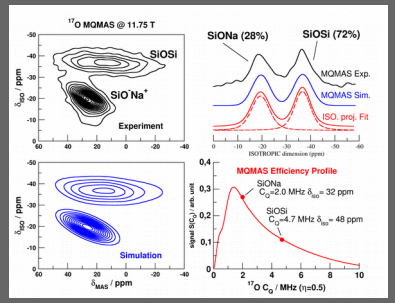
Mixed network formers and modifiers, borosilicate and boroaluminosilicate glasses : a NMR point of view



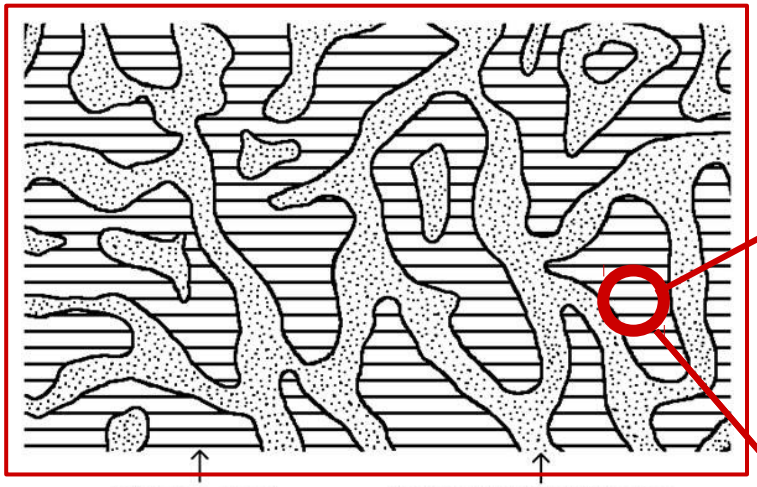


Thibault Charpentier
NIMBE, CEA, CNRS, Université Paris-Saclay, CEA Saclay France

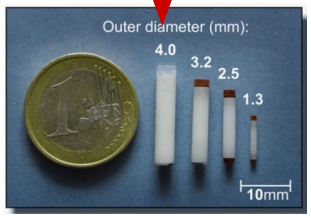
cnrs dépasser les frontières

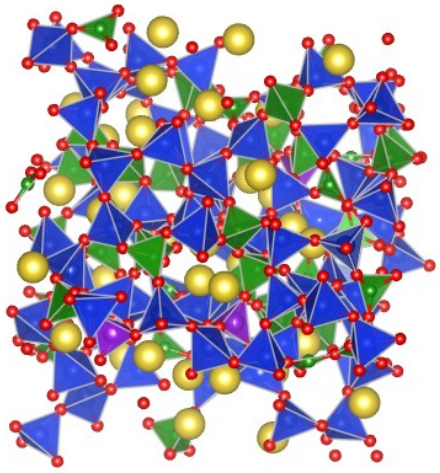
université PARIS-SACLAY

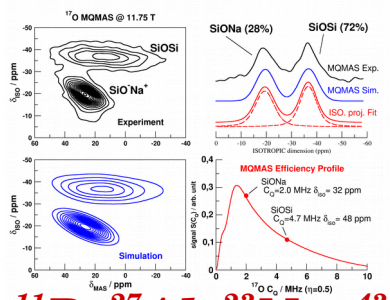
Mixing Network Former / Modifier in glasses
Answers from multinuclear NMR



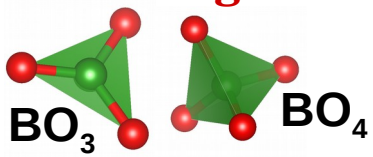
MAS NMR

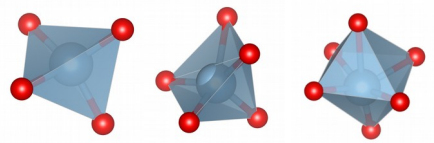




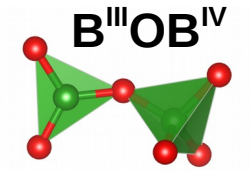


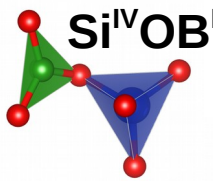
Building units

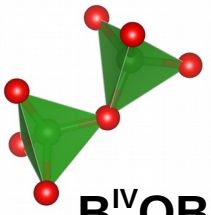




Connectivities -(^{17}O)

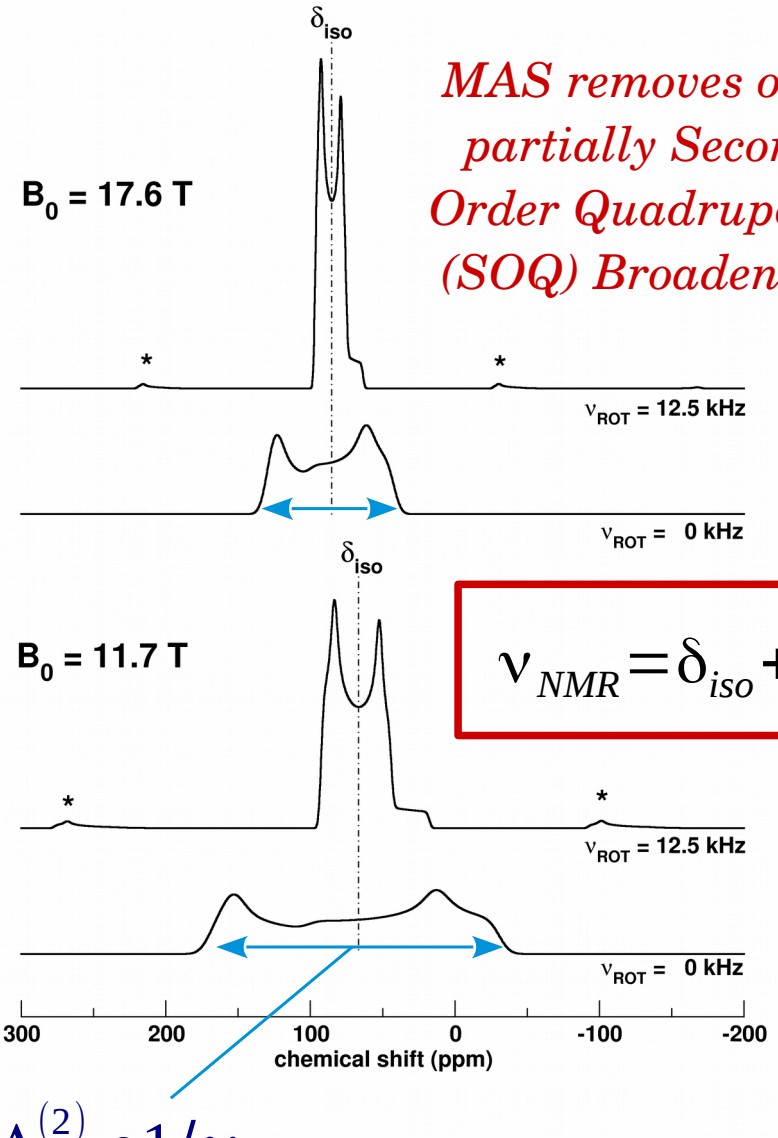






^{29}Si, ^{11}B, ^{27}Al, ^{23}Na, ^{43}Ca, … and ^{17}O

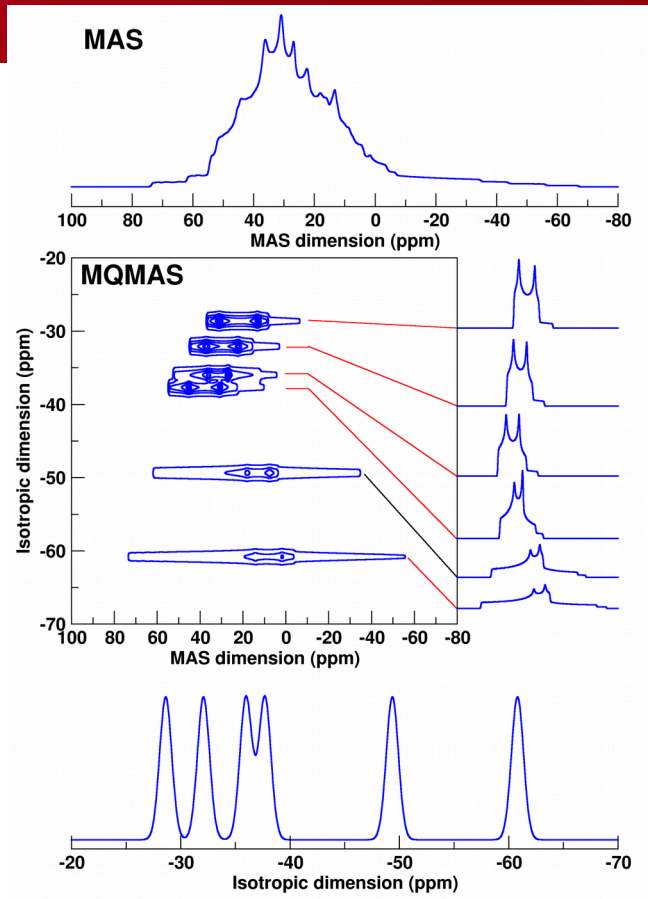
NMR Tools for quadrupolar nuclei (I>1/2)

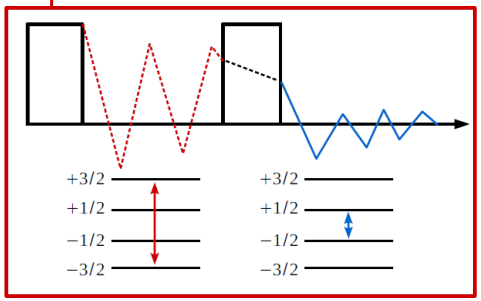


MAS removes only partially Second Order Quadrupolar (SOQ) Broadening

$$\nu_{NMR} = \delta_{iso} + \Delta_Q^{(2)}$$

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



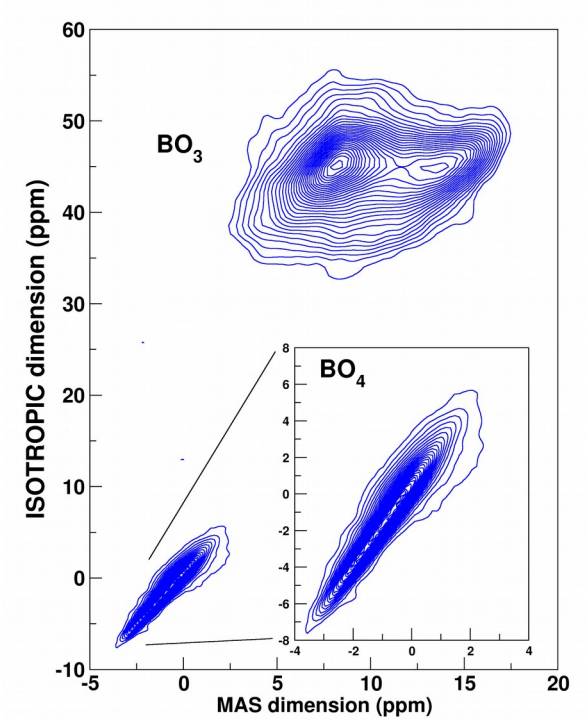


Multiple-Quantum MAS (2D) removes SOQ anisotropy

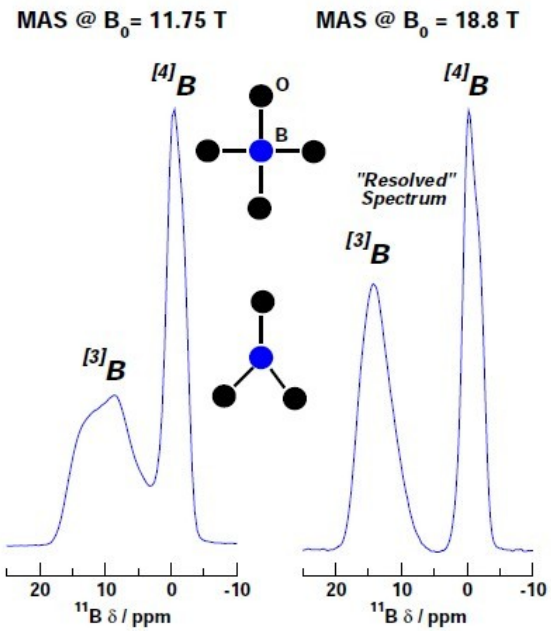
^{11}B MAS NMR in borosilicate glasses

^{11}B MAS NMR in Borosilicate Glasses

Direct access to boron speciation

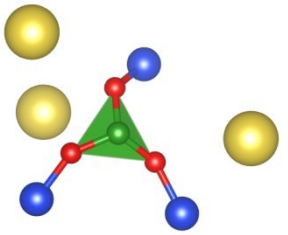


Identifying the structural units forming the glass network

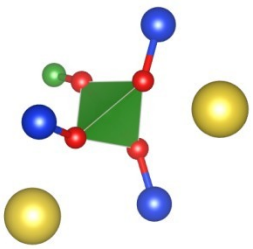


High Field MAS NMR: Boron speciation resolved

Planar BO_3 triangle unit



Tetrahedral BO_4 unit



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

Borosilicate glasses : Dell & Bray model

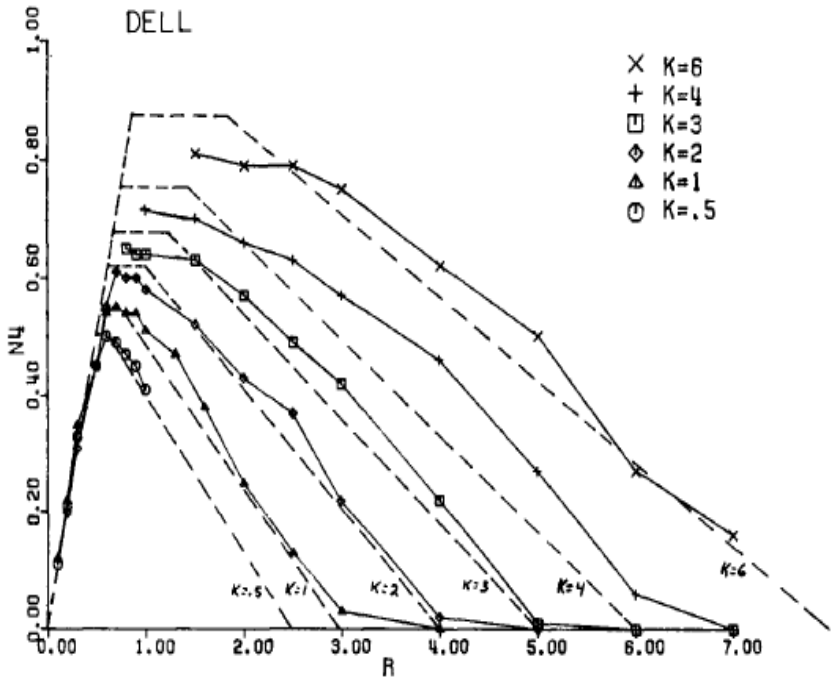


Fig. 9. Composite of N_4 data from ref. 1 and the present work. The dashed lines are predictions based on the model presented in the text. The dashed lines level off to a constant value at $R_{MAX} = \frac{1}{2} + \frac{1}{16}K$, begin to decrease at $R_{D1} = \frac{1}{2} + \frac{1}{4}K$, and drop to zero at $R_{D3} = 2 + K$.

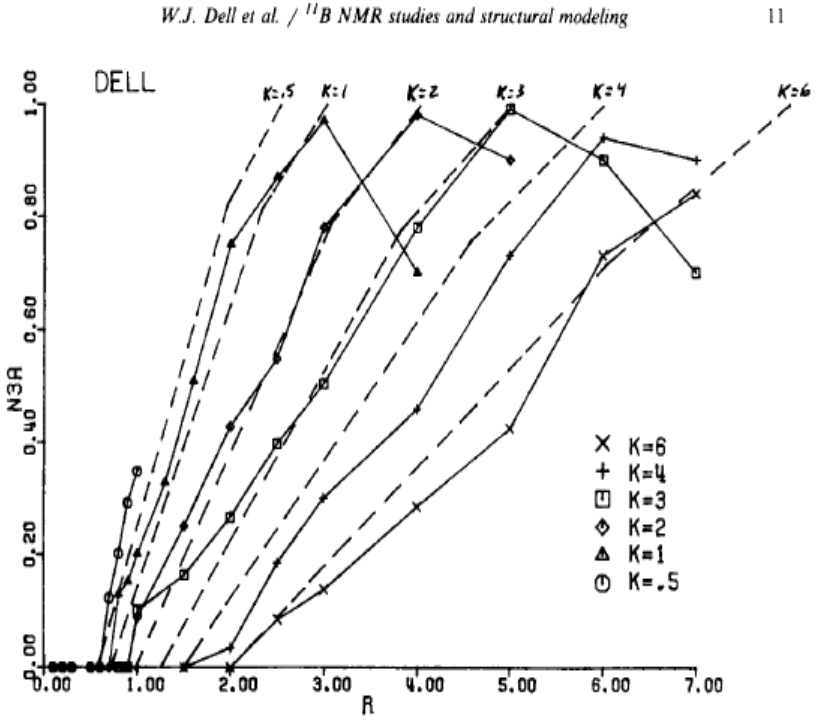


Fig. 10. Composite of N_{3A} data from ref. 1 and the present work. The dashed lines are predictions based on the model presented in the text. The dashed lines begin to rise at $R_{D1} = \frac{1}{2} + \frac{1}{4}K$, exhibit a small change in slope at $R_{D2} = \frac{3}{2} + \frac{3}{4}K$, and reach 1.0 at $R_{D3} = 2 + K$.

Model devised from wideline (CW) NMR for predicting the evolution of the fraction of BO_4 population (thanks to the good contrast between BO_4, BO_{3A}, BO_{3S} units in term of quadrupolar features)

W.J. Dell, P.J. Bray, S.Z. Xiao, Journal of Non-Crystalline Solids 58 (1983) 1-16.
Revision: Manara et al., Journal of Non-Crystalline Solids 355 (2009) 2528–2531

Borosilicate glasses : the Dell & Bray model

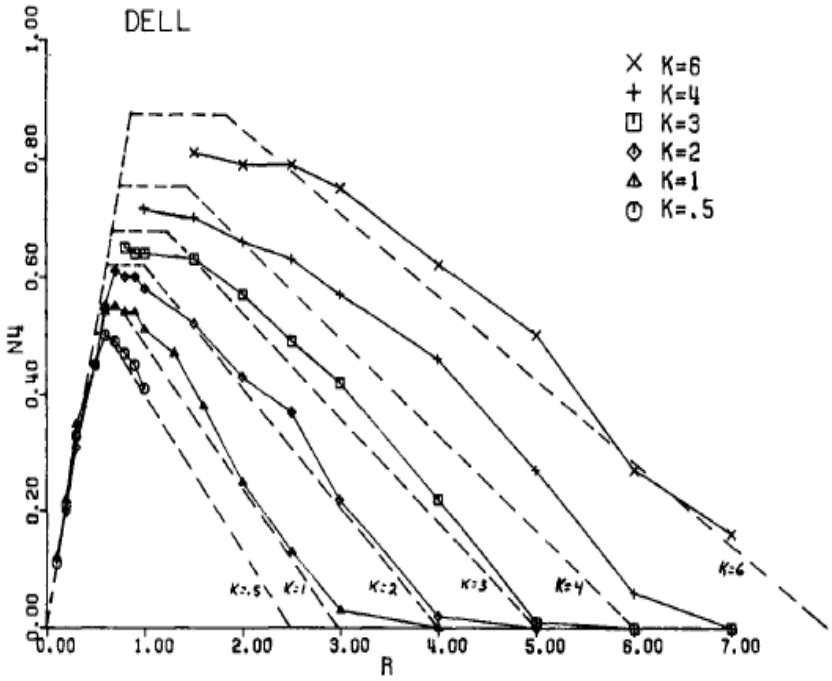


Fig. 9. Composite of N_4 data from ref. 1 and the present work. The dashed lines are predictions based on the model presented in the text. The dashed lines level off to a constant value at $R_{MAX} = \frac{1}{2} + \frac{1}{16}K$, begin to decrease at $R_{D1} = \frac{1}{2} + \frac{1}{4}K$, and drop to zero at $R_{D3} = 2 + K$.

$$R\ Na_2O\ .\ B_2O_3\ .\ K\ SiO_2$$

N_4 = BO_4 fraction

$R < R_{max}$: BO_3 to BO_4 conversion, $N_4 = R$

$R_{max} < R < R_{D1}$: creation of NBO (Si-Q3) and reedmegnerite units BO_4(4Si) (and danburite units BO_4(B,3Si))

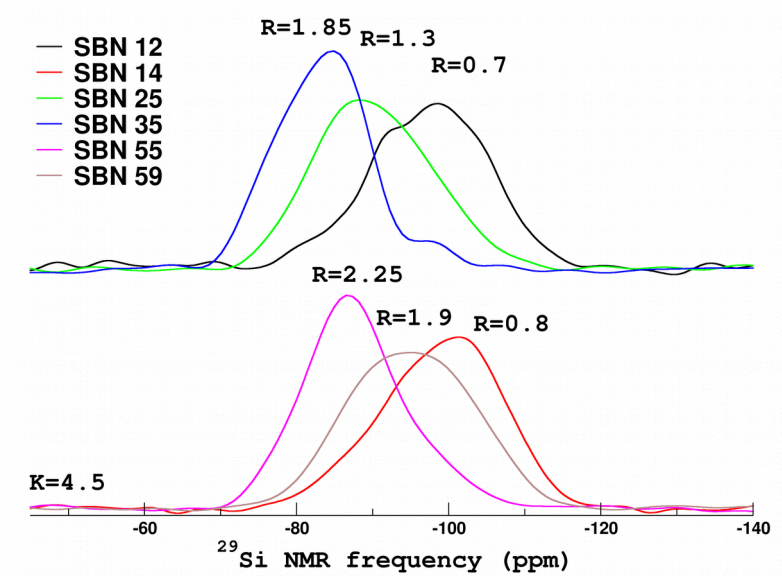
$R > R_{D1}$: creation of B-NBO

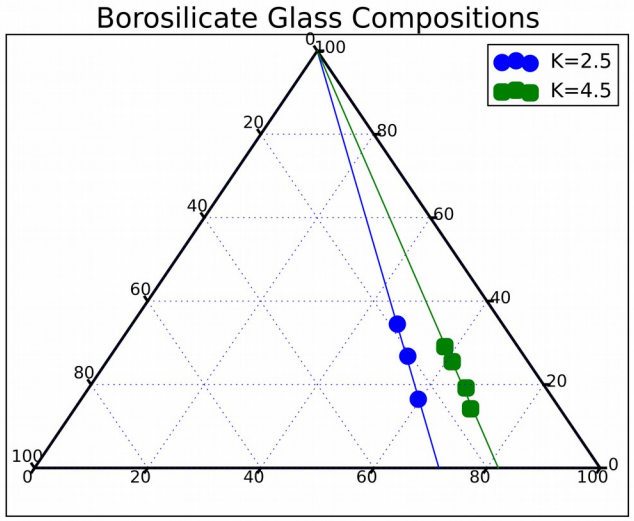
$R_{max} = 1/2 + K/16$

$R_{D1} = 1/2 + K/4$

W.J. Dell, P.J. Bray, S.Z. Xiao, Journal of Non-Crystalline Solids 58 (1983) 1-16.
Revision: Manara et al., Journal of Non-Crystalline Solids 355 (2009) 2528–2531

Multinuclear MAS NMR in ternary borosilicate glasses
^{29}Si MAS NMR

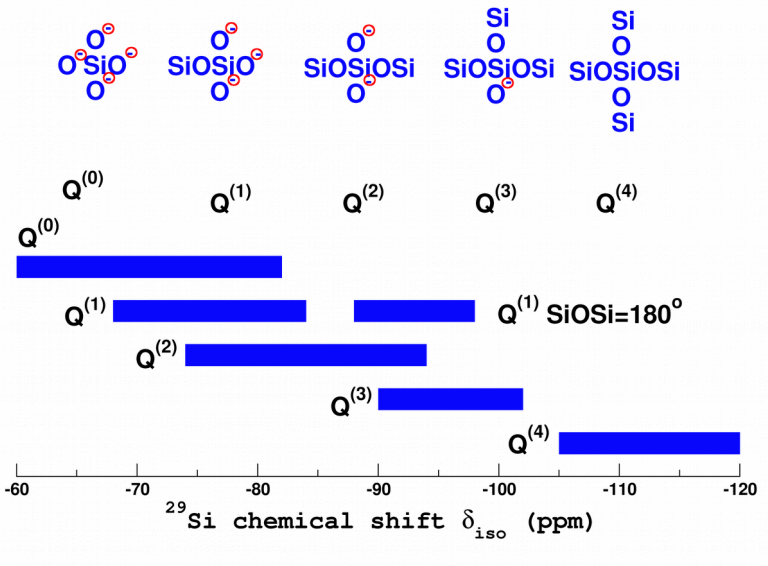




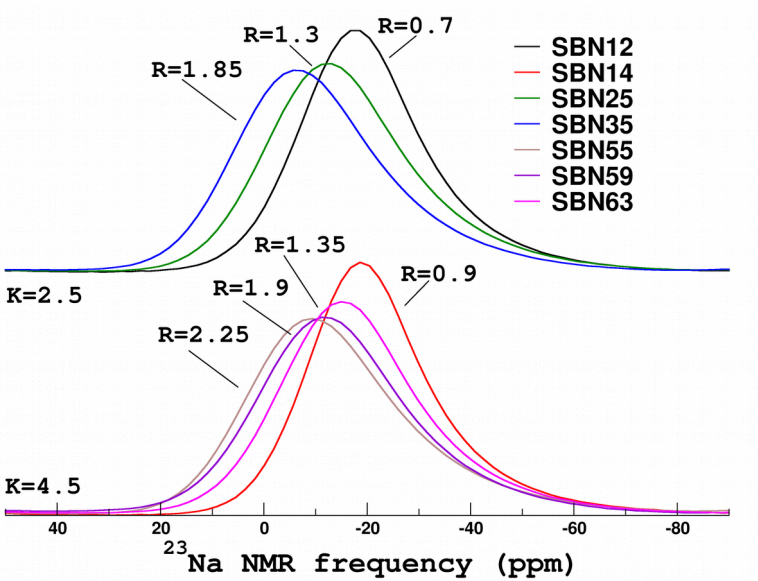
M. Barlet et al., JNCS 2013.

^{29}Si MAS NMR is a good probe of the global polymerizarion degree of the glass network, but :

- *Second neighborhood causes dispersion of the chemical shift range observed in simple silicates (Si-O-B, Si-O-Al,..)*
- *For example $^{[4]}$Si-O-$^{[4]}$B (Q^4) resonance at ~ 90 ppm (Nanba et al. GCA 2004) = $^{[3]}$Si-O-Si (Q^3) (1 NBO)*
- *Effect of B/Si on ^{29}Si chemical shift has not yet been clearly established (see Refs.)*

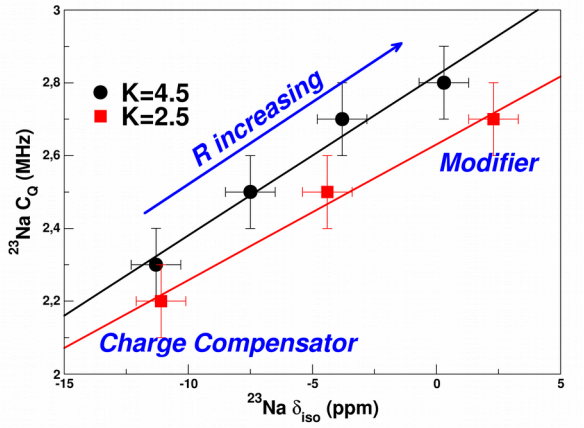


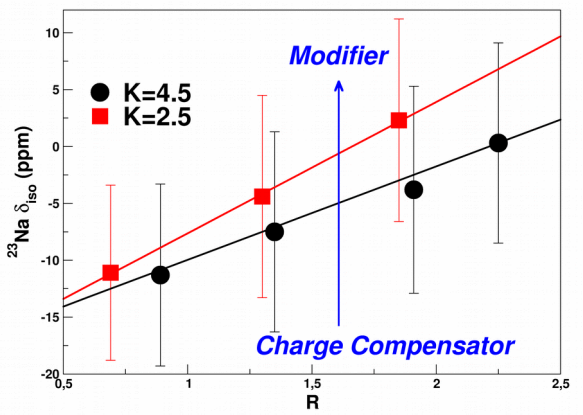
Multinuclear MAS NMR in ternary borosilicate glasses
^{23}Na MAS NMR and structural role

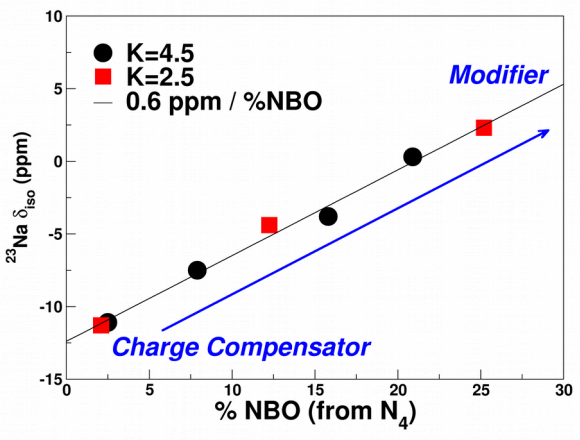


^{23}Na MAS NMR is a good probe of the global role of Na cation : modifier and/or charge compensator :

- *Isotropic chemical shift is primary governed by the average <Na-O> distance (Na-NBO<Na-BO)*
- *First coordination sphere not well defined (CN, distances) : broad distribution of NMR parameters*
- *In glasses, Na atoms are closed to both BO and NBO (see F. Angeli et al., GCA 2011).*
- *Its role between charge compensator and modifier might be not so well defined ...*



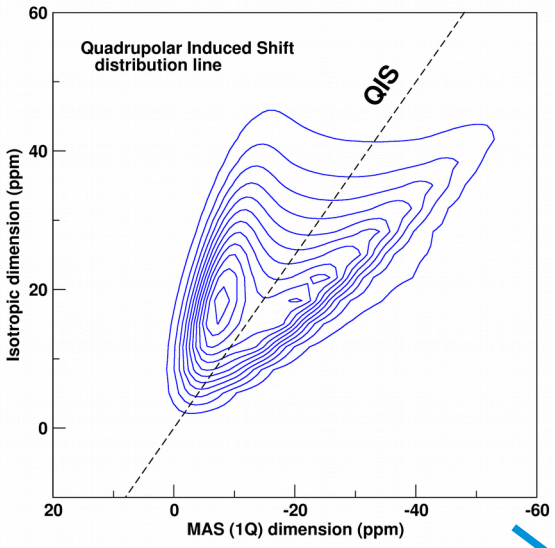


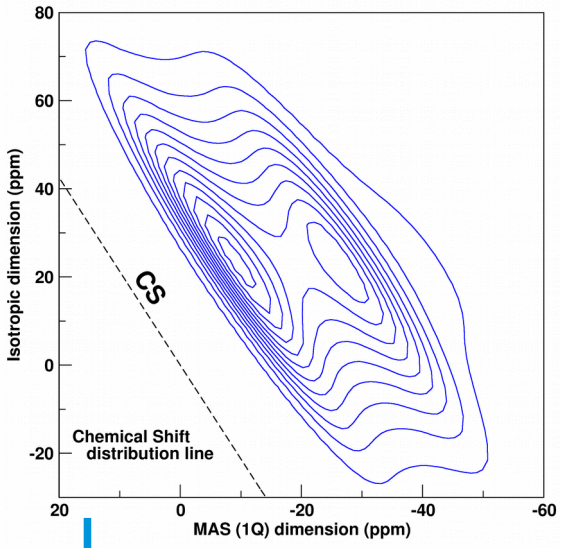


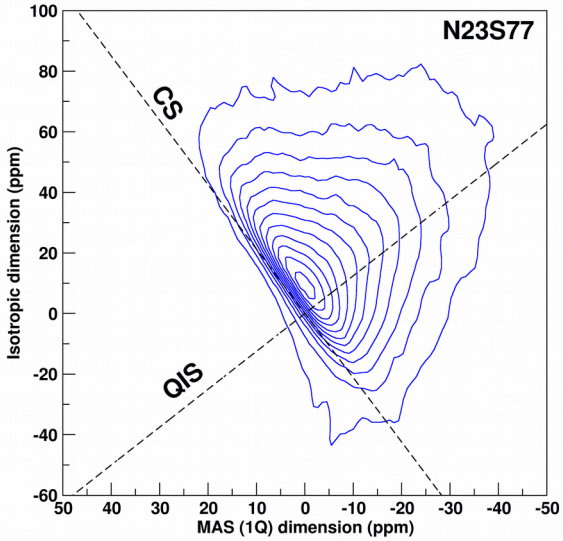
$$NBO = \frac{2 \times (R - N_4)}{(R + 2K + 3)}$$

In preparation.

