The Structure of Glass - Lecture 13: Nuclear Magnetic Resonance Spectroscopy of Glass Structure: Practice and Application of Dipolar Nuclei

Be able to predict alkali silicate glass structures from ^{29}Si MASS-NMR spectra

Be able to predict alkali phosphate glass structure from ^{31}P MASS NMR Spectra

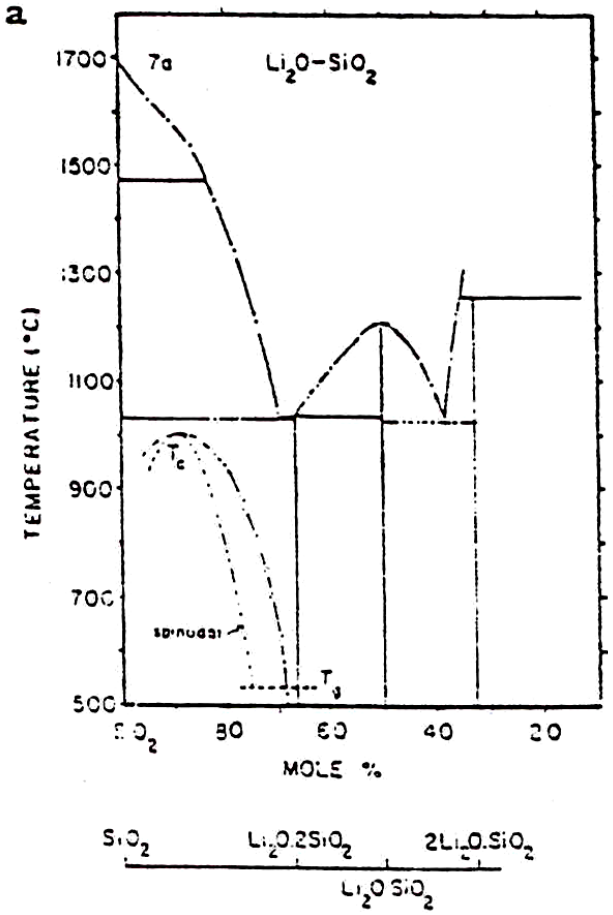
Be able to use ^{29}Si MASS NMR spectra to examine the glass structure of mixed glass former $M_2O + B_2O_3 + SiO_2$

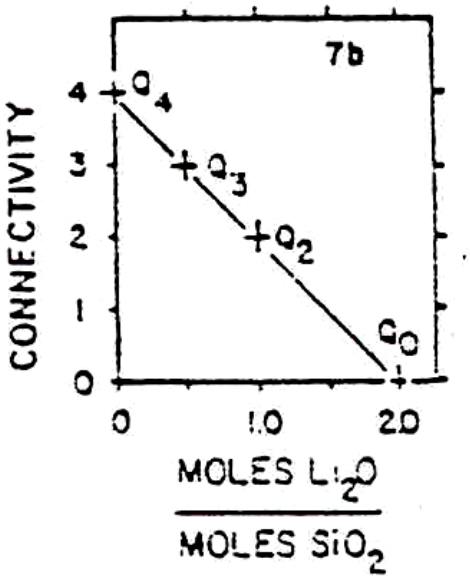
Be able to use ^{31}P MASS NMR spectra to examine the glass structure of mixed glass former $M_2O + SiO_2 + P_2O_5$

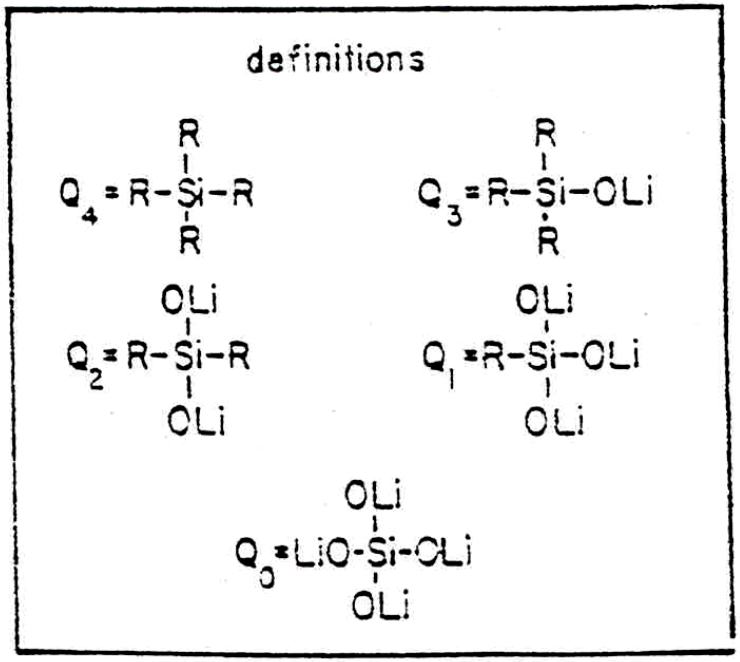
Be able to use ^{29}Si MASS NMR spectra to examine the glass structure of $M_2O + Al_2O_3 + SiO_2$

Application to Alkali Silicate Minerals - ^{29}Si MASS NMR

- ^{29}Si MASS NMR, spin ½, 4.5 % atomic abundance,





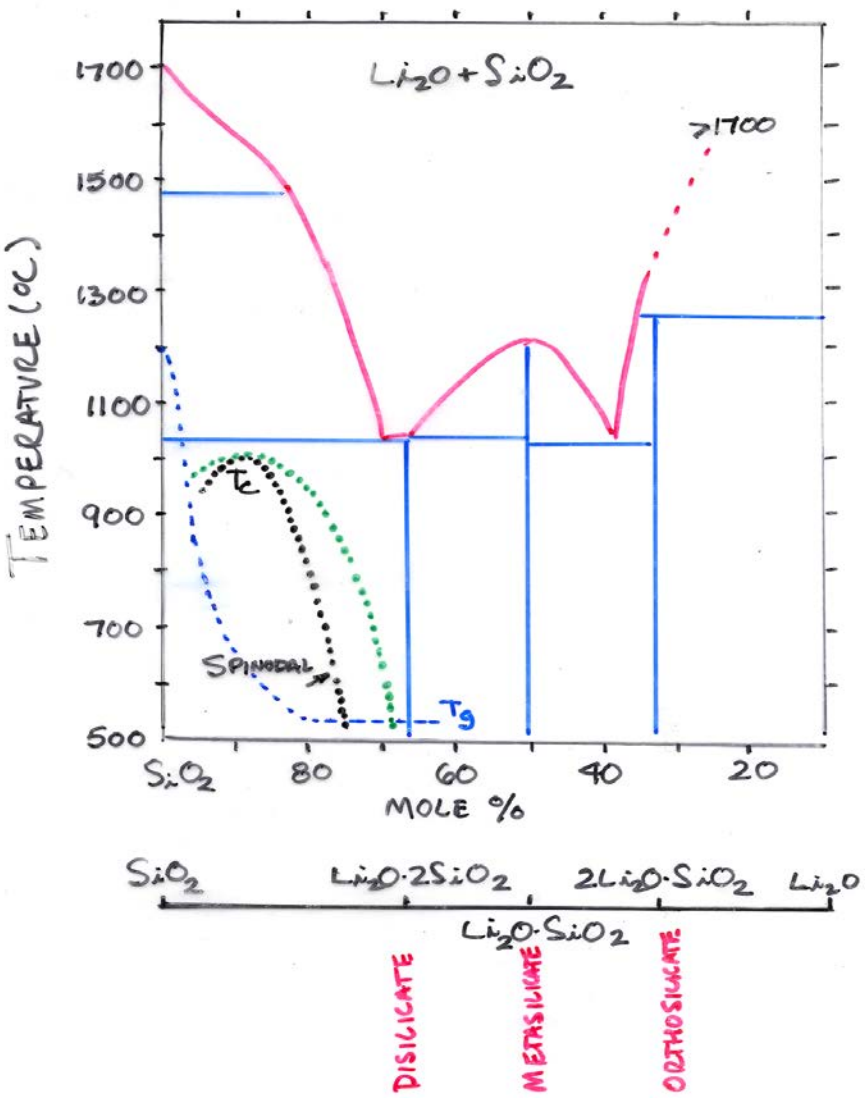


Quiz…

- For the different Q groups in $M_2O + SiO_2$
  - Write out the Chemical formula
  - Draw out the chemical structure
  - Calculate the mole fraction of M_2O
  - Calculate the fraction of bridging and non-bridging oxygens

Alkali Silicate Phase Diagram

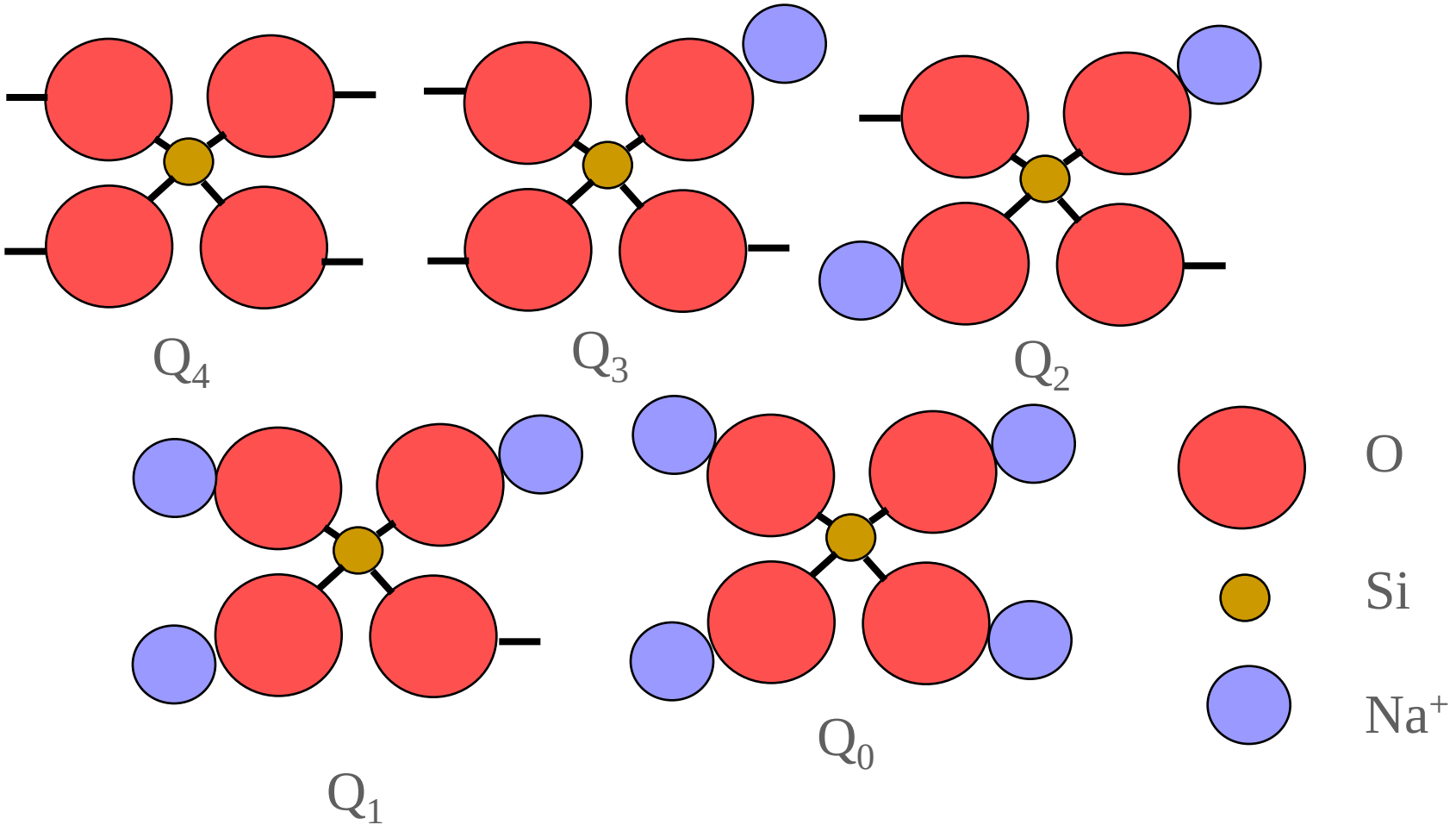
- Compounds are formed at stoichiometric ratios of M_2O to SiO_2
- Disilicate is $M_2O + 2SiO_2$
- Metasilicate is $M_2O + SiO_2$
- Orthosilicate is $2M_2O + SiO_2$
- From composition, write out SRS for each phase
- From Zacharaisen's Rules, which do you expect to be glass forming, which do you expect not to be?



