Some Interesting Observations on Oxygen Environments in Silicate Glasses with Implications for the Fitting of the High Frequency Raman Envelope

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M_2O-SiO_2 binaries: M = Li, Na, K, Rb, Cs

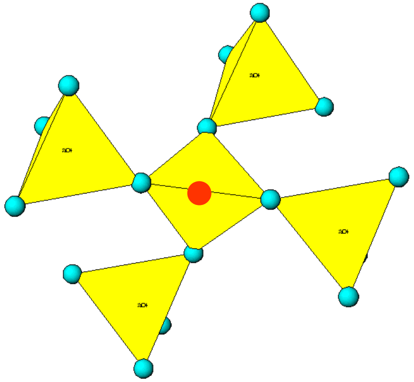
MO-SiO_2 binaries: M = Ca, Mg

Alkali silicates

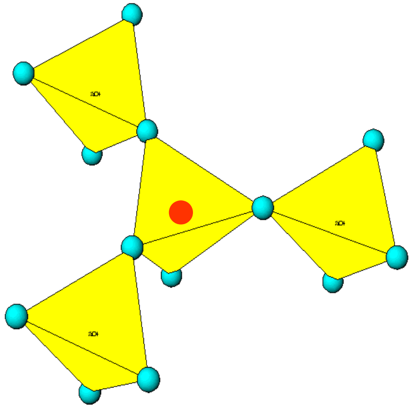
Network formers (Si, Al). Atoms that link together with BO to form network (form BOs) .

Network modifiers (Alkalis, Alkaline-earths). Atoms that break BOs to disrupt the network (create NBOs)

Q^n species (●): n= # of bridging oxygens (BO)

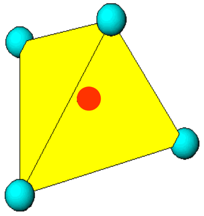


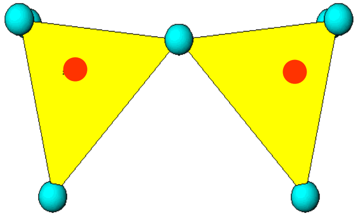
Q^4 35 possible arrangements



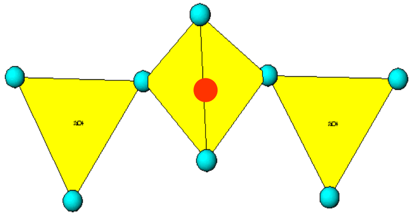
Q^3 20 possible arrangements

Q^0 1 possible arrangement





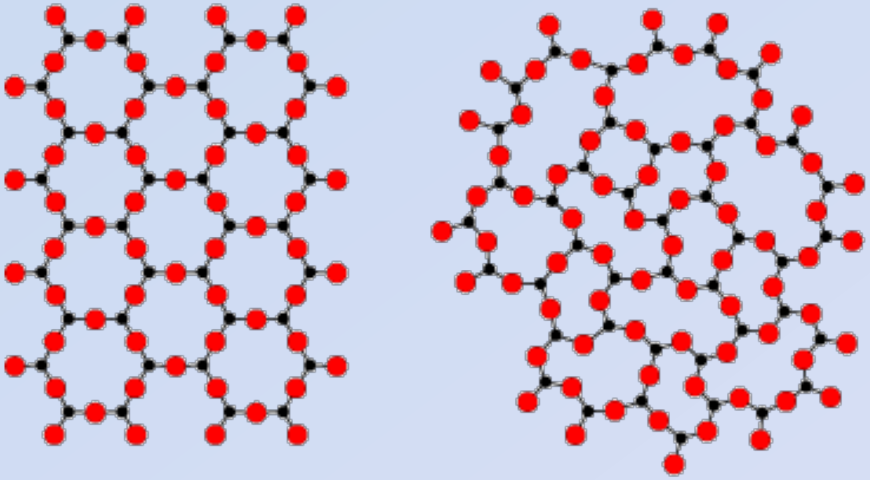
Q^1 4 possible arrangements



Q^2 10 possible arrangements

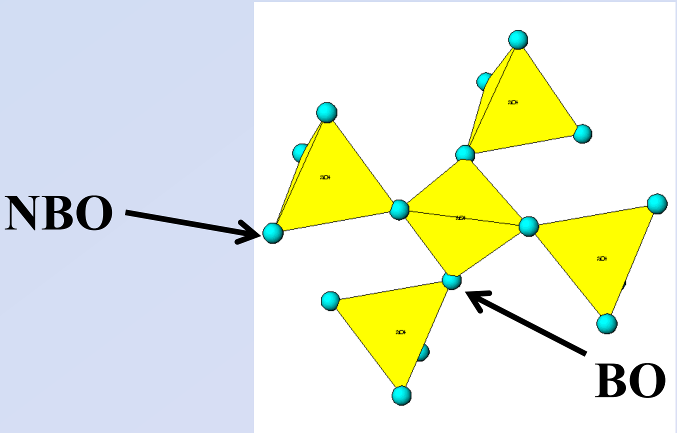
Proposed Oxide Glass Structures

The Continuous Random Network after Zachariasen and Warren (1930's)



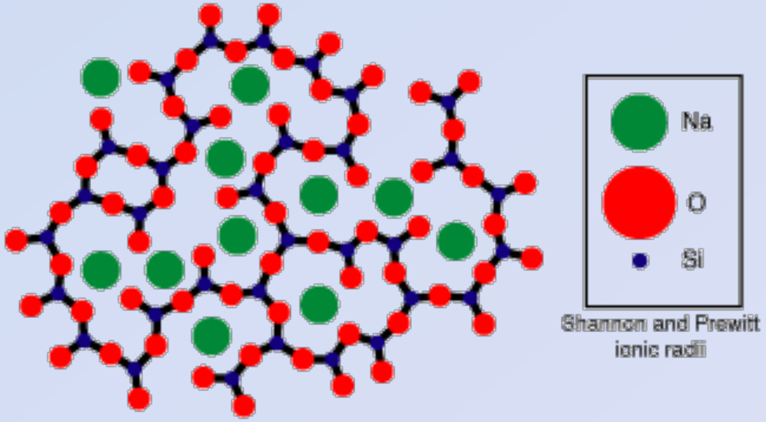
Crystalline A_2O_3

Glassy A_2O_3



Proposed Structure of Sodium Silicate Glass

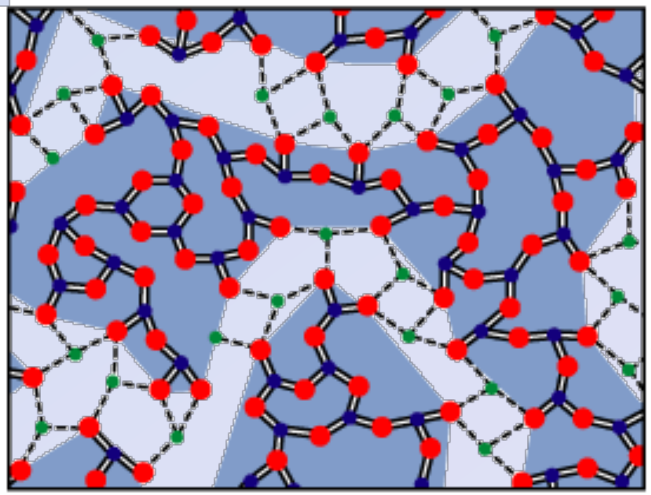
after Warren and Biscoe (1930's)



Modified Random Network

after Greaves

J. Non-Cryst. Solids, **71,** 203(1989)



Conventional thinking: Glasses have

- BO: Si-O-Si, O bonds to 2 network former
- NBO: Q^1, Q^2, Q^3, Q^4 plus combinations: Si-O, O bonds to 1 network former

- No free oxygen (O^{2-}): O not bonded to a network former (example: Na_2O)

Recent Studies : Glasses have

- NBO: Q^1, Q^2, Q^3, Q^4 plus combinations
- BO: 2 or more types (BO, MBO, MBOM, M_3BO)
- Free oxygen (O^{2-}) can be present at mol% levels
- Polymerization of melt generates O^{2-}
- Changes interpretation of NMR/Raman spectra of glasses and melts?

a) Disproportionation Reactions

$2Q^{n} \Leftrightarrow Q^{n-1} + Q^{n+1}$ e.g. $2Q^{3} \Leftrightarrow Q^{2} + Q^{4}$

No Change in polymerization!

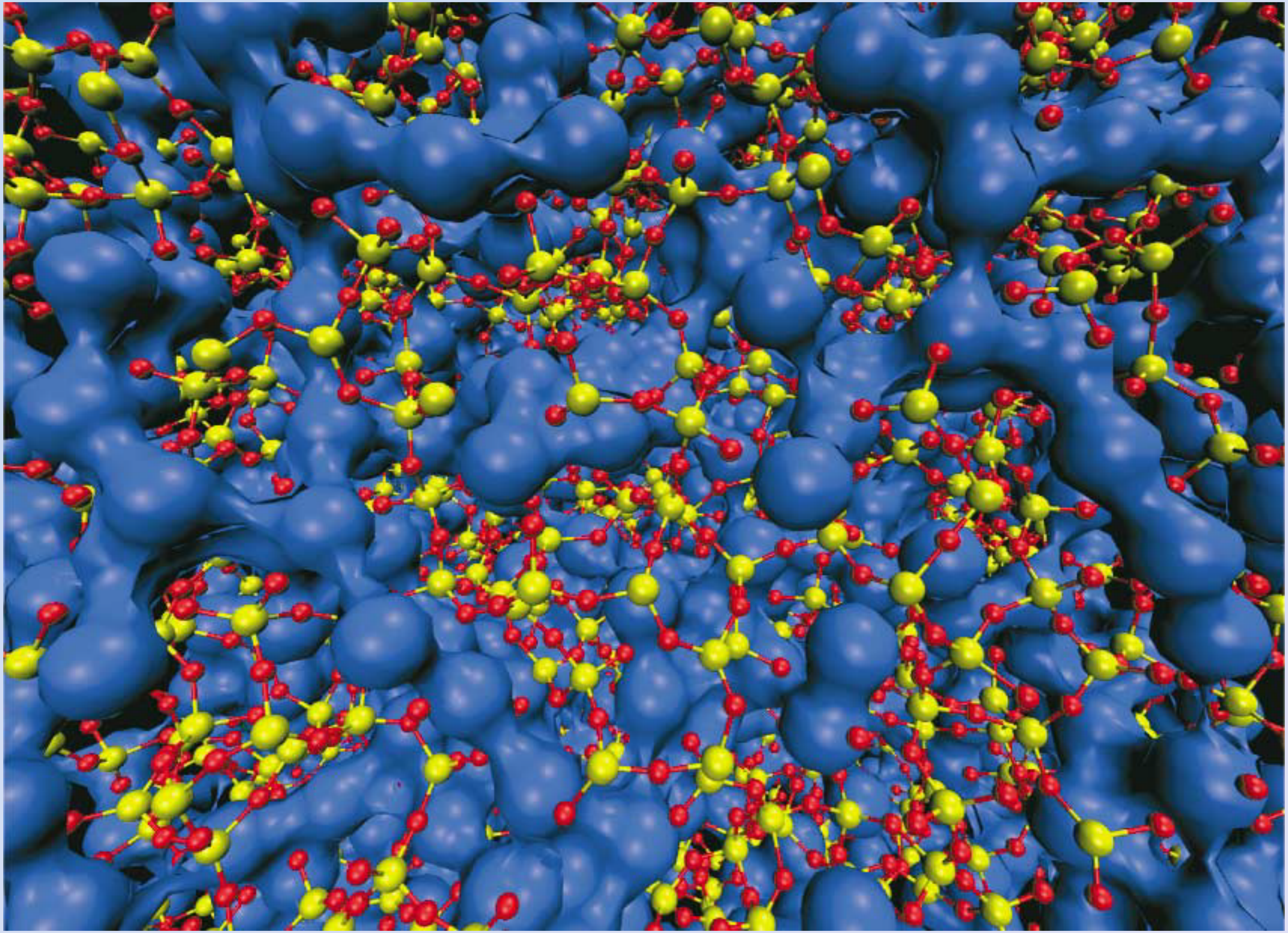
b) Polymerization Reactions

$2Q^{3} \Leftrightarrow Q^{4} + 2Na + O^{2-}$

Change in polymerization

$BO + O^{2-}$ (Na_2O) $\Leftrightarrow$ $2NBO^{-}$

O^{2-} = “free oxygen” = Non-network oxygen

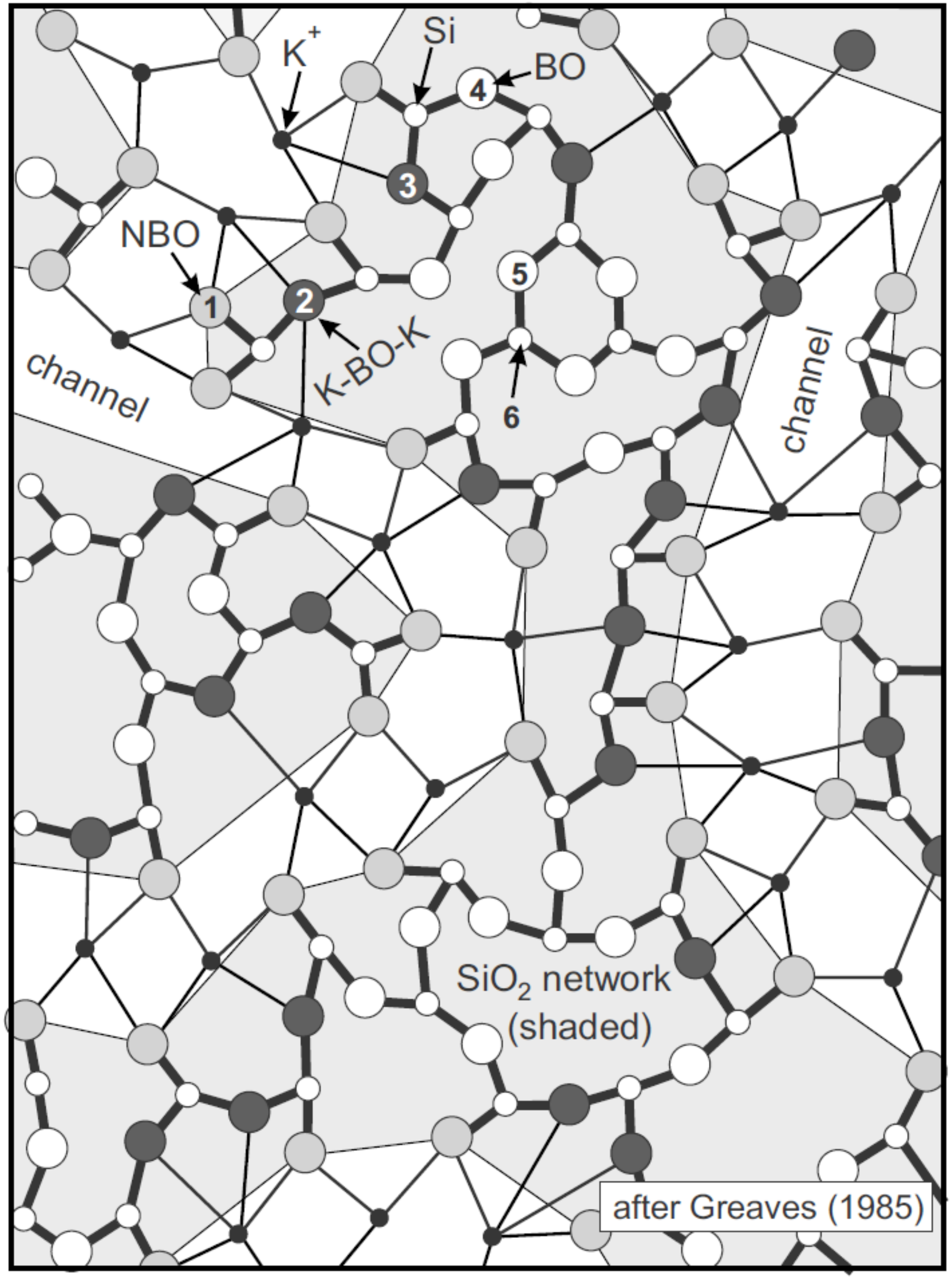


Meyer et al., 2004, Channel Formation and Intermediate Range Order in Sodium Silicate Melts and Glasses, PRL, 93, 027801.

Near channels and alkalis there will be a range of BO environments shown on right:

1) NBO
2) K-BO-K (MBOM)
3) K-BO (MBO)
4) BO
5) BO
6) Si

Away from the channels the rest of network has regular BO interactions



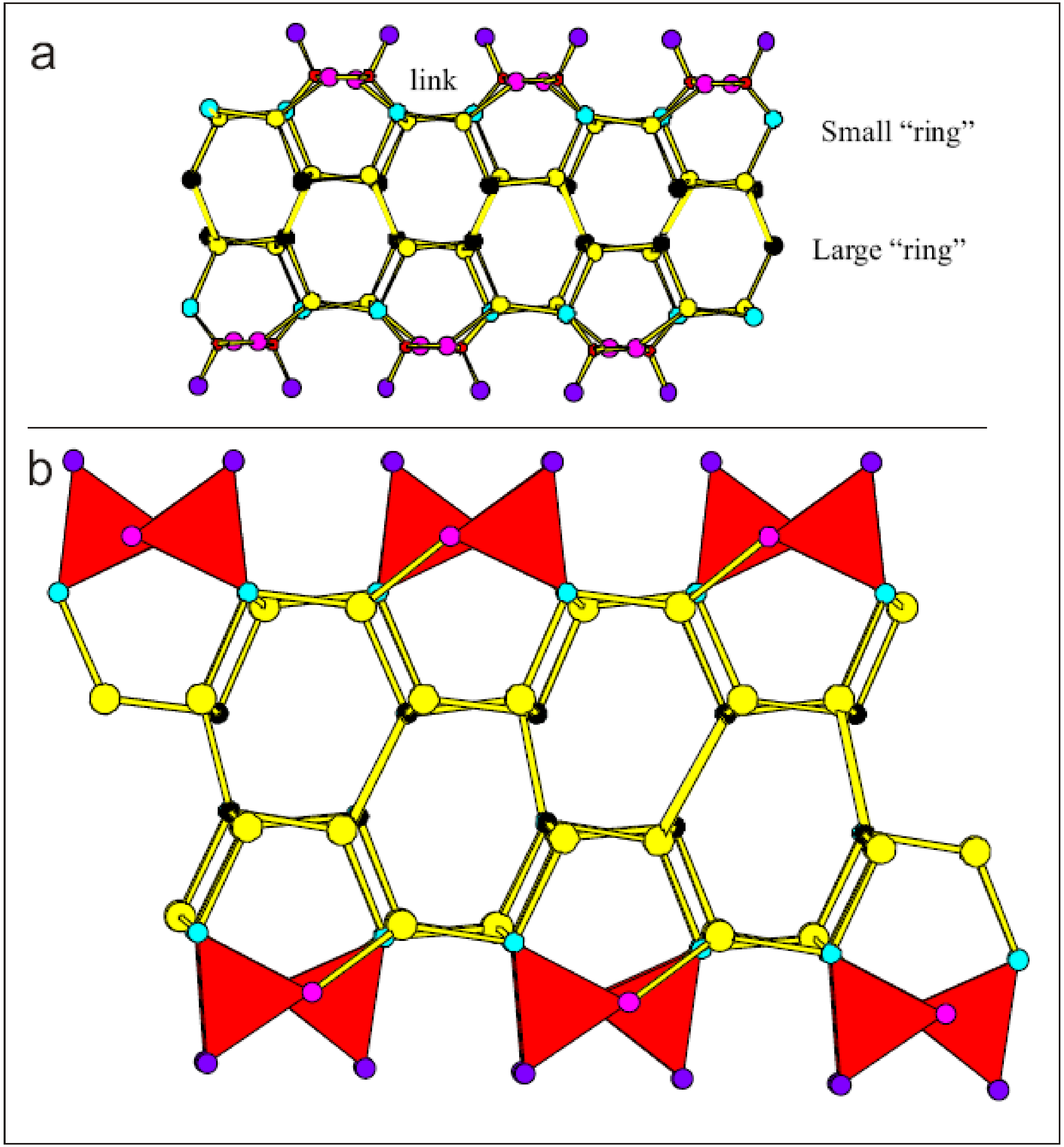
after Greaves (1985)

Channel Structure?

Probability of finding oxygen atoms NOT BONDED to Si is high

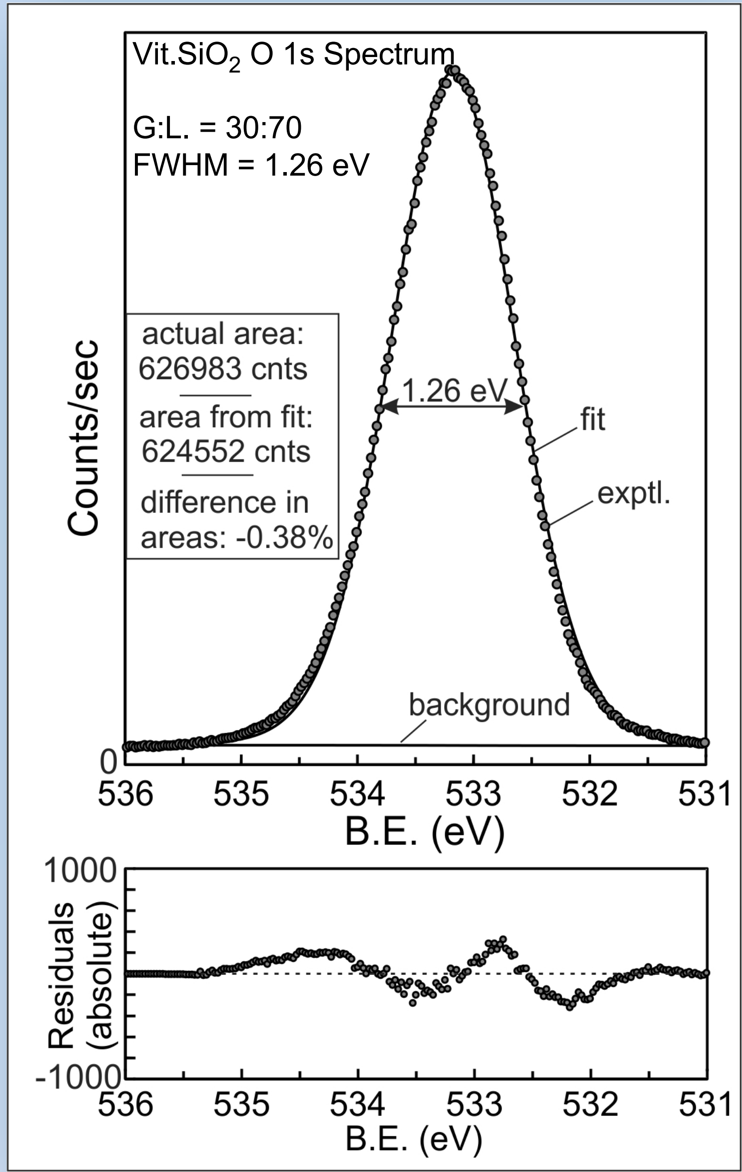
Called "free oxygen"

Nesbitt, Bancroft, Henderson, Ho, Dalby, Huang, Yan (2011), JNCS, 357, 170-180.

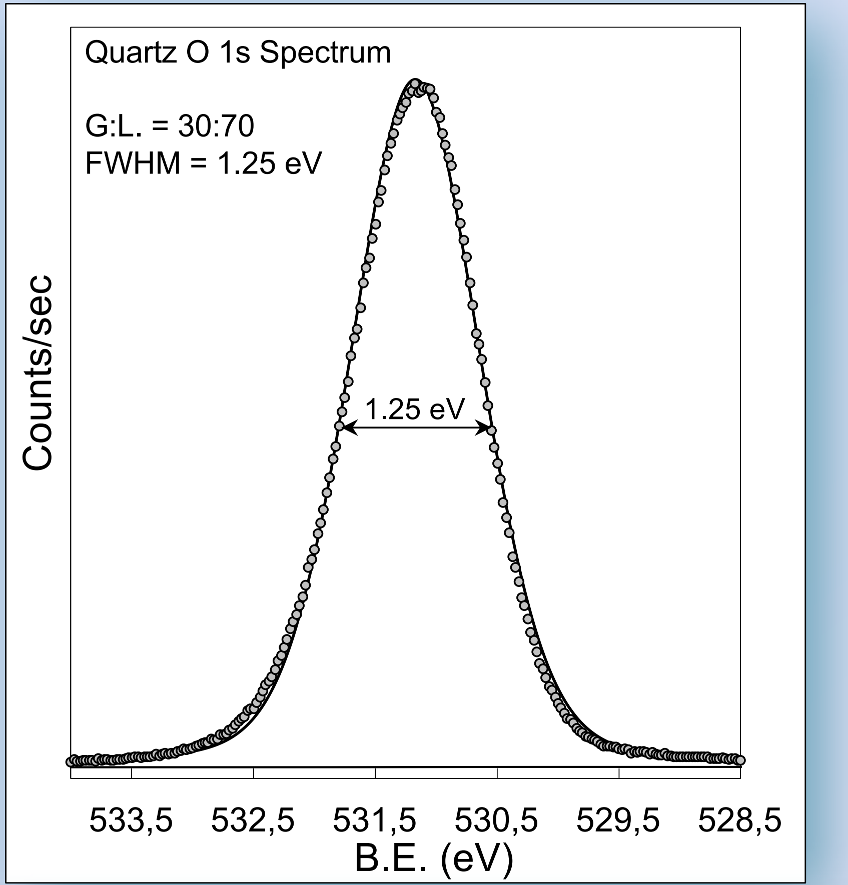


Part II, Quantification of O 1s Spectra: -- Evaluation of Peak Areas

Errors Associated with Symmetric Fits



Effect of State of Matter on Linewidths



Conclusions

1) For all silicates, O 1s linewidths ~1.25 ± 0.1 eV

2) If broader than ~ 1.35 eV, the peak likely is composite.

3) Peak shapes: ~ 30% Gaussian-70% Lorentzian

4) State of matter has little influence on linewidths.

Part III: To Evaluate Oxygen Speciation in Binary Silicate Glasses

BO = Si-O-Si moiety; NBO = Si-O-M moiety: O^{2-} = free oxygen = M-O-M moiety

Mass Balances and Thermodynamic Constraints

BO, NBO and O^{2-} are related through the reaction:

$$BO + O^{2-} \rightarrow 2NBO$$

and the mass action equation:

$$K_1 = (NBO)^2/\{(BO)(O2-)\}$$

where brackets = activities

To Determine X_{BO}, X_{NBO} and X_{O2-}

1) Measure areas under the BO and NBO+O^{2-} peaks and from these areas determine the Mole Fraction of BO ($\mathbf{X_{BOm}}$).

2) Calculate X_{BO} expected assuming the above reaction goes to completion. (i.e. $\mathbf{X_{BO}}^* = (2X_{SiO2} - X_{K2O})/(2X_{SiO2} + X_{K2O})$ where X_{SiO2} and X_{K2O} are mole fractions in the binary system).

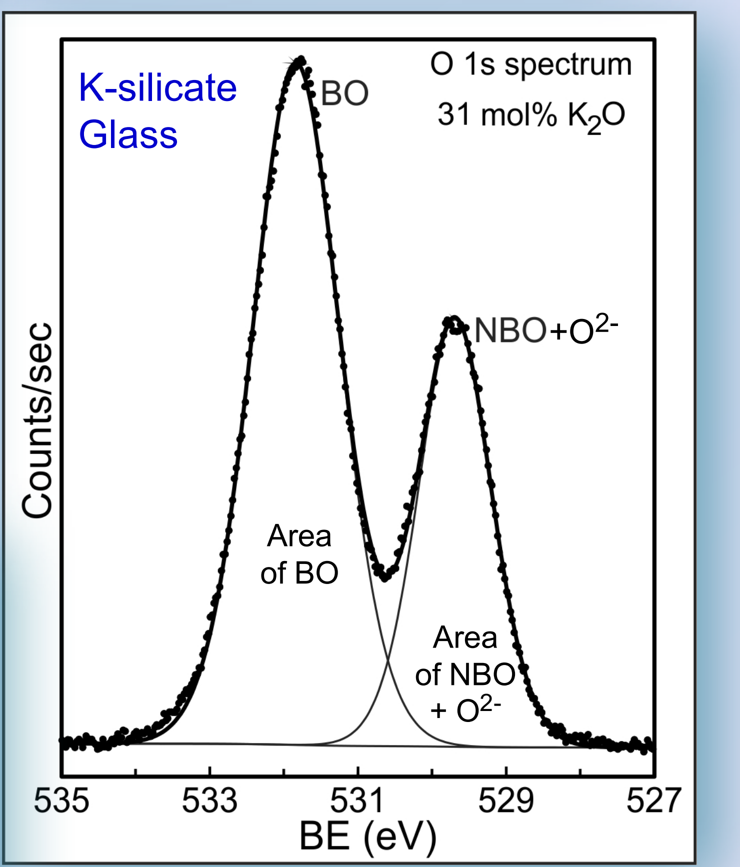
3) Compare X_{BOm} to X_{BO}^*

a) If $X_{BOm} < X_{BO}^*$ then the peak areas measured are incorrect.

b) If $X_{BOm} = X_{BO}^*$ then the reaction has gone to completion

c) If $X_{BOm} > X_{BO}^*$ then the reaction did not go to completion and there is free oxygen in the glass where X_{O2-} equals the amount for excess BO (i.e., $X_{BOm} – X_{BO}^*$)

4) X_{NBO} is calculated by difference (i.e., $X_{NBO} = 1.0 – X_{BO} – X_{O2-}$)



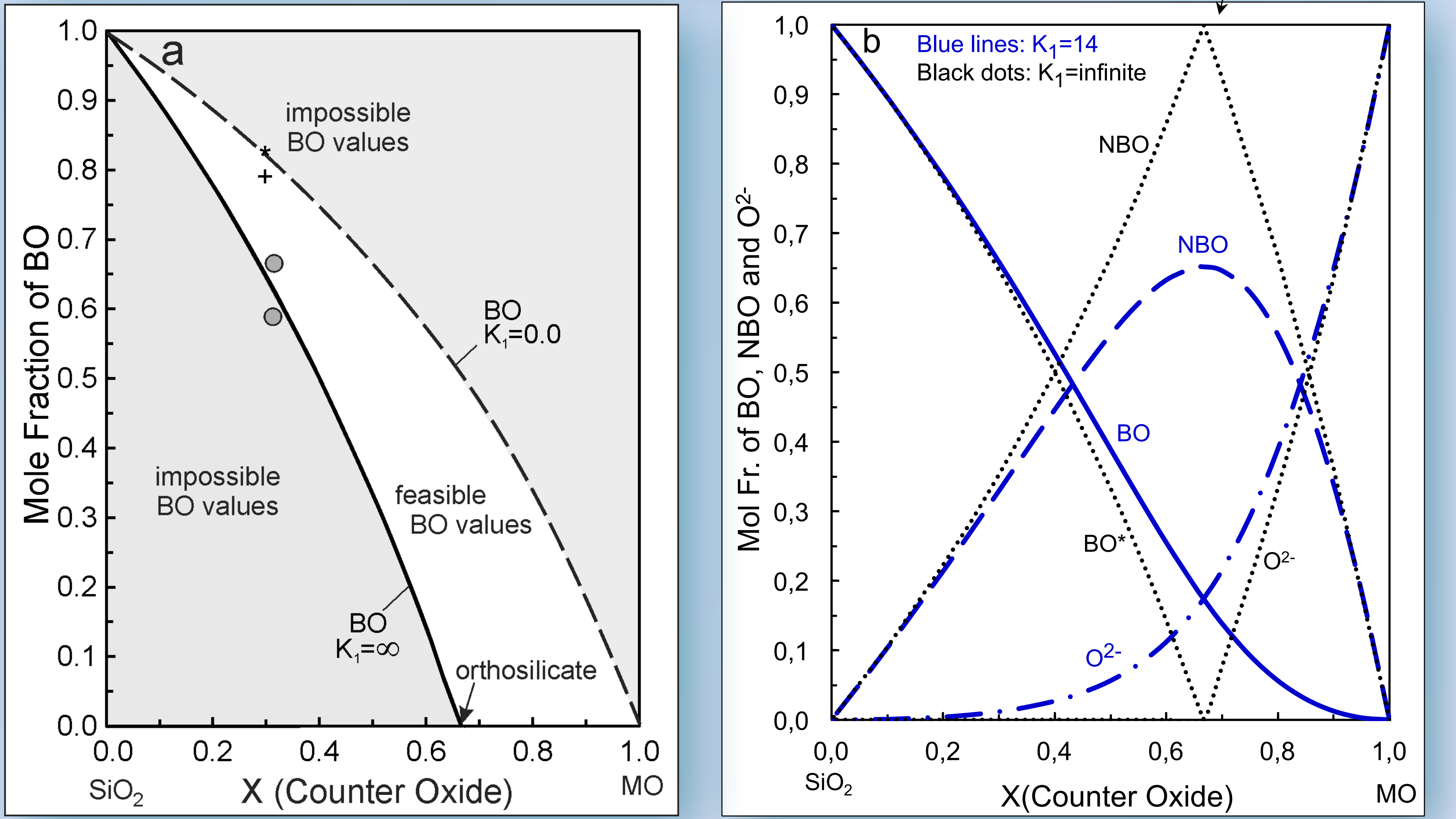
from Sawyer et al. (2014) Can. Jour. Chem. v.92, p. 1-14.

Part III: Oxygen Speciation in Binary Silicate Glasses

$BO + O^{2-} \rightarrow 2NBO$ and $K_1 = (NBO)^2/\{(BO)(O2-)\}$

At the orthosilicate composition, reaction stoichiometry requires $X_{BO} = X_{O2-}$

If K_1 is infinite then only NBO is present at the orthosilicate composition.



Oxygen Speciation in Na-Silicate Glasses

Consistency Of Results

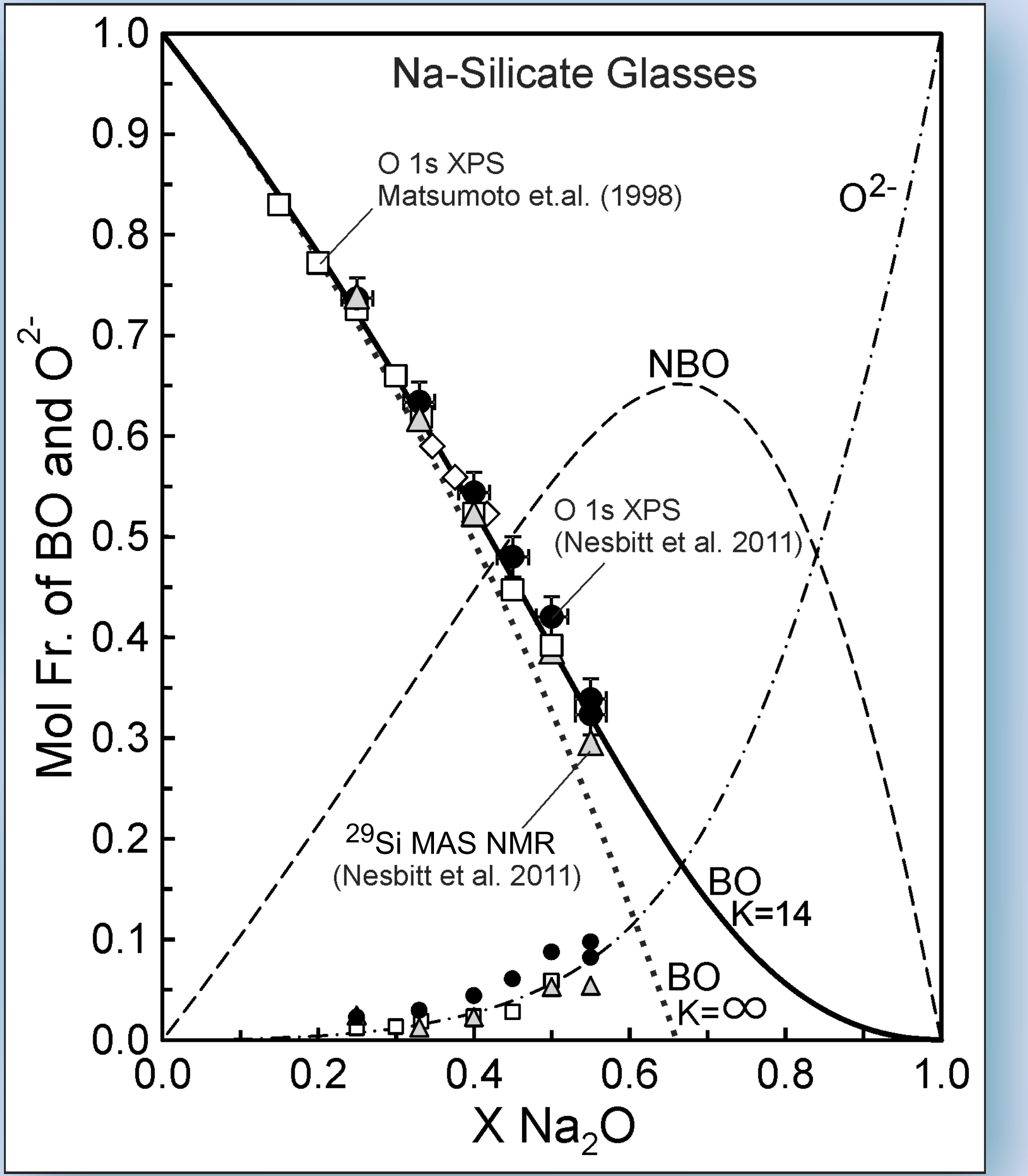
Experimental: Two O 1s XPS experiments and a ^{29}Si MAS NMR experiment yield similar X_{BO} results.

Thermodynamic: Within exptl. uncertainty the X_{BO} values conform to the mass action equation where the conditional equil. constant (K_1) ~ 14.

Conclusion

X_{BO} values are consistent with the presence of some free oxygen in Na-silicate glasses and indicate ~ 1-2 mol% O^{2-} in Na-disilicate glasses and increasing to ~ 4-6 mol% O^{2-} at the metasilicate composition.

Data from Nesbitt et al., (2011) J. Non-Cryst. Solids, v. 357, p. 170.
and
Matsumoto et al. (1998) Jour. Ceramic Soc. Japan, v. 106, p. 415.



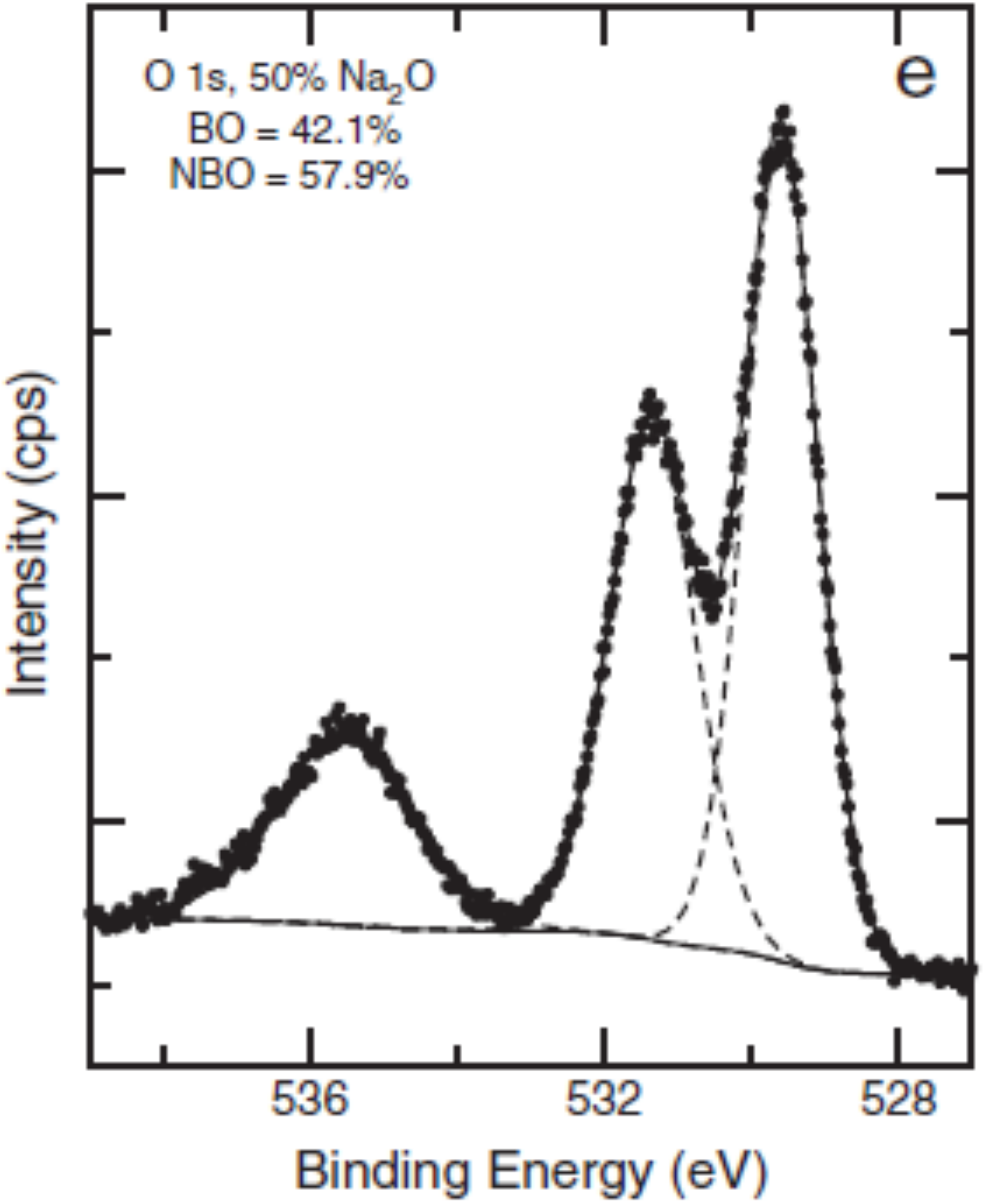
Na_2O-SiO_2 glasses must have O^{2-} present: Channels, NMR, thermodynamics/mass balance, MD

0.1% in 10 mol% Alkali, 3-6% in 50 mol% glasses

O^{2-} is under NBO

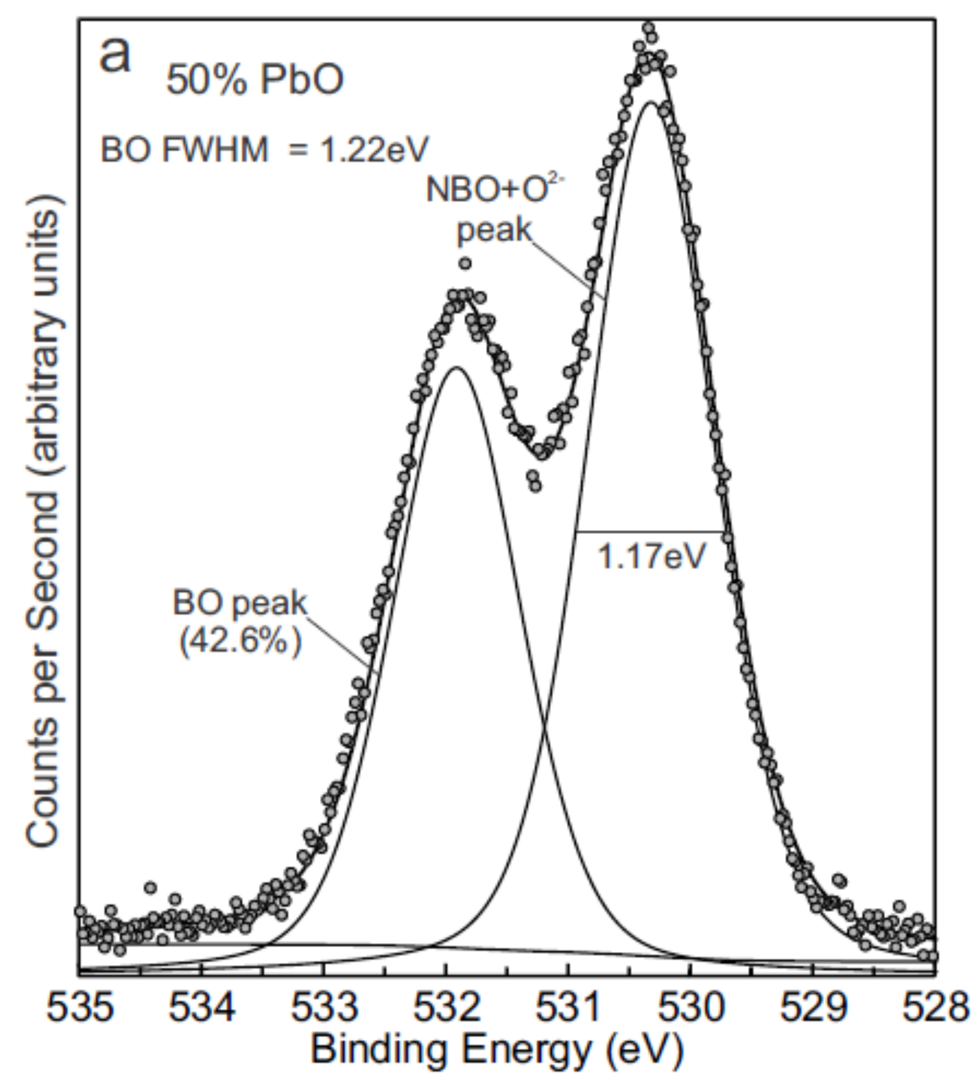
But don't see significant increase in FWHM

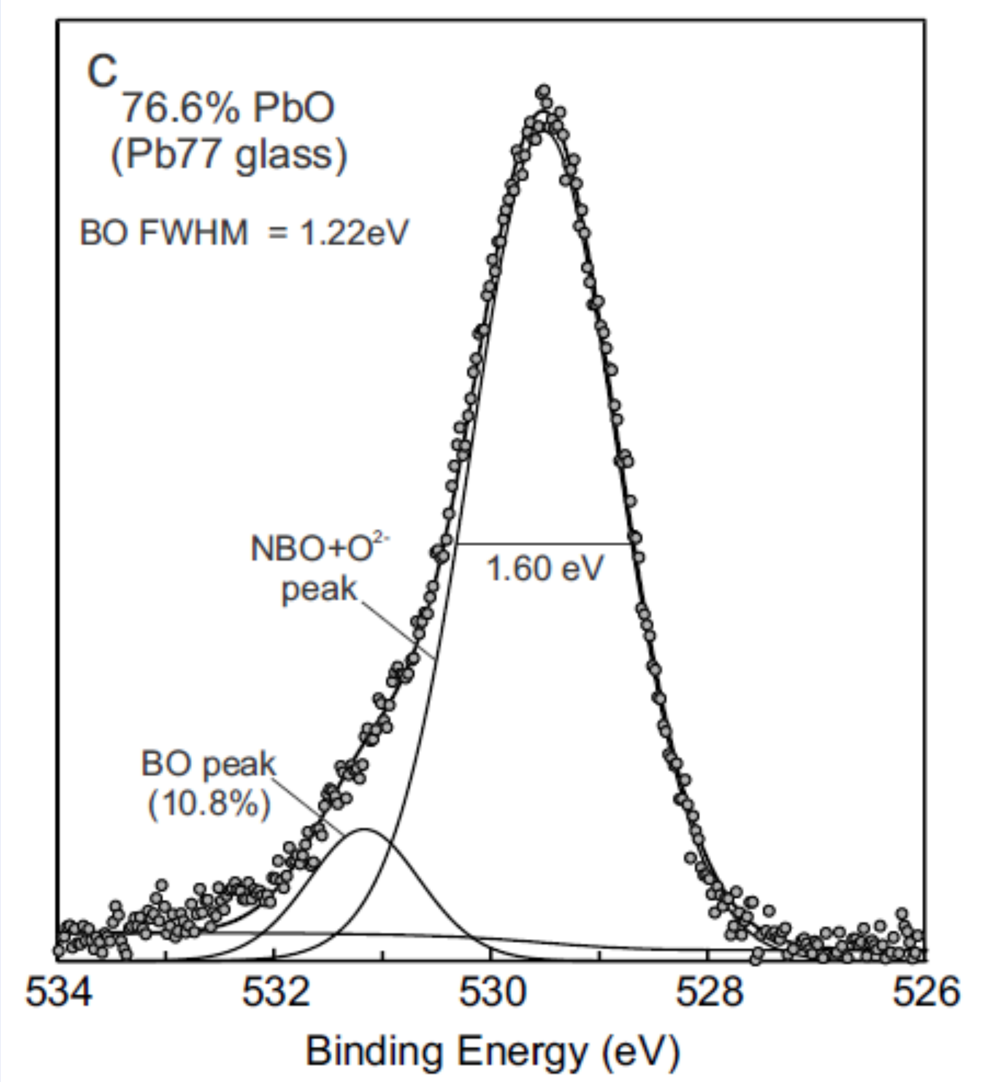
Can we see it?