How does disorder manifests itself in MQMAS ? Example of ^{23}Na MQMAS in glass



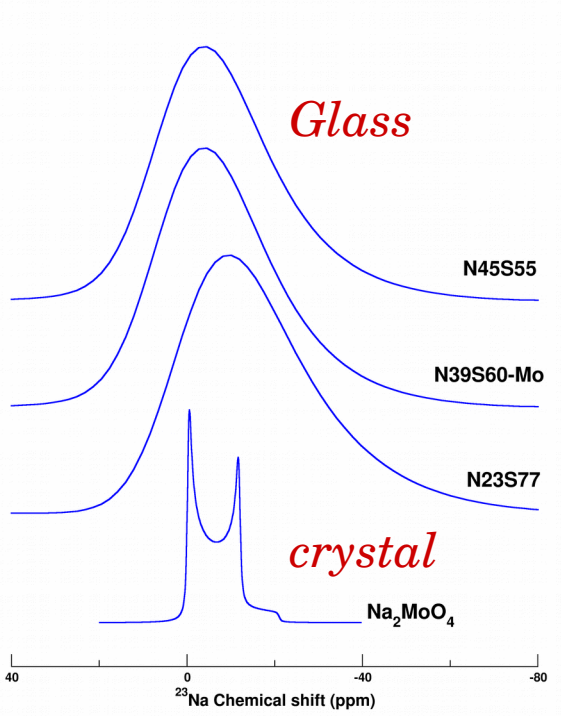




MQMAS enables to separate the broadening induced by the structural disorder :

- *Quadrupolar (QIS)*
- *Isotropic chemical shift (CS)*

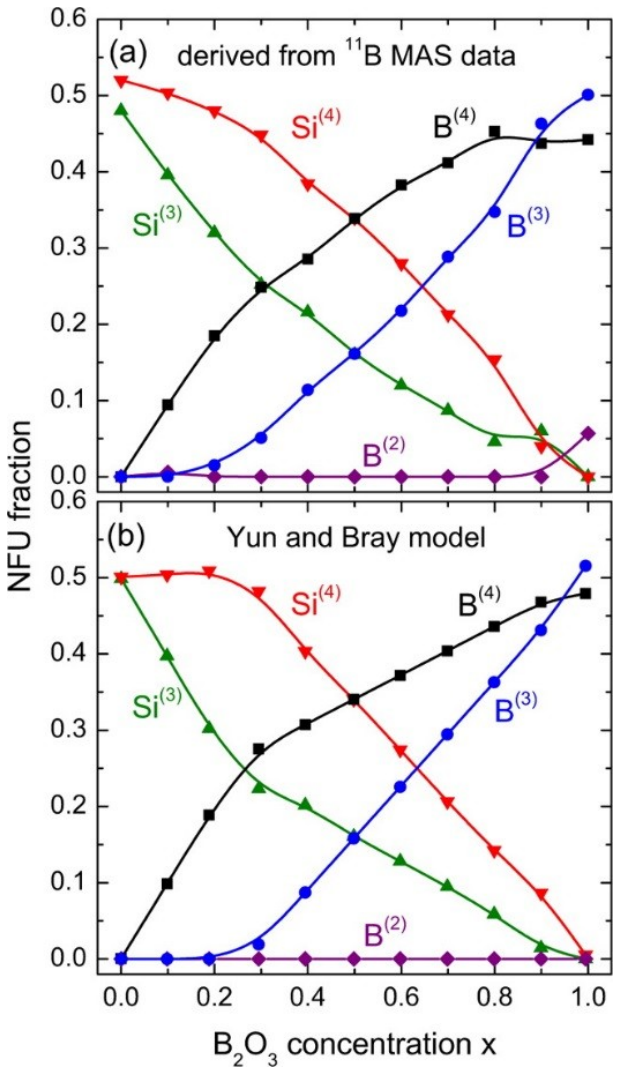
Lineshape in a glass ?



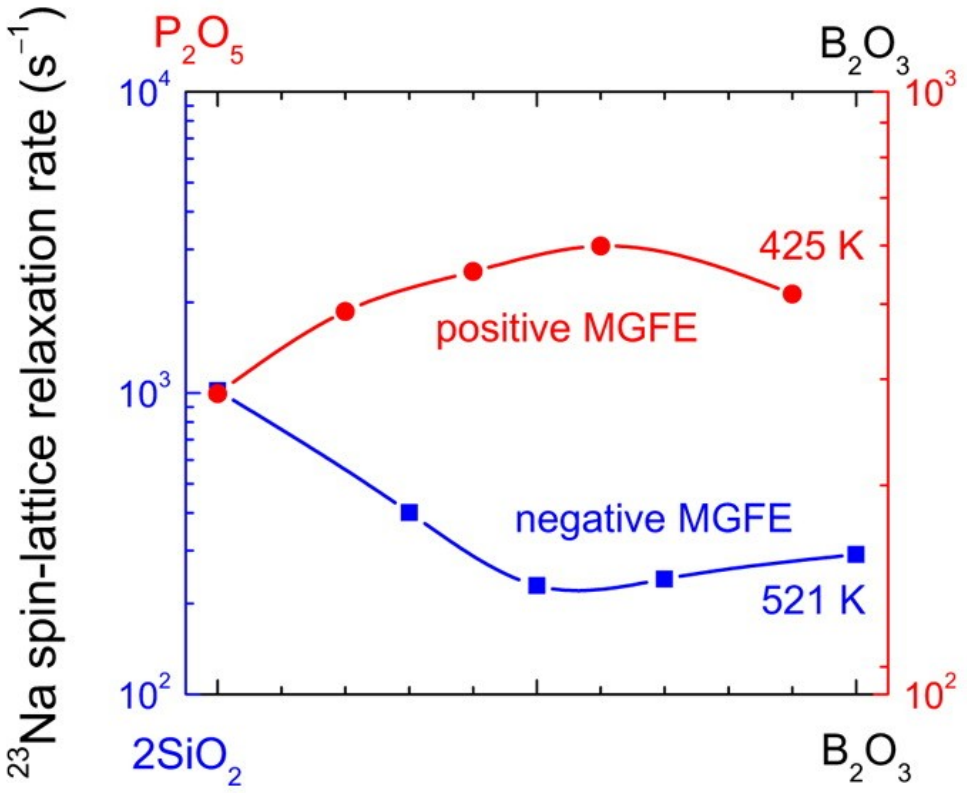
Na : first coordination sphere ill-defined (NaO_x) : broad NMR parameter distribution

Borosilicate glasses : Impact of Si/B (vs P/B) mixing

Network Forming Units



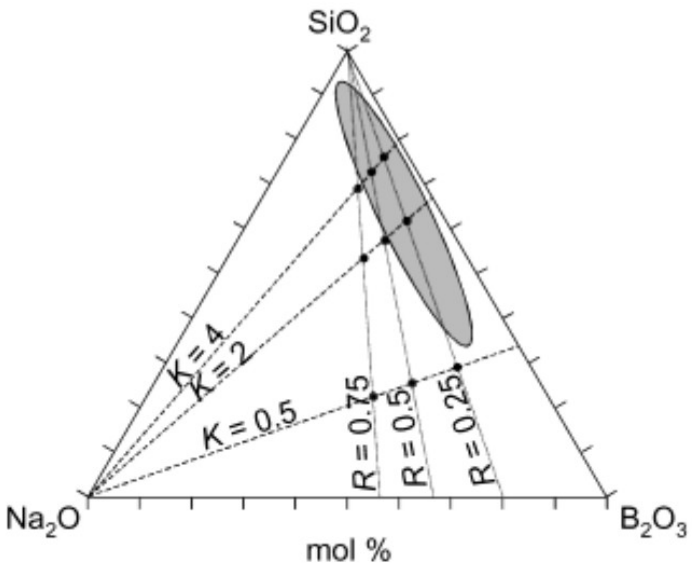
Mixing network former strongly impacts ionic mobility positively or negatively.

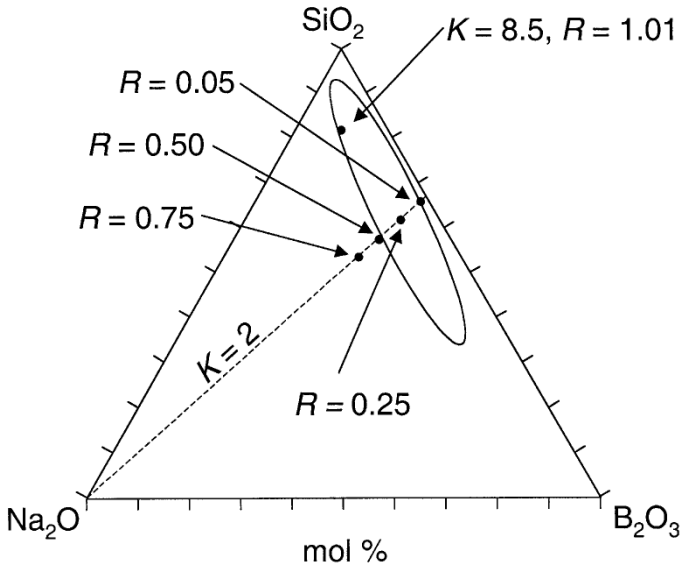


Mixed Glass Former Effect (MGFE)

Positive and Negative Mixed Glass Former Effects in Sodium Borosilicate and Borophosphate Glasses Studied by ^{23}Na NMR, M. Storek et al, J Phys. Chem. B 120, 4482-4495

Silicon-Boron Mixing in ternary borosilicate ^{11}B and ^{17}O MAS NMR at work





To which extent SiO_4 and BO_3 mix in (Li,K,Na)BS glasses ?

Effect of the modifier cation ? Dell&Bray model applicable ? Mixed-alkali effect ?

Influence of the B speciation on its connectivity to Si ?

Table 1. Sample Names and Nominal Compositions

	mole fraction (0.002)				
sample name	Li_2O	Na_2O	K_2O	B_2O_3	SiO_2
LBS	0.200			0.267	0.533
NBS		0.175		0.275	0.550
KBS			0.200	0.267	0.533
LN−BS	0.102	0.086		0.271	0.541
LK−BS	0.100		0.143	0.267	0.533
NK−BS		0.086	0.102	0.271	0.541

Lin-Shu Du and Jonathan F. Stebbins, J. Phys. Chem. B 2003, 107, 10063-10076

Lin-Shu Du and Jonathan F. Stebbins, Journal of Non-Crystalline Solids 315 (2003) 239–255

Lin-Shu Du and Jonathan F. Stebbins, Chem. Mater. 2003, 15, 3913-3921

Silicon-Boron Mixing in ternary borosilicate ^{11}B MAS NMR : evidence of superstructural units

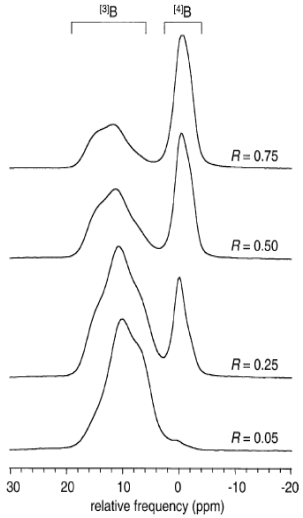


Fig. 2. Boron-11 MAS spectra for NBS-K2 glasses at $R = 0.05$–0.75. Here and in the following figures, the intensity of each spectrum is normalized to that of its highest peak.

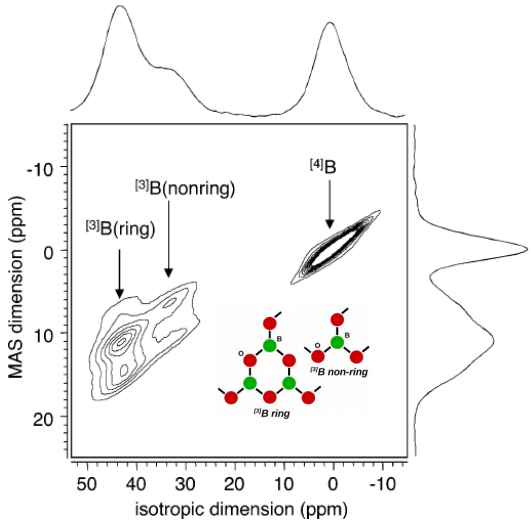


Figure 2. Contour plot of the ^{11}B 3QMAS spectrum for LBS glass. The spectra projected (summed) along both dimensions are also displayed adjacent to the axes.

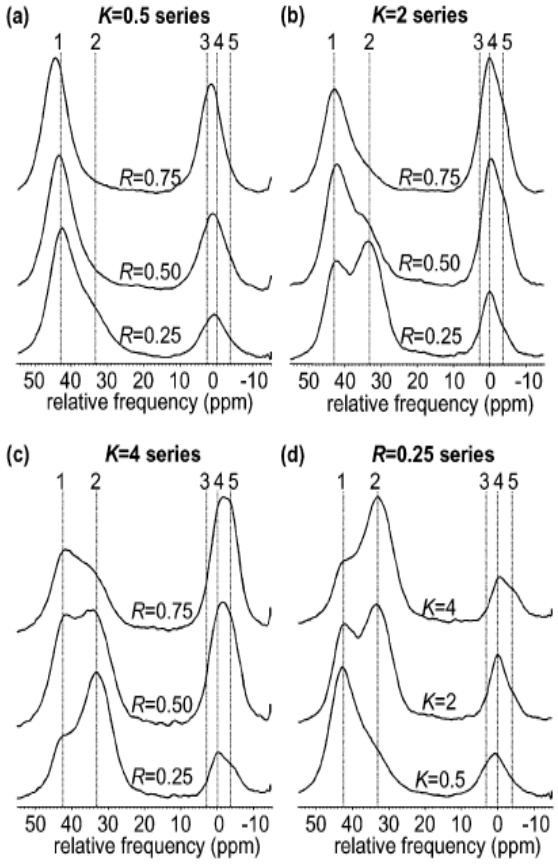


Figure 4. Isotropic projections of ^{11}B 3QMAS spectra for (a) NBS-K0.5, (b) NBS-K2, (c) NBS-K4, and (d) NBS-R0.25 glasses. The dotted lines are guides indicating the approximate positions of the peaks associated with [3]B(ring), [3]B(nonring), [4]B(2B,2Si), [4]B(1B,3Si), and [4]B(0B,4Si), labeled as 1, 2, 3, 4, and 5, respectively. Peak assignments are discussed in the text.

Different BO4 sites are observed (thanks to varying Si/B ratio, K) accroding to Si connectivity.

Peak interpretation still debated...

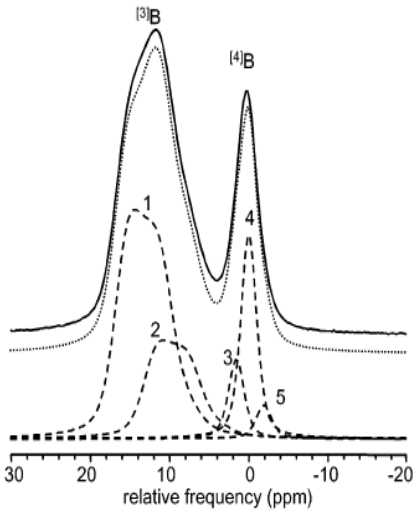
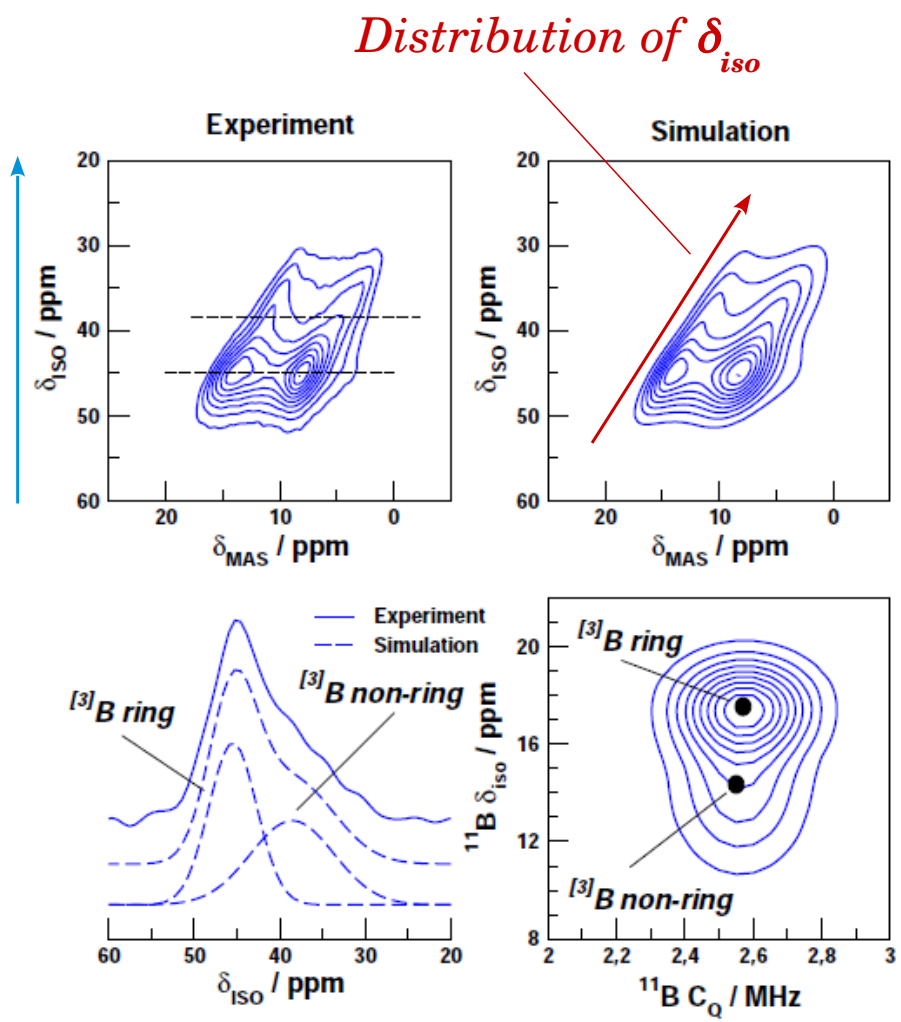


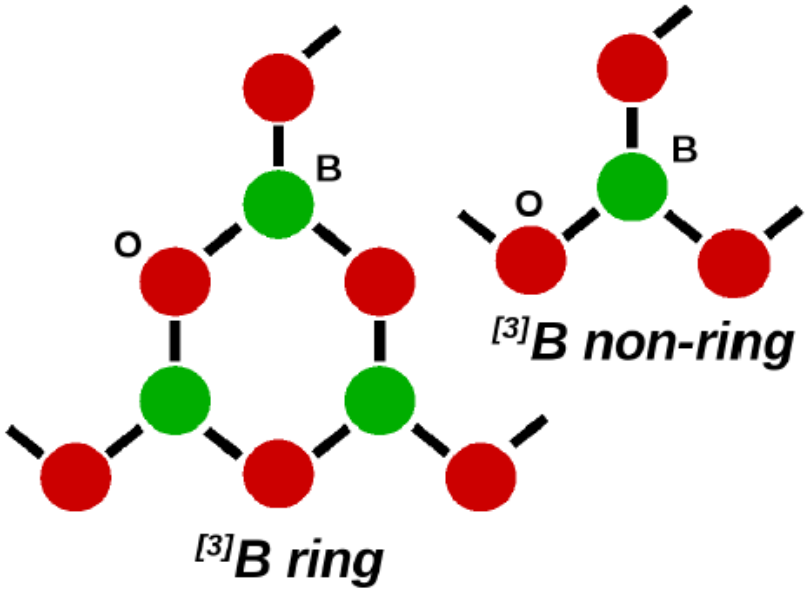
Figure 5. Experimental ^{11}B MAS NMR spectrum (solid line) and fitting results (dotted line, sum; dashed lines, components) for NBS-K0.5R0.25 glass. The peaks for [3]B(ring), [3]B(nonring), [4]B(2B,2Si), [4]B(1B,3Si), and [4]B(0B,4Si) are labeled as 1, 2, 3, 4, and 5, respectively. Fit parameters are given in Table 4.

Silicon-Boron Mixing in ternary borosilicate
^{11}B MQMAS NMR : evidence of superstructural units



^{11}B MQMAS (2D) NMR reveals how MAS lines are affected by disorder

⇒ ***distribution of NMR parameters***



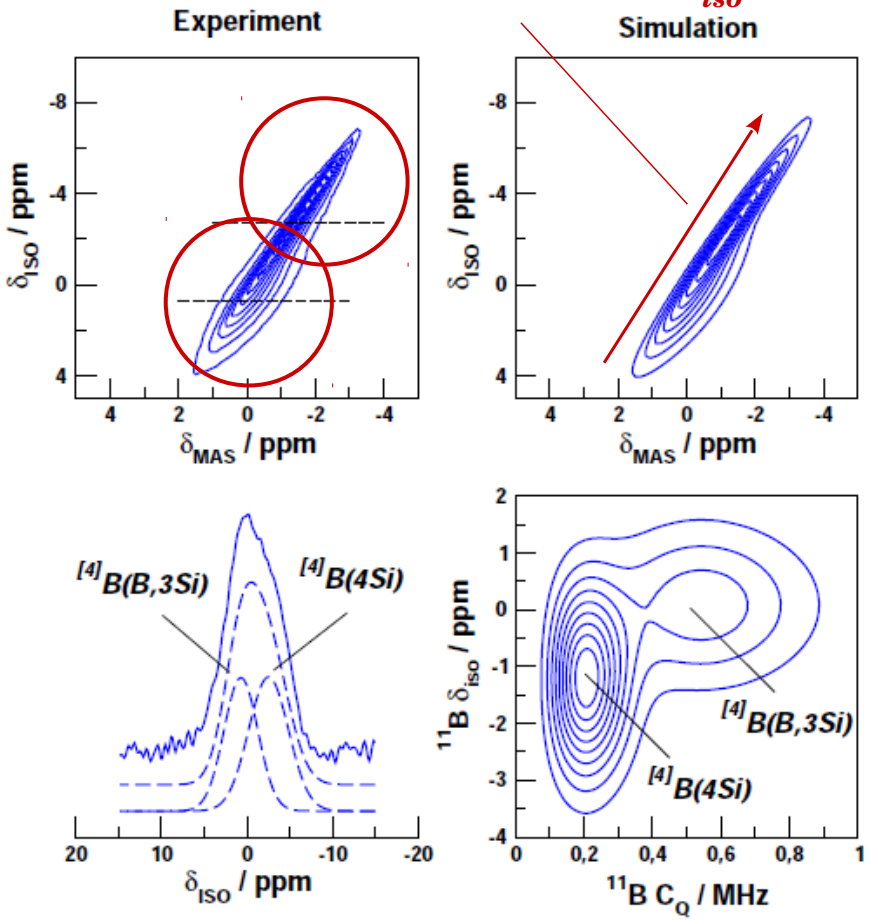
or BO3 in borate unit

^{11}B MQMAS (2D) NMR resolves two main BO3 lines.

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

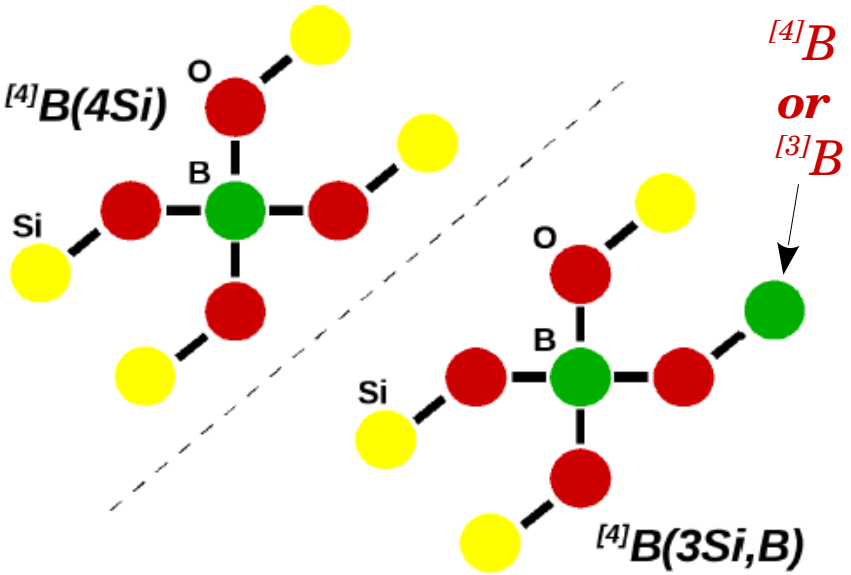
^{11}B MQMAS NMR : high resolution

Distribution of δ_{iso}



^{11}B MQMAS (2D) NMR reveals how MAS lines are affected by disorder

⇒ ***distribution of NMR parameters***



Sensitivy to ^{11}B / ^{29}Si connectivies
Effect of chemical disorder

^{11}B MQMAS (2D) NMR resolves - <u>at least</u> - two main BO4 lines.

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

Silicon-Boron Mixing in ternary borosilicate
^{11}B MAS NMR

MAS

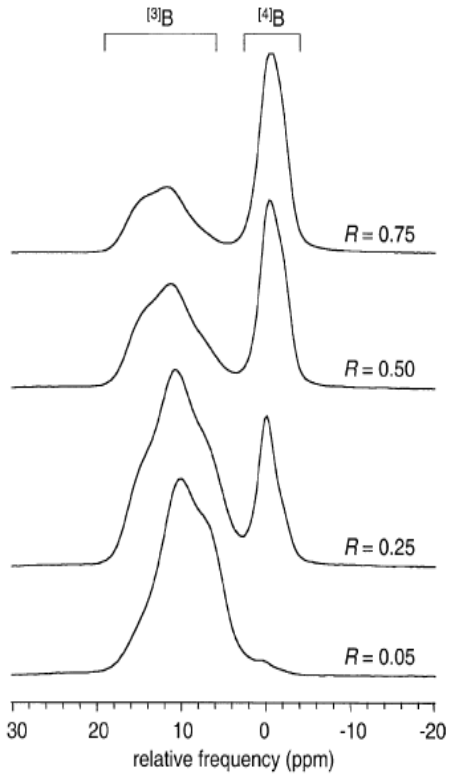


Fig. 2. Boron-11 MAS spectra for NBS-K2 glasses at $R = 0.05$–0.75. Here and in the following figures, the intensity of each spectrum is normalized to that of its highest peak.

MQMAS

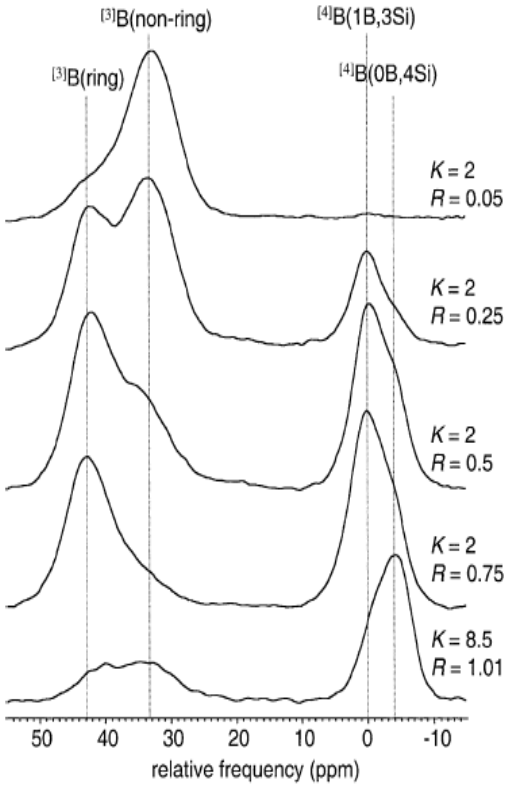


Fig. 4. Isotropic projections of ^{11}B 3QMAS spectra for NBS glasses. Peak assignments are labeled as discussed in text.