Alkali Silicate Glasses Reflect Local SRS Units

- Pure SiO_2 is made of $SiO_{4/2}$ units
  - Q_4 units with all "bridging" oxygens
- $Na_2O + 2SiO_2$ is made of $NaOSiO_{3/2}$ units
  - Q_3 units with one "non-bridging" and three bridging oxygens
- $Na_2O + SiO_2$ is made of $(NaO)_2SiO_{2/2}$
  - Q_2 units with two non-bridging and two bridging oxygens
- $3Na_2O + 2SiO_2$ is made of $(NaO)_3SiO_{1/2}$ units
  - Q_1 units with three non-bridging oxygens and one bridging oxygens
- $2Na_2O + SiO_2$ is made of $(NaO)_4Si$ units
  - Q_0 units with four non-bridging and no bridging oxygens
- Alkaline earth silicates ($MO + SiO_2$) behave similarly

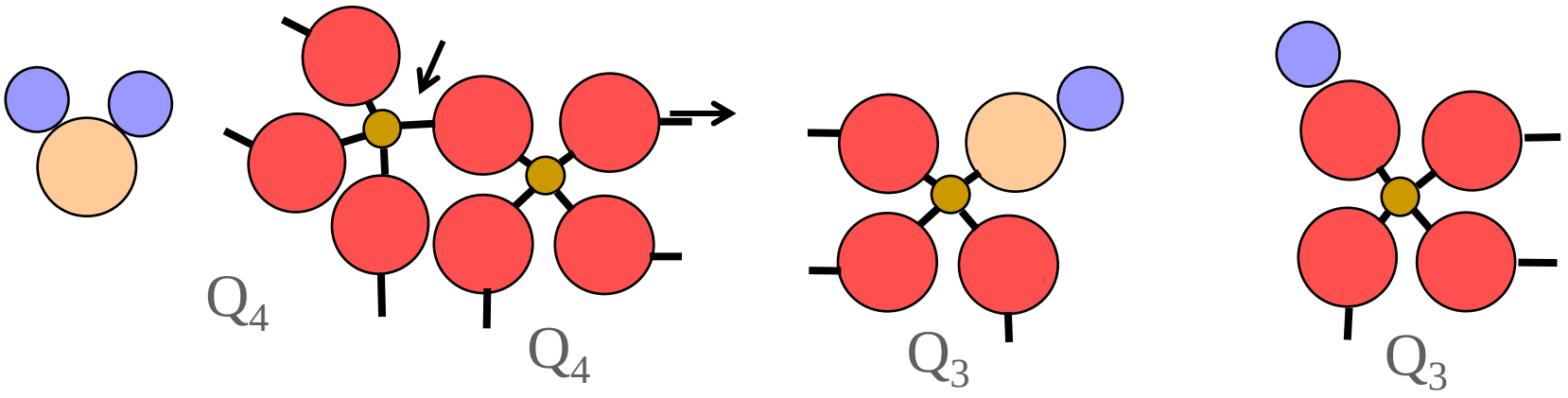
"Q_i" Units in Alkali Silicate Glasses



Calculating the Fraction of Non-Bridging Oxygens

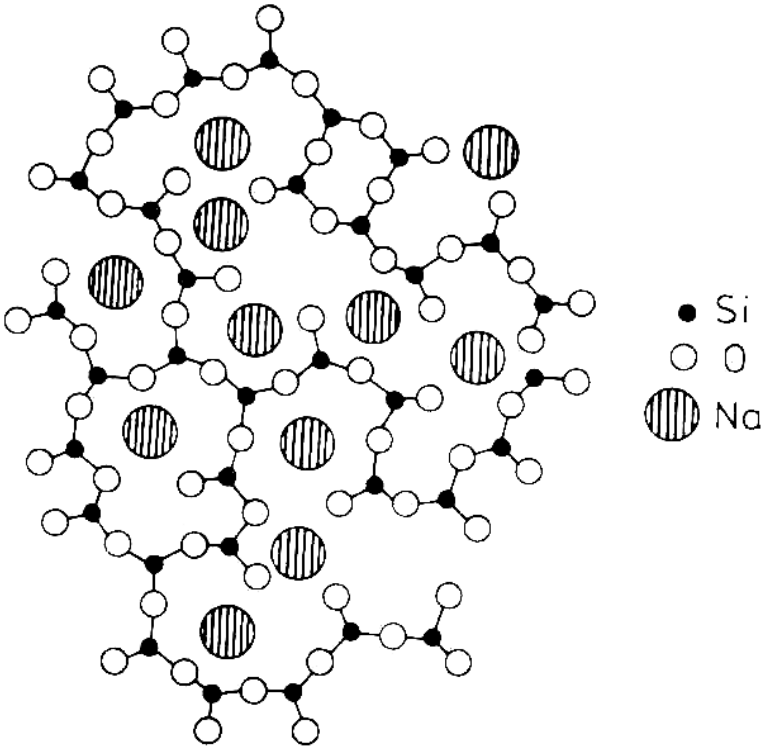
- Modifier M_2O or MO creates two NBOs per M_2O or MO added
- $xNa_2O + (1-x)SiO_2$ creates 2x NBOs
- f_{NBO} = NBOs/(NBOs + BOs)

  $= 2x/(x + 2(1-x)) = 2x/(2-x)$
- $f_{BO} = 1 - f_{NBO}$
- Calculate knob & f_{BO} for all the alkali silicate phases



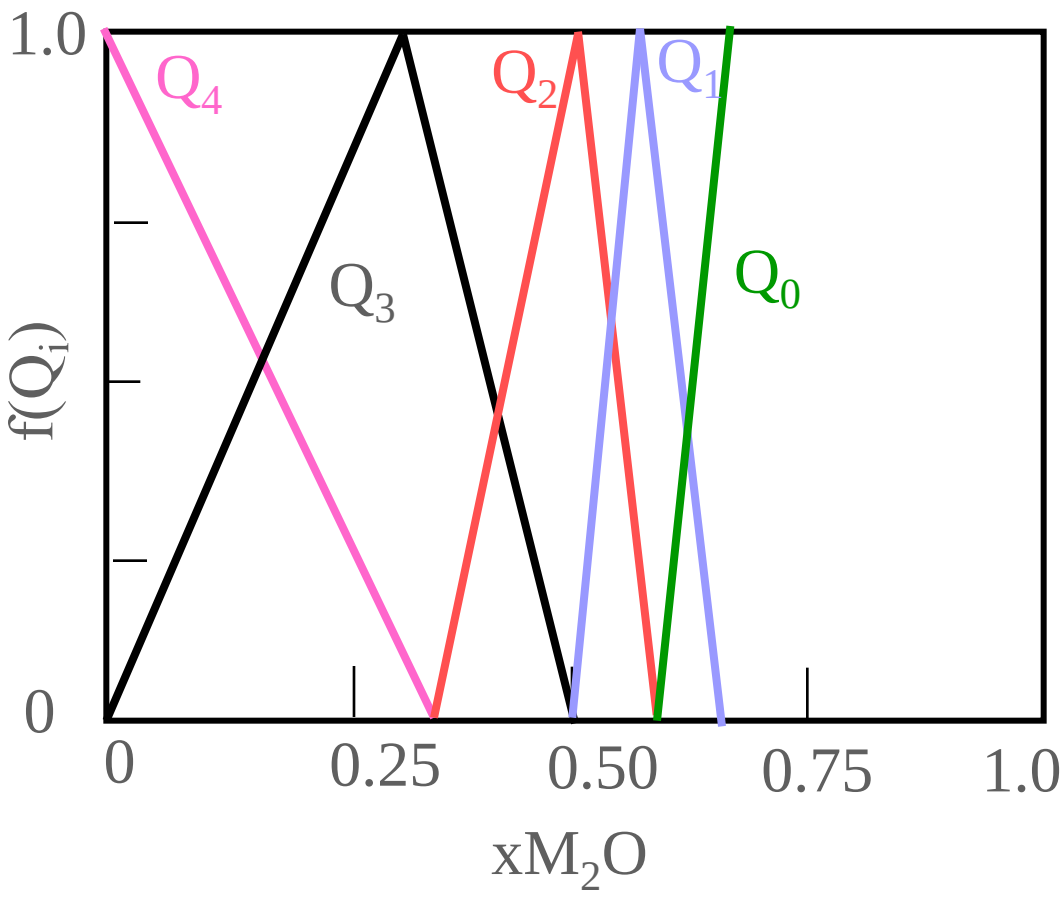
Q_i Unit Structures in Alkali Silicate Glasses

- Mixture of Q_4 and Q_3 sites
- Can you determine the fraction of Q_4 and Q_3 units in this structure?
- Can you determine the fraction of NBOs and BOs in this structure?
- Can you determine the alkali modifier oxide concentration?



Q_i sites and NBO/BO ratios are related

- Q_4 unit, all O are BO
- Q_0 unit, all O are NBO
- $2Q_4 + M_2O >> 2\ Q_3$
- $2Q_3 + M_2O >> 2\ Q_2$
- ….
- $2Q_1 + M_2O >> 2\ Q_0$



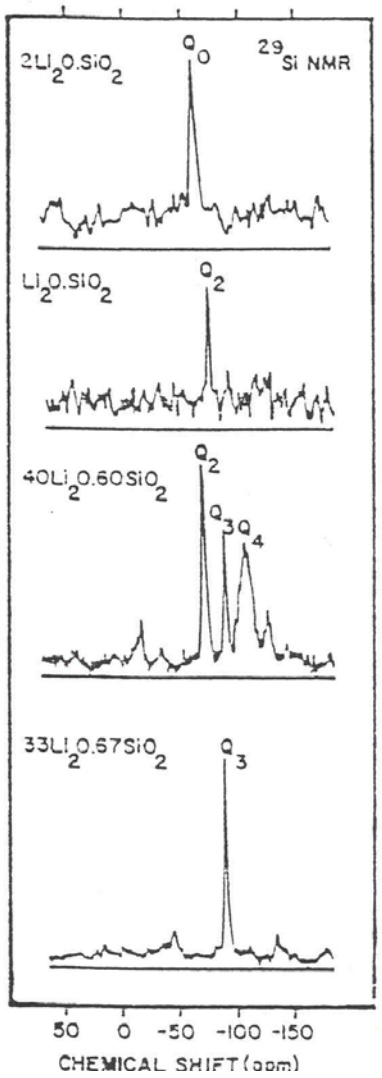
^{29}Si MASS NMR of Simple Alkali Silicates

$2Li_2O + SiO_2$

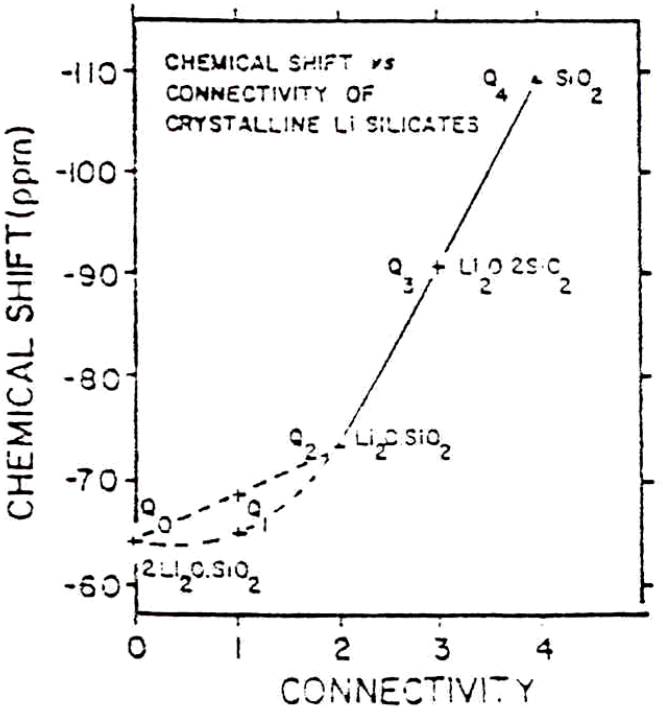
$Li_2O + SiO_2$

$2Li_2O + 3SiO_2$

$Li_2O + 2SiO_2$



Less shielded



Q_0 Q_1 Q_2 Q_3 Q_4

More shielded

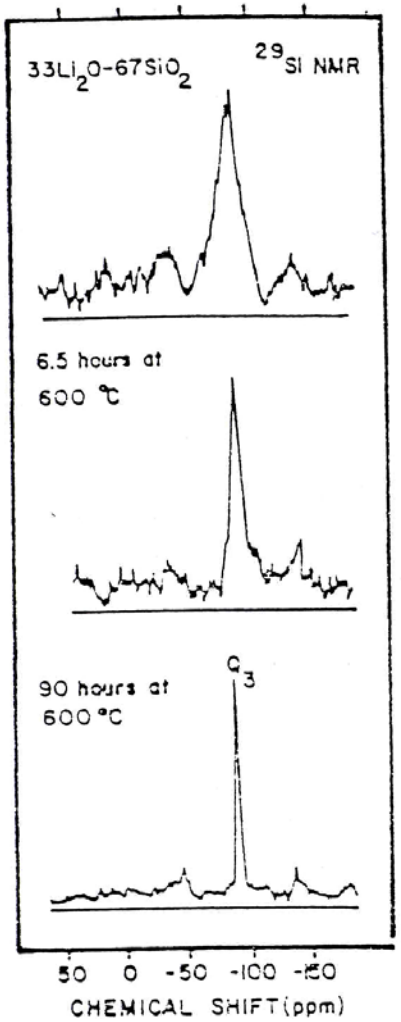
Amorphous versus Crystalline Silicates

Amorphous

$Li_2O + 2\ SiO_2 = Li_2SiO_3$

Q_2

Crystalline

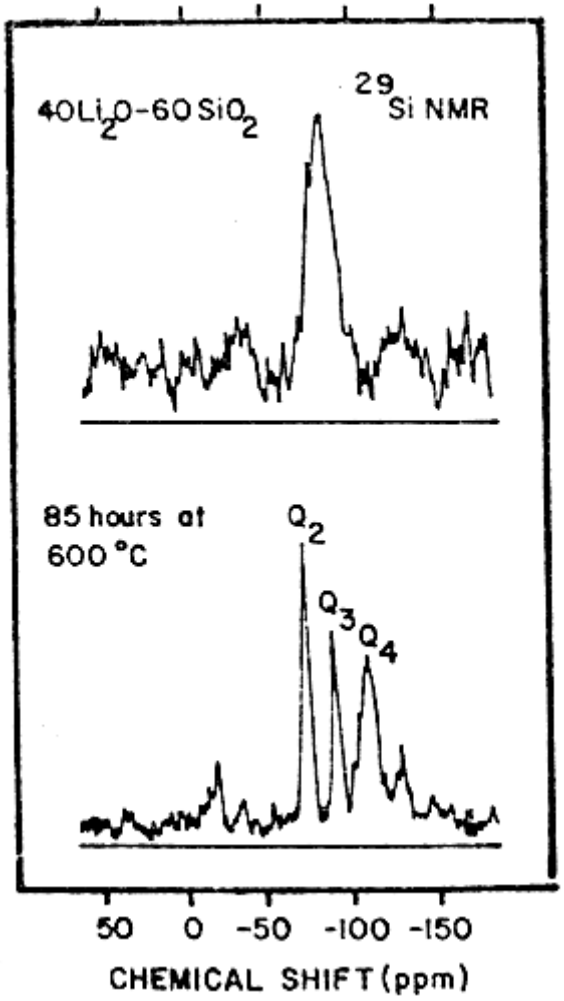


Amorphous

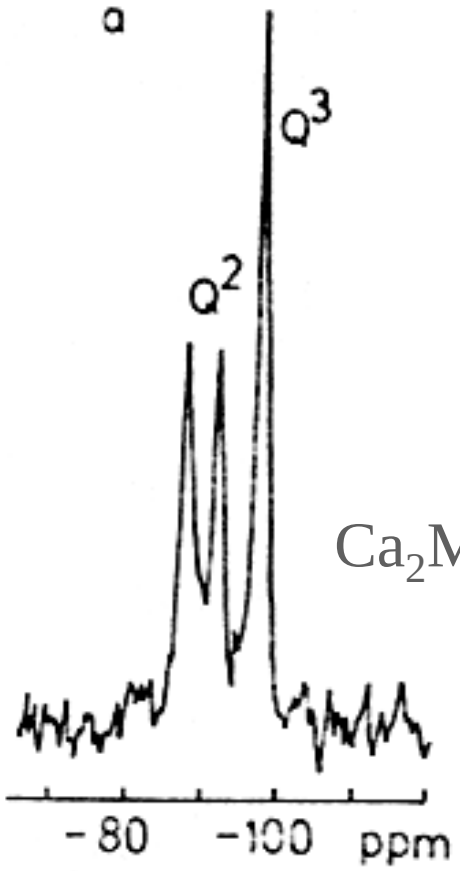
$2Li_2O + 3SiO_2 = Li_2SiO_3 + Li_2Si_2O_5$