$PbO-SiO_2$ glass can be made with very high amounts of PbO. Should have large amounts of O^{2-} (>30%).

FWHM of NBO peak increases with increasing PbO.





Determining the Mole Fractions of Oxygen Species in Binary Silicate Glasses

Fitting & Interpretation of O 1s Peaks

a: Two unconstrained peaks introduced
Test : FWHM conform to theoretical value of 1.25 +/- 0.1 eV.

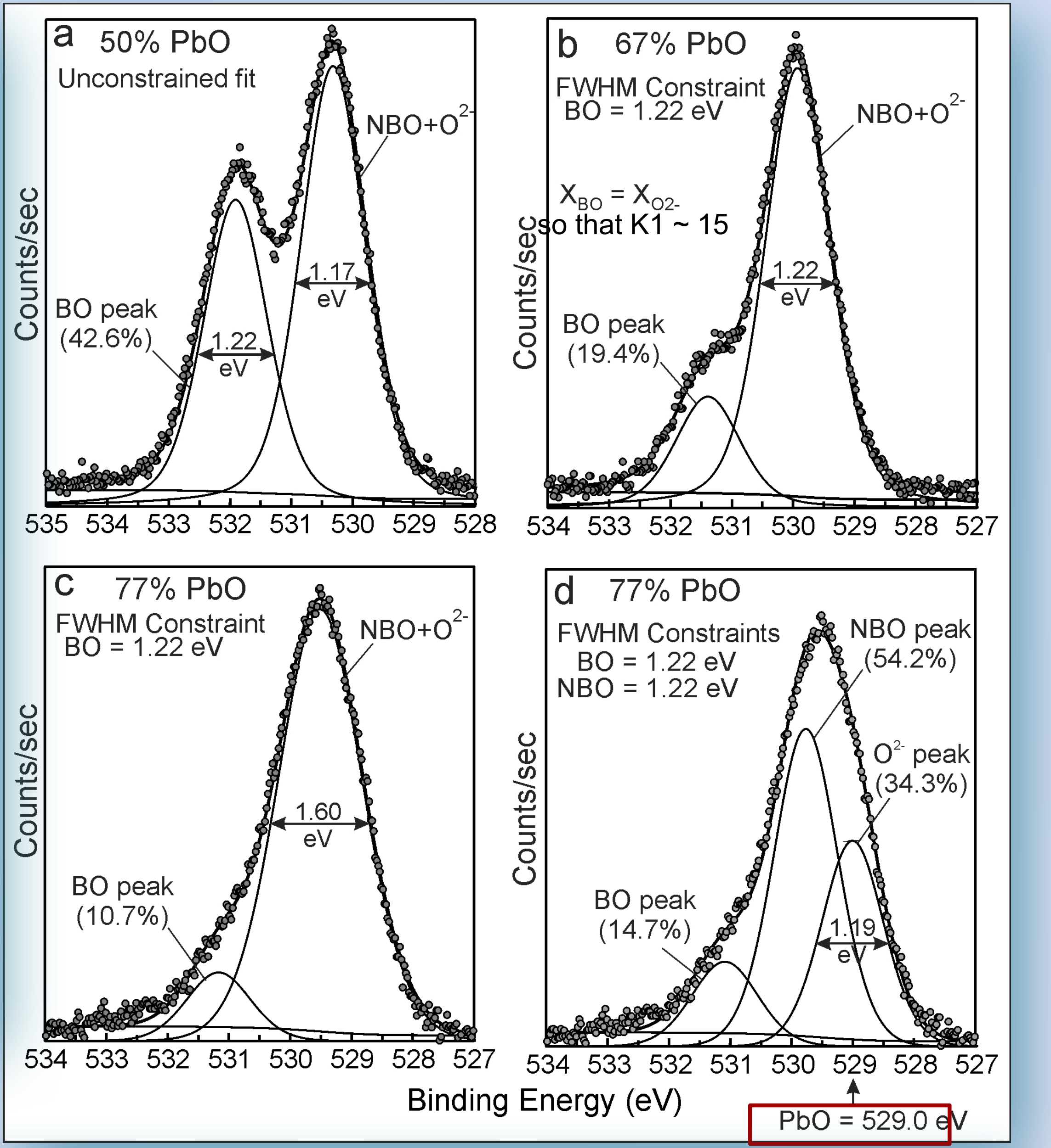
b: BO peak constrained to 1.22 eV and NBO+O^{2-} was unconstrained.

c: BO peak constrained to 1.22 eV and NBO+O^{2-} was unconstrained. An unacceptably large FWHM is obtained and needs explanation.

d: BO and NBO constrained to 1.22 eV. A third unconstrained peak was fitted.

Interpretation: Broadened peak in ‘c’ is due to a very strong O^{2-} signal.

O 1s XPS Spectra of Pb-Silicate Glasses



From Dalby et al. (2007) GCA, v.71, p. 4297, and Nesbitt et al. (2015), Am. Min. 100, 2566..

Spectroscopic and Thermodynamic Tests for Consistency

Spectroscopic Consistency

BO abundances obtained from ^{29}Si MAS NMR measurements (Fayon et al. (1998) are plotted as squares.

BO abundances from O 1s XPS results (Dalby et al., 2007) are plotted as shaded circles.

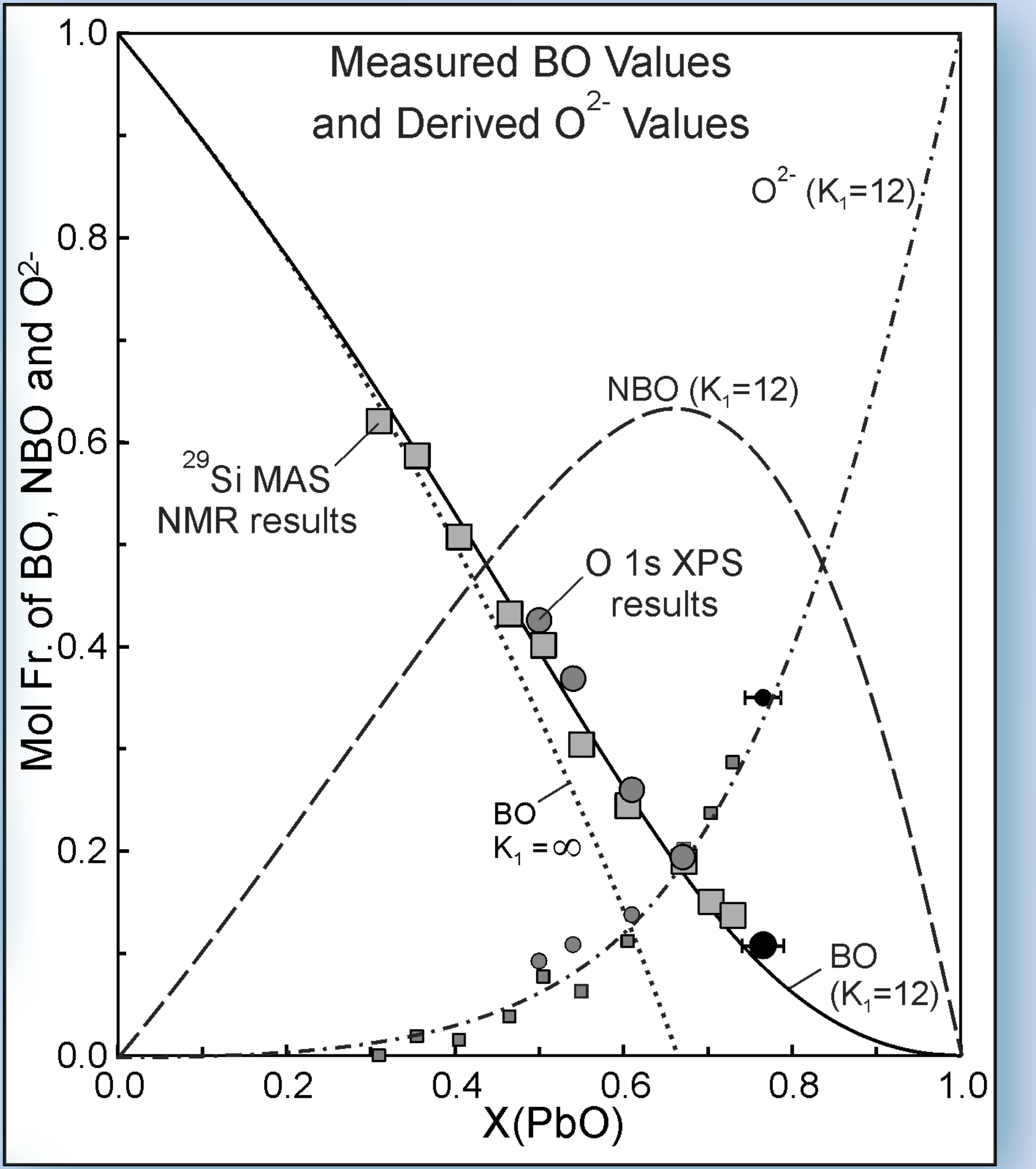
Thermodynamic Consistency

The NMR and XPS results are consistent with the mass action equation (K_1 ~ 12) and the consistency holds over a large compositional range.

Mole fractions of BO, NBO and O^{2-} were used in place of activities so that K1 is a conditional equilibrium constant.

Evaluation of Free Oxygen

For each measured XBO value, K1 = 12, and the reaction stoichiometry, a X_{O2-} has been calculated and is plotted.



from Nesbitt et al. (2015) American Mineral, 100, 2566

Some observations

Free oxygen widely accepted in glass and materials science communities. Existence is denied by Earth science community

13 separate Raman and NMR studies of Mg/Ca silicate glasses indicate the presence of free oxygen (O^{2-})
23 separate NMR and Raman studies indicate its presence in alkaline earth silicate glasses
21 numerical simulations on alkaline-Earth glasses indicate free oxygen

All indicate ~1-2.6 mol% in metasilicate glasses and ~5-10 mol% in orthosilicate glasses.

What is the importance of “free” oxygen (O^{2-})?

For over 100 years no mechanism to explain melting of silicate minerals

Proposed mechanism involving “free” oxygen (O^{2-})

1) **Breaking of weak M-O bonds prior to melting, to produce itinerant M^+ and $Si\text{-}O^-$ moieties attached to chains**
2) **Reaction of $Si\text{-}O^-$ to form cross-chain linkages which produces free oxygen (O^{2-})**
3) **Reaction of O^{2-} with SiO_3 chains to depolymerize (rupture) them causing melting.**
4) **O^{2-} plays essential and critical role in melting and crystallization of silicate minerals!**

Nesbitt, Bancroft, Henderson, Richet, O’Shaughnessy, Melting, crystallization, and the glass transition: Toward a unified description for silicate phase transitions, Am Min 102, 412, 2017

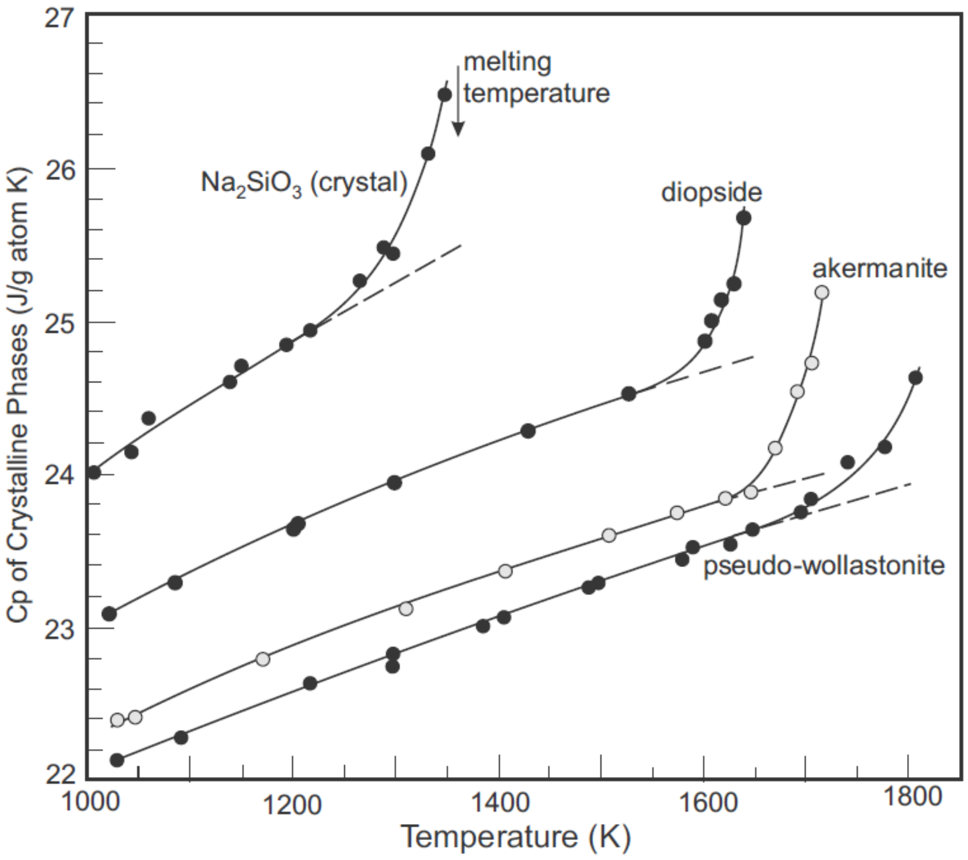
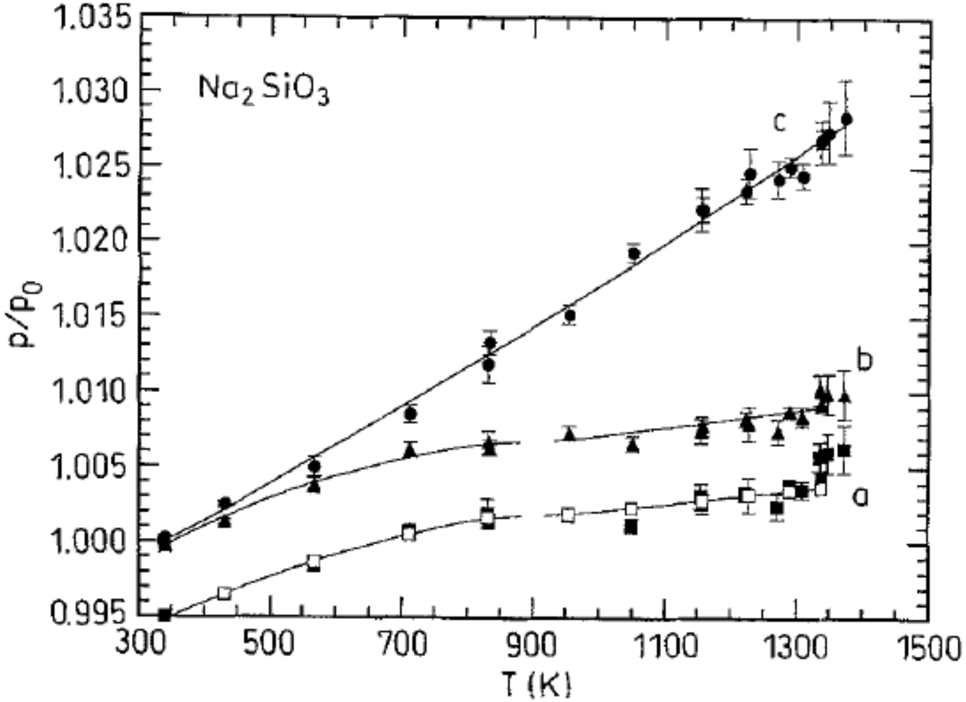


Fig. 2

Heat Capacity (Cp) exhibits inflexion before melting point Implies pre-melting phenomenon

In crystalline metasilicate (Na_2SiO_3)
a-b plane undistorted
c axis exhibits linear changes with T

Richet et al., 1996 Phys. Chem. Mineral., 23, 157.
Richet et al., 1998 Phys. Chem. Mineral., 25, 401.



Similarity between NMR and Raman spectra

Q^2 dominate spectra

$Q^3 > Q^1$

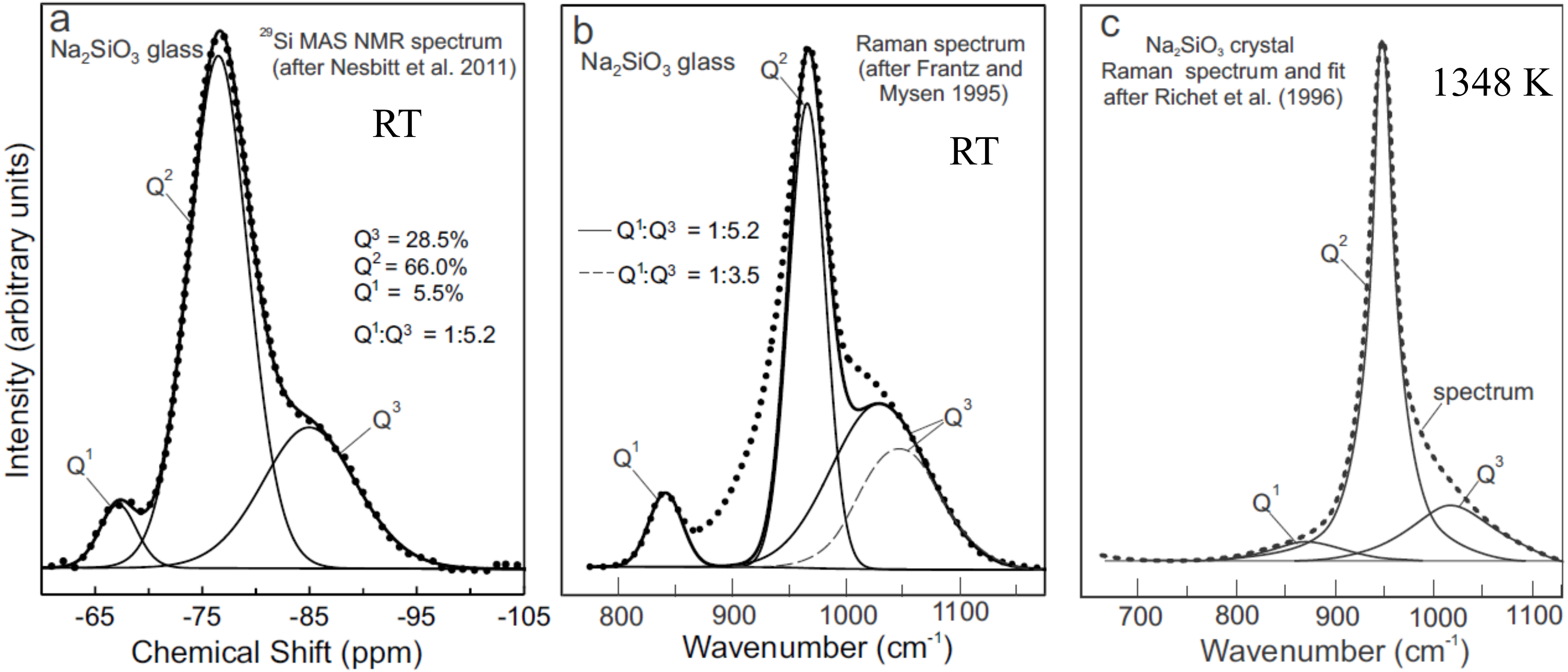


Fig. 3

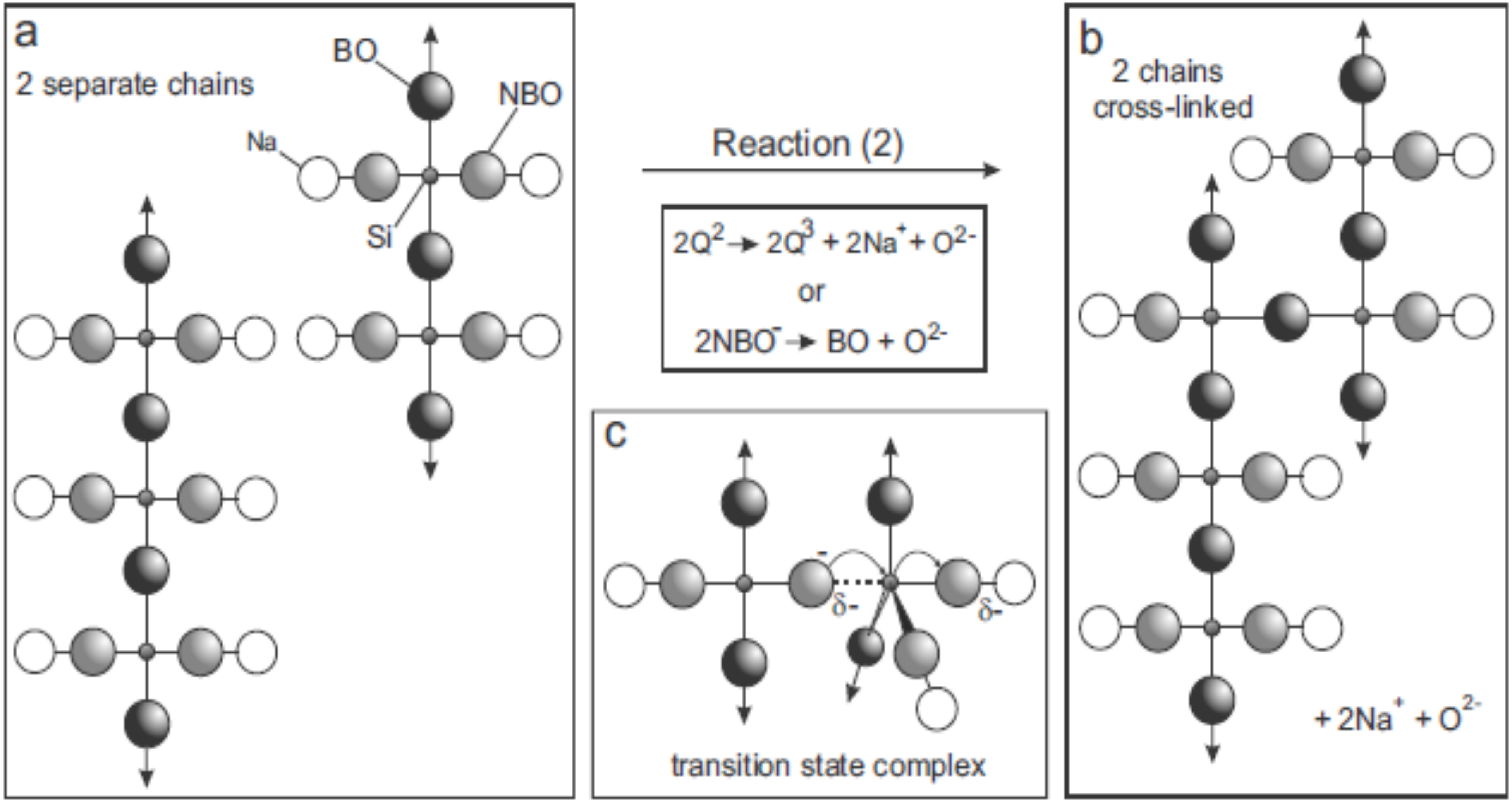
Nesbitt et al., 2011, JNCS, 357, 170. Frantz and Mysen, 1995, Chem. Geol. 121, 155..
Richet et al., 1998, Phys. Chem. Mineral., 23, 157.

Pre-melting reactions

$2Q^2 \rightarrow 2Q^3 + 2Na^+ + O^{2-}$ indicated by Q^3 in Raman

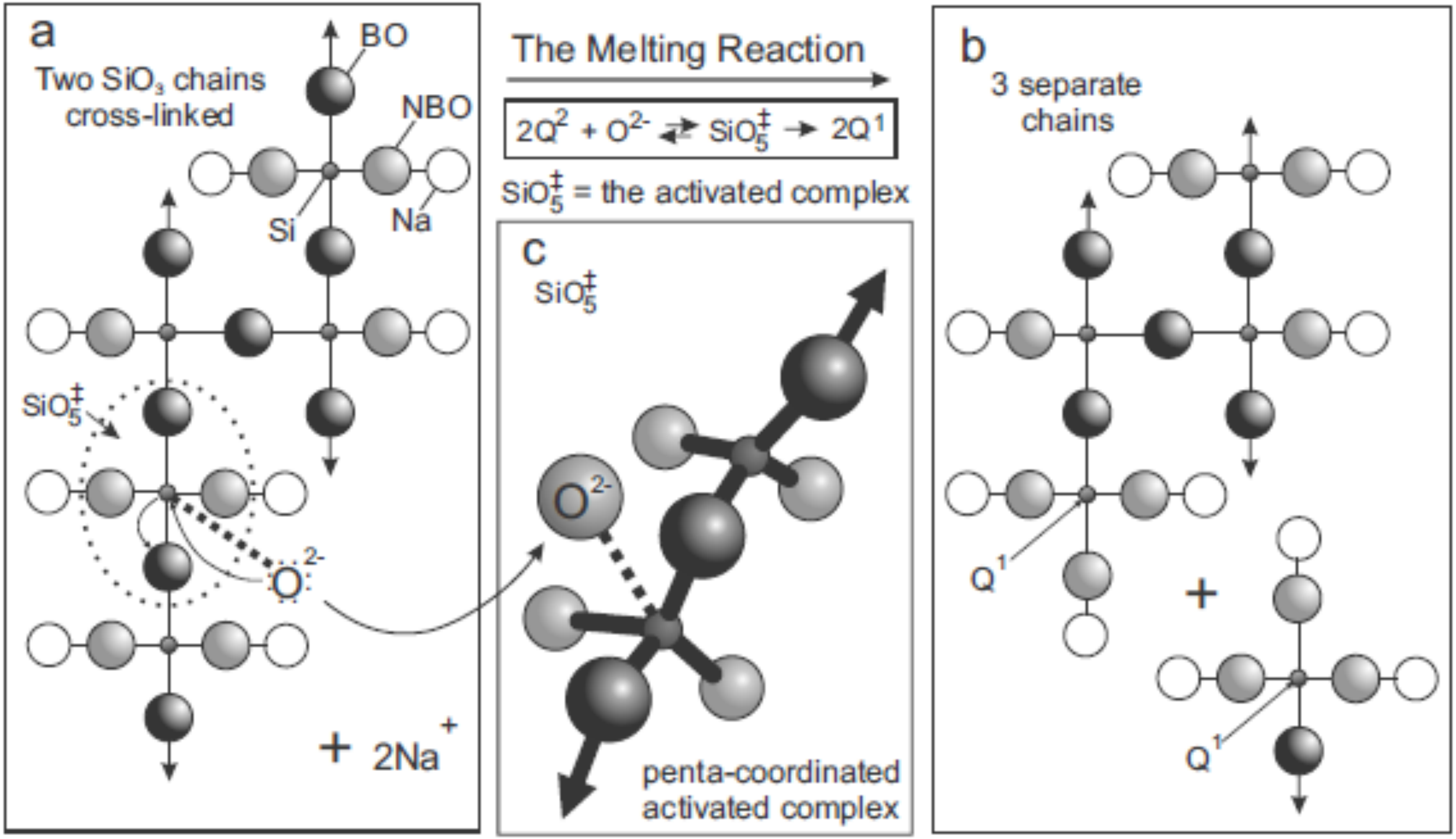
Q^3 form in a/b plane, prevent expansion

$Si\text{-}O^- + Q^2 \rightleftharpoons [(Si\text{-}O\text{-}Q^2)\text{-}]^{\ddagger} \rightarrow 2Q^3 + Na^+ + O^{2-}$



Melting Reaction

$$2Q^2 + O^{2-} \rightleftharpoons SiO_5^{\ddagger} \rightarrow 2Q^1$$

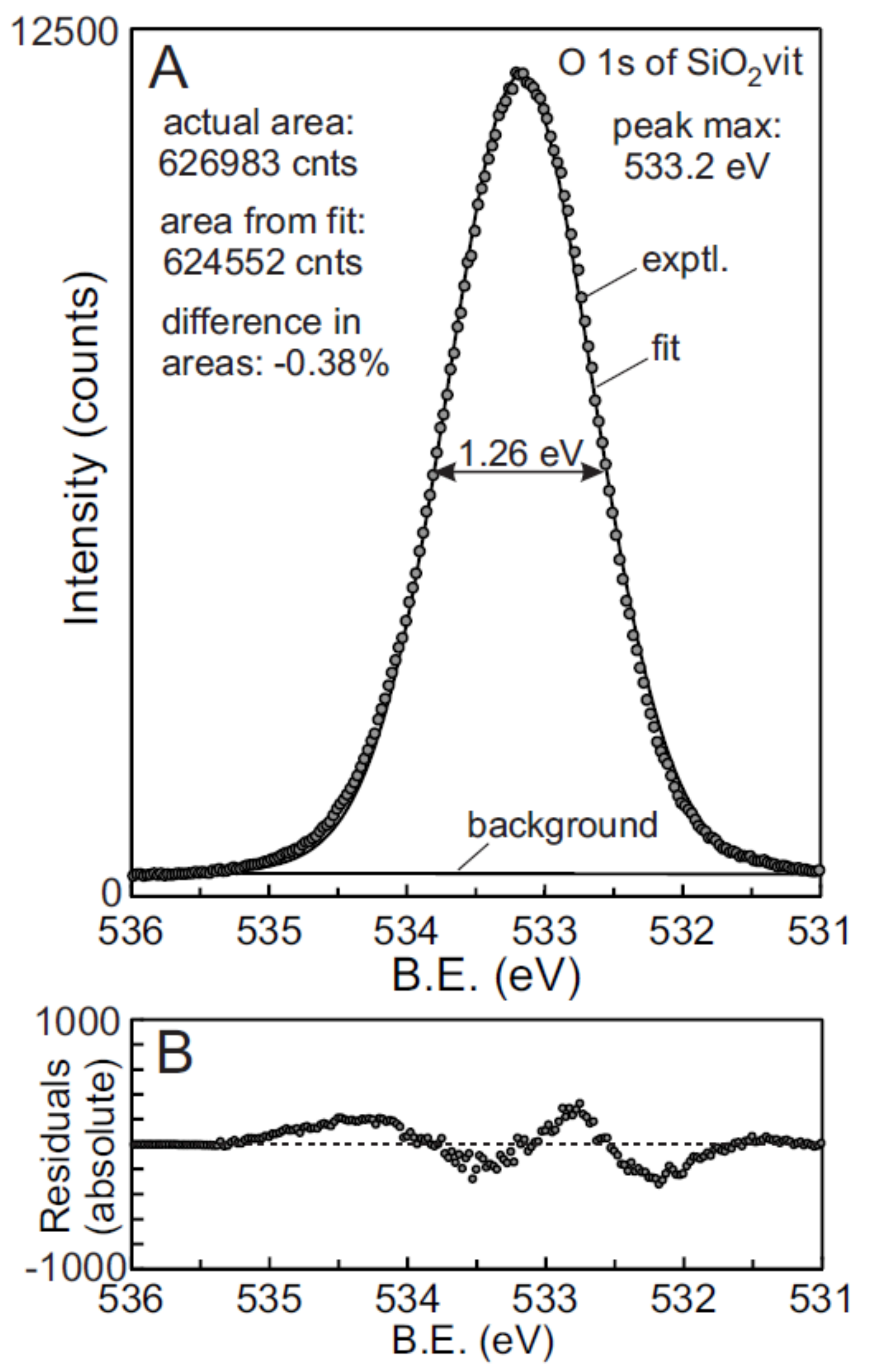


What about the presence of MBOs?

Theoretical line widths (FWHM) of O 1s spectra in all glasses should be ~1.25 eV

Observed line widths (FWHM) of O 1s spectra in silicate glasses are 1.22- 1.26 eV

Observed line widths (FWHM) of O 1s spectra in silicate glasses close to theoretical FWHM!

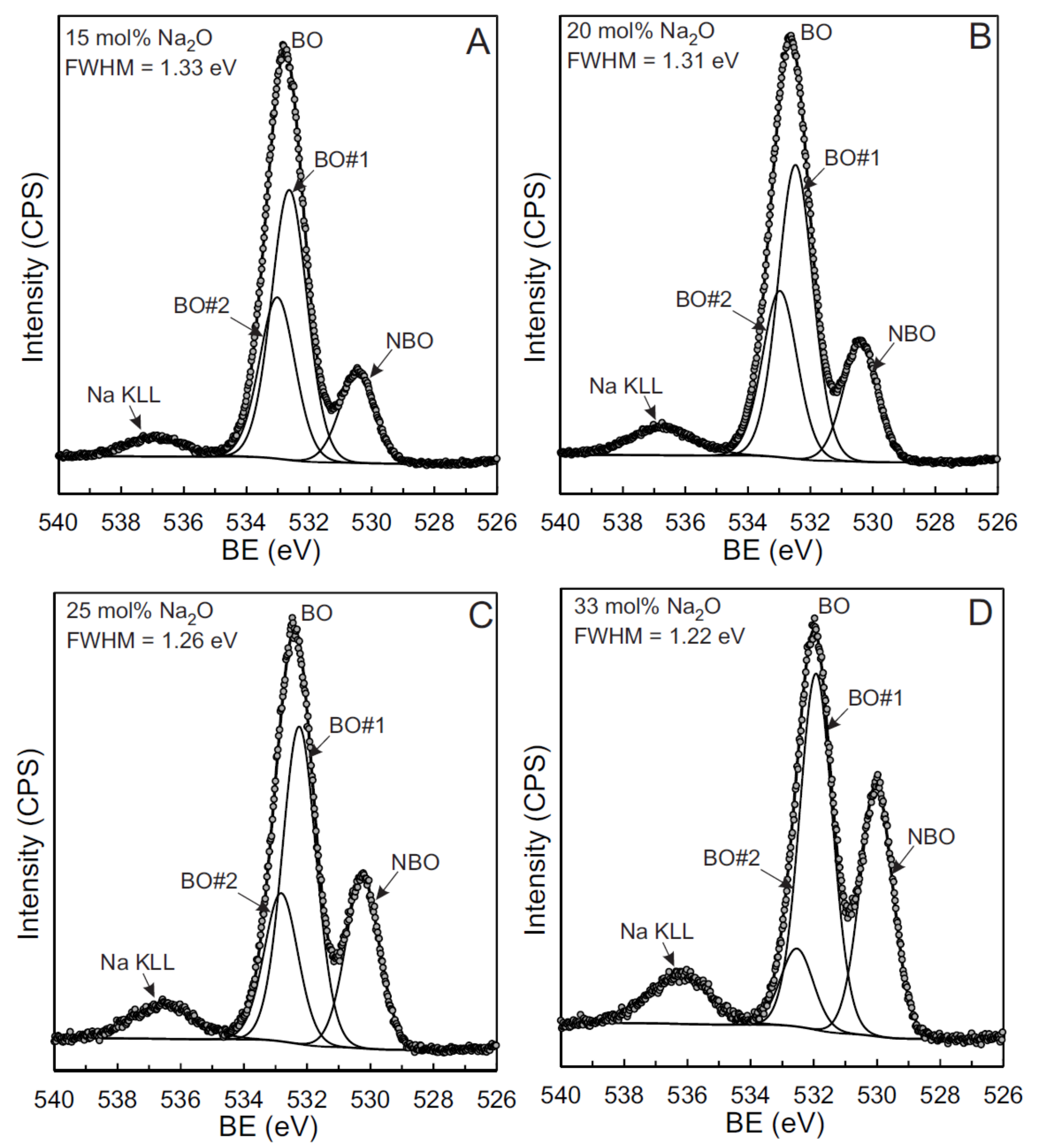


BO FWHM increases with increasing alkali (1.26 to 1.57 eV)

Suggests that 2nd BO species present (MBO)

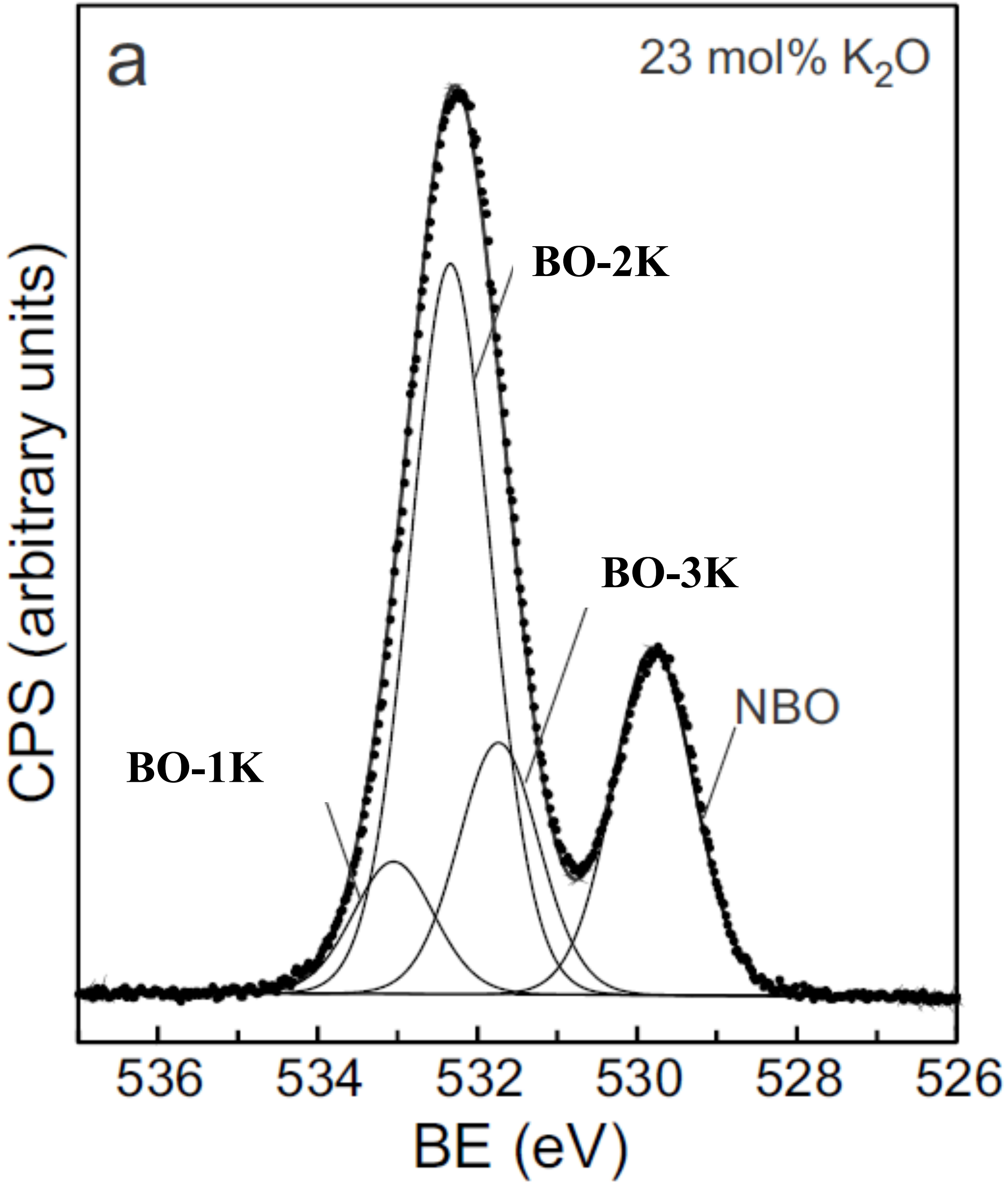
Two peak (BO, MBO) fit with both FWHM constrained to 1.25 eV: MBO>BO

Will affect density and volume of magma and ascent rates



Nesbitt, Henderson, Bancroft, Ho (2015), JNCS, 409, 139-148.

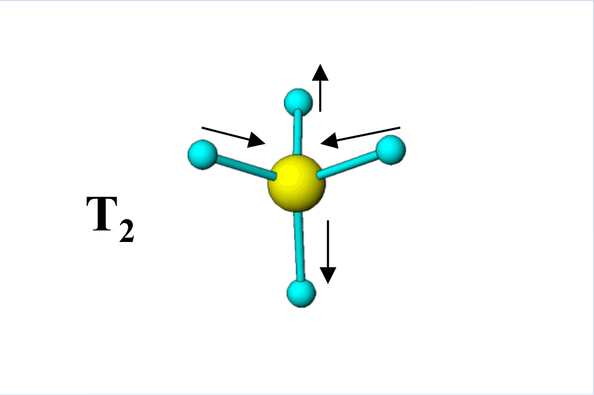
- Fit to BO peak in $K_2Si_2O_5$ glass indicates 3 BO peaks
- Crystal structure of $K_2Si_2O_5$ (de Jong et al (1998) Acta Cryst, B54, 568) has 15 unique oxygen sites
- With cutoff of 3.25Å have 1 BO-K, 6 BO-2K, 2 BO-3K
- BE will decrease as K atoms approach BO
- Fit has approximate ratio of 1:6:2
- BO peaks are consistent with MBO combinations derived from crystal structure.
- Does approach of alkali to BO affect Raman and NMR frequencies of Q species? E.g., increase in Q^4 intensity.

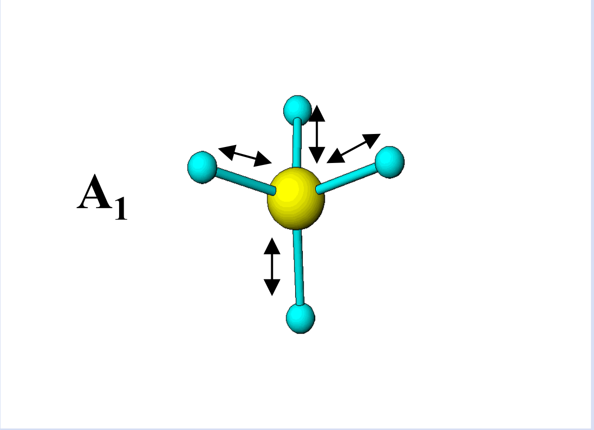


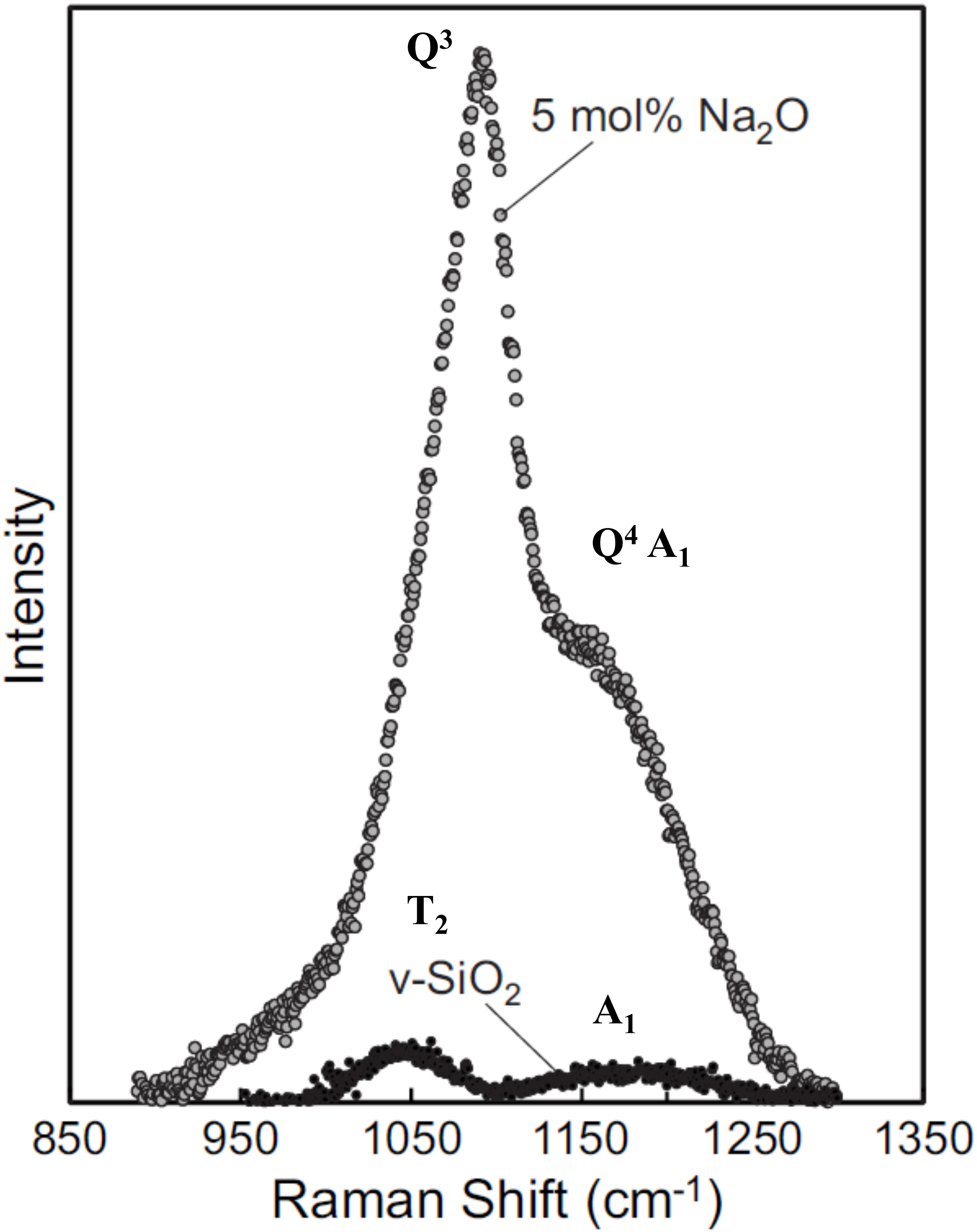
Nesbitt et al., 2017a, Chem Geol, in press

The addition of small amounts of alkali greatly increase Q^4 A_1 band intensity.