Effect of R=Na_2O/B_2O_3

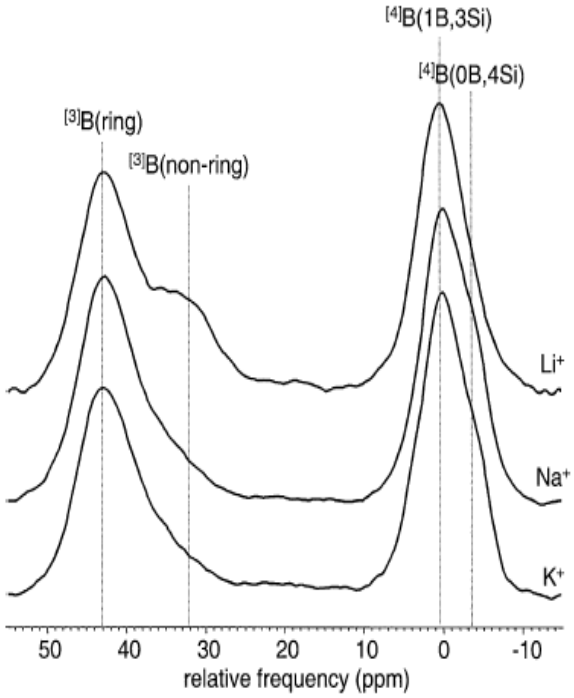
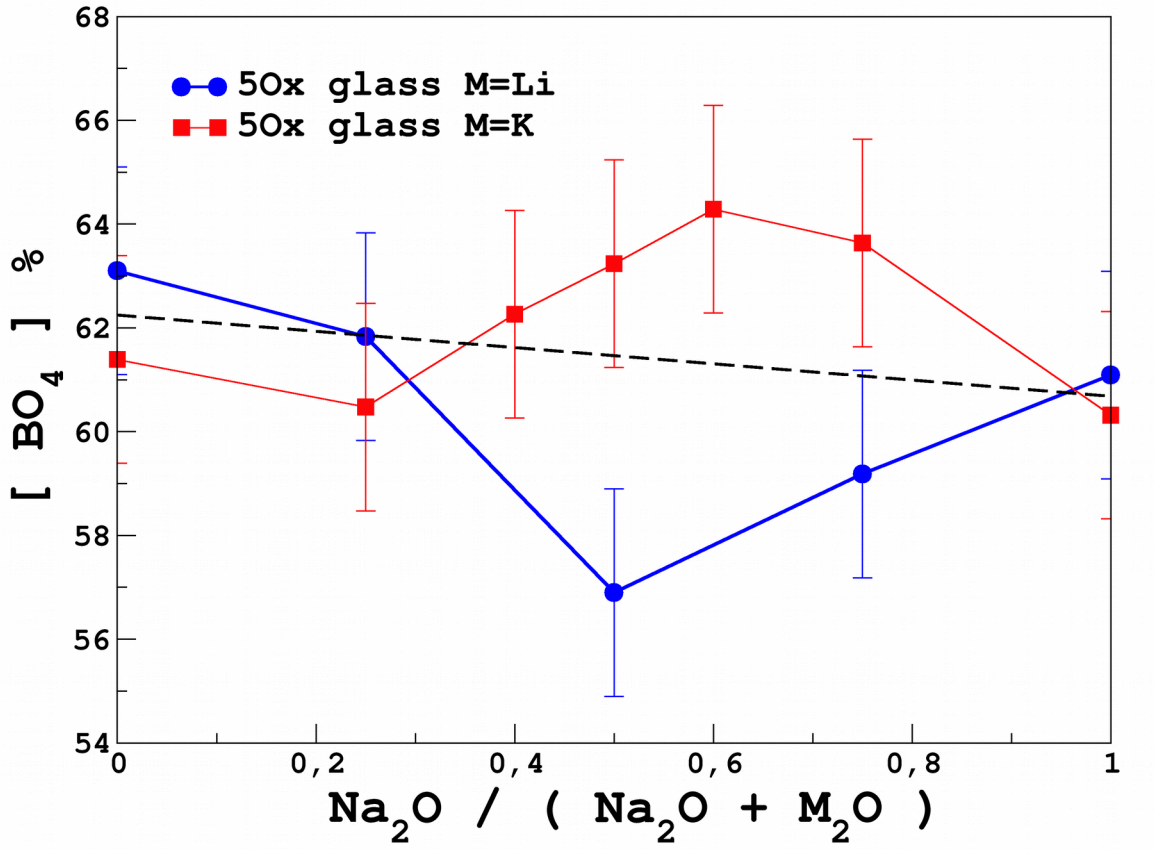


Fig. 8. Isotropic projections of ^{11}B 3QMAS spectra for Li, Na and K borosilicate glasses at a composition of $K = 2$ and $R = 0.75$.

Effect of the modifier cation which affects both %BO_4 and BO_3 speciation

Silicon-Boron Mixing in ternary borosilicate
^{11}B MAS NMR : Mixed Alkali Effet



Non-linear Mixed Alkali effect on the glass structure (in 5 Oxides Simplified Nuclear Waste Glass)

N. Ollier et al., J. Non-Cryst. Solids 2004

Silicon-Boron Mixing in ternary borosilicate
The power of ^{17}O MAS / MQMAS NMR

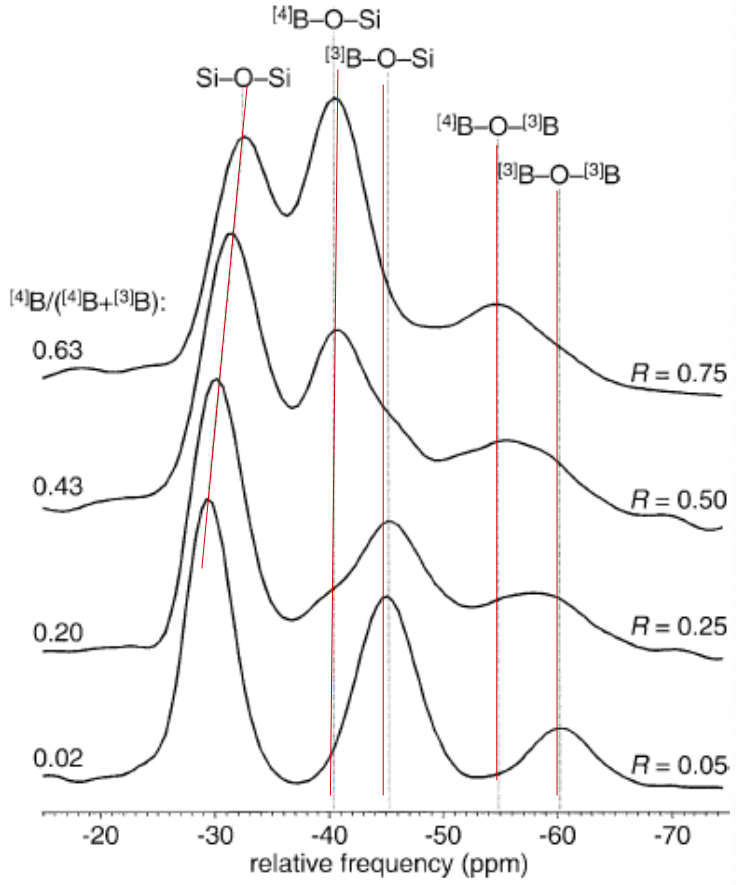


Fig. 10. Isotropic projections of ^{17}O 3QMAS spectra for NBK2 glasses with $R = 0.05–0.75$.

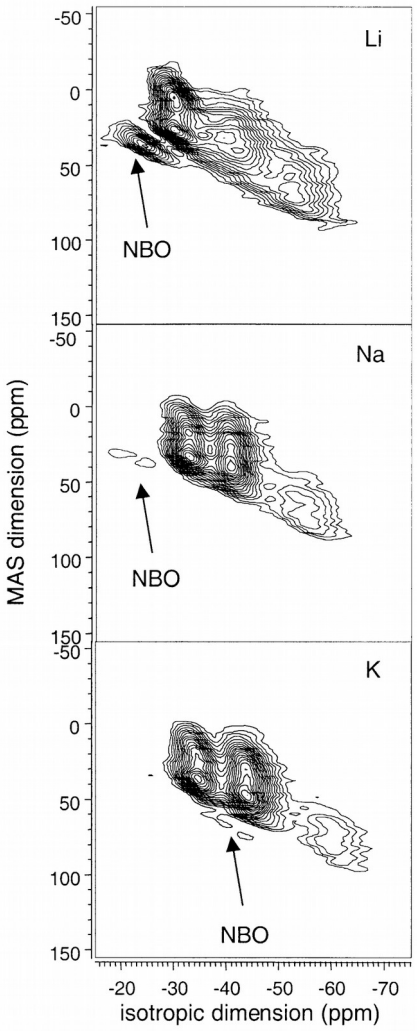


Fig. 12. Oxygen-17 3QMAS spectra for Li, Na and K borosilicate glasses at a composition of $K = 2$ and $R = 0.75$.

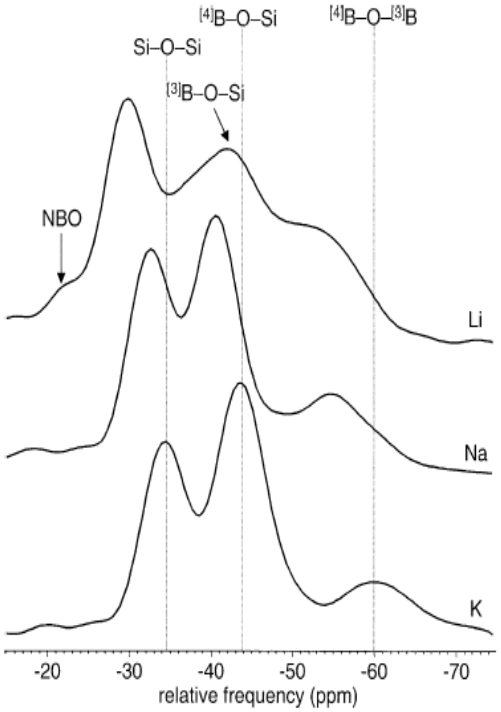


Fig. 13. Isotropic projections of ^{17}O 3QMAS spectra for Li, Na and K borosilicate glasses at a composition of $K = 2$ and $R = 0.75$. Vertical dotted lines indicate peak positions in potassium borosilicate spectrum.

Increased disorder (line width) with high field modifier cations (Li)

^{17}O MQMAS NMR resolve the « chemical disorder » (Si / B mixing)

$^{[4]}B$-O-$^{[4]}B$ avoidance is assumed for the interpretation of the data

Silicon-Boron Mixing in ternary borosilicate
The power of ^{17}O MQMAS NMR

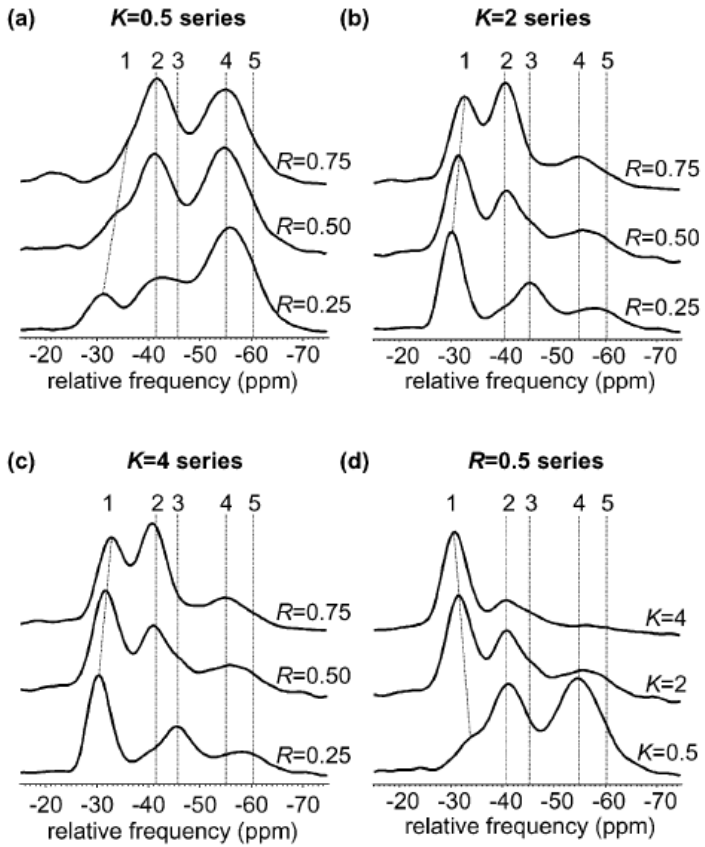


Figure 7. Isotropic projections of ^{17}O 3QMAS spectra for (a) NBS-K0.5, (b) NBS-K2, (c) NBS-K4, and (d) NBS-R0.5 glasses. The dotted lines are guides indicating the approximate positions of the peaks for Si−O−Si, Si−O−$^{[4]}$B, Si−O−$^{[3]}$B, $^{[4]}$B−O−$^{[3]}$B, and $^{[3]}$B−O−$^{[3]}$B, labeled as 1, 2, 3, 4, and 5, respectively.

Deviation of %NBO (also determined from N4) from Dell&Bray model (homogenous) might be indicative of heterogeneity at nanoscale.

Resolution of the Si/B mixing (think configuratinal entropy) with ^{17}O MQMAS NMR

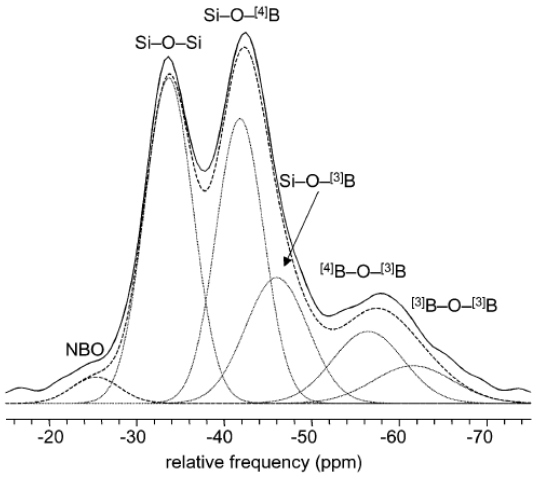


Figure 7. Experimental ^{17}O isotropic projection (solid line) and typical fitting results (dashed line, sum; dotted lines, components) for NK−BS glass. Fit parameters are given in Table 3.

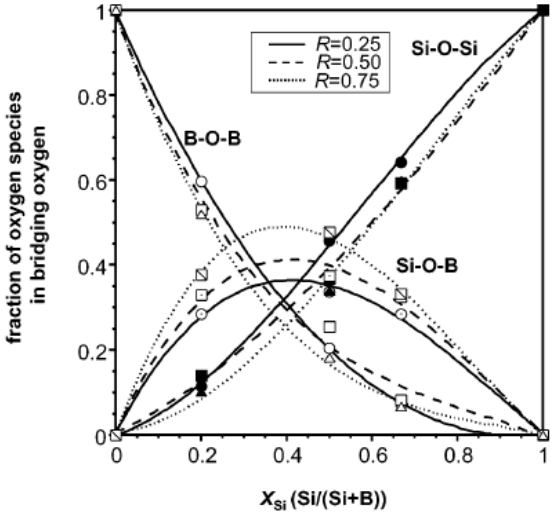


Figure 16. Variations in the fraction of oxygen species in bridging oxygens with X_{Si} for NBS-R0.25, NBS-K0.5, and NBS-R0.75 glasses.

Nature of Silicon-Boron Mixing in Sodium Borosilicate Glasses : A High-Resolution ^{11}B and ^{17}O NMR study, L. Du et al. J. Phys. Chem. B 107, 10063 (2003).

Silicon-Boron Mixing in ternary borosilicate
One step further !

^{11}B and ^{17}O MQMAS NMR provides the fractions of Si-O- $^{[3]}B$, $^{[3]}B$(ring) and $^{[3]}B$(non-ring). Question : How are $^{[3]}B$(ring) and $^{[3]}B$(non-ring) are connected to Si ? $^{[3]}B$(ring) and $^{[3]}B$(non-ring) connected in average to m and n Si, respectively.

$$\left(\frac{R+2K+3}{2}\right)\times I_{B^{[3]}OSi} = m\,J_{B^{[3]}(ring)} + n\,J_{B^{[3]}(non-ring)}$$

Number of Oxygen atoms in $RNa_2O.B_2O_3$-$KSiO_2$

Fraction of Si-O- $^{[3]}B$

Fraction of $^{[3]}B$(ring)

Fraction of $^{[3]}B$(non-ring)

$I_{B^{[3]}OSi}$

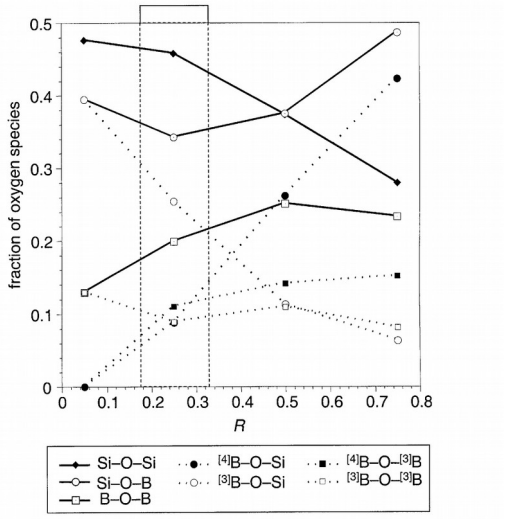


Fig. 16. Variations in the fractions of bridging oxygens with R, as given in Table 3.

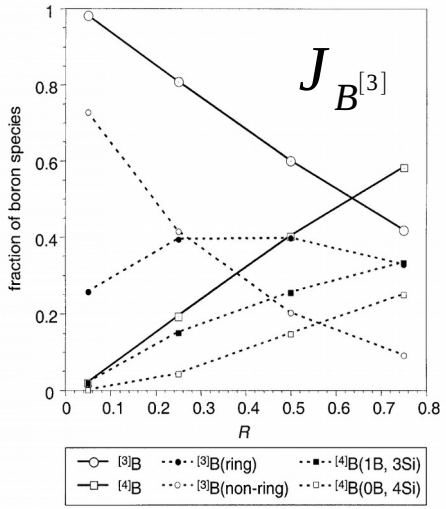


Fig. 15. Variations of the fractions of boron species (relative to total boron) with R, as given in Table 2.

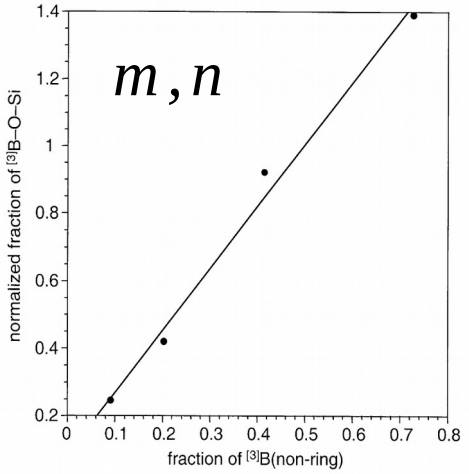


Fig. 19. Variation of the fraction of $^{[3]}$B–O–Si multiplied by $(R+2K+3)/2$ with the fraction of non-ring $^{[3]}$B groups, with the line fitted by linear regression.

Lin-Shu Du and Jonathan F. Stebbins, Journal of Non-Crystalline Solids 315 (2003) 239–255

Silicon-Boron Mixing in ternary borosilicate (KBS)
One step further !

$$\left(\frac{R+2K+3}{2}\right)\times I_{B^{[3]}OSi} = m\,J_{B^{[3]}(ring)} + n\,J_{B^{[3]}(non-ring)}$$

Number of Oxygen atoms in $RNa_2O.B_2O_3\text{-}KSiO_2$

Fraction of Si-O- $^{[3]}B$

Fraction of $^{[3]}B$*(ring)*

Fraction of $^{[3]}B$*(non-ring)*

$K=SiO_2/B_2O_3$		0.5	2	4
$^{[3]}B$*(non-ring)*	n	0.52	1.68	2.02
$^{[3]}B$*(ring)*	m	0.17	0.27	0.48

$^{[3]}B$(ring) connect more to boron (~1/3 to Si) and $^{[3]}B$(non-ring) preferentially bonds to Si.
Interpretation : $^{[3]}B$(ring) ($^{[3]}B$(non-ring) are species more connected to B (Si, respectively)
m<n/3 suggest aggregates of B-ring region.

Mixing to the silicate network in the order : $^{[4]}B$ > $^{[3]}B$(non-ring) > $^{[3]}B$(ring)

Lin-Shu Du and Jonathan F. Stebbins, Journal of Non-Crystalline Solids 315 (2003) 239–255

The case of Aluminoborosilicate glasses
Resolution of Al-O-Si

Network connectivity in aluminoborosilicate glasses: A high-resolution ^{11}B, ^{27}Al and ^{17}O NMR study, L. Du et al., Journal of Non-Crystalline Solids 351 (2005) 3508–3520

Effect of the cation field strengths

High field strength modifier cations favor BO_3

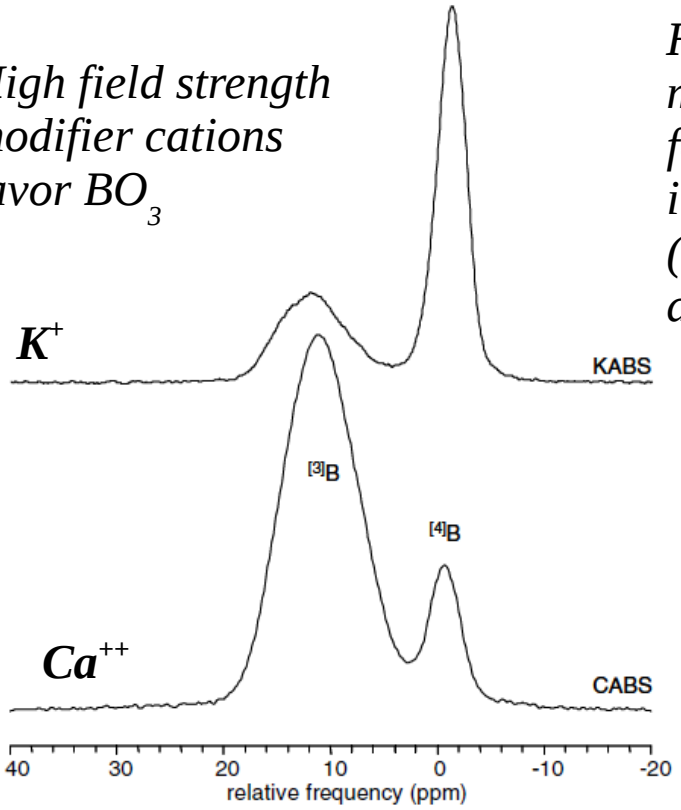


Fig. 1. Boron-11 MAS spectra for the KABS and CABS glasses collected at 14.1 T. Here and in the following figures, the intensity of each spectrum is normalized to that of its highest peak.

High field strength modifier cations favor formation of B-NBO and increase linewidth (higher topological disorder).

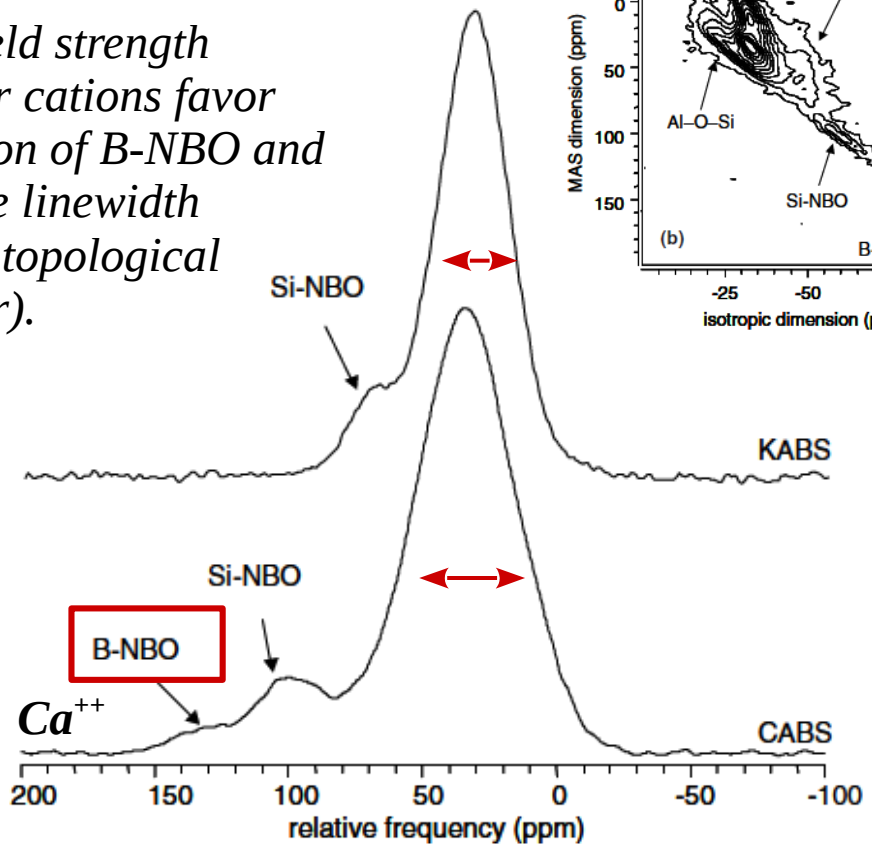
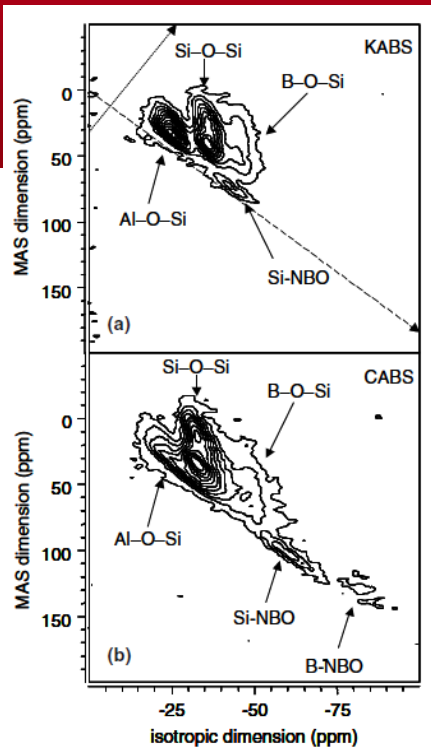


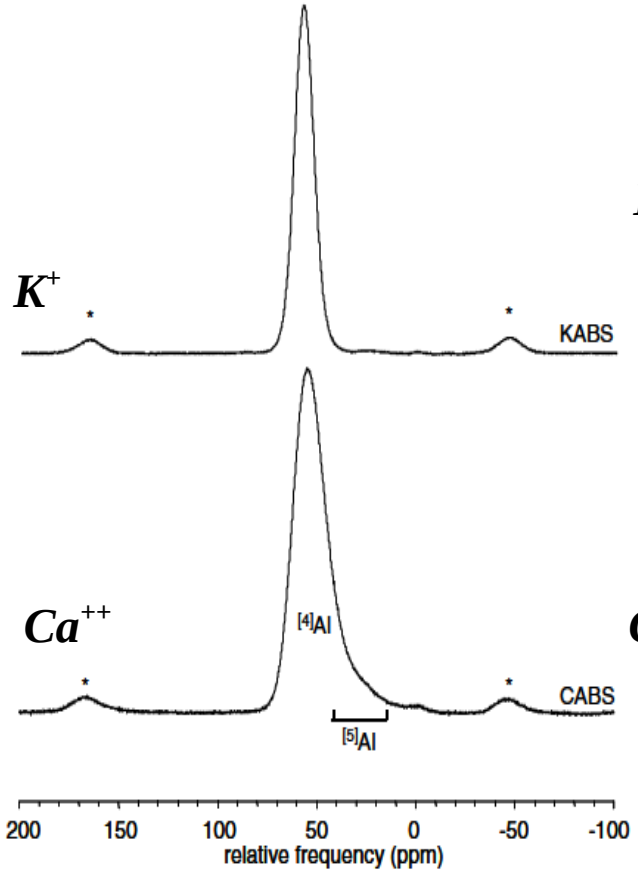
Fig. 3. Oxygen-17 MAS spectra for the KABS and CABS glasses collected at 14.1 T.