$= Q_2 + Q_1$

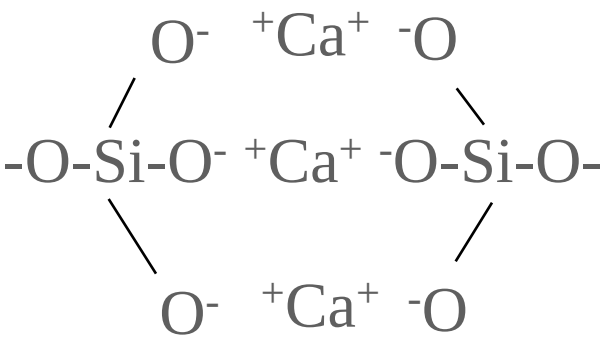
Crystalline



"Simple" silicate crystals

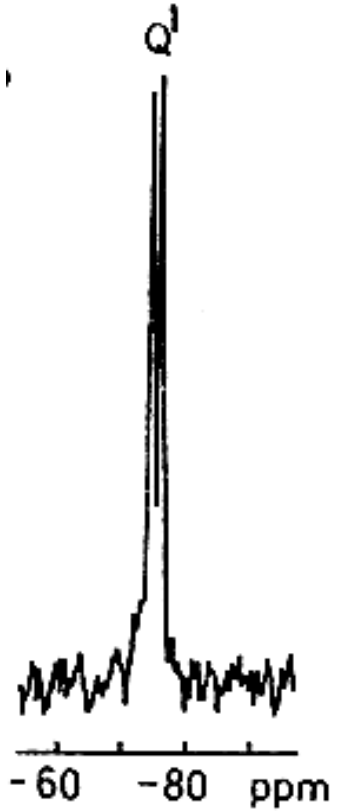


Synthetic $Ca_3Si_2O_7$



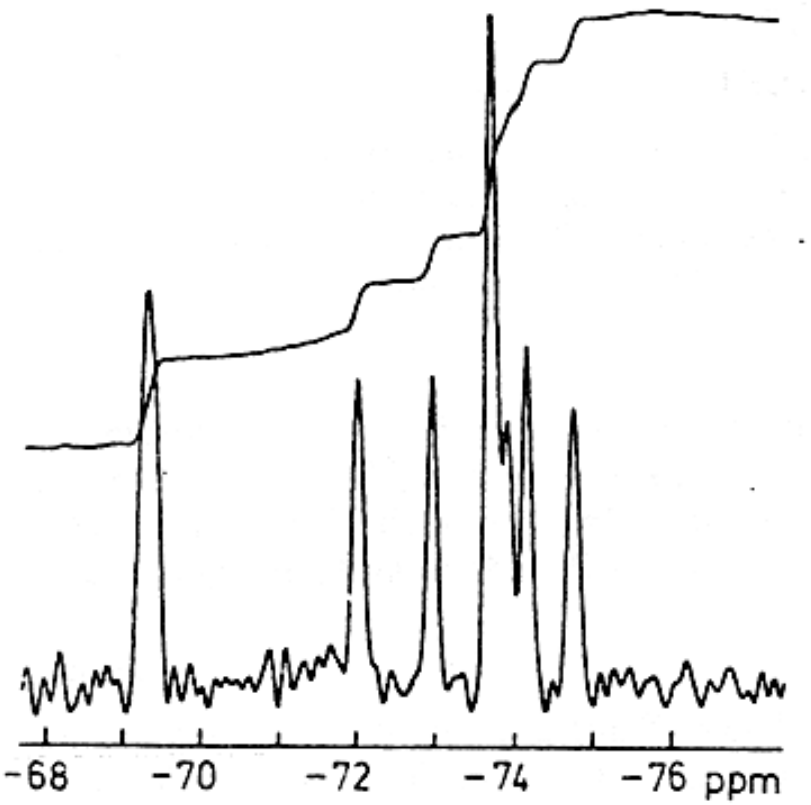
$Ca_2Mg_2[Si_4O_{11}]_2(OH)_2$

Can you sketch this structure?
How many predicted Si sites?



^{29}Si MASS of $3CaO + SiO_2$, Ca_3SiO_5

- Can you predict this structure?
- Crystalline compound possess multiple chemical sites, each with their unique chemical shift
- Chemical shift difference is greater than dipolar broadening, “spun down”
- So that individual sites can be observed
- Note long relaxation time of ^{29}Si required 12 hour accumulation!



^{29} Si MASS NMR of Crystalline Silicates

TABLE III: ^{29}Si Isotropic Chemical Shifts of Inosilicates and Cyclosilicates (Q^2)

silicate	mineral	origin	δ_{Si} from Me_4Si
	Inosilicates		
Li_2SiO_3		synth	−74.5
Na_2SiO_3		synth	−76.8
$Mg_2Si_2O_6$	orthoenstatite	Bamle (Norway)	−82[a]
$CaMgSi_2O_6$	diopside	Zillertal (Austria)	−84[a]
$Ca_2[SiO_3](OH)_2$	hillebrandite	synth	−86.3
$Ca_2NaH[Si_3O_9]$	pectolite	synth	−86.3
$Ca_4[Si_3O_9](OH)_2$	foshagite	synth	−84.8; −86.4[b]
$Ca_6[Si_6O_{17}](OH)_2$	xonotlite	synth	−86.8[c]
β-$Ca_3[Si_3O_9]$	β-wollastonite	synth	−89.0
$Ca_2Mg_5[Si_4O_{11}]_2(OH)_2$	fibrous tremolite	St. Gothard	−87.8; −92.2[d]
$LiAl[Si_2O_6]$	spodumene	Branchville (USA)	−91.6
$NaAl[Si_2O_6]$	jadeite	Burma	−91.8
	Cyclosilicates		
α-$Ca_3[Si_3O_9]$	pseudowol-lastonite	synth	−83.5
$K_4H_4[Si_4O_{12}]$		synth	−87.5
$BaTi[Si_3O_9]$	benitoite	California	−94.2
$Al_2Be_3[Si_6O_{18}]$	beryl	Urals	−102.6

^{29}Si MASS NMR Chemical Shifts for Silicates

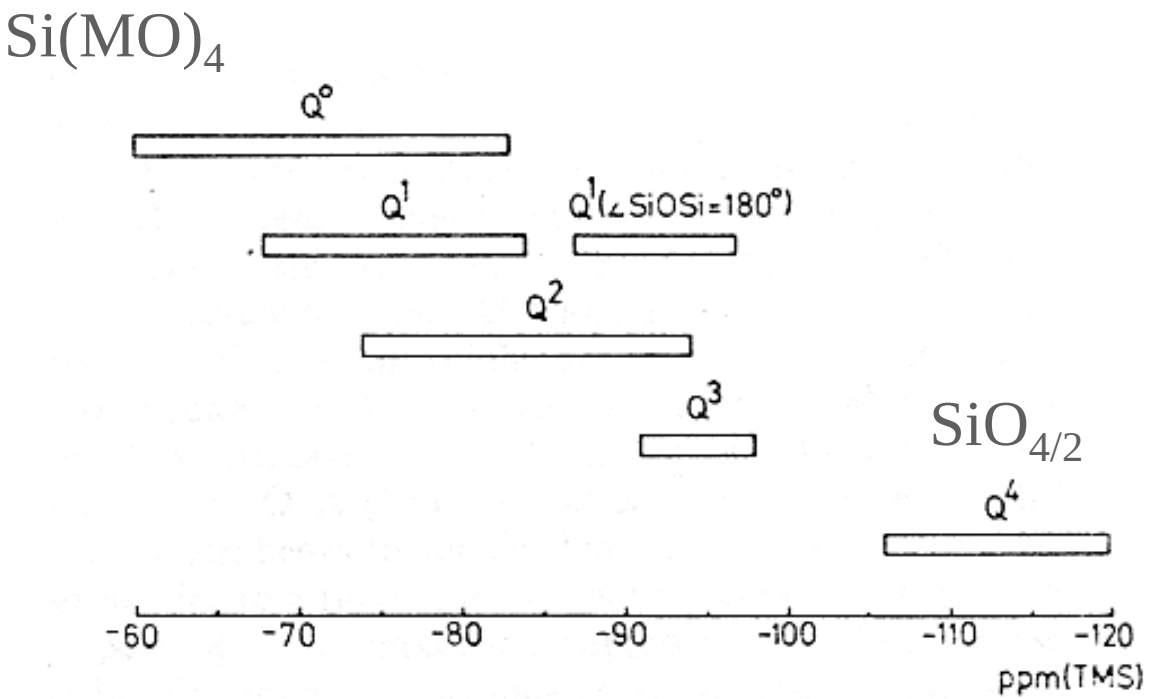
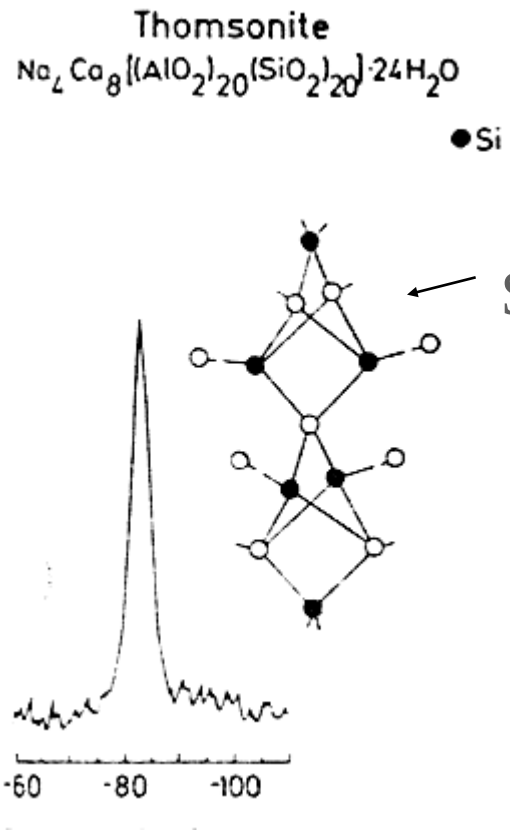


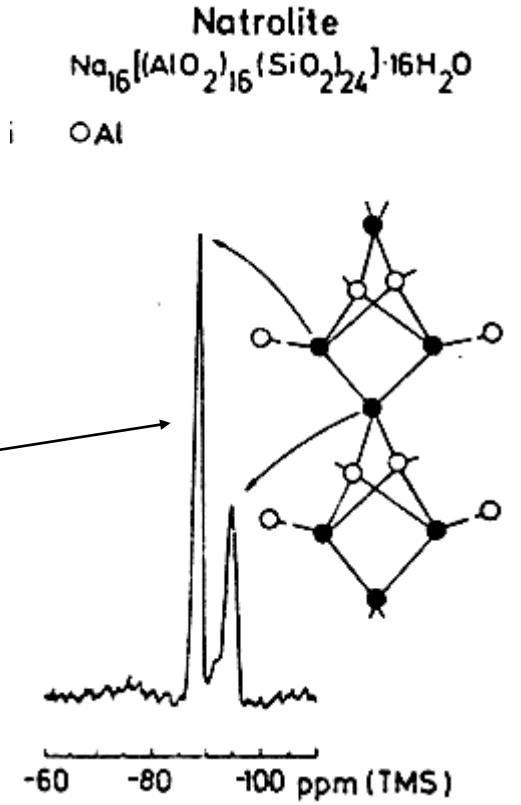
Figure 3. ^{29}Si chemical shift ranges of silicates with a different degree of condensation of SiO_4 tetrahedra (Q^0, nesosilicates; Q^1, sorosilicates; Q^2, inosilicates; Q^3, phyllosilicates; Q^4, SiO_2 polymorphs). Silicates containing four-coordinated Al and Be are excluded (see text).

