Structural role of elements in glasses and melts :

Link between structure and properties

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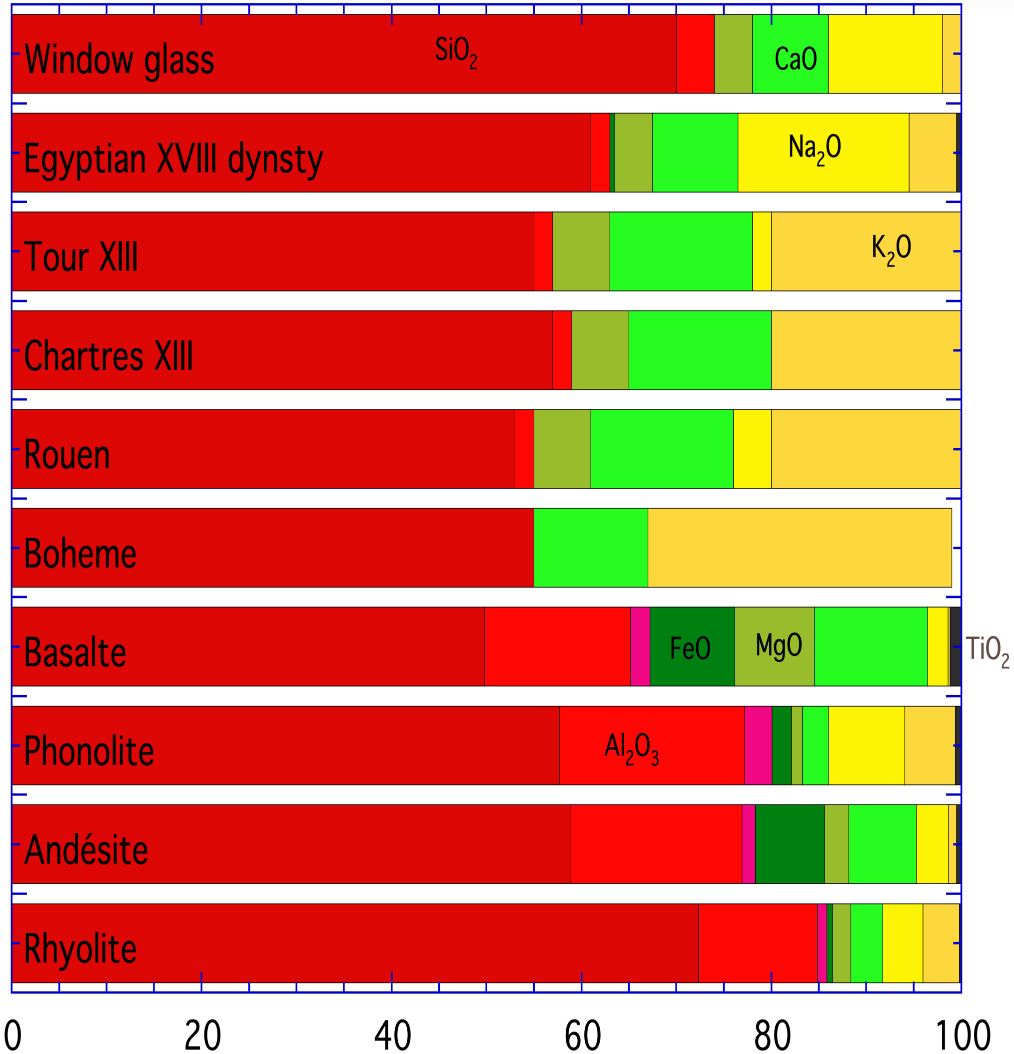
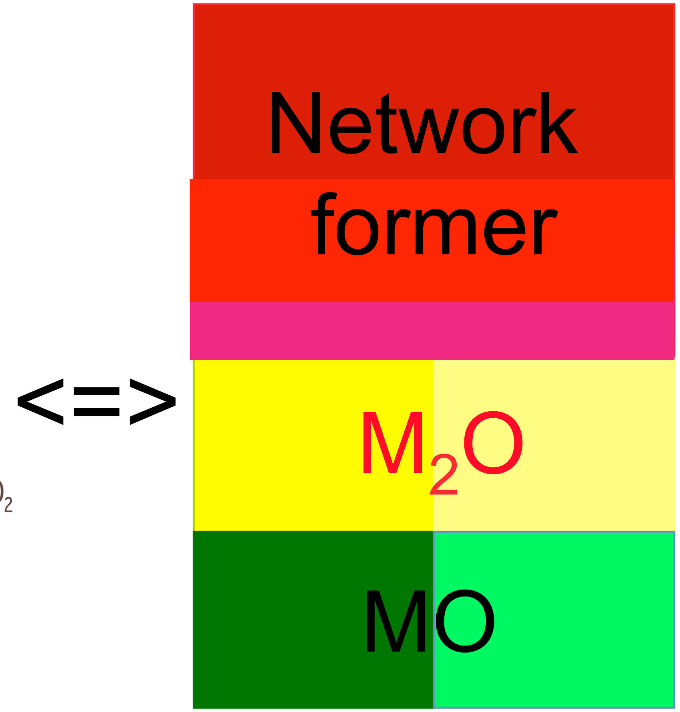
TO_2-MO-M'_2O, with T= Si, Al, Fe^{3+}, M=Mg, Ca, Fe^{2+}, M'=Li, Na, K





Properties versus Structure ?

TO_2-MO-M'_2O, avec T= Si, Al, Fe^{3+}, M=Mg, Ca, Fe^{2+}, M'=Li, Na, K

Glasses, melts = network former + alkali or earth-alkaline elements + transition elements

What is a network modifier or charge compensator ?

Why alkaline or earth-alkaline element changes role?

What happens in the case of transition elements?

What happens during nucleation processes?

TO_2-MO-M'_2O, avec T= Si, Al, Fe^{3+}, M=Mg, Ca, Fe^{2+}, M'=Li, Na, K

How network former can be mixed?

What is the redox effect on glass forming?

How made an invert glasses?

How elaboration processes can influence glass forming ability?

Fragility and ability of glass forming?

Role of element can change as a function of their content?

TO_2-MO-M'_2O, avec T= Si, Al, Fe^{3+}, M=Mg, Ca, Fe^{2+}, M'=Li, Na, K

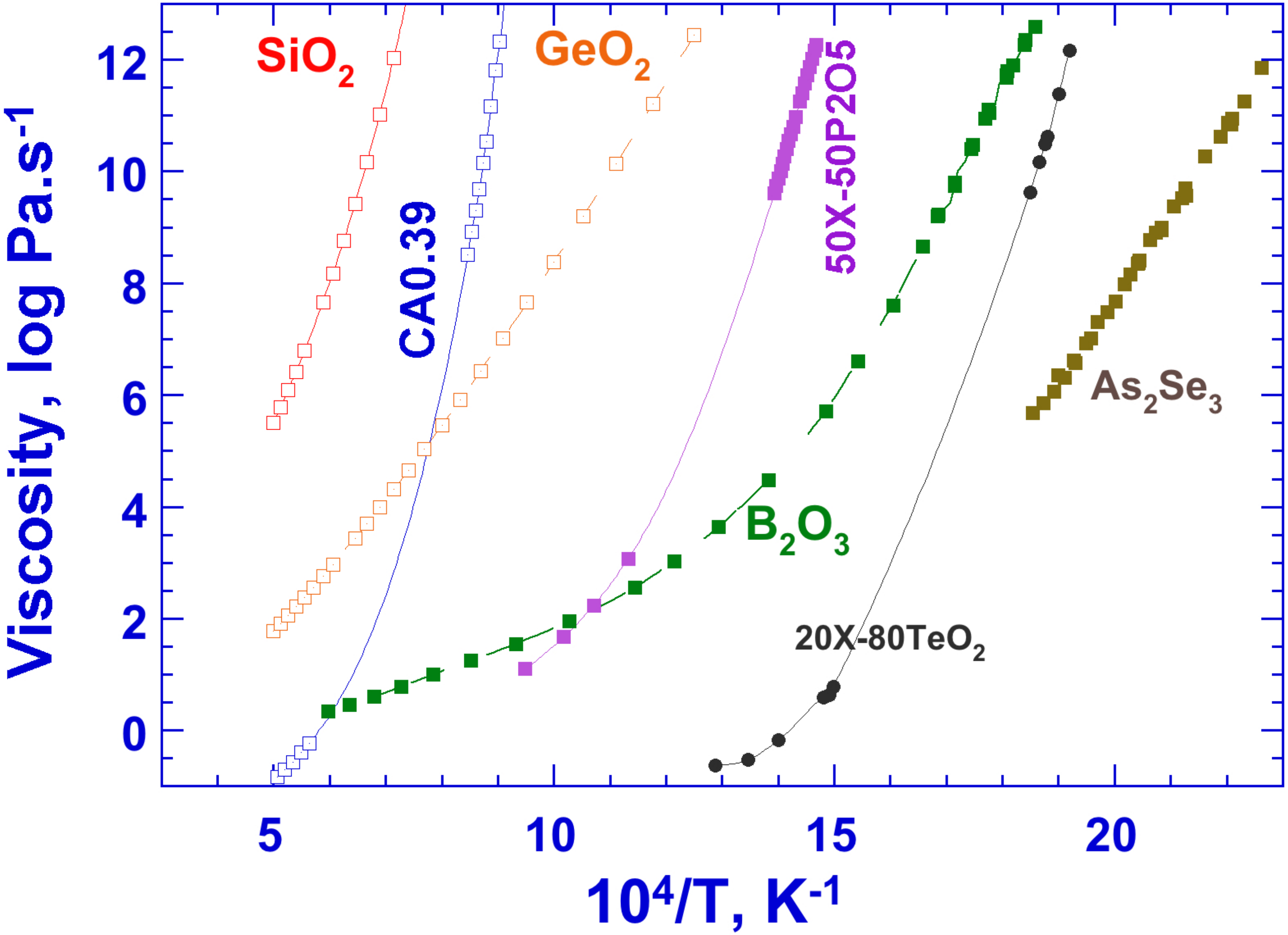
Is there and universal definition of glass former?

Does the definition of glass formers depends on the type of glass systems?

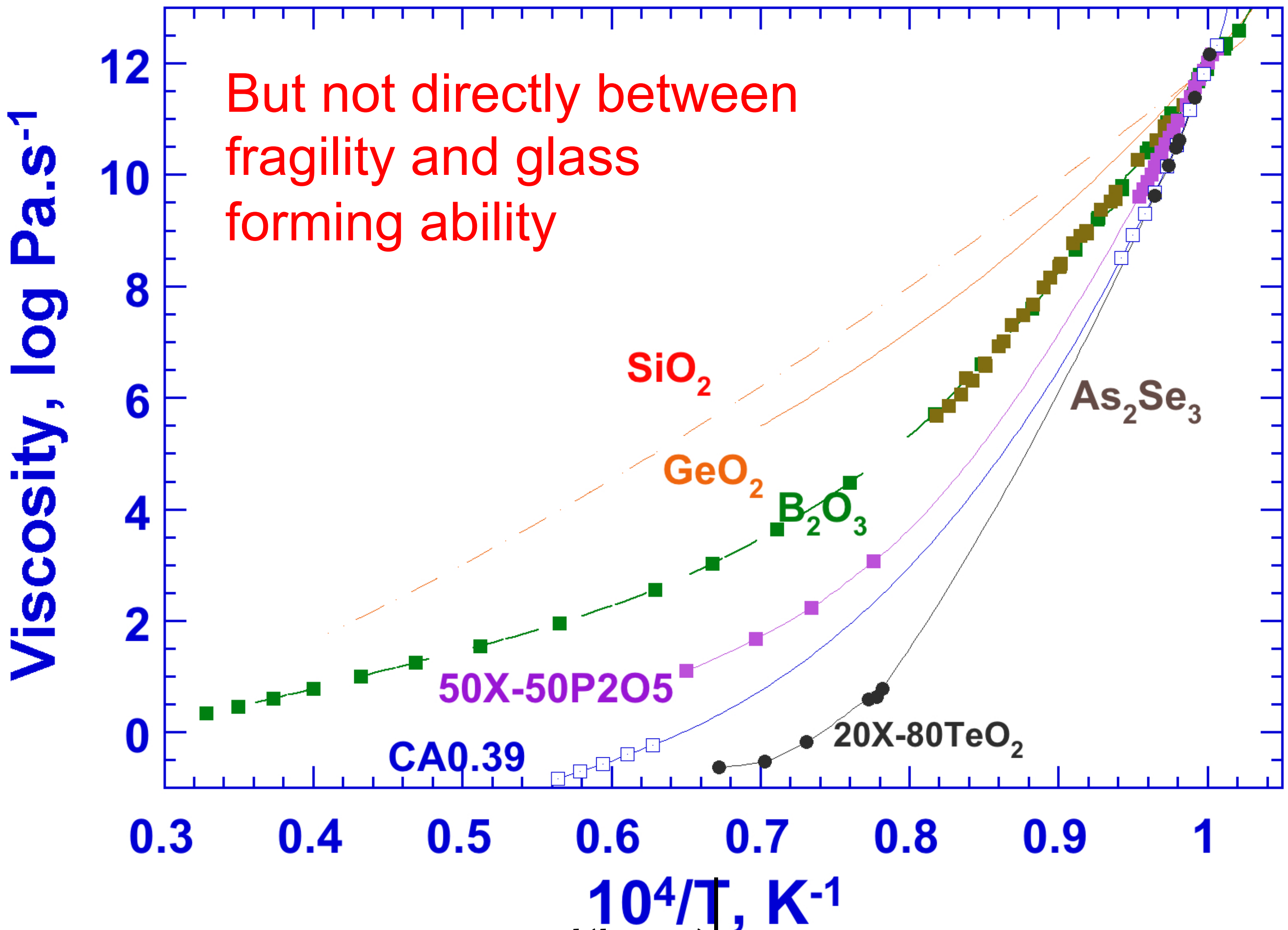
Does the definition of glass formers evaluate with new analytical tools?

Does modelisation enable to get a different view of glass forming effect?

Viscosity versus chemical composition



Fragility versus chemical composition



Fragility can be express : $m = \left.\frac{d(log_{10}\eta)}{d(\frac{T_g}{T})}\right|_{T=T_g}$ And also by Cpl/Cpg(Tg)

Network former…

SiO_2

GeO_2

B_2O_3

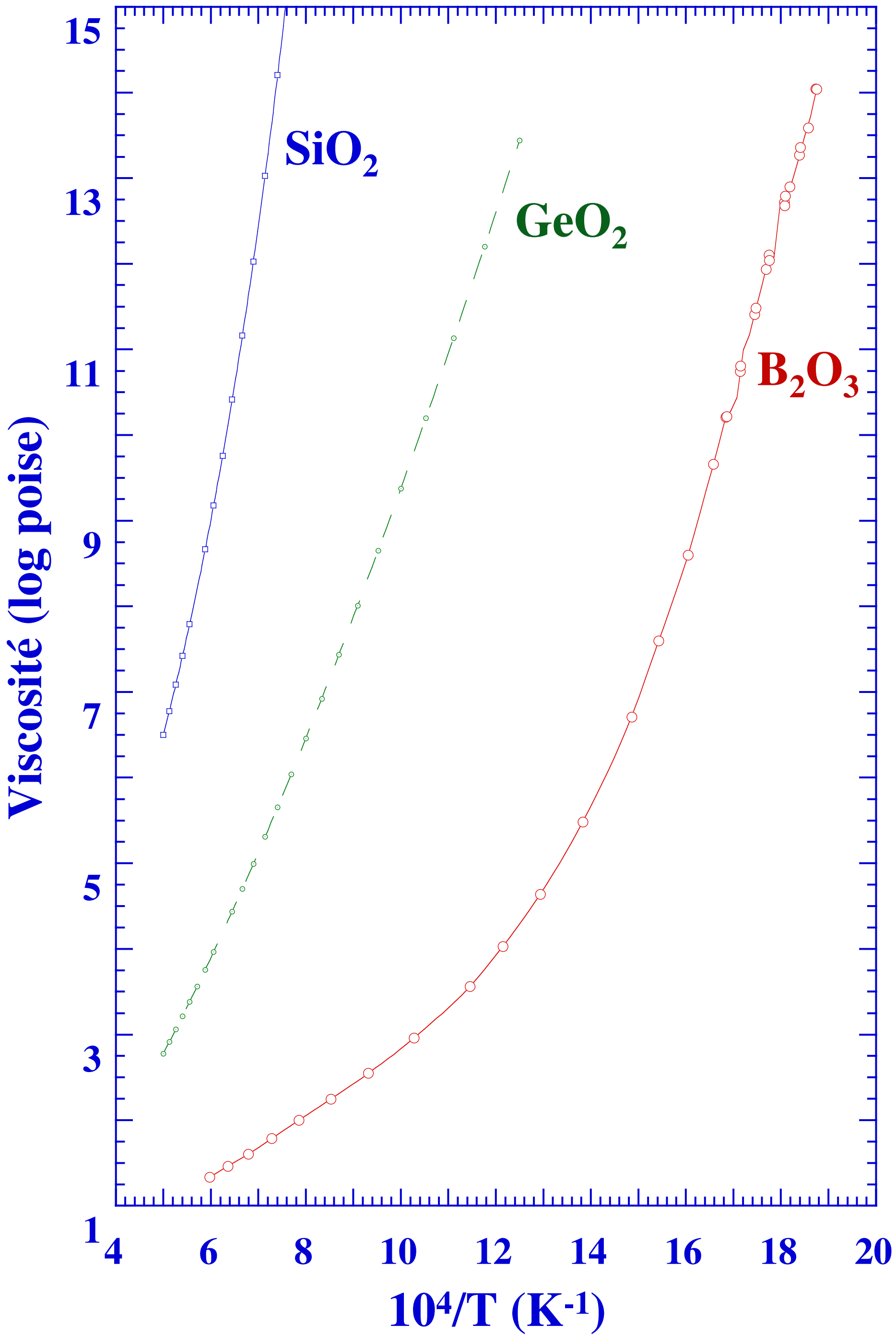
As_2Se_3

TeO_2

Al_2O_3

Fe_2O_3….