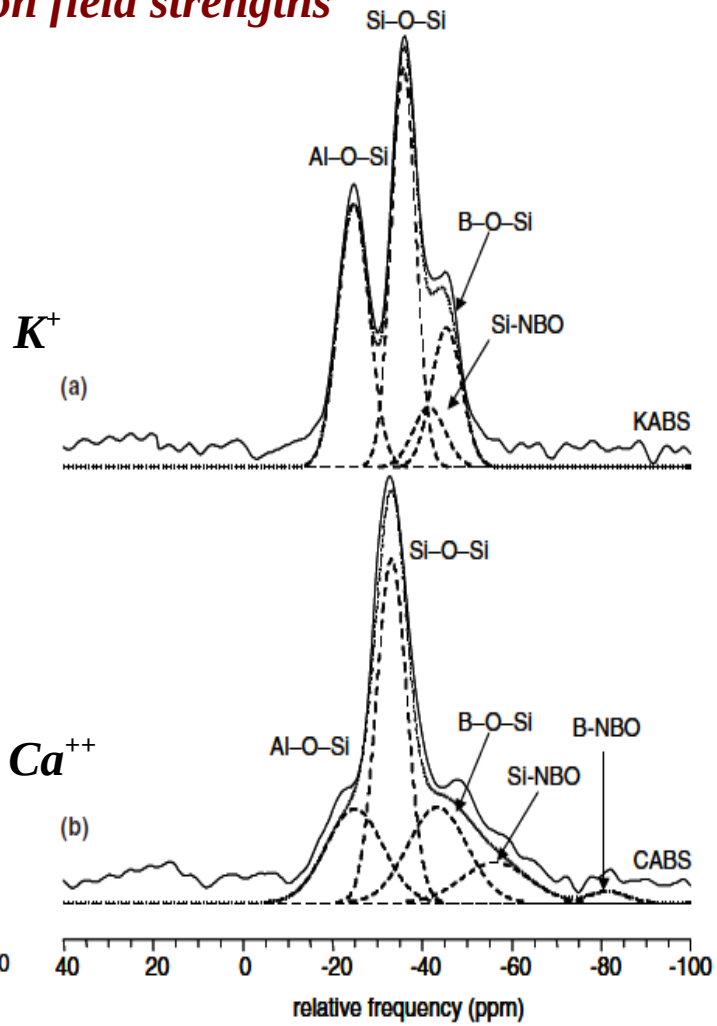
The case of Aluminoborosilicate glasses
Resolution of Al-O-Si

Network connectivity in aluminoborosilicate glasses: A high-resolution ^{11}B, ^{27}Al and ^{17}O NMR study, L. Du et al., Journal of Non-Crystalline Solids 351 (2005) 3508–3520

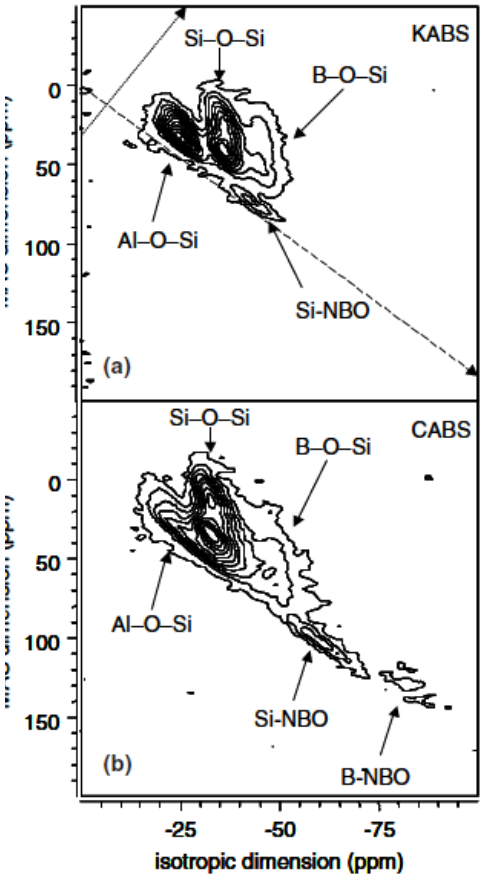
Effect of the cation field strengths



^{27}Al MAS NMR



^{17}O MQMAS NMR



Aluminoborosilicate glasses : Search for a generalized Dell&Bray model

Network connectivity in aluminoborosilicate glasses: A high-resolution ^{11}B, ^{27}Al and ^{17}O NMR study, L. Du et al., Journal of Non-Crystalline Solids 351 (2005) 3508–3520

Alkali first charge compensate AlO_4 :

effective R ratio $R^*=(Na_2O\text{-}Al_2O_3) / B_2O_3$

$Na_2O\text{-}Al_2O_3$ is the effective number of Na_2O

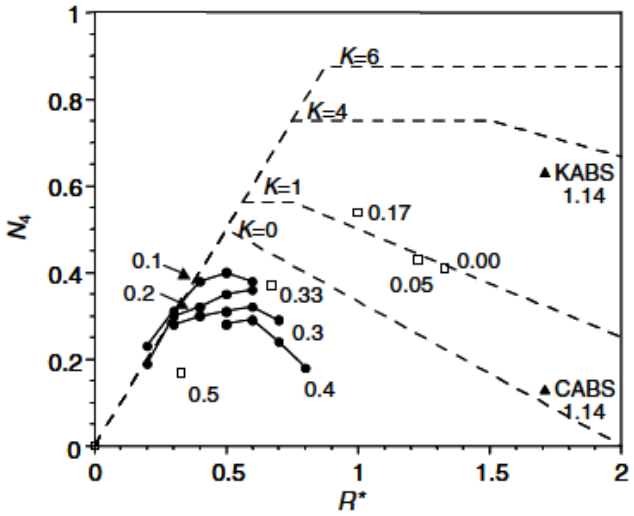


Fig. 7. Variation of N_4 with R^* from a previous NMR study on sodium aluminoborosilicate glasses [30] (□), a previous NMR study on potassium aluminoborosilicate glasses [27] (● connected by solid lines for each series with the same Al/B ratio), trends predicted by Dell and Bray model at several K values (---) and our experimental data (▲). Numbers shown near experimental data are the Al/B ratios.

It works sometimes ...

New model : treat Al_2O_3 (AlO_4) as B_2O_3

$R'=Na_2O/(Al_2O_3 + B_2O_3)$

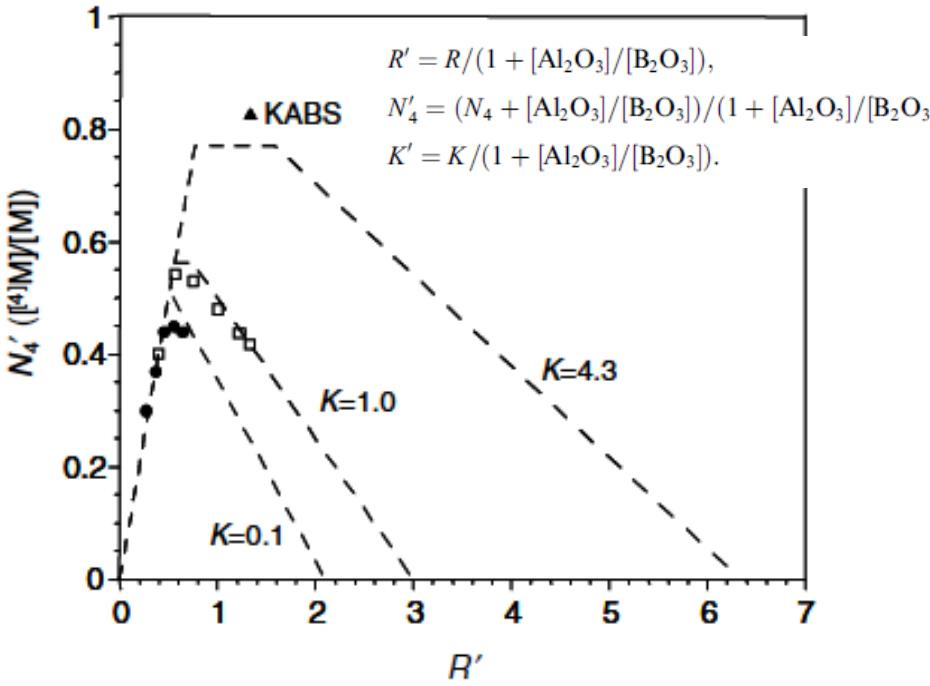
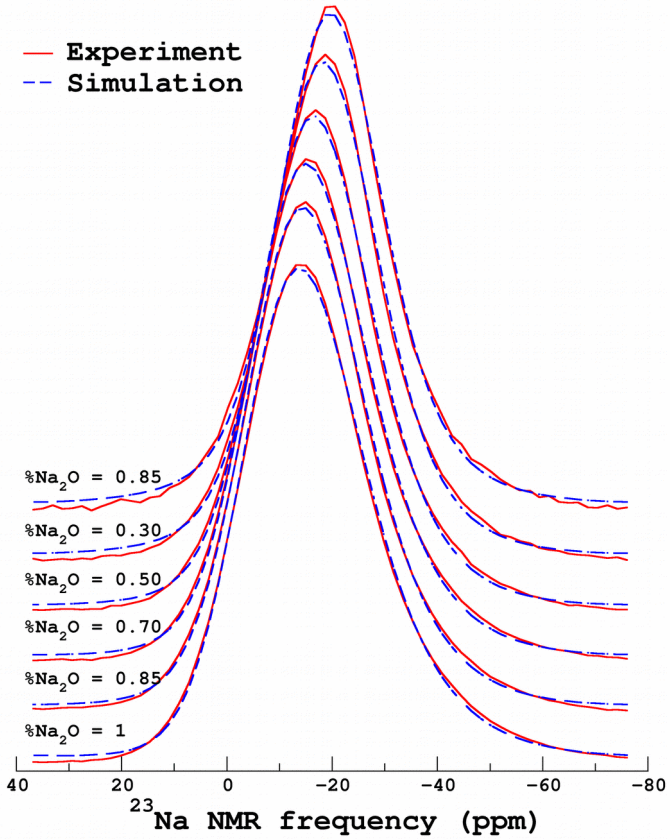


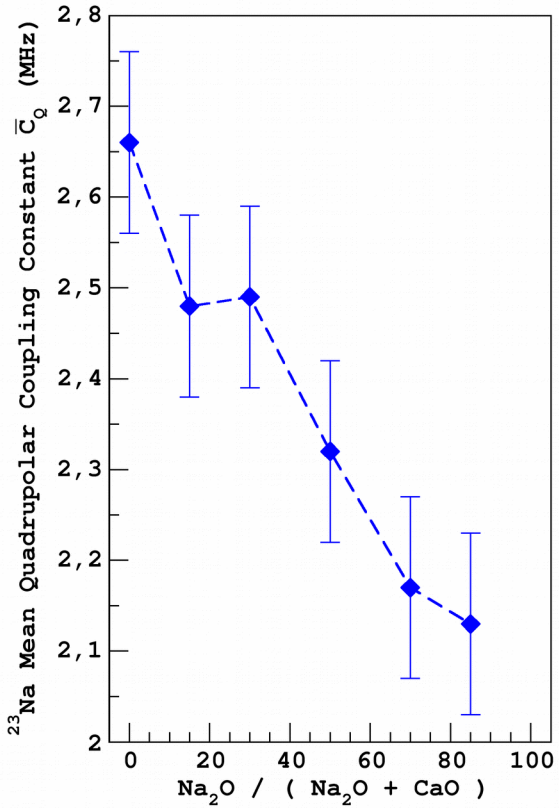
Fig. 9. Variation of calculated N'_4 with R' for potassium aluminoborosilicates [27] at $K' = 0.1$ (●), sodium aluminoborosilicates [30] (□), trends predicted by Dell and Bray model for various K values (---) and our data for KABS (▲).

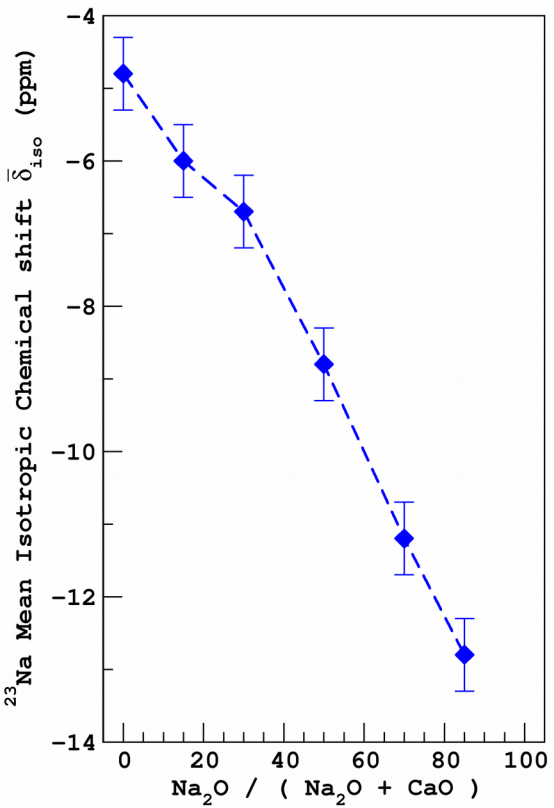
Applicable when AlO_5, AlO_6 ?

(Complex) Aluminoborosilicate glasses : Effect of cation field strength ^{23}Na MAS NMR

$62SiO_2$ – $9B_2O_3$ - 20 (Na_2O+CaO) – $3Al_2O_3$ – $2ZrO_2$ - $3.5La_2O_3$





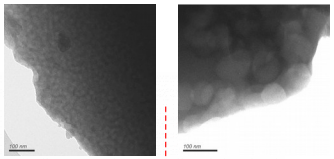


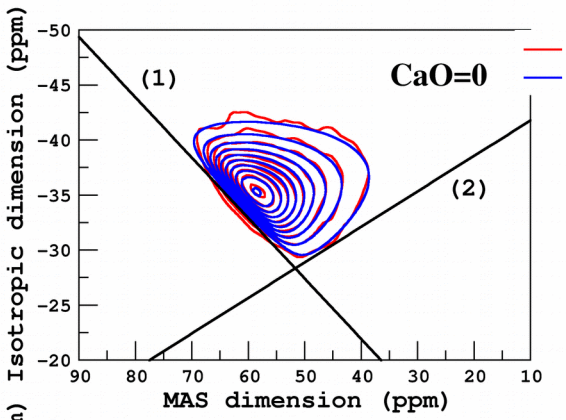
Strong variation of the ^{23}Na NMR parameters : Ca/Na mixing

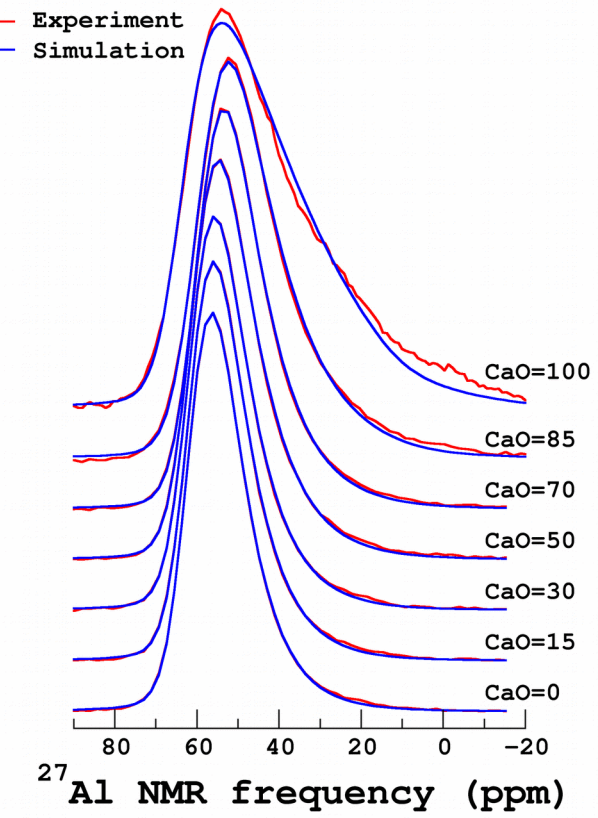
A. Quintas et al. Journal of Applied Magnetic Resonance 2007

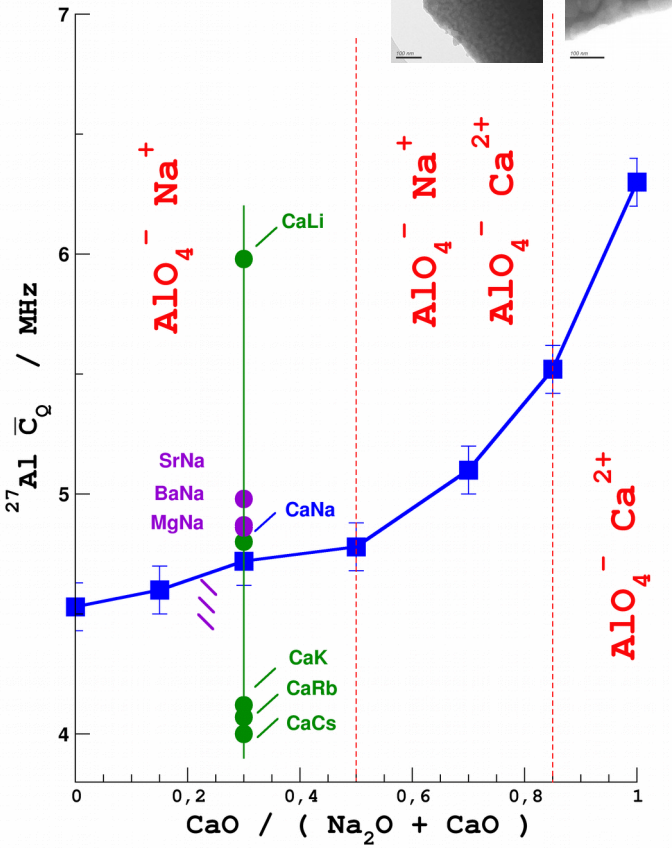
(Complex) Aluminoborosilicate glasses : Effect of cation field strength ^{23Al} MAS NMR

$62SiO_2$ – $9B_2O_3$ - 20 (Na_2O+CaO) – $3Al_2O_3$ – $2ZrO_2$ - $3.5La_2O_3$







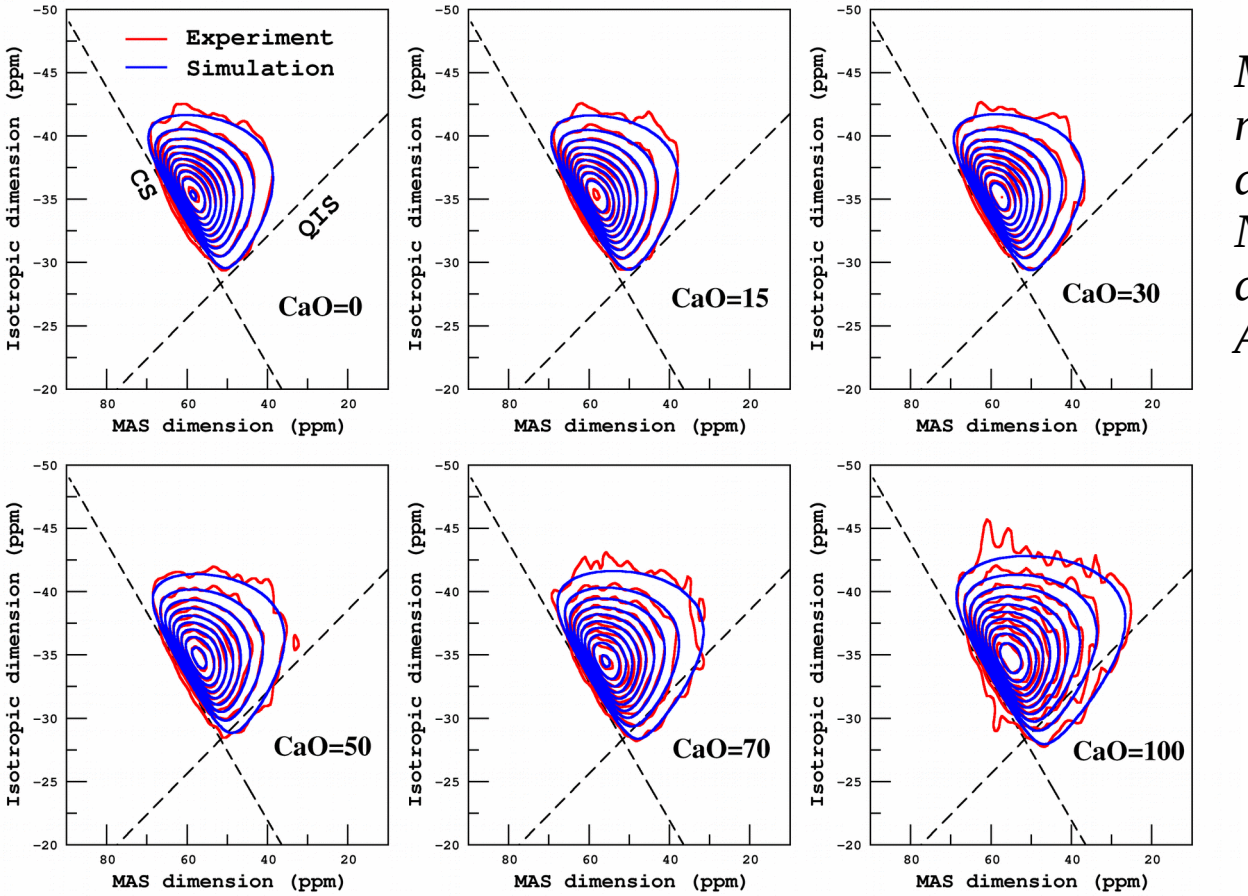


Changes in the ^{27}Al NMR parameters : variation of the charge compensation mechanism

A. Quintas et al. Journal of Applied Magnetic Resonance 2007

(Complex) Aluminoborosilicate glasses : Effect of cation field strength ^{27}Al MAS NMR

$62SiO_{2-}\ 9B_2O_3$ - 20 (Na_2O+CaO) – $3Al_2O_{3-}\ 2ZrO_2$ - $3.5La_2O_3$



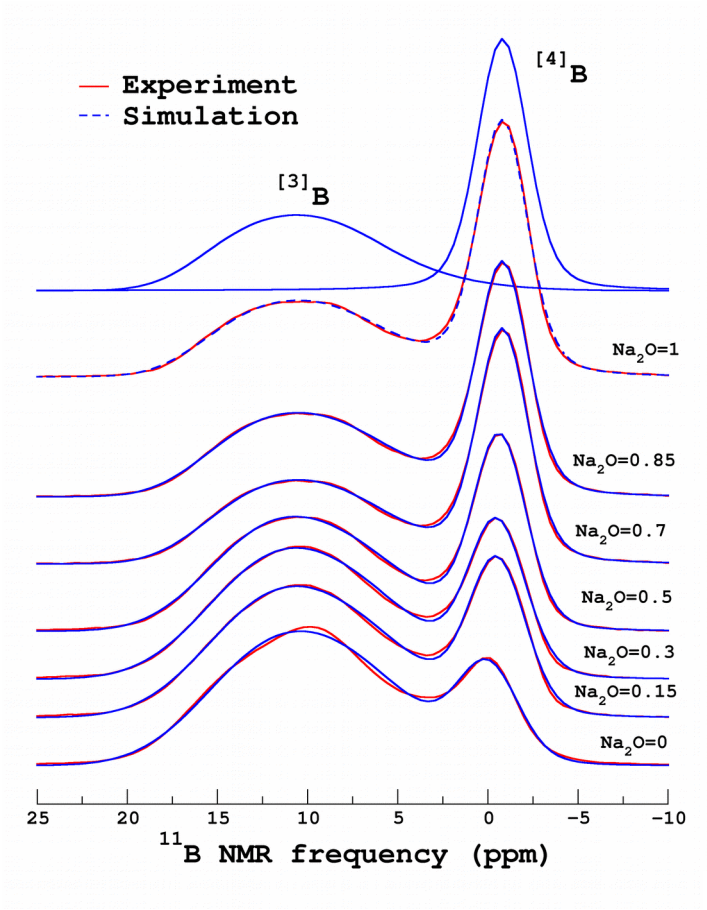
MQMAS if often needed for accurate determination of the NMR parameters and extraction of $AlO_{5,6}$ peaks

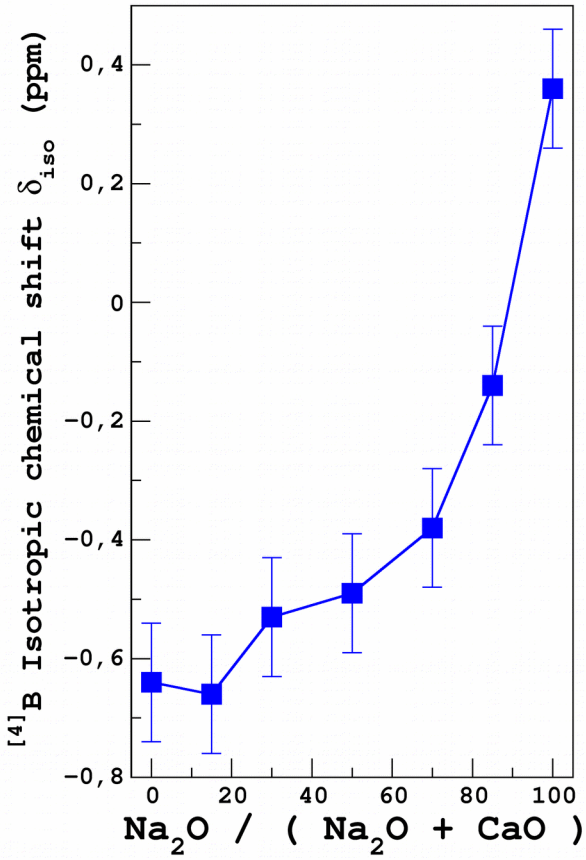
Changes in the ^{27}Al NMR parameters : variation of the charge compensation mechanism

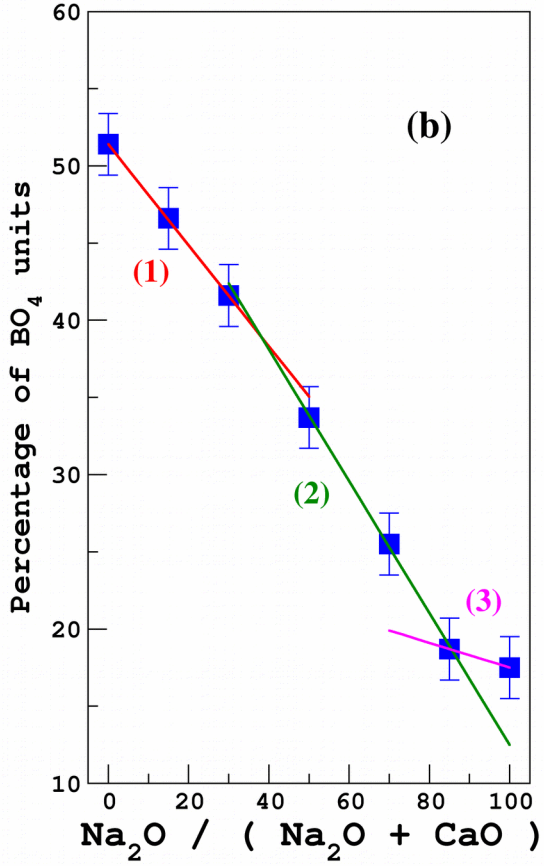
A. Quintas et al. Journal of Applied Magnetic Resonance 2007

(Complex) Aluminoborosilicate glasses : Effect of cation field strength ^{11}B MAS NMR

$62SiO_2$ – $9B_2O_3$ - 20 (Na_2O+CaO) – $3Al_2O_3$ – $2ZrO_2$ - $3.5La_2O_3$





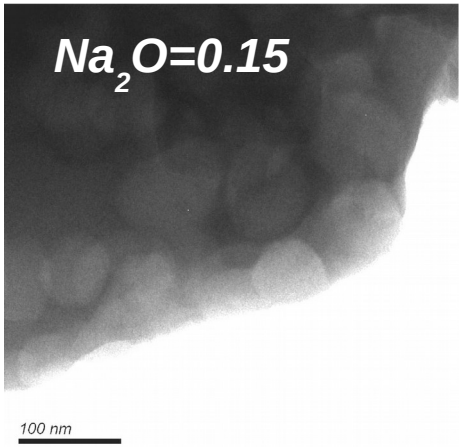


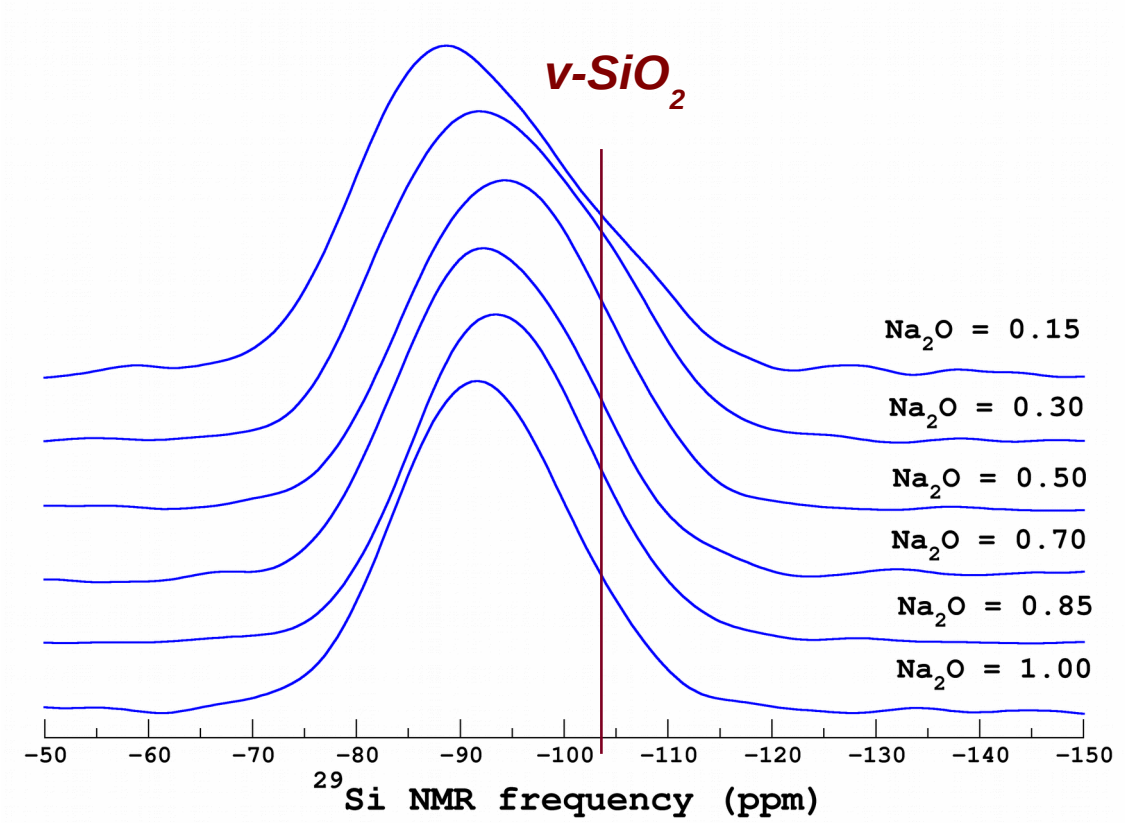
Changes in the ^{11}B NMR parameters and speciation : conversion of BO4 to BO3