^{29}Si MASS NMR of Aluminosilicate Zeolites



Single Si site

Two Si sites



Less alkali, mostly Al and Si

More alkali, more Si sites

Affect of Si/Al ratio

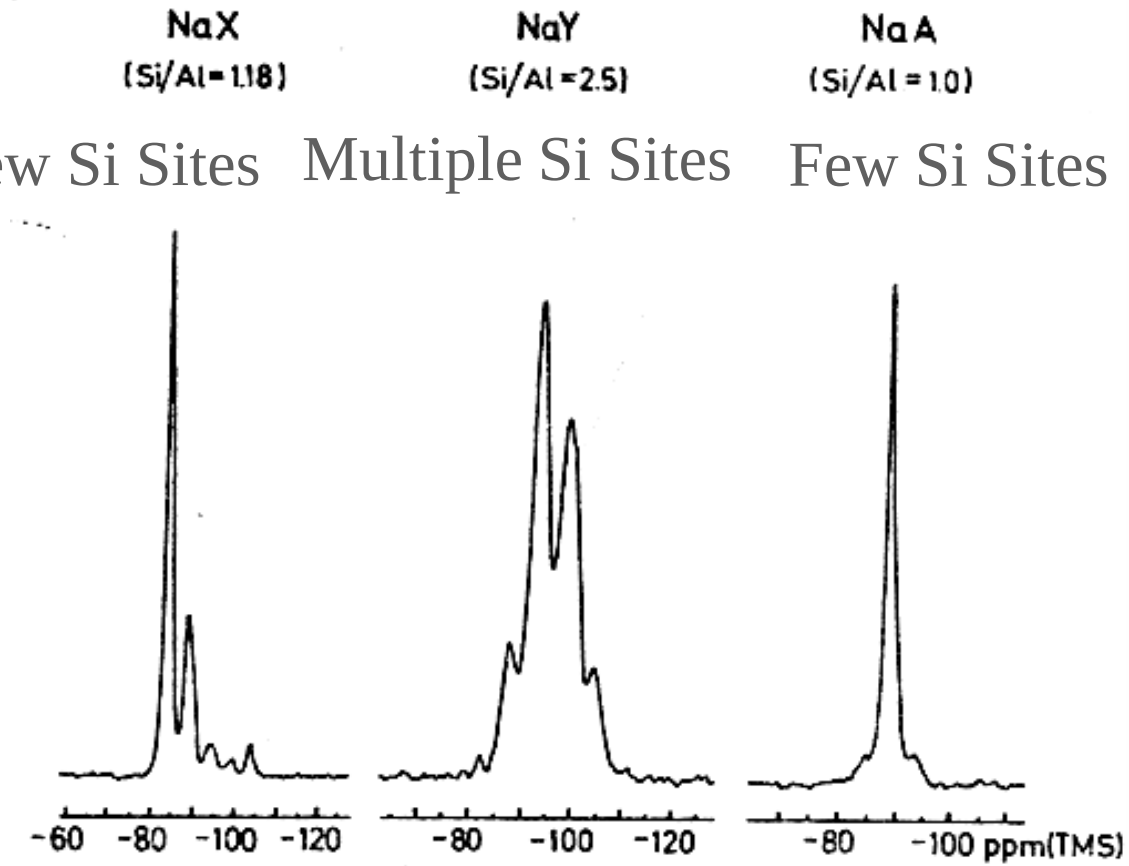


Figure 2. ^{29}Si NMR spectra of NaX, NaY, and NaA zeolites.

Typical Aluminosilicate Zeolite Structure

Lippmaa et al.

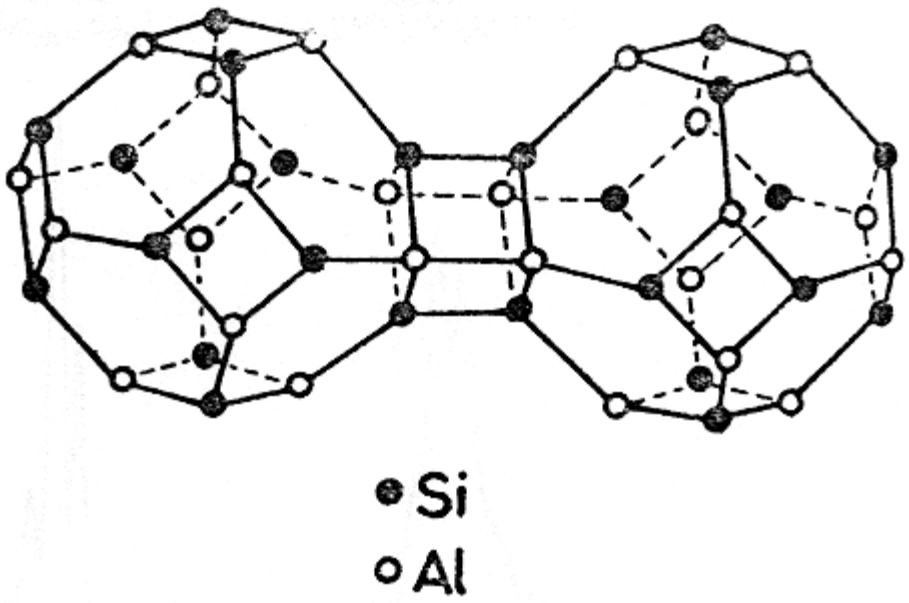
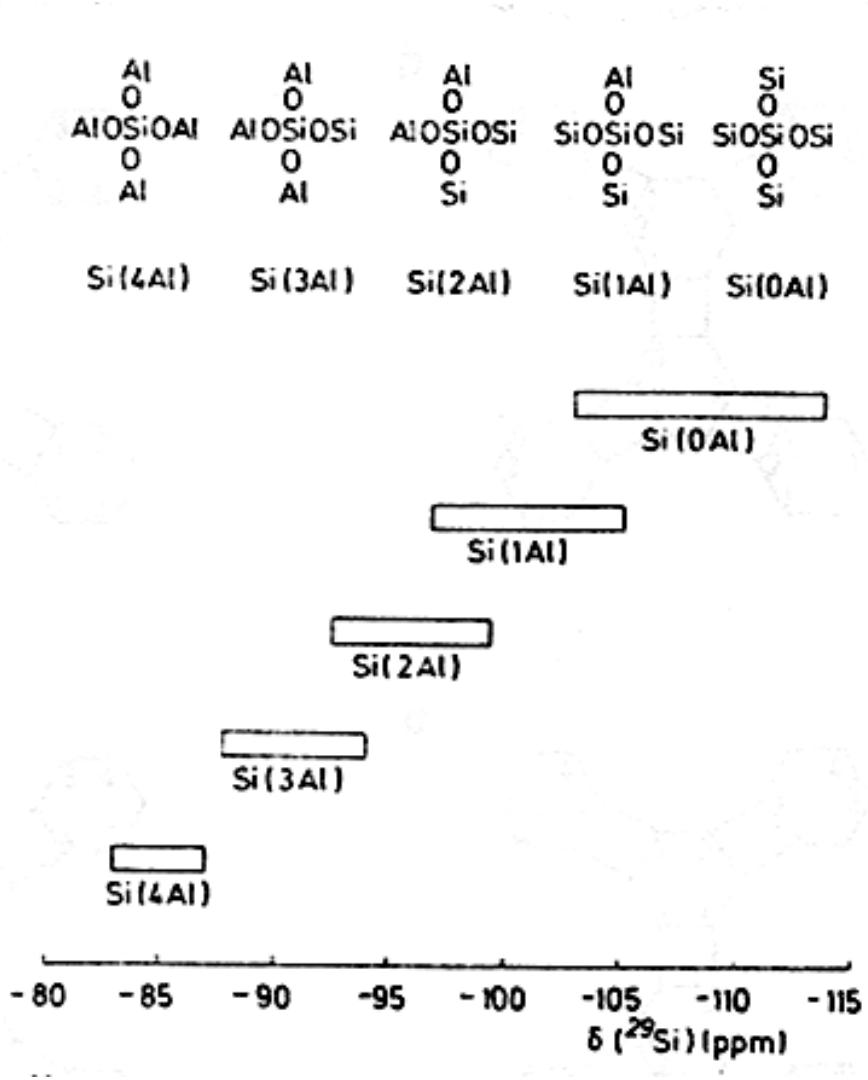
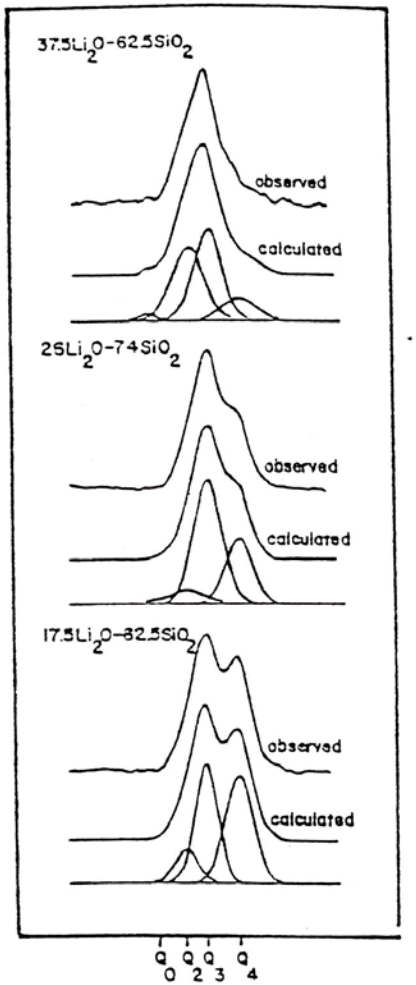


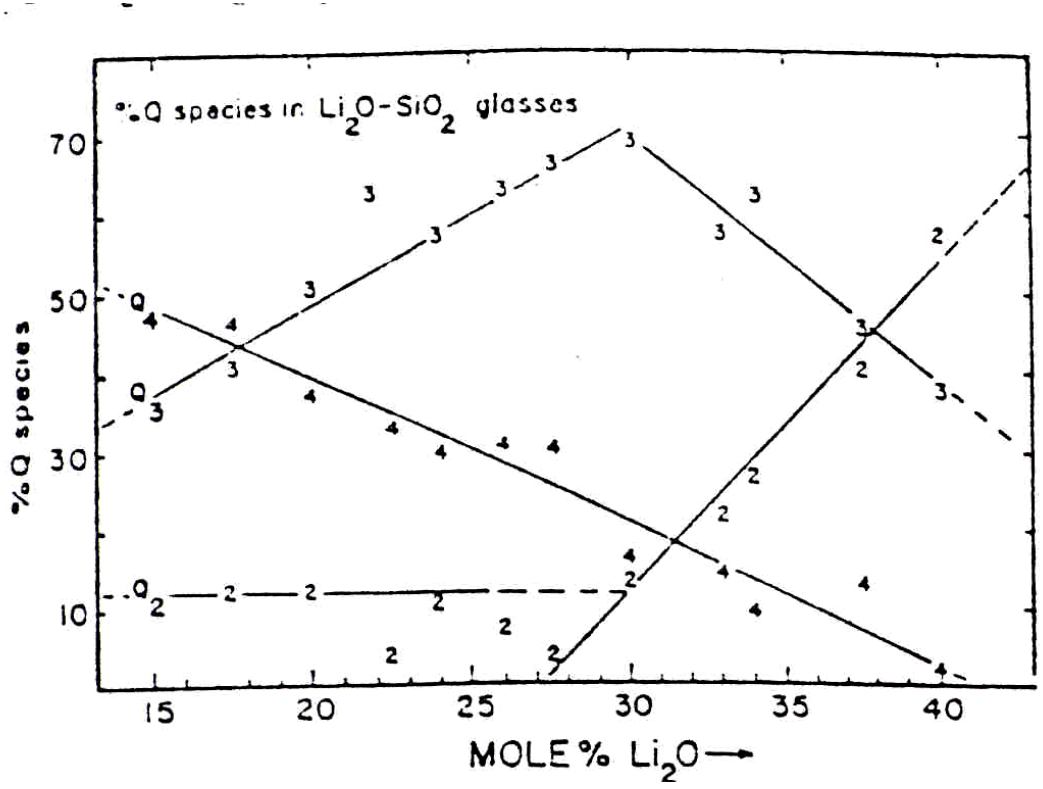
Figure 4. Si/Al distribution in the proposed model structure of the NaA zeolite consisting of Si(3Al) units. Only the central atoms of the tetrahedra in two interconnected cubooctahedra of the three-dimensional framework are shown.

Affect of Al coordination upon ^{29}Si MASS shift



^{29}Si MASS NMR of Glasses – Amorphous Materials





PPM scale in terms of glass chemistry

^{29} Si MASS NMR of Silicate Glasses

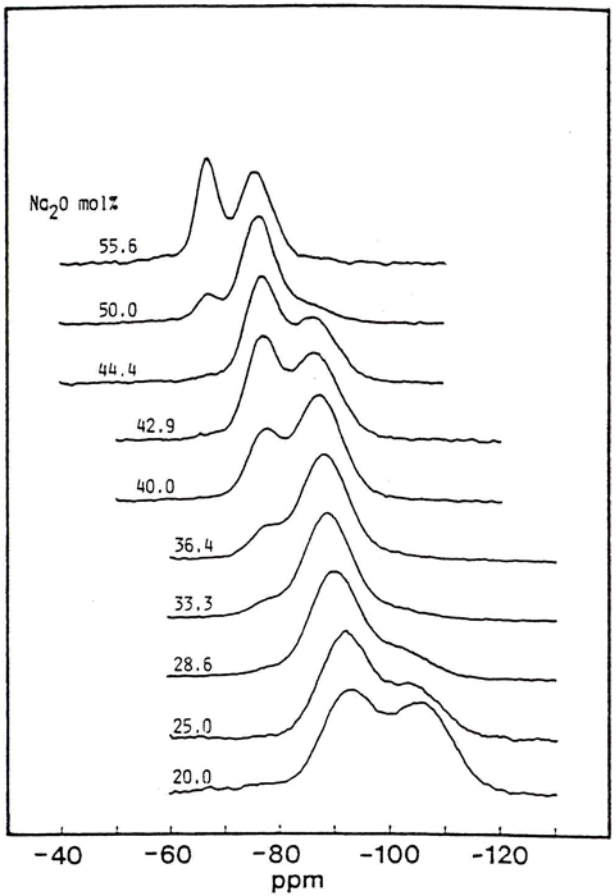


Fig. 1. ^{29}Si MAS-NMR spectra of sodium silicate glasses.