Why?







Raman Spectral Fitting and Interpretation

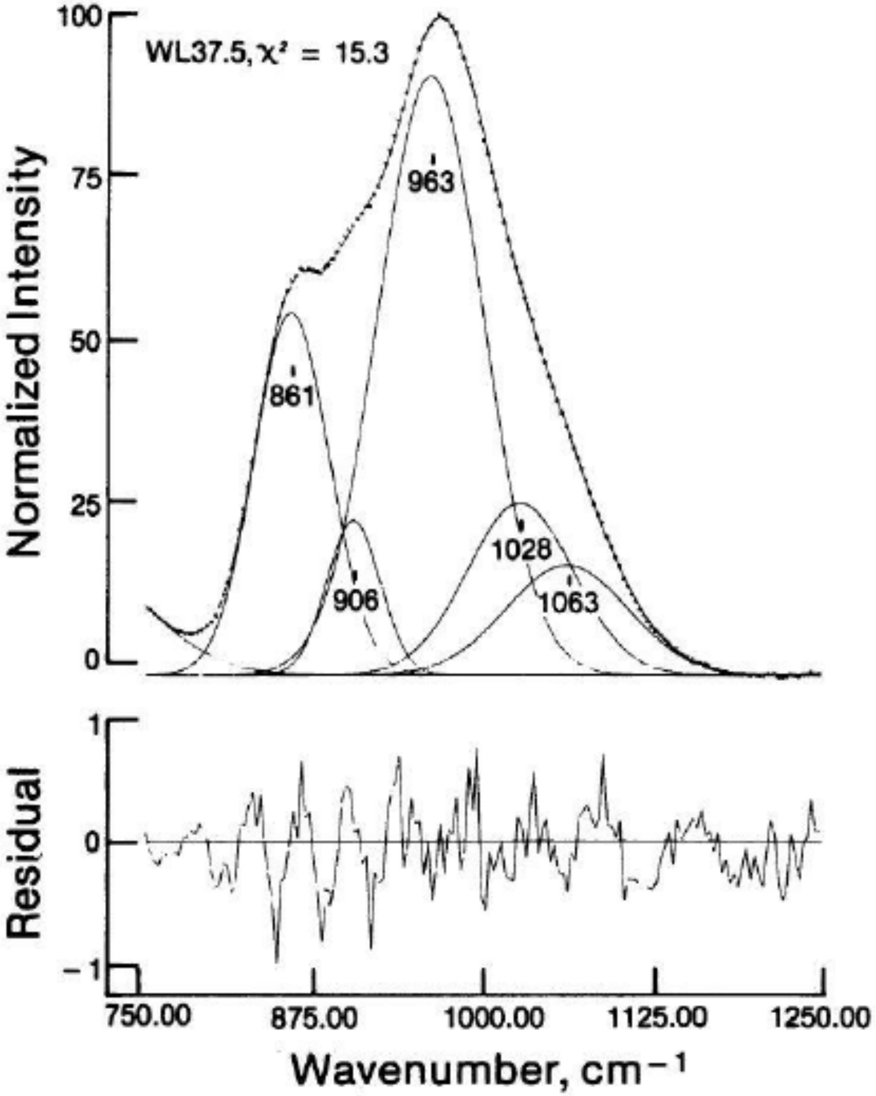
Three main types of fitting procedures

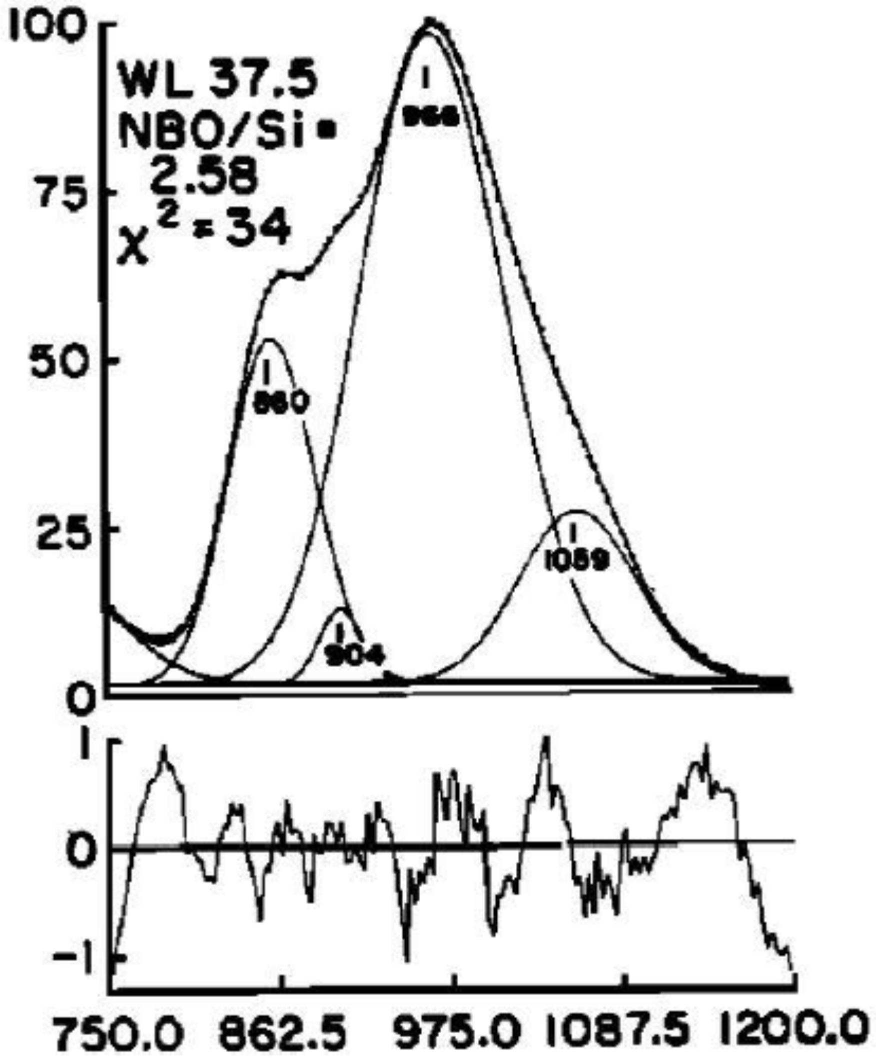
1) Fitting of spectral envelope with well constrained Gaussian peaks with well recognized peak positions for Q species: Q^0, Q^1, Q^2, Q^3 (~850, 900, 970, 1100 cm^{-1}) and Q^4
    - a) Dominant peaks of the crystal spectrum appear in the glass spectrum
    - b) All fits yield more than the minimum number of peaks for the possible Q species
    - c) Often the FWHM of the fitted peaks vary widely
    - d) Peaks usually fit with Gaussian peaks

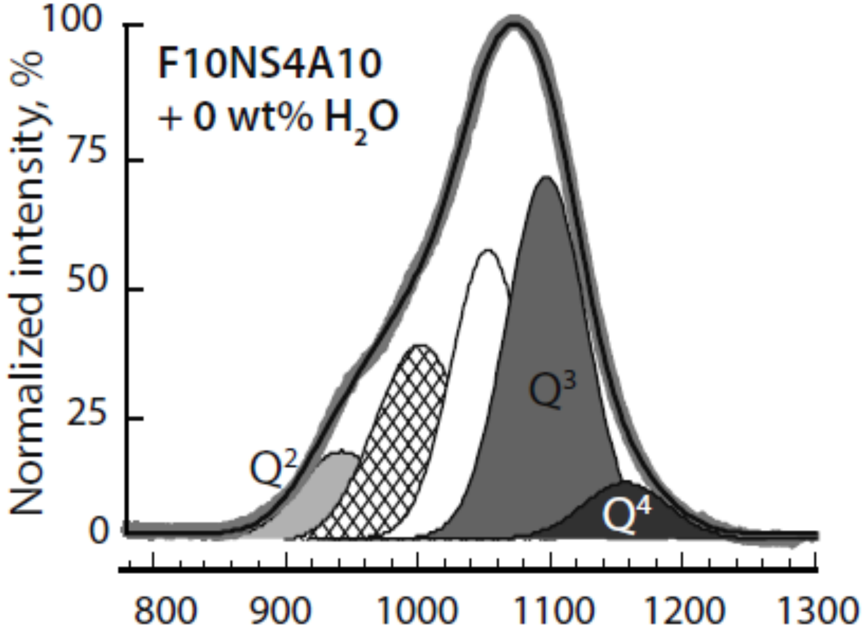
2) Partial Component Analysis (PCA): Use many Raman spectra of different compositions, no a priori control of line widths, shapes or positions.
    - a) Ca silicate glasses produces split peaks over 100 cm^{-1} apart (Q^3 and Q^2)
    - b) Q^1 is split into 3 peaks with a total width of 150 cm^{-1}

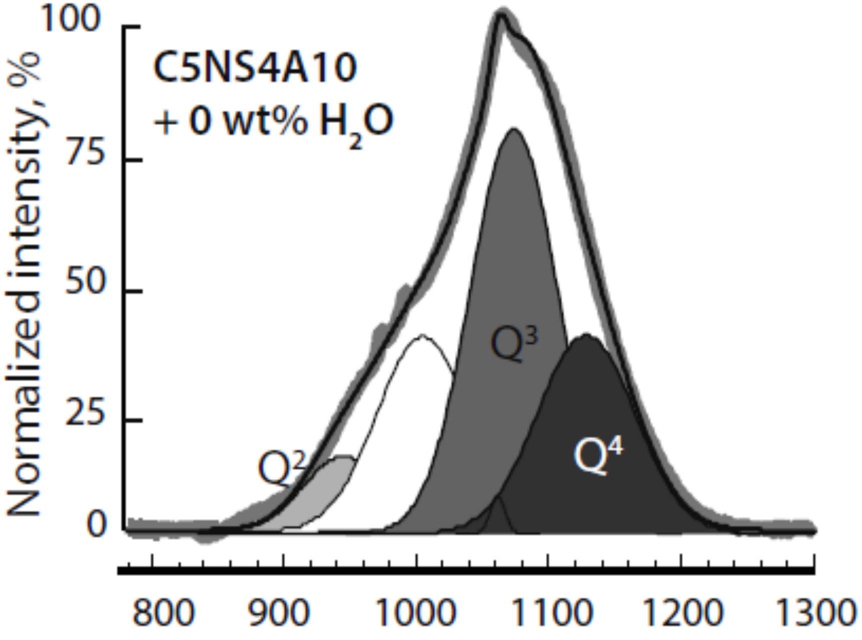
3) Variation of first method: peak widths constrained. However, extra peaks still have to be fit

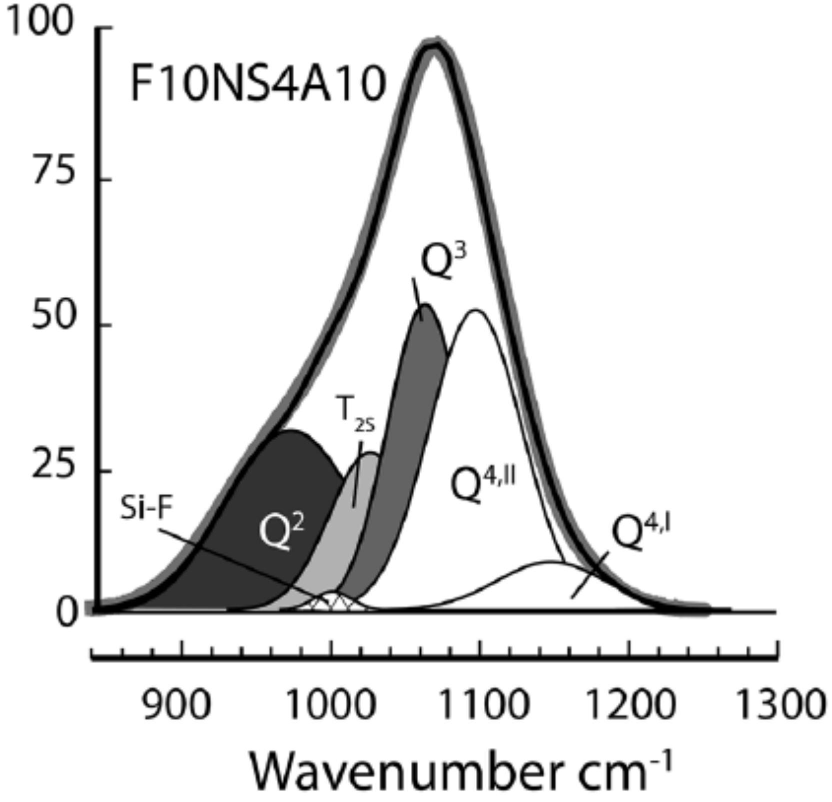
Same composition WL37.5 (CaO-SiO2)

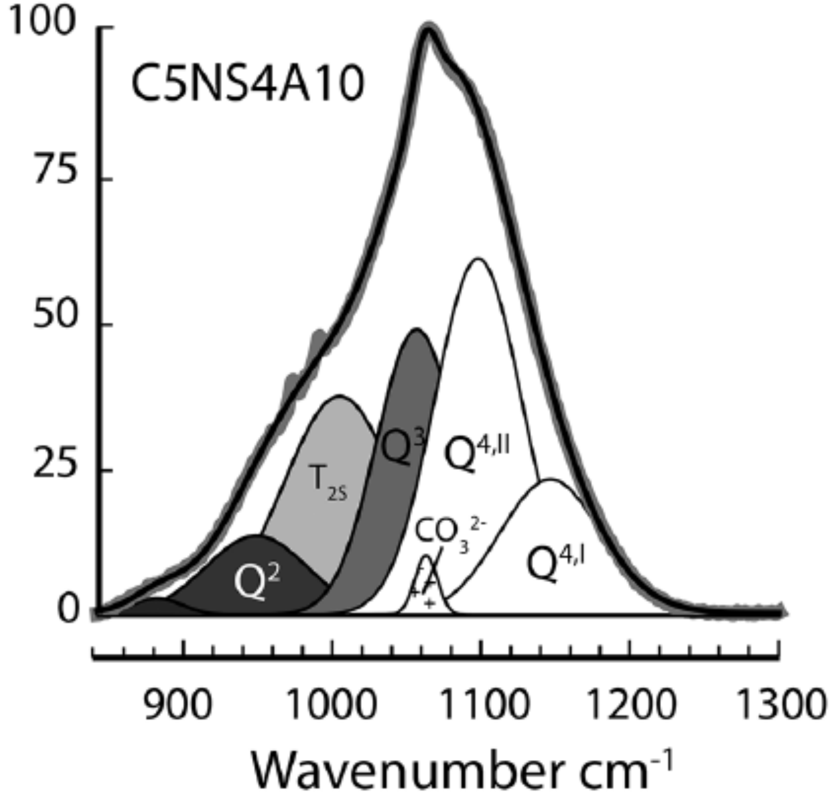





F10NS4A10
+ 0 wt% H$_2$O
Normalized intensity, %
100
75
50
25
0
Q^2
Q^3
Q^4
800
900
1000
1100
1200
1300

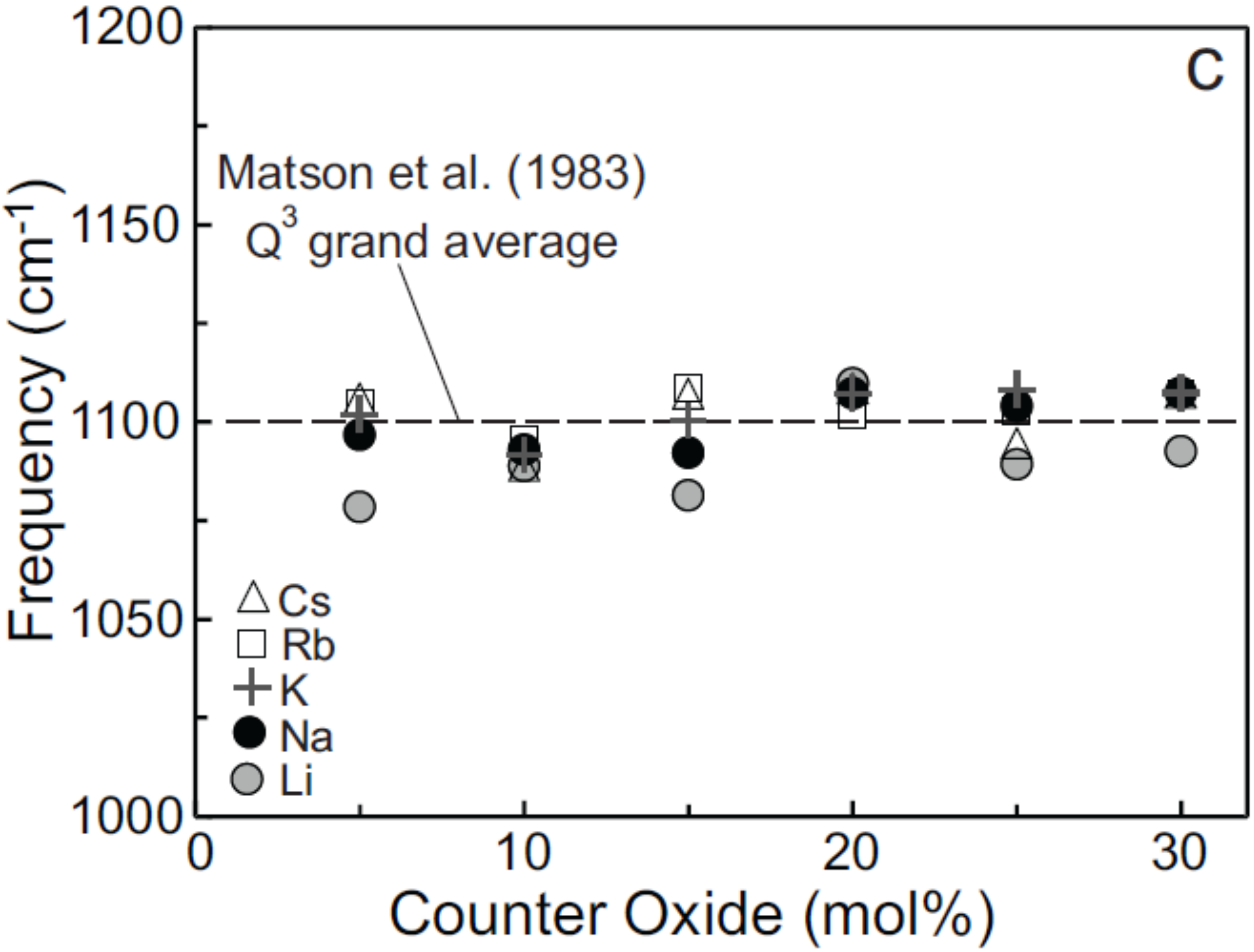

C5NS4A10
+ 0 wt% H$_2$O
Normalized intensity, %
100
75
50
25
0
Q^2
Q^3
Q^4
800
900
1000
1100
1200
1300

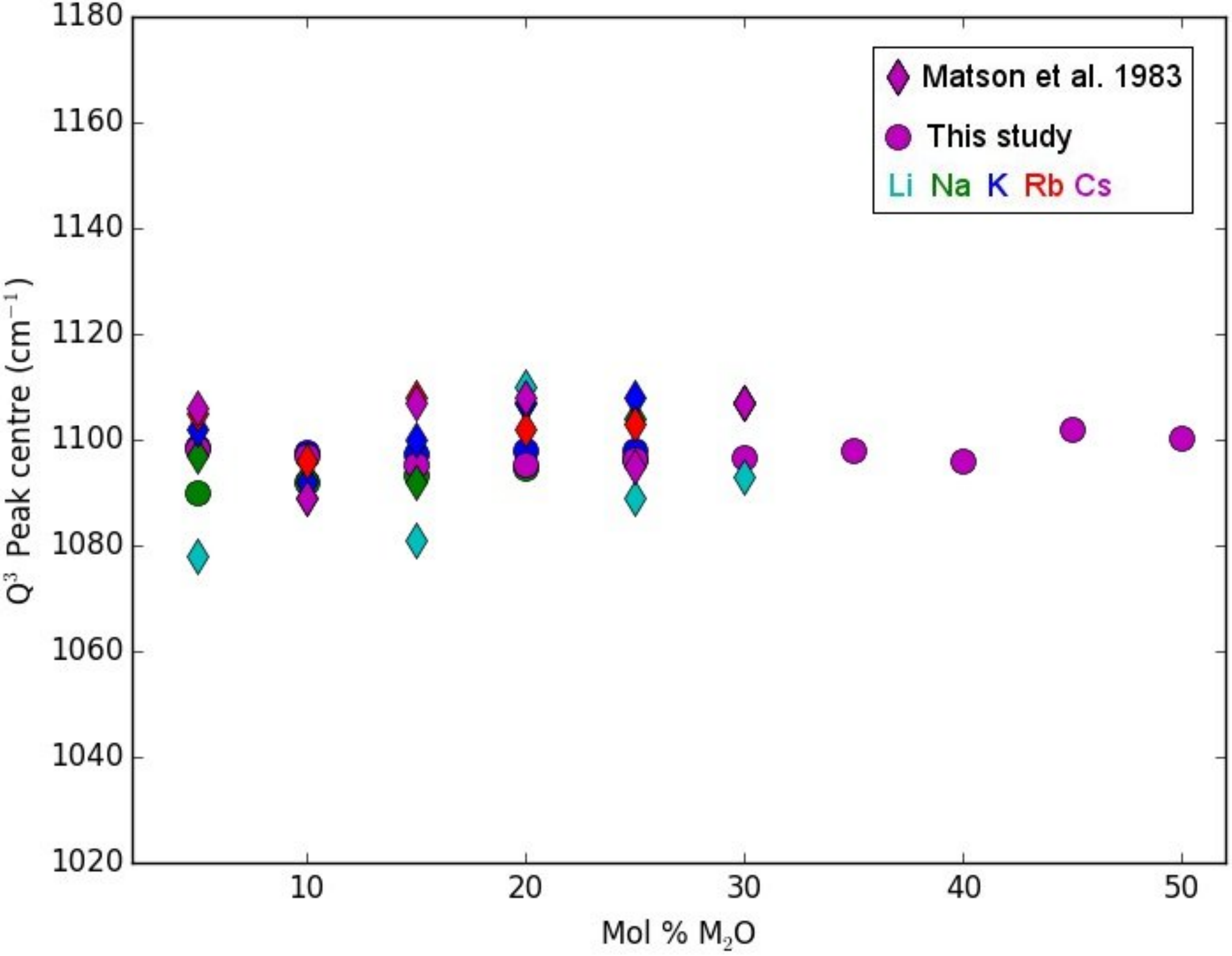

F10NS4A10
100
75
50
25
0
Q^3
T$_{2S}$
Q^{4,II}
Si-F
Q^2
Q^{4,I}
900
1000
1100
1200
1300
Wavenumber cm^{-1}


C5NS4A10
100
75
50
25
0
T$_{2S}$
Q^3
Q^{4,II}
CO$_3^{2-}$
Q^2
Q^{4,I}
900
1000
1100
1200
1300
Wavenumber cm^{-1}

Some Raman observations

- Q species Raman bands are independent of alkali composition and type of alkali.
- Raman bands assigned to Q species are essentially always at same Raman Shift (cm^{-1}). We know where the Q species bands are.
- The addition of small amounts of alkali greatly increase Q^4 vibrational band intensity
- Q species frequency depends on the number of BOs


C
Matson et al. (1983)
Q3 grand average
Frequency (cm-1)
1200
1150
1100
1050
1000
Counter Oxide (mol%)
0
10
20
30
Cs
Rb
K
Na
Li

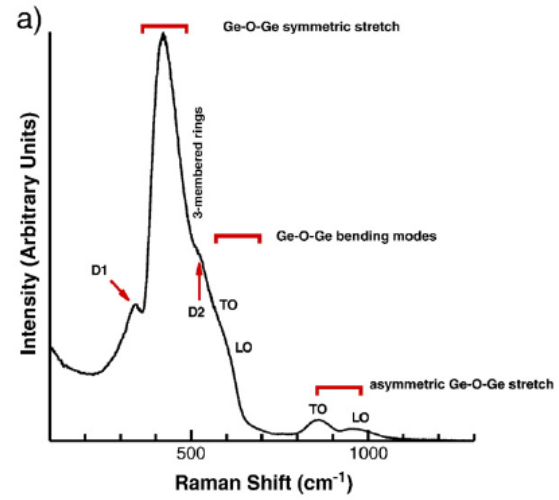

Matson et al. 1983
This study
Li Na K Rb Cs
Q^3 Peak centre (cm^{-1})
1020
1040
1060
1080
1100
1120
1140
1160
1180
10
20
30
40
50
Mol % M$_2$O

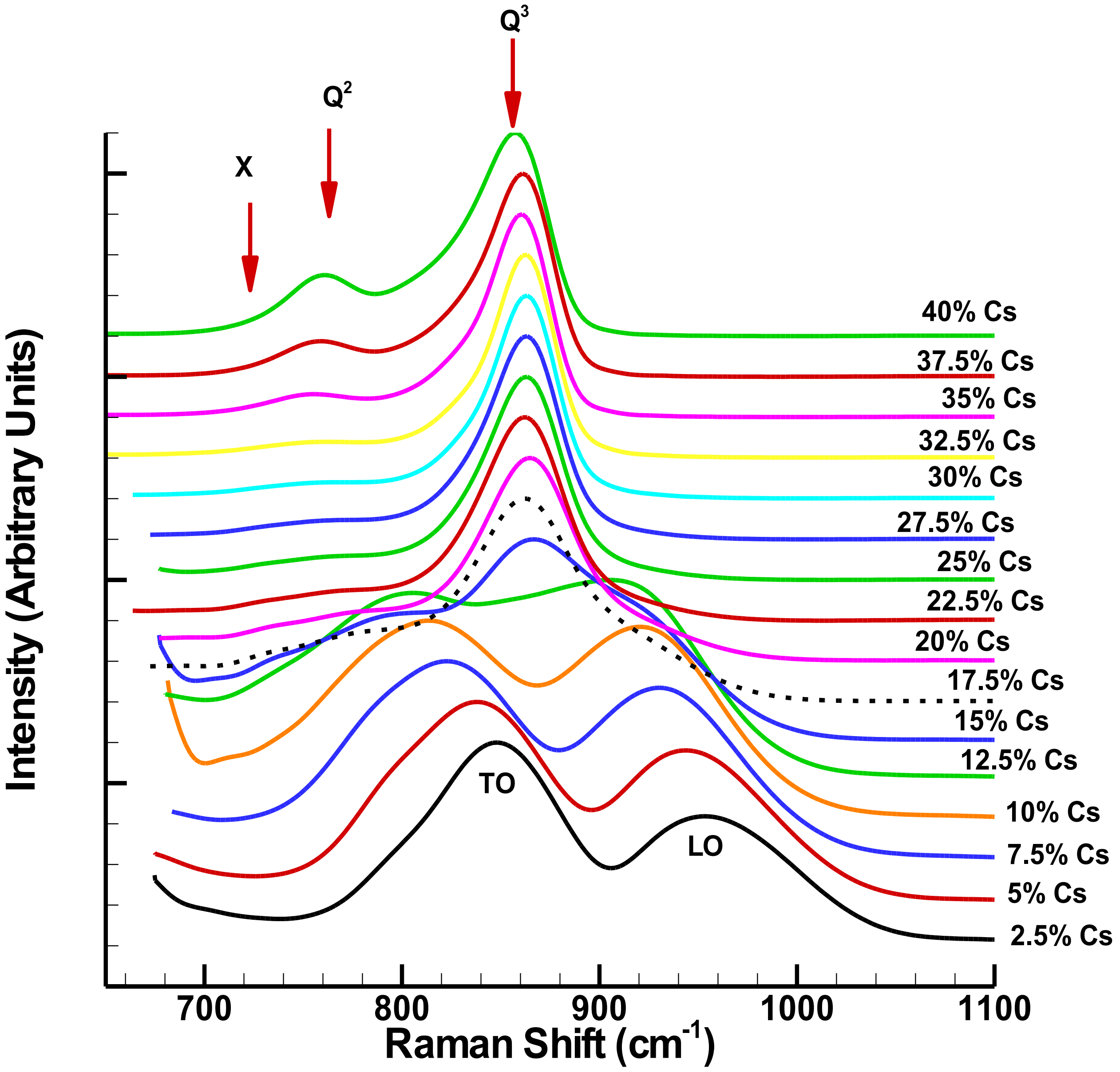
Other alkalis

- Q^2/Q^3 ratio: $Cs_2O<Rb_2O<K_2O<Na_2O$
- X intensity: $Cs_2O/Rb_2O < K_2O/Na_2O$
- Q3' at 35 mol% Na_2O

  25 mol% K_2O/Rb_2O

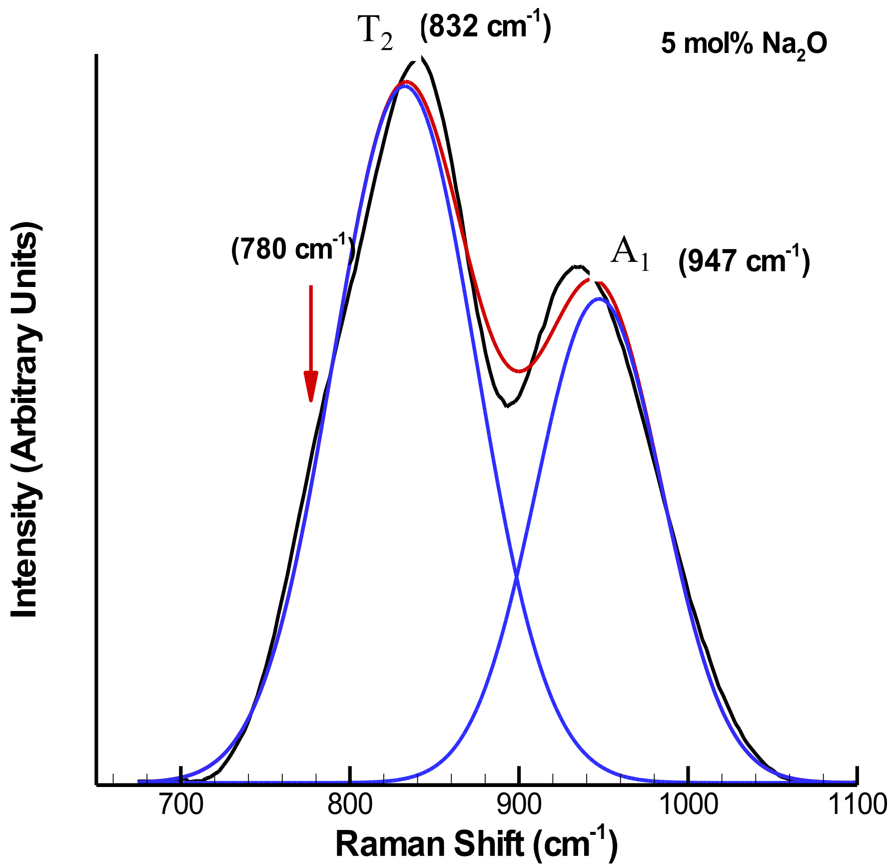
  20 mol% Cs_2O

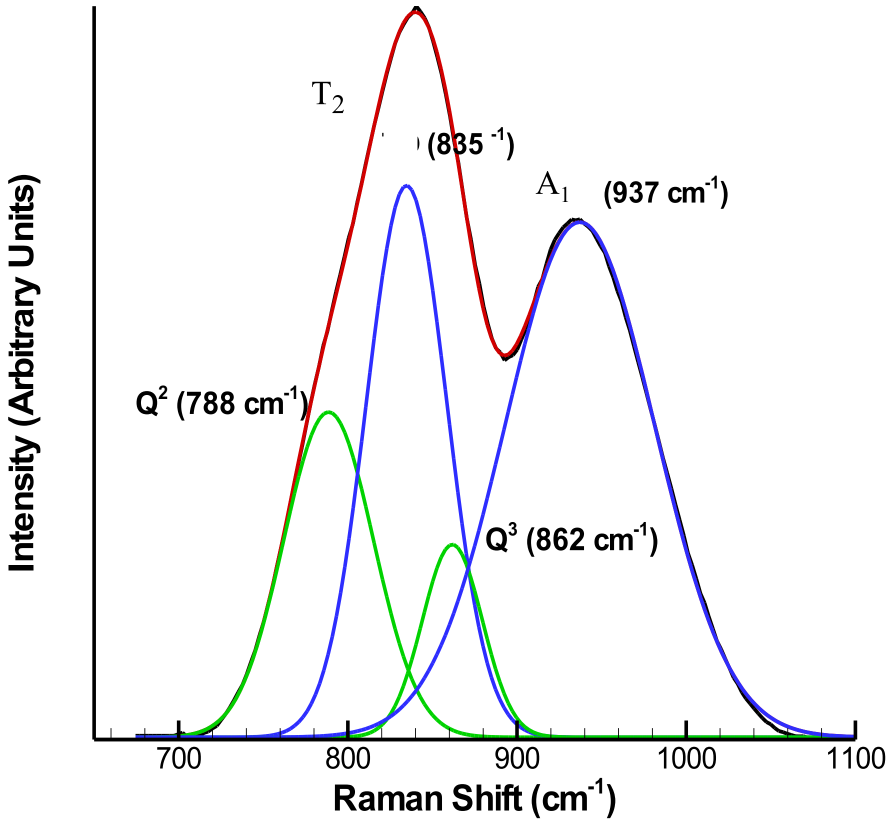




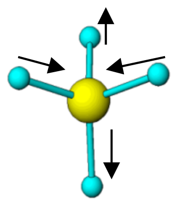
5 mol% Na_2O-GeO_2

- 2-peak fit doesn't account for shoulder
- Requires 4 peak fit with Q^2 and Q^3

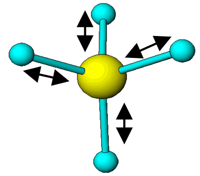




T_2

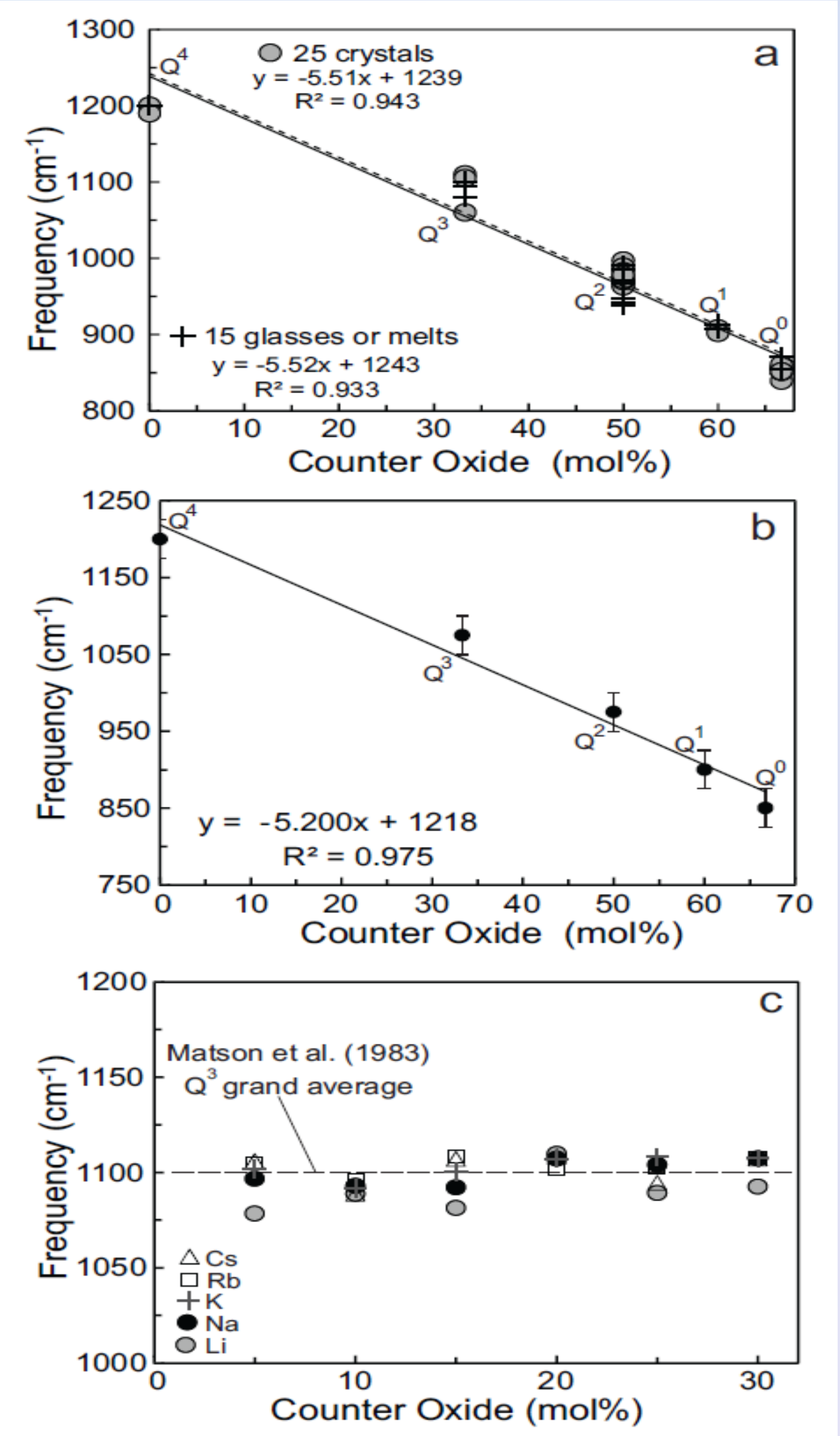


A_1

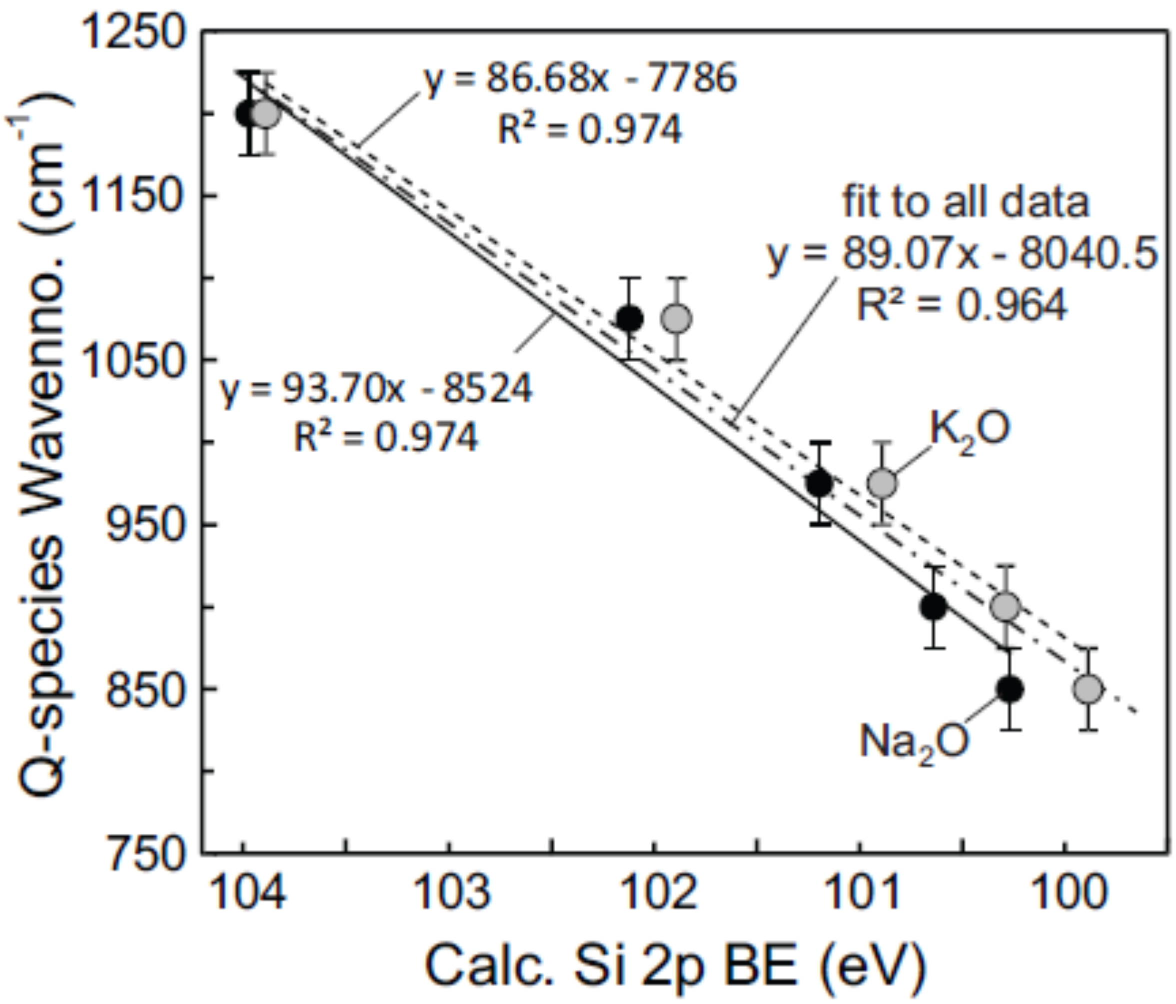


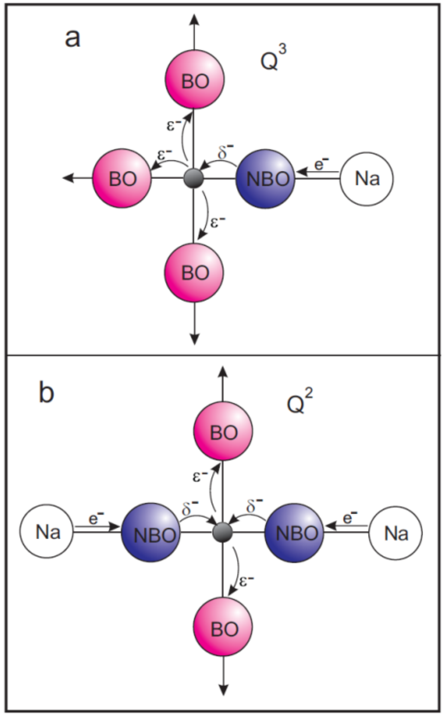
- **dominant Q species in crystals is the one observed in comparable glasses (with additional peaks); No effect crystal vs glass**
- **No effect of mass on frequencies (for alkali and alkaline-earths).**
- **Strong correlation between frequency and composition**
- **Alkali oxide concentration determines type of Q species but frequency depends on the number of NBOs.**

Nesbitt et al., 2017b, Chem Geol, in press



- **Si 2P chemical shift near linear with composition**
- **Q frequencies related to electronic charge in the valence band**
- **Perturbation of the electron density over an atom in the Si tetrahedron results in changes to the coulombic interactions and force constants.**





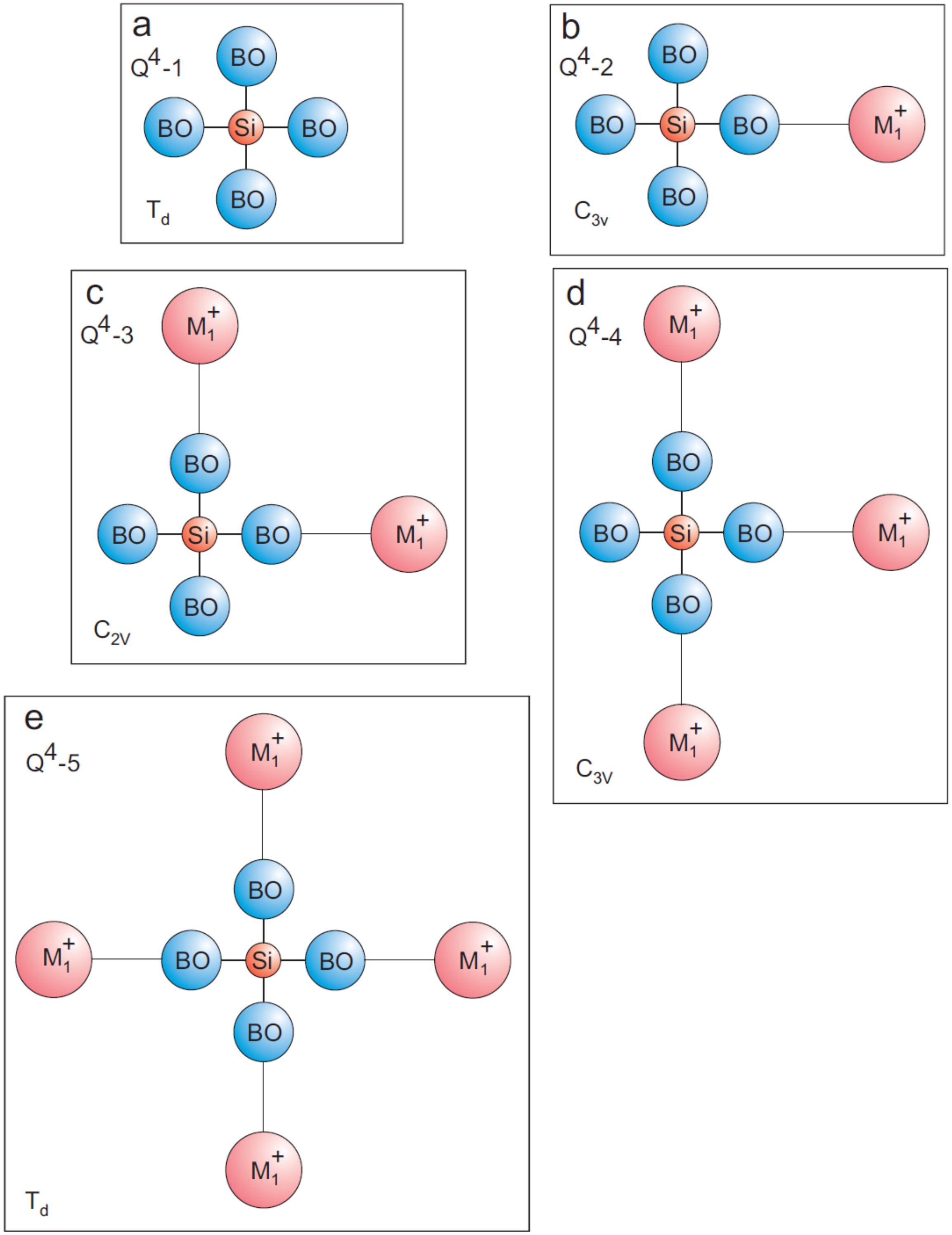
- **Na transfers 3s electron to NBO**
- **Transfer of NBO fractional charge to Si (via sp^3) and redistribution around other BO (via σ)**
- **This (total number of electrons transferred) determines Q^n frequency**

M-BO Q^4 tetrahedra have:
2 sites with T_d symmetry
2 sites with C_{3V} symmetry
1 site C_{2V} symmetry

Possibilities expand with M-BO-M etc.