A. Quintas et al. Journal of Applied Magnetic Resonance 2007

(Complex) Aluminoborosilicate glasses : Effect of cation field strength ^{23}Al MAS NMR

$62SiO_2$ – $9B_2O_3$ - 20 (Na_2O+CaO) – $3Al_2O_3$ – $2ZrO_2$ - $3.5La_2O_3$





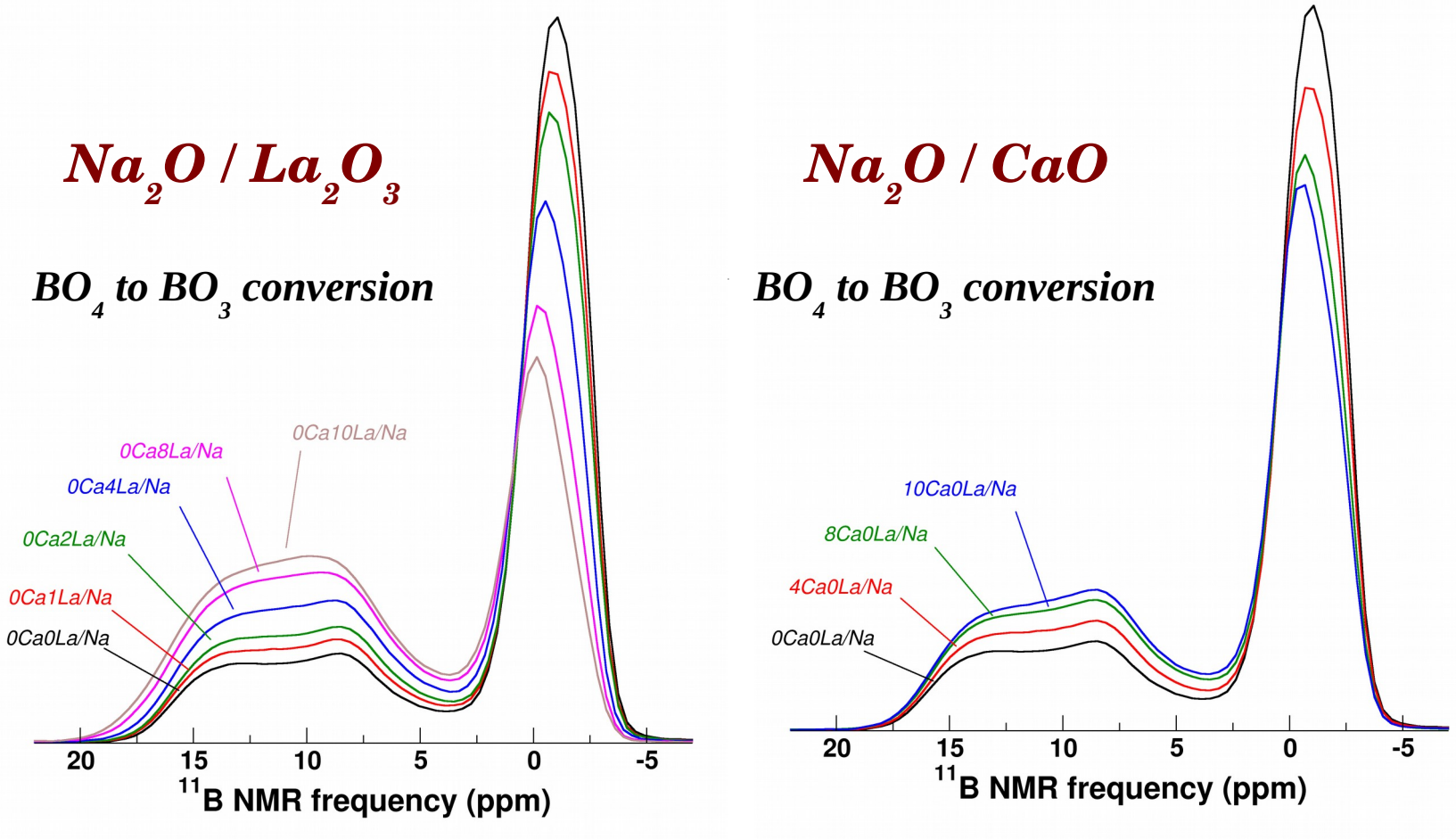
Slight changes in the ^{29}Si MAS NMR spectra. At high CaO content, spectrum broadening and shift to lower (depolymerized) and higher (vitreous silica) chemical shift values, in agreement with the observed phase separation.

A. Quintas et al. Journal of Applied Magnetic Resonance 2007

Incorporation of Lanthanum in borosilicate glasses
^{11}B MAS NMR at work

$60\ SiO_2 - 18B_2O_3 - (20\text{-}x)\ Na_2O - x\ \{ CaO \text{ or } La_2O_3 \}$

La_2O_3 : network former or modifier ?

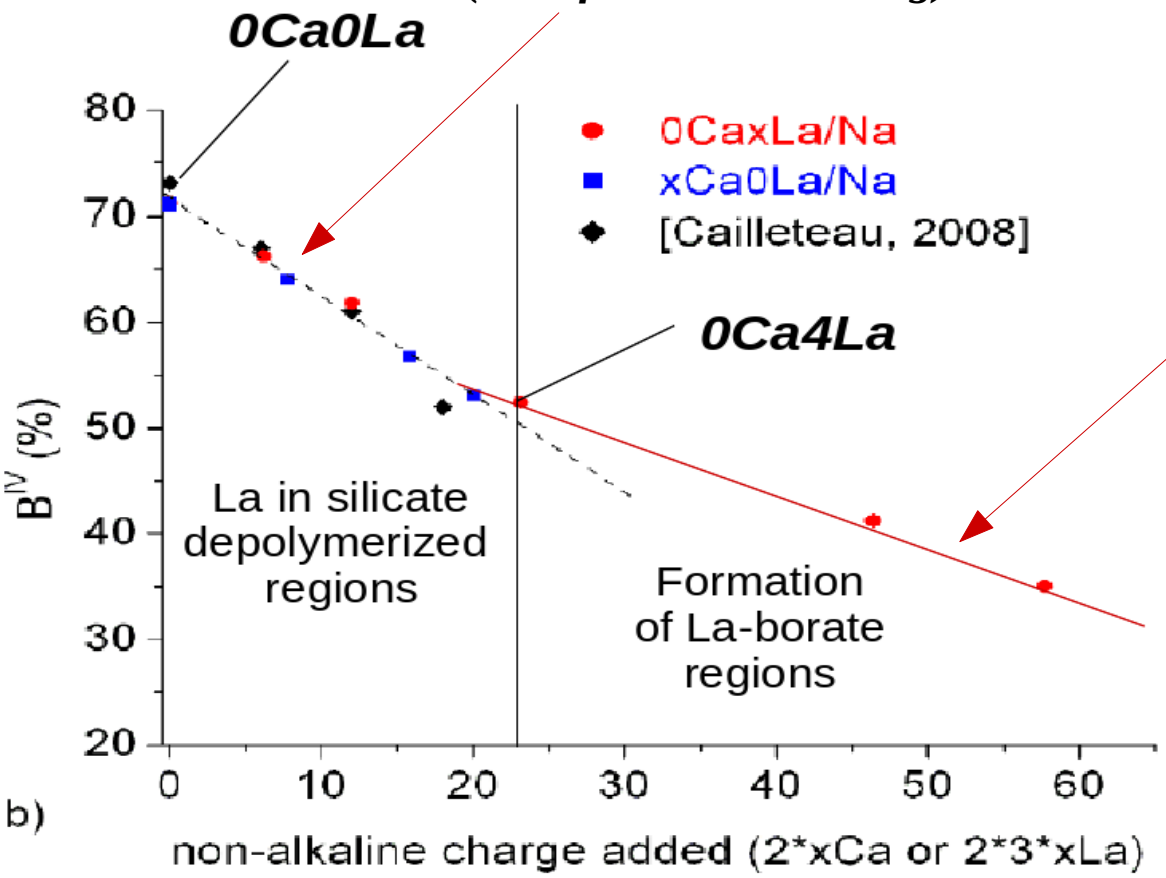


F. Angeli, T. Charpentier et al., JNCS 2013

Incorporation of Lanthanum in borosilicate glasses
^{11}B MAS NMR at work

$60\ SiO_2 - 18B_2O_3 - (20\text{-}x)\ Na_2O - x\ \{\ CaO\ or\ La_2O_3\ \}$

BO_4 to BO_3 conversion + Na consumption
(modifier cation mixing)



Formation of BO_3 - NBO ?
Borate (nano)-clustering

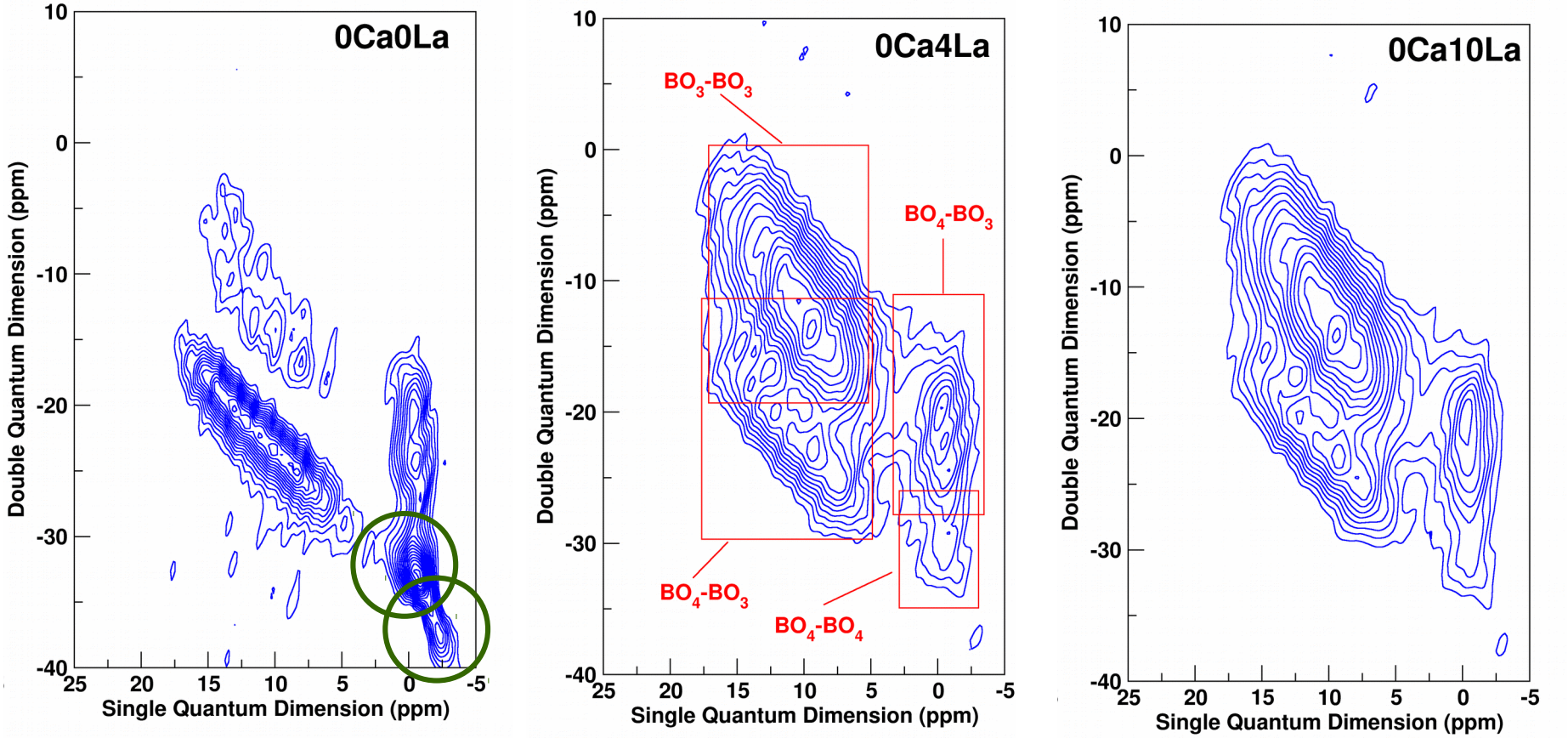
Possible NMR approaches :

- ***^{17}O MQMAS / MAS***
- ***2D NMR (^{11}B-^{11}B)***

F. Angeli, T. Charpentier et al., JNCS 2013

Incorporation of Lanthanum in borosilicate glasses
^{11}B- ^{11}B Dipolar Double Quantum Correlation (DQC)

60 SiO_2 - 18B_2O_3 - (20-x) Na_2O – x { CaO or La_2O_3}



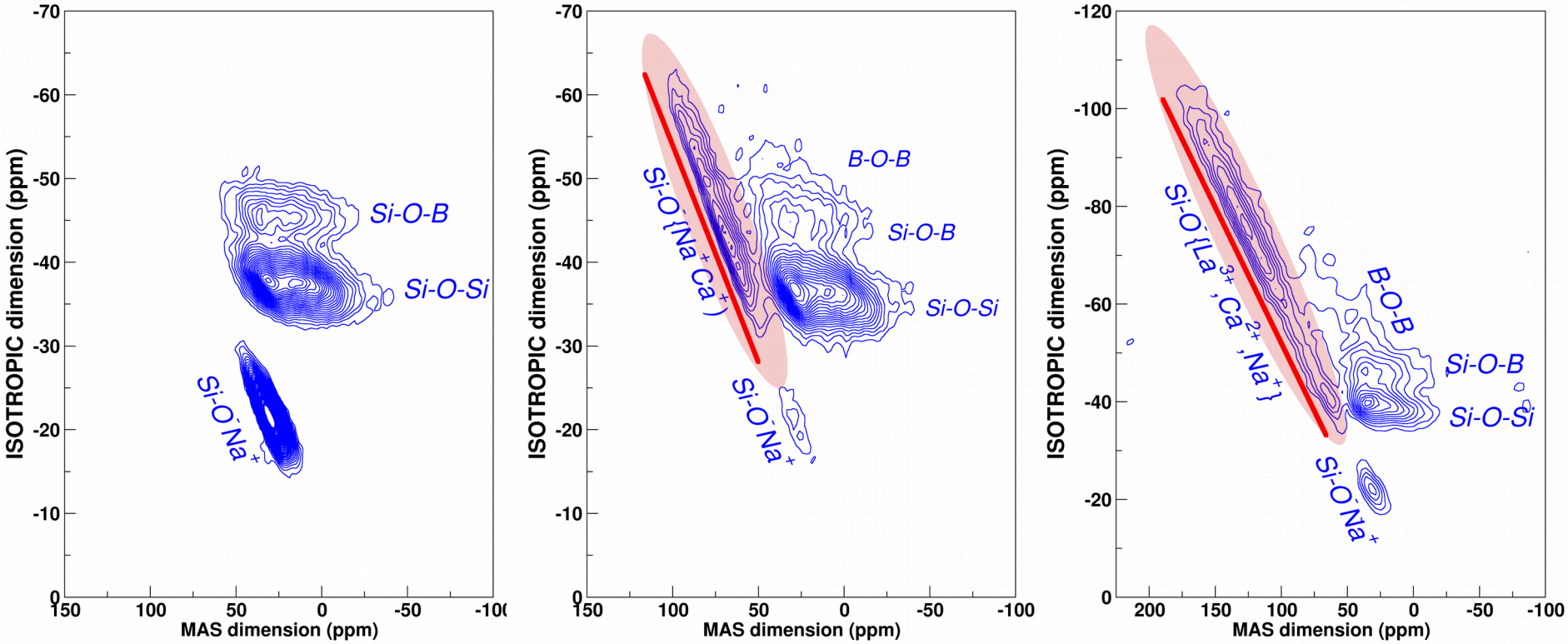
Dipolar-DQC : Boron clustering for high La content : Metaborate environment (LaB_3O_6, RAMAN).

Caution : dipolar = spatial proximity, not chemical bonding !!

T. Charpentier et al., in preparation

Incorporation of Lanthanum in borosilicate glasses
^{17}O MQMAS NMR at work

$SiO_2 – B_2O_3 – Na_2O$ + CaO + La_2O_3

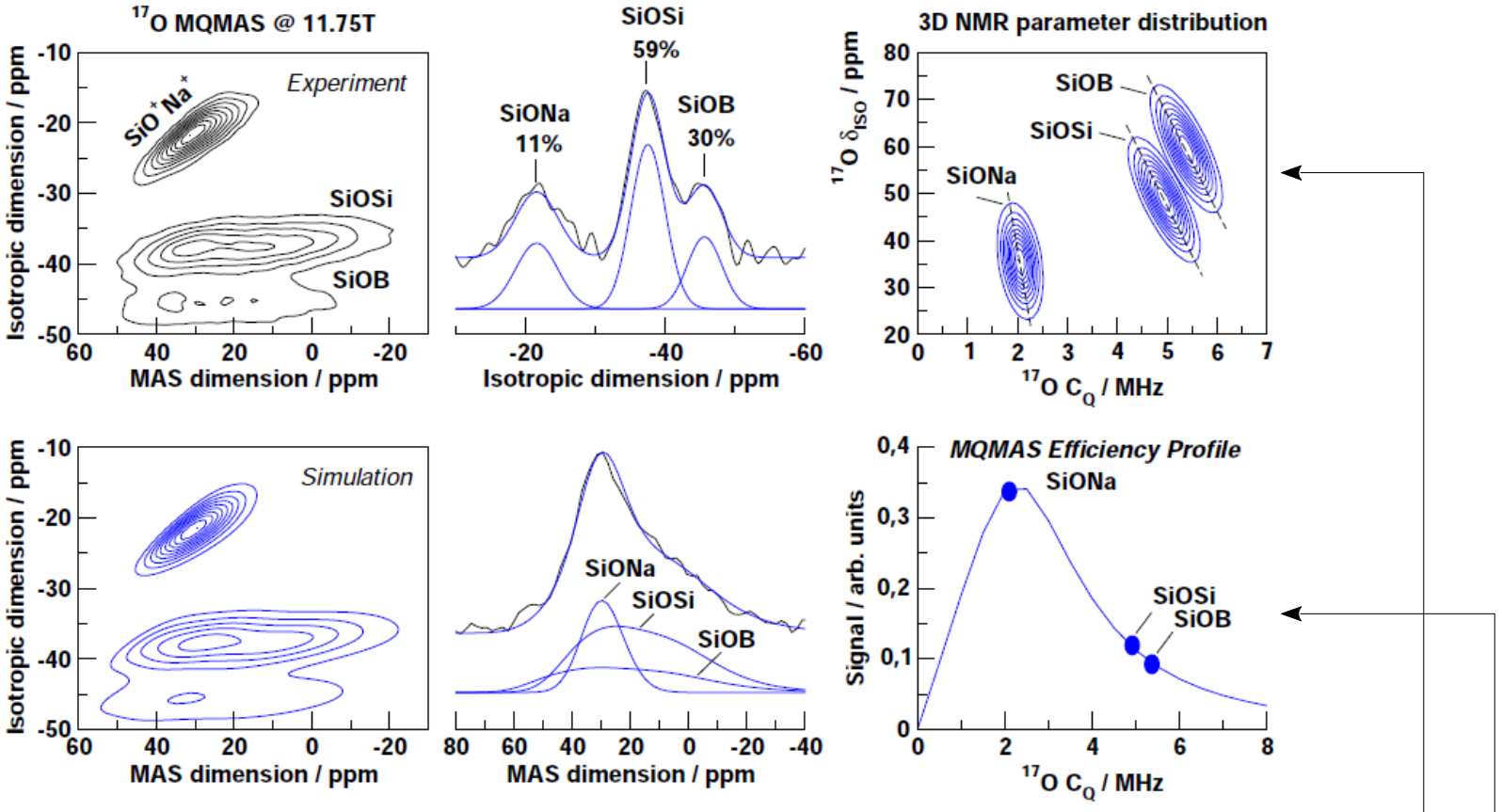


Mixed Oxide Region

Quantitative information : accurate modeling needed

F. Angeli, T. Charpentier et al., JNCS 2013

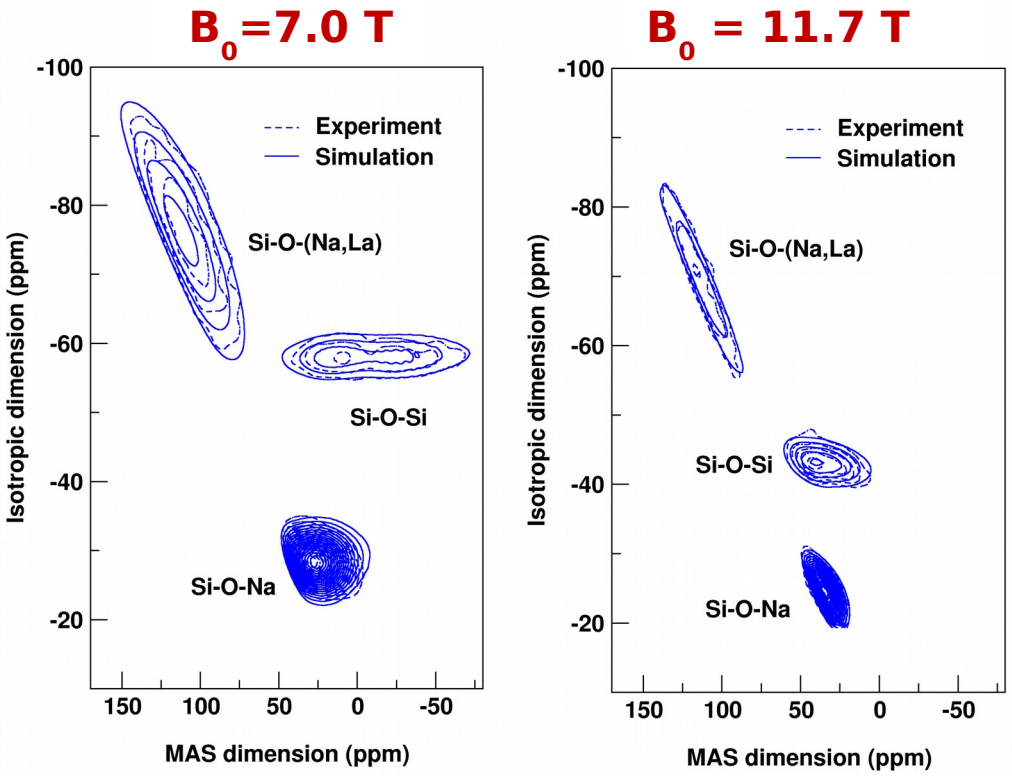
^{17}O MAS & MQMAS NMR : modeling and Quantification



- Specific model of NMR parameter distribution: $p(C_Q, \eta, \delta_{iso})$
- Simulation of the (full) MQMAS experiment for quantitativeness

See F. Angeli, T. Charpentier et al., JNCS 2008 & GCA 2011

Investigation of lanthanum environment by ^{17}O MQMAS NMR spectra



$$60\,SiO_2 - 35\,Na_2O - 5\,La_2O_3$$

Experimental data reproduced considering La-Na mixing:

3.3Na^+ as second-neighbors of **1La^{3+}**

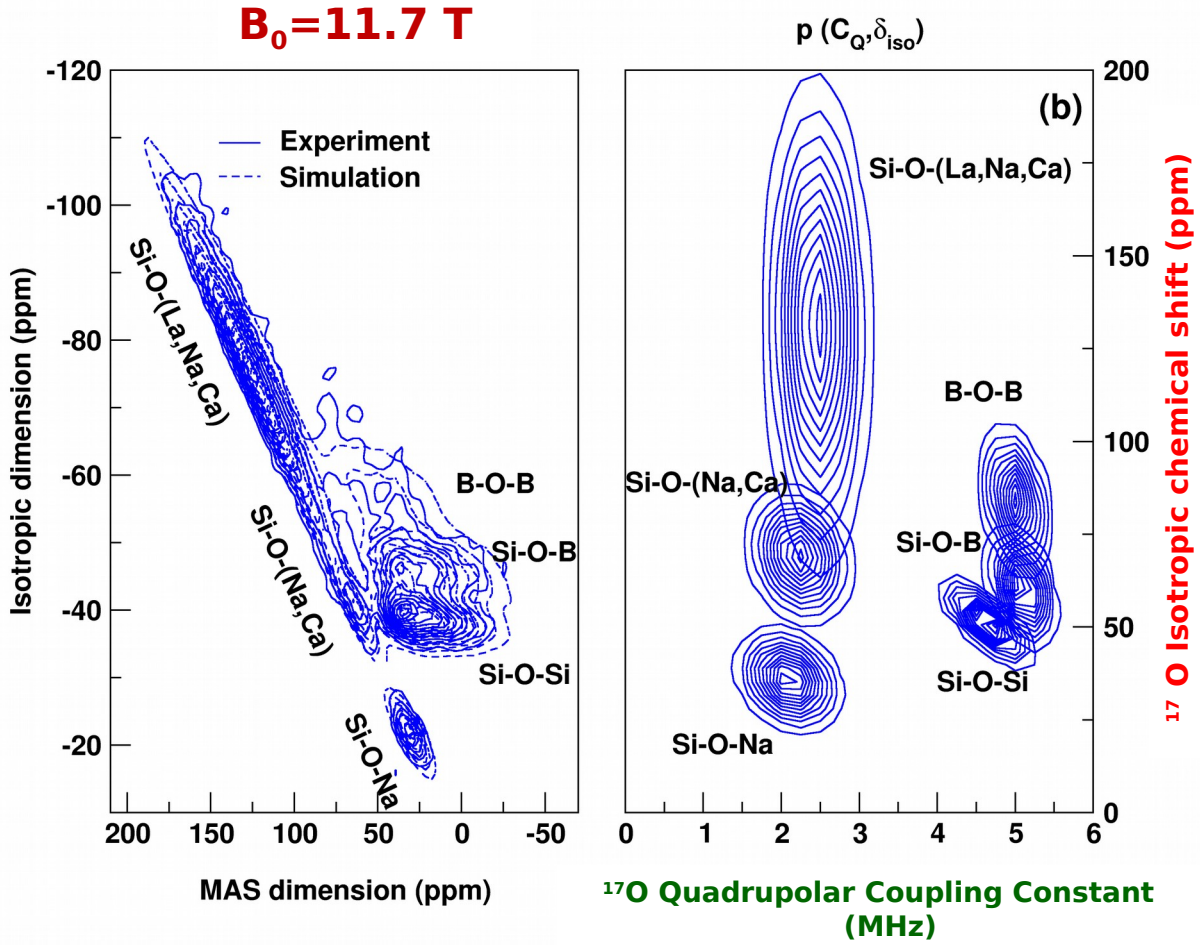
La-Na mixing: 6.3 positive charges

- requires equivalent NBOs
- La coordination ~ 6 (EXAFS)

5La	7.0 T	11.7 T	Calculation (random distrib.)	Calculation (xNa=3.3)
Si-O-Si	42	43	42.5	42.5
Si-O-Na	**23**	**23**	41.3	**23.4**
Si-O-(Na,La)	**35**	**34**	16.3	**34.2**
NBO	58	57	57.5	57.5

Increasing the complexity of the system (soda-lime borosilicates)

$54SiO_2 – 17B_2O_3 – 20Na_2O – 5CaO – 4La_2O_3$



*Lee and Stebbins (2003), *J. Phys. Chem. B*, -> Na_2O-CaO-$3SiO_2$:

formation of Na-Ca pairs

**Angeli, Charpentier et al. (2013), *J. Non-Cryst. Solids*

^{17}O quantification

2 cation mixing sites:

- **Si-O-(Na-Ca)***
- **Si-O-(La-Na-Ca)****:

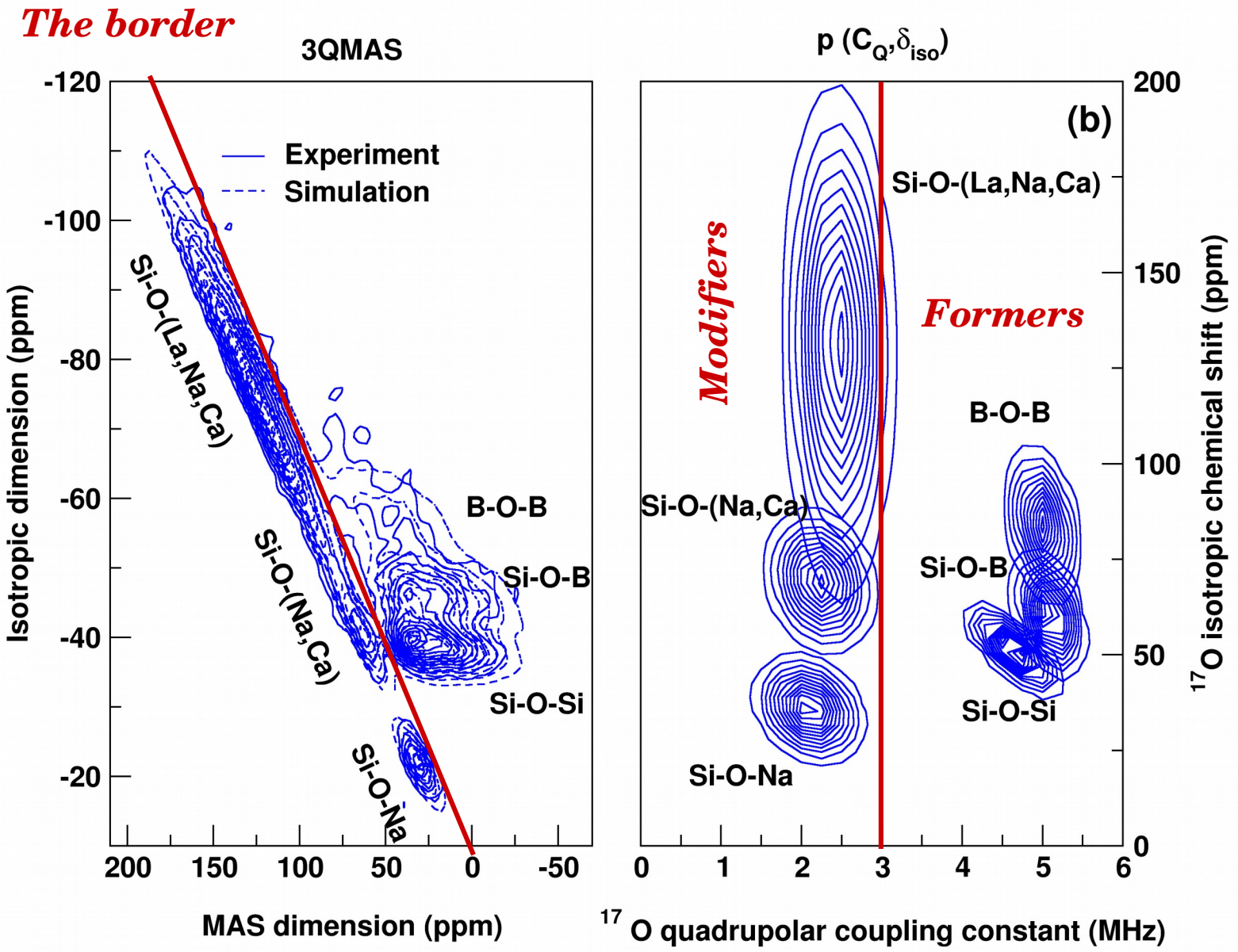
2.2 Na^+, 0.5 Ca^{2+} for 1 La^{3+}

-> 6.2 positive charges

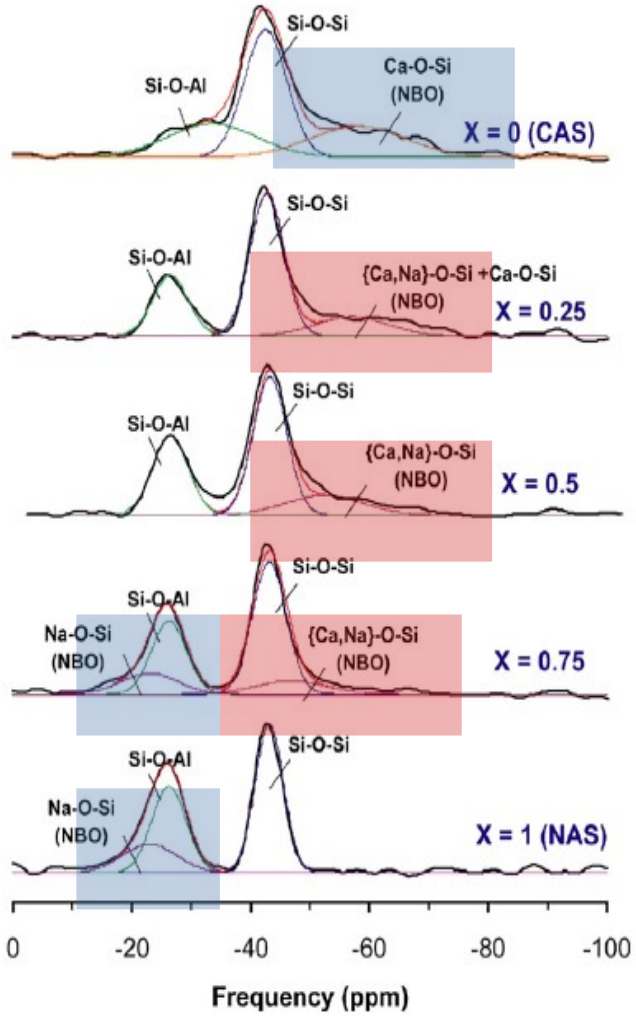
-EXAFS (La-L_3-edge):

- La coordination ~ 6
- Si 2nd neighbors

^{17}O MQMAS NMR
Network modifier vs former : a ^{17}O landscape ...