Formateurs de réseau



SiO_2 liaison covalente

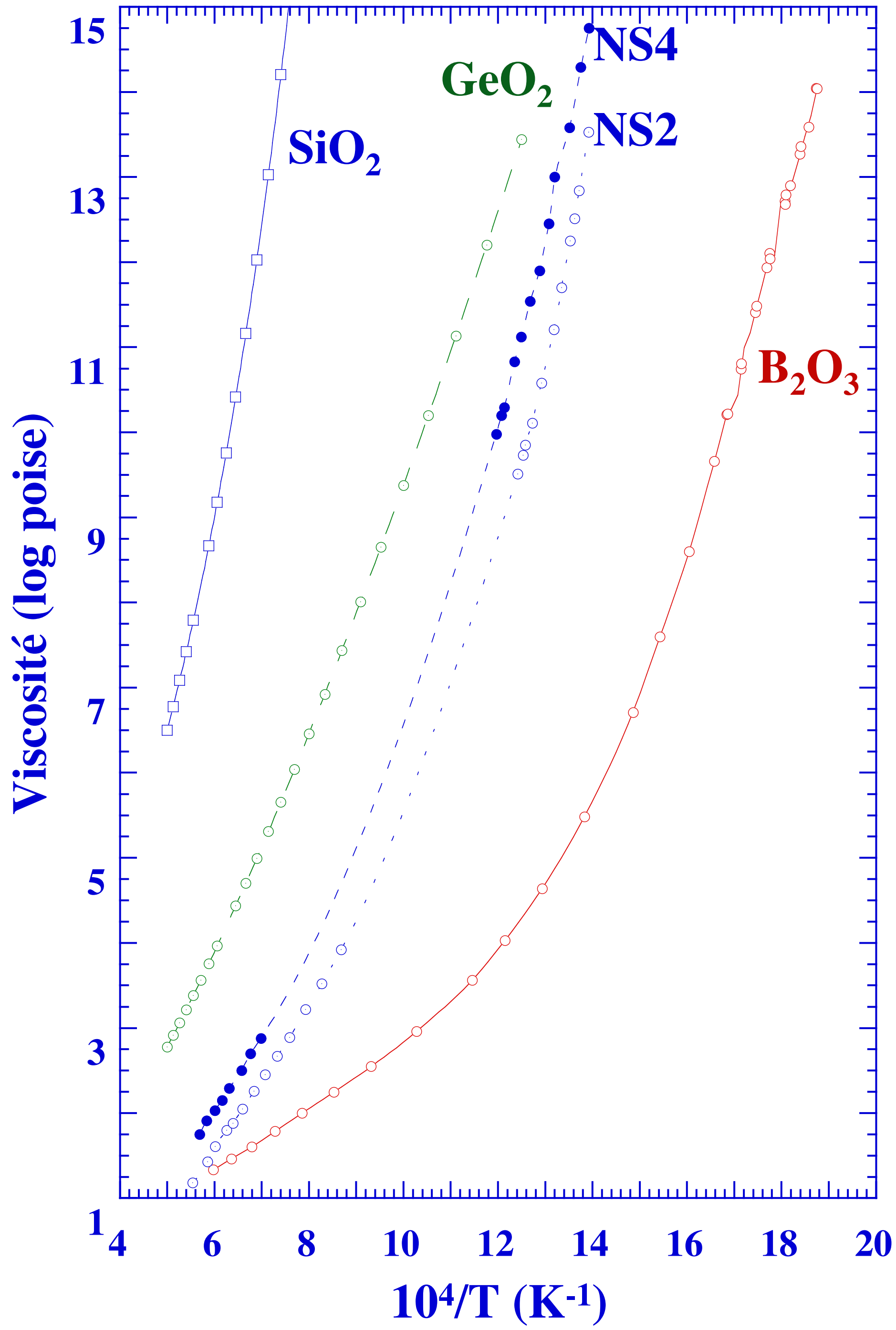
tétraèdre SiO_4

GeO_2 liaison covalente

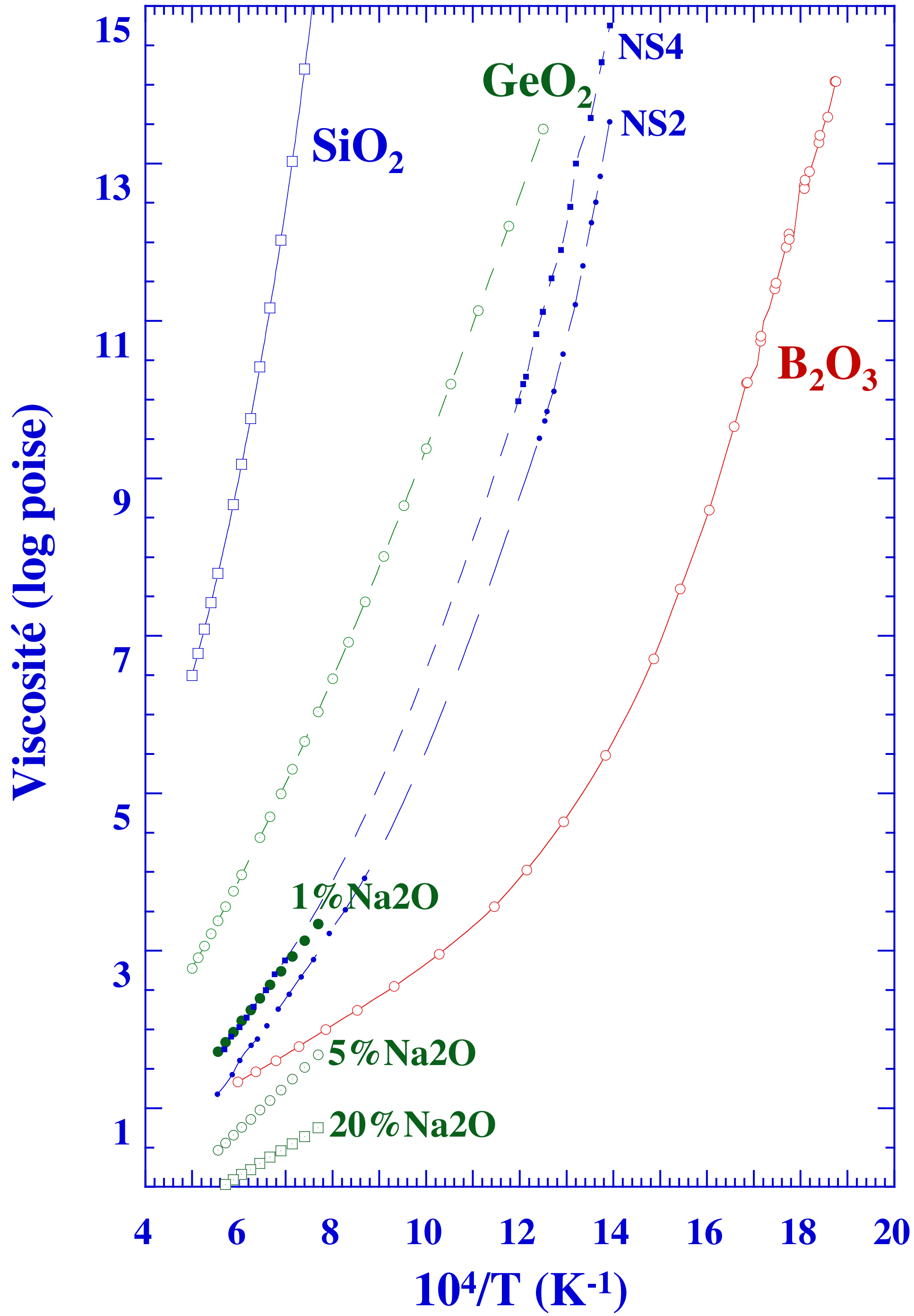
tétraèdre GeO_4

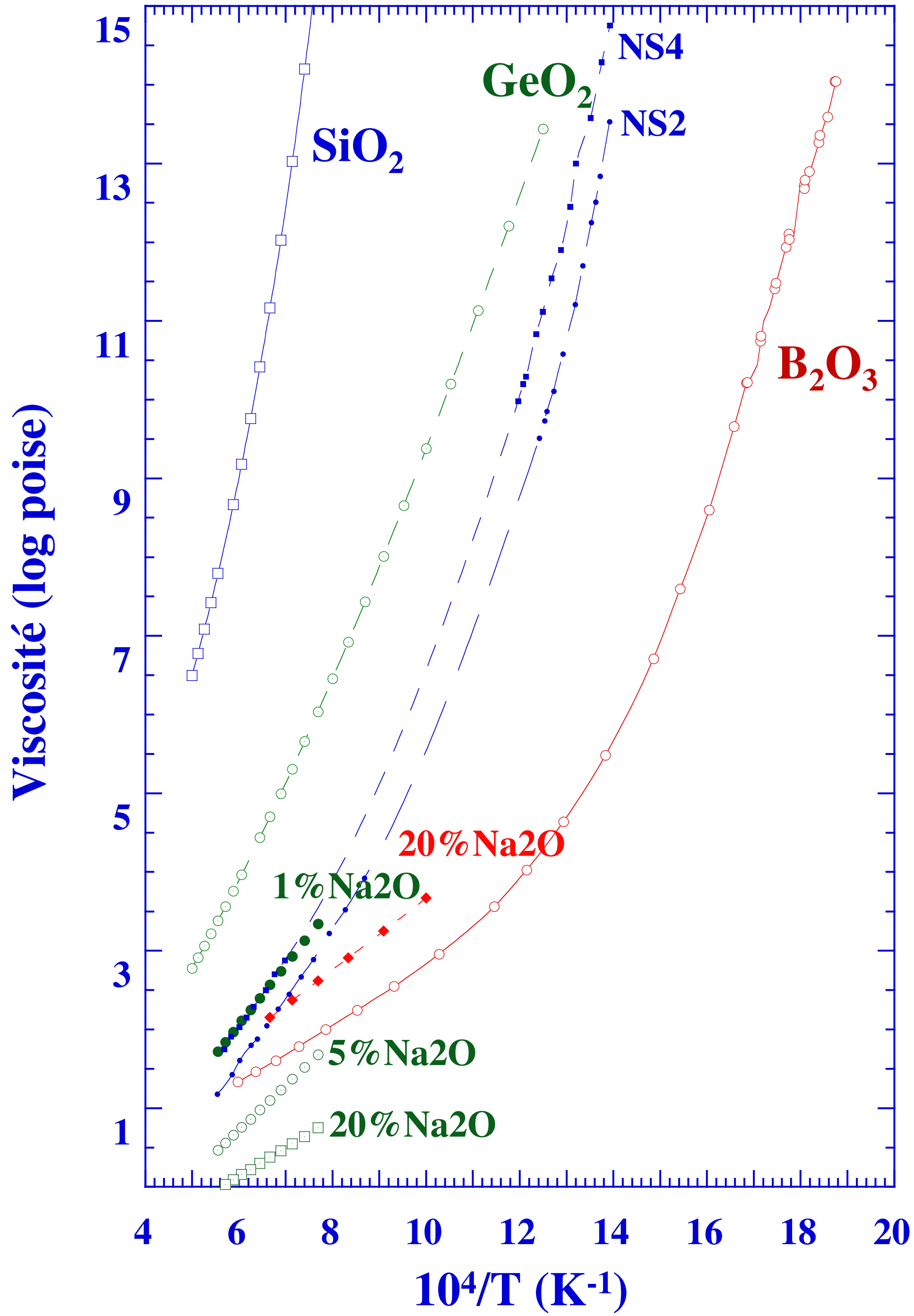
B_2O_3 liaison covalente

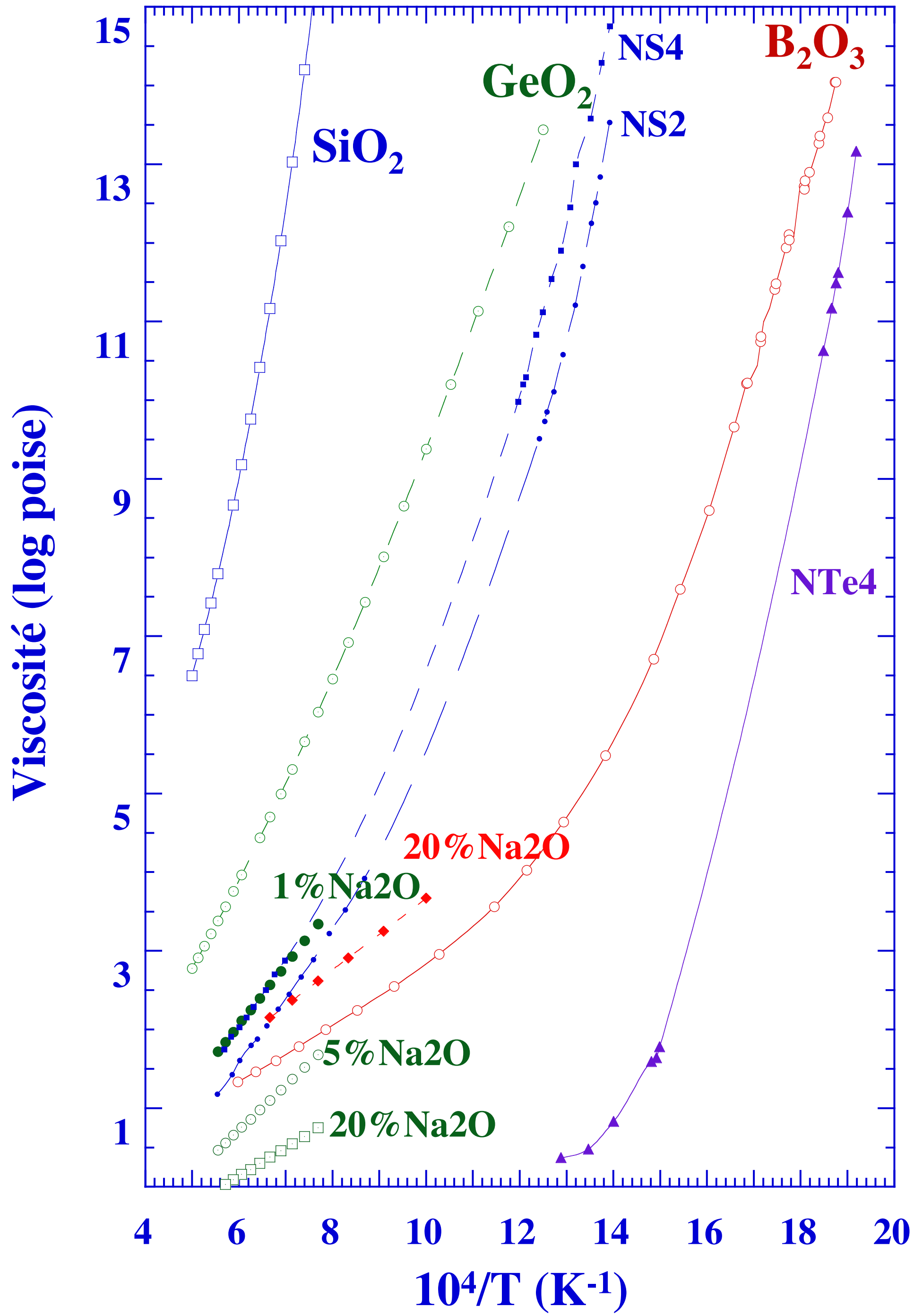
Triangle BO3 et
tétraédre BO4



SiO2
GeO2
NS4
NS2
B2O3
Viscosité (log poise)
10⁴/T (K⁻¹)
1
3
5
7
9
11
13
15
4
6
8
10
12
14
16
18
20


Viscosité (log poise)
10⁴/T (K⁻¹)
SiO2
GeO2
NS4
NS2
B2O3
1%Na2O
5%Na2O
20%Na2O
15
13
11
9
7
5
3
1
4
6
8
10
12
14
16
18
20


Viscosité (log poise)
10⁴/T (K⁻¹)
SiO2
GeO2
NS4
NS2
B2O3
20%Na2O
1%Na2O
5%Na2O
20%Na2O
15
13
11
9
7
5
3
1
4
6
8
10
12
14
16
18
20


Viscosité (log poise)
10⁴/T (K⁻¹)
SiO2
GeO2
NS4
NS2
B2O3
NTe4
20%Na2O
1%Na2O
5%Na2O
20%Na2O
15
13
11
9
7
5
3
1
4
6
8
10
12
14
16
18
20

Network former

SiO_2 : SiO_4 tetrahedra, increase connectivity, viscosity and Tg, = strong liquid

Alkalin broke network, viscosity decreases, Tg…..

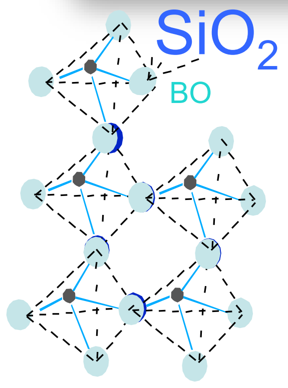
GeO_2 : GeO_4 tetrahedra, increase connectivity, viscosity and Tg, = strong liquid

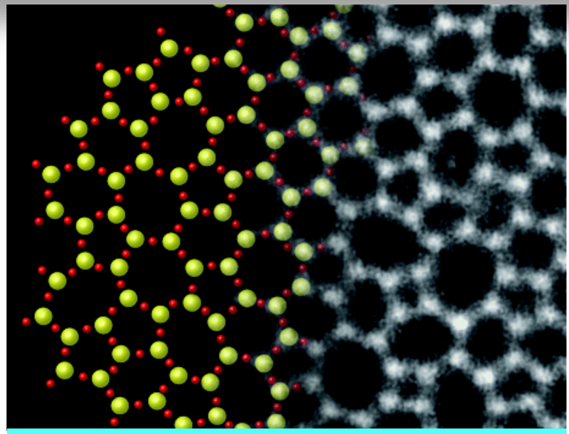
Alkalin broke network, viscosity decreases, Tg…..

B_2O_3 : BO3 triangle, 2D connectivity, low viscosity, Tg… fragile liquid

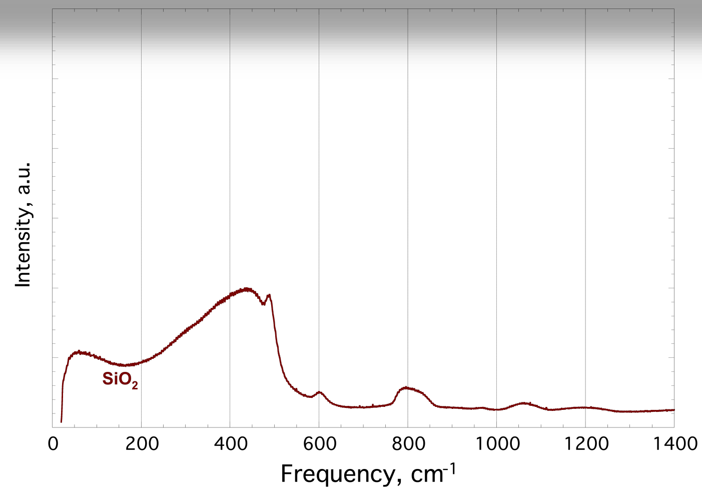
With M_2O BO3 =>BO4

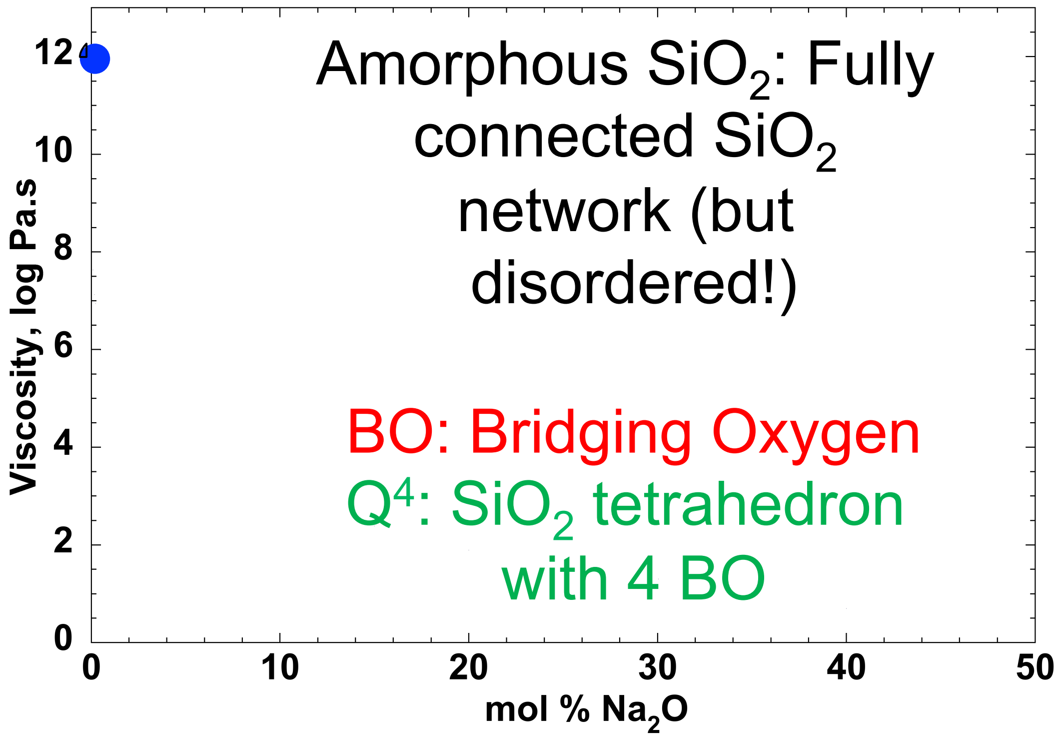
Structure versus properties of silicate melts