Effect on Q vibrational band position, shape, numbers?

5 possible bands for Q^4
4 bands with Q^3
3 bands with Q^2
2 bands with Q^1
1 band with Q^0



At least 4 major questions must be addressed before we can fit spectra with confidence

1) Are all peaks in the 800-1200 cm^{-1} region due to SiO_4 symmetric stretches (NBO vibrations of Q species)

2) Are these peaks at well defined energies (wavenumbers)

3) Are the linewidths for glasses and melts similar

4) What are the additional peaks due to?

FWHM taken from published spectra or fit by us. Line widths are accurate to ± $1 cm^{-1}$ for crystals and < $3 cm^{-1}$ for glasses and melts

Investigated Q^1 and Q^2 peaks (well defined and separate)

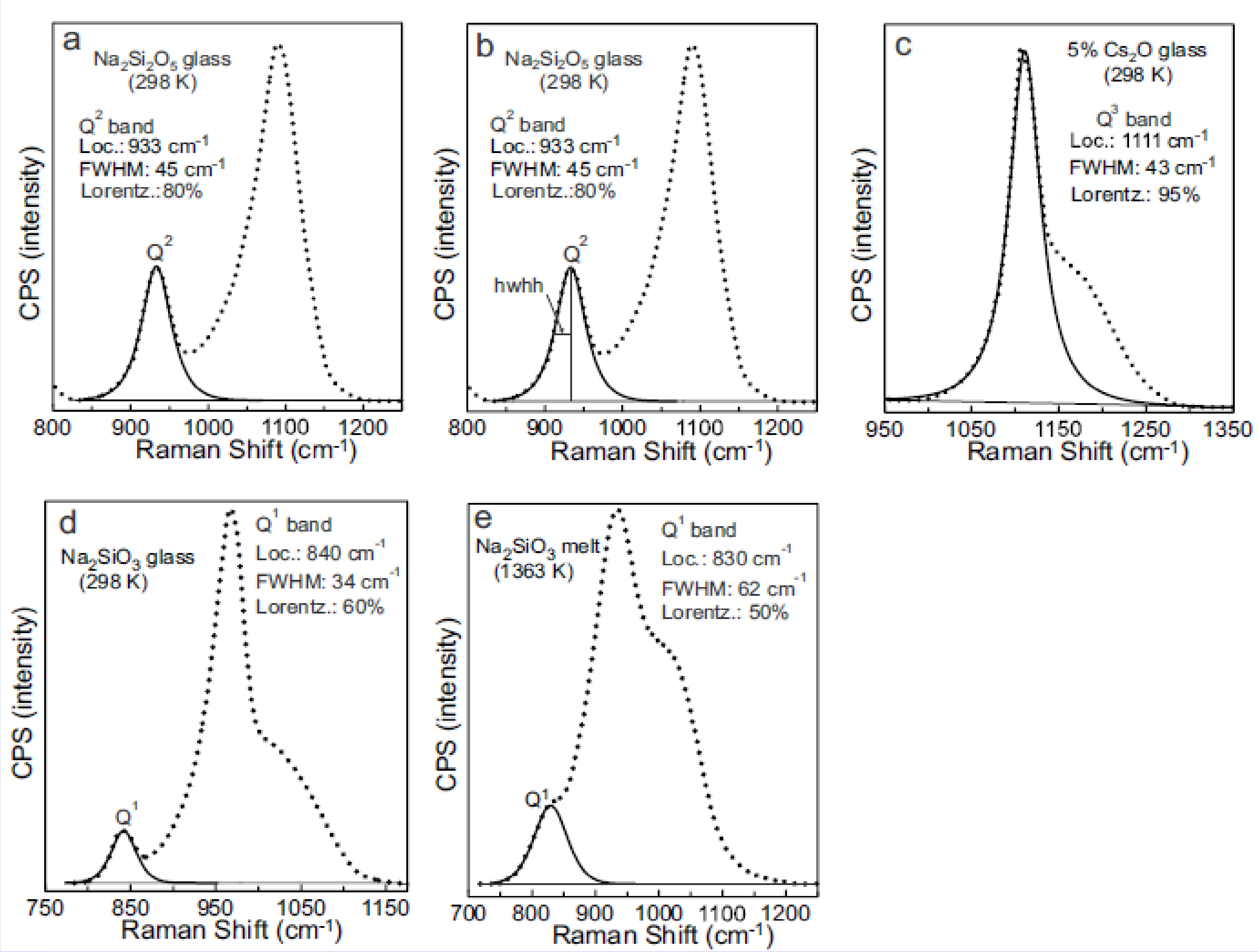
Peaks should be 100% Lorentzian in crystals (true)

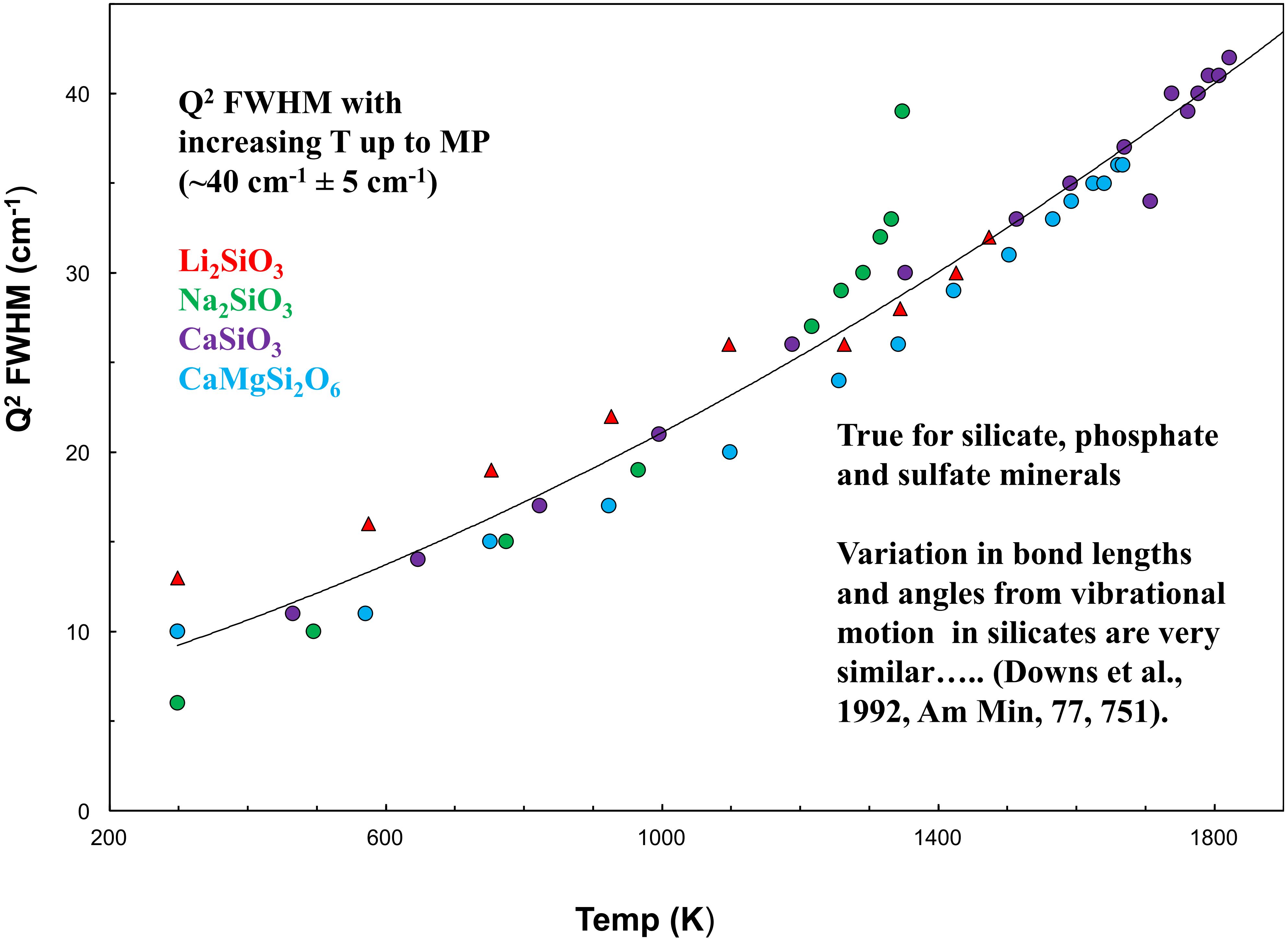
Peak shapes in glasses are predominantly Lorentzian with some Gaussian component

80% Lorentzian/ 20% Gaussian (best fit for Na_2SiO_3).

Acceptable fits up to 30% Lorentzian and 70% Gaussian but depends on composition

Fitted linewidths have small sensitivity to large differences in Gaussian component



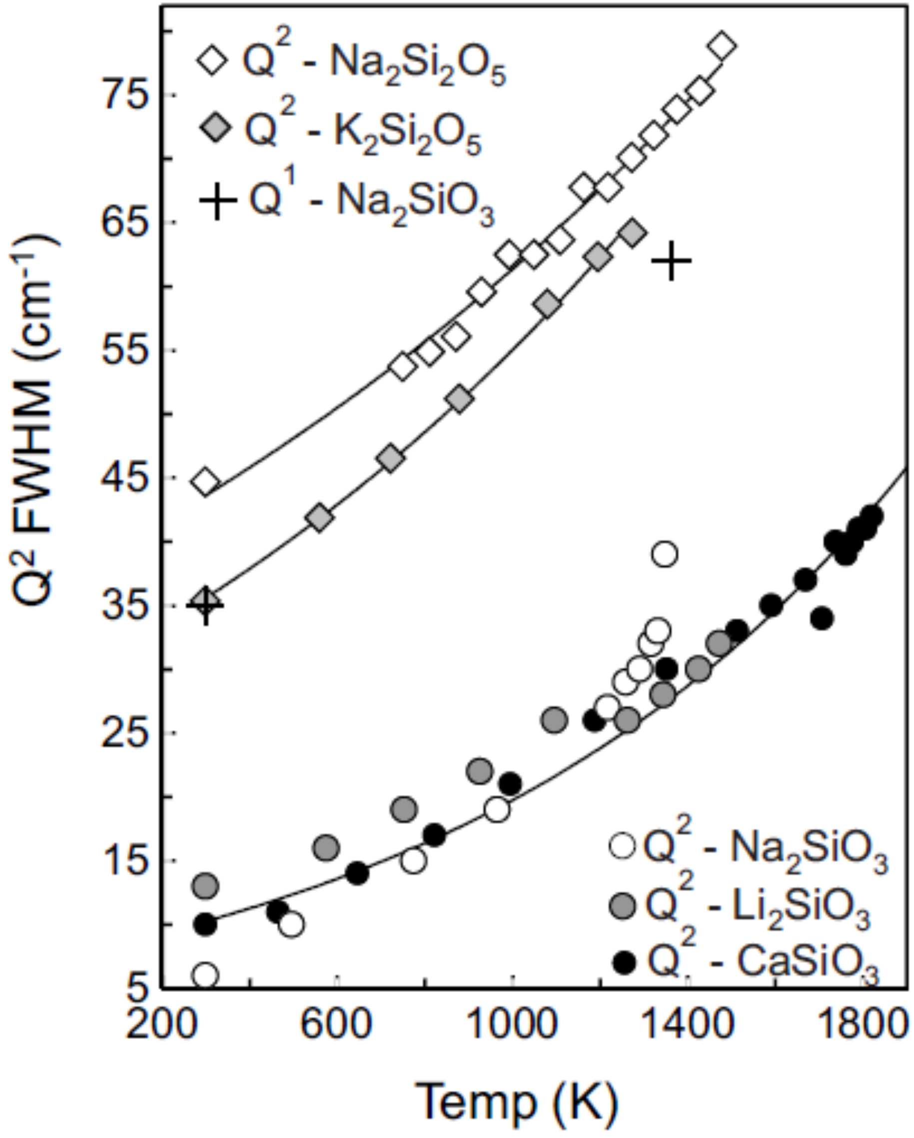


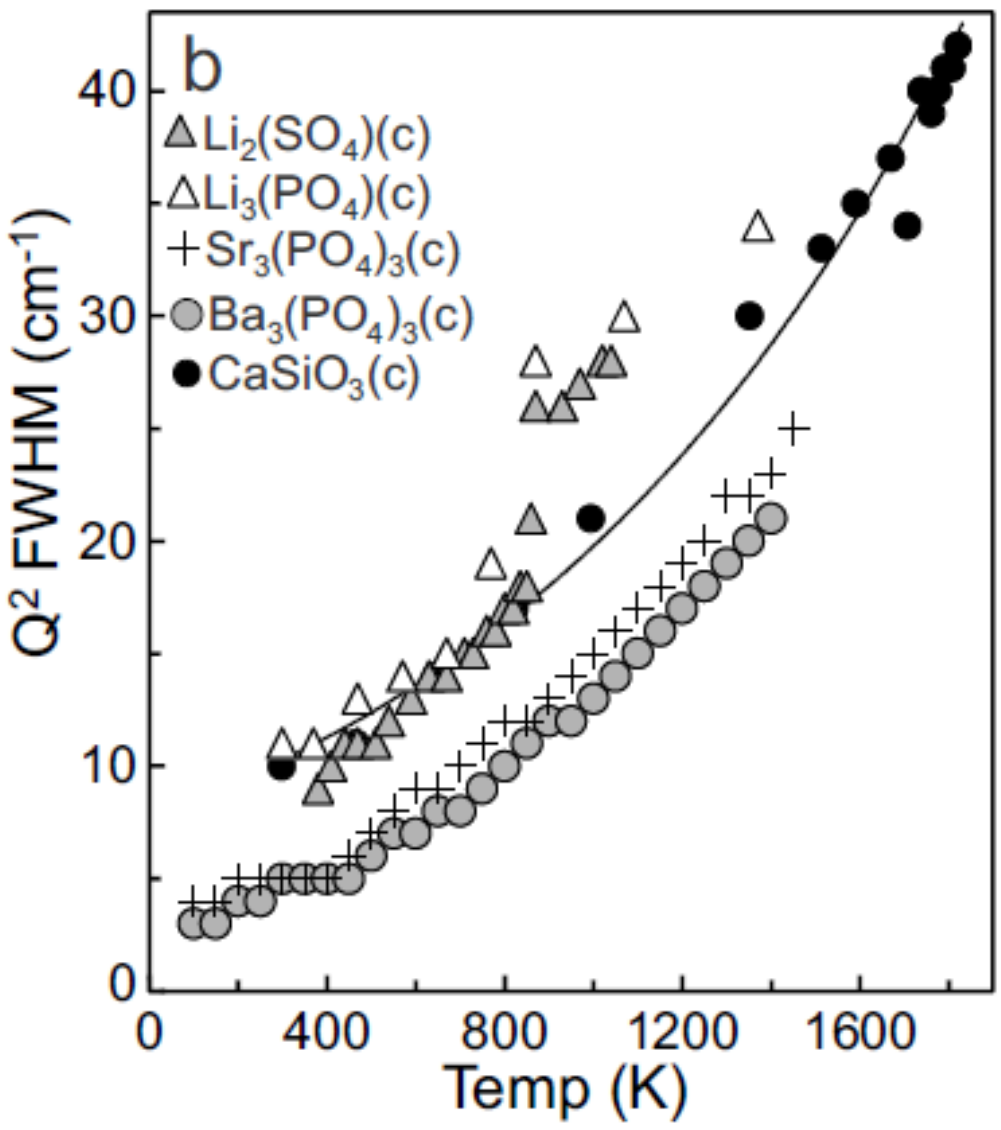
Q^2 FWHM with increasing T up to MP (~40 cm^{-1} ± 5 cm^{-1})

True for silicate, phosphate and sulfate minerals

Variation in bond lengths and angles from vibrational motion in silicates are very similar….. (Downs et al., 1992, Am Min, 77, 751).

Silicate FWHM increases from ~10 to ~40 cm^{-1} at MP
True for Q^{0-3}
Similar for phosphates, sulphate and germanate glasses
All linewidths for all crystalline materials are very similar at a given T regardless of chemical composition





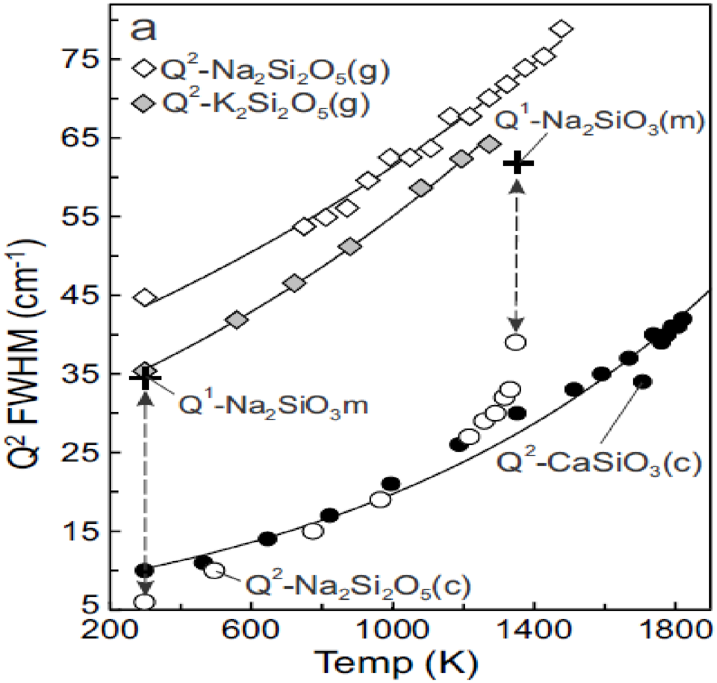
Glasses versus Melts

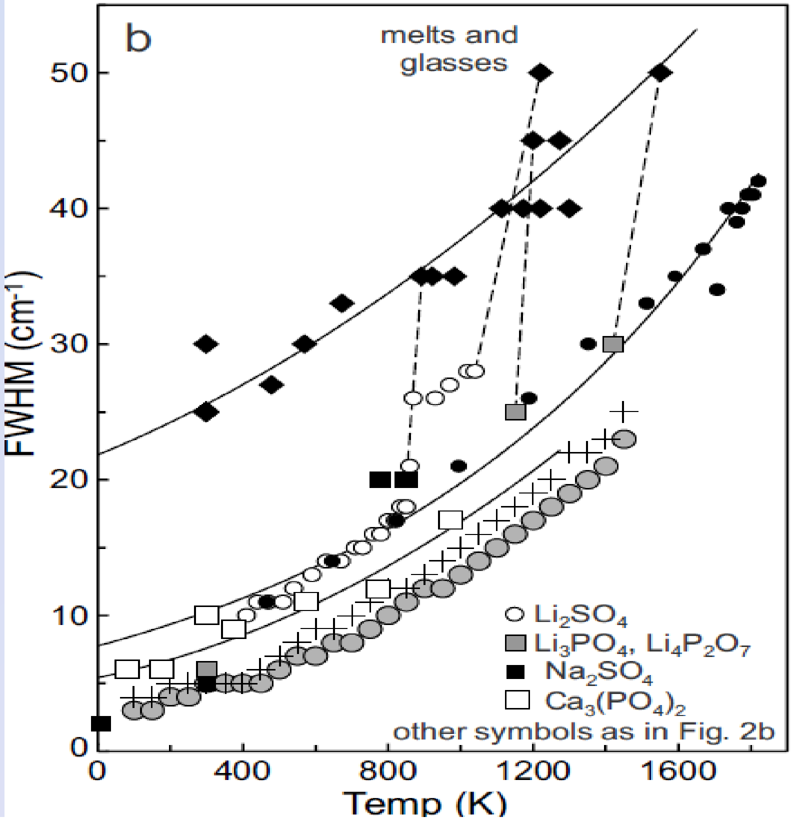
Linewidths for 3 glasses and melts are within 10cm^{-1} for all T: $Na_2Si_2O_5$ and $K_2Si_2O_5$ glasses , 45 and 35 cm^{-1} at 298K, 72 and 64 cm^{-1} at 1270K

Glass/melt linewidth much larger than crystalline compounds: ~35-45 cm^{-1} glasses, 5-10 cm^{-1} crystals (well known): Q^1 Na_2SiO_3 (g) 35 cm^{-1}, Na_2SiO_3 (m) 62 cm^{-1}

No significant increase in FWHM at Tg

Like crystalline silicates the glass/melt FWHM only depends on T





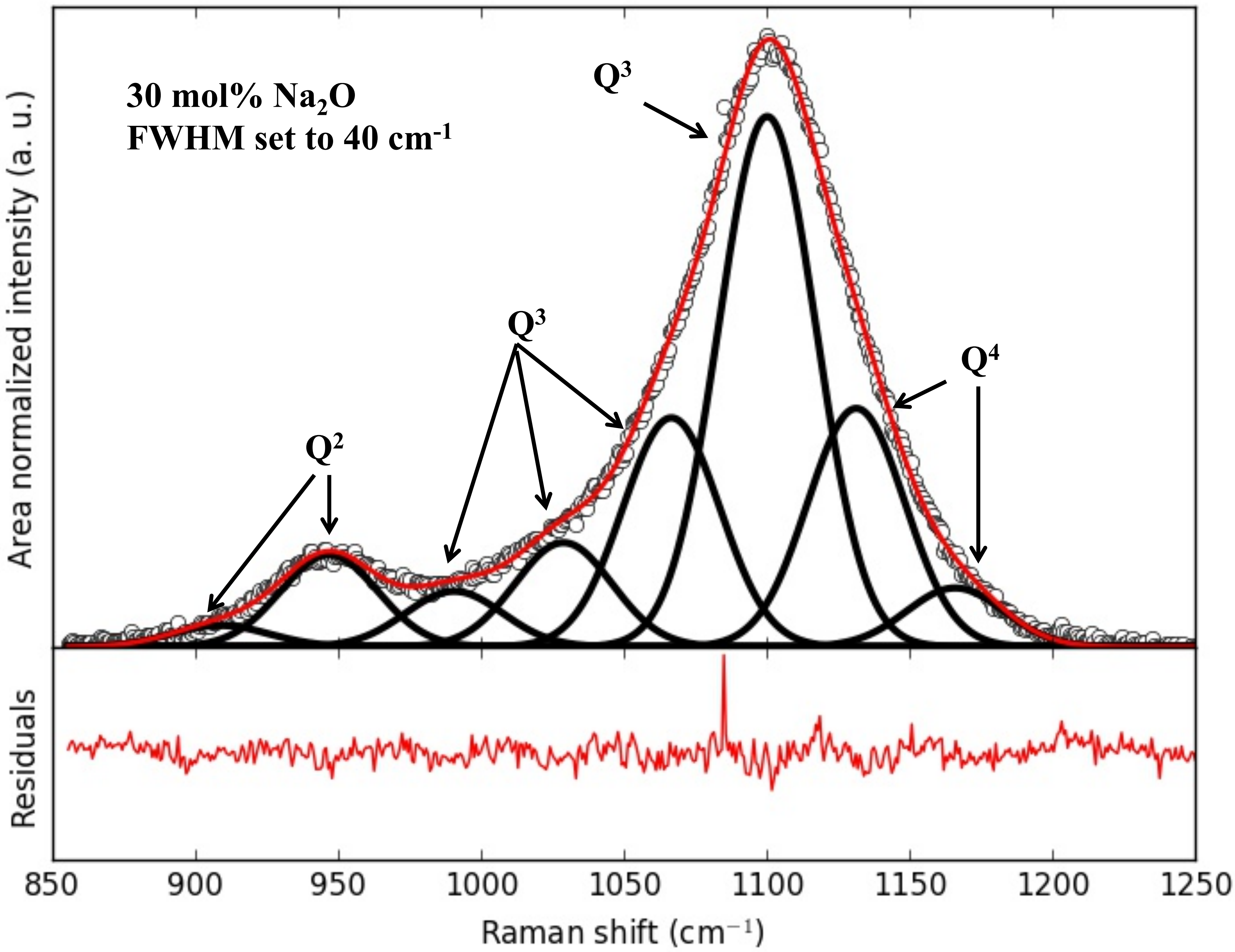
At least 4 major questions must be addressed before we can fit spectra with confidence

1) Are all peaks in the 800-1200 cm^{-1} region due to SiO_4 symmetric stretches (NBO vibrations of Q species). YES THEY ARE for Q^{0-3}

2) Are these peaks at well defined energies (wavenumbers). YES THEY ARE

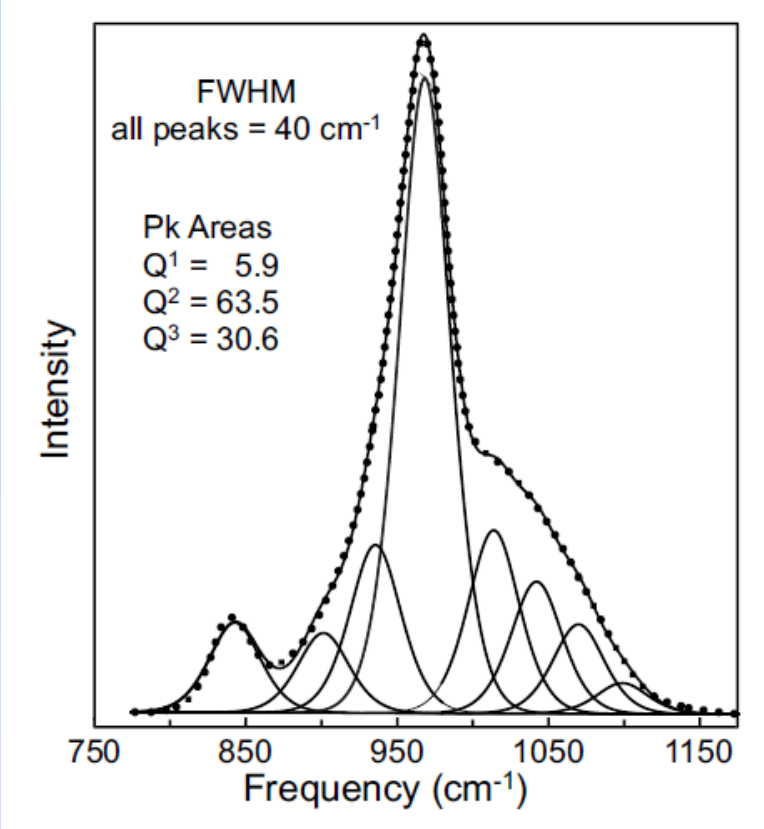
3) Are the linewidths for glasses and melts similar YES THEY ARE. All Lorentzian (some Gaussian component) with FWHM well defined at a given T

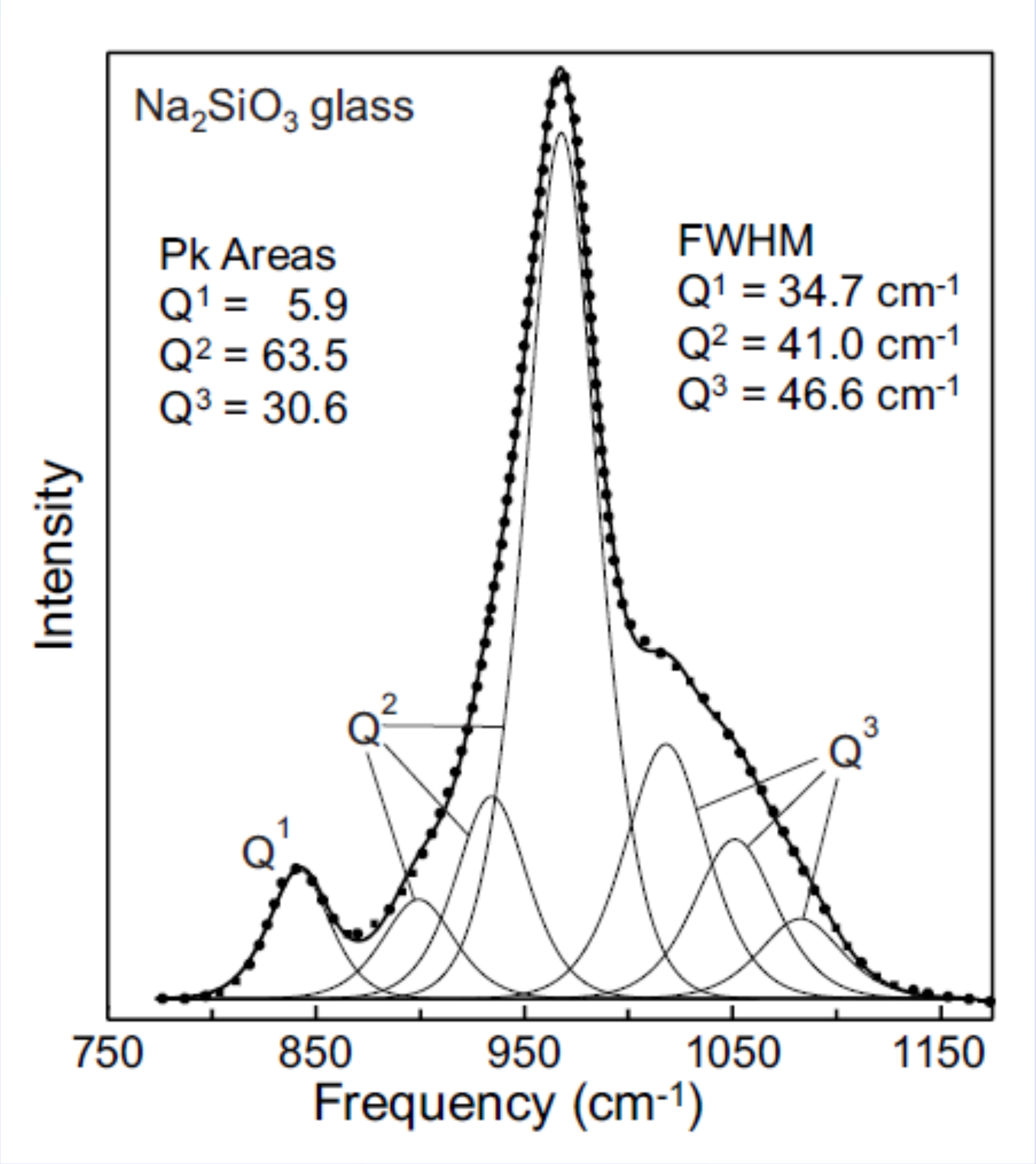
4) What are the additional peaks due to? MBO vibrations associated with Q^{0-3}


30 mol% Na_2O
FWHM set to 40 cm^{-1}
Q^3
Q^3
Q^2
Q^4
Area normalized intensity (a. u.)
Residuals
850
900
950
1000
1050
1100
1150
1200
1250
Raman shift (cm^{-1})

Maekawa et al., 1991 (NMR)
$Q^0 = 1$
$Q^1 = 13$
$Q^2 = 70$
$Q^3 = 16$

Nesbitt et al., 2011 (NMR)
$Q^1 = 5.5$
$Q^2 = 66.0$
$Q^3 = 28.5$





A more detailed investigation of the temperature dependence of the Raman shift (Ω) and FWHM at temperature (T).

Use Balkanski et al., 1983 to model Raman shifts (Ω) and FWHM at different Ts for metasilicate minerals

$$\Omega(T) = \omega^* + C[1 + 2/(ex - 1)] + D[1 + 3/(ey - 1) + 3/(ey - 1)2] \qquad (1)$$

C and D are constants, ω^* is the Einstein frequency of the Raman shift, $x = h\omega^*/2kT$, $y = h\omega^*/3kT$, h is Planck's constant and k is Boltzmann's constant. Also, $h\omega^*/k$ = the Einstein temperature (θE) for the Raman oscillator, and the terms $2/(ex - 1)$ and $3/(ey - 1)$ are closely related to the average energy of the Raman oscillator (εR) at thermal equilibrium ($\varepsilon R = h\omega^*/(eh\omega^*/kT -1)$. Expansion of the equation and collection of constants yields:

$$\Omega(T) = \Omega^*(0) + C[2/(ex - 1)] + D[3/(ey - 1) + 3/(ey - 1)2] \qquad (2)$$

where $\Omega^*(0)$ is the Raman shift at absolute zero and is equal to ω^*+C+D.

Balkanski, M., Wallis, R.F., and Haro, E. (1983) Anharmonic effects in light scattering due to optical phonons in silicon, Phys. Rev B 28, 1928-1934

The temperature dependence of FWHM:

$$\mathrm{FWHM}(T) = A[1 + 2/(ex - 1)] + B[1 + 3/(ey - 1) + 3/(ey - 1)2] \tag{3}$$

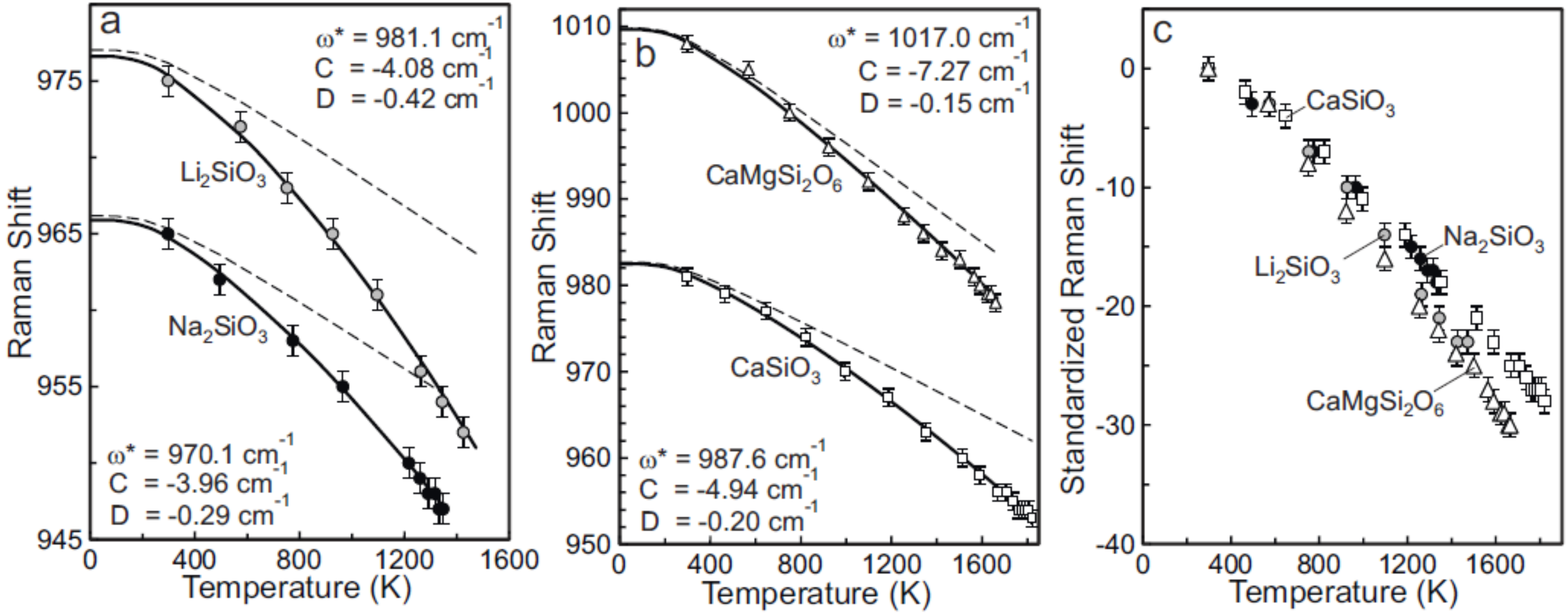
where FWHM(T) is the linewidth at temperature T and A and B are constants.

Other terms are as for Equation (1). Expansion of the equation and collection of the constants yields:

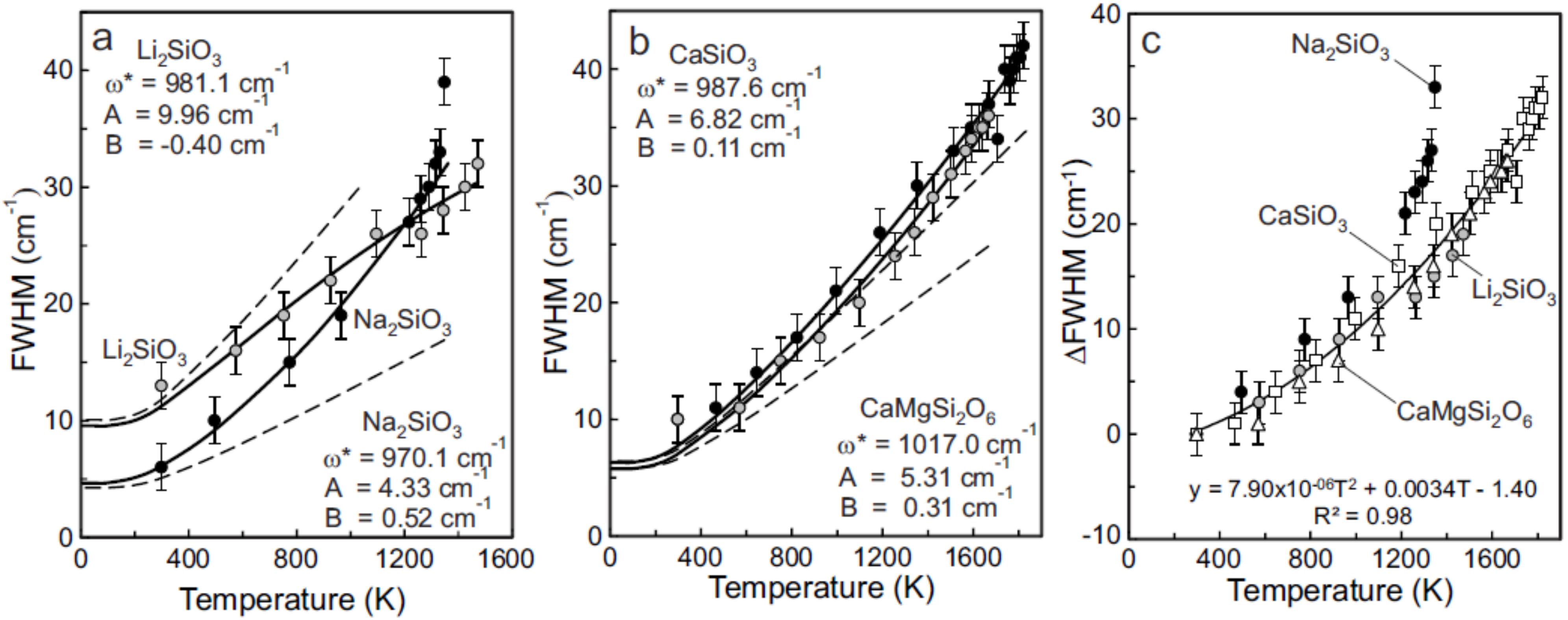
$$\mathrm{FWHM}(T) = \mathrm{FWHM}^*(0) + A[2/(ex - 1)] + B[3/(ey - 1) + 3/(ey - 1)2] \tag{4}$$

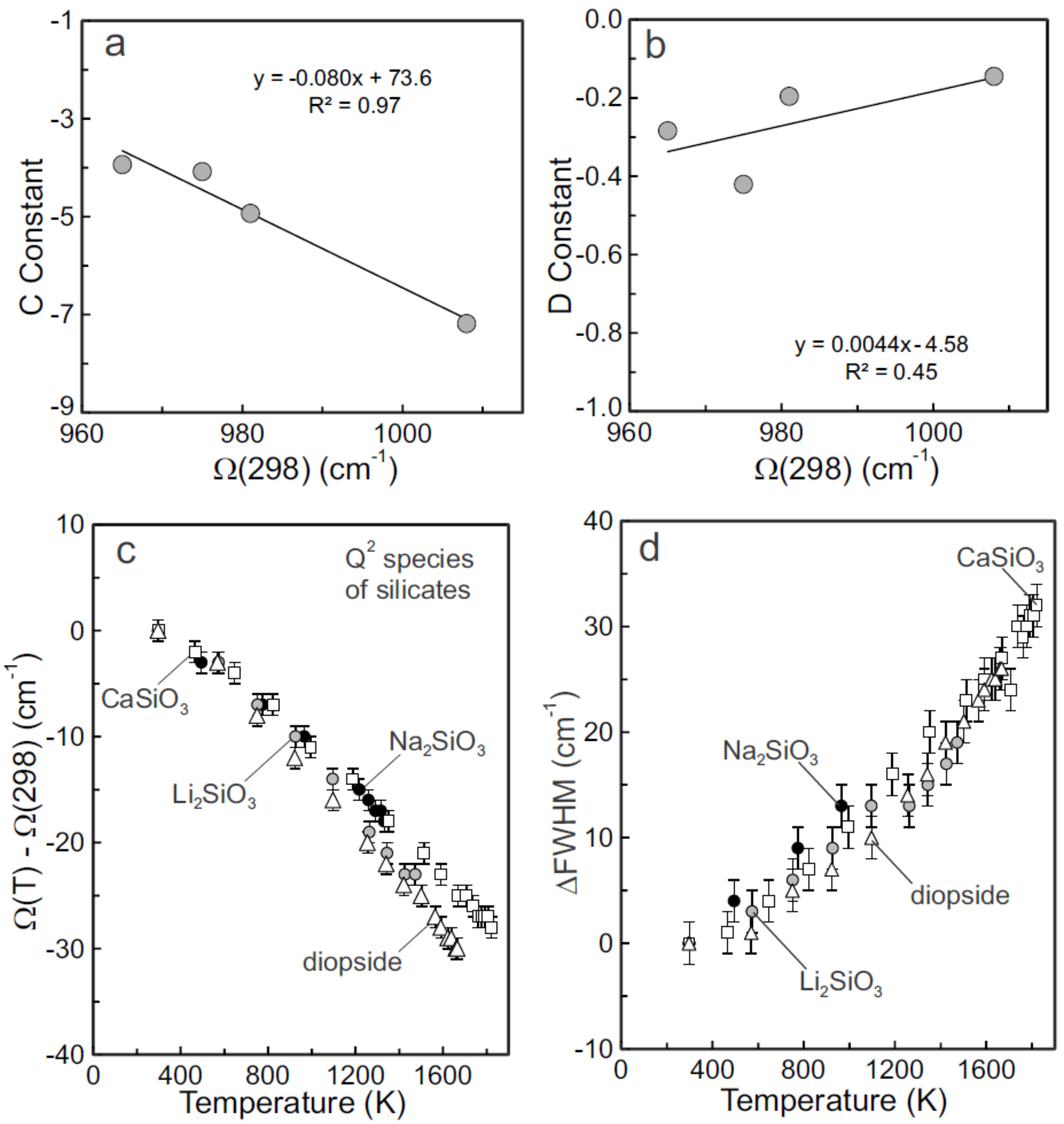
where FWHM*(0) is the linewidth at absolute zero and is equal to A+B. The constants, ω*, A, B, C and D must be evaluated from experimental data.