^{17}O MQMAS NMR in aluminosilicate glasses : Modifier cation mixing



The effect of network-modifying cations on the structure and disorder in peralkaline Ca–Na aluminosilicate glasses: O-17 3QMAS NMR studyS.K. Lee et al., Chemical Geology 256 (2008) 326–333

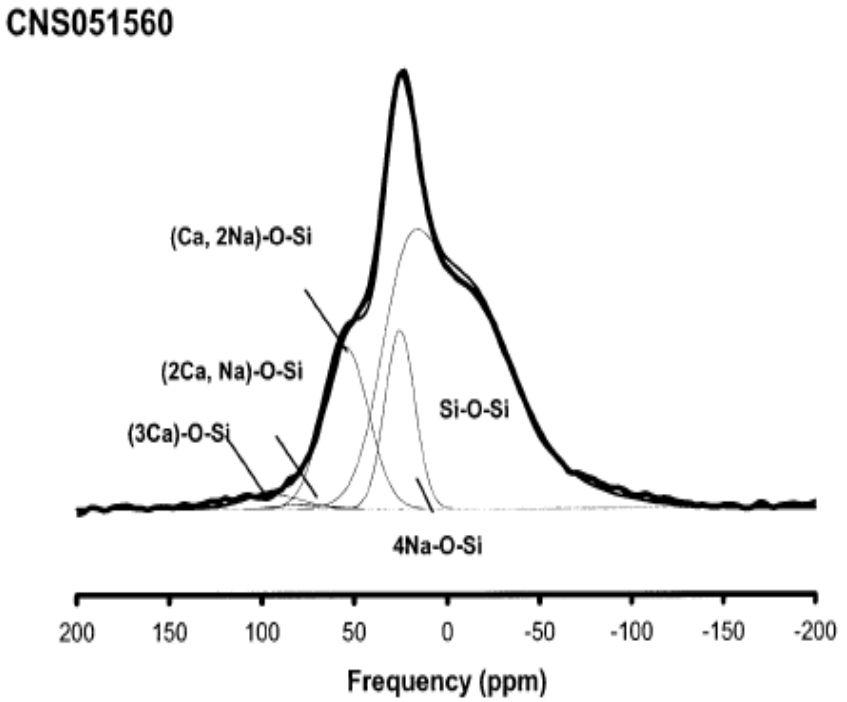


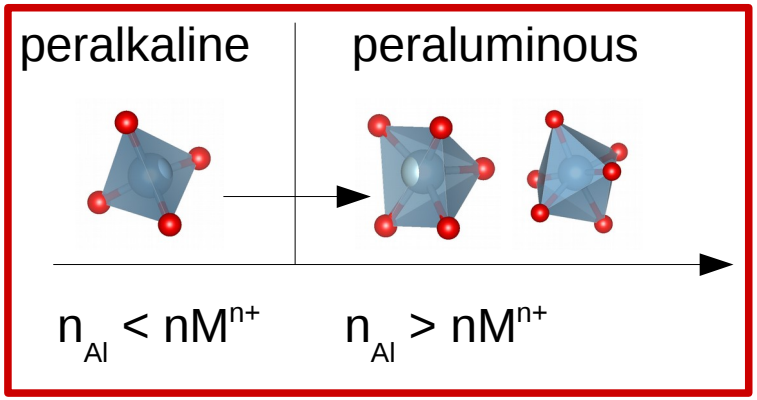
Figure 7. Fitting results of ^{17}O MAS NMR spectrum for CNS116 and CNS051560. Thick and thin lines refer to experimental and fitting results.

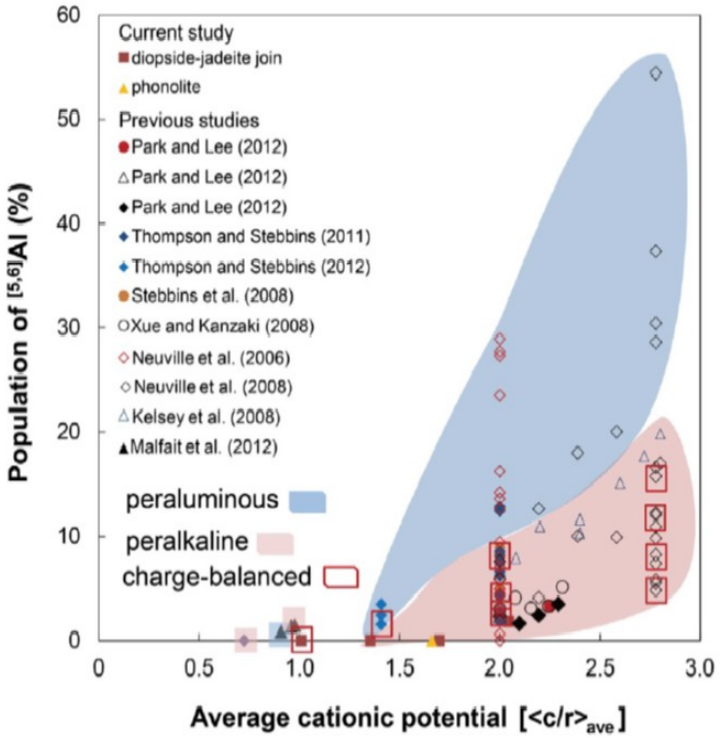
Nature of Cation Mixing and Ordering in Na-Ca Silicate Glasses and Melts, Sung Keun Lee and Jonathan F. Stebbins, *J. Phys. Chem. B* **2003,** *107,* 3141-3148

^{27}Al MQMAS NMR in aluminosilicate glasses : AlO_5

Structural of Aluminum

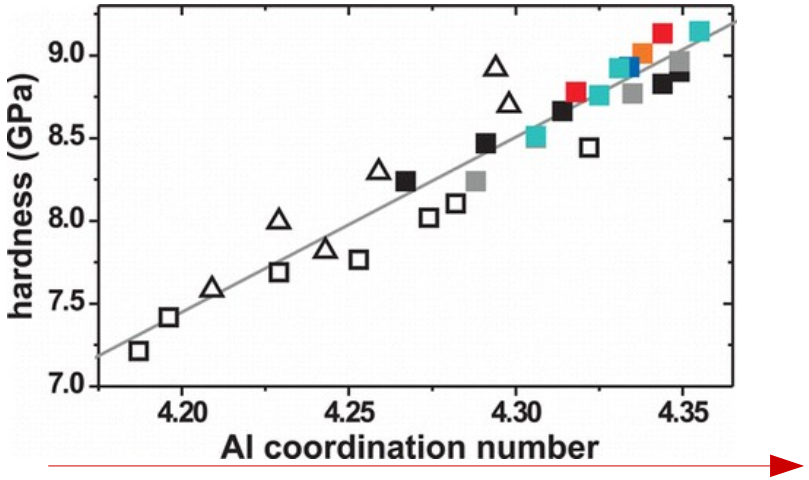
- ***AlO_4 : former (charge-balance needed)***
- ***AlO_5, AlO_6: modifier or charge compensator (still debated)***





S.K. Lee et al Geochimica et Cosmochimica Acta, 147, 2014, 26–42

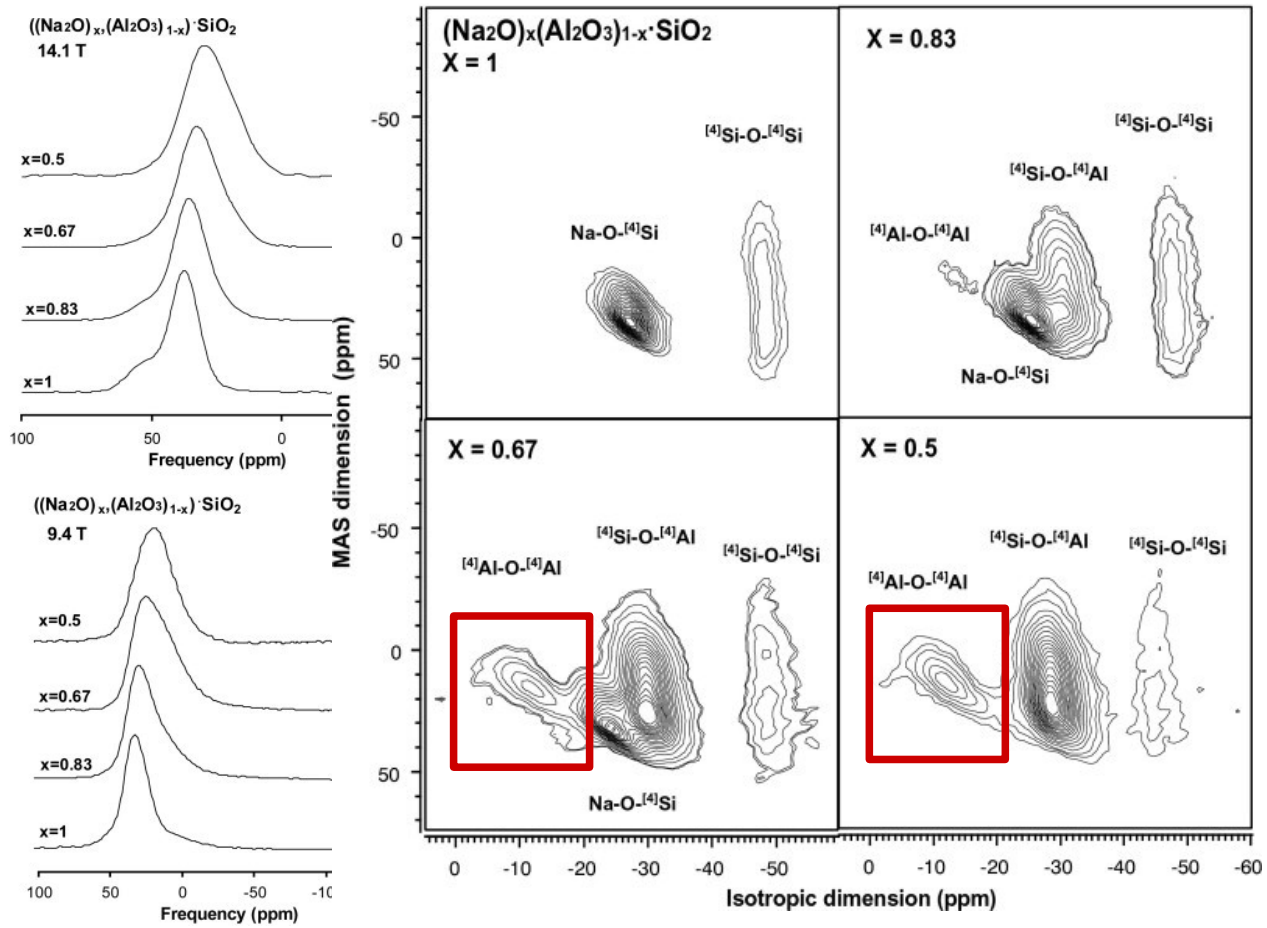
Strong correlation of hardness with Al coordination number in RE (Y, La, Lu, Sc) AluminoSilicate Glasses.

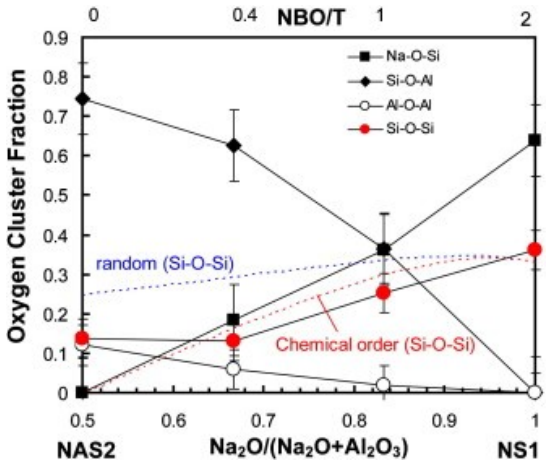


%AlO_5 increasing

D. Iftekhar et al ;J. Phys. Chem. C 2012, 116, 18194-18406

^{17}O MQMAS NMR in aluminosilicate glasses : Tri-coordinated Oxygen atoms

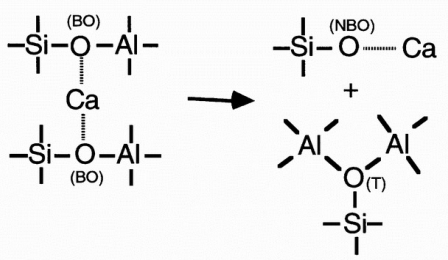




Strong chemical ordering (non-random T-O-T population) in sodium aluminosilicate glasses

Al-O-Al avoidance rule (which applies in crystalline systems) in partially violated in glasses

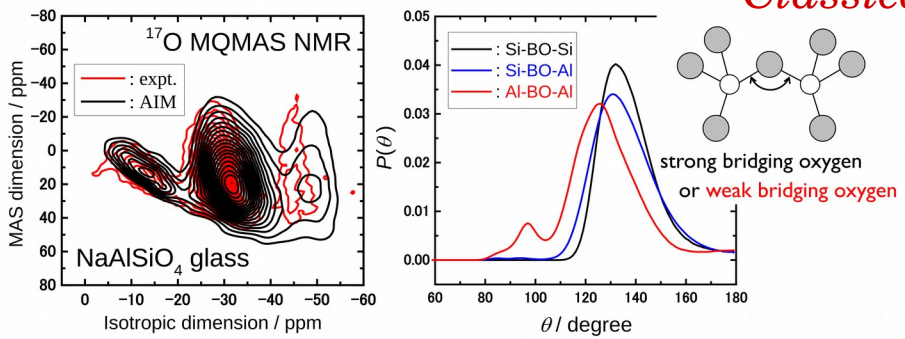
Role of Oxygen Triclusters ? (peaks unresolved in NMR)

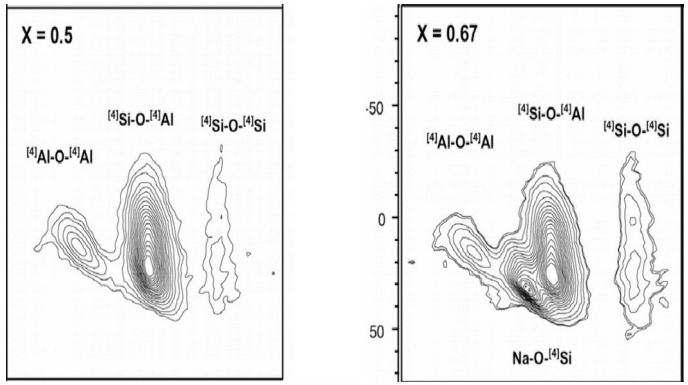


S.K. Lee, J.F. Stebbins, Geochimica et Cosmochimica Acta, Volume 73, 2009

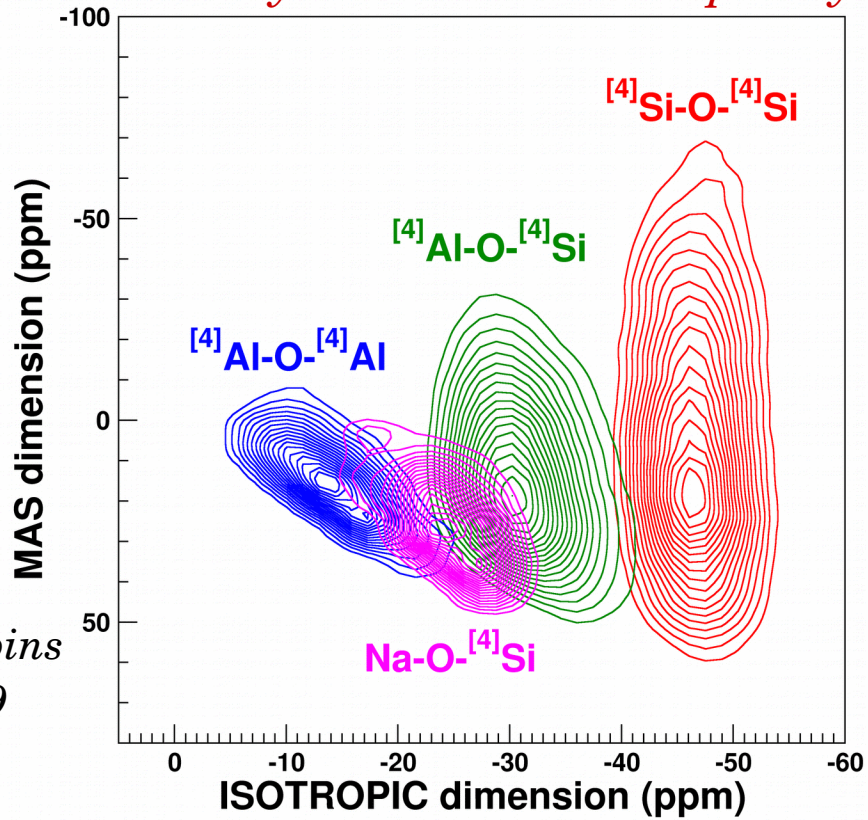
Aspherical Ionic Model (AIM) Polarisable force fields : MD with DFT quality Potentials

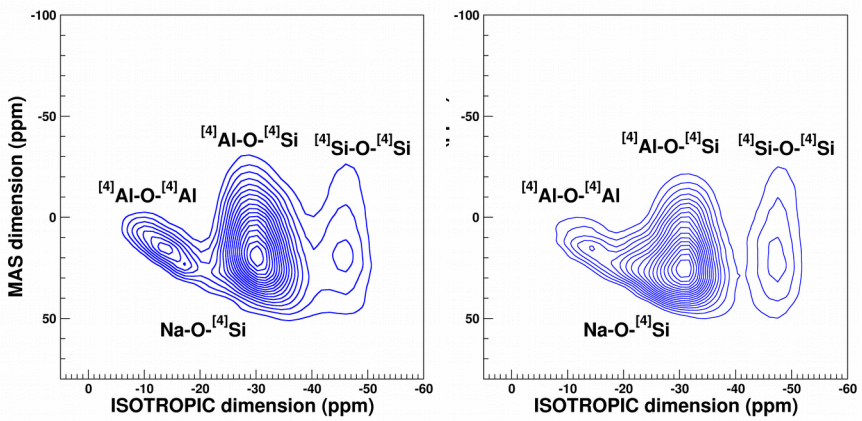
Classical Molecular Dynamics with DFT-quality





Lee, Stebbins et al. 2009





- *Polarisable Model + Aspherical Ionic Model (AIM) with parameters fitted to DFT calculations*
- *Yoshiki Ishii et al., J. Phys. Chem. C 2016.*

Thank you for your attention

29Si MAS NMR in borosilicate glasses : interpretation

Borosilicate glasses : Possible mis-interpretation of ^{29}Si MAS NMR

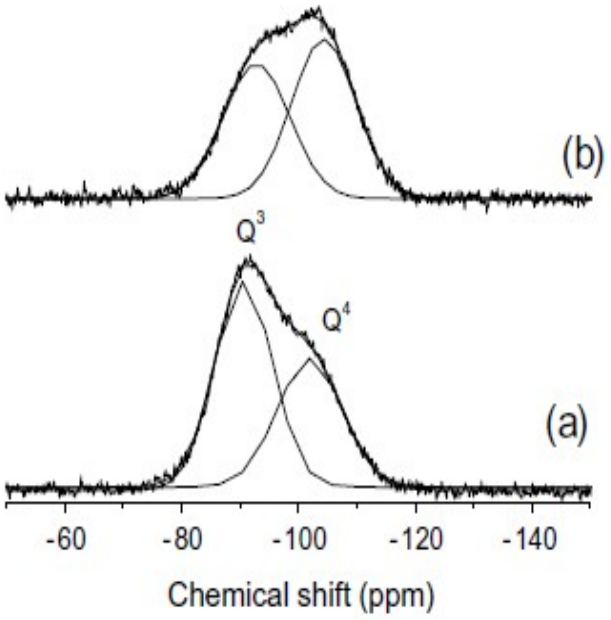
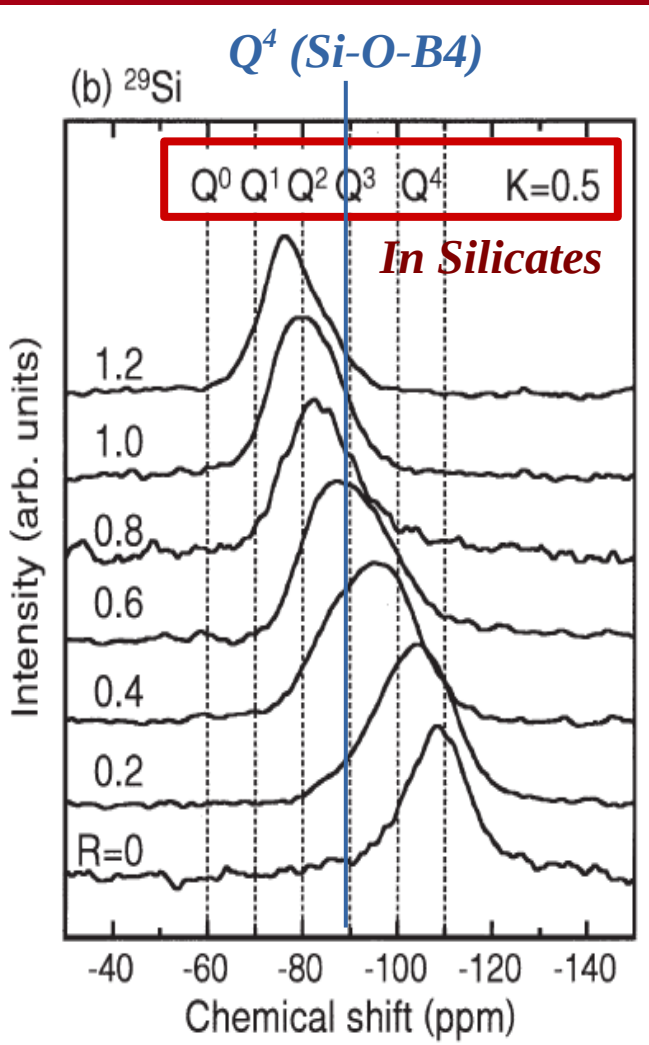
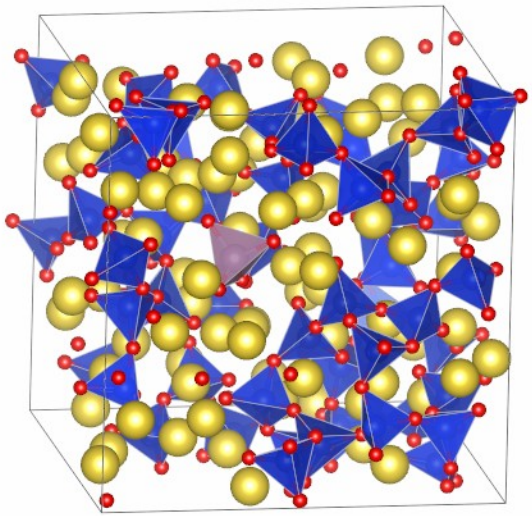


Fig. 1. ^{29}Si MAS NMR patterns for $(Na_2O)_{0.27-x}(K_2O)_{0.029}(B_2O_3)_x(SiO_2)_{0.69}(Al_2O_3)_{0.011}$ glasses (series I) with (a) $x = 0.05$ (b) $x = 0.10$ (c) $x = 0.15$, (d) $x = 0.17$, (e) 0.20 and (f) $x = 0.22$.