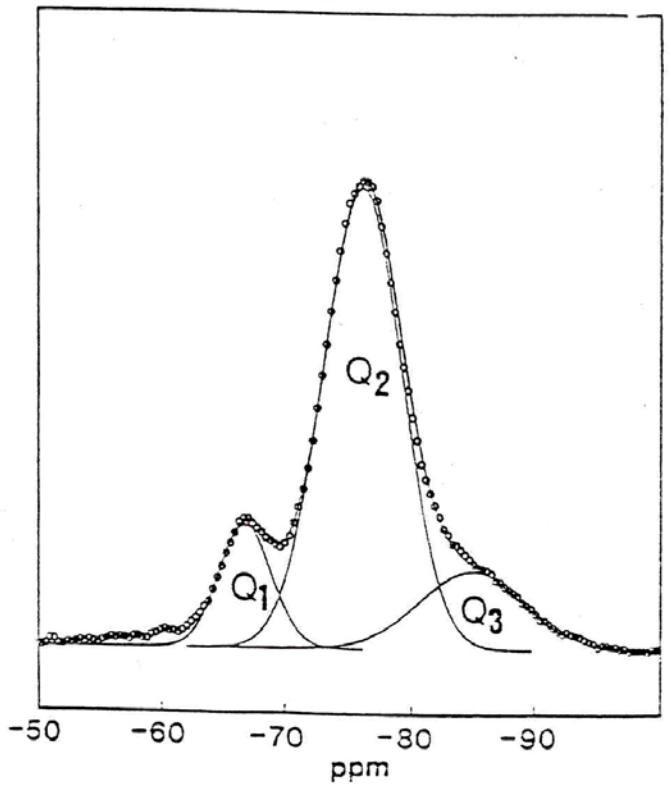
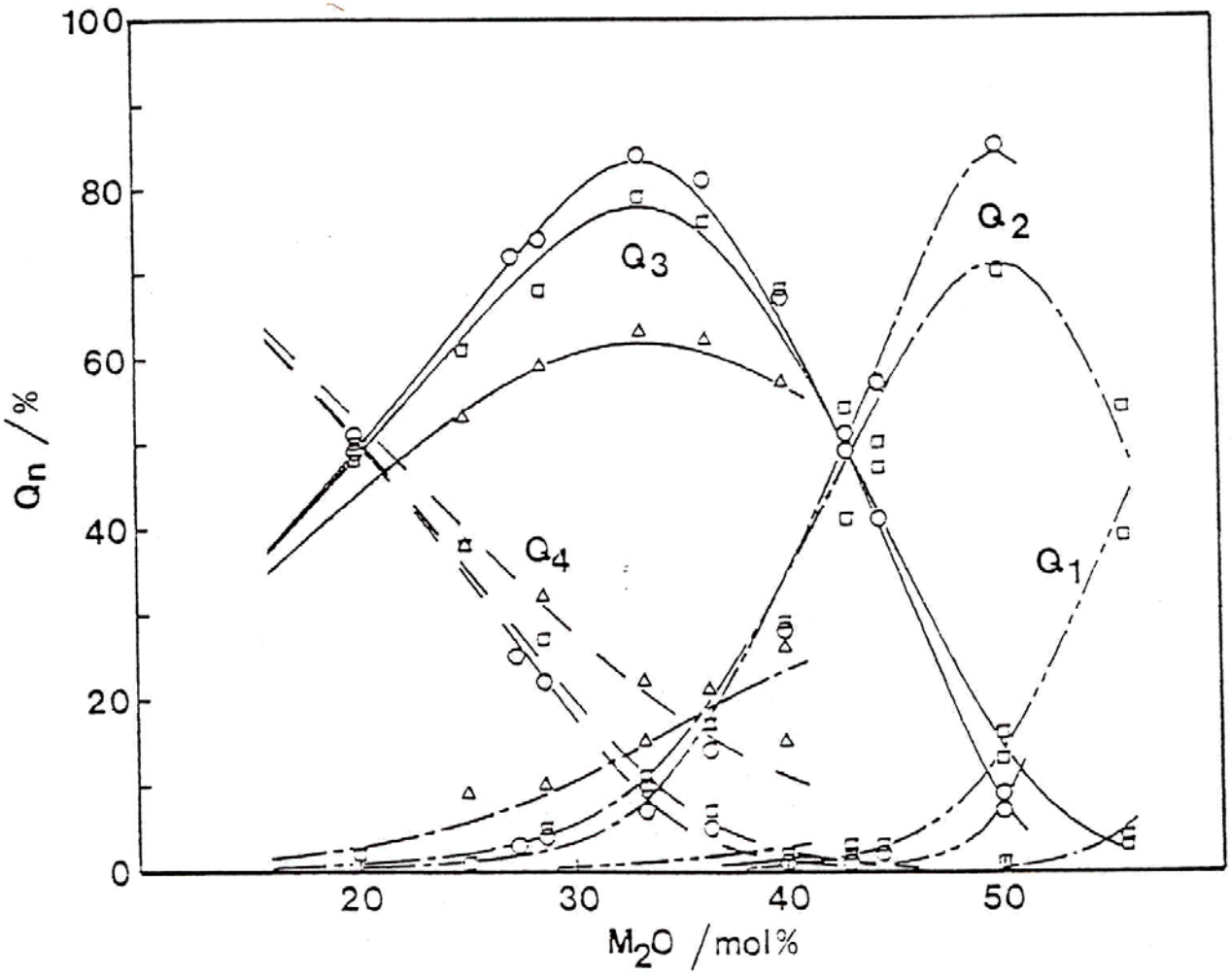


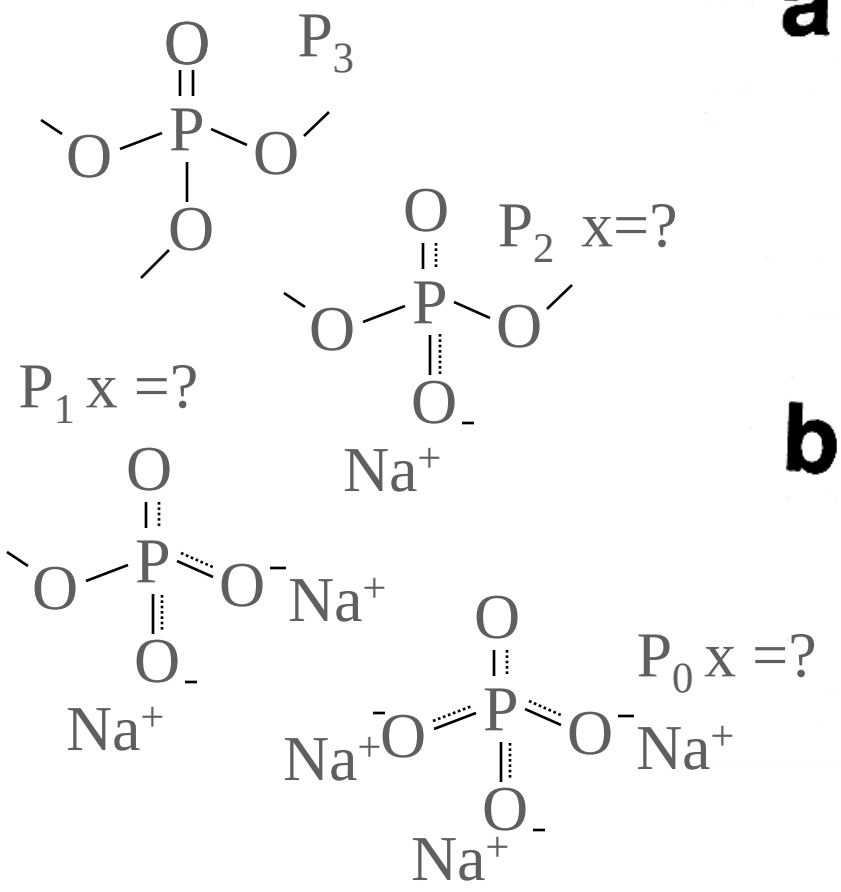
Fig. 3. ^{29}Si MAS-NMR spectrum of sodium metasilicate glass.

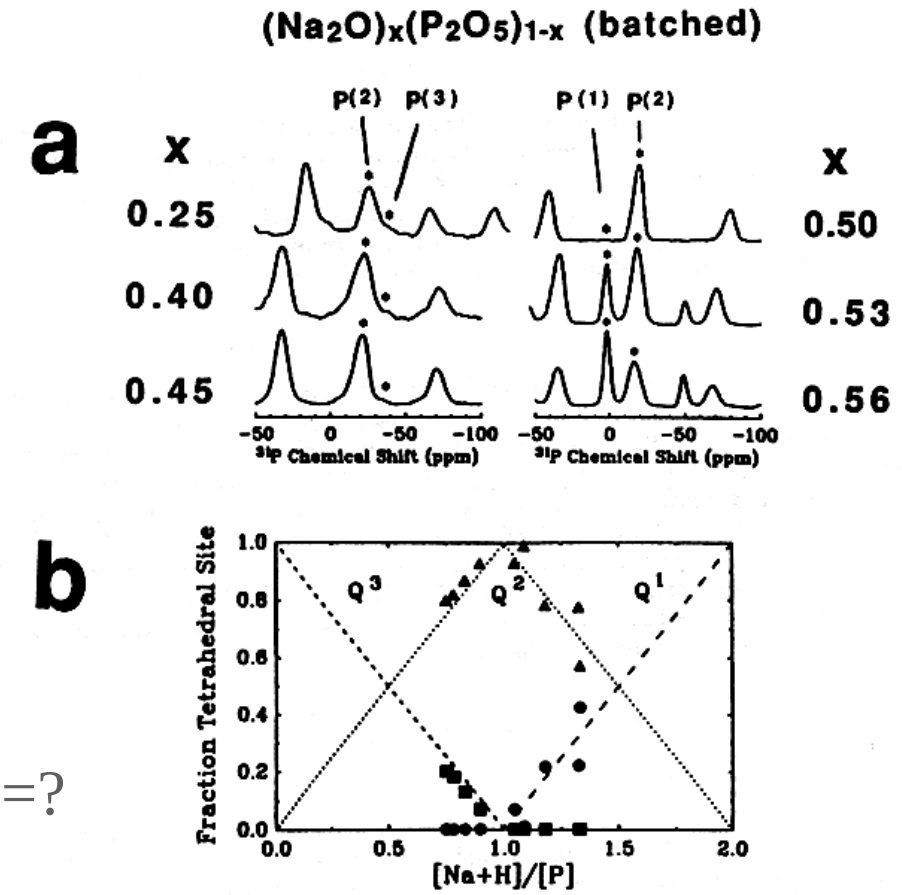
Speciation of Silicate Groups in Silicate Glasses