Temperature dependence of the Q^2 band position in four metasilicate, minerals (a,b) modelled using Eqn 1, c) Best fits standardized to 298 K, error bars ± $1 cm^{-1}$

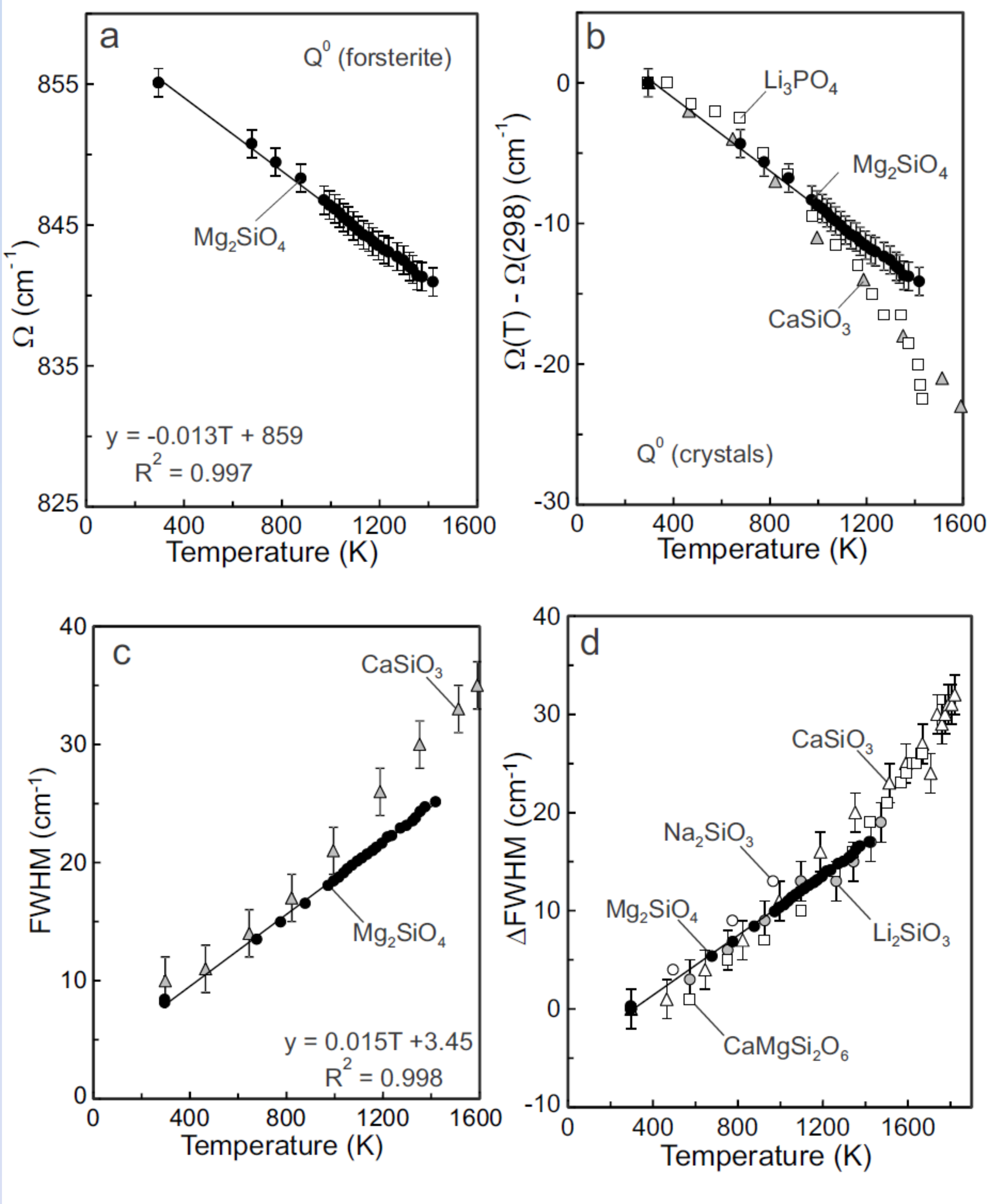


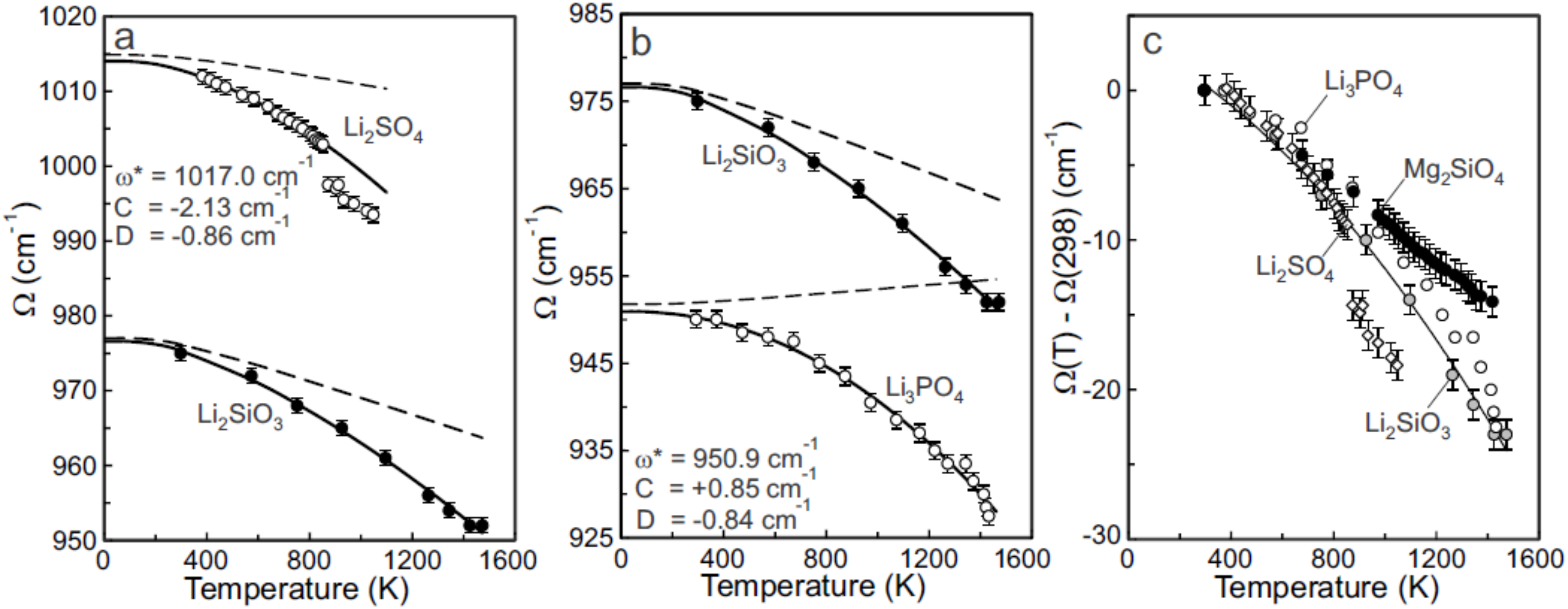
Temperature dependence of the Q^2 FWHM in four metasilicate, minerals (a,b) modelled using Eqn 1, c) Best fits standardized to 298 K. Error bars are ± 2 cm^{-1}




a
y = -0.080x + 73.6
R² = 0.97
C Constant
-1
-3
-5
-7
-9
960
980
1000
Ω(298) (cm-1)
b
y = 0.0044x - 4.58
R² = 0.45
D Constant
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
960
980
1000
Ω(298) (cm-1)
c
Q2 species of silicates
CaSiO3
Li2SiO3
Na2SiO3
diopside
Ω(T) - Ω(298) (cm-1)
10
0
-10
-20
-30
-40
0
400
800
1200
1600
Temperature (K)
d
CaSiO3
Na2SiO3
diopside
Li2SiO3
ΔFWHM (cm-1)
40
30
20
10
0
-10
0
400
800
1200
1600
Temperature (K)

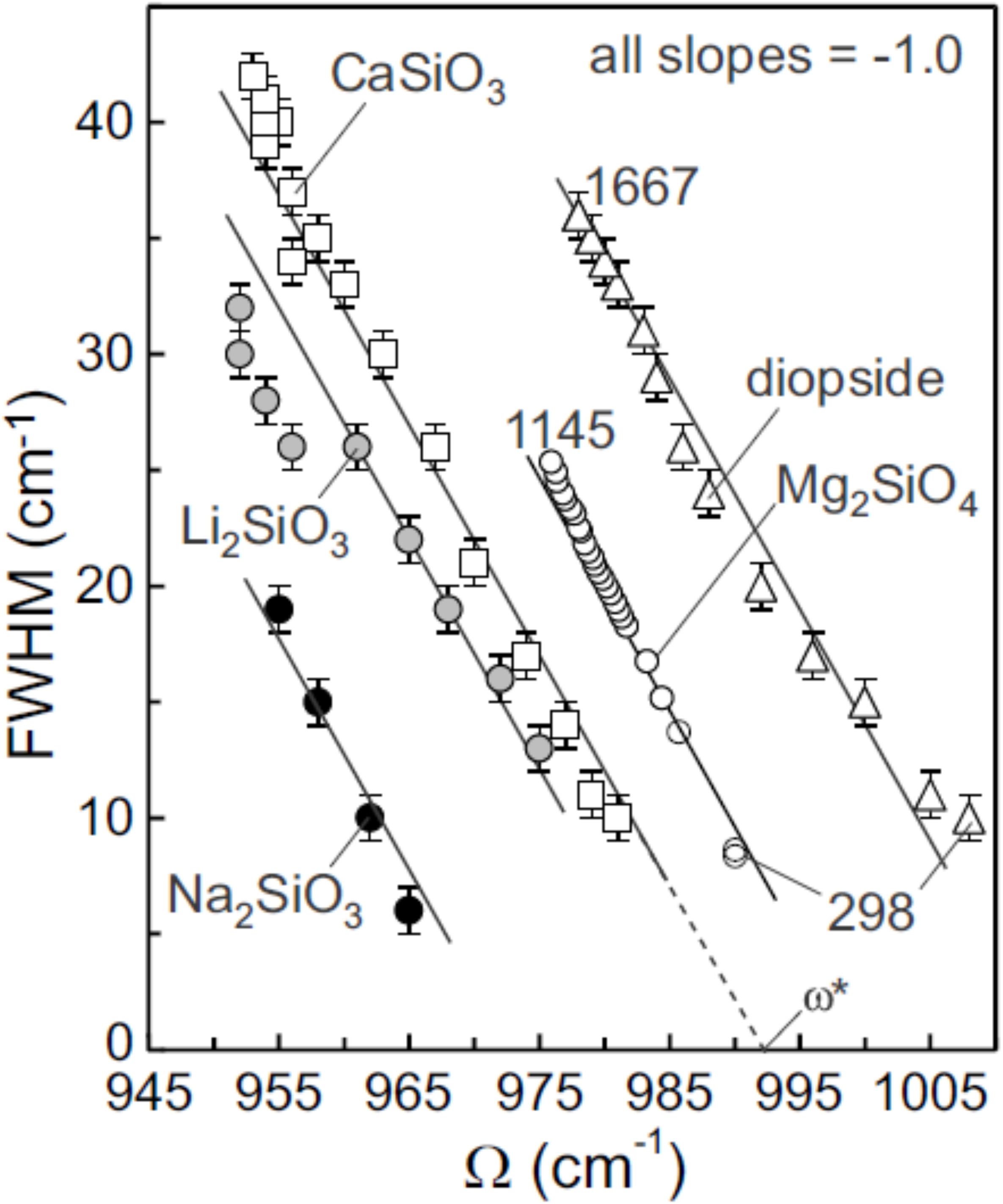
Temperature dependence of the Q^0 band position for forsterite in four metasilicate, minerals (a,b) modelled using Eqn 1, c) Best fits standardized to 298 K, error bars ± 1cm^{-1}

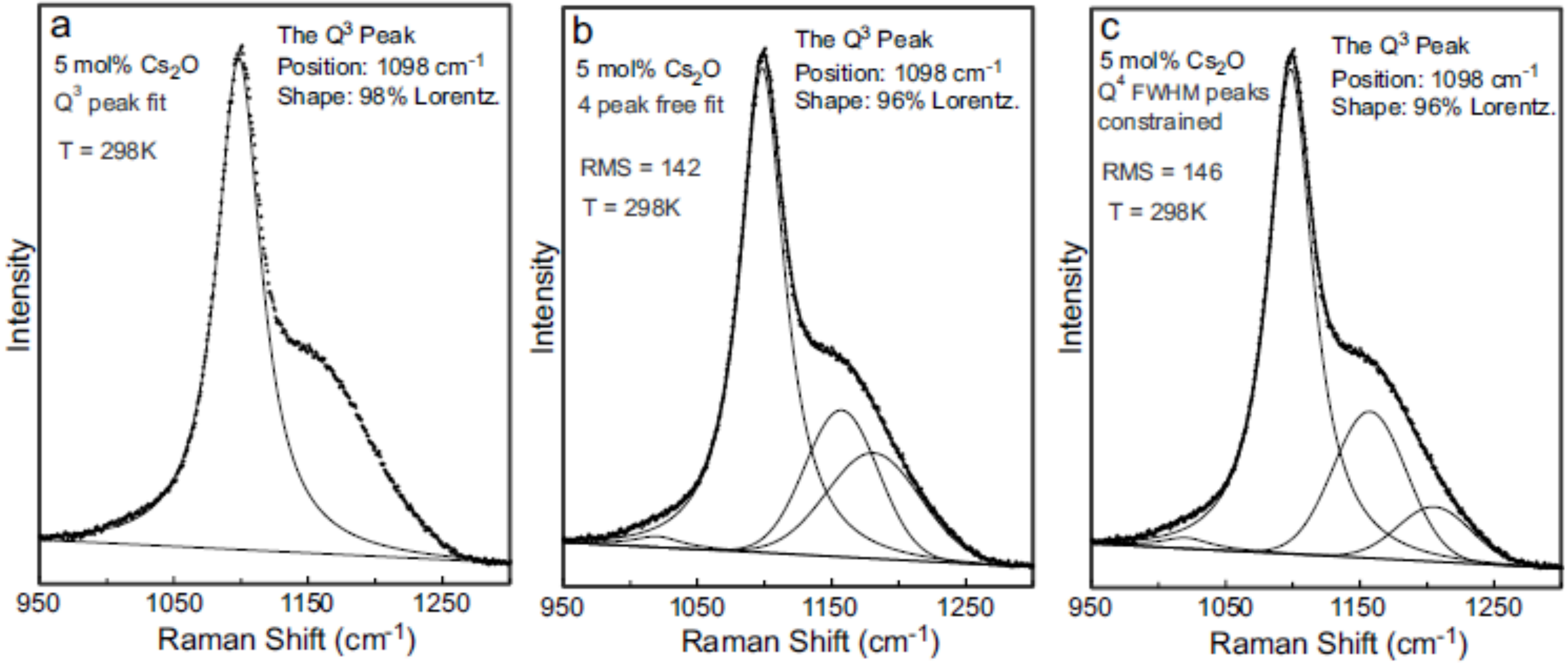


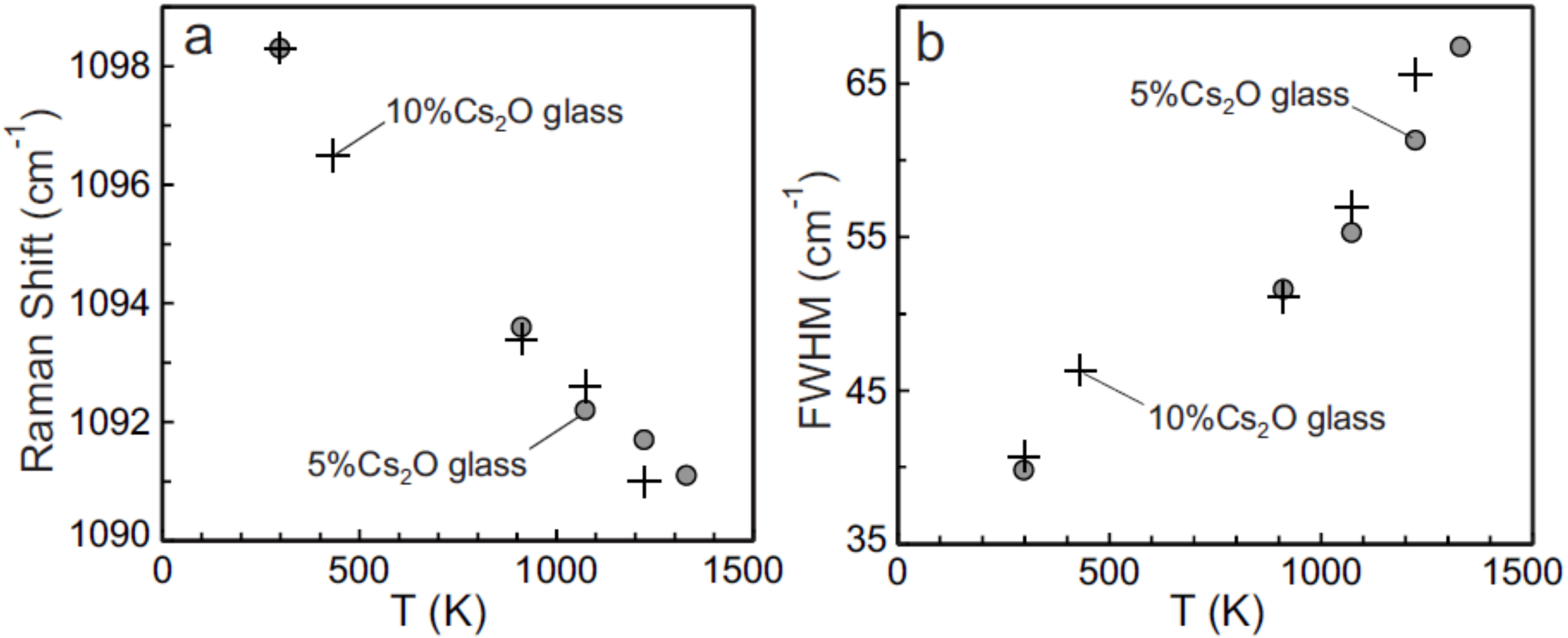

a
Ω (cm^{-1})
1020
1010
1000
990
980
970
960
950
0
400
800
1200
1600
Temperature (K)
Li_2SO_4
ω^* = 1017.0 cm^{-1}
C = -2.13 cm^{-1}
D = -0.86 cm^{-1}
Li_2SiO_3
b
Ω (cm^{-1})
985
975
965
955
945
935
925
0
400
800
1200
1600
Temperature (K)
Li_2SiO_3
Li_3PO_4
ω^* = 950.9 cm^{-1}
C = +0.85 cm^{-1}
D = -0.84 cm^{-1}
c
Ω(T) - Ω(298) (cm^{-1})
0
-10
-20
-30
0
400
800
1200
1600
Temperature (K)
Li_3PO_4
Mg_2SiO_4
Li_2SO_4
Li_2SiO_3

If we know FWHM at RT can predict FWHM at higher Ts.

FWHM has a linear dependence on T




a
5 mol% Cs_2O
Q^3 peak fit
T = 298K
The Q^3 Peak
Position: 1098 cm^{-1}
Shape: 98% Lorentz.
Intensity
950
1050
1150
1250
Raman Shift (cm^{-1})
b
5 mol% Cs_2O
4 peak free fit
RMS = 142
T = 298K
The Q^3 Peak
Position: 1098 cm^{-1}
Shape: 96% Lorentz.
Intensity
950
1050
1150
1250
Raman Shift (cm^{-1})
c
5 mol% Cs_2O
Q^4 FWHM peaks constrained
RMS = 146
T = 298K
The Q^3 Peak
Position: 1098 cm^{-1}
Shape: 96% Lorentz.
Intensity
950
1050
1150
1250
Raman Shift (cm^{-1})



Q3 Properties for 5% Cs2O glass

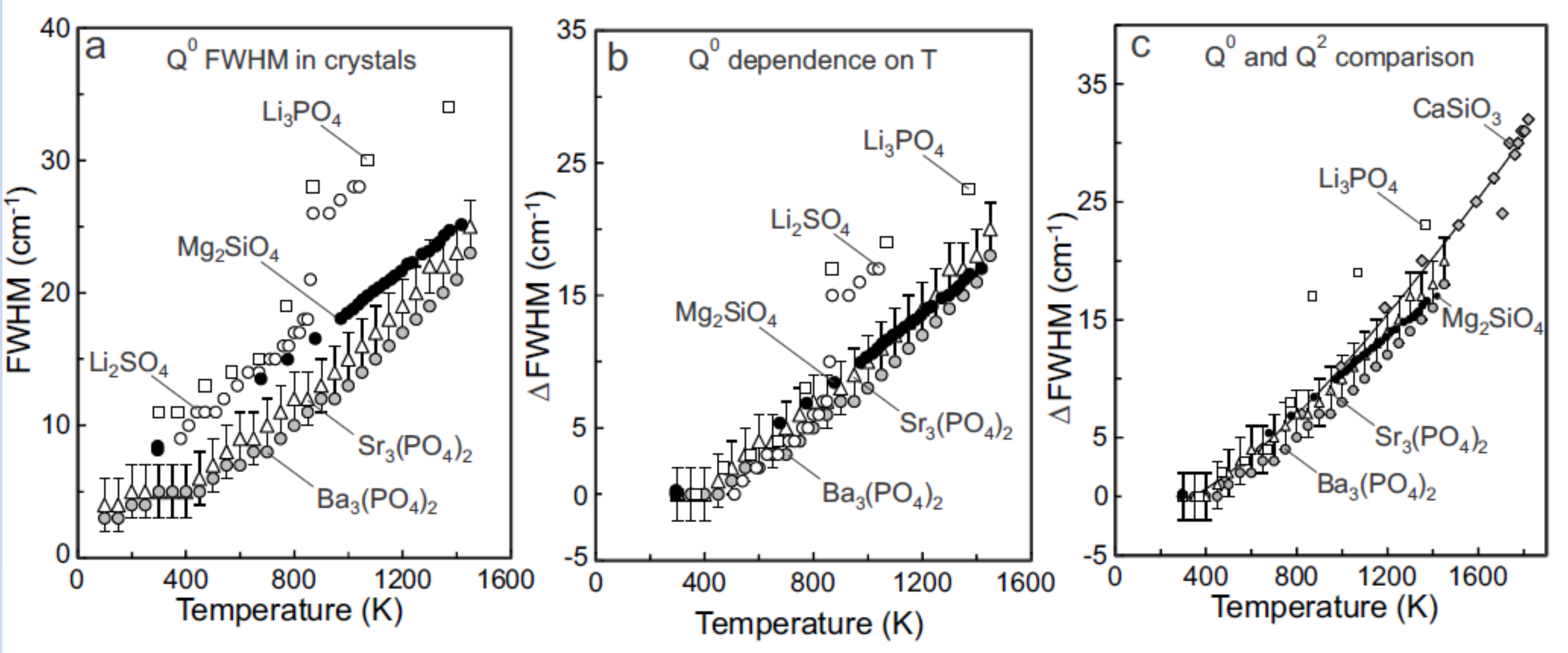
T	Lorentz.	Position	FWHM
298	95	1098.3	39.8
911	93	1093.6	51.6
1073	92	1092.2	55.3
1223	91	1091.7	61.3
1330	85	1091.1	67.4

Q3 Properties for 10% Cs2O glass

T	Lorentz.	Position	FWHM
298	92	1098.3	40.7
432	88	1096.5	46.3
911	85	1093.4	51.1
1073	83	1092.6	57.0
1223	81	1091	65.6

O’Shaughnessy, Henderson, Nesbitt, Bancroft, Neuville, 2017, in prep

[redacted]


a
Q^0 FWHM in crystals
FWHM (cm-1)
Temperature (K)
Li3PO4
Mg2SiO4
Li2SO4
Sr3(PO4)2
Ba3(PO4)2
0
10
20
30
40
0
400
800
1200
1600
b
Q^0 dependence on T
ΔFWHM (cm-1)
Temperature (K)
Li3PO4
Li2SO4
Mg2SiO4
Sr3(PO4)2
Ba3(PO4)2
-5
0
5
15
25
35
c
Q^0 and Q^2 comparison
ΔFWHM (cm-1)
Temperature (K)
CaSiO3
Li3PO4
Mg2SiO4
Sr3(PO4)2
Ba3(PO4)2
-5
0
5
15
25
35

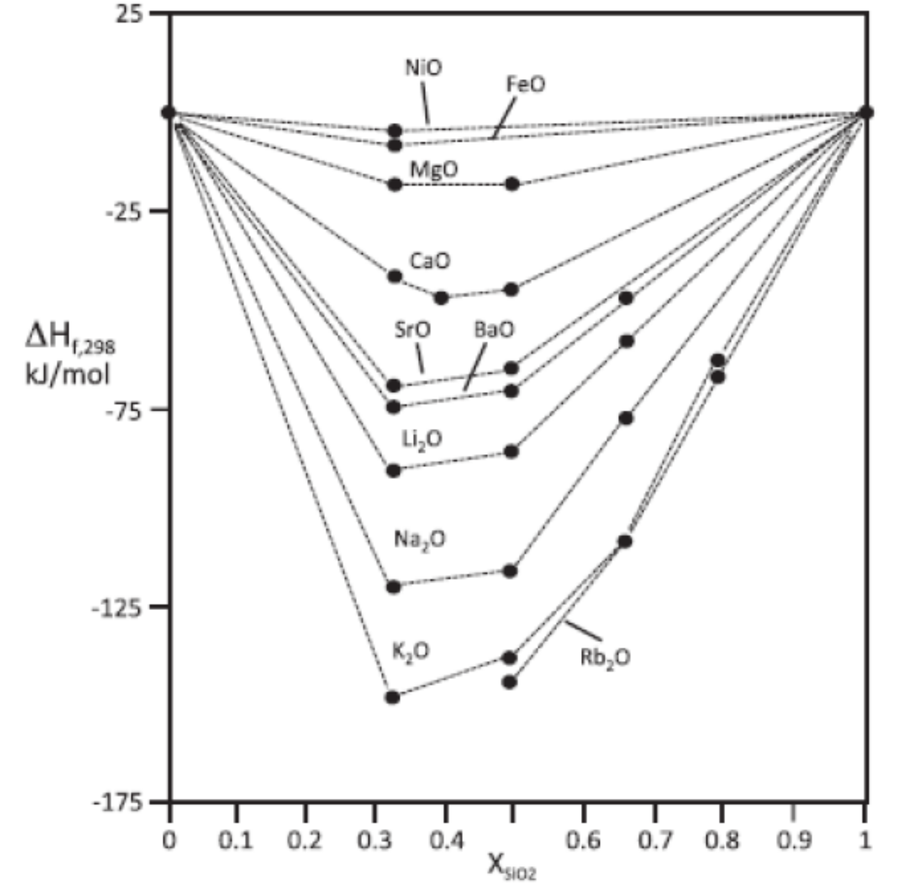
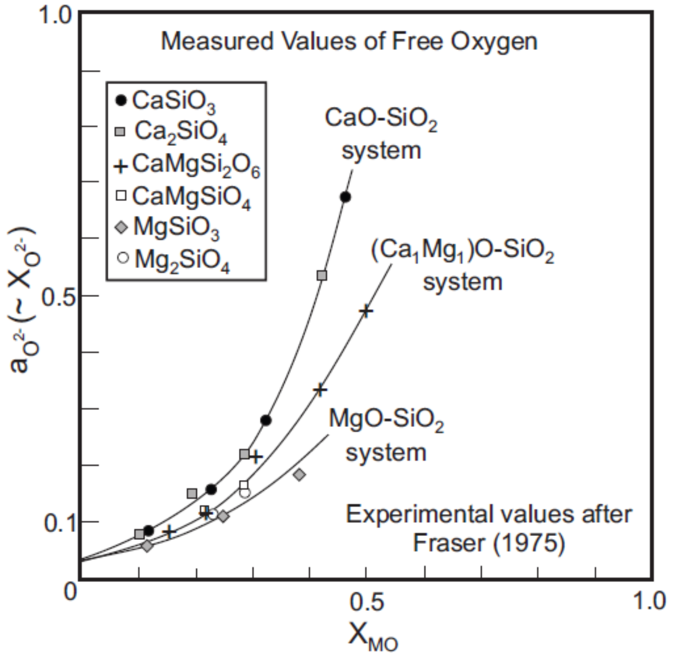


Fig. 4. Heats of formation (298 K) from the simple oxides for crystalline silicates, in kJ per one mole of oxide.

From Stebbins, 2016, reproduced from Hess 1995.

$$a_{Na2O} = (a_{Na+})^2(a_{O2-})$$

There is no obvious relationship between the Heats of Formation of crystalline binary phases and the activity or mole fraction of free oxygen. This has been demonstrated long ago by Fraser (1975; 1977)



Quote from Fraser (in Thermodynamics of Silicate Melts 1977, p. 318)

"The curves (in the figure) are of some interest because the cation effect (on free oxygen) is the opposite of that which might be predicted from studies of the effects of cation polarizing power" (ie., Z/r^2, also referred to as cation field strength).

Referring to the polymerization reactions:

2NBO • BO + O^{2-}

Hess (1971) argues that the product side of the reaction should be favoured by cations with high field strength (i.e., greater Z/r^2 values) so that X_{O2-} should be greater in Mg-bearing melts and glasses than in Ca-bearing systems.

The above experimental results demonstrate that the prediction is incorrect and that one cannot predict free oxygen (or oxide ion) activities or mole fractions based on cation field strength.

Hess, 1995, Reviews in Mineralogy and Geochemistry, 32, 145
Stebbins 2016 Chem Geol, preprint
Fraser 1975, GCA 39, 1525

XPS O 1s Spectra of Na-Silicate Glasses

Spectral Peaks
2 O 1s Peaks: BO and NBO+O^{2-}
1 Auger Peak: Na KLL

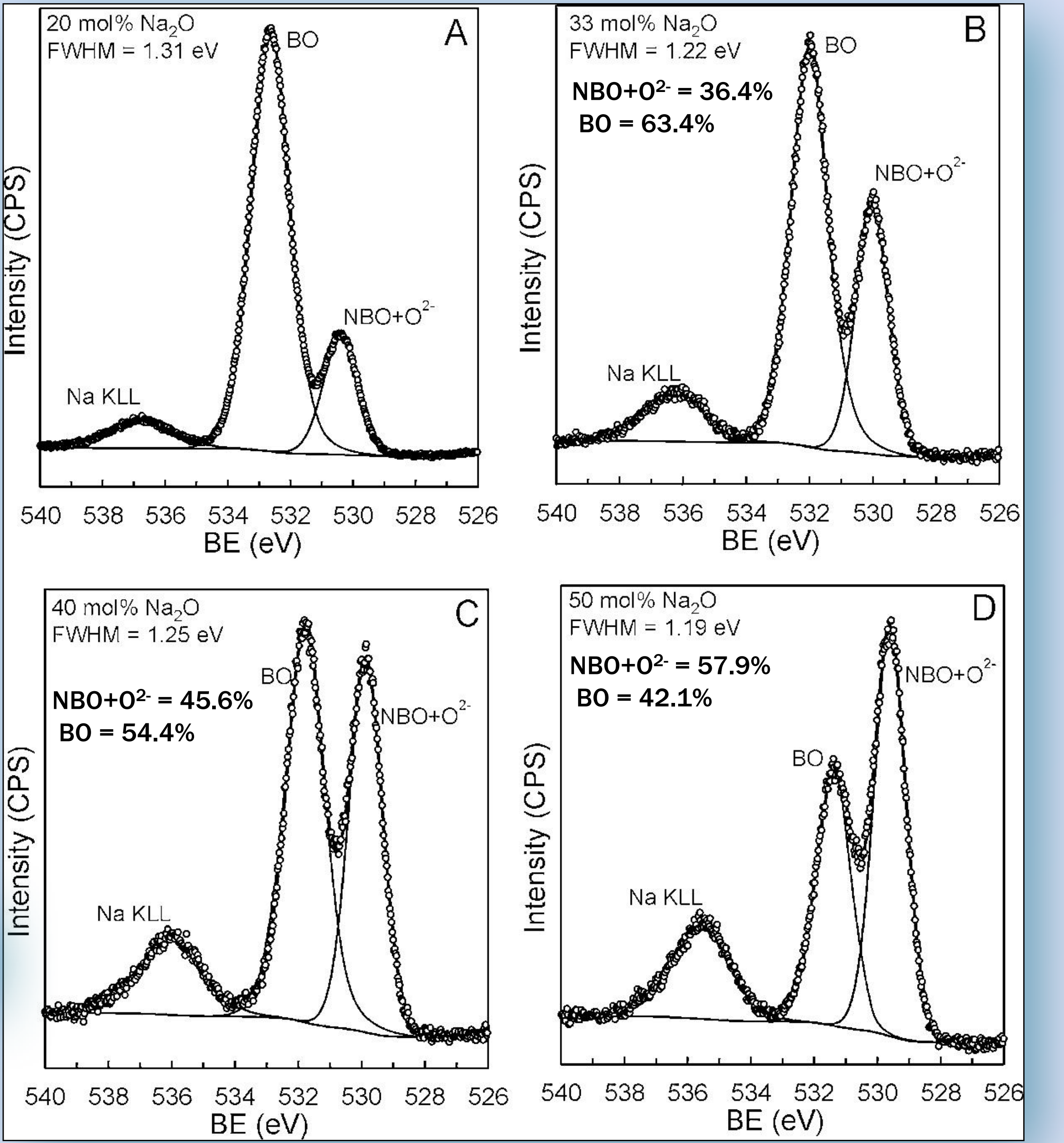
Results: for all compositions X_{BO} is greater than expected if the following reaction had gone to completion:

$$\mathbf{BO + O^{2-} \rightarrow 2NBO}$$

The excess BO must be matched by an equal excess of O^{2-}. Measurement of X_{BO} alone is sufficient to determine X_{O2-} in a glass or melt.

Implication: there is free oxygen in the Na-silicate glasses.

from Nesbitt et al., (2011) J. Non-Cryst. Solids v. 357, p. 170.



Oxygen Speciation in Na-Silicate Glasses

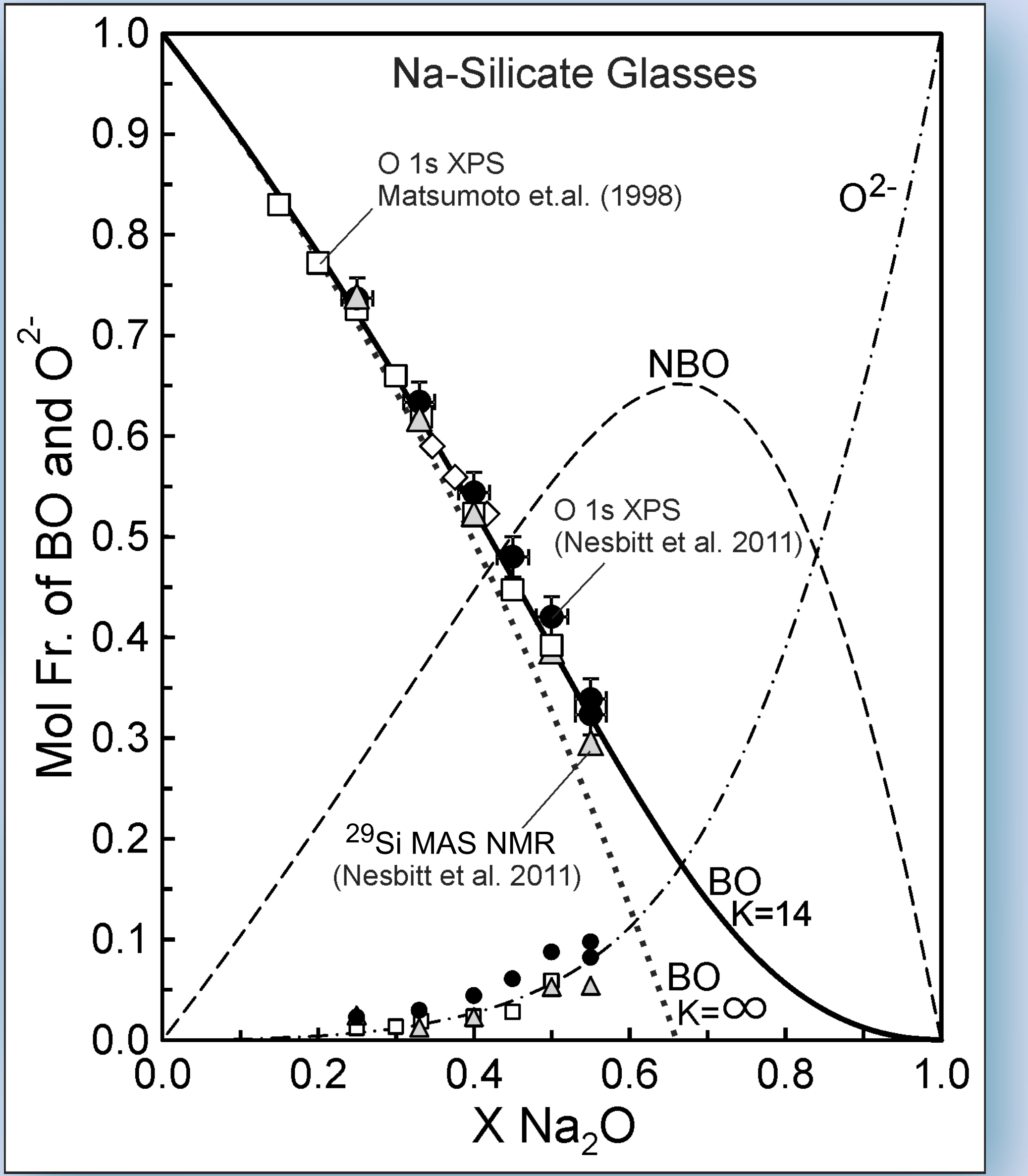
Consistency Of Results

Experimental: Two O 1s XPS experiments and a ^{29}Si MAS NMR experiment yield similar X_{BO} results.

Thermodynamic: Within exptl. uncertainty the X_{BO} values conform to the mass action equation where the conditional equil. constant (K_1) ~ 14.

Conclusion

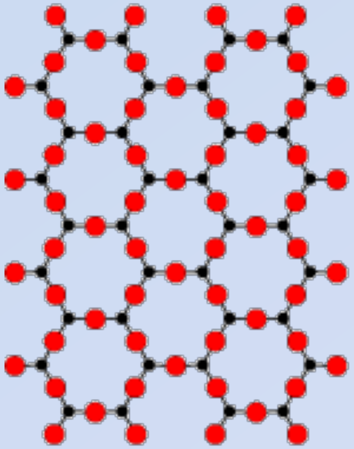
X_{BO} values are consistent with the presence of some free oxygen in Na-silicate glasses and indicate ~ 1-2 mol% O^{2-} in Na-disilicate glasses and increasing to ~ 4-6 mol% O^{2-} at the metasilicate composition.



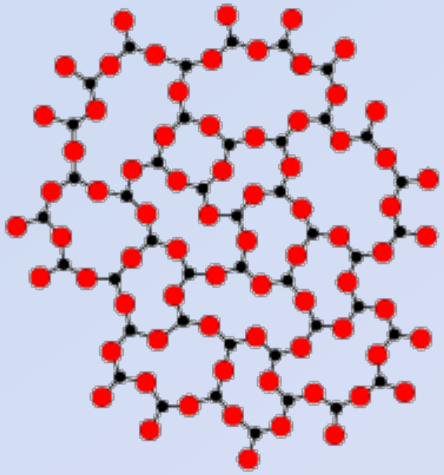
Data from Nesbitt et al., (2011) J. Non-Cryst. Solids, v. 357, p. 170.
and
Matsumoto et al. (1998) Jour. Ceramic Soc. Japan, v. 106, p. 415.

Proposed Oxide Glass Structures

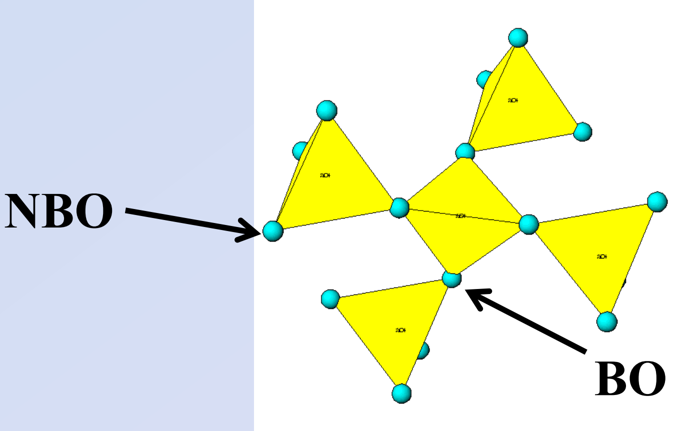
The Continuous Random Network after Zachariasen and Warren (1930's)



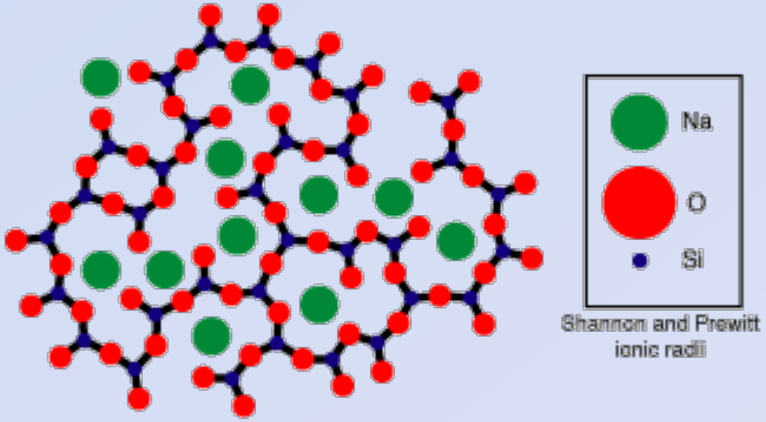
Crystalline A_2O_3



Glassy A_2O_3



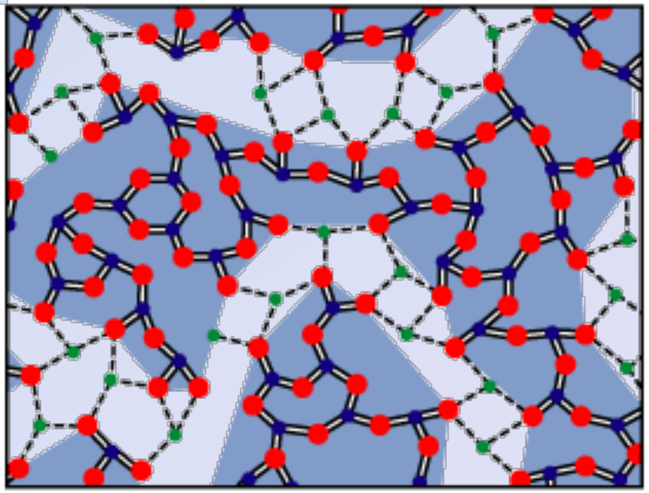
Proposed Structure of Sodium Silicate Glass
after Warren and Biscoe (1930's)



Modified Random Network

after Greaves

J. Non-Cryst. Solids, **71**, 203(1989)



Some Raman observations

- Q species Raman bands are independent of alkali composition and type of alkali.
- Raman bands assigned to Q species are essentially always at same Raman Shift (cm^{-1}). We know where the Q species bands are.
- Q^4 band intensity increases when alkalis present
- CN of Na is NOT 1 when Si-O-Na formed: 5-6. Na-BO > BO. Effect on NBO Q species vibrations?

Raman Fitting Issues

- Q species bands are always in the same positions
- Can assign Q species bands but then have extra bands. What are they?

Problems

- Don't know FWHM of bands
- Have not considered the influence of MBO on Q species vibrations

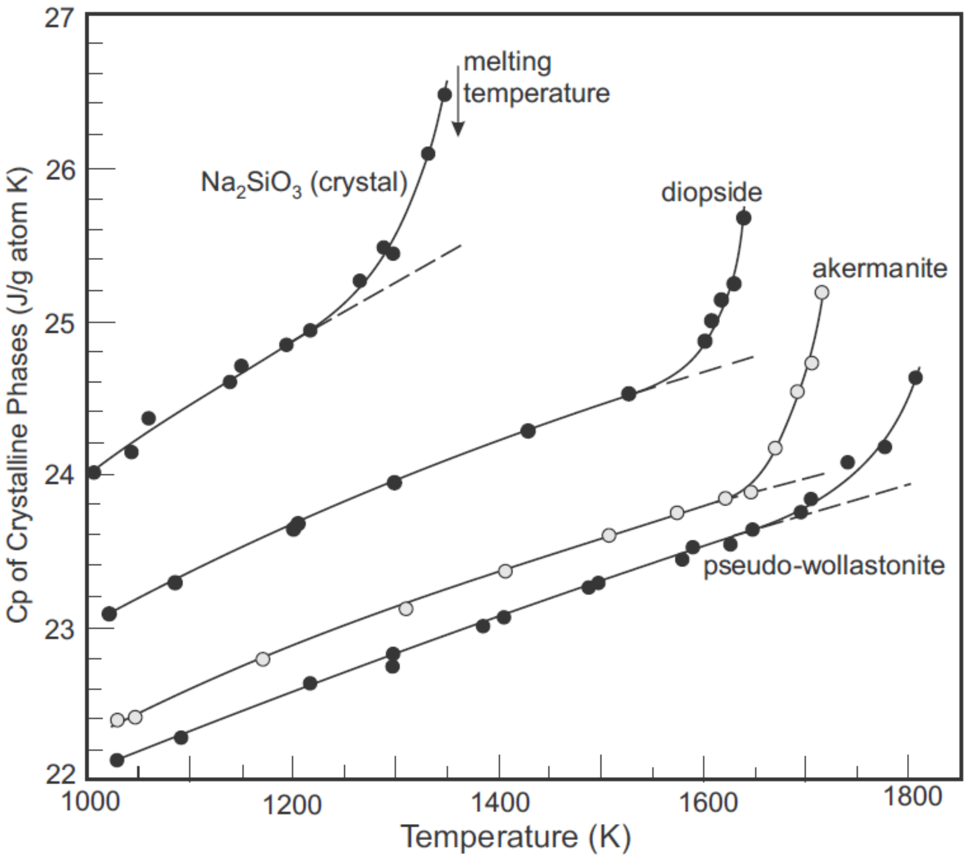
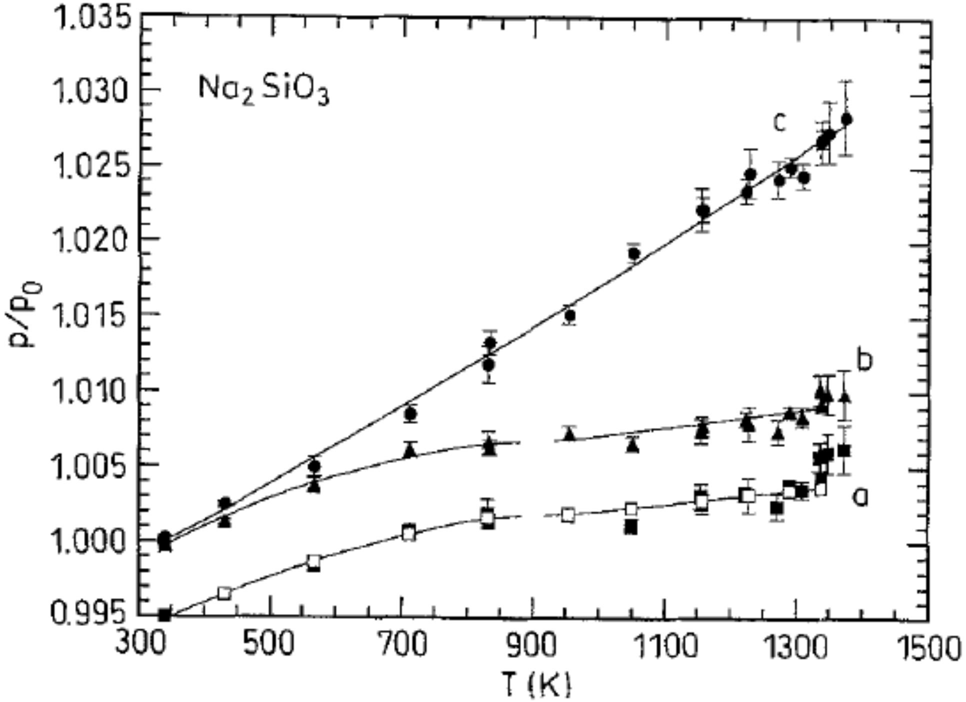


Fig. 2

Heat Capacity (Cp) exhibits inflexion before melting point Implies pre-melting phenomenon

In crystalline metasilicate (Na_2SiO_3)
a-b plane undistorted
c axis exhibits linear changes with T

Richet et al., 1996 Phys. Chem. Mineral., 23, 157.
Richet et al., 1998 Phys. Chem. Mineral., 25, 401.