Huang et al. (2012): HRTEM picture of thin film of amorphous SiO_2

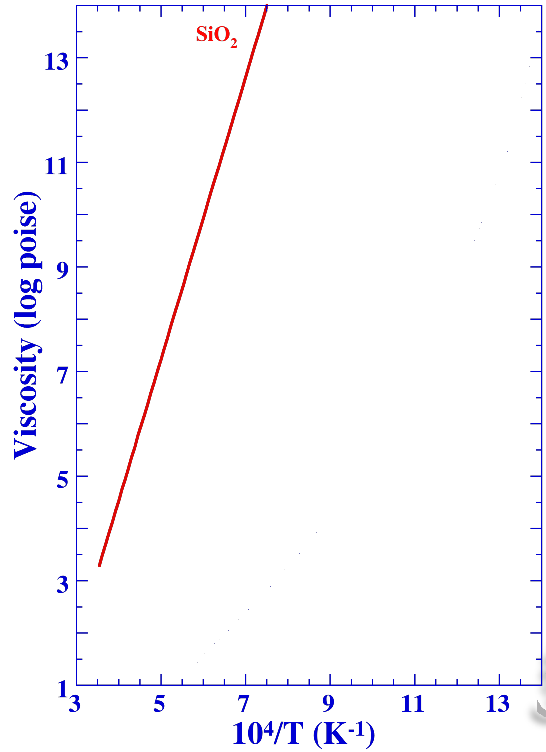




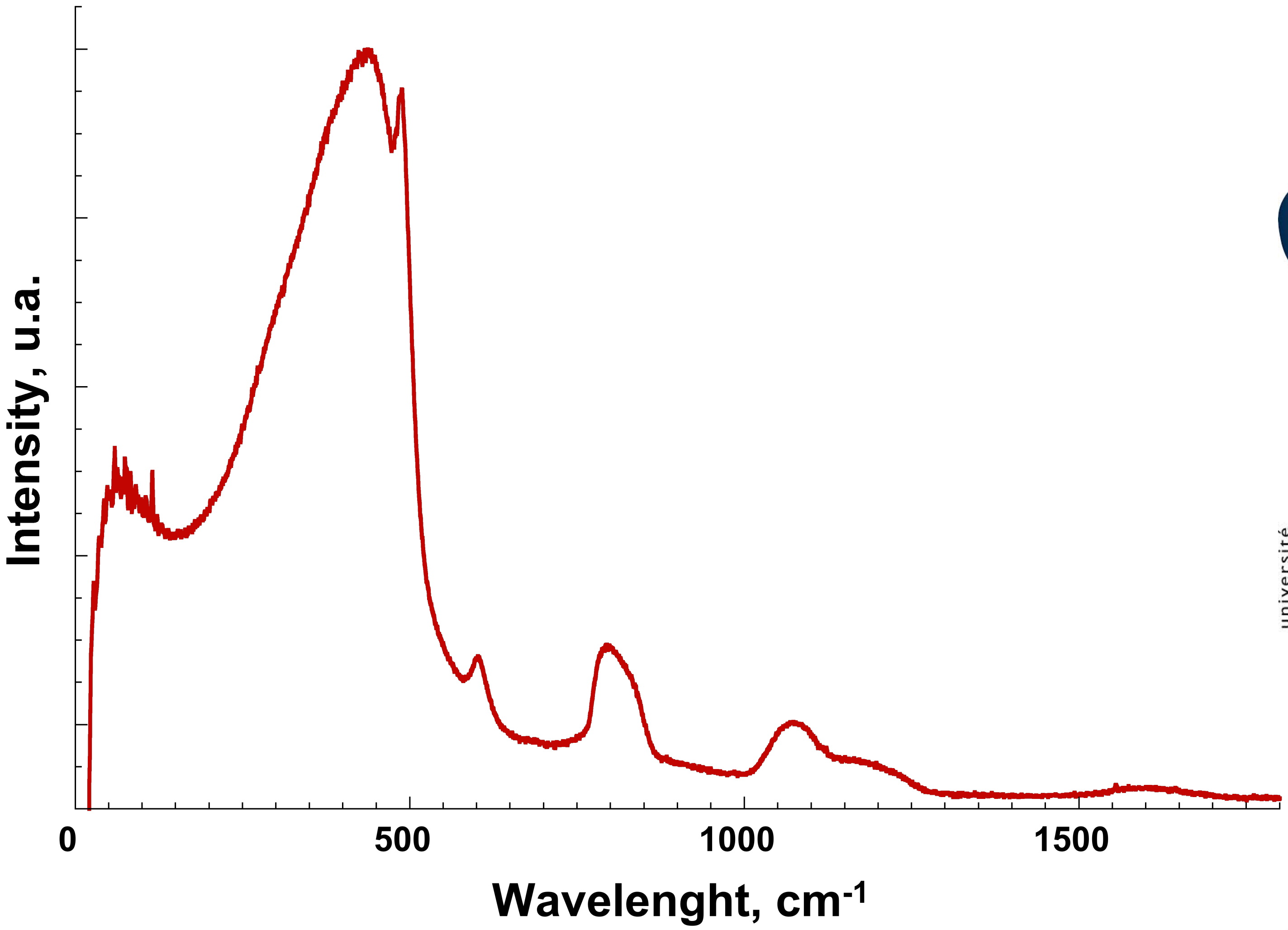
Amorphous SiO_2: Fully connected SiO_2 network (but disordered!)

BO: Bridging Oxygen

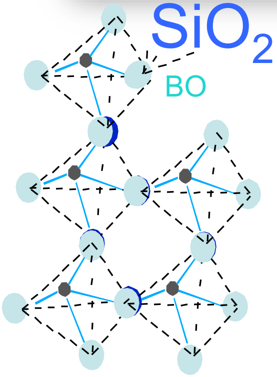
Q^4: SiO_2 tetrahedron with 4 BO



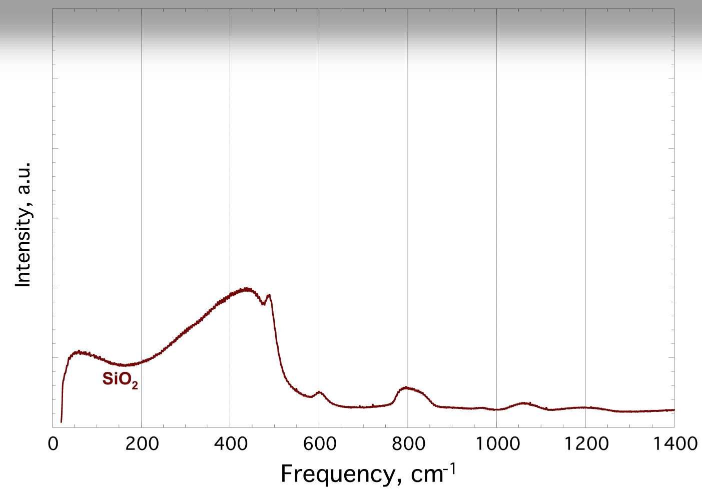
Raman : vibrations of v-SiO_2

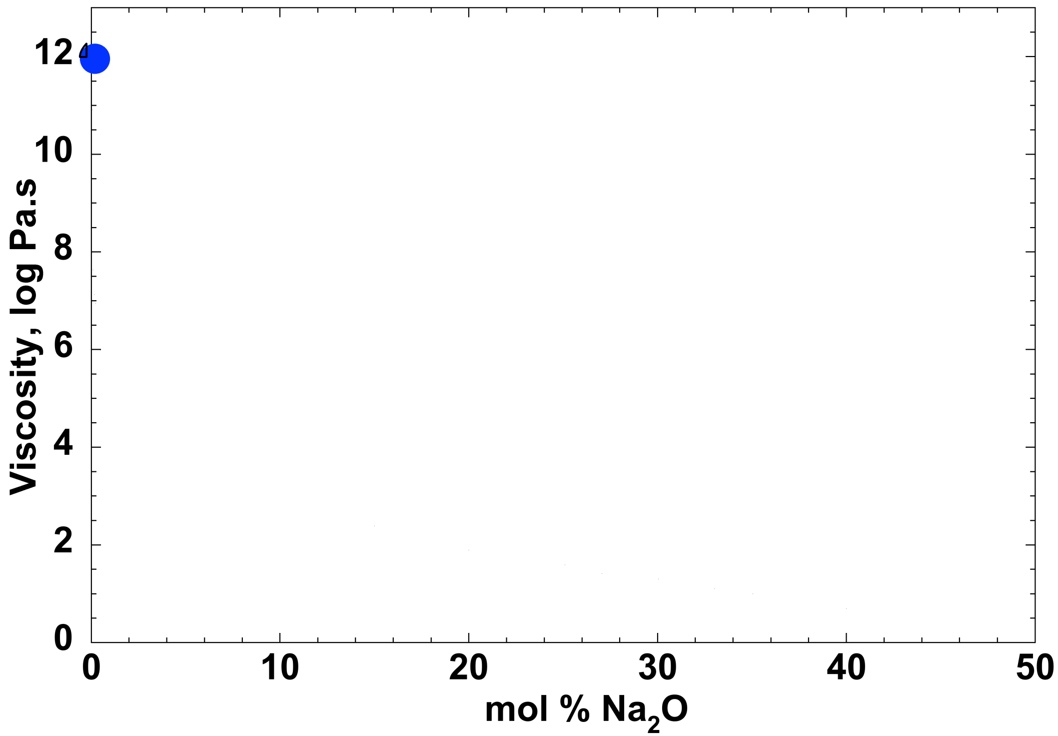


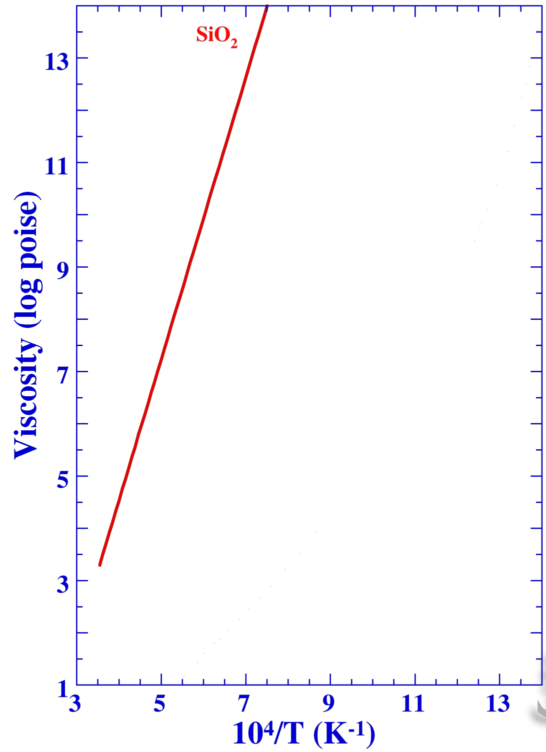
Structure versus properties of silicate melts



1200°C

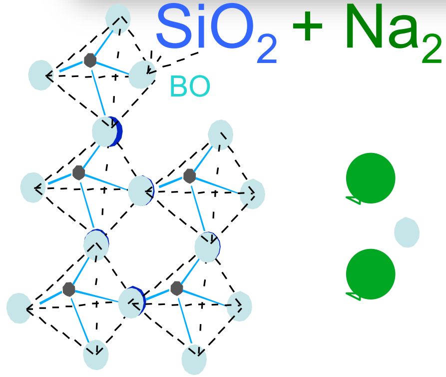




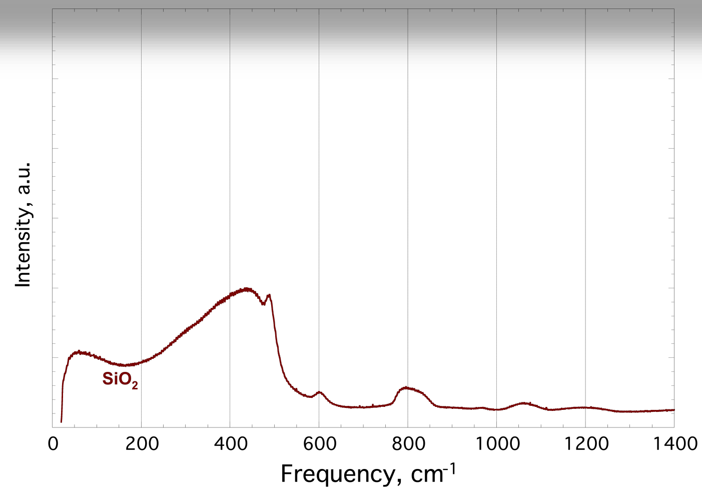


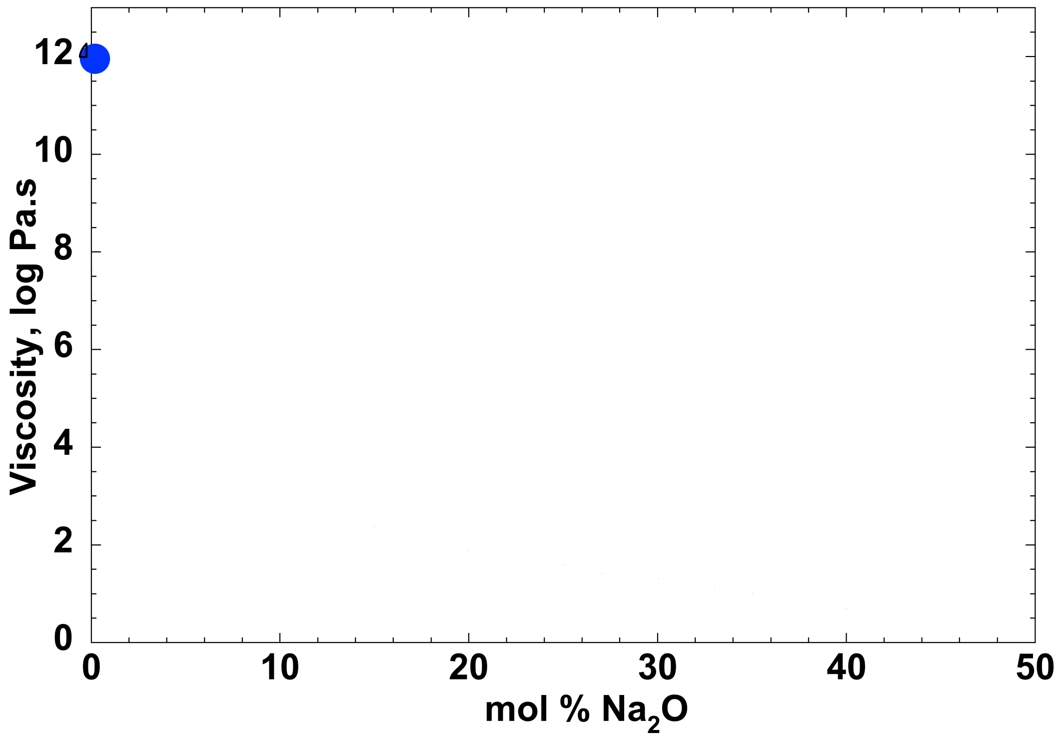
Structure versus properties of silicate melts

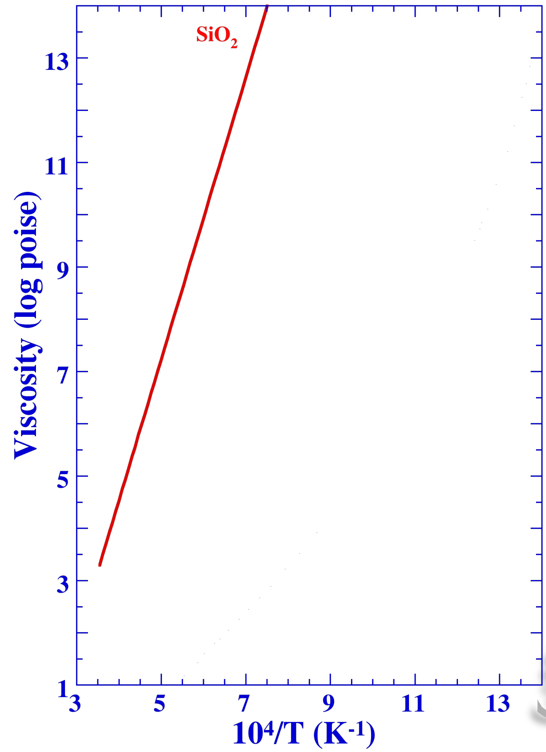
SiO_2 + Na_2O



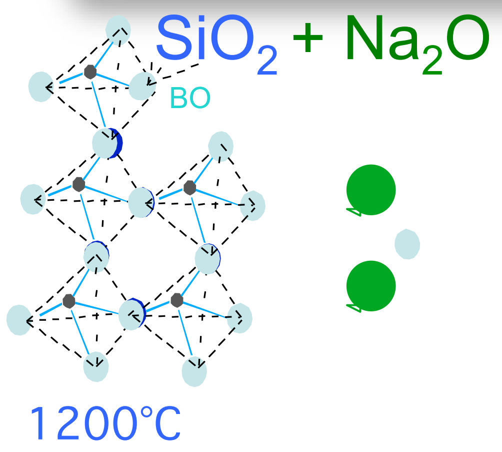
1200°C

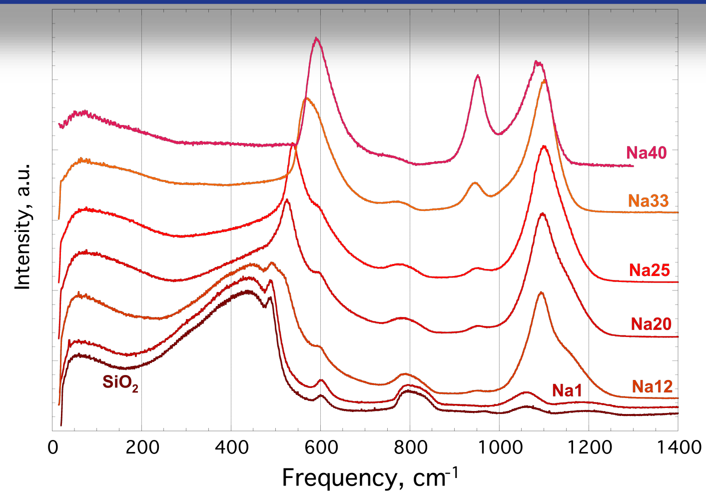


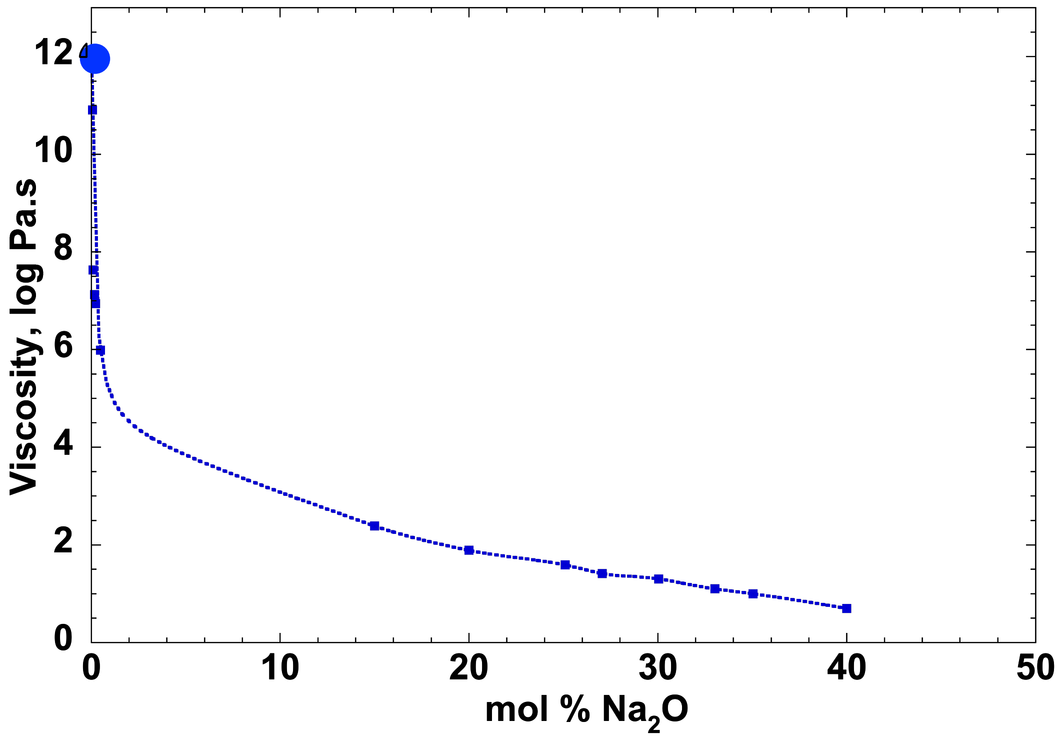


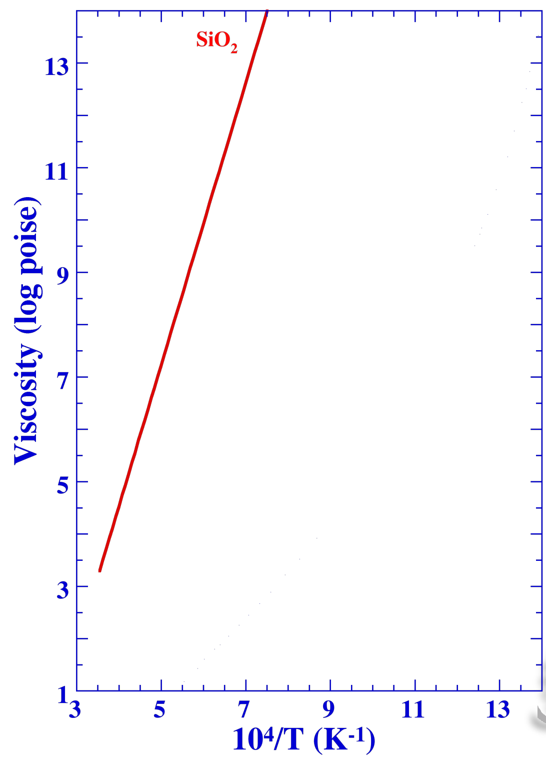


Structure versus properties of silicate melts









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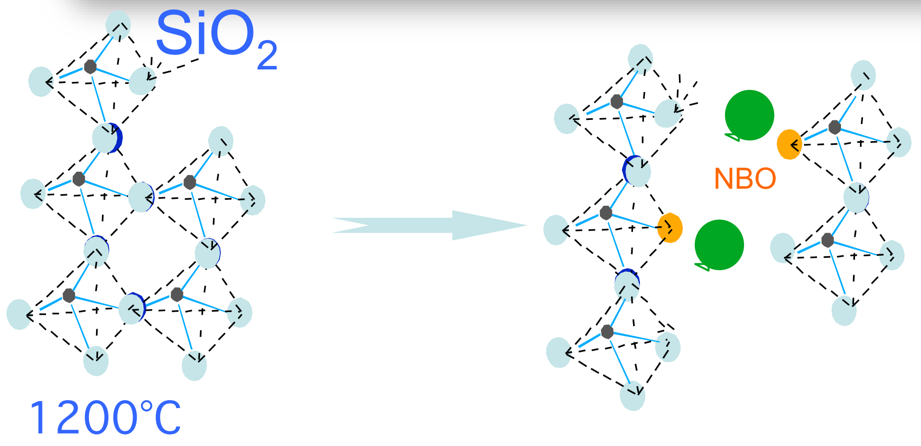