^{31}P MASS NMR $Na_2O + P_2O_5$

- $xM_2O + (1-x)P_2O_5$
- x = 0, P_2O_5





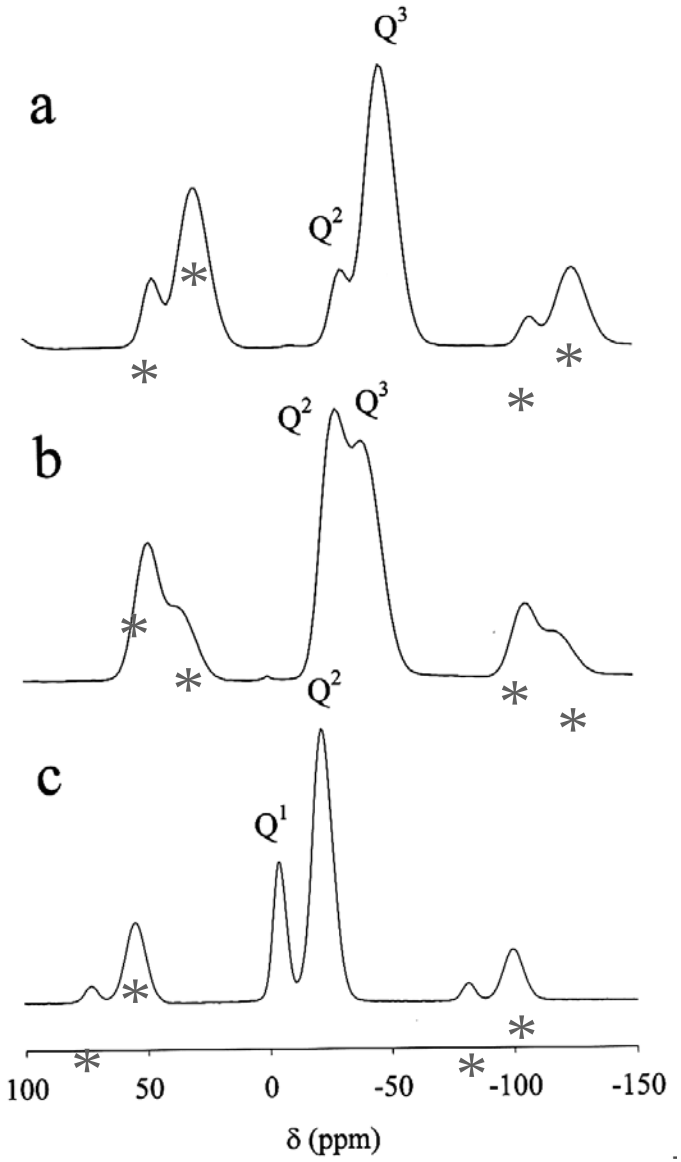
^{31}P MASS NMR

$15Li_2O + 85P_2O_5$

$35Li_2O + 65P_2O_5$

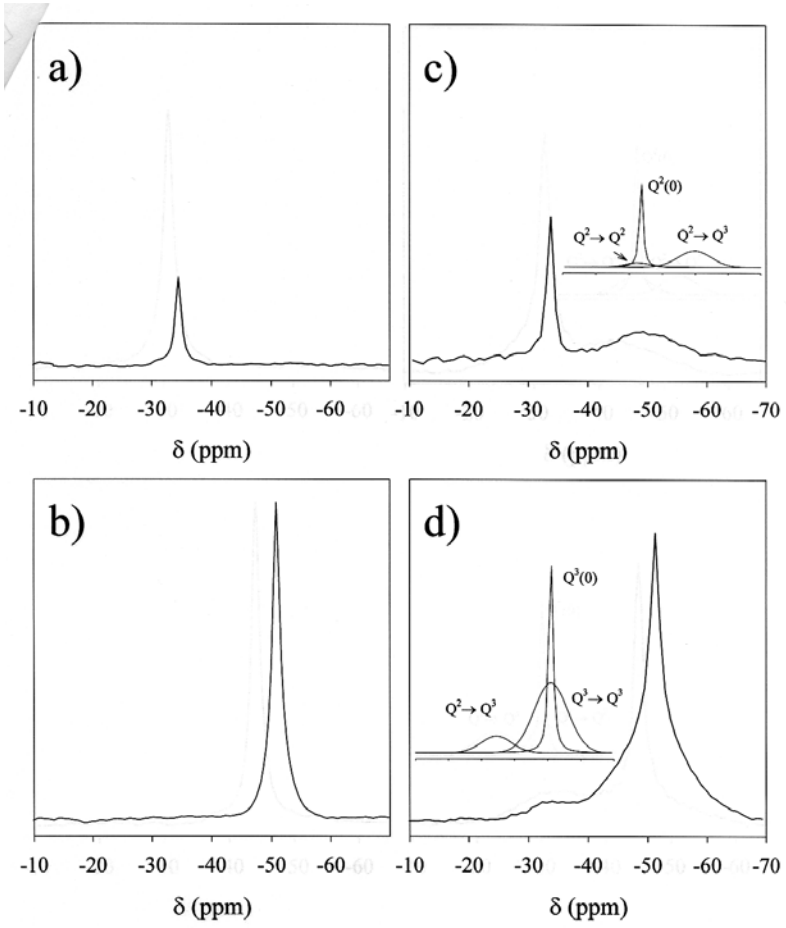
$55Li_2O + 45P_2O_5$

* Spinning side bands

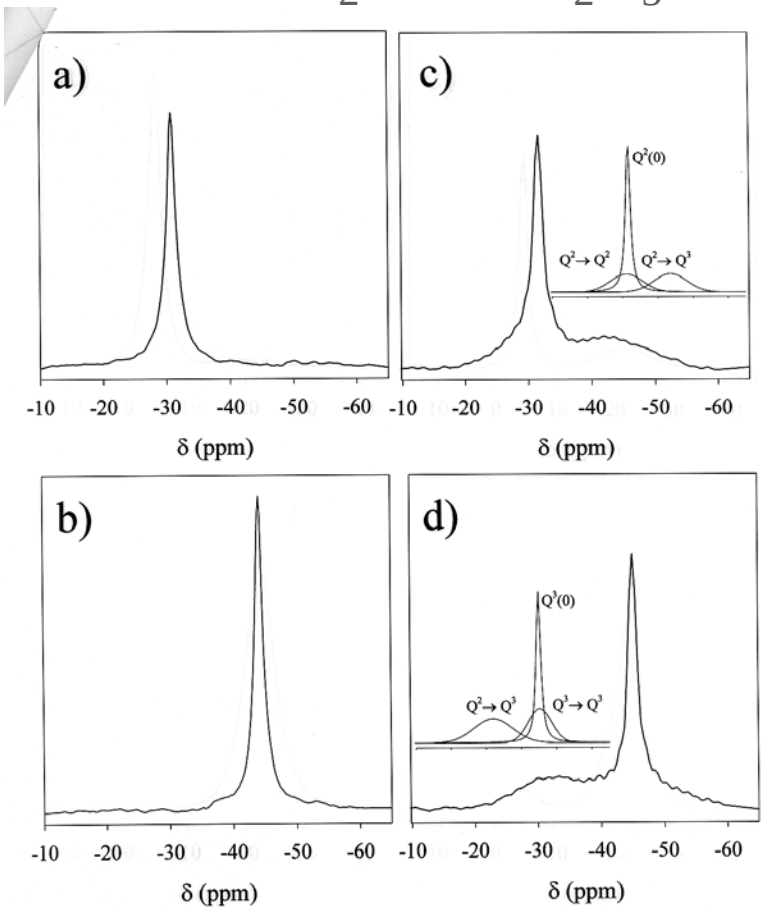


Site specific ^{31}P MASS 2D NMR

$15Li_2O + 85P_2O_5$

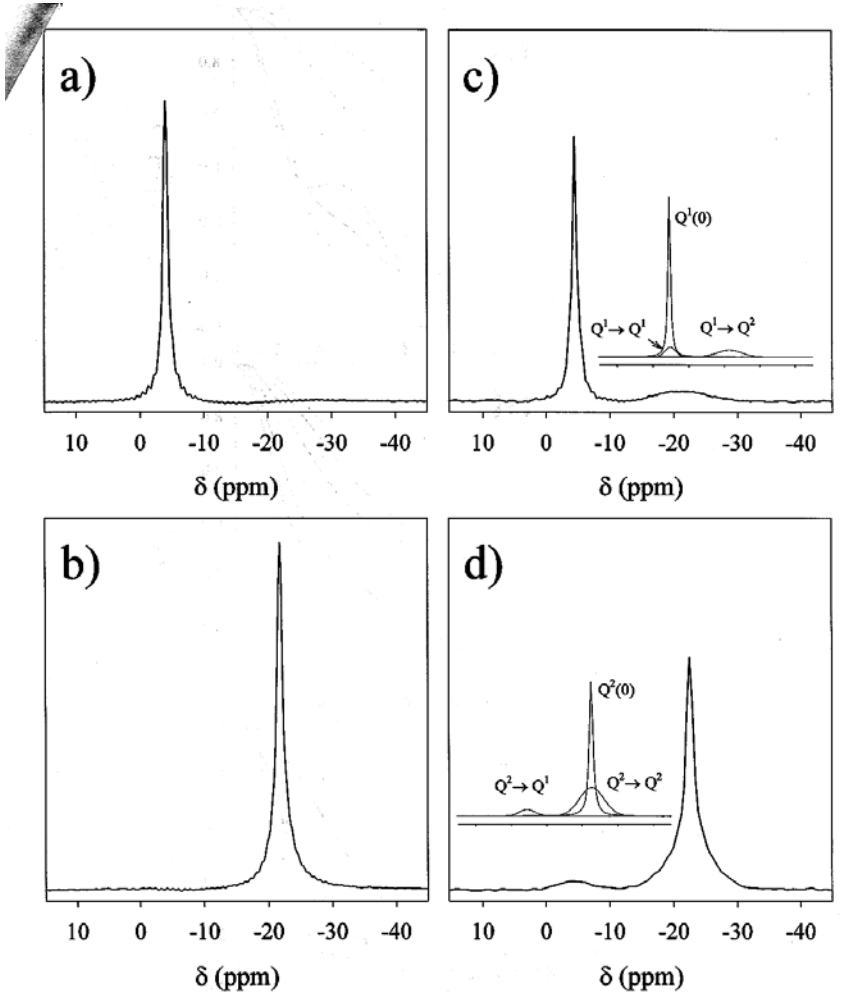


$35Li_2O + 65P_2O_5$