Similarity between NMR and Raman spectra
Q^2 dominate spectra
$Q^3 > Q^1$

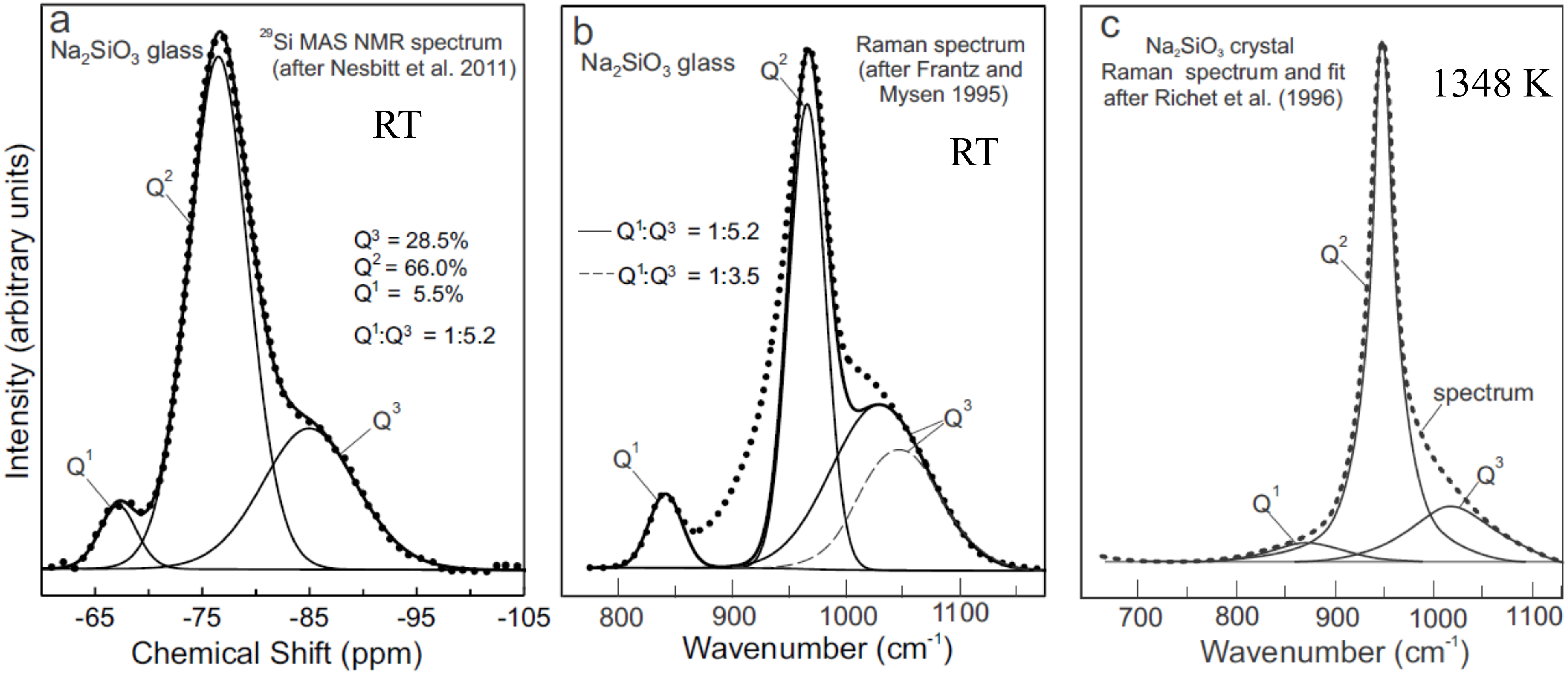


Fig. 3

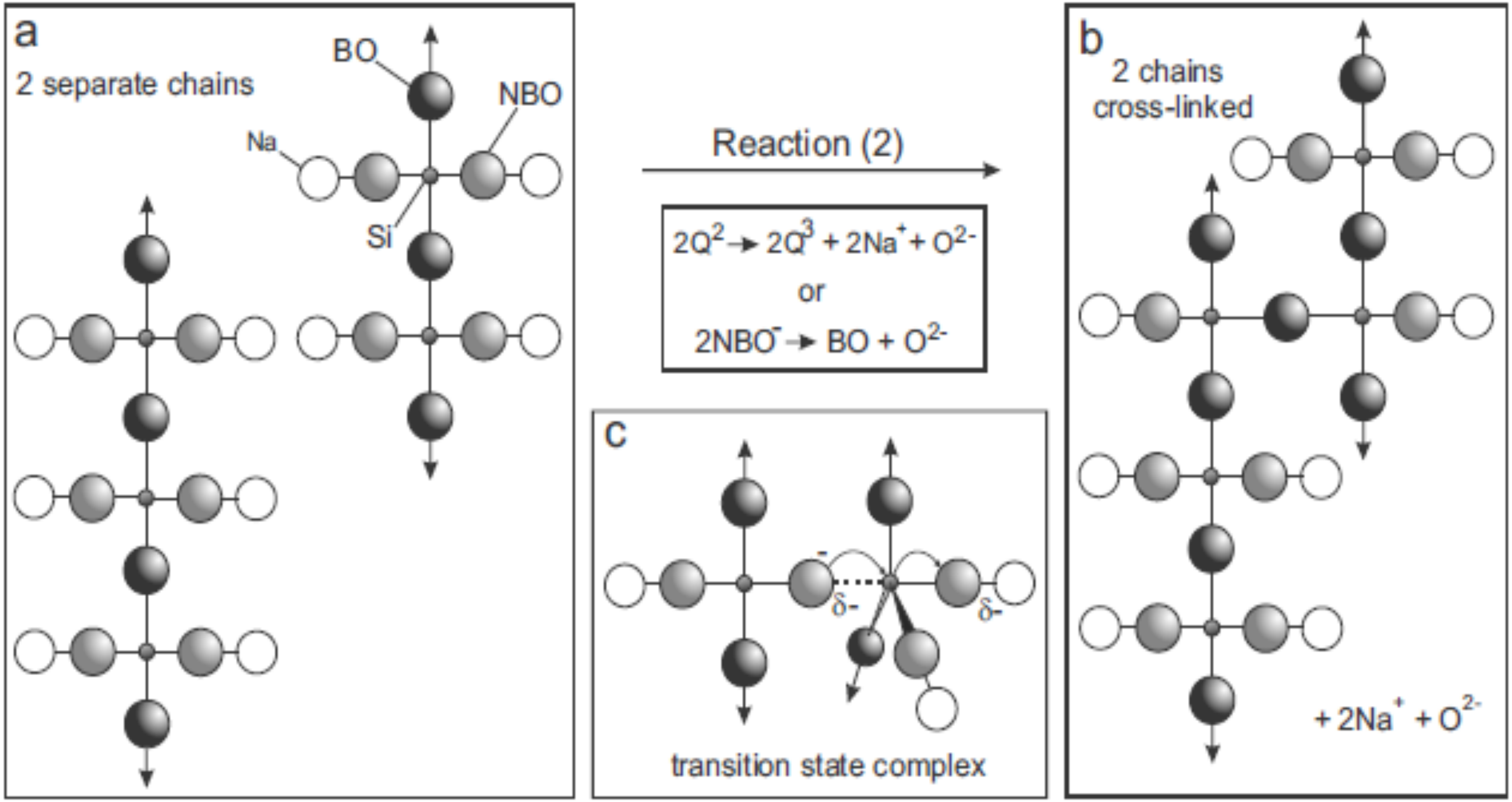
Nesbitt et al., 2011, JNCS, 357, 170. Frantz and Mysen, 1995, Chem. Geol. 121, 155.. Richet et al., 1998, Phys. Chem. Mineral., 23, 157.

Pre-melting reactions

$2Q^2 \rightarrow 2Q^3 + 2Na^+ + O^{2-}$ indicated by Q^3 in Raman

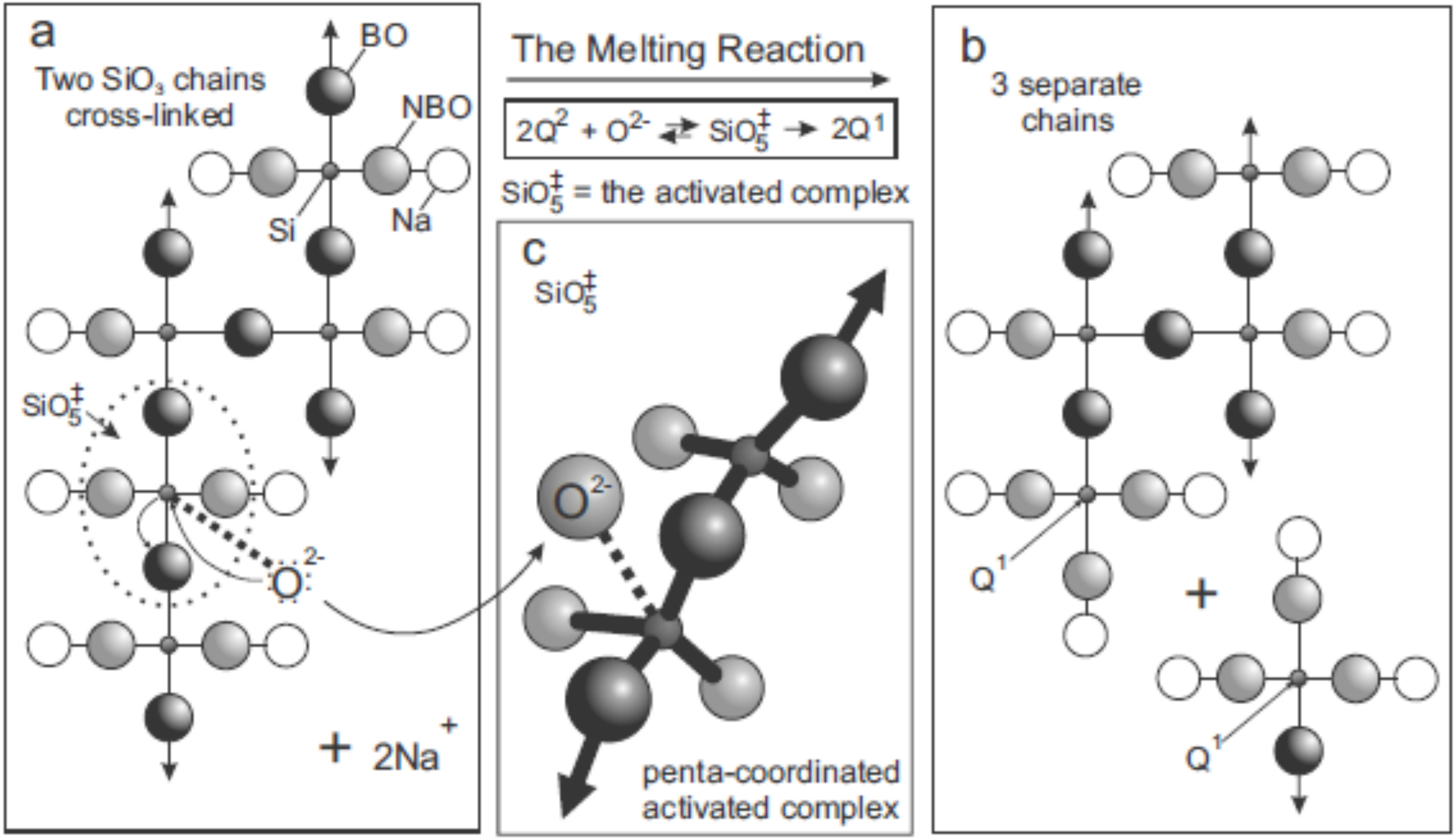
Q^3 form in a/b plane, prevent expansion

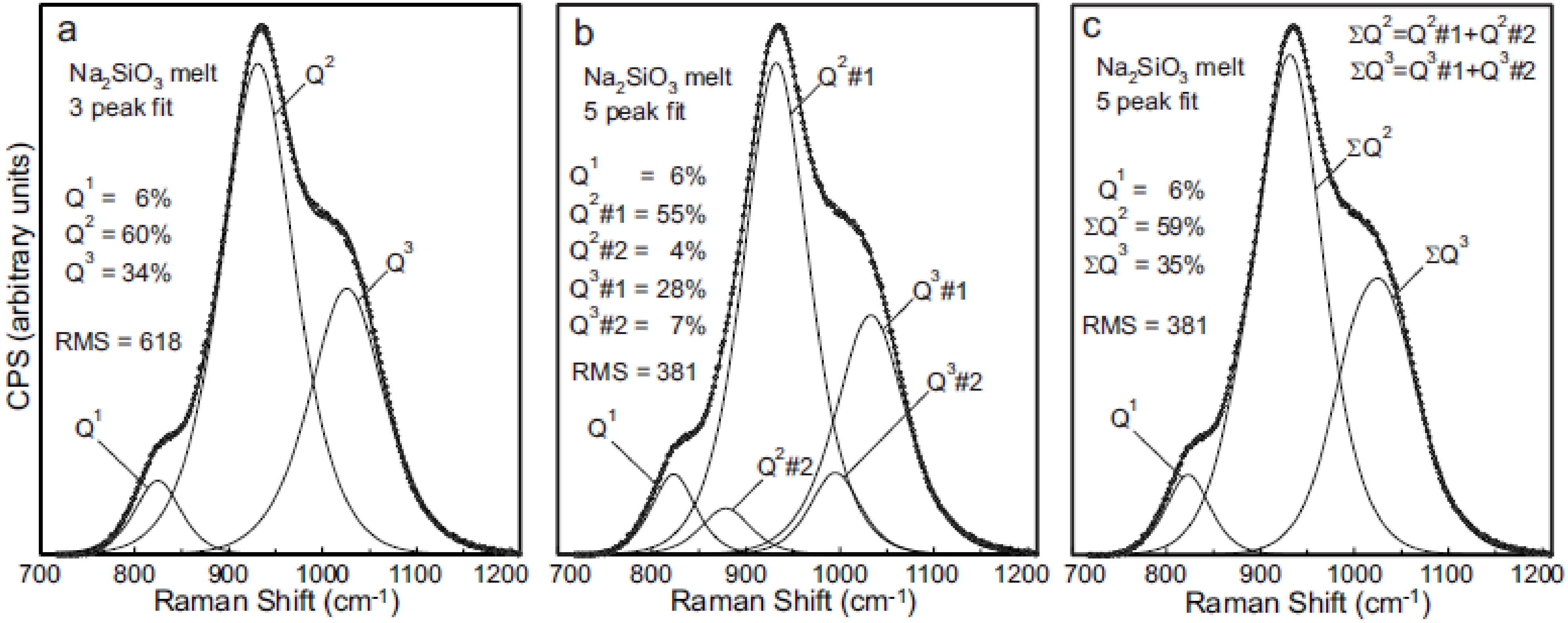
$\text{Si-O}^- + Q^2 \rightleftharpoons [(\text{Si-O-}Q^2)\text{-}]^{\ddagger} \rightarrow 2Q^3 + Na^+ + O^{2-}$



Melting Reaction

$$2Q^2 + O^{2-} \rightleftharpoons SiO_5‡ \rightarrow 2Q^1$$



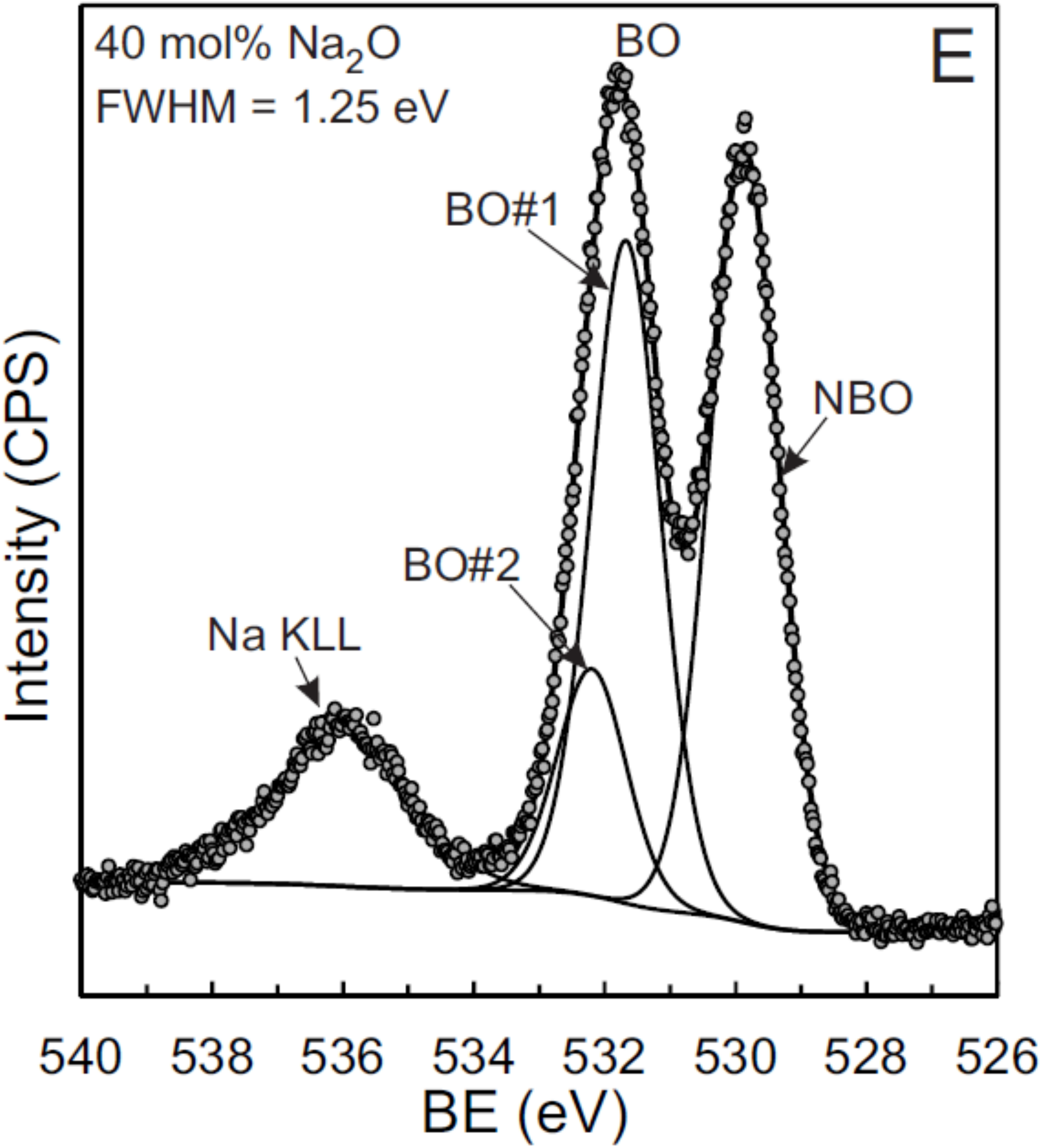

a
Na$_2$SiO$_3$ melt
3 peak fit
Q^1 = 6%
Q^2 = 60%
Q^3 = 34%
RMS = 618
Q^1
Q^2
Q^3
b
Na$_2$SiO$_3$ melt
5 peak fit
Q^1 = 6%
Q^2#1 = 55%
Q^2#2 = 4%
Q^3#1 = 28%
Q^3#2 = 7%
RMS = 381
Q^1
Q^2#1
Q^2#2
Q^3#1
Q^3#2
c
$\Sigma Q^2 = Q^2\#1 + Q^2\#2$
$\Sigma Q^3 = Q^3\#1 + Q^3\#2$
Na$_2$SiO$_3$ melt
5 peak fit
Q^1 = 6%
ΣQ^2 = 59%
ΣQ^3 = 35%
RMS = 381
Q^1
ΣQ^2
ΣQ^3
CPS (arbitrary units)
700
800
900
1000
1100
1200
Raman Shift (cm^{-1})

BO FWHM increases with increasing alkali

Suggests that 2nd BO species present (MBO)

Two peak (BO, MBO) fit with both FWHM constrained to 1.25 eV: MBO>BO

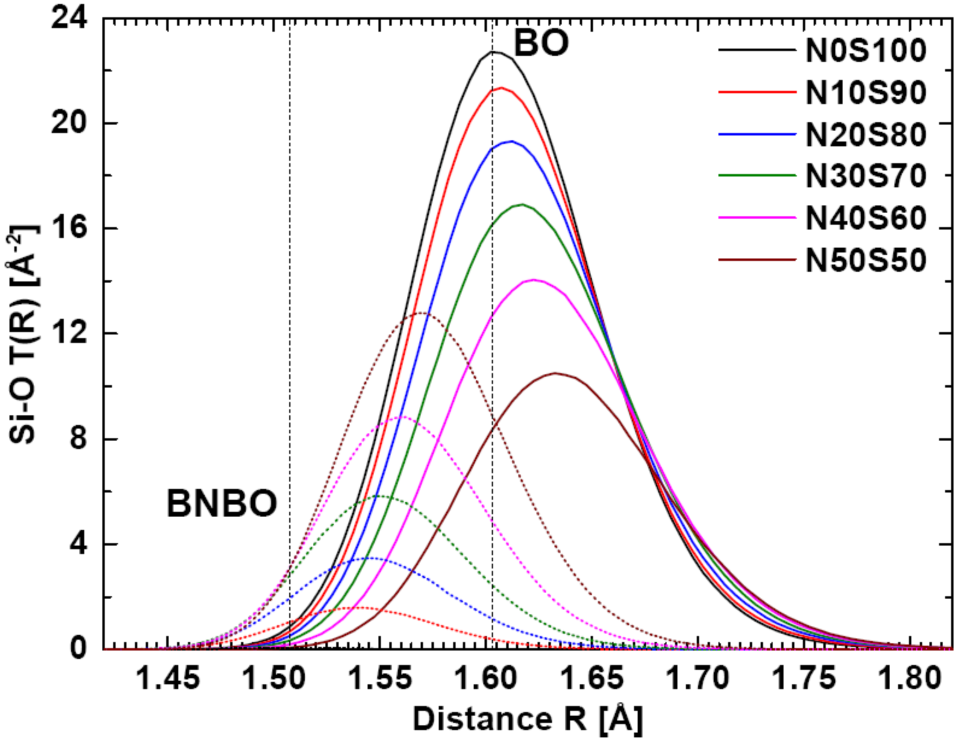
Will affect density and volume of magma and ascent rates

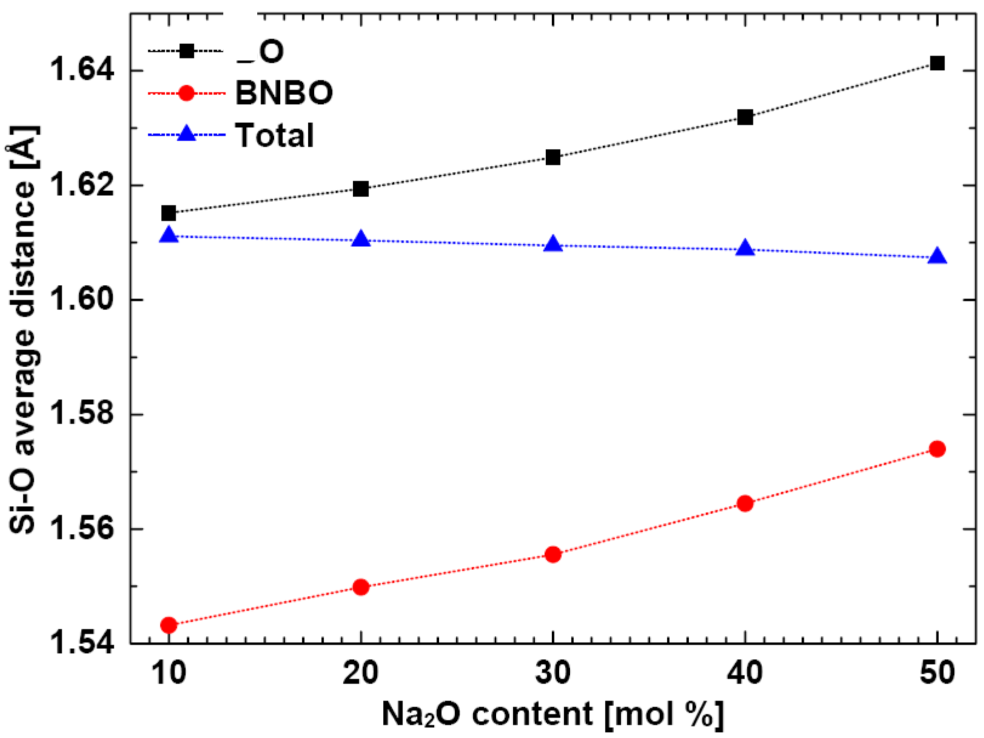


Nesbitt, Henderson, Bancroft, Ho (2015), JNCS, 409, 139-148.

Crystalline β-$Na_2Si_2O_5$/Na_2SiO_3 : Only have Na-BO or Na-BO-Na linkages
Crystalline α-$Na_2Si_2O_5$: has BO and Na-BO in 1:2 ratio
Si-BO bond length increases from 1.61 to 1.67 Å going from BO → BO-Na → Na-BO-Na

1. **Si-NBO bonds are shorter than Si-BO bonds**
2. **both Si-NBO and Si-BO bonds get longer as Na content increases**
   - **note: average Si-O bond remains constant**





Unpublished data courtesy of Gavin Mountjoy

Some observations

- Do channels exits? No real experimental evidence

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- If so why are experimental data not interpreted in terms of channel model?

Some observations

- Do channels exits? No real experimental evidence
- If so why are experimental data not interpreted in terms of channel model?
- Free oxygen widely accepted in glass and materials science communities. Existence is denied by Earth science community
- Q species Raman bands are independent of alkali composition and type of alkali.
- Q^4 band intensity increases when alkalis present
- Na-NBO: Doesn’t mean Na has CN=1. Na-BO > BO
- Same composition fit multiple ways by same authors.

Conventional thinking: Melts have

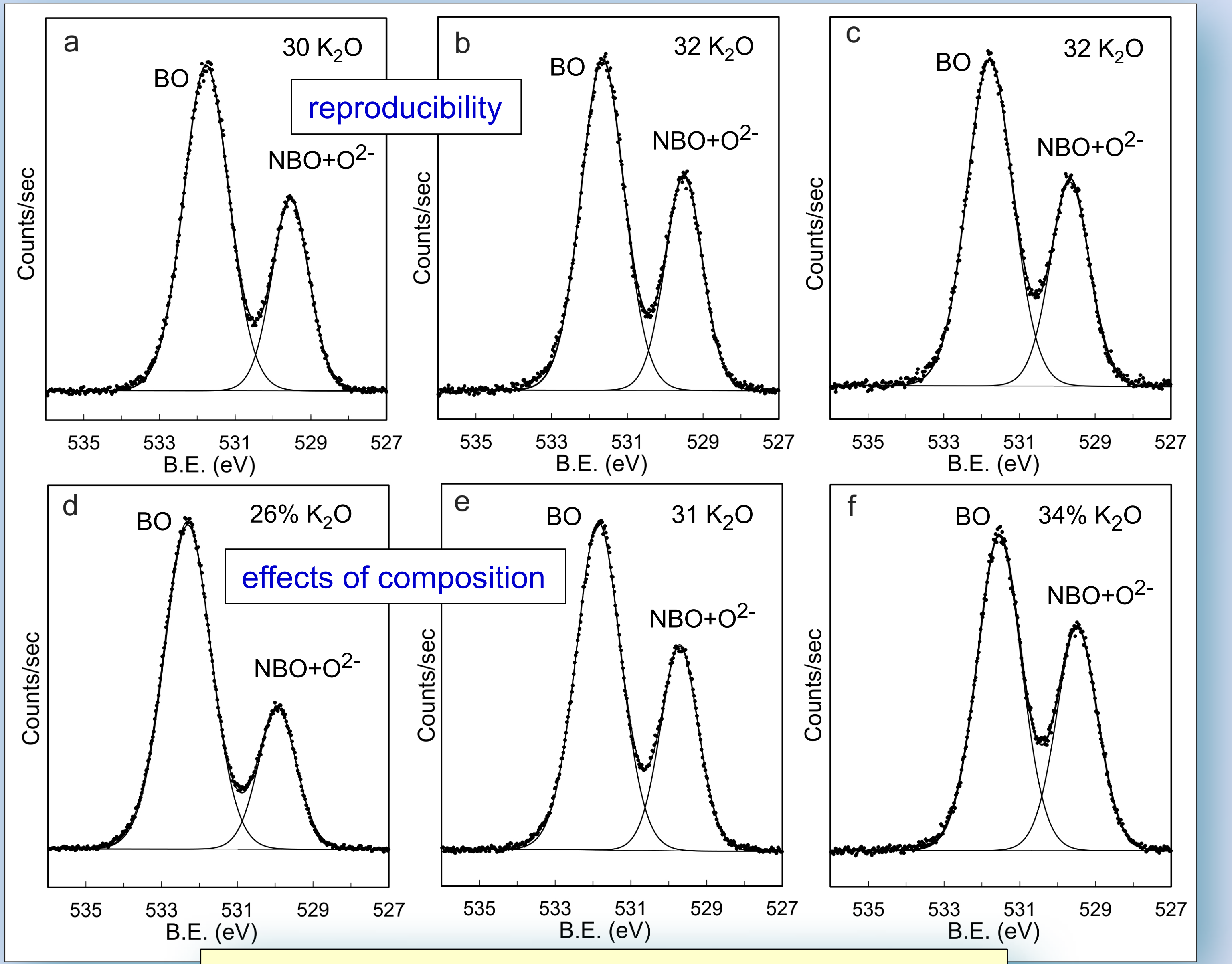
- BO
- NBO: Q^1, Q^2, Q^3, Q^4 plus combinations
- No free oxygen

Recent Studies : Melts have

- BO: 2 or more types (BO, MBO, MBOM, M_3BO)
- Changes interpretation of NMR/Raman spectra of glasses and melts
- NBO: Q^1, Q^2, Q^3, Q^4 plus combinations
- Free oxygen (O^{2-}) can be present at mol% levels
- Polymerization of melt generates O^{2-}

Part II: O 1s Spectra of K-Silicate Glasses near the Disilicate Composition

Peaks are effectively symmetric, well resolved and peak areas can be accurately measured.



reproducibility

effects of composition

Data from Sawyer et al. (2014), Can. Jour. Chem. v.92, p. 1-14.

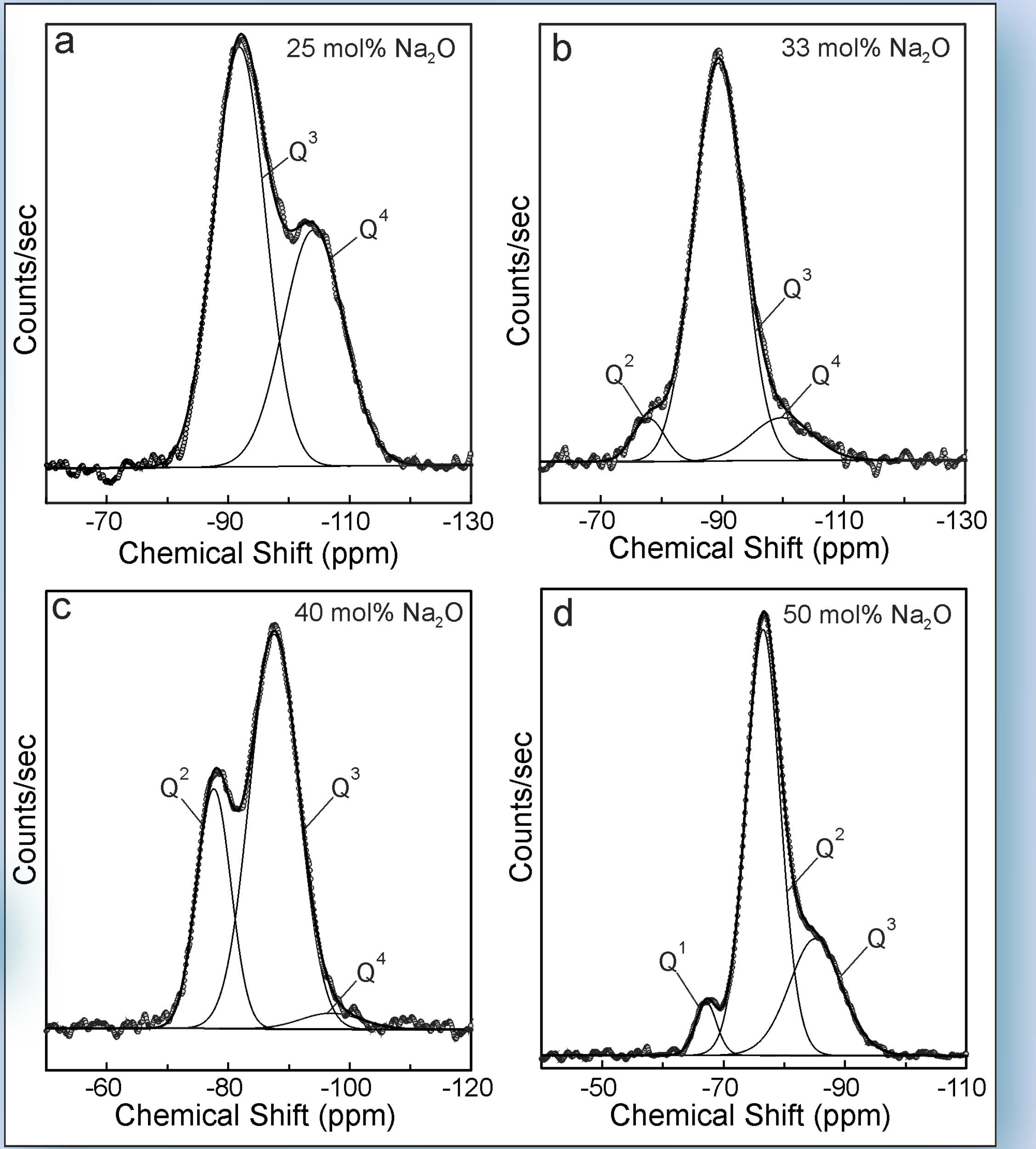
^{29}Si MAS NMR Spectra for Na-Silicate Glasses

Spectral Peaks
All fitted peaks were Gaussian in shape.

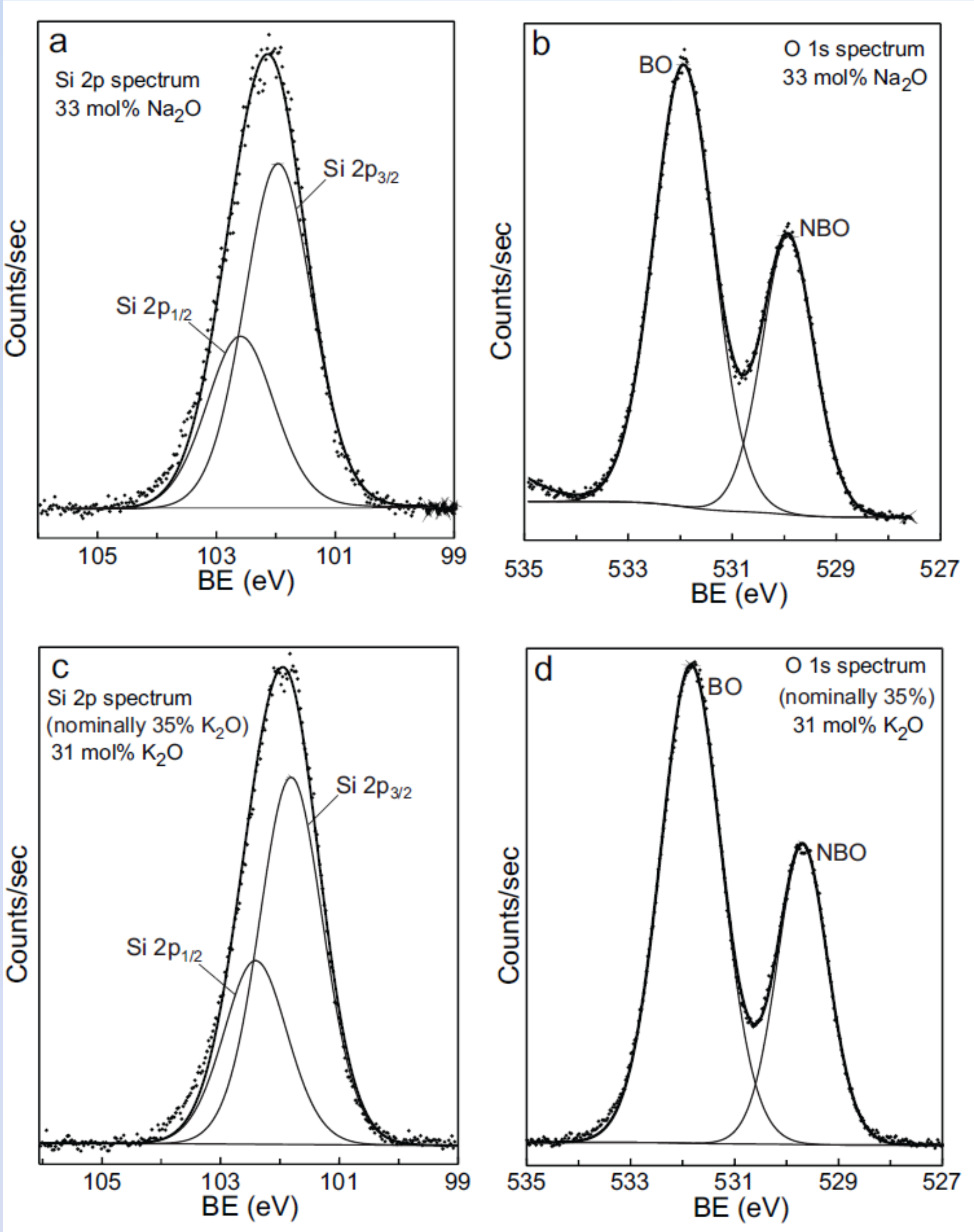
All glasses indicate an excess of BO over that expected if the following reaction went to completion.

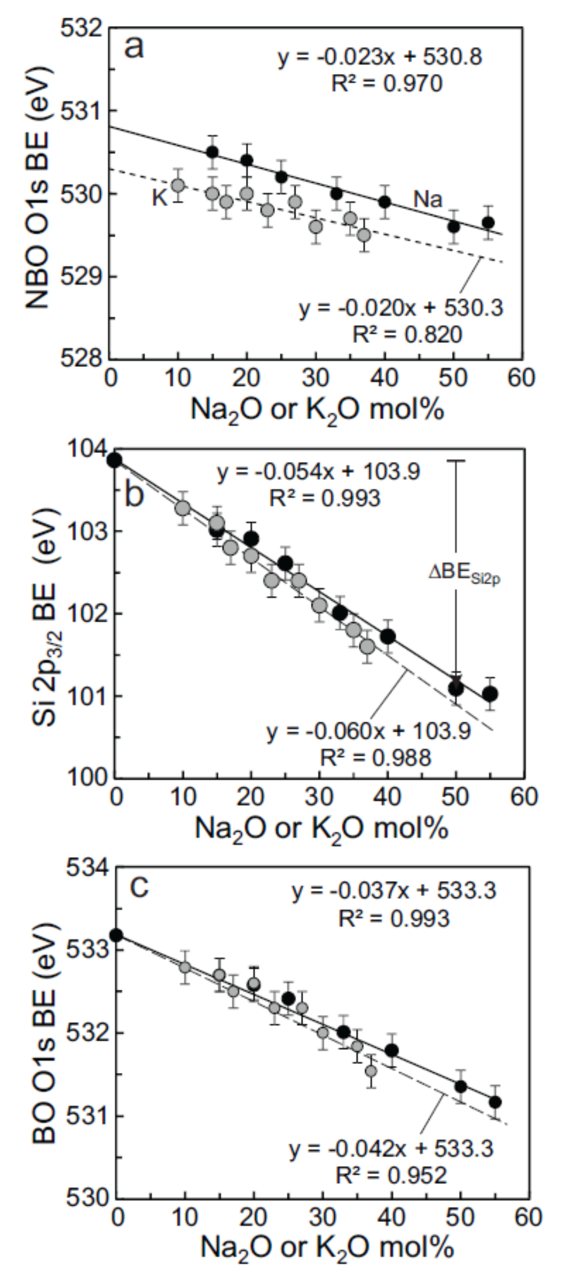
$$\mathbf{BO + O^{2-} \rightarrow 2NBO}$$

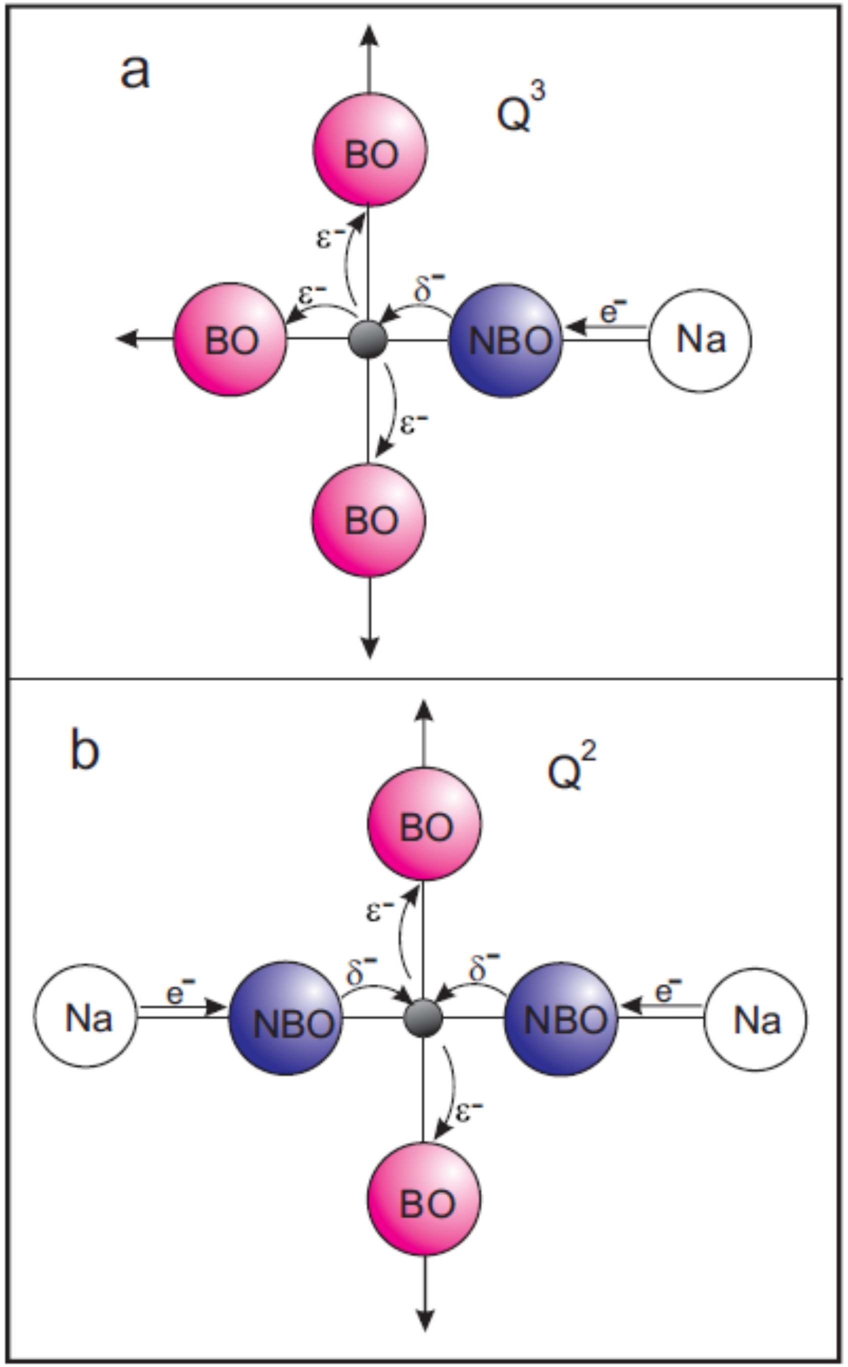
implying the presence of free oxygen.



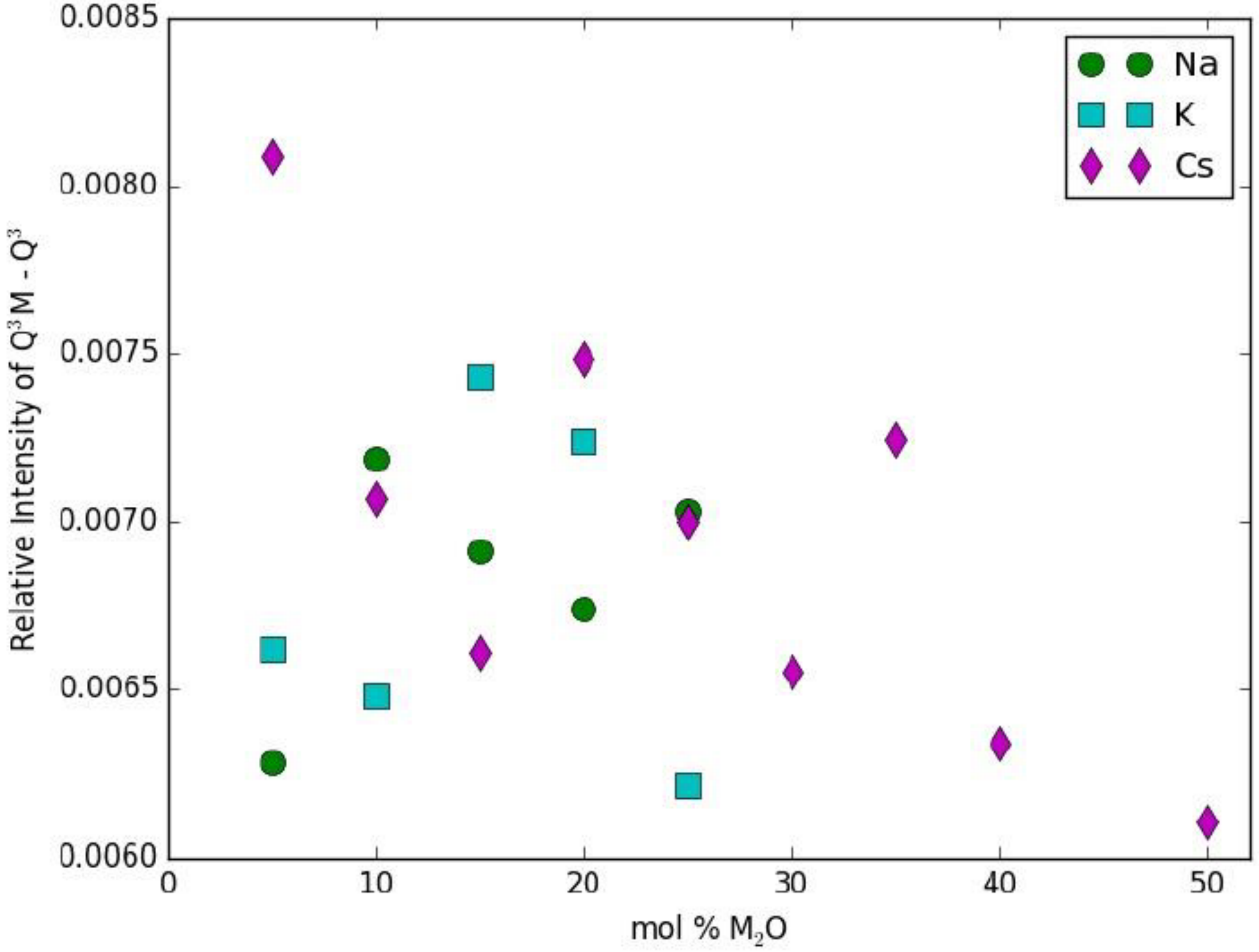
from Nesbitt et al., (2011) J. Non-Cryst. Solids v. 357, p. 170.