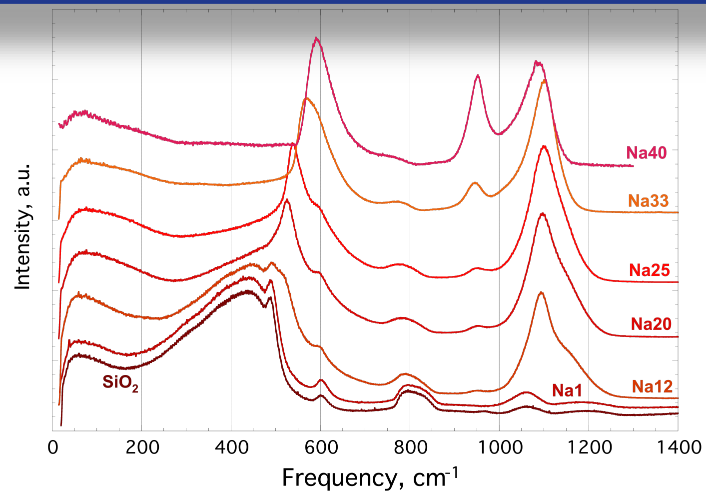

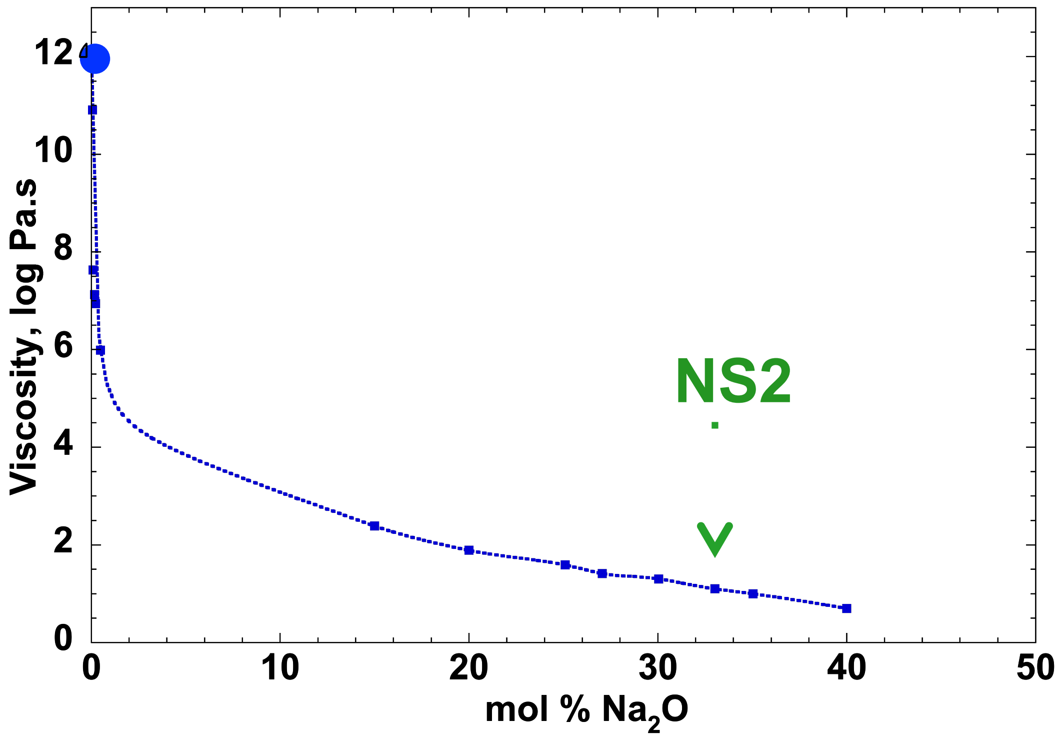

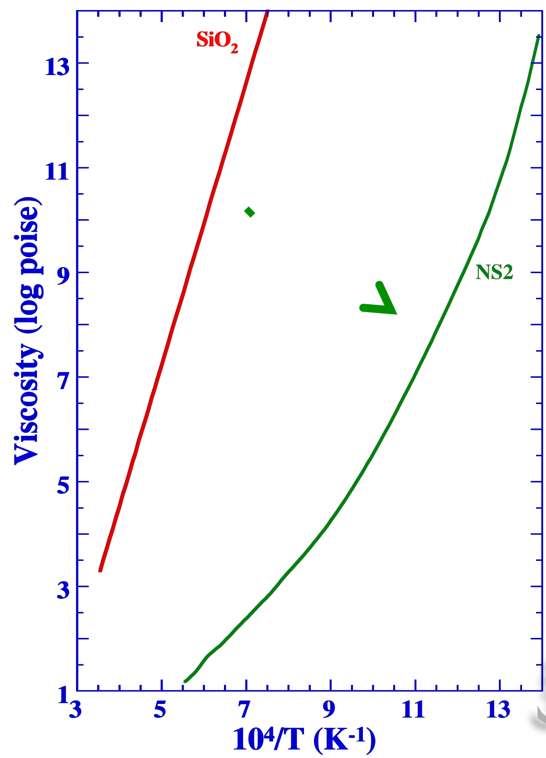

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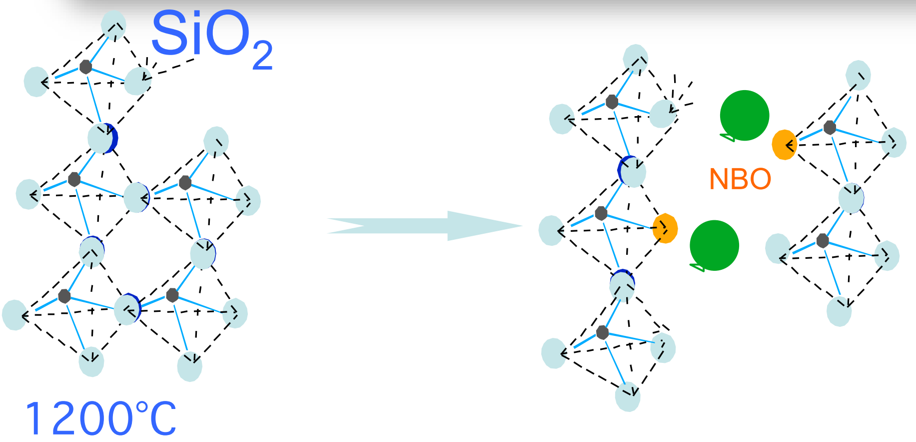
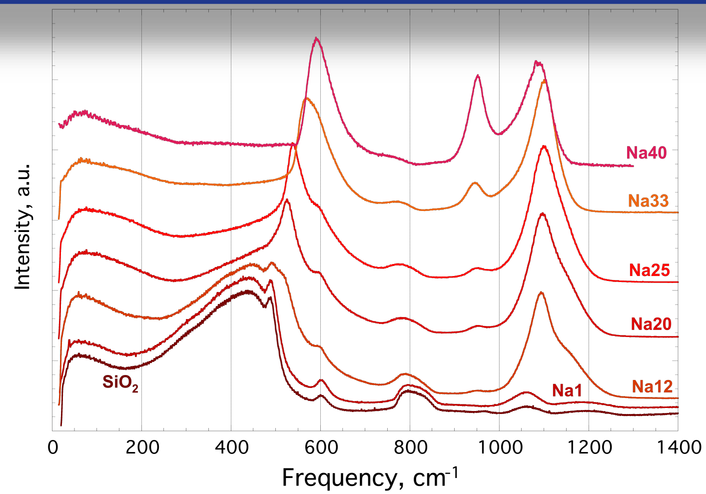
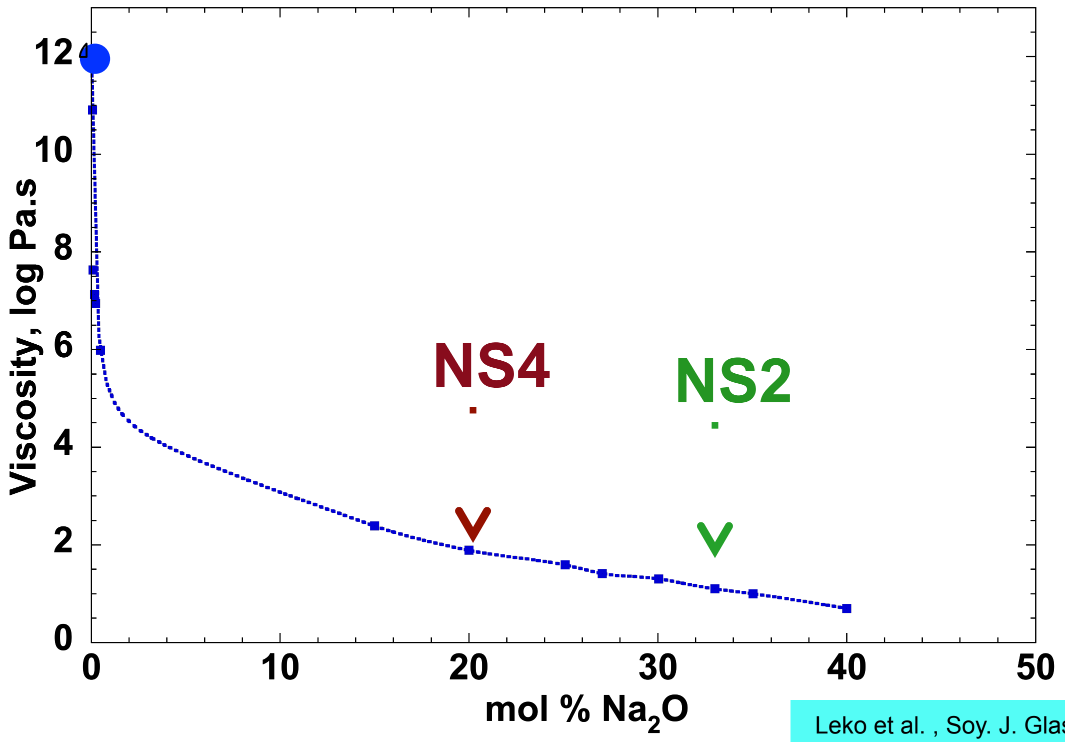
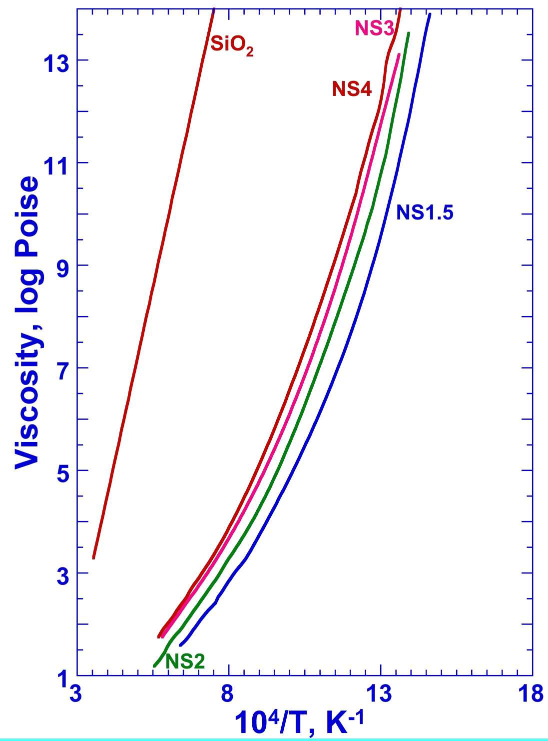


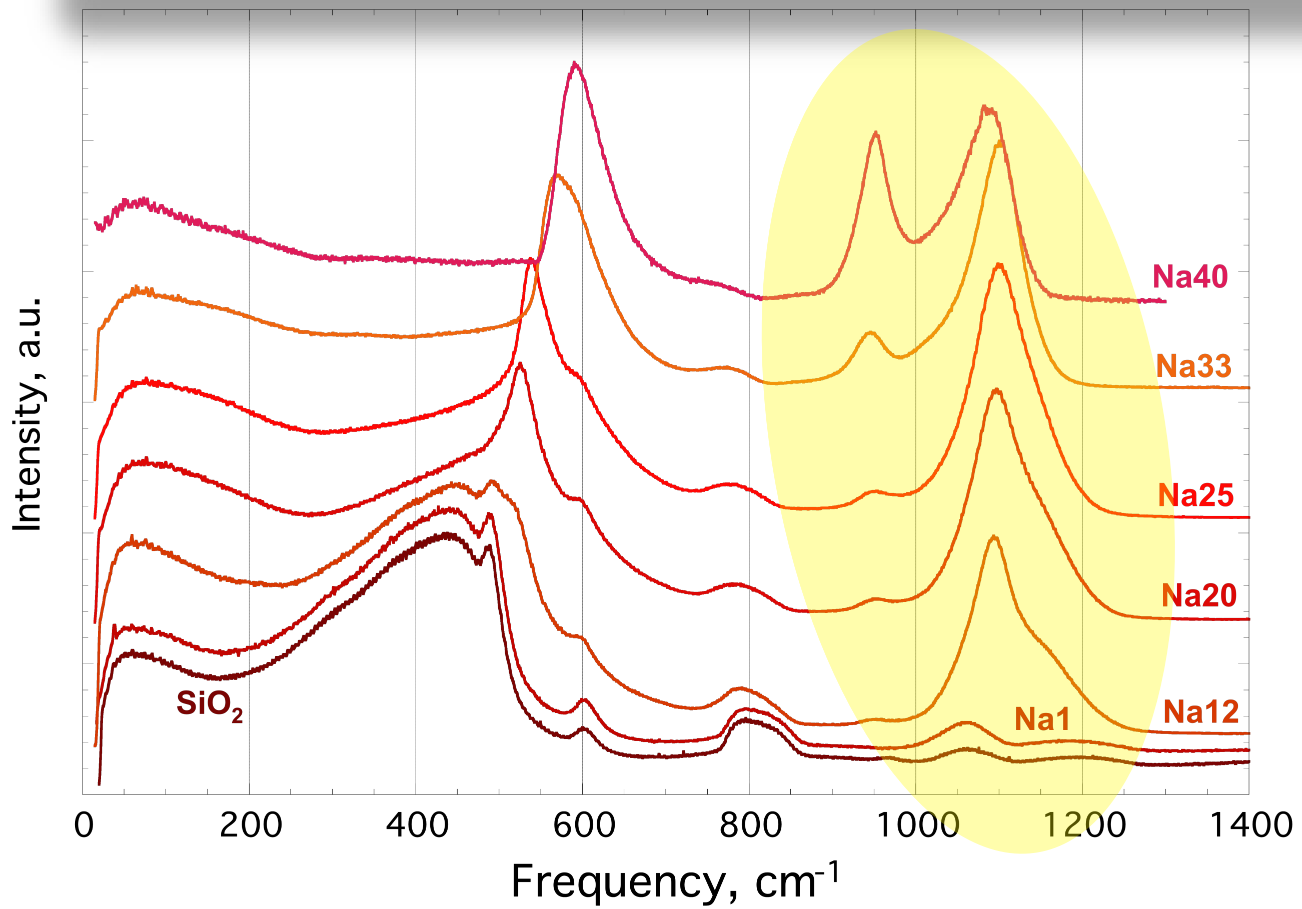






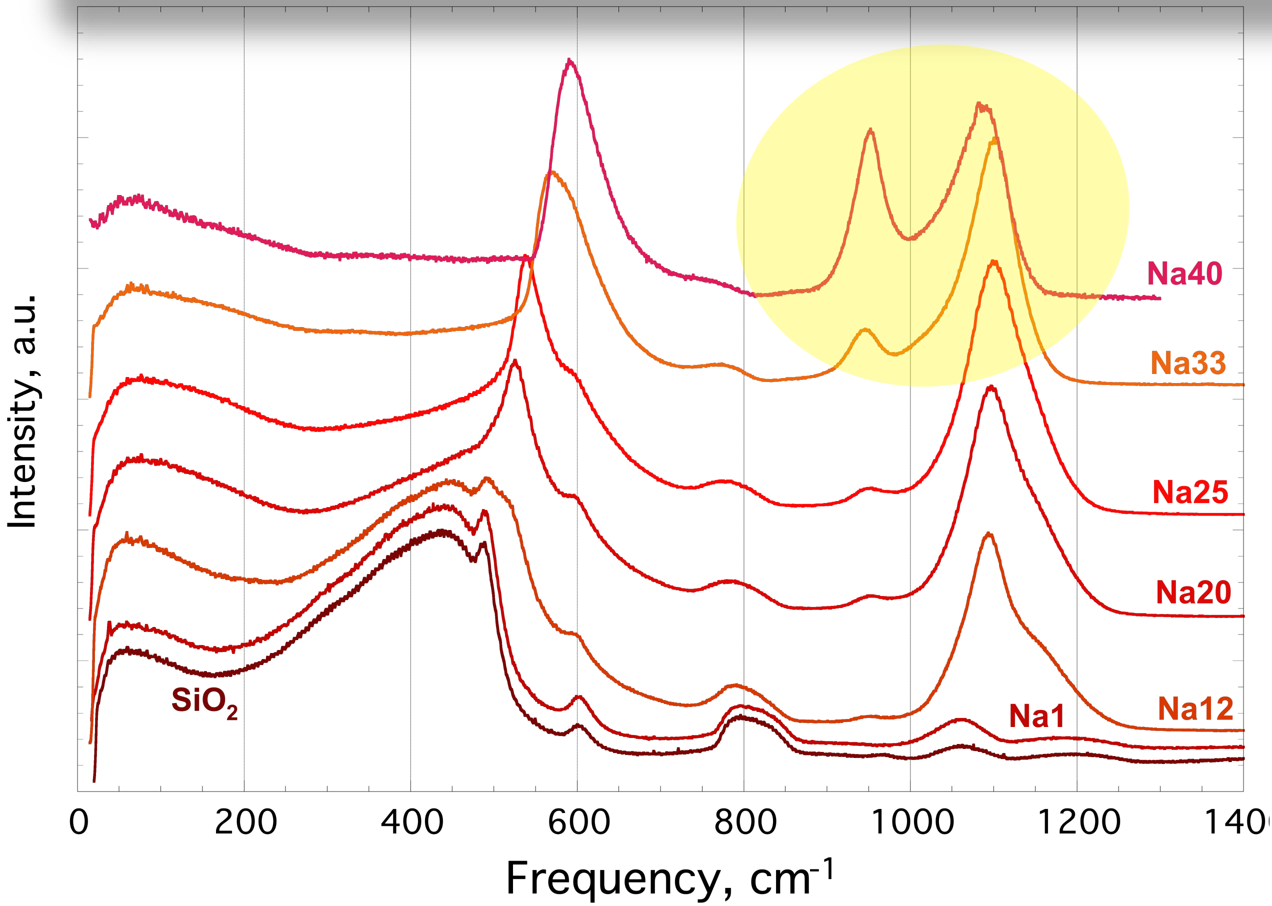
Leko et al. , Soy. J. Glass Phys. Chem., 1977, 3, 204-210 and Neuville, Chem Geol, 2006, 229, 28-42