Structural studies on boroaluminosilicate glasses
Jayshree Ramkumar a, V. Sudarsan b, S. Chandramouleeswaran a, V.K. Shrikhande c, G.P. Kothiyal c, P.V. Ravindran a, S.K. Kulshreshtha b, T. Mukherjee**Journal of Non-Crystalline Solids 354 (2008) 1591–1597**

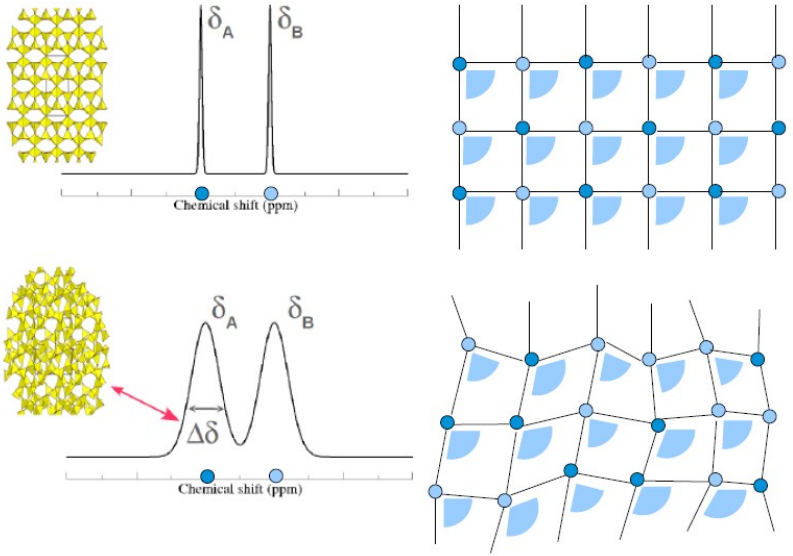


A theoretical interpretation of the chemical shift of ^{29}Si NMR peaks in alkali borosilicate glasses, TOKURO NANBA,* MITSUNORI NISHIMURA, and YOSHINARI MIURA, Geochimica et Cosmochimica Acta, Vol. 68, No. 24, pp. 5103–5111, 2004



Perspectives :
Modelling NMR from first-principles

Combining MD simulations with DFT NMR calculations

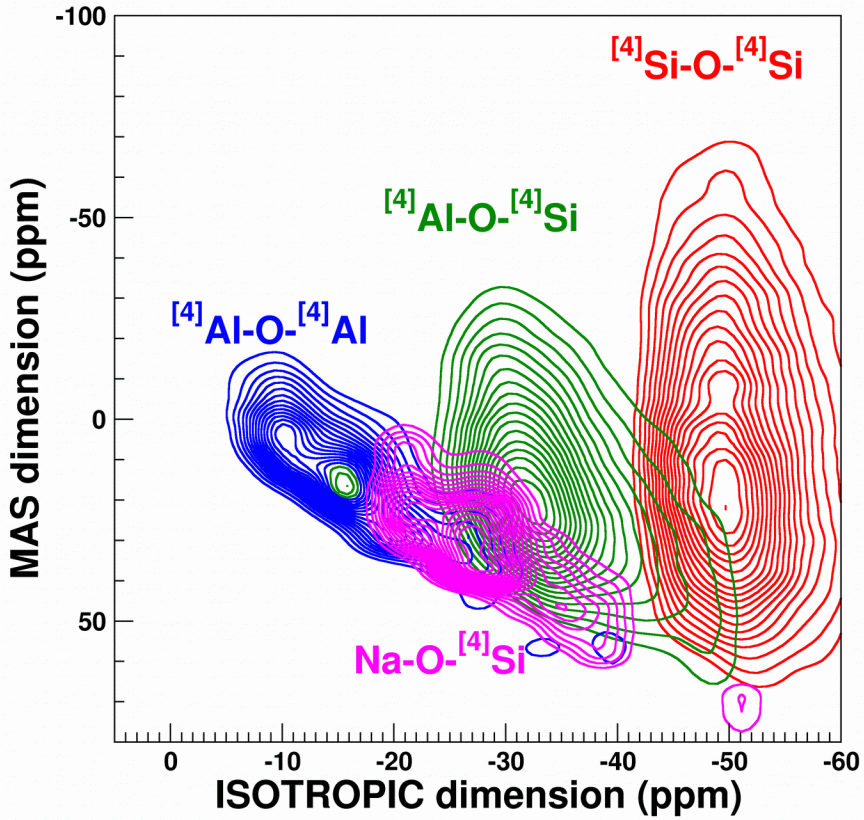


- MD simulations can (now) be compared to NMR experiments
- Effect of structural and chemical disorder on NMR
- NMR / structure (bond angle, distance, . . .) relationships

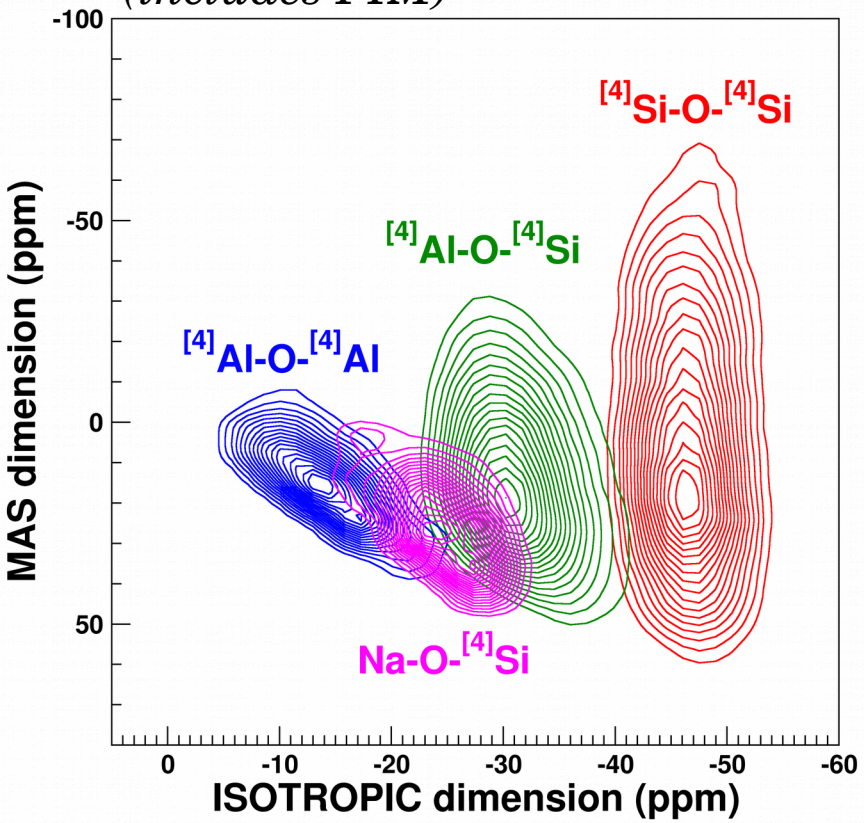
Towards an Integrated NMR Computational Approach

MD : DFT quality Potentials

Polarisable Model : PIM MD



Aspherical Ionic Model : AIM MD (includes PIM)

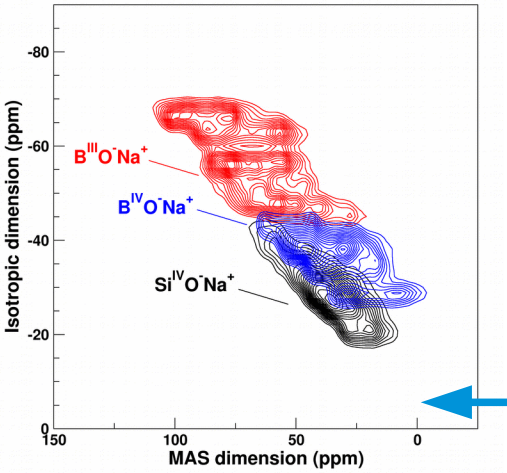


- *Most of Force fields produce too broad NMR (^{17}O)*
- *AIM MD seems to properly reproduce the width of ^{17}O NMR lines (related to narrow Bond Angle Distribution, except for Al-O-Al)*

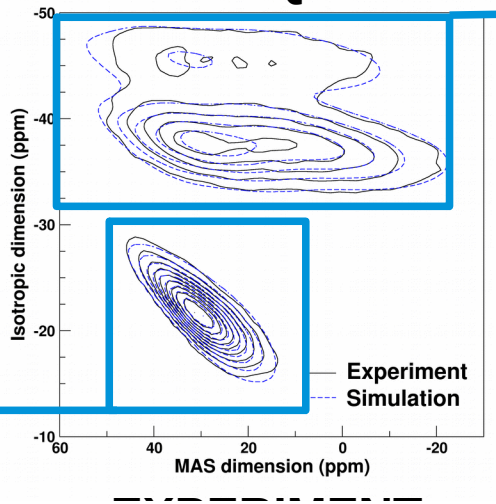
Y. Ishii et al. Submitted.

MD-GIPAW of borosilicates

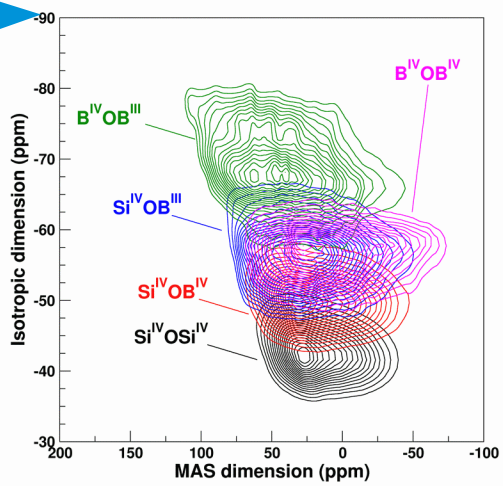
THEORY : MD-GIPAW



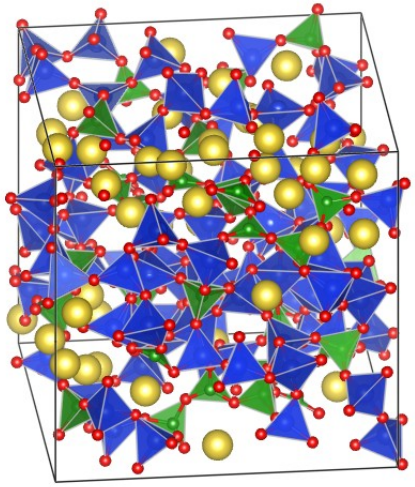
EXPERIMENT 17O MQMAS NMR



THEORY : MD-GIPAW



THEORY : MD



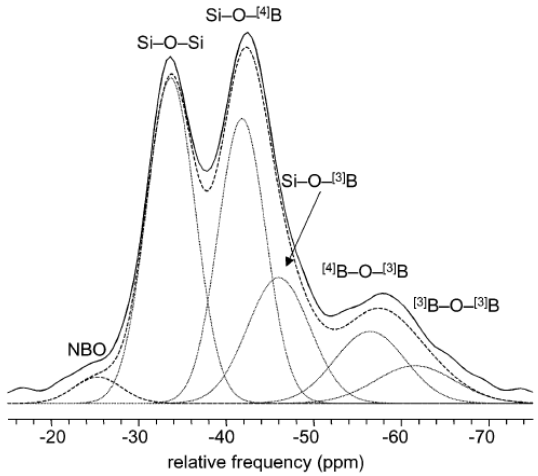
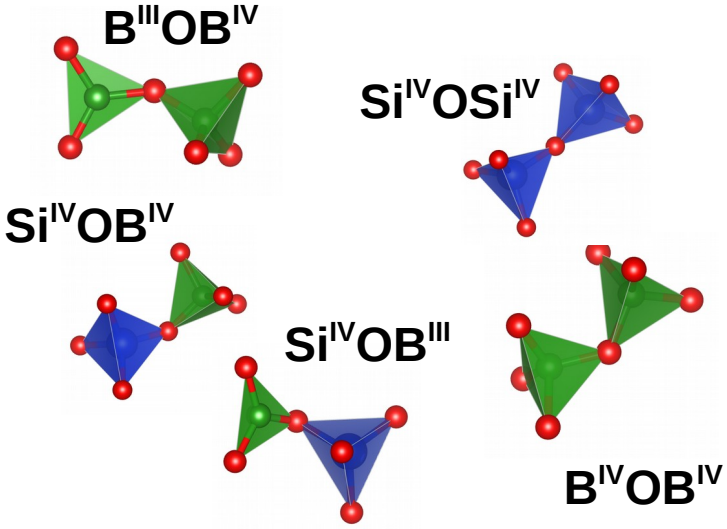
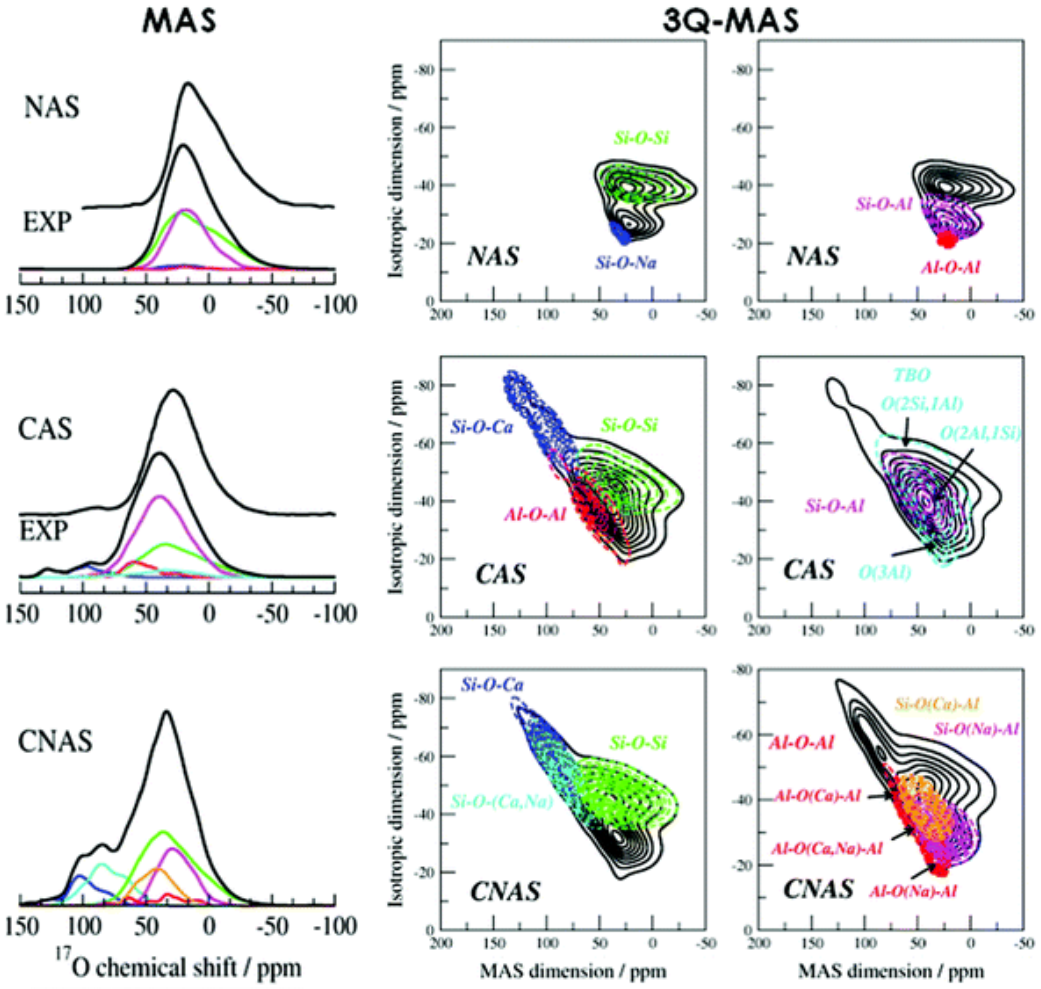


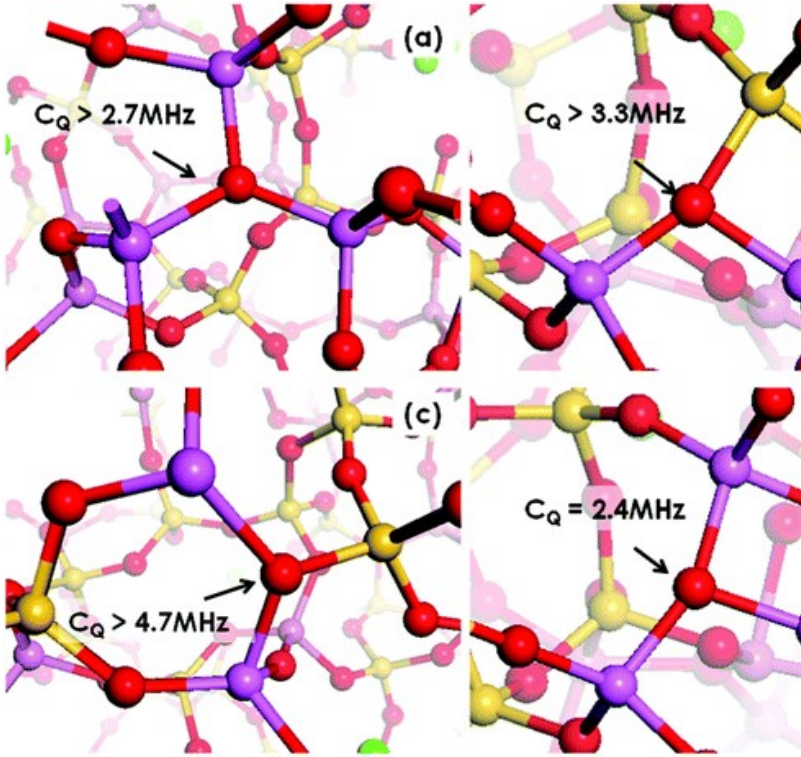
Figure 7. Experimental ^{17}O isotropic projection (solid line) and typical fitting results (dashed line, sum; dotted lines, components) for NK–BS glass. Fit parameters are given in Table 3.

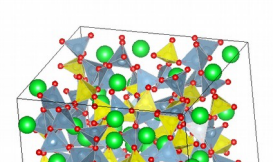


Combining DFT-NMR with MD simulations

NMR parameters can be calculated with DFT (GIPAW Method)







Data interpretation

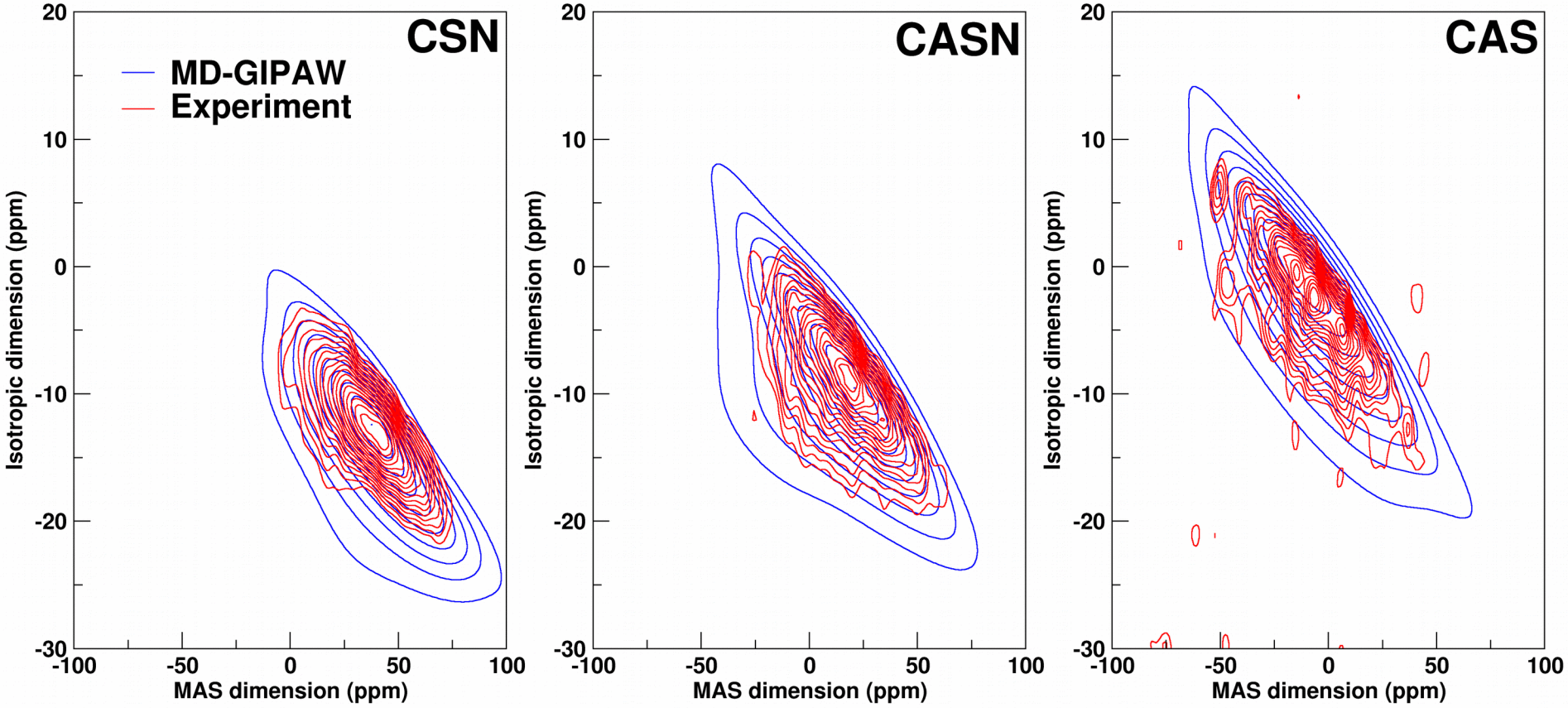
Relationships between NMR and local structure : extraction of the structural information underlying the NMR parameter

^{43}Ca MQMAS NMR in Aluminosilicates

$60SiO_2$-$20Na_2O$-$20CaO$

$60SiO_2$-$10Al_2O_3$ -$10Na_2O$-$10CaO$

$60SiO_2$-$20Al_2O_3$-$20CaO$



Shell-model MD in SiO_2-Al_2O_3-CaO-Na_2O

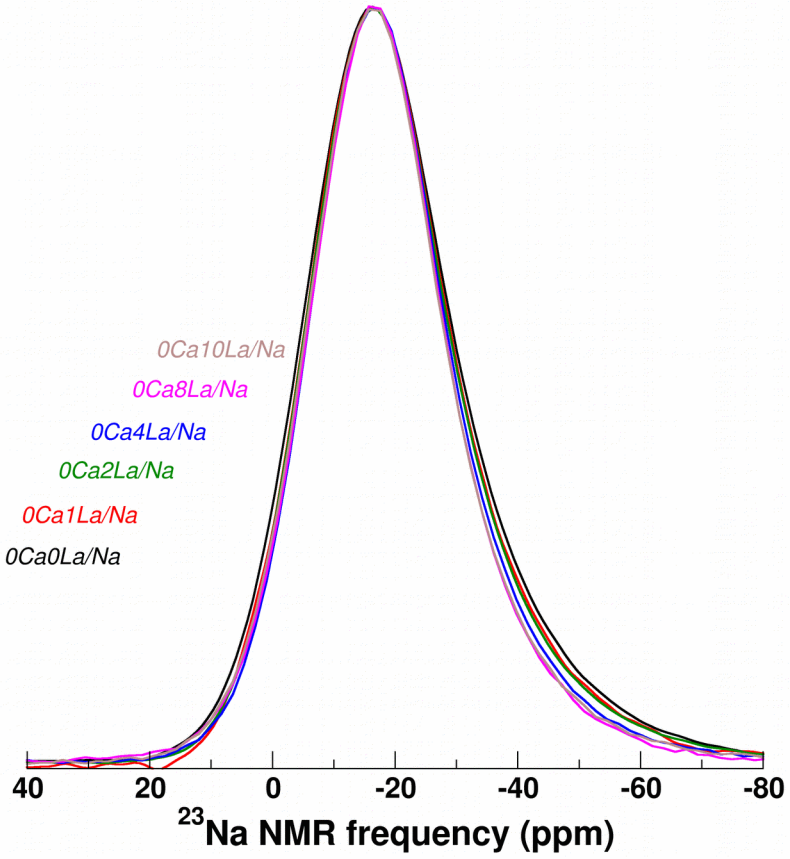
E. Gambuzzi et al. Solid state NMR 2015

Binary borosilicate glasses

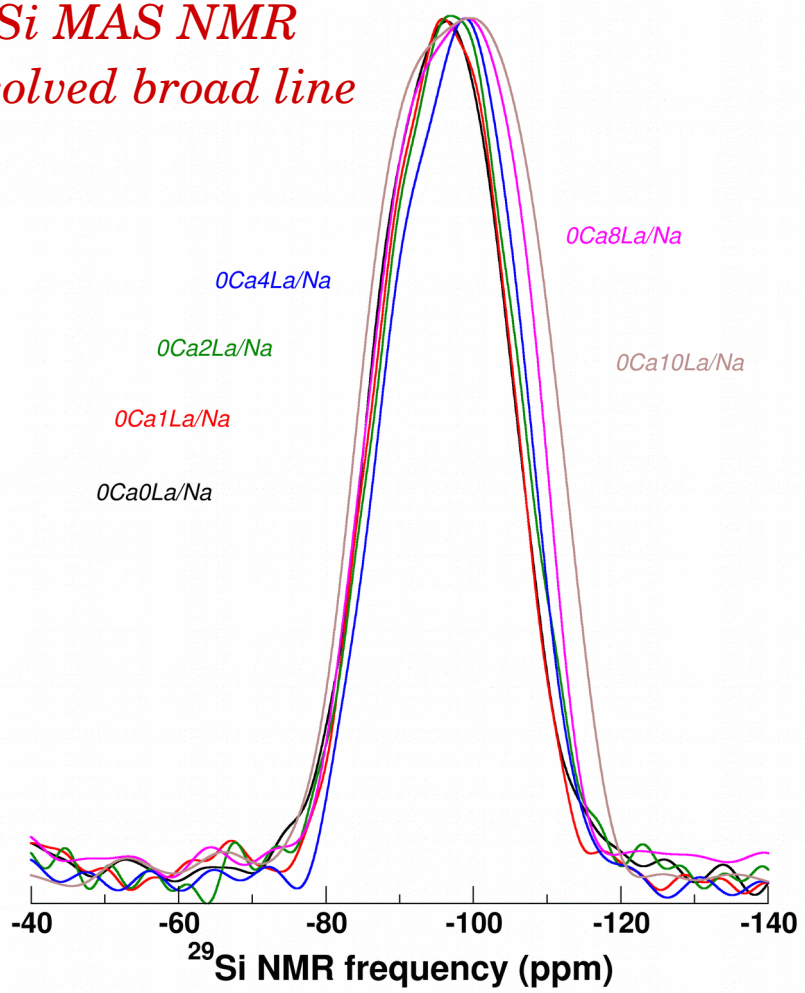
Incorporation of Lanthanum in borosilicate glasses
^{23}Na and ^{29}Si MAS NMR

$$60\ SiO_2 - 18\ B_2O_3 - (20 - x)\ Na_2O - x\ \{La_2O_3\ or\ CaO\}$$

23Na MAS NMR is much less informative

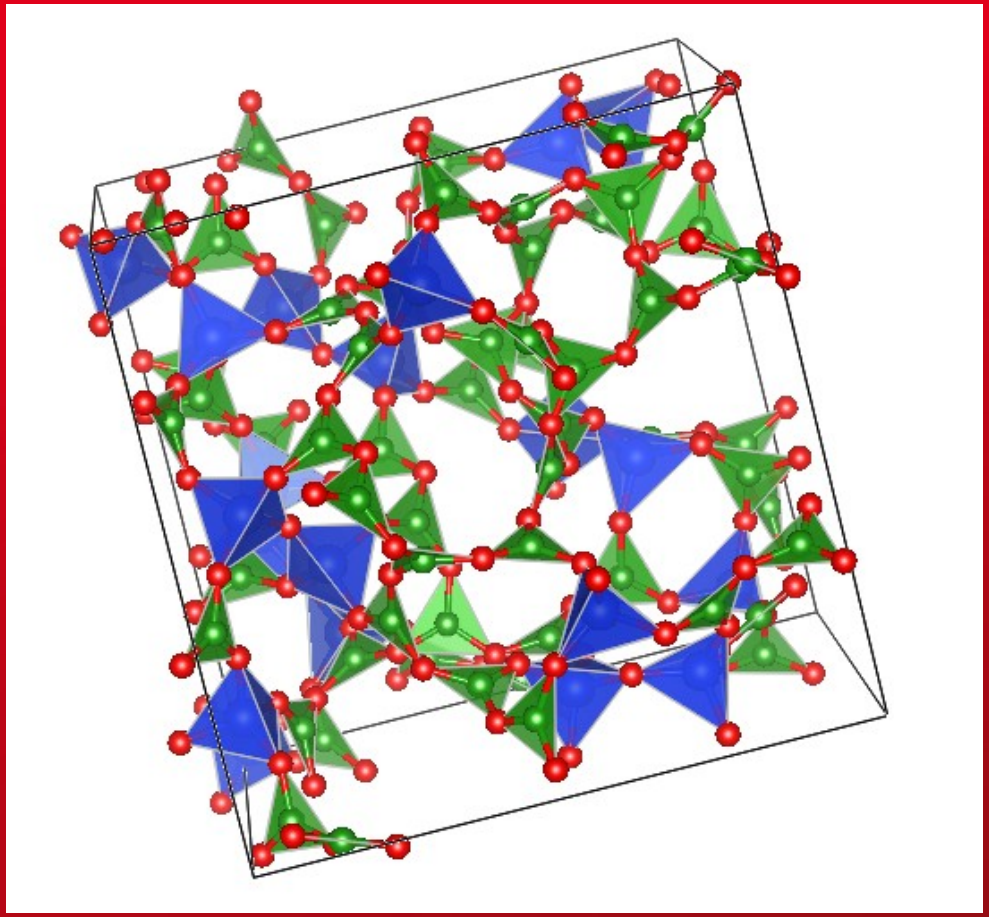


29Si MAS NMR unresolved broad line

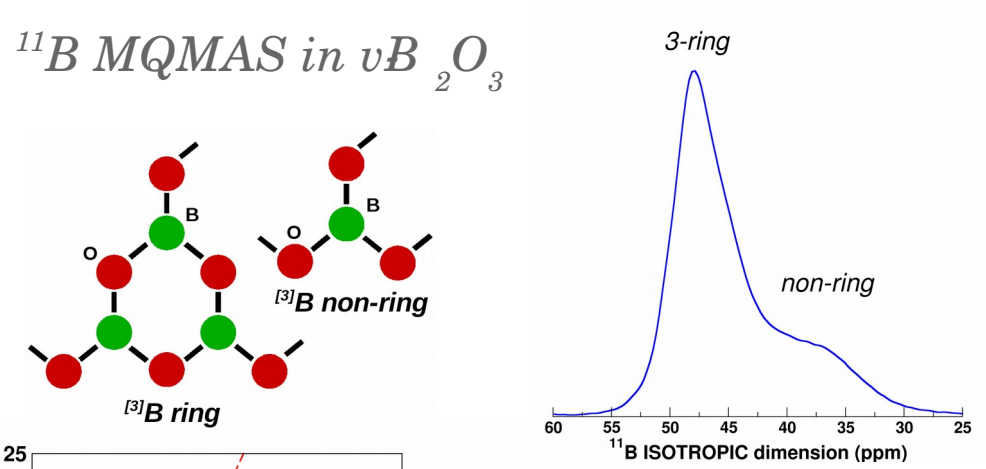


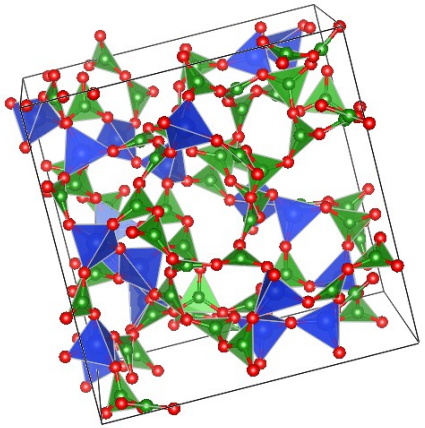
F. Angeli, T. Charpentier et al., JNCS 2013

Lanthanum in borosilicate glasses



Si/B Mixing in binary SiO_2/B_2O_3





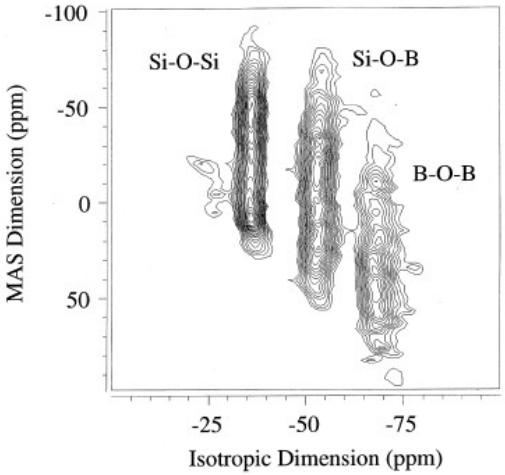


Fig. 2. Two-dimensional ^{17}O-MQMAS spectrum of borosilicate glass with 40 mol% of B_2O_3 and 60 mol% of SiO_2.