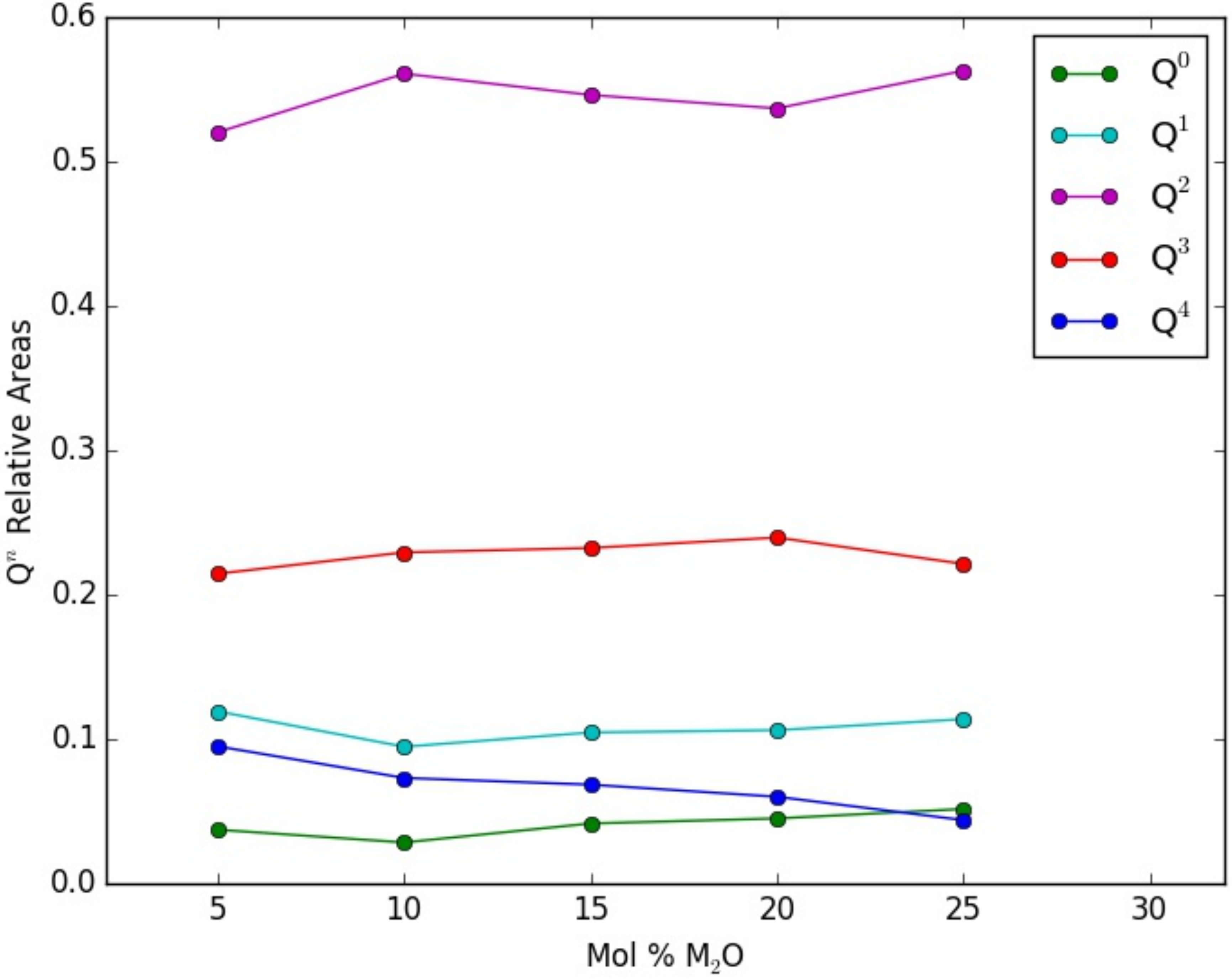

a
Si 2p spectrum
33 mol% Na_2O
Si $2p_{3/2}$
Si $2p_{1/2}$
Counts/sec
105
103
101
99
BE (eV)
b
O 1s spectrum
33 mol% Na_2O
BO
NBO
Counts/sec
535
533
531
529
527
BE (eV)
c
Si 2p spectrum
(nominally 35% K_2O)
31 mol% K_2O
Si $2p_{3/2}$
Si $2p_{1/2}$
Counts/sec
105
103
101
99
BE (eV)
d
O 1s spectrum
(nominally 35%)
31 mol% K_2O
BO
NBO
Counts/sec
535
533
531
529
527
BE (eV)


a
y = -0.023x + 530.8
R² = 0.970
y = -0.020x + 530.3
R² = 0.820
K
Na
NBO O1s BE (eV)
532
531
530
529
528
0
10
20
30
40
50
60
Na2O or K2O mol%
b
y = -0.054x + 103.9
R² = 0.993
ΔBESi2p
y = -0.060x + 103.9
R² = 0.988
Si 2p3/2 BE (eV)
104
103
102
101
100
0
10
20
30
40
50
60
Na2O or K2O mol%
c
y = -0.037x + 533.3
R² = 0.993
y = -0.042x + 533.3
R² = 0.952
BO O1s BE (eV)
534
533
532
531
530
0
10
20
30
40
50
60
Na2O or K2O mol%

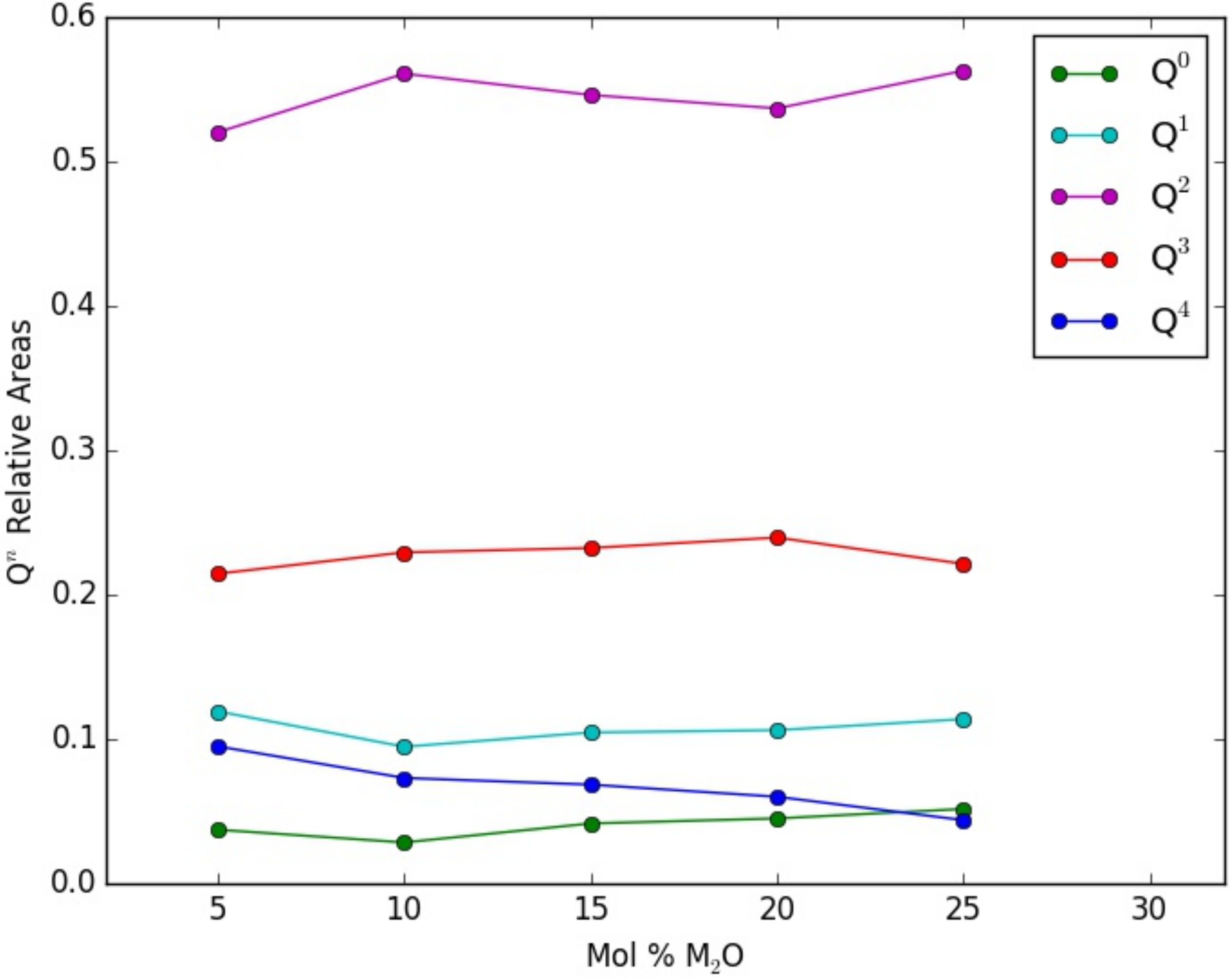

a
Q^3
BO
BO
NBO
Na
BO
ε⁻
ε⁻
δ⁻
e⁻
ε⁻
b
Q^2
BO
ε⁻
δ⁻
δ⁻
Na
e⁻
NBO
NBO
e⁻
Na
ε⁻
BO

Difference in peak Q^3M-Q^3 intensity





0.6
0.5
0.4
0.3
0.2
0.1
0.0
Q^n Relative Areas
5
10
15
20
25
30
Mol % M_2O
Q^0
Q^1
Q^2
Q^3
Q^4


0.6
0.5
0.4
0.3
0.2
0.1
0.0
Q^n Relative Areas
5
10
15
20
25
30
Mol % M_2O
Q^0
Q^1
Q^2
Q^3
Q^4

What is the importance of “free” oxygen (O^{2-})?

For over 100 years no mechanism to explain melting of silicate minerals

Proposed mechanism involving “free” oxygen (O^{2-})

1) Breaking of weak M-O bonds prior to melting, to produce itinerant M^+ and $Si\text{-}O^-$ moieties attached to chains
2) Reaction of $Si\text{-}O^-$ to form cross-chain linkages which produces free oxygen (O^{2-})
3) Reaction of O^{2-} with SiO_3 chains to depolymerize (rupture) them causing melting.
4) O^{2-} plays essential and critical role in melting and crystallization of silicate minerals!

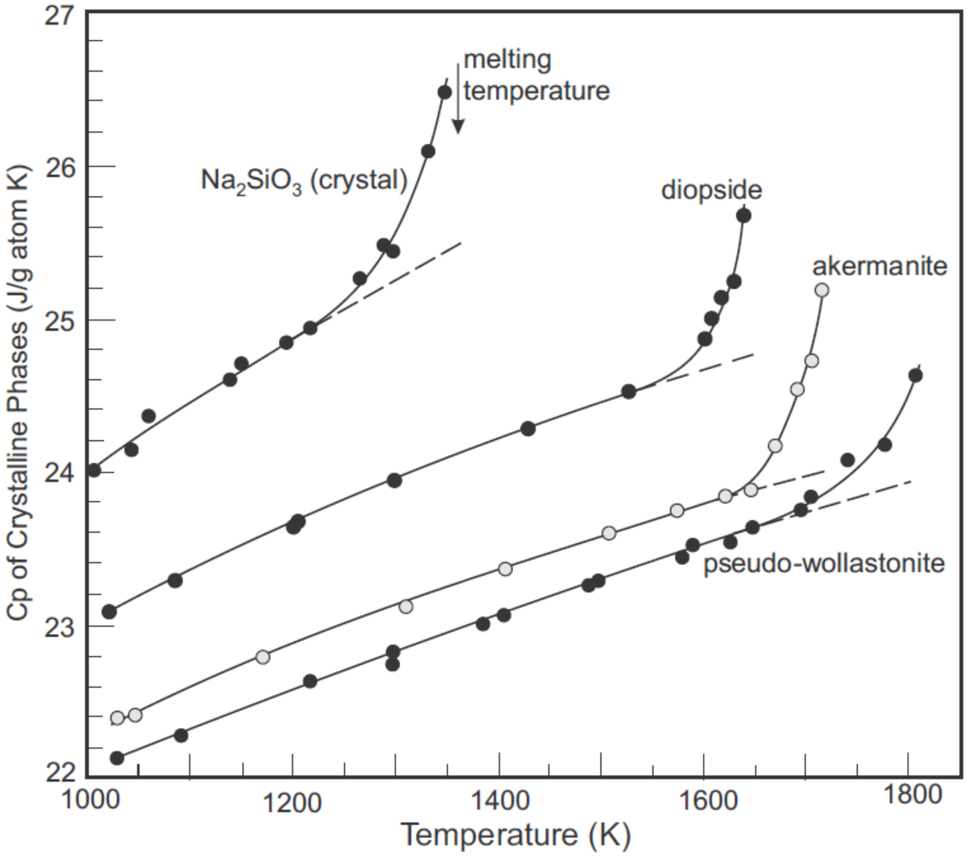


Fig. 2

Heat Capacity (Cp) exhibits inflexion before melting point Implies pre-melting phenomenon

In crystalline metasilicate (Na_2SiO_3)
a-b plane undistorted
c axis exhibits linear changes with T

Richet et al., 1996 Phys. Chem. Mineral., 23, 157.
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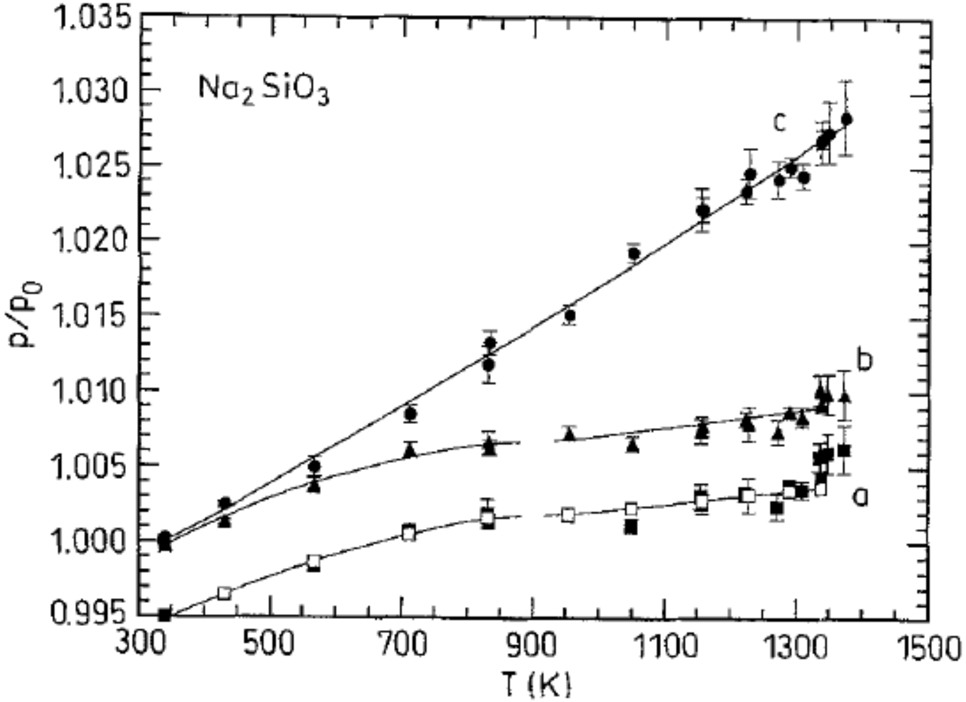


Similarity between NMR and Raman spectra
Q^2 dominate spectra
$Q^3 > Q^1$

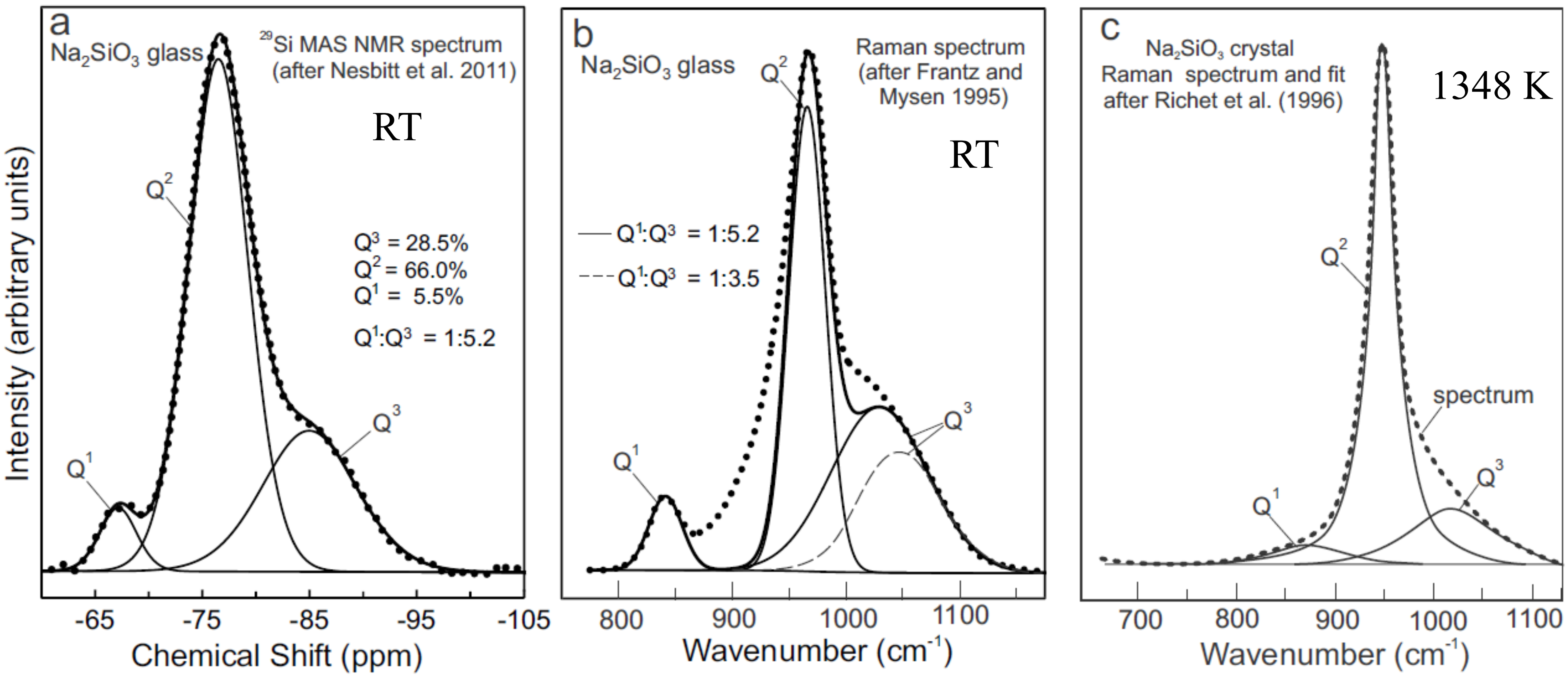
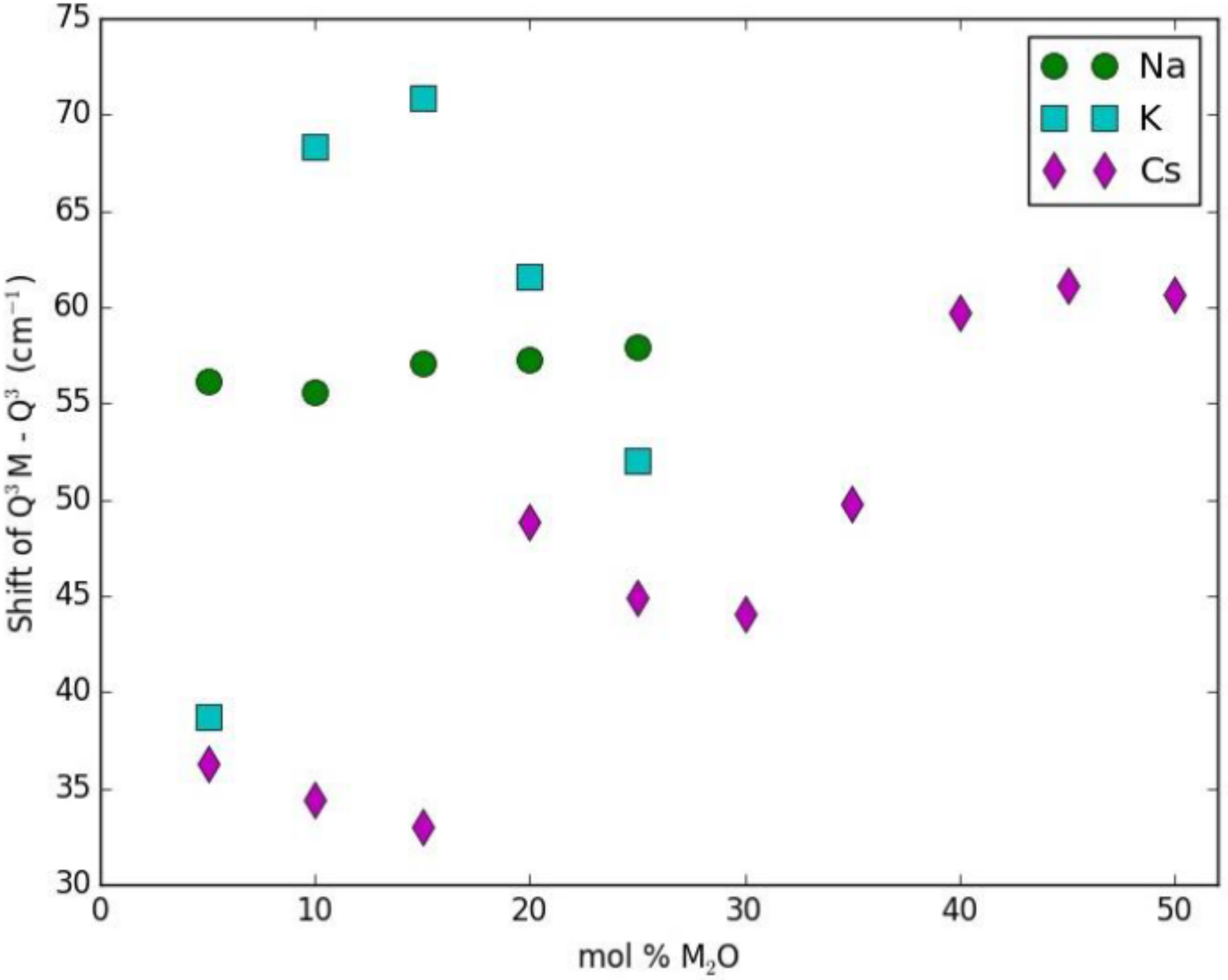


Fig. 3

Nesbitt et al., 2011, JNCS, 357, 170. Frantz and Mysen, 1995, Chem. Geol. 121, 155..
Richet et al., 1998, Phys. Chem. Mineral., 23, 157.

Difference in peak Q^3M-Q^3 position



Summary

1) Charging of silicate minerals and glasses has been circumvented by new charge neutralization technologies found on the new generation of XPS instruments.

2) O 1s spectral lines can now be accurately fitted with symmetric line shapes. A 30:70 Gaussian-Lorentzian convolution is used to fit all our spectra.

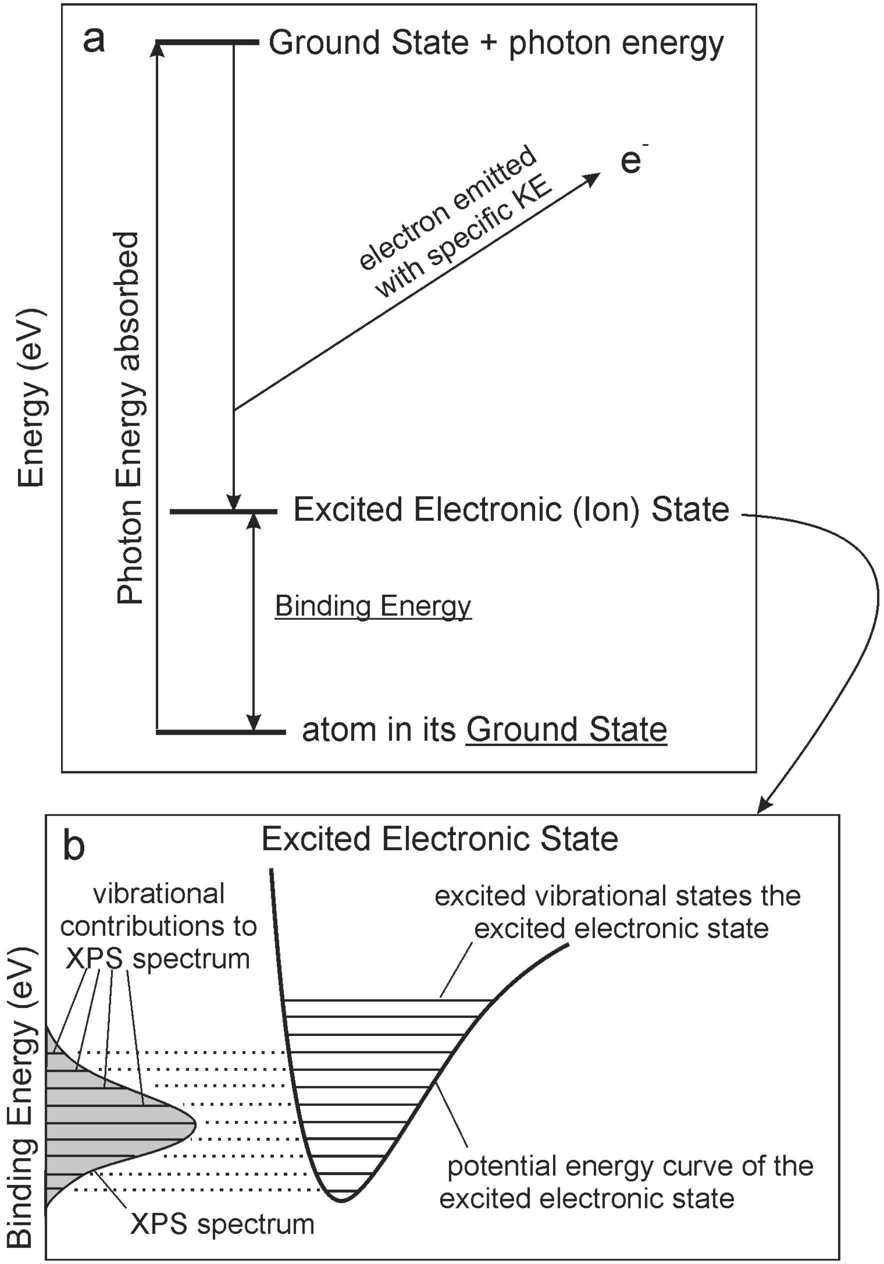
3) The O 1s XPS linewidths of silicates are effectively constant at ~ 1.25 +/- 0.1 eV. Widths greater than about 1.4 eV indicate that the peak is composite.

4) O 1s XPS spectra of Pb-Silicate, Na-Silicate and K-silicate glasses indicate that free oxygen is present in glasses containing more than about 20 mol% counter oxide.

5) Determination of O^{2-} abundance is important because its strong basicity makes it the most reactive of oxygen species in glasses and melts.

Moreover, there is a large reservoir of O^{2-} in glasses and melts in that free oxygen consumed by a reaction with reagents will be replaced by conversion of NBO to BO and O^{2-} according to the principle of Le Chatelier.

Part II: Vibrational and Phonon Broadening Controls Si 2p and O 1s Linewidths



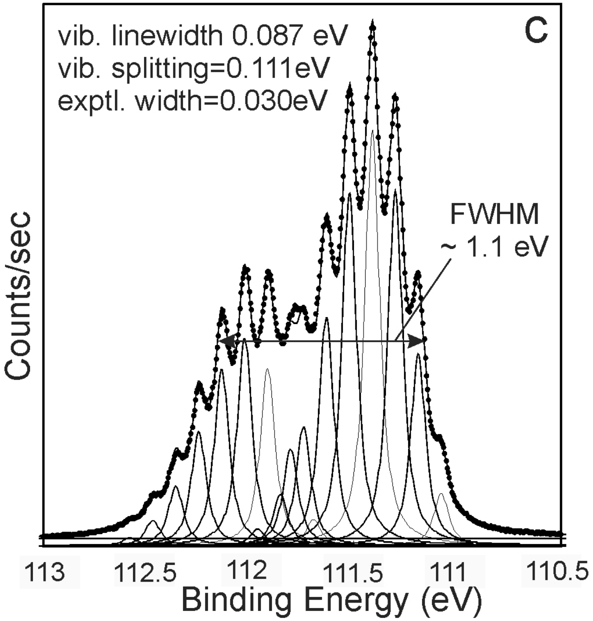
Consequences of Absorption of a Photon by an Atom

(Bancroft et al. (2009) Phys. Rev. B v.80, 075405)

From Bancroft et al. (2009) Phys. Rev. B v.80, 075405 and Thomas et al. (2002) Phys. Rev. B, v.89, p.223001

Si 2p spectrum of SiF_4 (gas phase)

Each Si 2p contribution is composed of a Si $2p_{3/2}$ and a Si $2p_{1/2}$ signal, the later being half the intensity of the $2p_{3/2}$ peak.



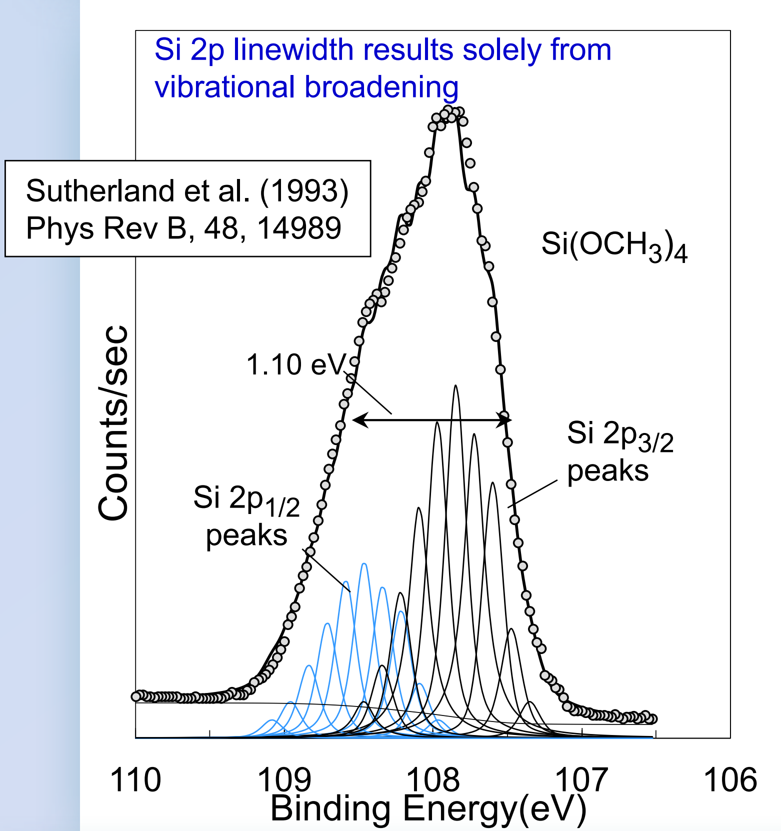
Part II: Contributions to Si 2p and O 1s Spectral Linewidths

Si 2p Spectrum of Tetramethoxysilane (gas)

Si-O bond length = 1.61Angstroms
Vibrational frequency = 840 cm^{-1}
Instrumental Linewidth = 0.05 eV
Vibrational Linewidth = 0.170 eV
Vibrational Energy Splitting = 0.125 eV

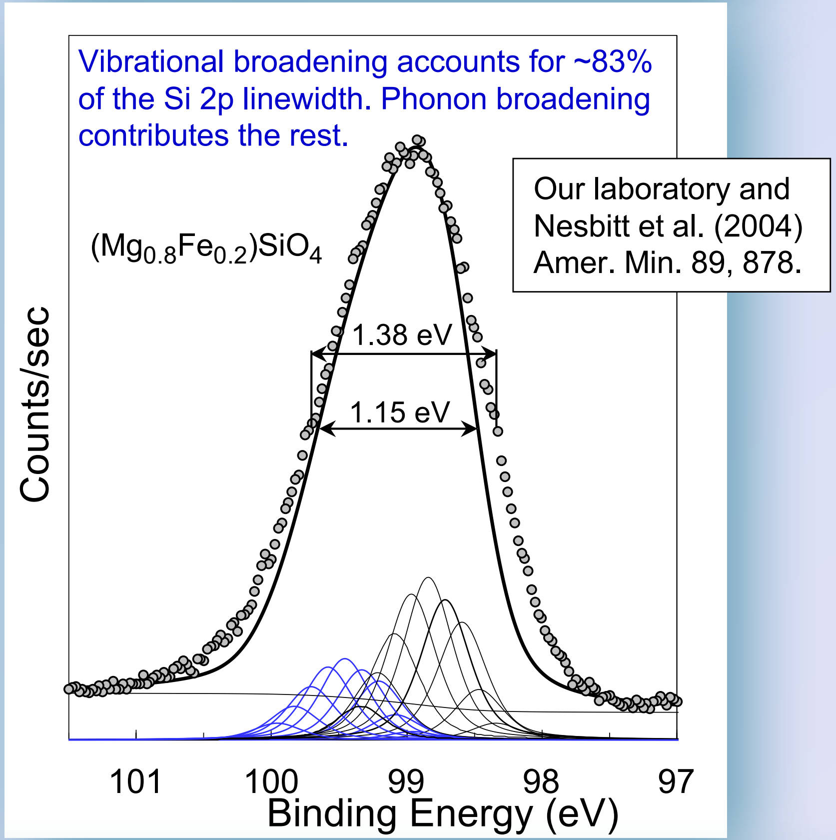
Si 2p Spectrum of Olivine

Si-O bond length = 1.63 Angstroms
Vibrational frequency = 863 cm^{-1}
Instrumental Linewidth = 0.40 eV
Vibrational Linewidth = 0.40 = Instr. width
Vibrational Splitting = 0.125 eV
Relative intensities of the peaks as for TMOS



Si 2p linewidth results solely from vibrational broadening

Sutherland et al. (1993)
Phys Rev B, 48, 14989



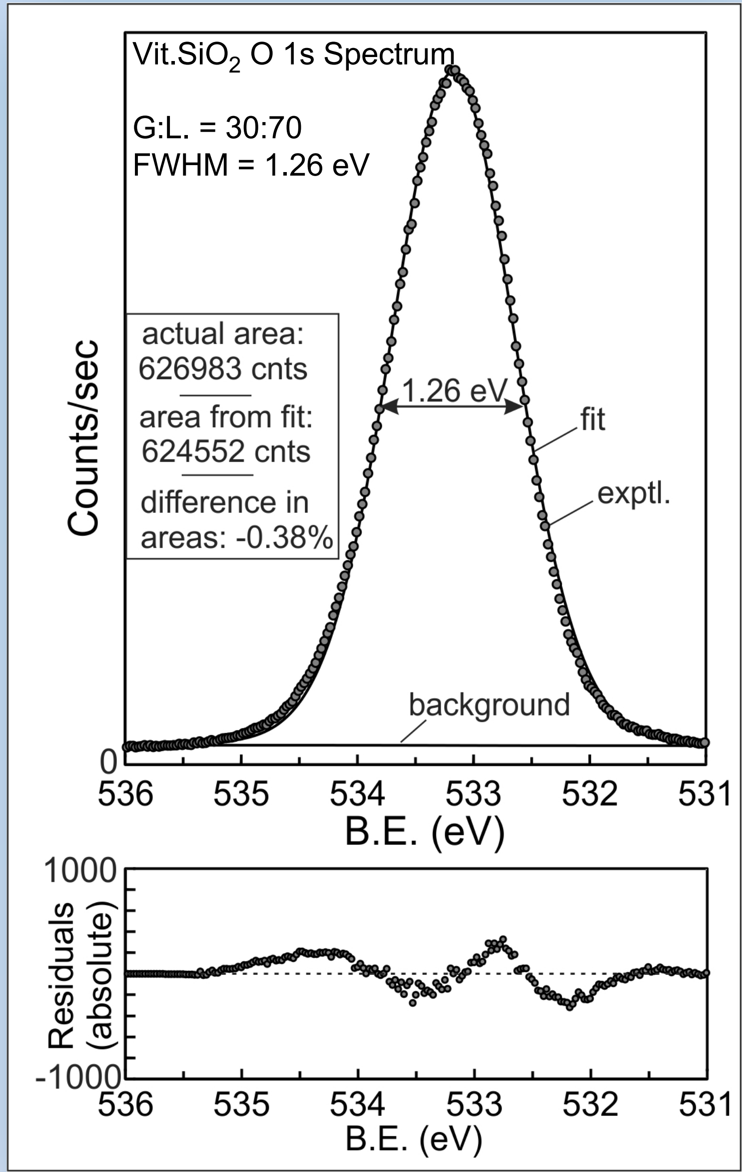
Vibrational broadening accounts for ~83% of the Si 2p linewidth. Phonon broadening contributes the rest.

Our laboratory and
Nesbitt et al. (2004)
Amer. Min. 89, 878.

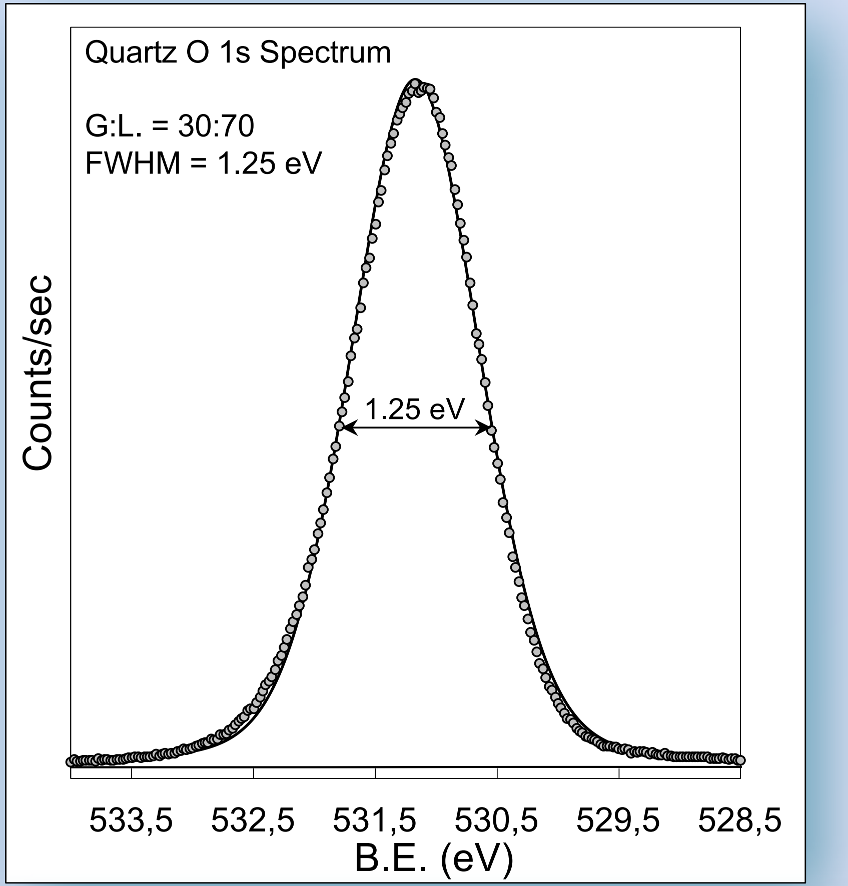
Si 2p and O 1s minimum linewidths are ~ 1.35 (± 0.1) eV and ~ 1.25 (± 0.1) eV respectively
(Bancroft et al., 2009, Phys. Rev. B v.80, 075405)

Part II, Quantification of O 1s Spectra: -- Evaluation of Peak Areas

Errors Associated with Symmetric Fits



Effect of State of Matter on Linewidths



Conclusions

1) For all silicates, O 1s linewidths ~1.25 ± 0.1 eV

2) If broader than ~ 1.35 eV, the peak likely is composite.

3) Peak shapes: ~ 30% Gaussian-70% Lorentzian

4) State of matter has little influence on linewidths.

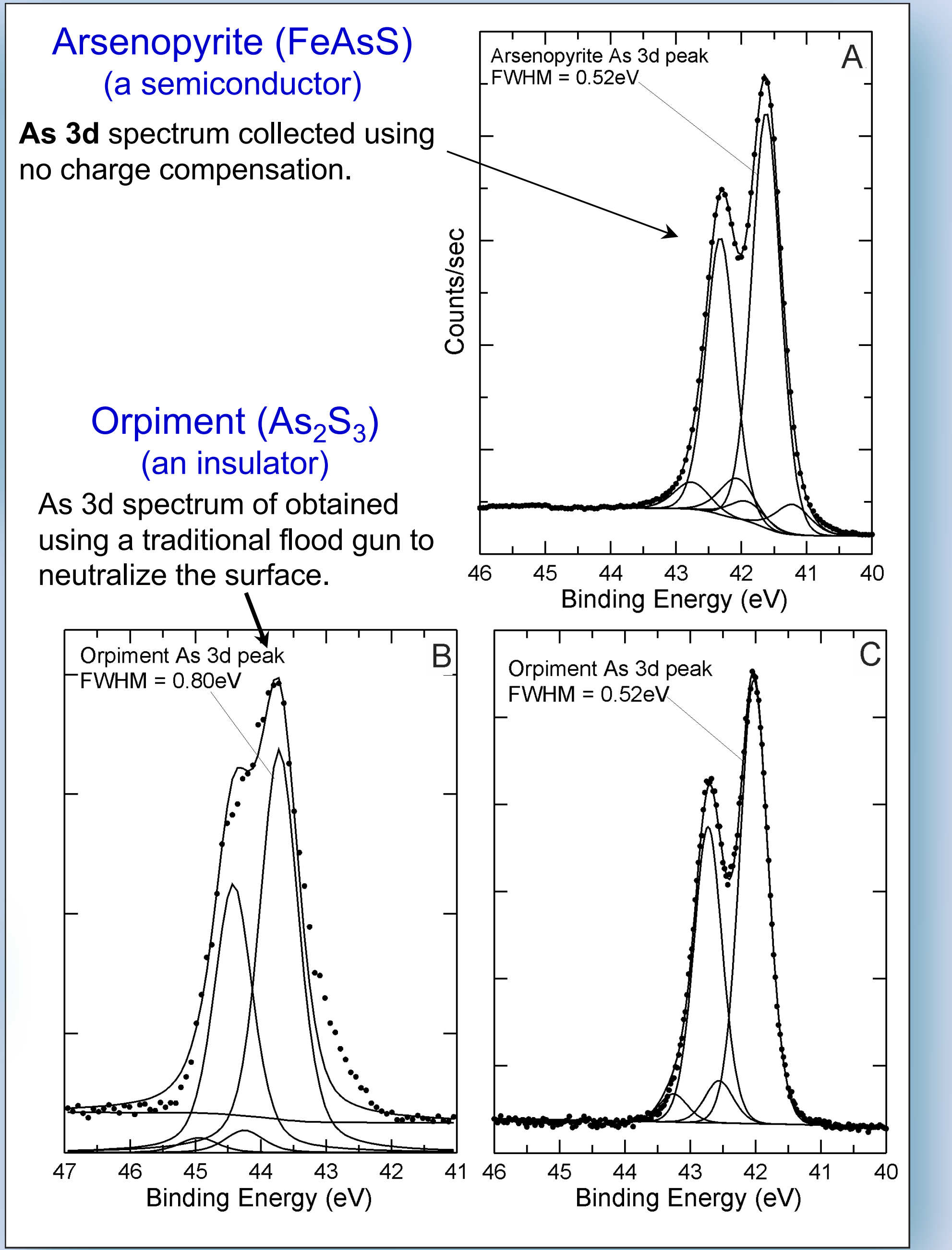
Part I, a Disadvantage: Difficult to Collect XPS Spectra of Insulators

The Problem: Prior to the mid 1990’s, XPS spectra of ***insulators*** were difficult and often impossible to collect due to charging of surfaces.

The Advance: Kratos Instruments developed an effective charge compensation system in the 1990’s. Other manufacturers now have effective charge compensation systems.

A Test: An As 3d spectra of a semiconductor (FeAsS) and an insulator (As_2S_3) were collected and the linewidths are identical for both using the Kratos charge compensation system.

From Nesbitt et al. (2004) Amer. Min. v.89, p.878.