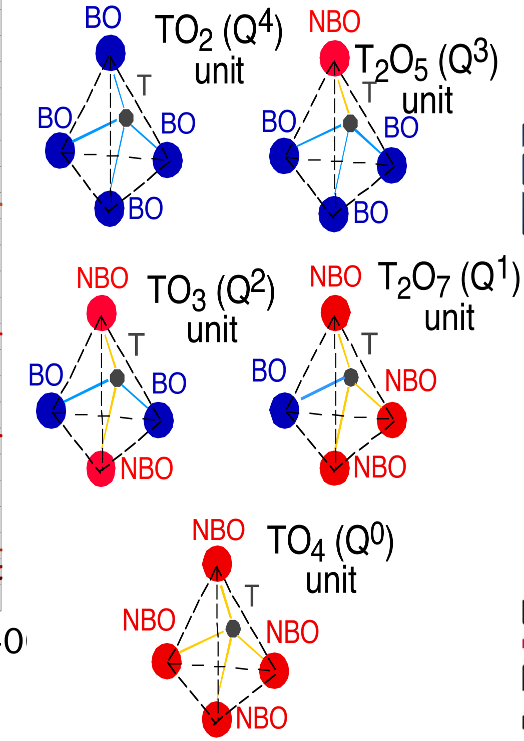
Raman spectra of SiO_2-Na_2O glass

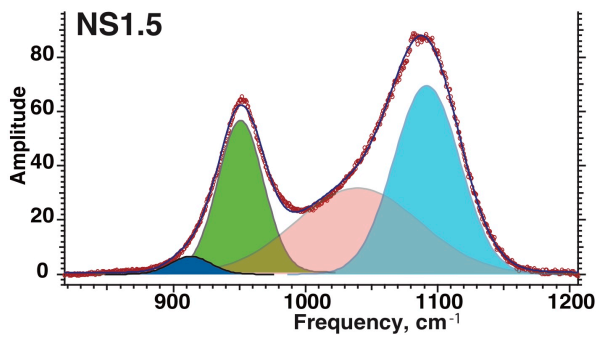


Neuville et al., Review in Min & Geo, 78, 509-541

Raman spectra of SiO_2-Na_2O glass



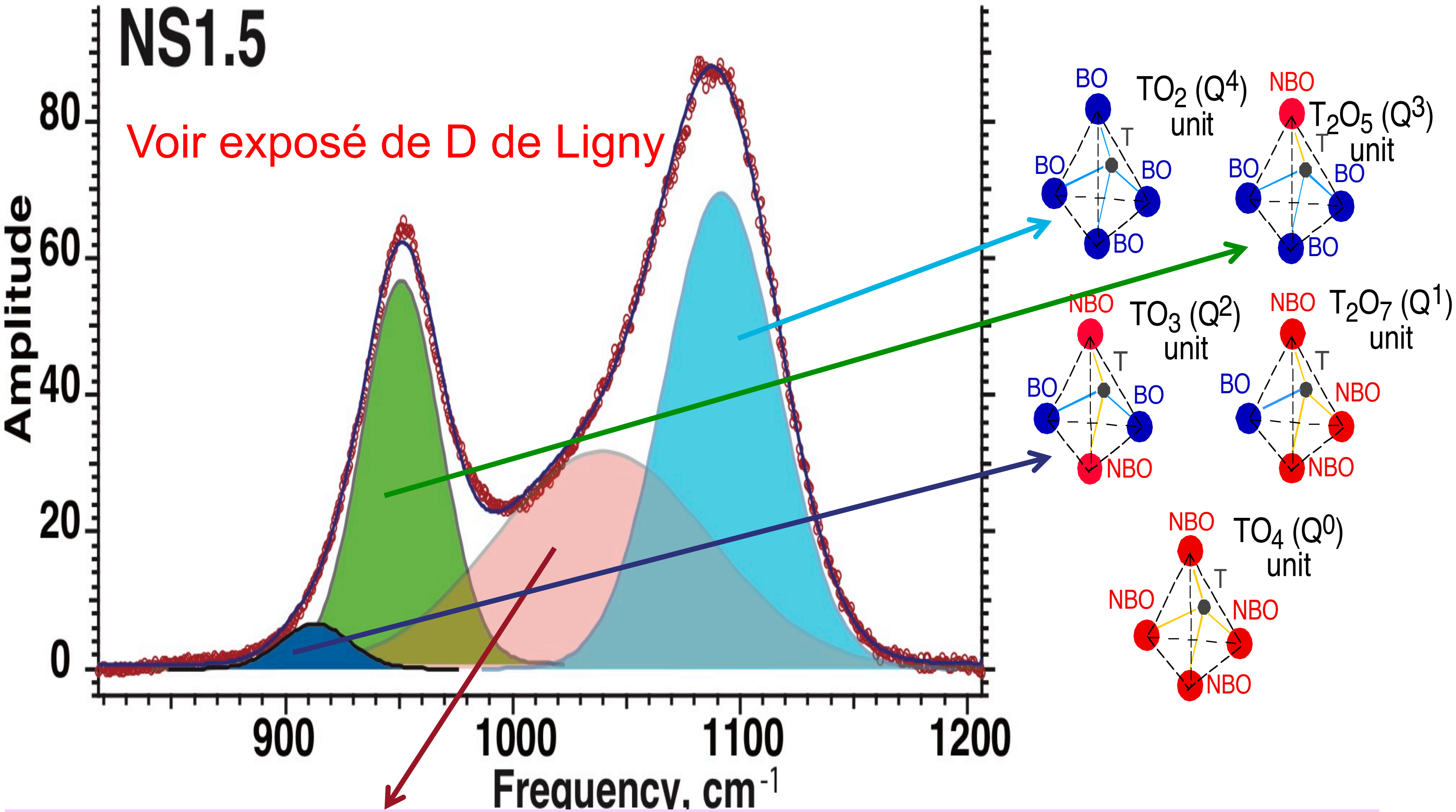




Raman spectra of SiO_2-Na_2O glass

Q^n species

T-O-T stretching vibration

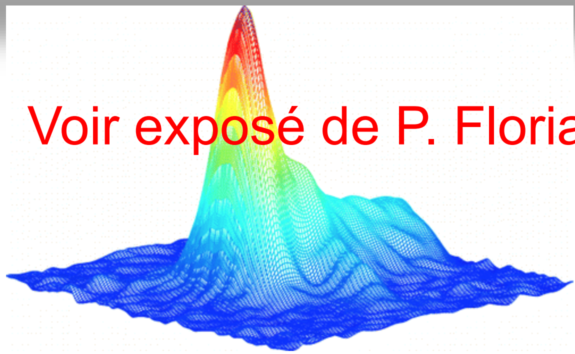


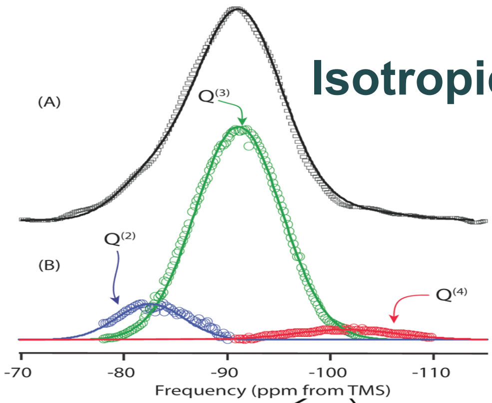
T_2 mode of TO^4 tetrahedra, Q^4, two oxygen atoms moving closer to the central Si atom while the two others oxygen atoms are moving away (Sarnthein et al. 1997; Taraskin and Elliott 1997; Pasquarello et al. 1998)

Neuville, Chem Geol, 2006, 229, 28-42

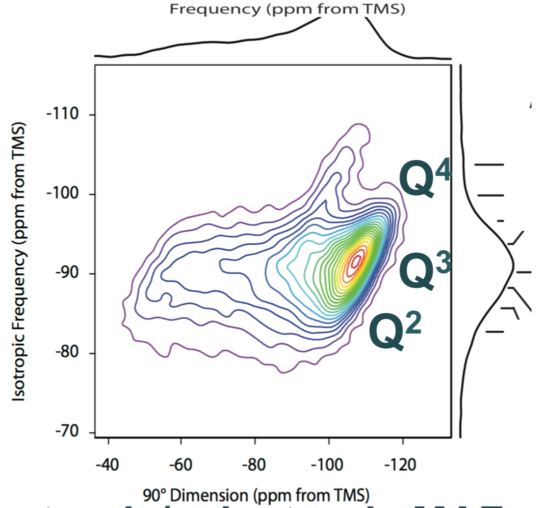
NMR — Q^n species — X-ray absorption

Voir exposé de P. Florian





Isotropic MAS



Isotropic/anisotropic MAF

^{29}Si MAF Spectrum of K_2O-2SiO2 glass

Davis et al., J. Phys. Chem. A, 2010, 114 5503–5508

Voir exposé de G. Calas

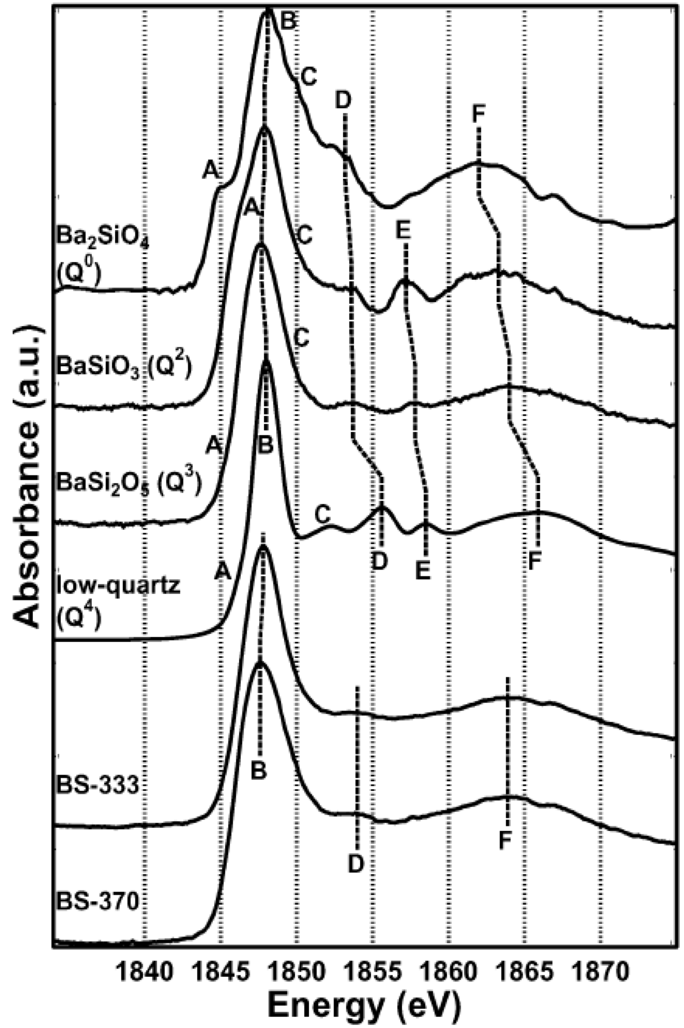
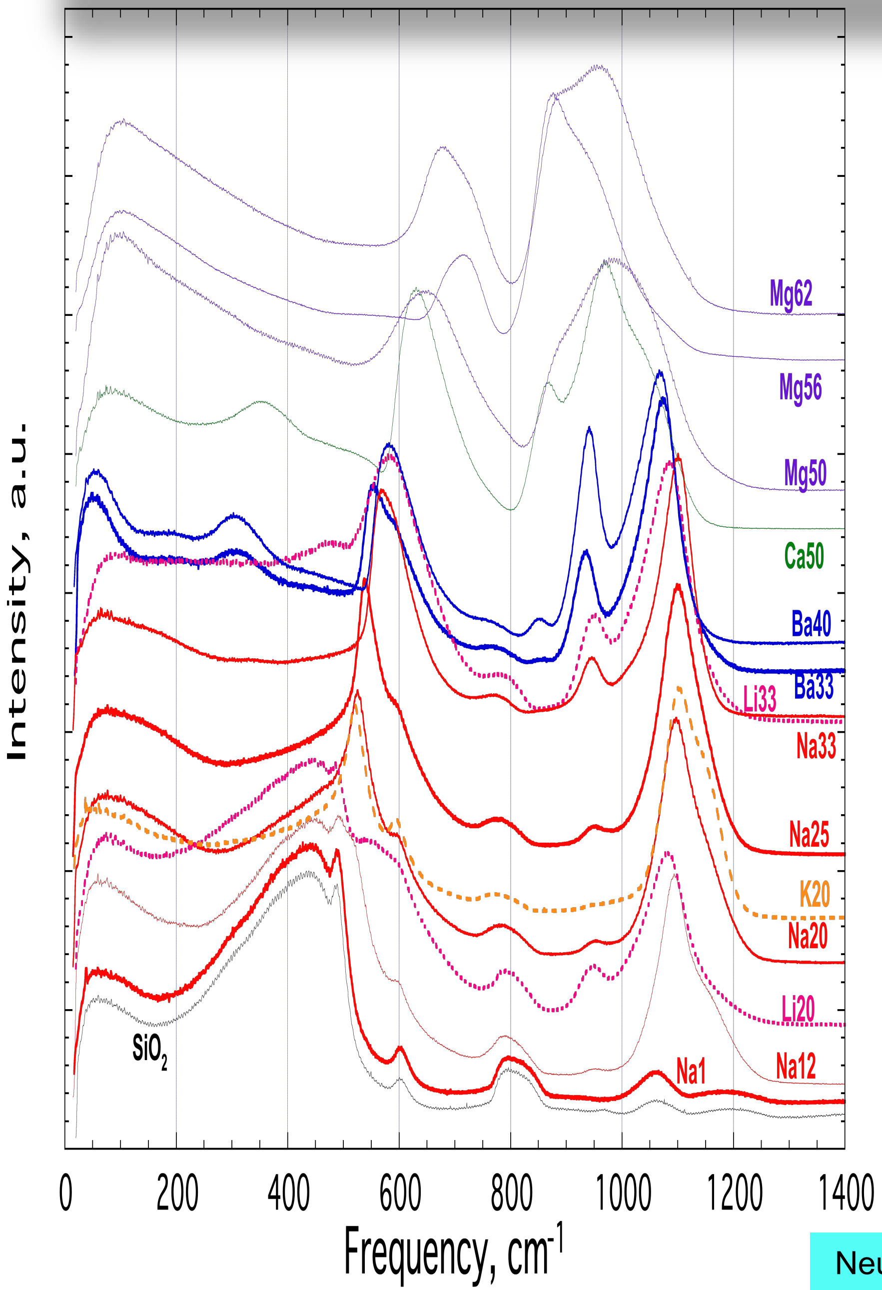
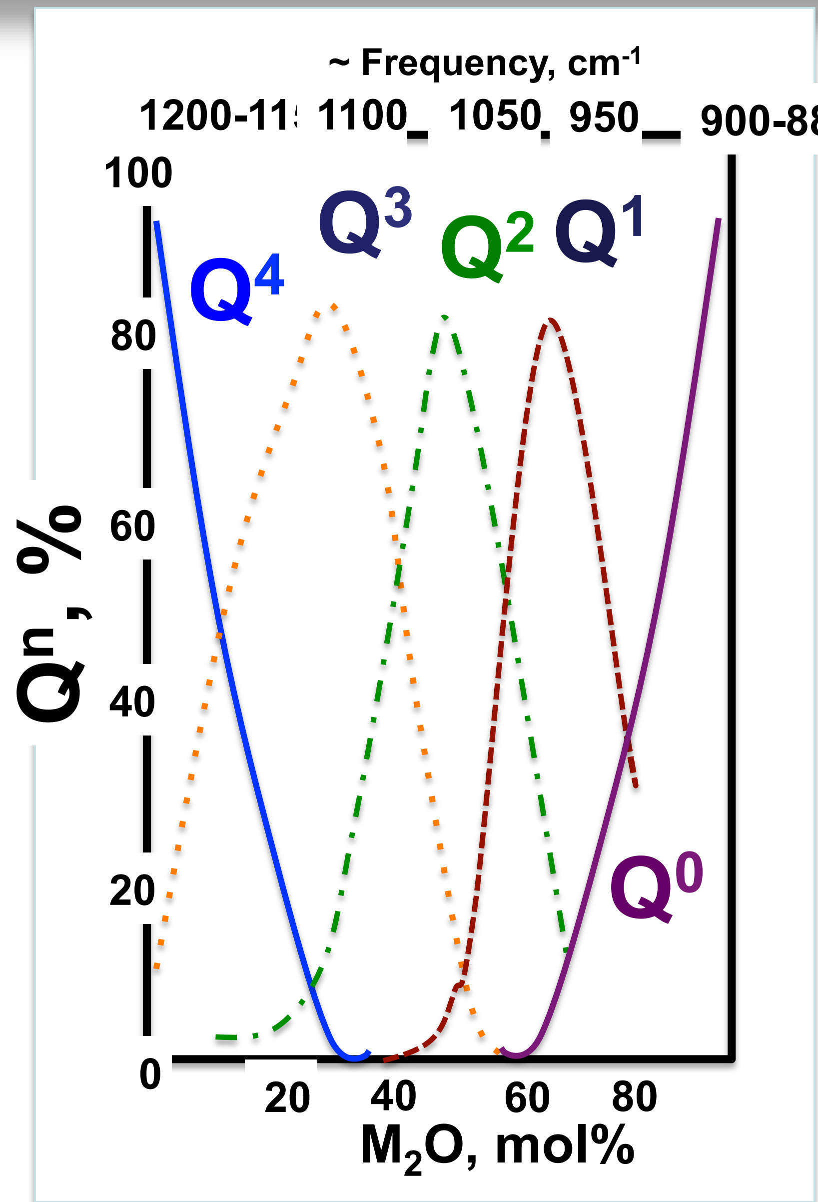


Fig. 1. Si K-XANES spectra of barium silicates, low quartz and the amorphous samples BS-333 and BS-370.