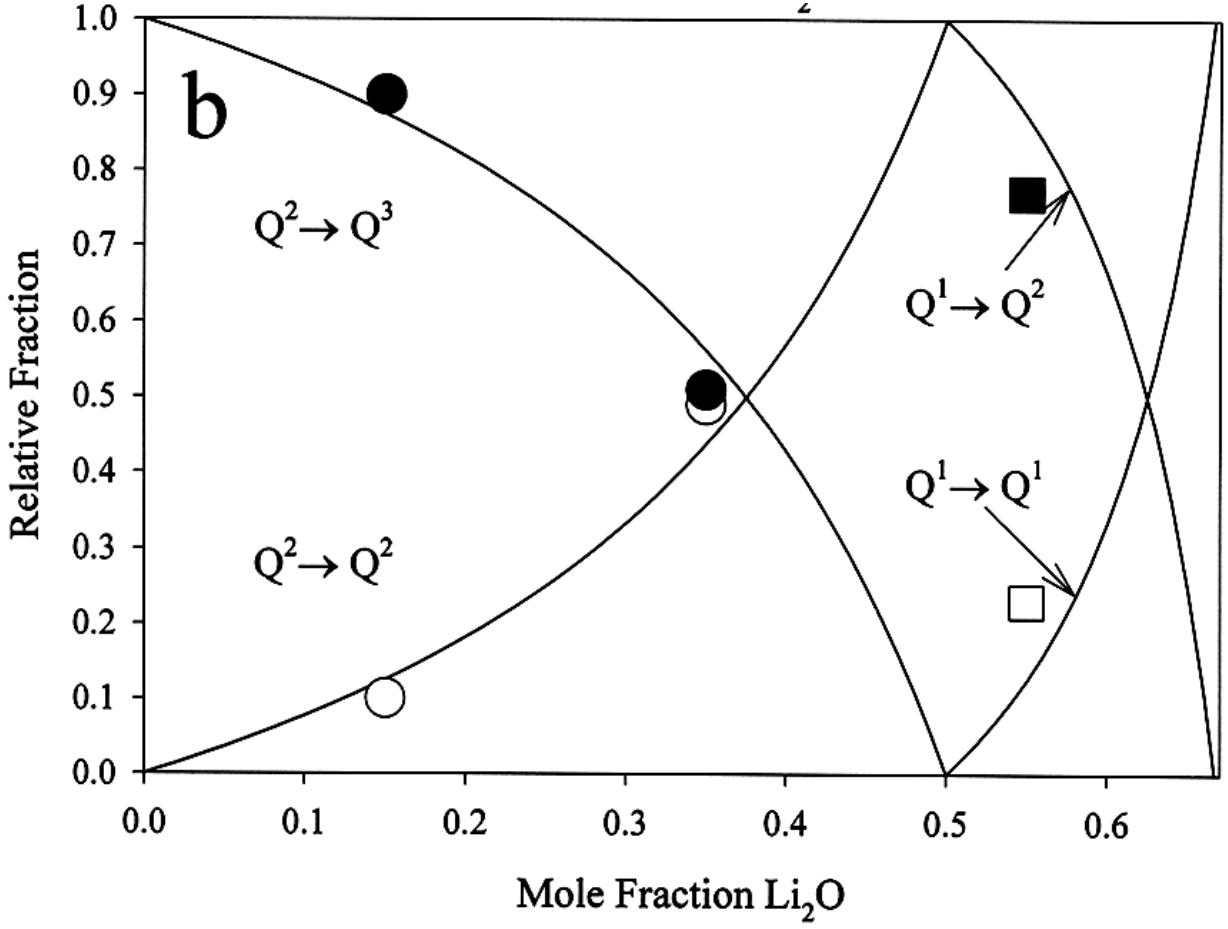


Site specific ^{31}P MASS 2D NMR

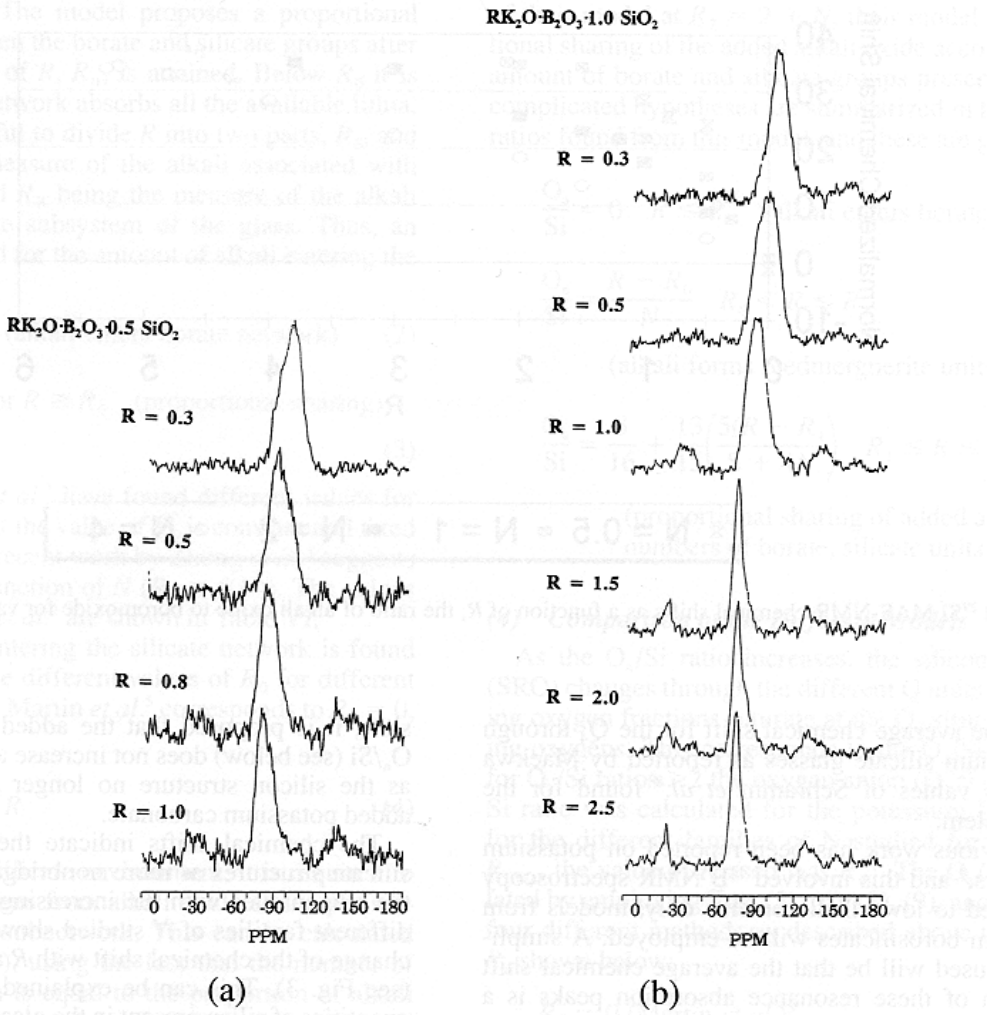
- $55Li_2O + 45P_2O_5$



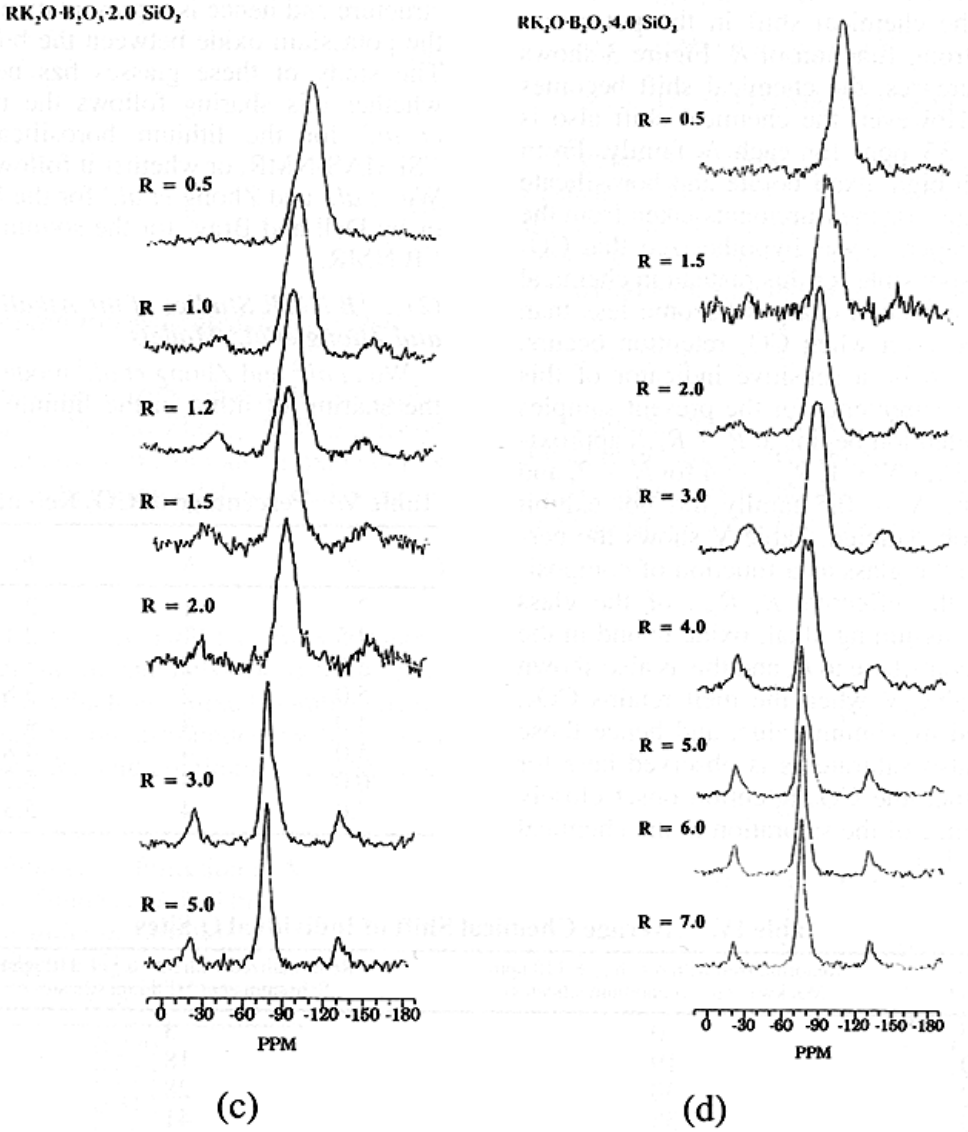
Composition dependence of Phosphate groups



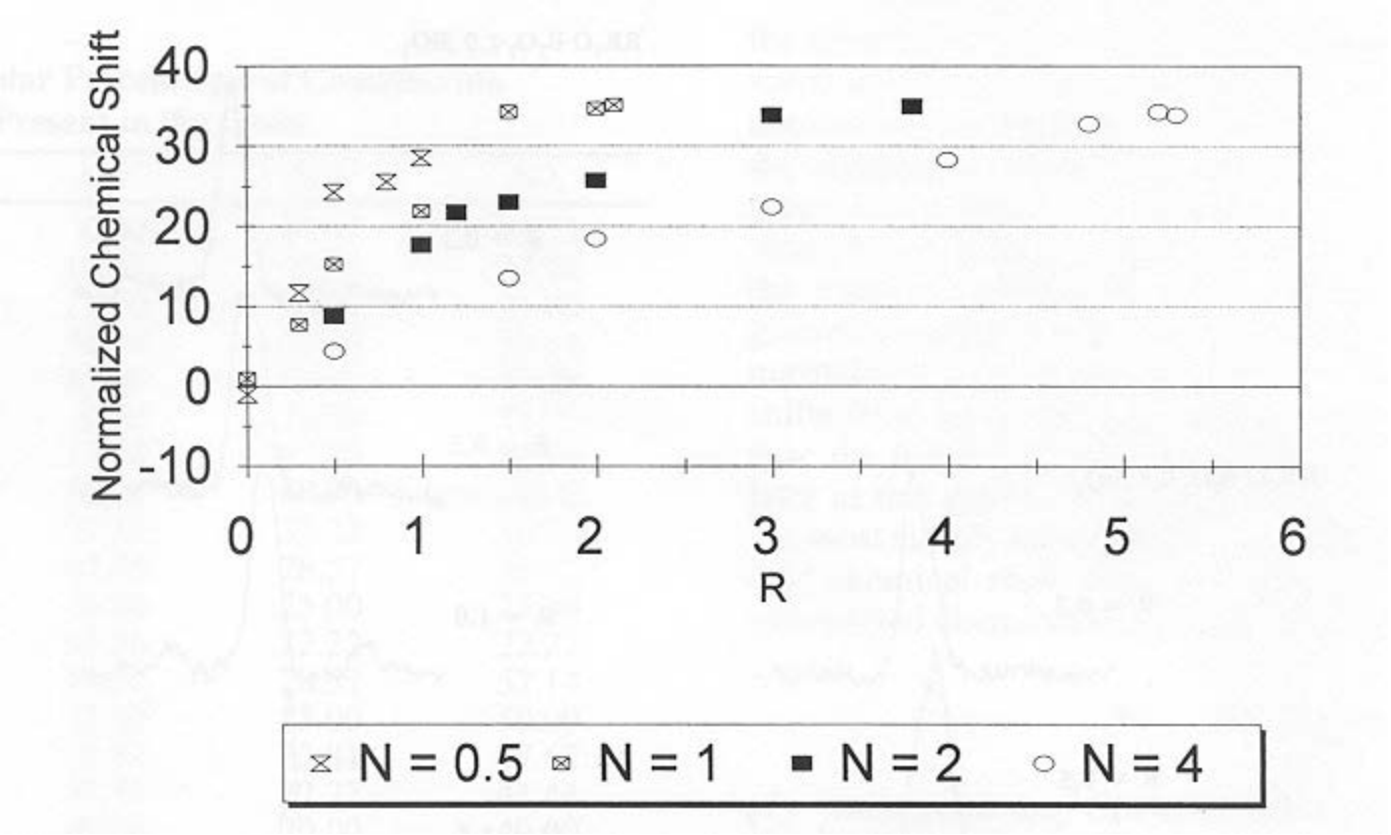
^{29}Si MASS NMR of Potassium borosilicate glasses



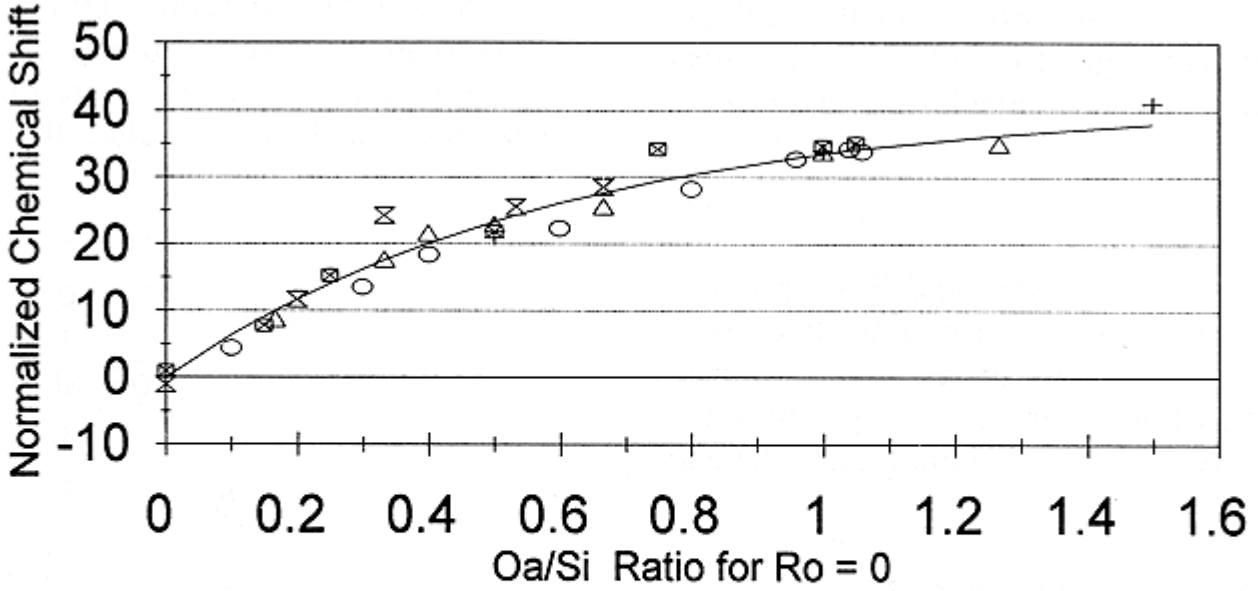
^{29}Si MASS NMR of Potassium borosilicates