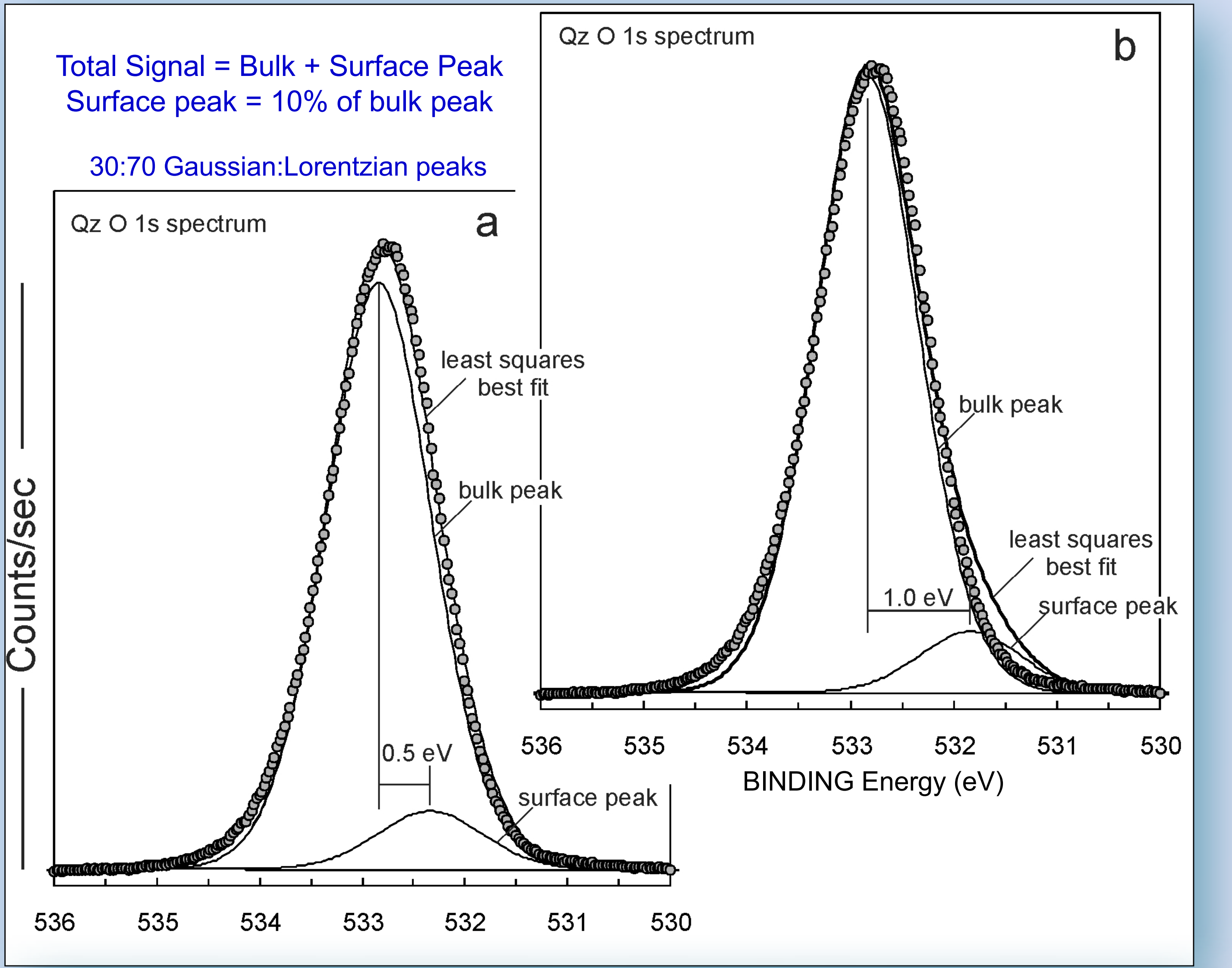
Arsenopyrite (FeAsS)
(a semiconductor)

As 3d spectrum collected using no charge compensation.

Orpiment (As_2S_3)
(an insulator)

As 3d spectrum of obtained using a traditional flood gun to neutralize the surface.

Part II, Effect of Bulk and Surface Peaks on O 1s Spectra



Total Signal = Bulk + Surface Peak
Surface peak = 10% of bulk peak

30:70 Gaussian:Lorentzian peaks

From: Nesbitt and Bancroft (2014) Reviews in Mineralogy & Geochemistry. Mineralogical Soc. America, v.78, p. 278-337.

Part II, Treatment and Quantification of O 1s Spectra: -- Uncertainties

Analytical Uncertainties

Determination of BO% in Glass

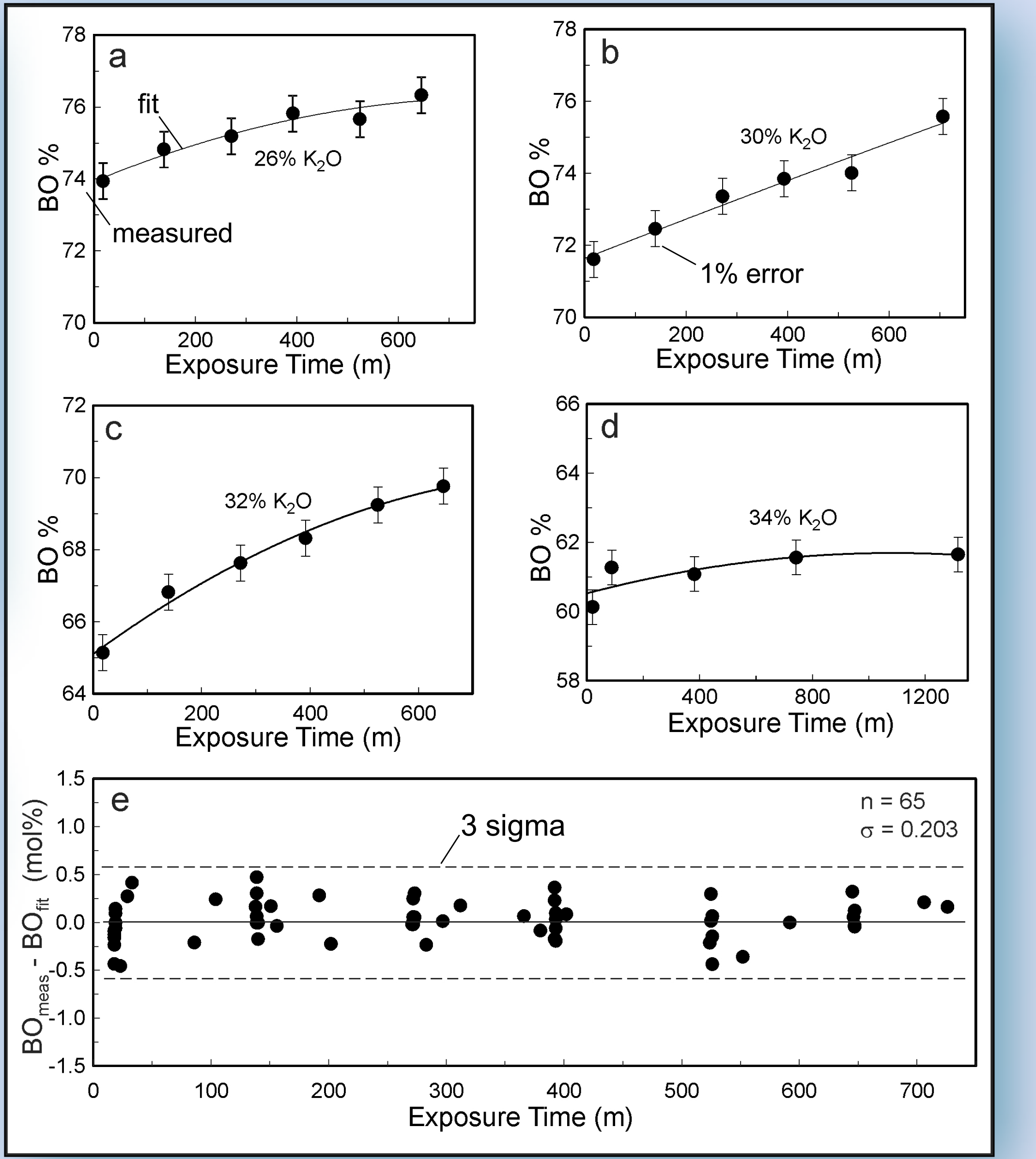
1) The X-ray beam causes damage to glasses as shown in diagrams ‘a’ to ‘d’.
2) A quadratic is fitted and the intercept is taken as the BO% prior to X-ray exposure.

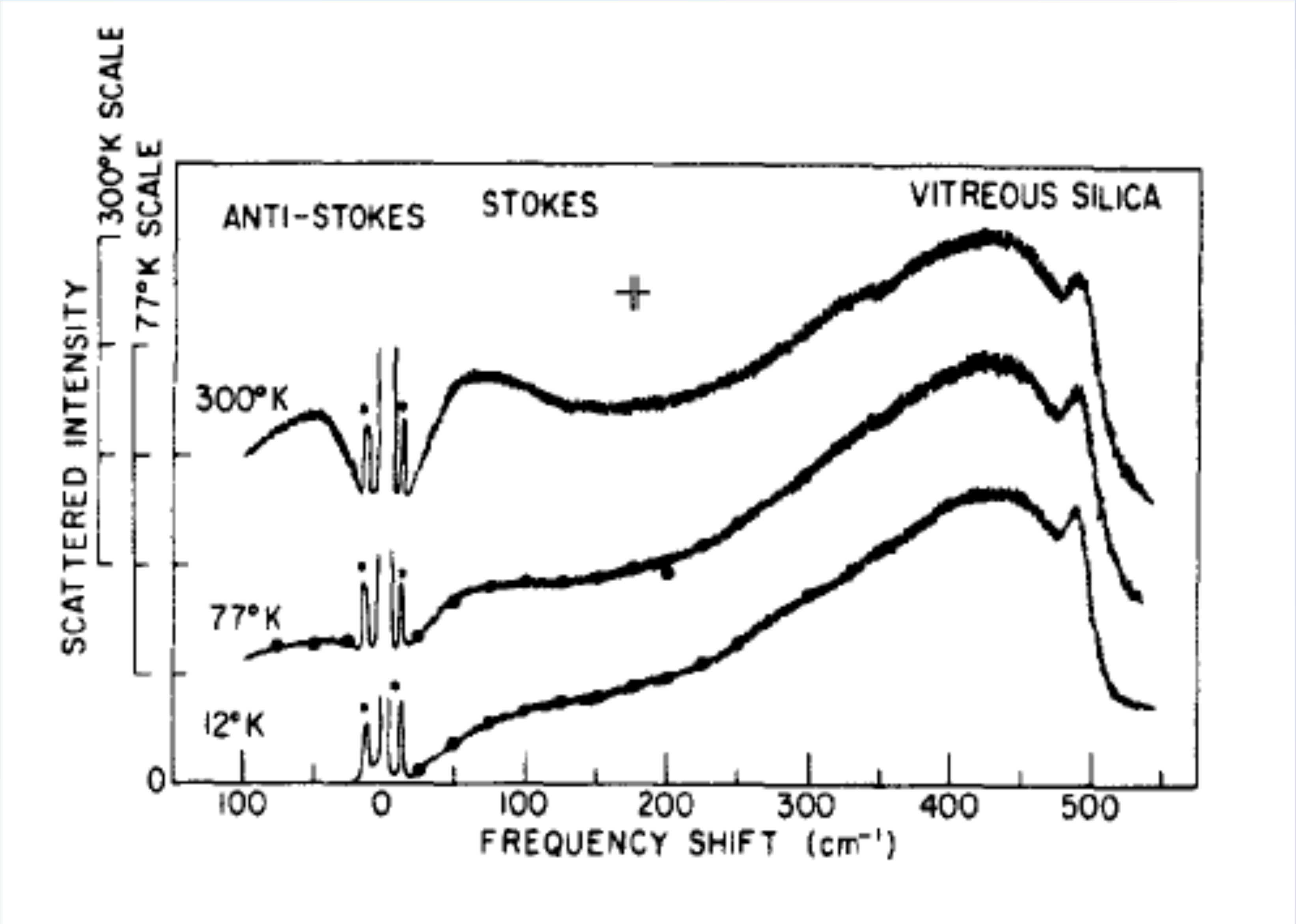
Uncertain in an Individual Analysis

1) 5 or 6 spectra are collected for each glass.
2) Each is fitted and BO% determined.
3) Deviations from the best fit are plotted on ‘e’ as a function of X-ray exposure time.
4) 3 standard deviation units plus the error associated with extrapolation indicates an uncertainty of ~1 mol% in BO.

Data from Sawyer et al. (2014), Can. Jour. Chem. v.92, p. 1-14.

Effect of the X-ray Beam on BO Abundances

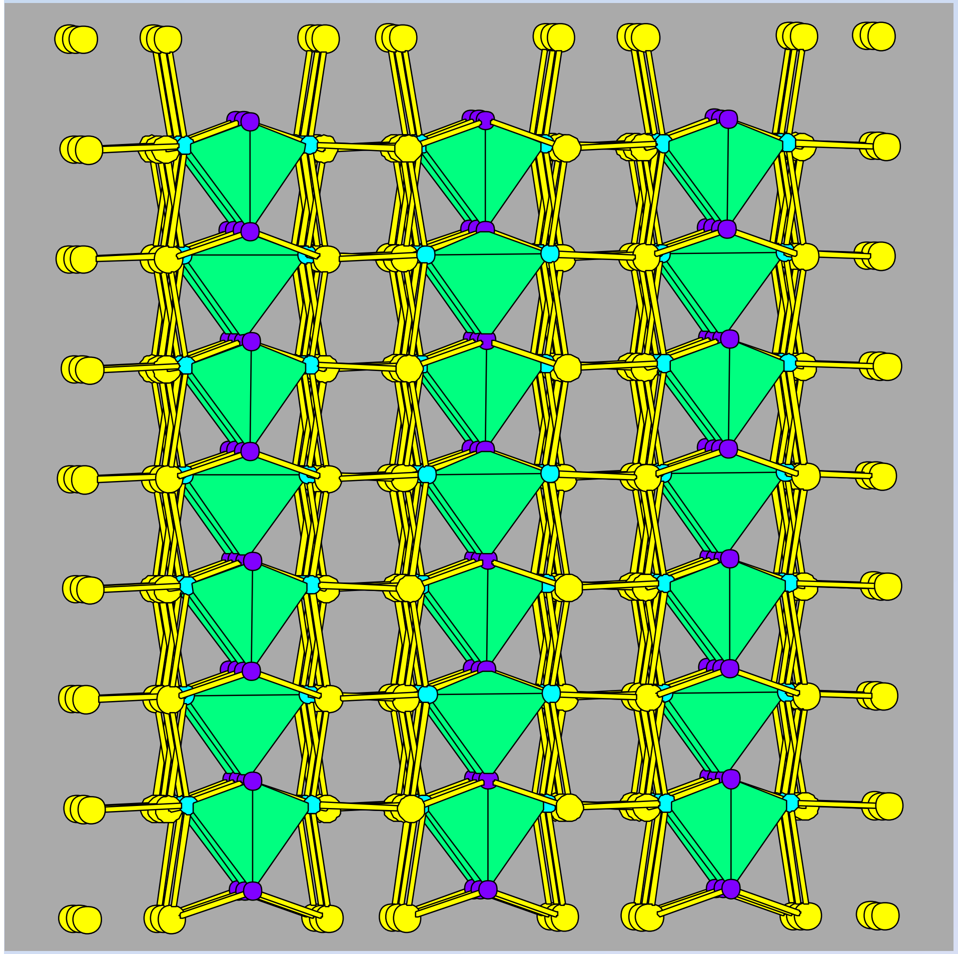




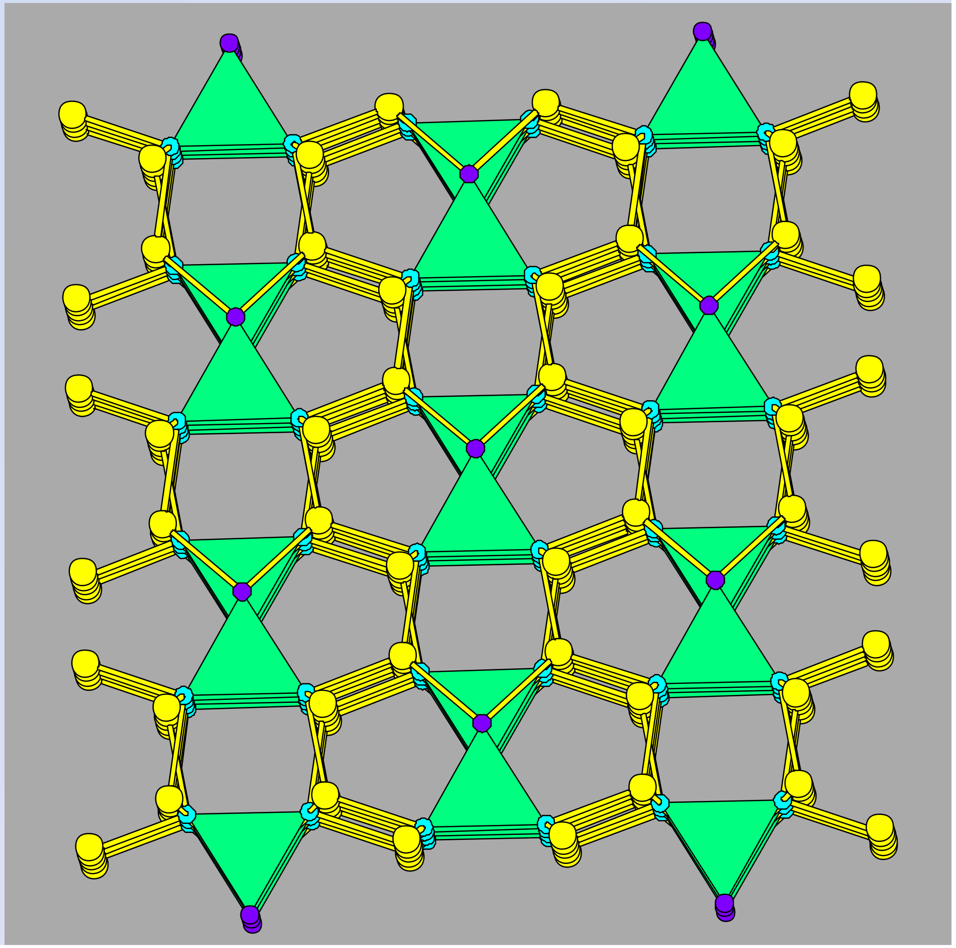
"It can be seen from Fig.1 that the Raman spectrum of vitreous silica is highly temperature dependent below 100 cm^{-1}, but is only slightly temperature dependent in the higher frequency region above 300 cm^{-1}". (Hass 1970)

Hass 1969 Solid state communications 7, 1069-1071.

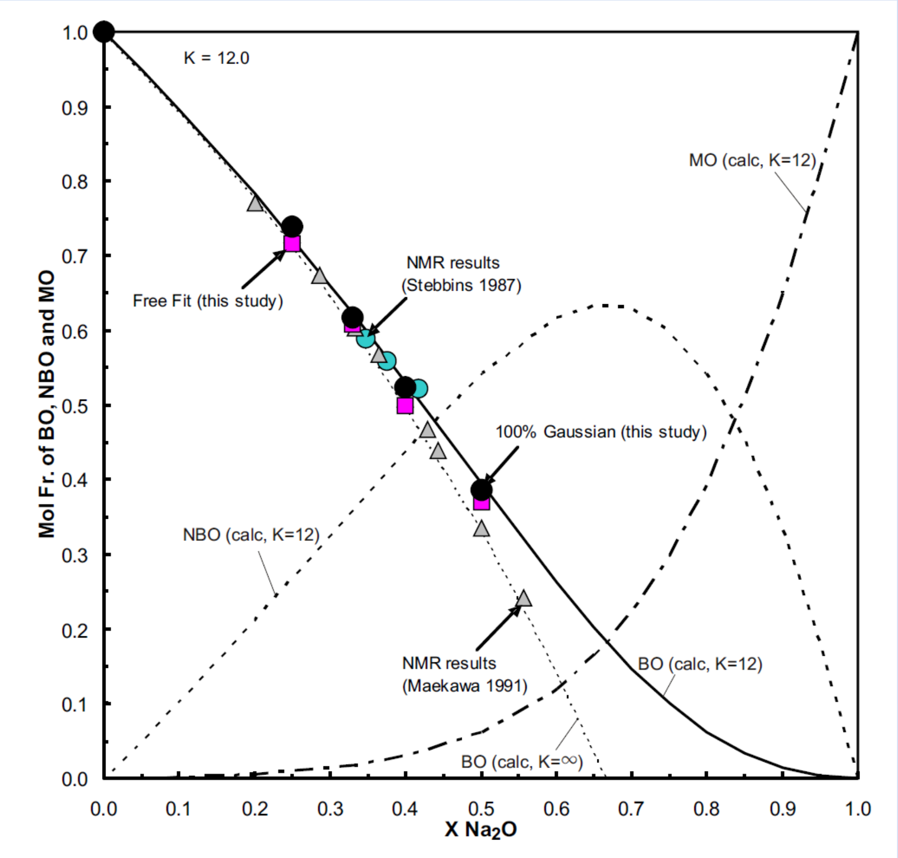
Crystalline sodium metasilicate (Na_2SiO_3) orthorhombic ($Cmc2_1$), McDonald and Cruickshank, 1967, Acta Cryst., 22, 37.

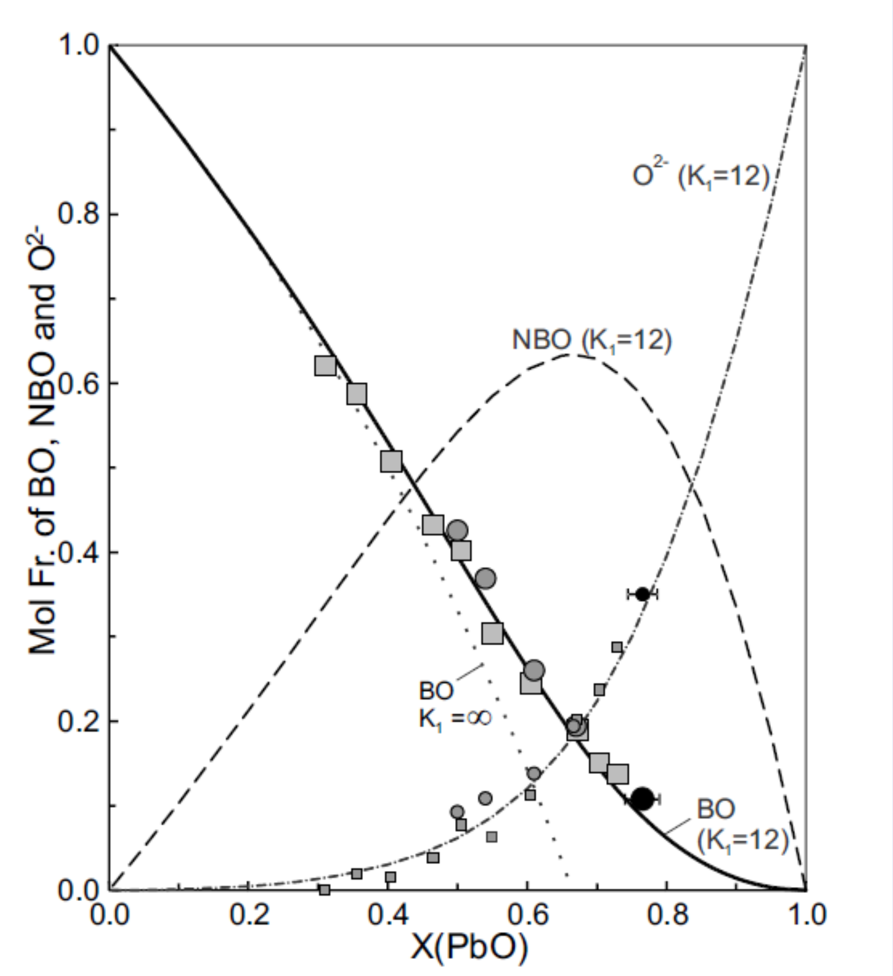


SiO_4 tetrahedra (all Q^2 tetrahedra) in chains along c-axis



Chains cross linked by Na atoms


K = 12.0
MO (calc, K=12)
Free Fit (this study)
NMR results
(Stebbins 1987)
100% Gaussian (this study)
NBO (calc, K=12)
NMR results
(Maekawa 1991)
BO (calc, K=12)
BO (calc, K=∞)
Mol Fr. of BO, NBO and MO
X Na2O
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0

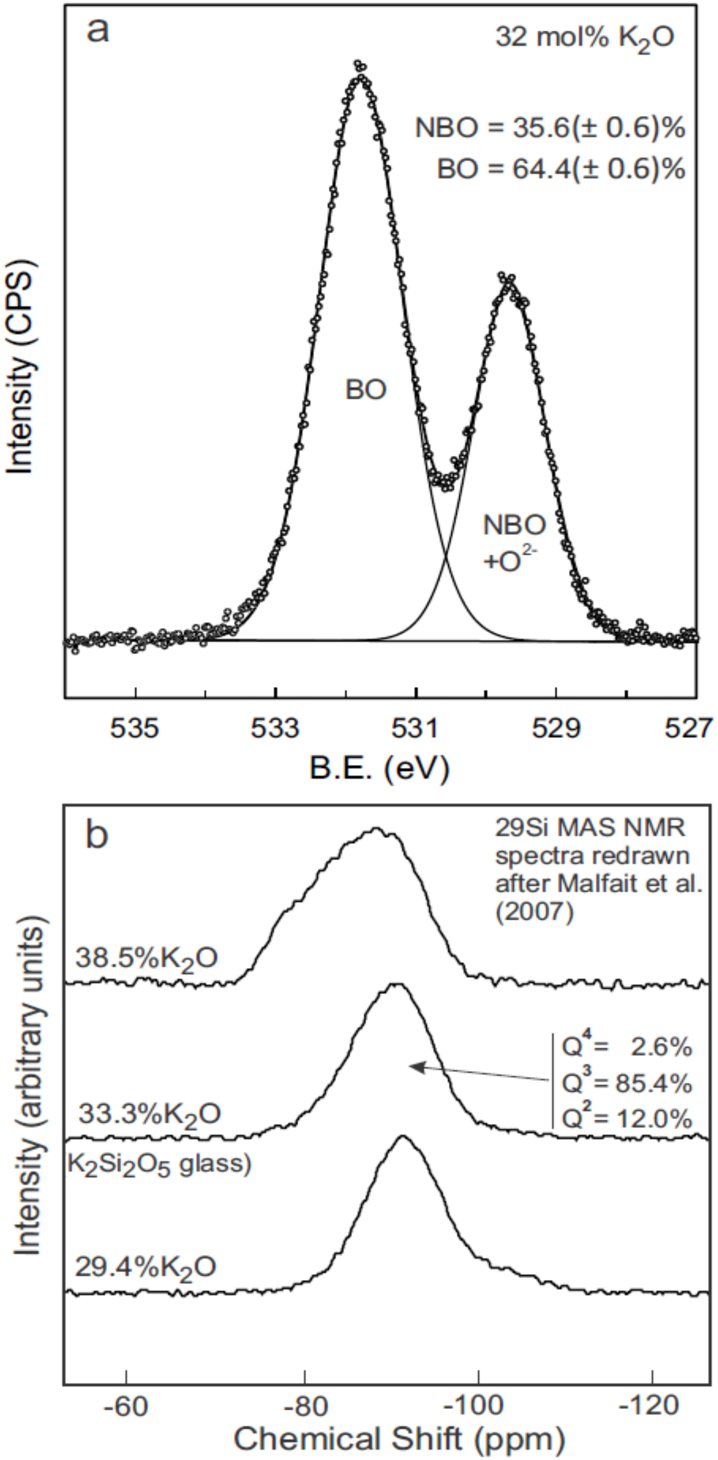

O2- (K1=12)
NBO (K1=12)
BO
K1 =∞
BO
(K1=12)
Mol Fr. of BO, NBO and O2-
X(PbO)
1.0
0.8
0.6
0.4
0.2
0.0
0.0
0.2
0.4
0.6
0.8
1.0

a) XPS spectrum of BO and NBO of K_2O-SiO_2 glass

Clear discrimination of BO and NBO peaks

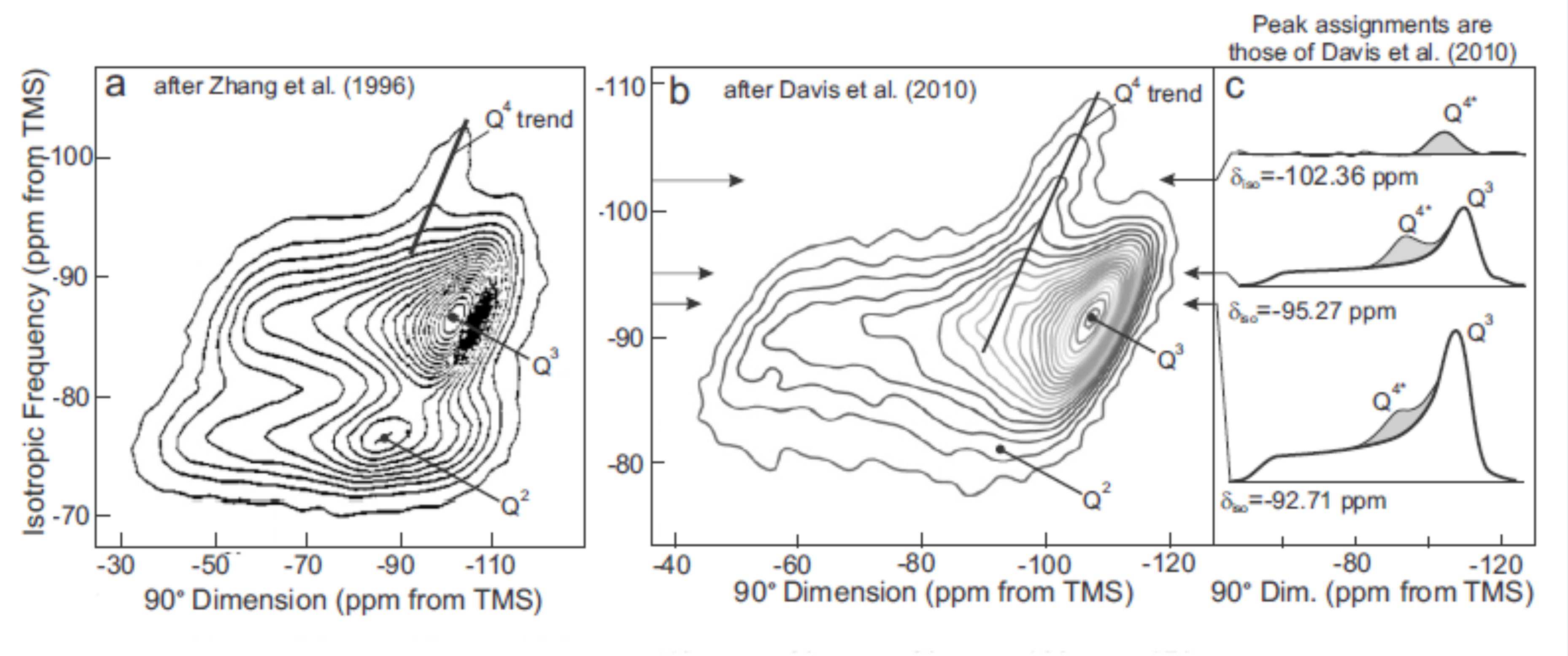
b) ^{29}Si MAS NMR spectrum of BO and NBO of K_2O-SiO_2 glass

Peaks must be curve fit to extract quantitative numbers



3Q MAS/F NMR spectroscopy

$2Q^3 \Leftrightarrow Q^2 + Q^4$ holds for Na_2O BUT NOT for K_2O glasses

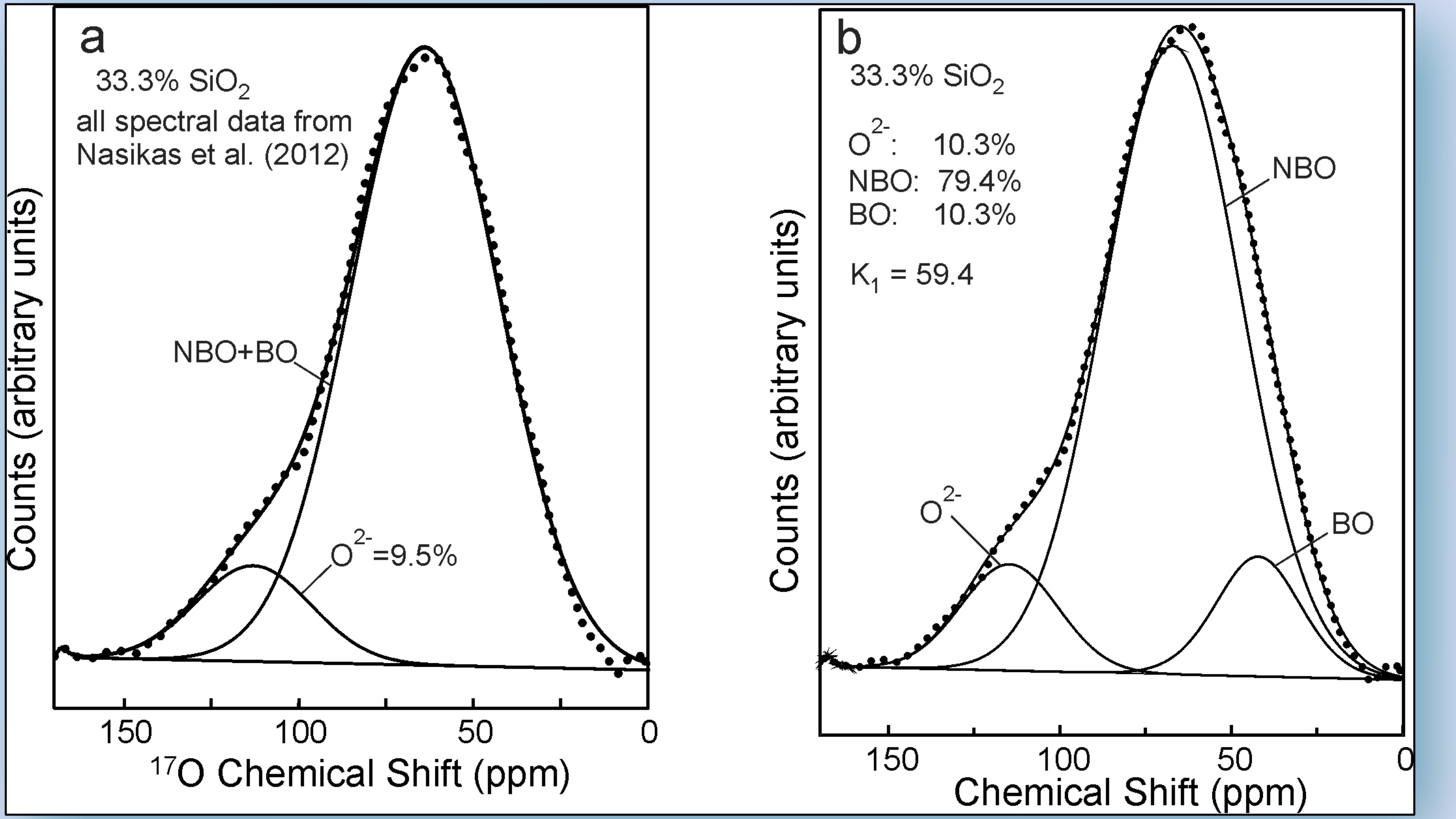


Na-silicate **K-silicate**

An Important Contribution: a ^{17}O NMR of a $CaMgSIO_4$ Glass

(first spectroscopic evidence for O^{2-} in silicate glass)

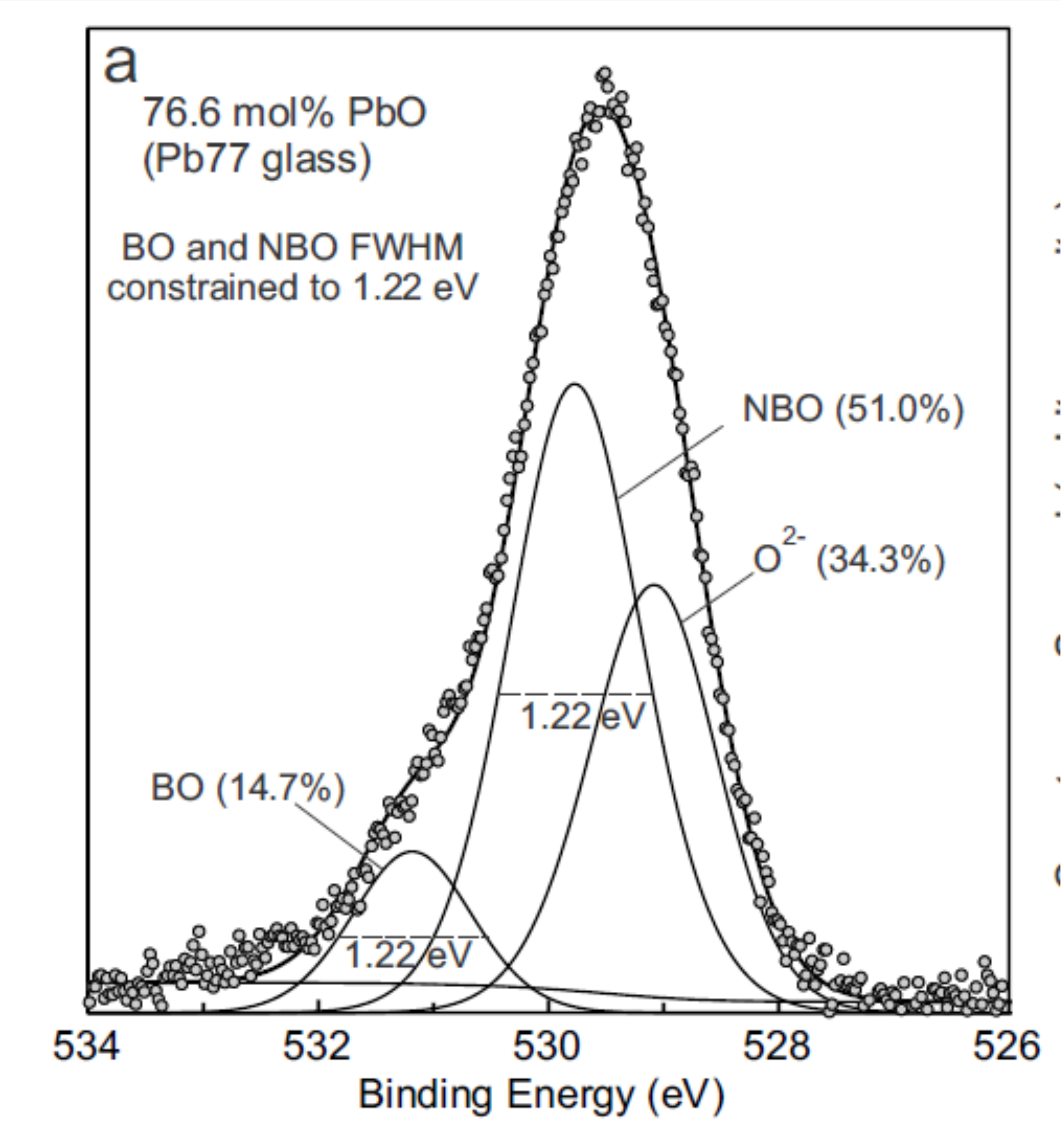
The spectrum is after Nasikas et al. (2012) but no fit was provided.



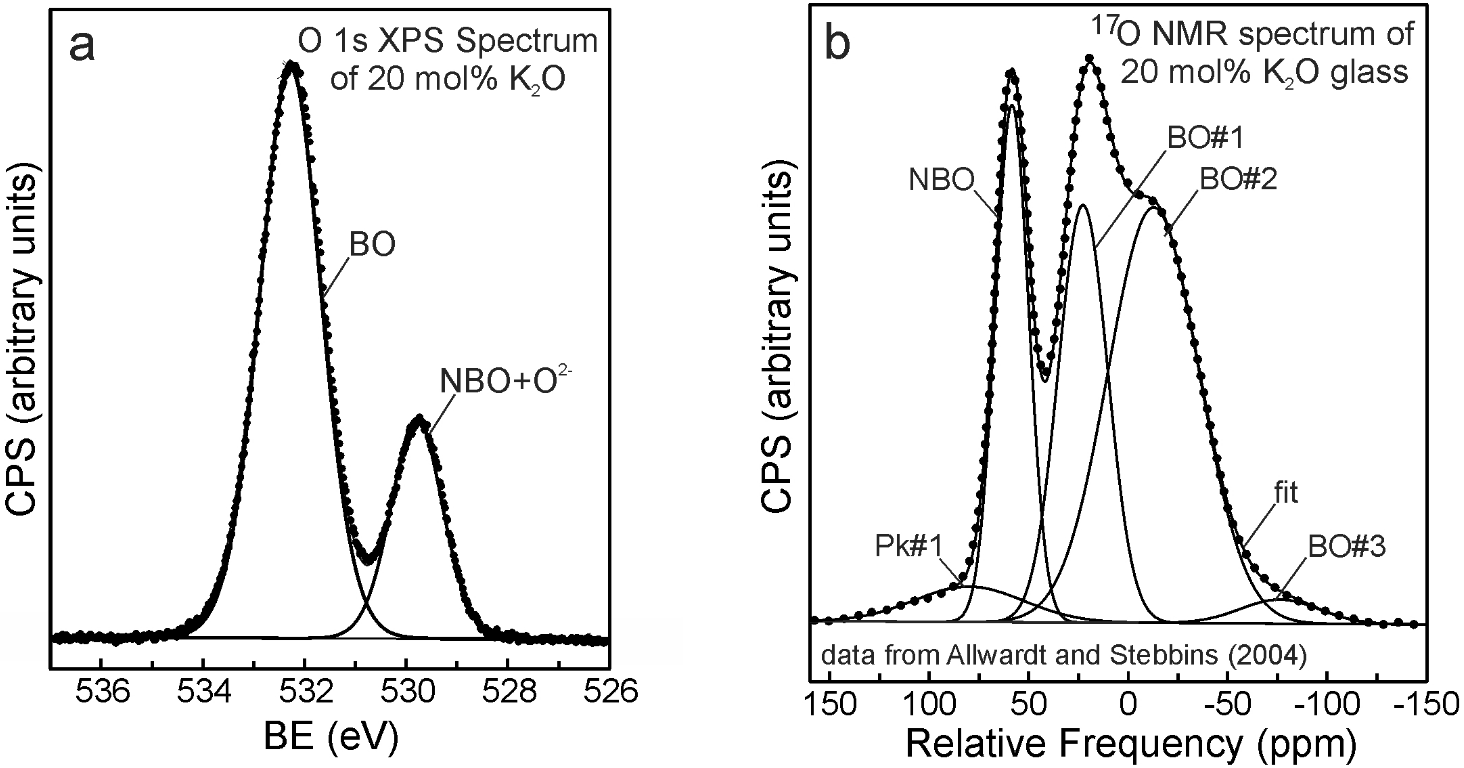
Two peaks fit: FWHM constrained to observed and theoretical values

Observe ~34% O^{2-}

Consistent with thermodynamic/mass balance arguments



Comparison of O 1s XPS and ^{17}O NMR Results



Peak Areas

NBO+O^{2-} = 21.5 ± 1mol%

BO = 78.5 ± 1mol%

At 20 mol% K_2O, O^{2-} is less than 1 mol%
(data from Sawyer et al., 2014 and
Nesbitt et al. in prep.)

Peak Areas

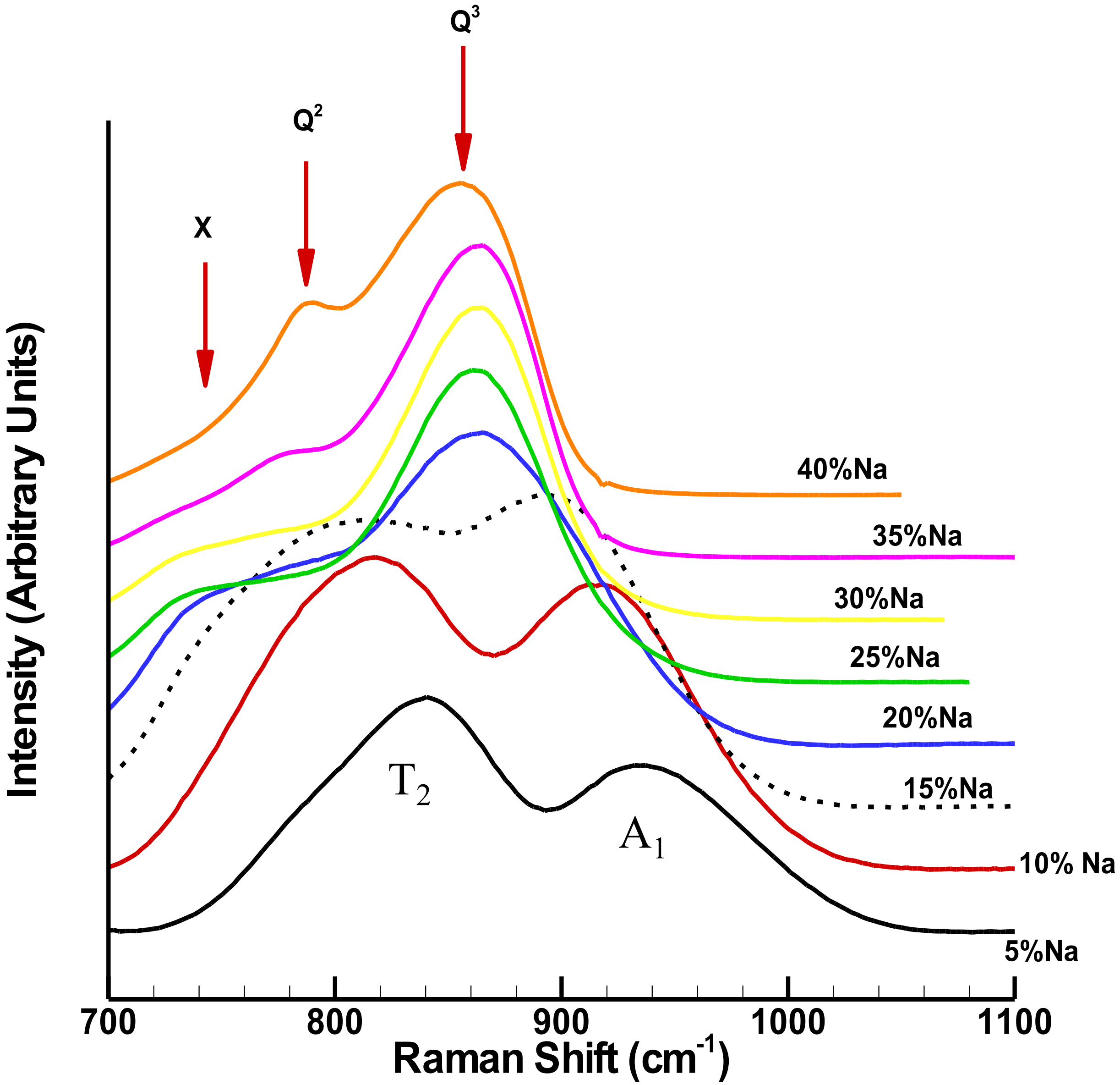
NBO = 21.3%

BOtot = 78.7%

where
Pk#1 = 4.7%
BO#1 = 25.4%
BO#2 = 46.3%
BO#3 = 2.3%

Na_2O

- $T_2 > A_1$ below anomaly maximum
- A_1 FWHM > T_2
- Shoulder at 788 cm^{-1} (Q^2)
- $Q^2 > Q^3$ up to anomaly maximum
- $Q^3 > Q^2$ after anomaly maximum
- X observed at 10 mol%
- Maximum X at 20 mol%



What is the importance of “free” oxygen (O^{2-})?

For over 100 years no mechanism to explain melting of silicate minerals

Proposed mechanism involving “free” oxygen (O^{2-})

1) **Breaking of weak M-O bonds prior to melting, to produce itinerant M^+ and $Si\text{-}O^-$ moieties attached to chains**
2) **Reaction of $Si\text{-}O^-$ to form cross-chain linkages which produces free oxygen (O^{2-})**
3) **Reaction of O^{2-} with SiO_3 chains to depolymerize (rupture) them causing melting.**
4) **O^{2-} plays essential and critical role in melting and crystallization of silicate minerals!**