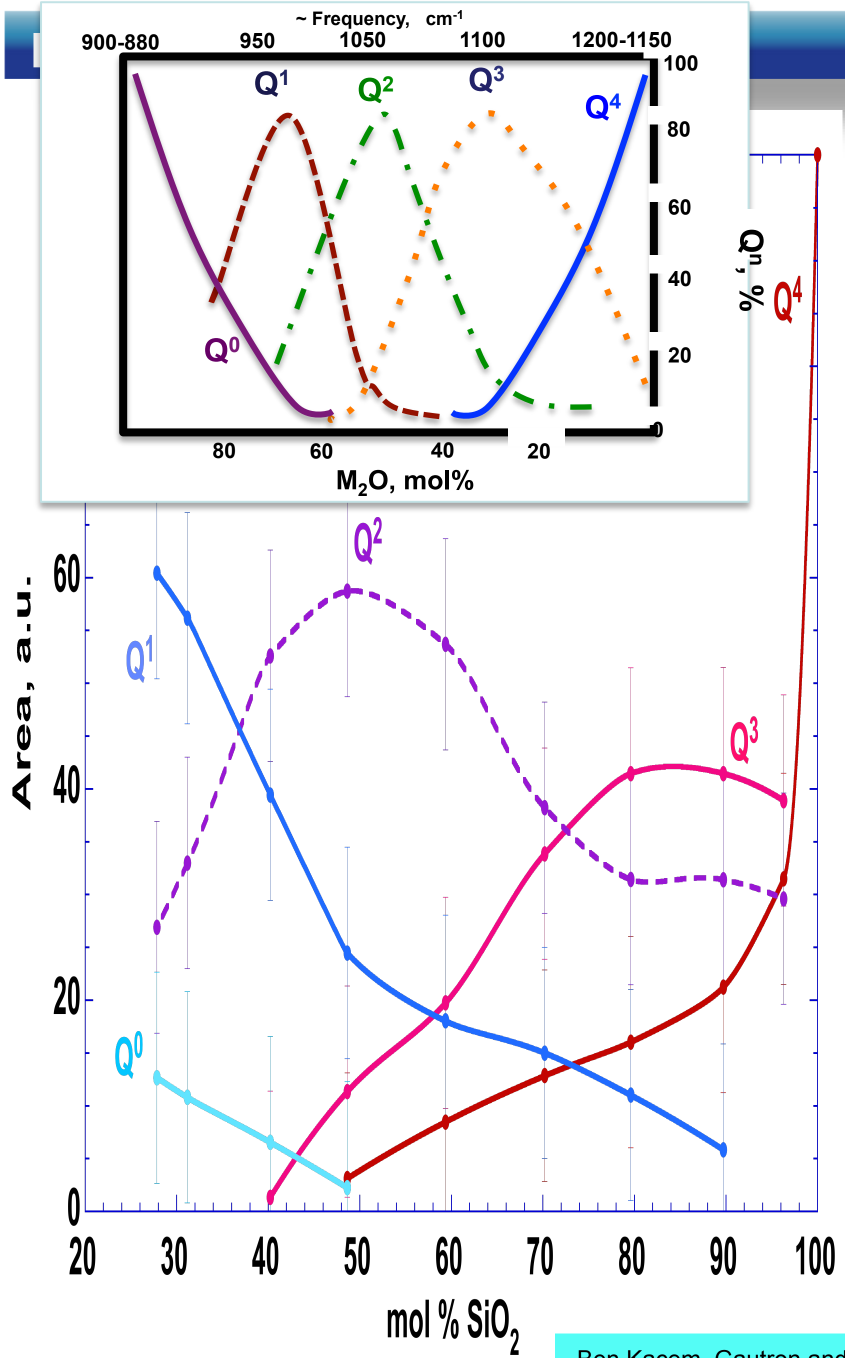
Si K-edge of BaO-SiO_2 glass
Bender et al., JNCS, 2002, 298, 99-108

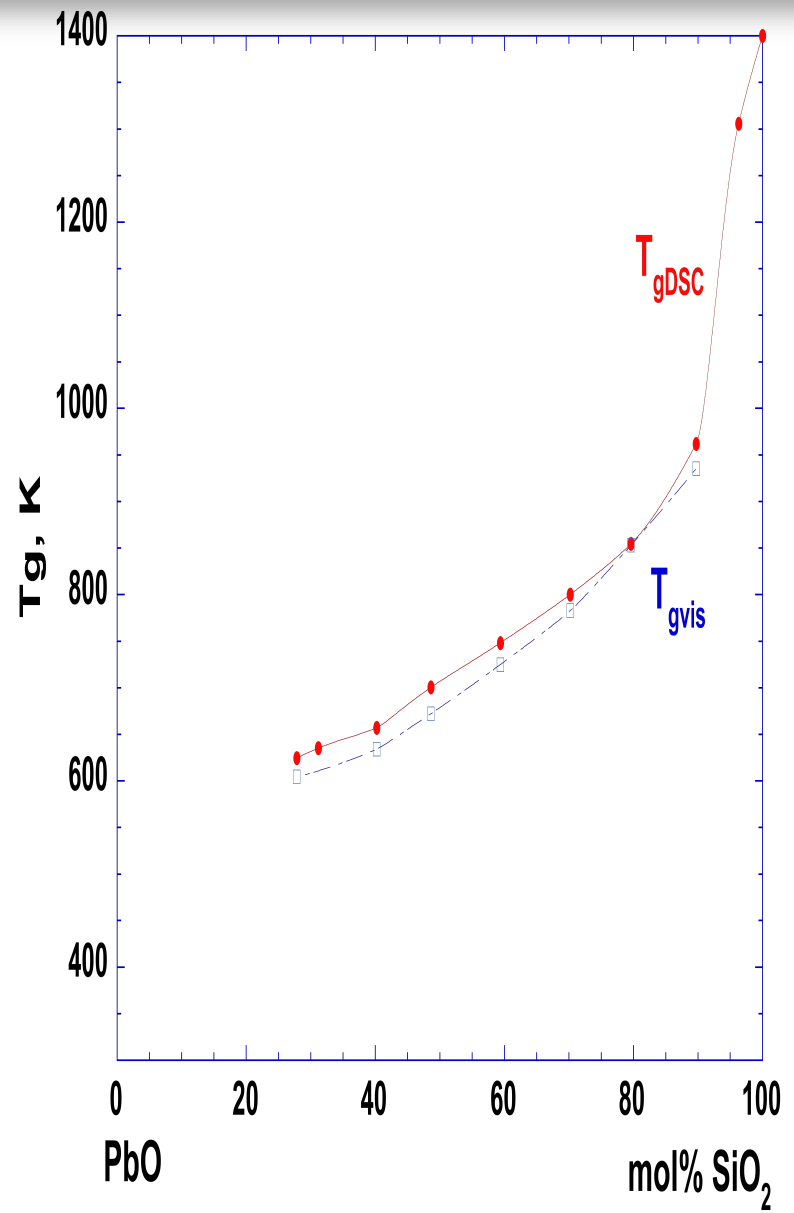
Q^n species



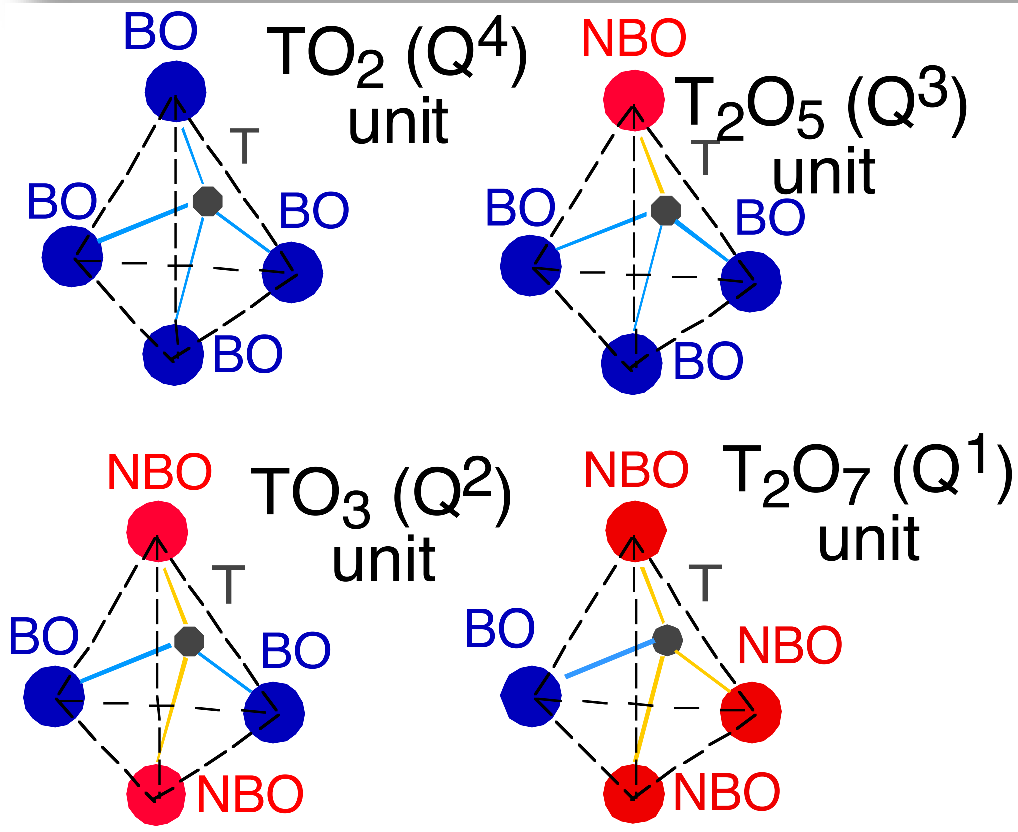


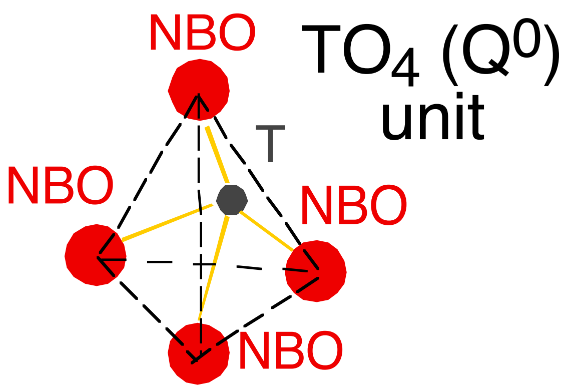
Neuville, Henderson, de Ligny Review in Min & Geo, 78, 509-541





Ben Kacem, Gautron and Neuville Structure and properties of lead silicate glasses and melts. Chem Geol. 2017



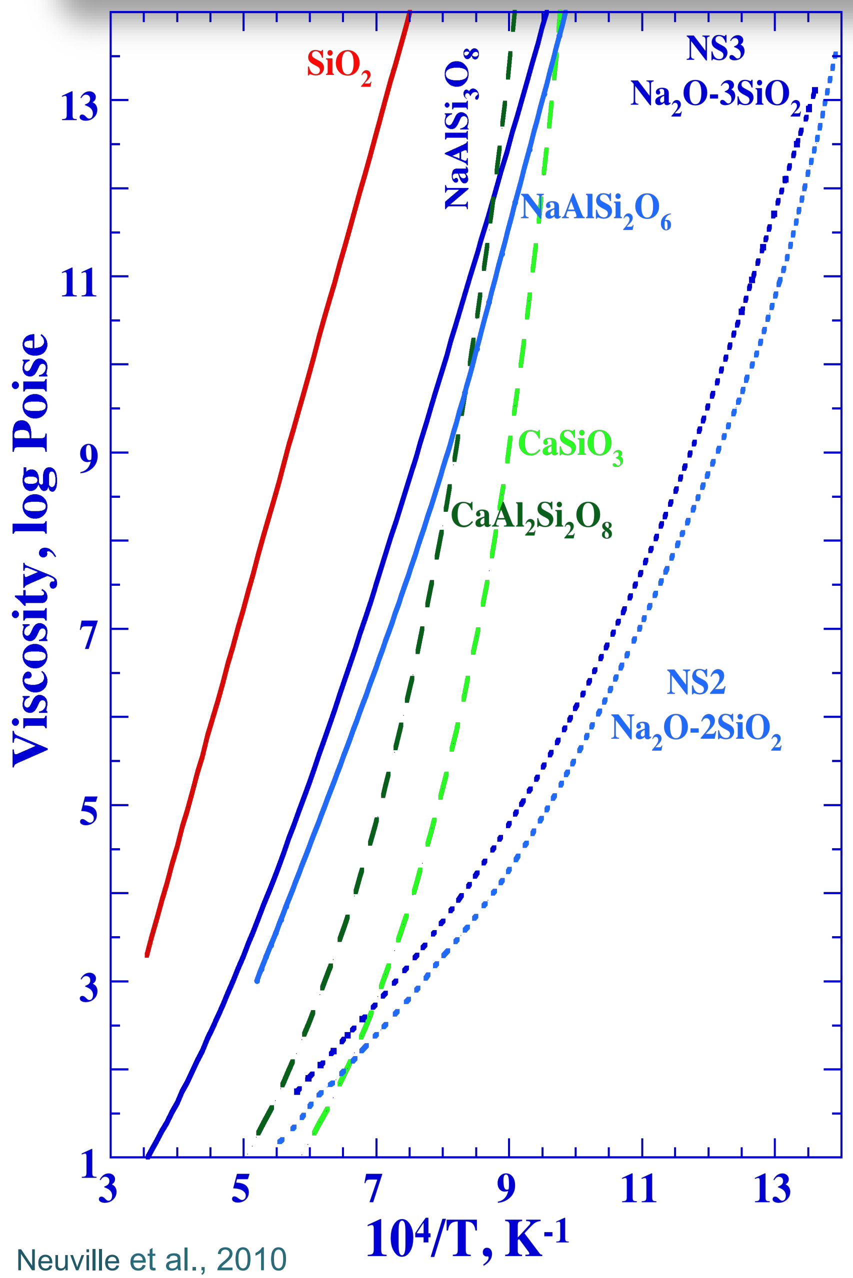


Network modifier with Si^{4+}

=> Li^+, Na^+, K^+

=> Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}

How fit viscosity



Neuville et al., 2010

Arrhenius :

$$\eta(T) = A.\exp(E/RT)$$

$$\Leftrightarrow \log \eta = A + B/T$$

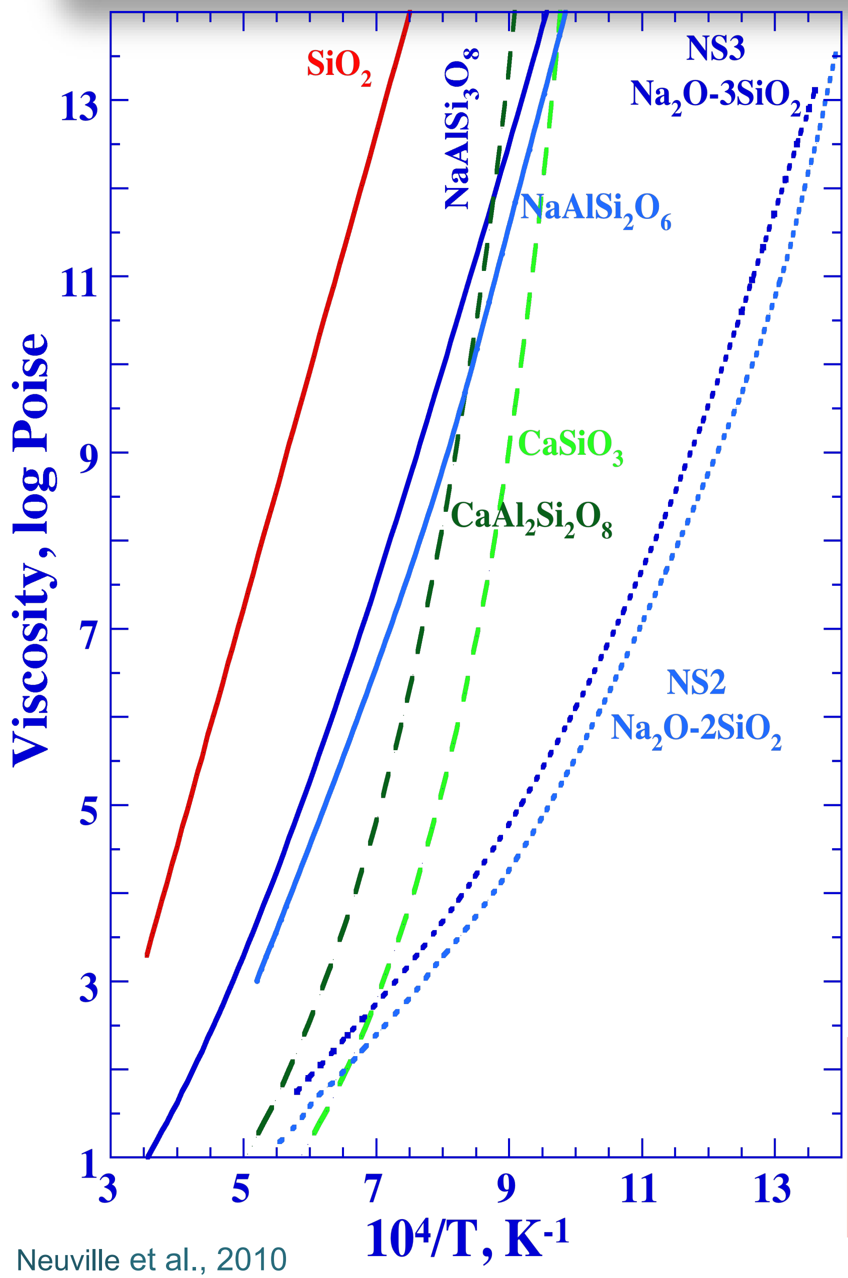
Yes but only for SiO_2, GeO_2, $NaAlSiO_8$, $KAlSiO_8$ because activation energy change from 2000kJ/mol at 1000K up down 300kJ/mol at 1800K for NS3.

Need TVF equation

$$\log \eta = A_1 + B_1/(T-T_1)$$

But, just a fit …..

How fit viscosity



Neuville et al., 2010

$$\eta(T) = A_e.\exp[B_e/TS^{conf}(T)]$$

Proposed by Adam and Gibbs, 1964

First used to silicate melts by Urbain, 1972, Scherer, 1984, Richet, 1984, Neuville and Richet, 1991….