Chemical Shift for different B/Si ratios

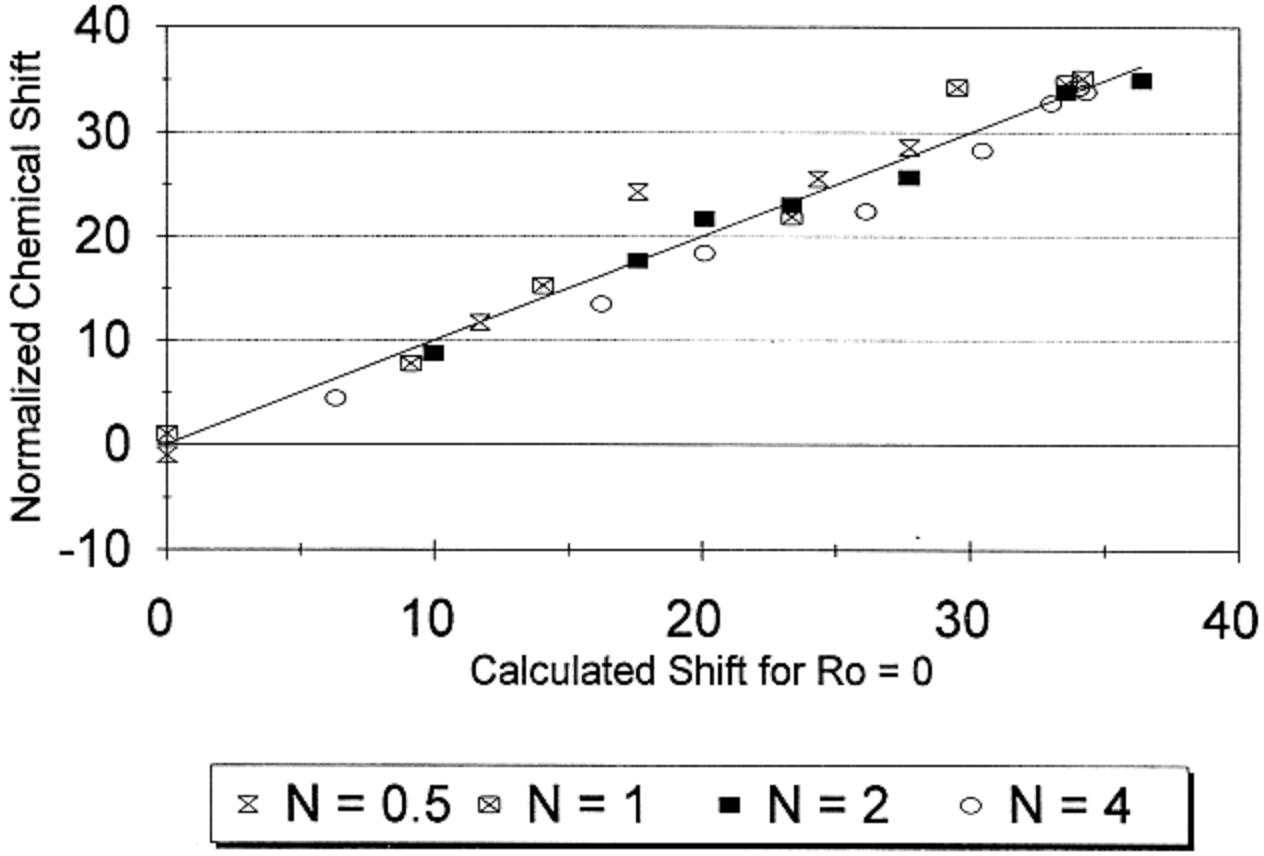


Chemical Shift versus added O/Si ratio



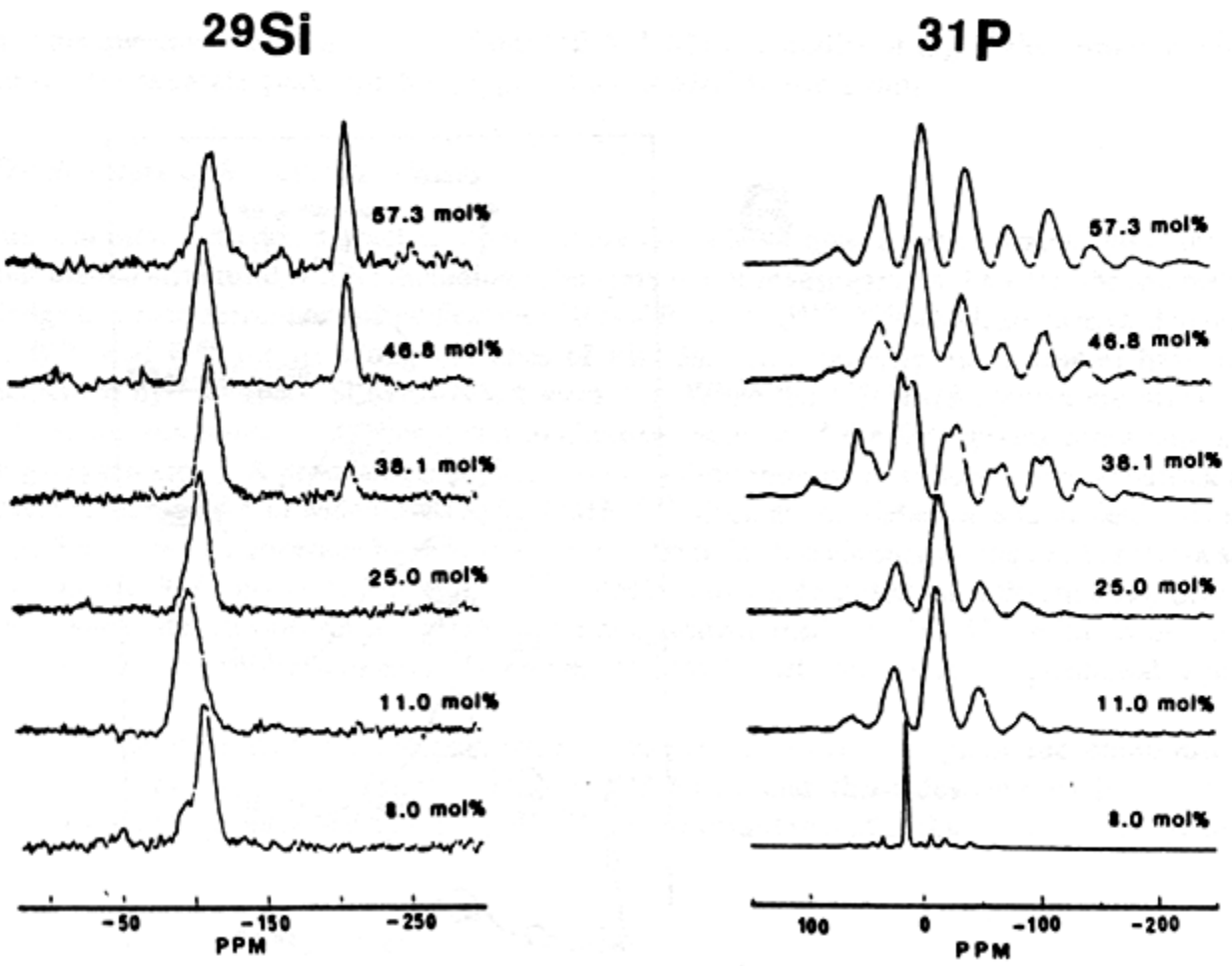
Chemical Shift versus calculated chemical shift

ALL added K_2O is equally shared between B_2O_3 and SiO_2 from $0K_2O$

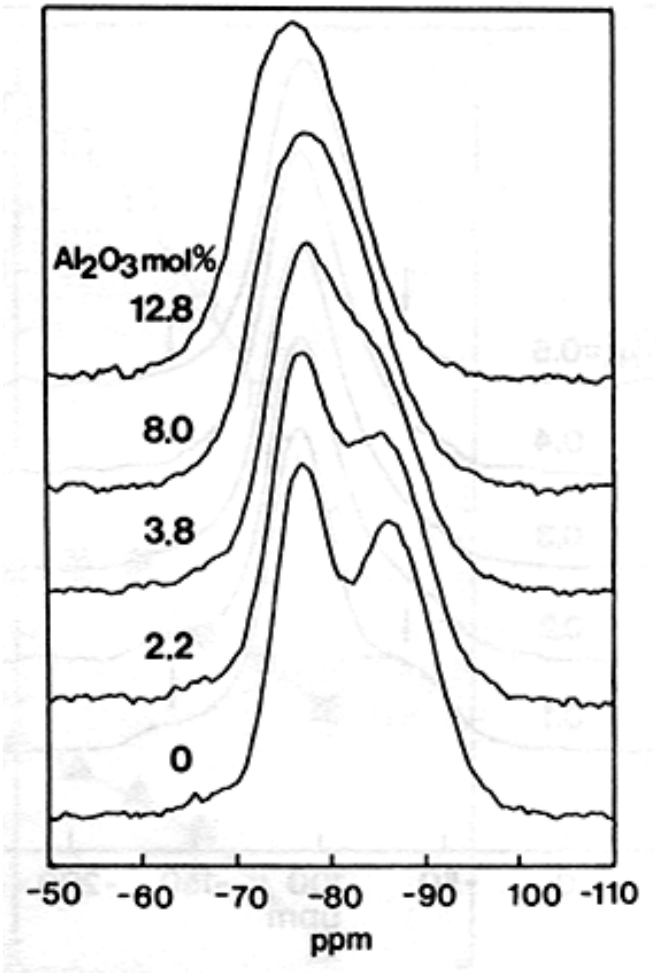


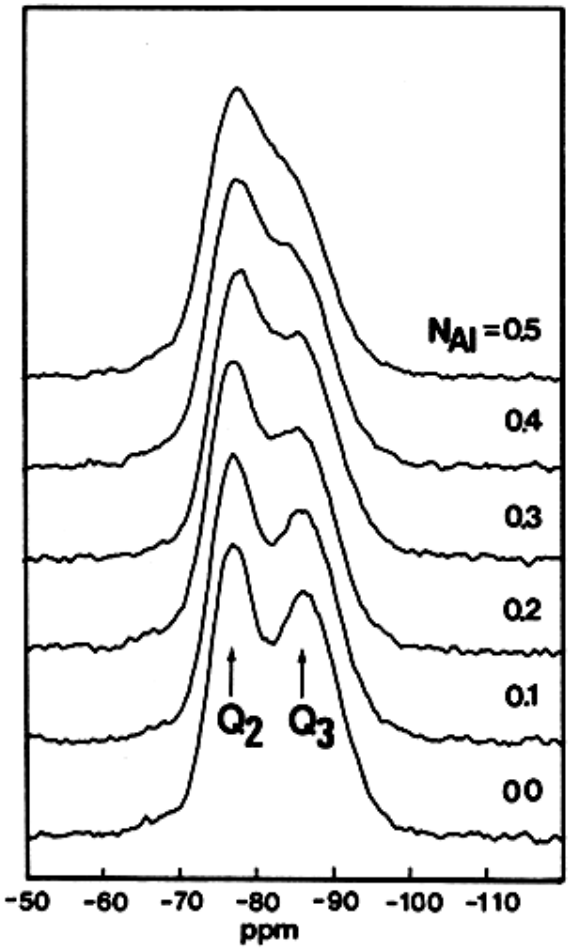
$Na_2O + P_2O_5 + SiO_2$ Glasses

- Two NMR active nuclei add to the level of structural analysis
- Site specific information around Si and P nuclei
- Combine this information to determine complete structure of the glass



^{29}MASS NMR of $Na_2O + Al_2O_3 + SiO_2$ Glasses





Ternary $Na_2O + Al_2O_3 + SiO_2$ System

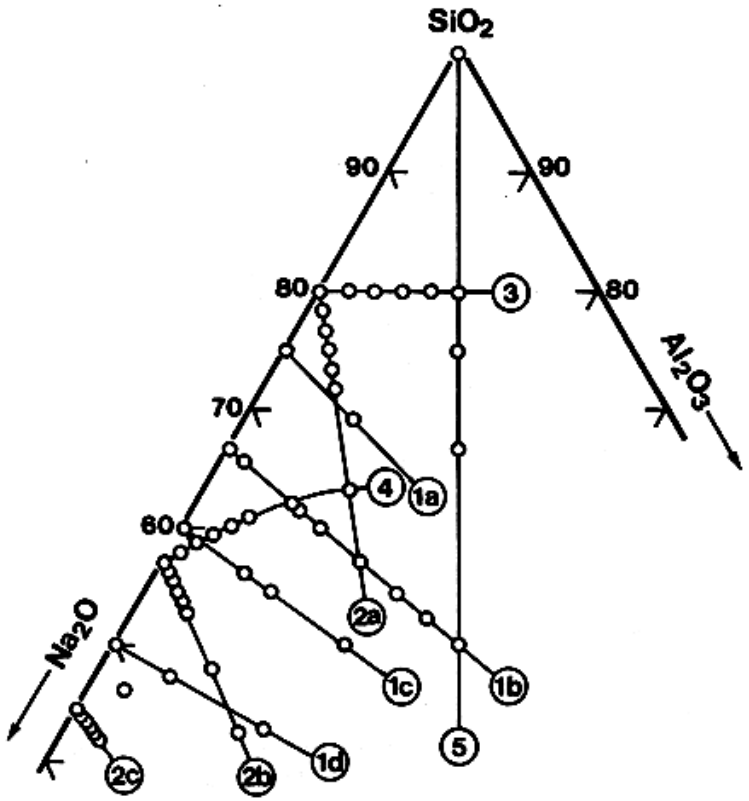
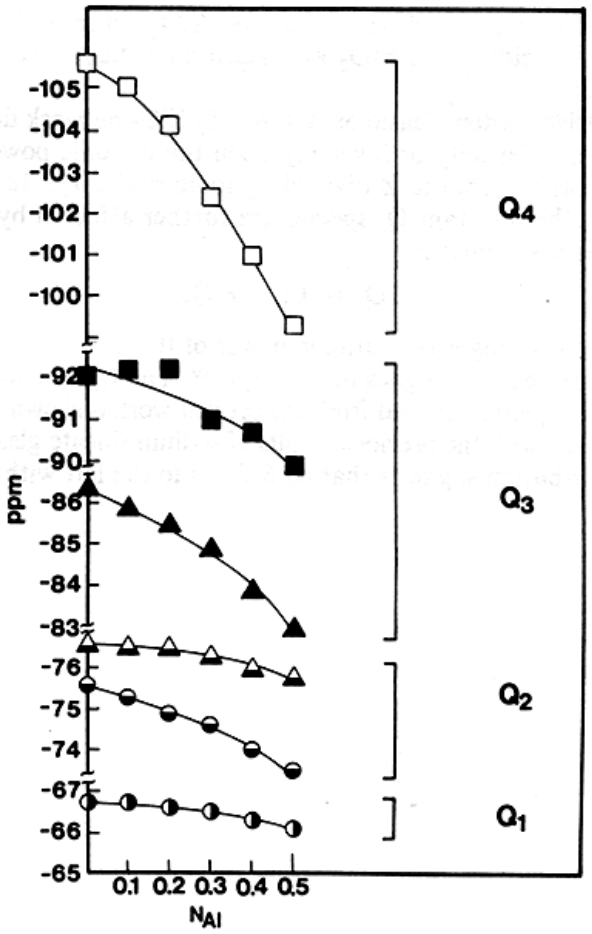


Figure 1. Five series of the glasses shown in the composition diagram for Na_2O–Al_2O_3–SiO_2 system.

Composition dependence of Chemical Shift

$Na_2O + Al_2O_3 + SiO_2$ Glasses



Composition dependence of Q fractions

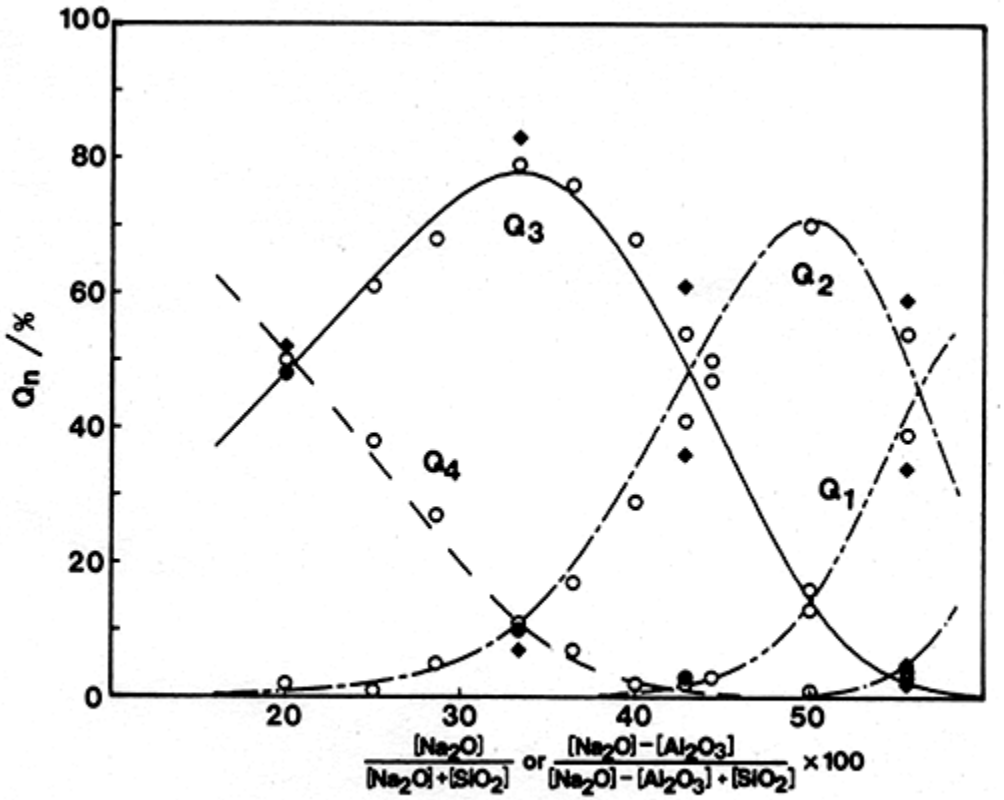


Figure 8. Q_n distribution as a function of contents of Na_2O: (O) for binary sodium silicate glass;[21] (◆) present work at $N_{Al} = 0.5$.