On the structure of borosilicate glasses : a triple-quantum magic-angle spinning ^{17}O nuclear magnetic resonance study, S. Wang et al. J. Non-Cryst. Solids 231, 286 (1998).

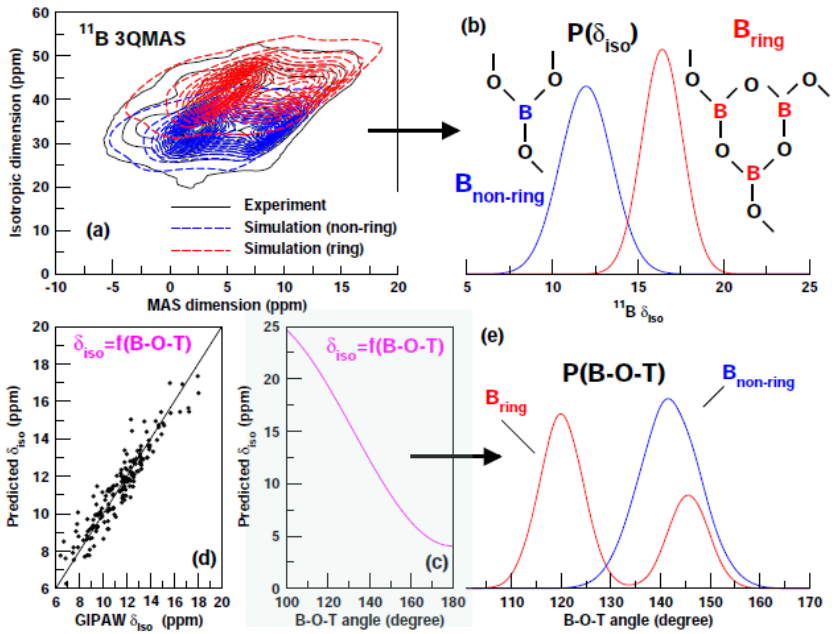
Topological Disorder and Reactivity of Borosilicate Glasses: Quantum Chemical Calculations and 17 O and 11 B NMR Study S. K. Lee et al., J. Phys. Chem. B 2001, 105, 12583-12595

MD-GIPAW : towards *NMR structural* inversion (^{11}B)

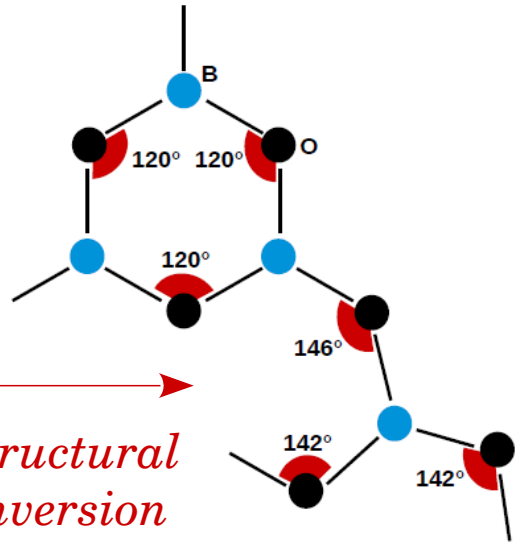
Reconstructing the Bond Angle Distribution (*P*BAD)

Improved Analysis of NMR data

Improved Interpretation of NMR parameters



Structural Inversion



Magn. Reson. Chem. 48 2010

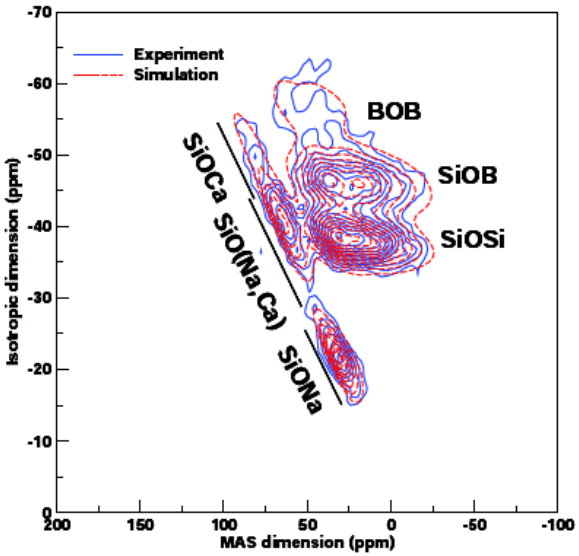
- Vitreous SiO_2-B_2O_3 system
- ^{11}B NMR parameter distribution of BO_3 units
- ^{11}B NMR (δ_{iso}) vs B-O-(B,Si) bond angles
- model: $\delta_{iso} = \sum_k F_k(\theta_k)$: j specie $p_j(\delta_{iso})$ inversion $\Rightarrow p_j(\theta)$

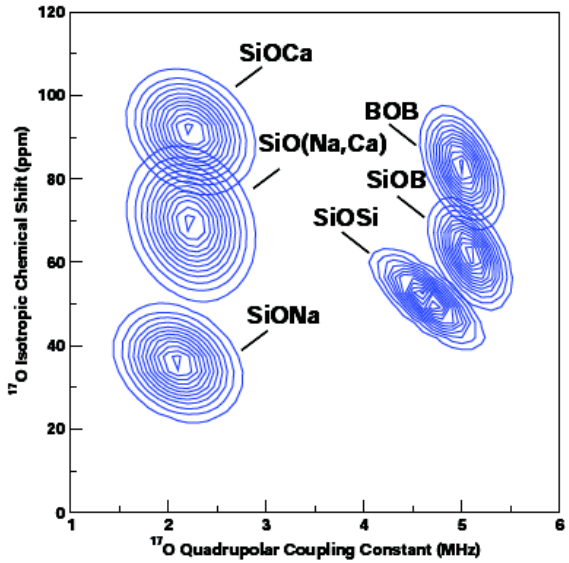
Soleilhavoup et al. Magn. Reson. Chem. 2010

Quantification of ^{17}O MQMAS NMR spectra

^{17}O MAS & MQMAS NMR : modeling and Quantification

60.4 SiO_2 - 15.3 B_2O_3 - 19 Na_2O - 5.2 CaO



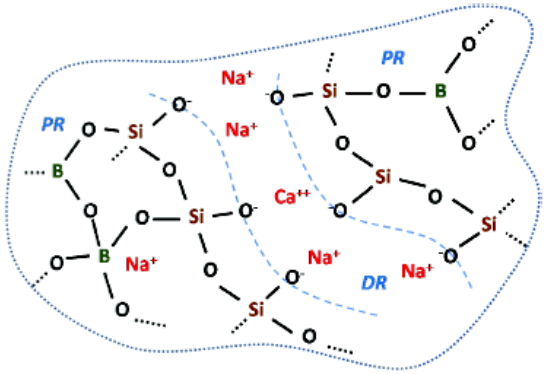


Si/B random mixing

	Theory	^{17}O
Si-O-Si	34.1	35.6
Si-O-B	42.1	42.8
B-O-B	13.0	11.3
NBO	10.8	10.2

- Data in agreement with Si/B random mixing
- Evidence of Na/Ca mixing in depolymerized regions (DR)
- Ca is modifier (^{11}B NMR: $BO_4^- \rightarrow BO_3$)

J. Am. Ceram. Soc **93** 2010; J. Non Cryst. Solids **354** 2008



Coll. F. Angeli, P. Jollivet, CEA/DEN

^{43}Ca MAS NMR in aluminosilicate glasses

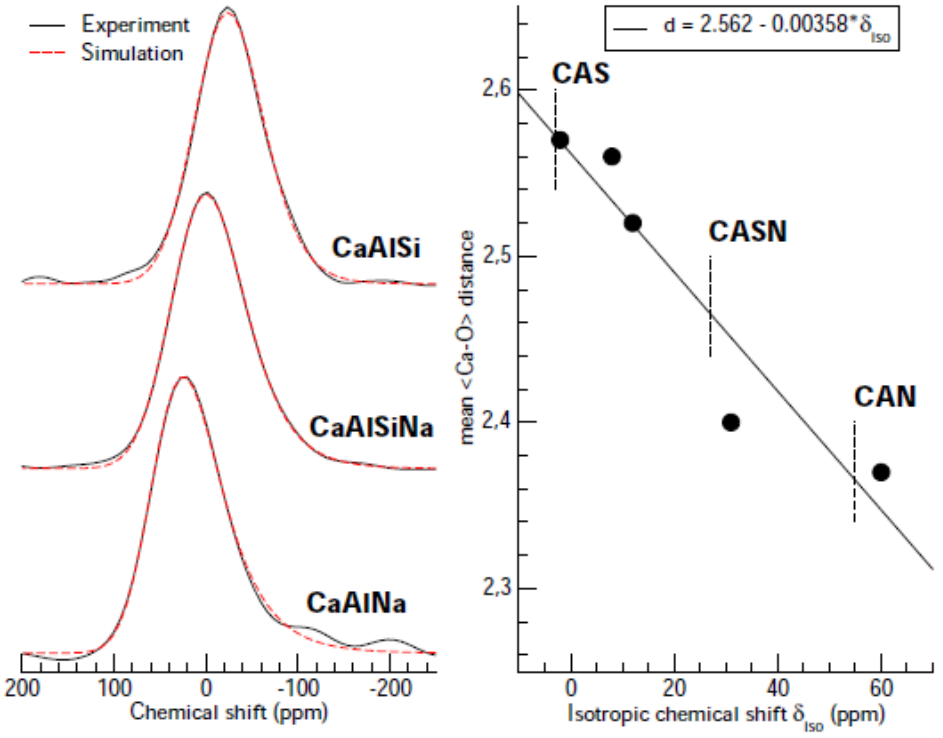
^{23}Ca MAS NMR in aluminosilicate glasses

Broad MAS NMR spectra of cation (^{23}Na, ^{43}Ca)

High disorder in first-coordination sphere

Analysis with NMR parameter distribution

See Angeli et al. Chem. Phys Lett. 2007

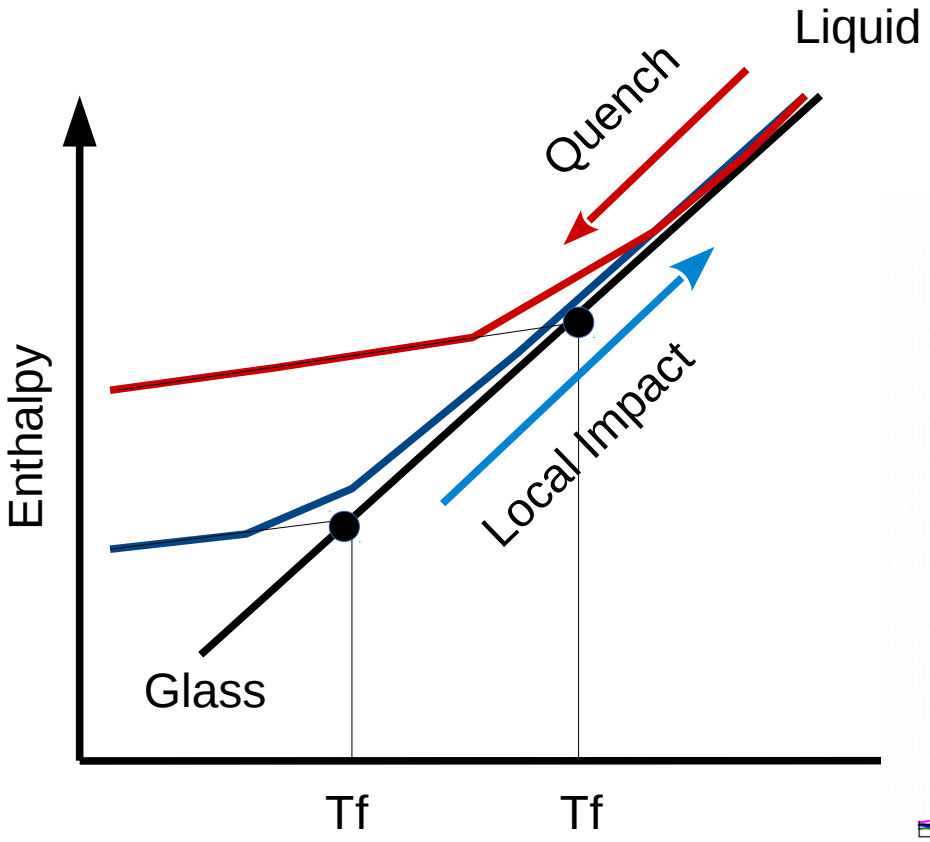


⇒ Exploring Ca environement in vitreous borosilicates . . .

Similarly to ^{23}Na, ^{43}Ca isotropic chemical shift is sensitive to the mean <Ca-O> distance.

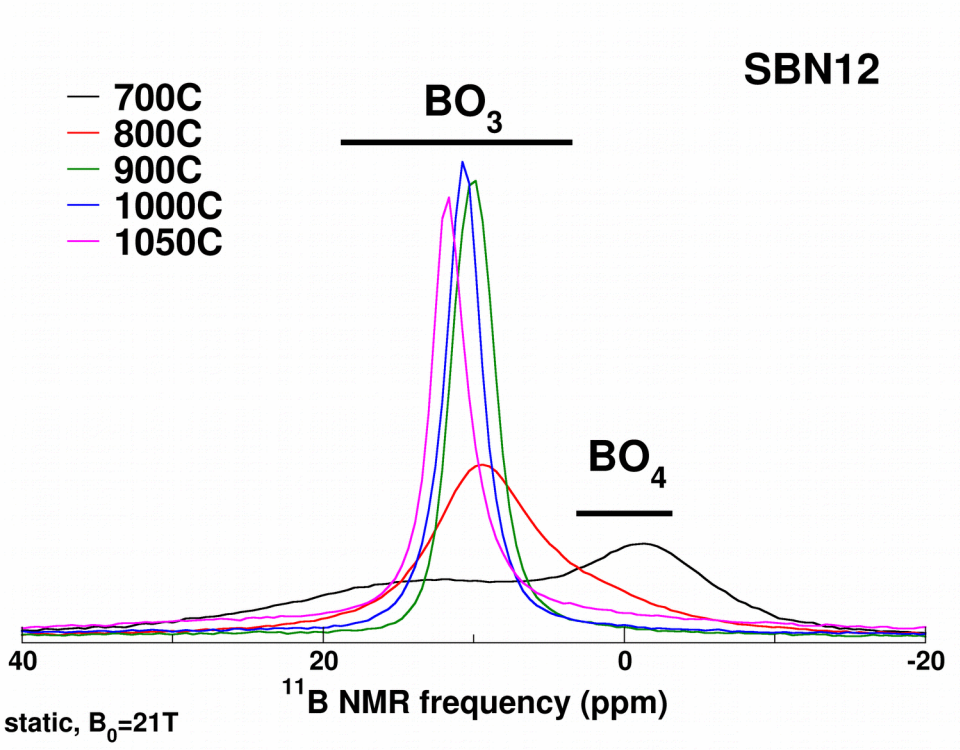
High Temperature NMR

Irradiated glasses : NMR & fast melt-quenched events



Tf : fictive temperature

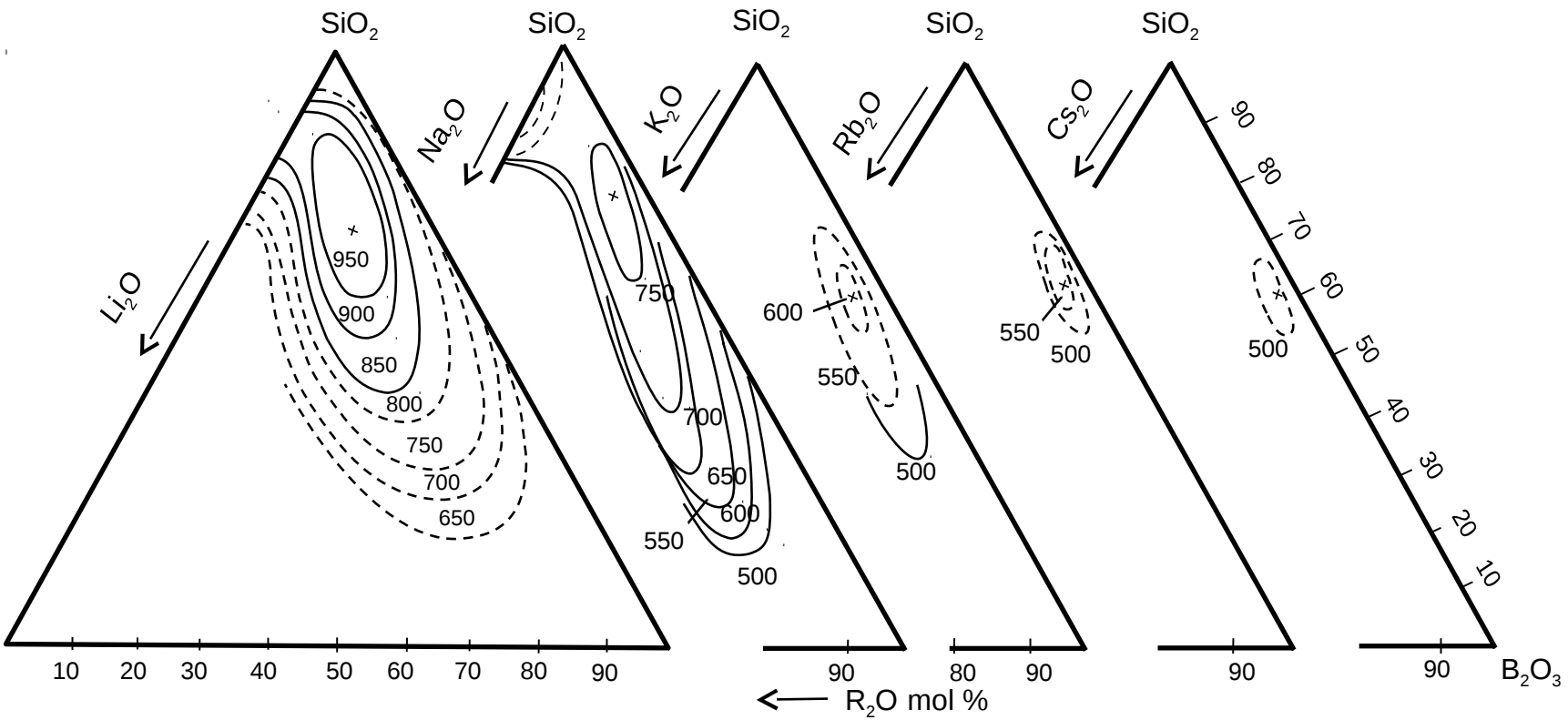
At high temperature, in the melt, BO_3 is the favored configuration for boron.



High Temperature NMR, CNRS CEMTHI Orléans
Coll. J.M. Delaye, F. Pacaud

Demixion in borosilicate glasses

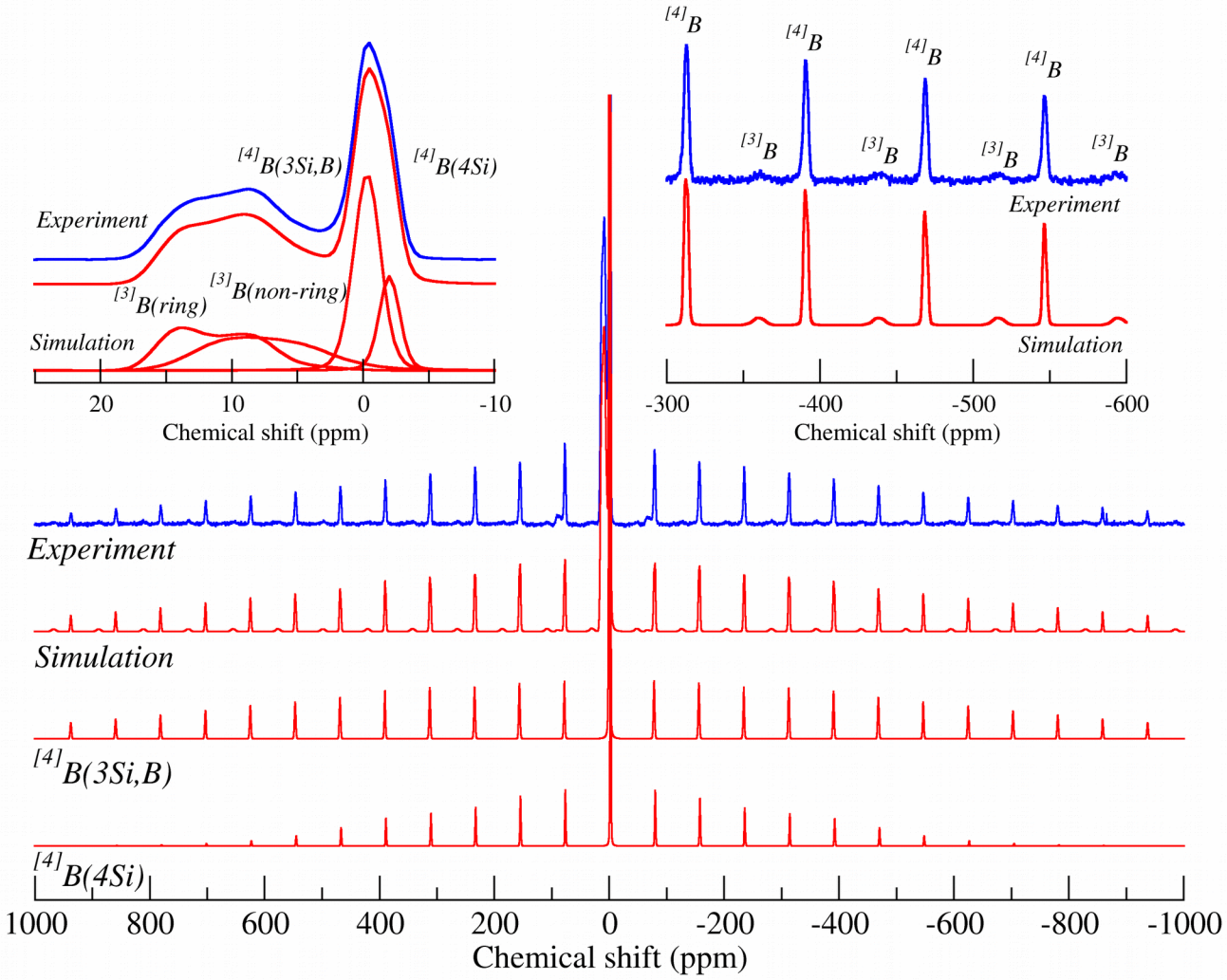
Demixion in borosilicate glasses



Courstesy of S. Schuller, CEA DEN.

More borosilicate glasses

^{11}B MAS NMR

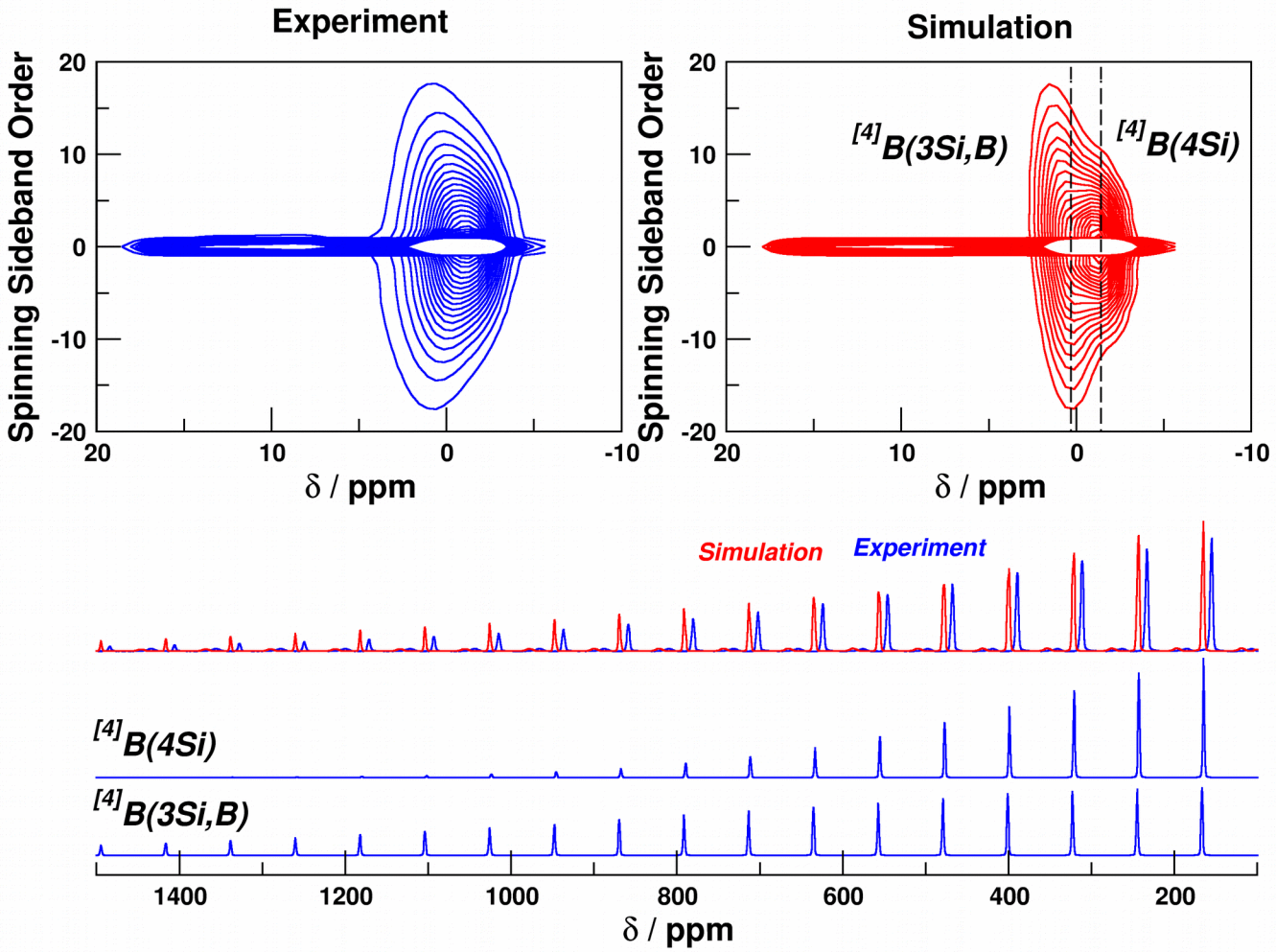


See F. Angeli et al., JACerS 93 (2010)

BORON-11 MAS NMR : TOP ANALYSIS

***TOP** : **T**WO-DIMENSIONAL **O**NE **P**ULSE*

BO_4 lines (CT+ST) well described by a Czjzeck distribution of the EFG (Gaussian Isotropic Model)



See F. Angeli et al., JACerS 93 (2010) & J. Hopt et al. GCA 181 (2016)

SUPERSTRUCTURAL UNITS IN BORATE

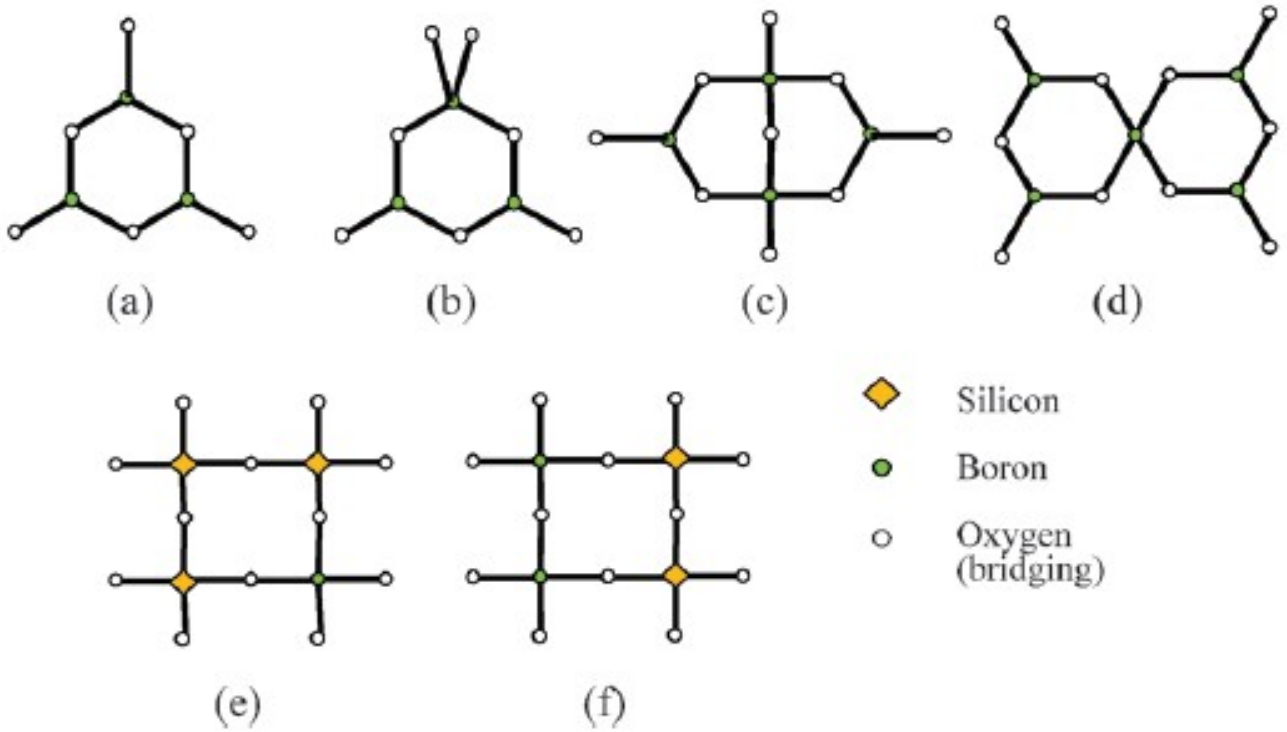


Fig. 1 Two dimensional representation of the superstructural units predicted to be present in Pyrex® using the Model of Associated Solutions: (a) boroxol; (b) triborate; (c) diborate; (d) pentaborate; (e) reedmergnerite; (f) danburite.