$$S^{conf}(T) = S^{conf}(Tg) + \int_{Tg}^{T} Cp^{conf} / T dt$$

$$Cp^{conf}(T) = Cpg(Tg) - Cpl(T)$$

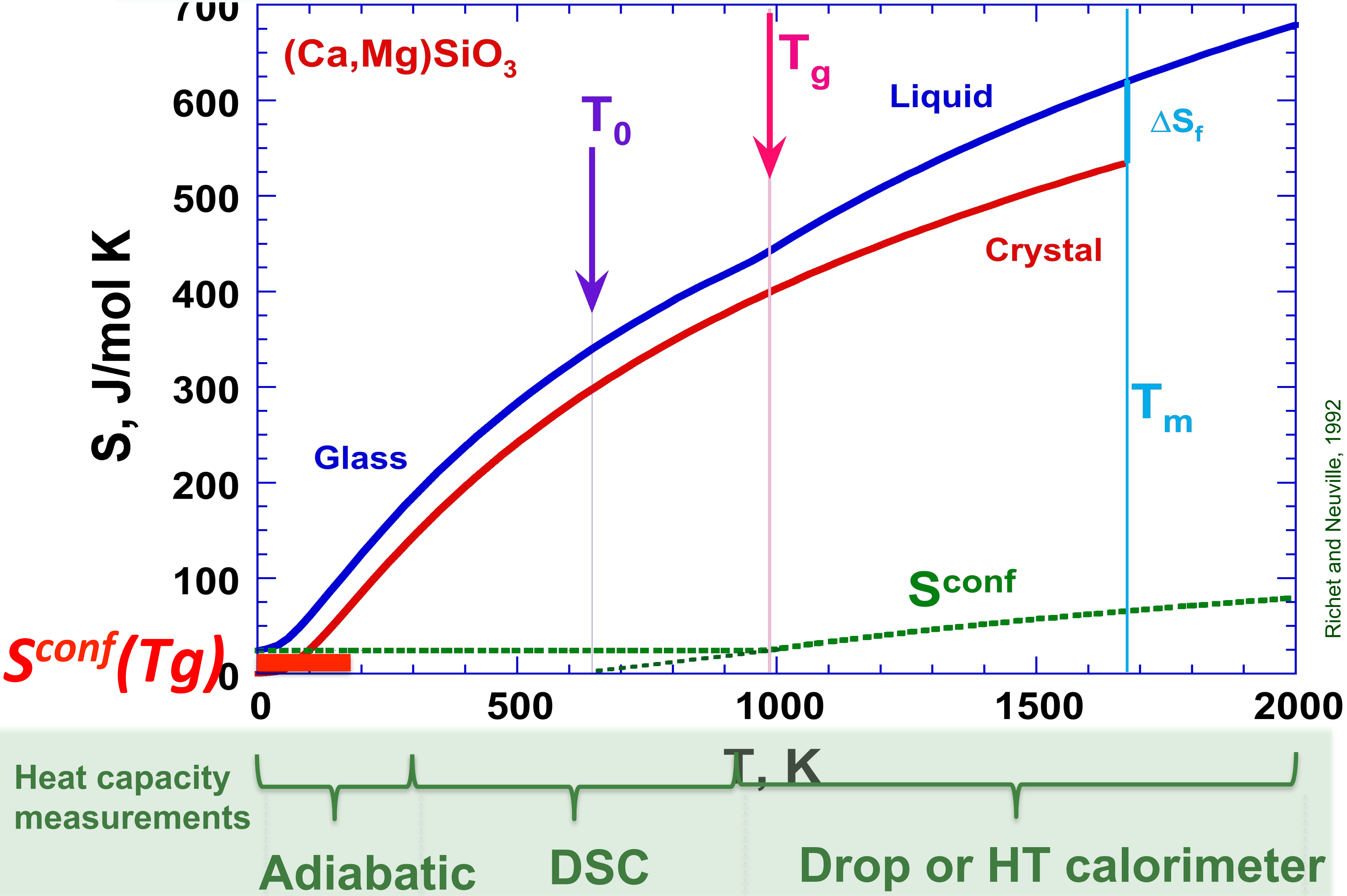
Calorimetry measurements => Easy

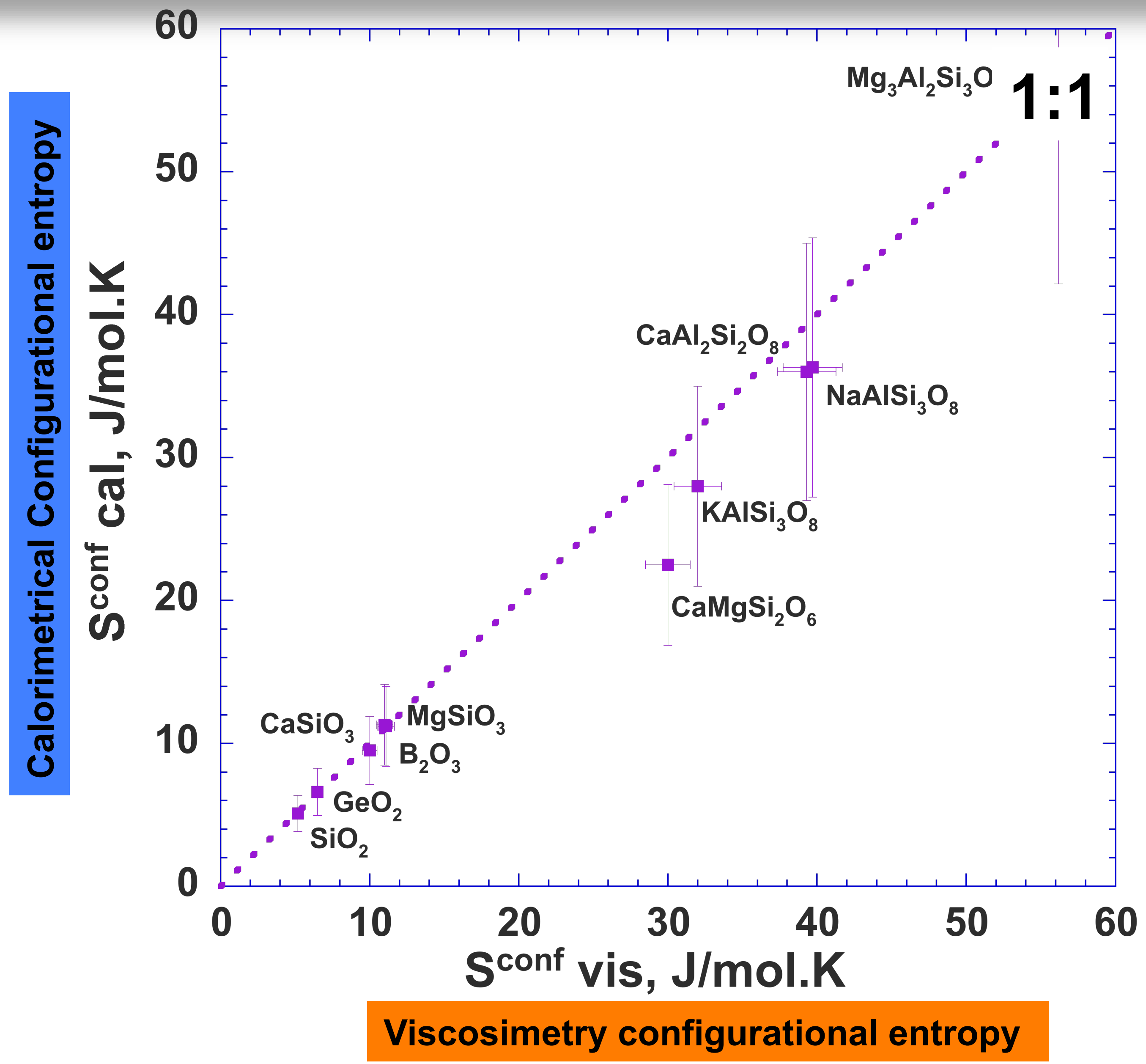
$S^{conf}(Tg)$

⇒ What is that ?

Configurational entropy

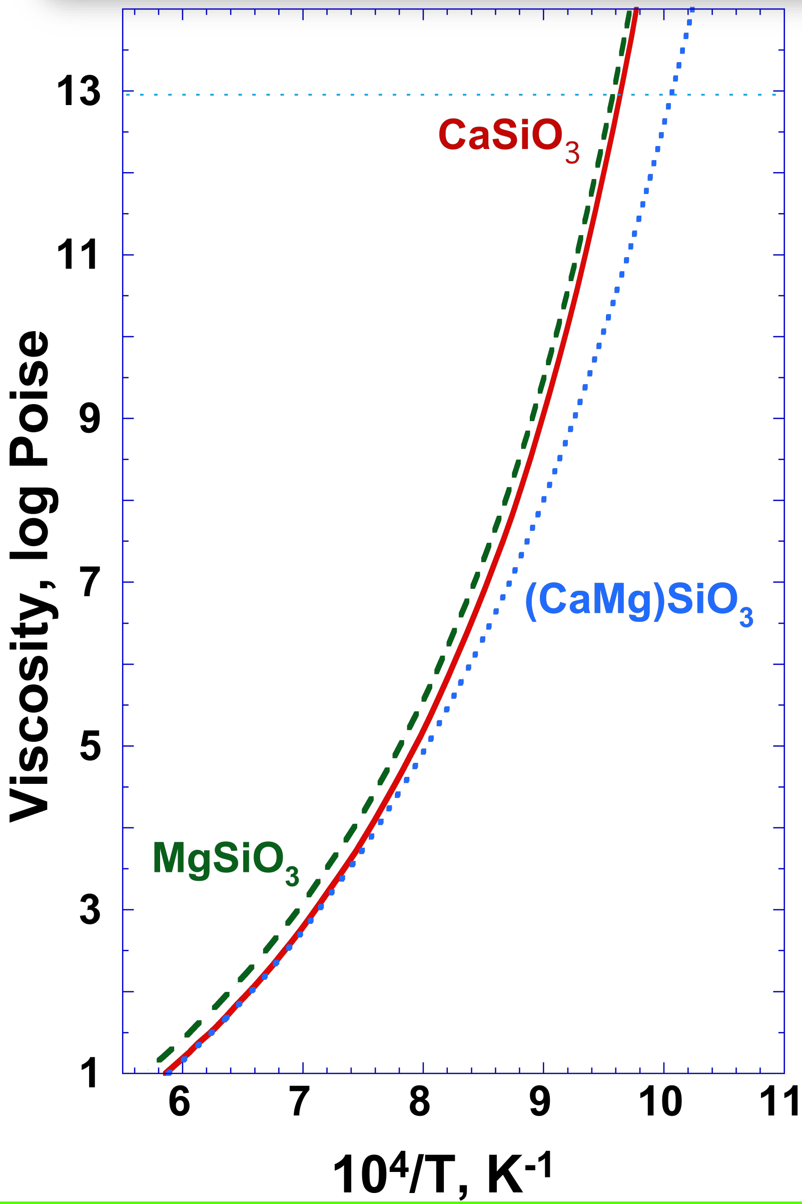
$$S^{conf}(Tg) = \int_0^{Tm} \frac{Cp^{Crystal}}{T}.dT + \Delta S_f + \int_{Tm}^{Tg} \frac{Cp^{liquid}}{T}.dT + \int_{Tg}^{0} \frac{Cp^{glass}}{T}.dT$$

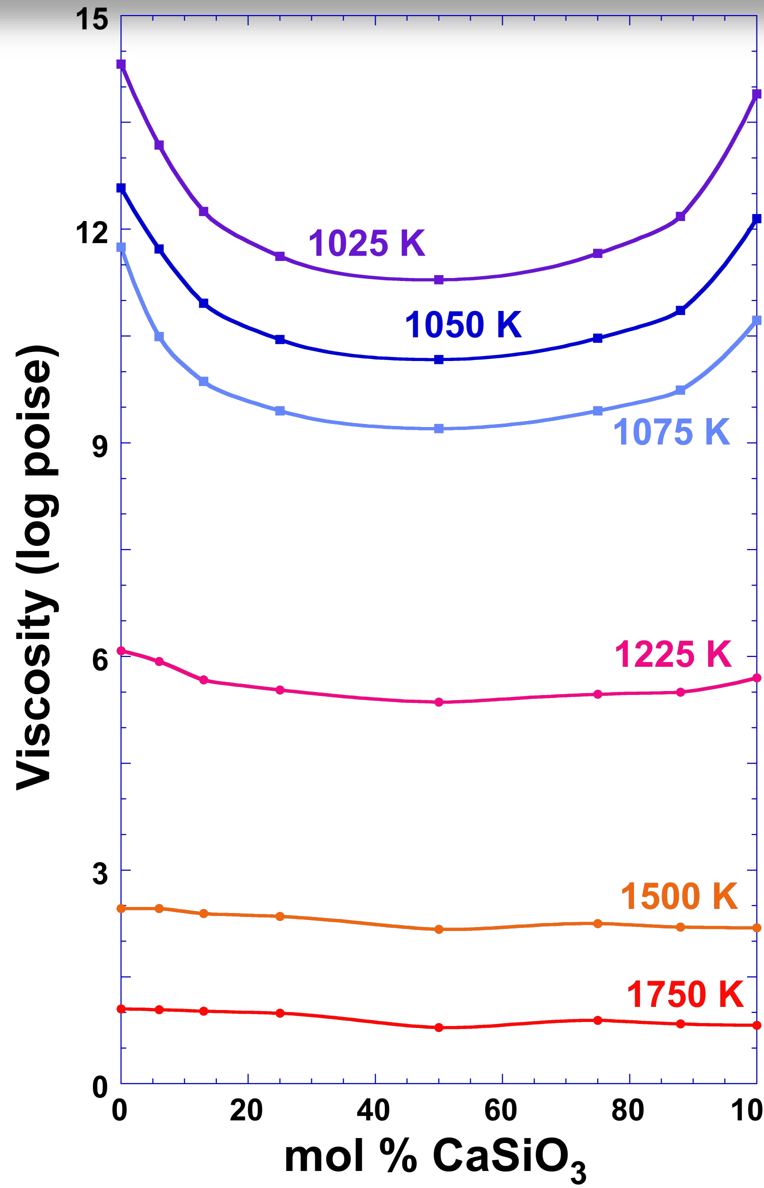




Adapted from Richet and Neuville, 1992

Ca/Mg Mixing ?

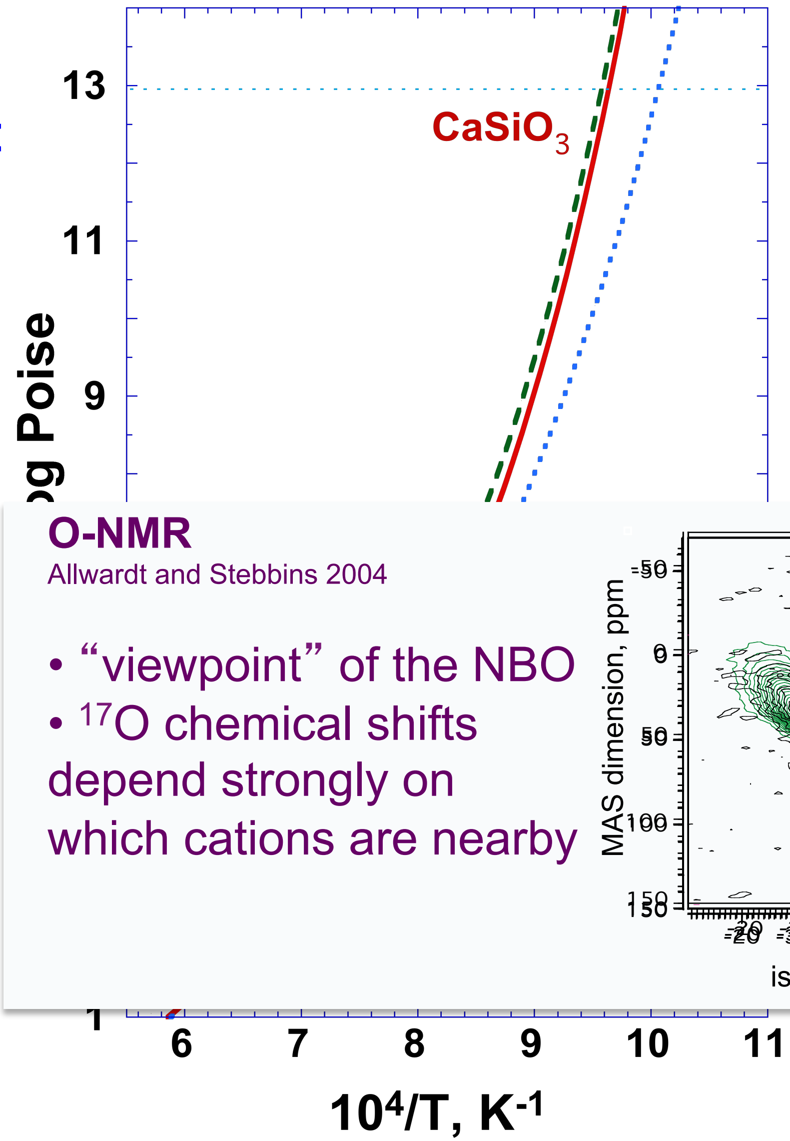


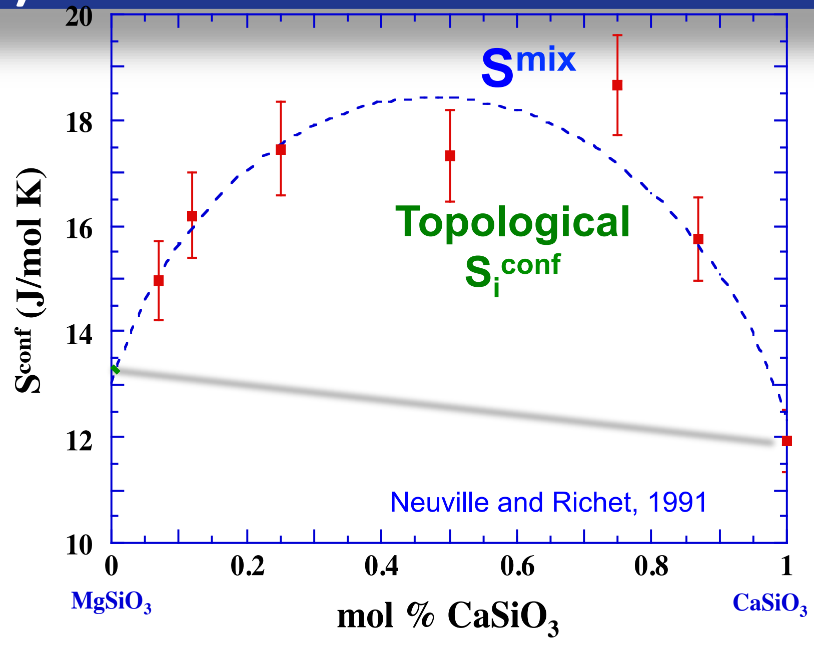


Neuville D.R. and Richet P. (1991) Viscosity and mixing in molten (Ca,Mg) pyroxenes and garnets. Geochim. Cosmochim. Acta., 55, 1011-1021.

Entropy theory (Adam et Gibb, 1965)

$$\log \eta = A_e + B_e/TS^{conf}(T)$$



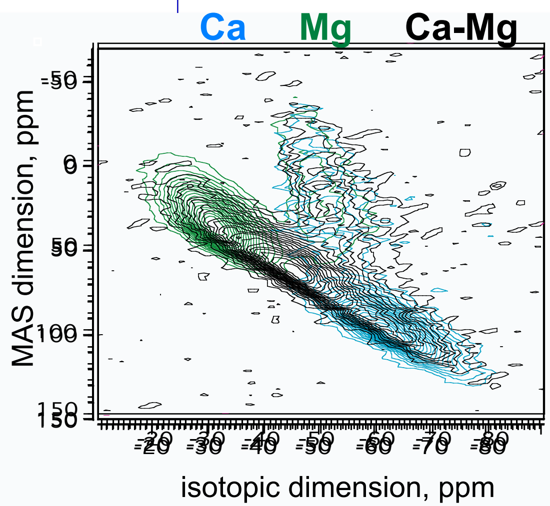


Mg)

O-NMR

Allwardt and Stebbins 2004

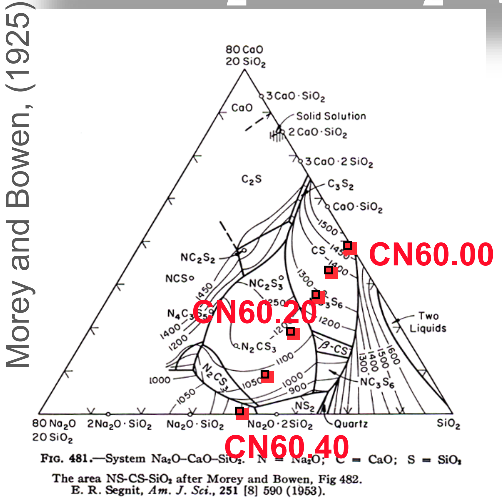
- "viewpoint" of the NBO
- ^{17}O chemical shifts depend strongly on which cations are nearby

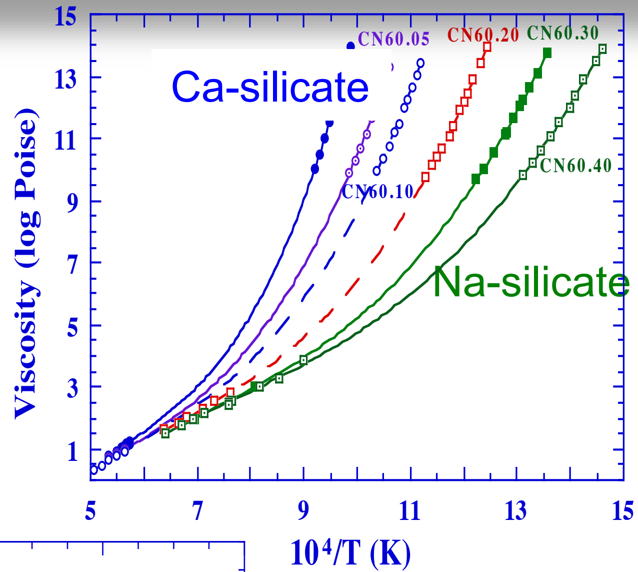


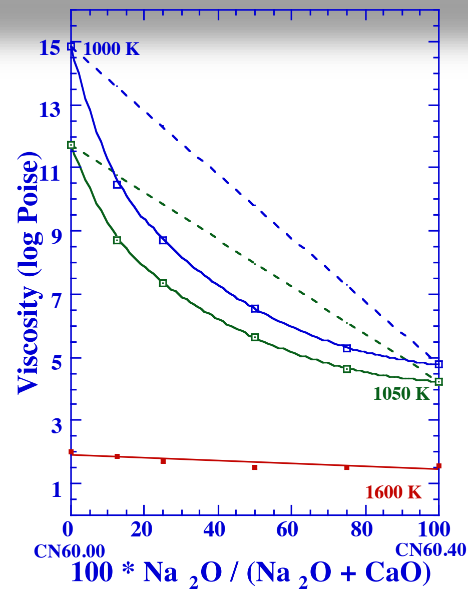
- **detailed analyses of spectra support almost random distribution of Ca + Mg around NBO**
- **size difference of Ca^{2+} and Mg^{2+} is insufficient to cause ordering**

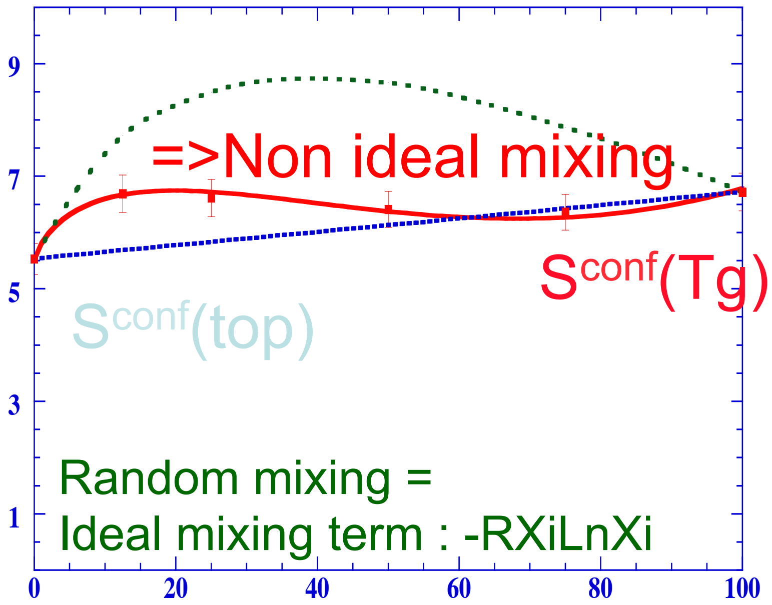
py: a "picture" of the network structure

$CaO-Na_2O-SiO_2$ system

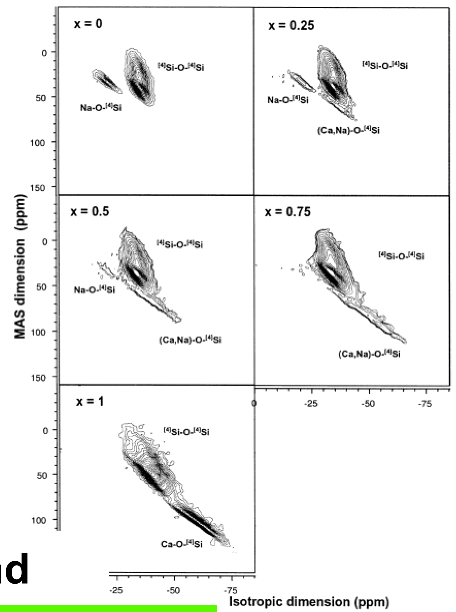








Ideal mixing does not work between Na/Ca and



Raman spectrocopy (Neuville, 2006) and ^{17}O NMR (Lee and Stebbins, 2003) show a **non random distribution of Na and Ca.**

Neuville D.R., (2005) Structure,properties in (Sr, Na) silicate glasses and melts. Phys Chem Glasses, 46, 112-119
Neuville D.R. (2006) Viscosity, structure and mixing in (Ca, Na) silicate melts. Chem. Geol., 229, 28-42

The Adam and Gibbs relaxation theory

A_e pre-exponential term
Viscosity at "infinite" temperature

B_e proportional to the energy barriers $\Delta\mu$ to viscous flow

$$\log(\eta) = A_e + \frac{B_e}{T\,S^{conf}(T)}$$

$$S^{conf}(T_g) + \int_{T_g}^{T} \frac{C_p^{conf}}{T} dt$$

Viscous flow occurs through cooperative rearrangements of subunits

The Adam and Gibbs relaxation theory

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$$S^{conf}(T_g) + \int_{T_g}^{T} \frac{C_p^{conf}}{T} dt$$

Viscous flow occurs through cooperative rearrangements of subunits

In silicate melts, viscous flow is related to exchange of oxygen by and interactions between tetrahedral SiO_4 and AlO_4 units

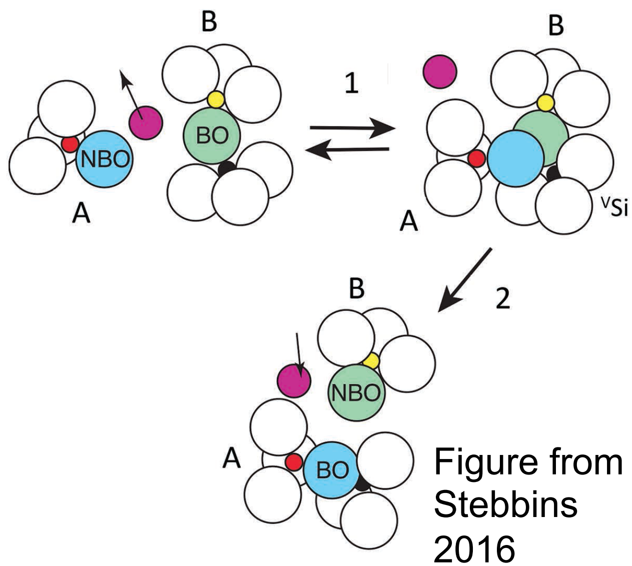
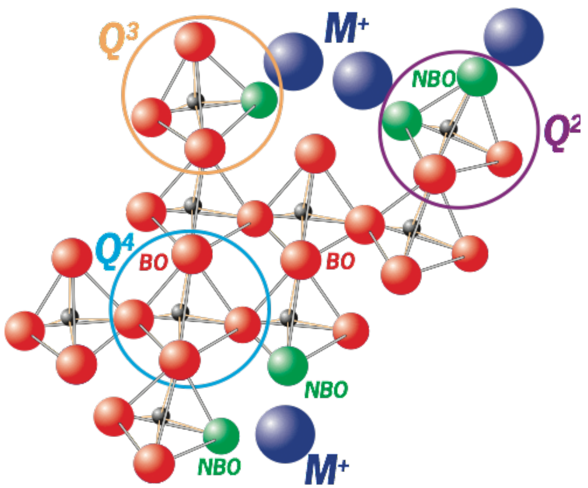


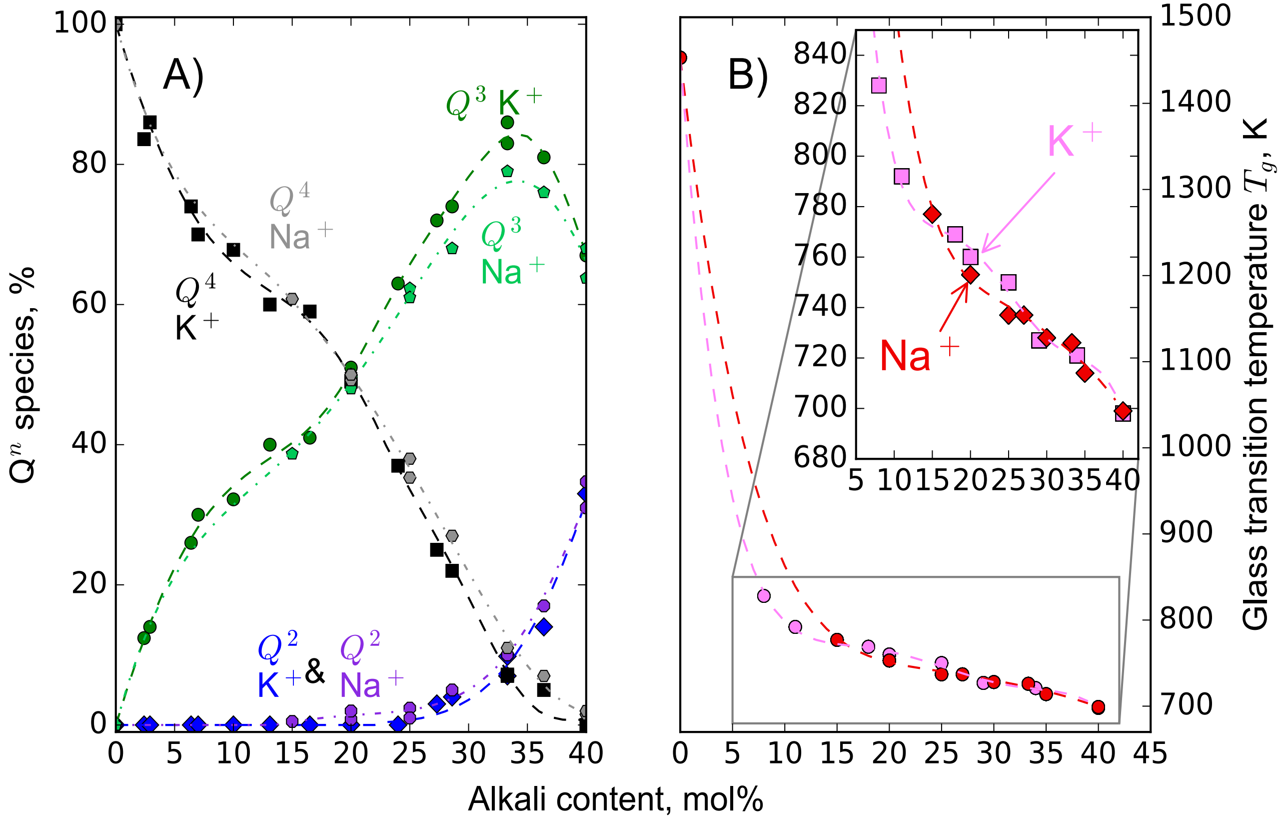
Figure from Stebbins 2016

Na_2O - K_2O - SiO_2 melts → extensive dataset

- glass and liquid heat capacity (e.g., Richet and Bottinga 1985, Richet 1987)
- glass molecular structure (e.g. from ^{29}Si NMR: Maekawa et al. 1991, Sen and Yougman 2003)
- liquid viscosity (e.g., Bockris 1954, Poole 1949, Sipp and Richet 2002, Neuville 2006)



BO:bridging oxygen
NBO: non-bridging
M+: alkali cation



Le Losq Ch., Neuville D.R. (2017) Molecular structure, configurational entropy and viscosity of silicate melts: link through the Adam and Gibbs theory of viscous flow. Journal of Non-Crystalline Solids

Linking structure, thermodynamic and rheology:

$$\log(\eta) = A_e + \frac{B_e}{T\left(S^{conf}(T_g) + \int_{T_g}^{T} \frac{C_p^{conf}}{T} dT\right)}$$

B_e and $S^{conf}(T_g)$ = sum of partial B_e and $S^{conf}(T_g)$ molar values for each tetrahedral species

Na_2SiO_3 and K_2SiO_3 (Na-Q^2 and K-Q^2)

$Na_2Si_2O_5$ and $K_2Si_2O_5$ (Na-Q^3 and K-Q^3)

SiO_2 (Q^4)

Need to add to $S^{conf}(T_g)$:

- ideal mixing of Si between Q^2, Q^3 and Q^4 units
- ideal mixing of Na and K (Richet, 1984) in network modifier channels

Need to add to B_e:

- the above ideal mixing terms, scaled by two coefficients

Le Losq Ch., Neuville D.R. (2017) Molecular structure, configurational entropy and viscosity of silicate melts: link through the Adam and Gibbs theory of viscous flow. Journal of Non-Crystalline Solids

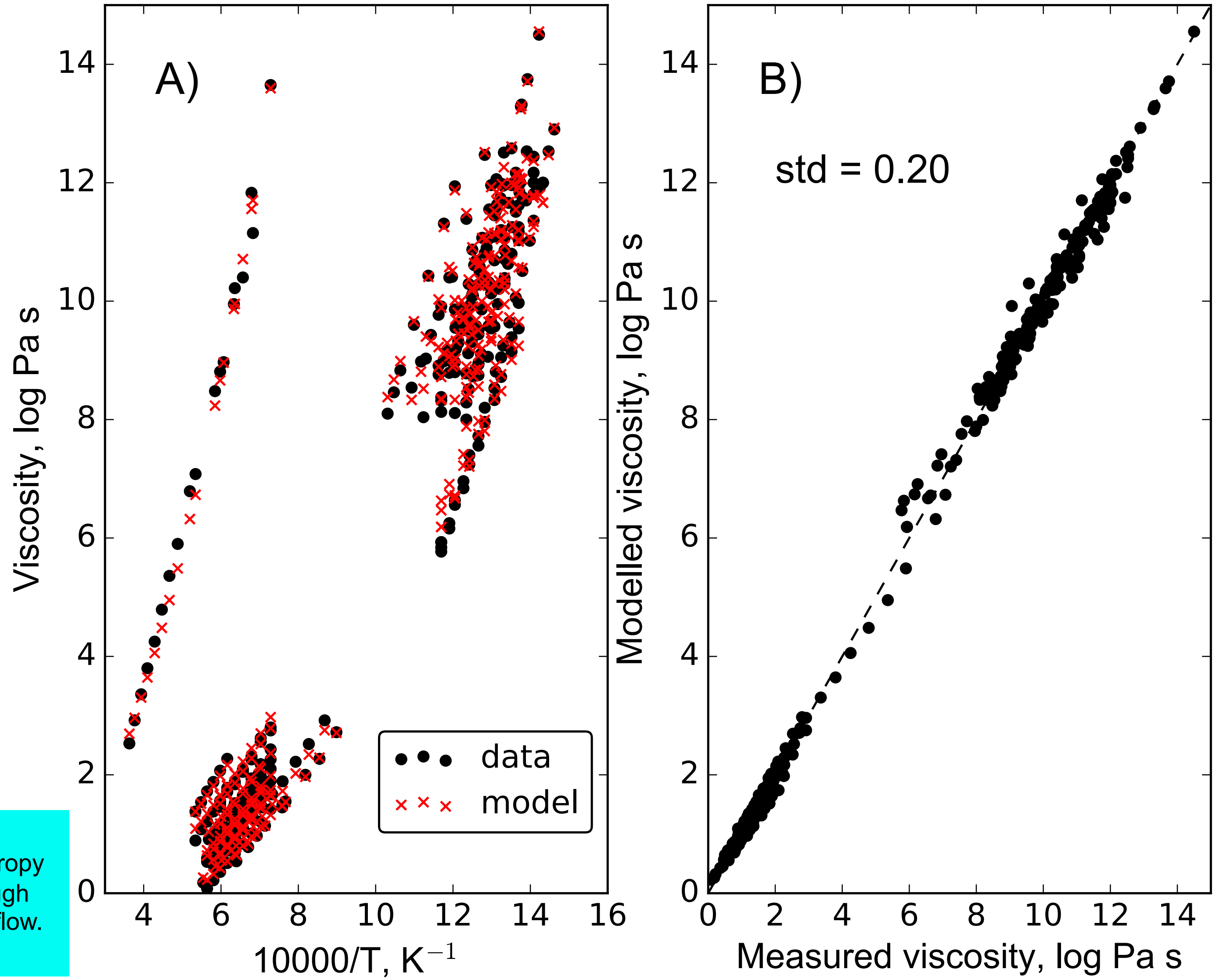
- 13 parameters, 326 data points, from 60 to 100 mol% SiO_2
- Minimisation of the least-square criterion using the Ipopt (Wächter and Biegler 2006) and Knitro (Byrd et al. 2006) solvers, and error calculation via non-parametric bootstrapping (20 000 re-sampling done)

Partial $S^{conf}(T_g)$, $J\ mol^{-1}\ K^{-1}$

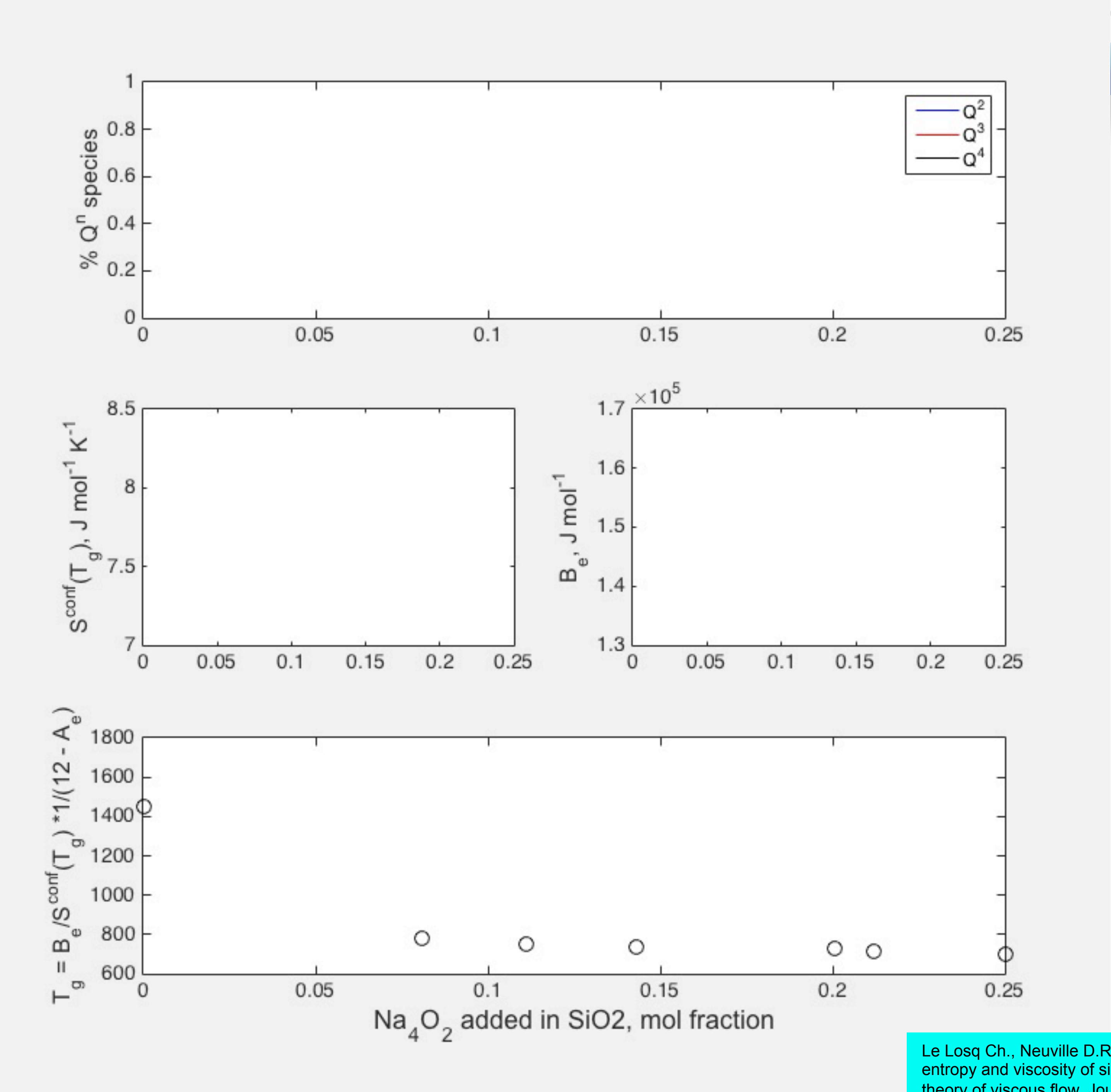
Na-Q^2:5.8 [4.8 - 6.9]
Na-Q^3: 0.9 [0.3 - 1.3]

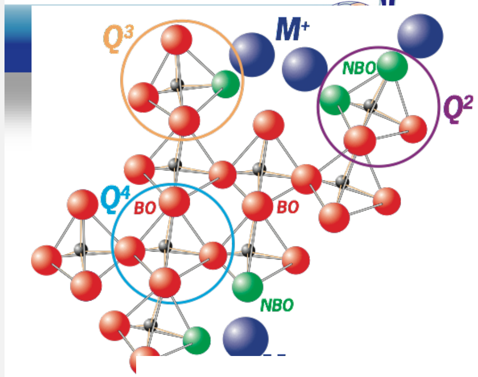
K-Q^2: 12.0 [6.8 - 20.4]
K-Q^3: 4.4 [3.3 - 5.4]

Q^4: 7.9 [7.1 - 8.4]
SiO_2 exp. is 5.1 ±2



Le Losq Ch., Neuville D.R. (2017) Molecular structure, configurational entropy and viscosity of silicate melts: link through the Adam and Gibbs theory of viscous flow. Journal of Non-Crystalline Solids





$$\log(\eta) = A_e + \frac{B_e}{T\left(S^{conf}(T_g) + \int_{T_g}^{T} \frac{C_p^{conf}}{T} dT\right)}$$

Example of model prediction along the join Na_2O-SiO_2

Le Losq Ch., Neuville D.R. (2017) Molecular structure, configurational entropy and viscosity of silicate melts: link through the Adam and Gibbs theory of viscous flow. Journal of Non-Crystalline Solids

M^+, M^{++} : Network modifier

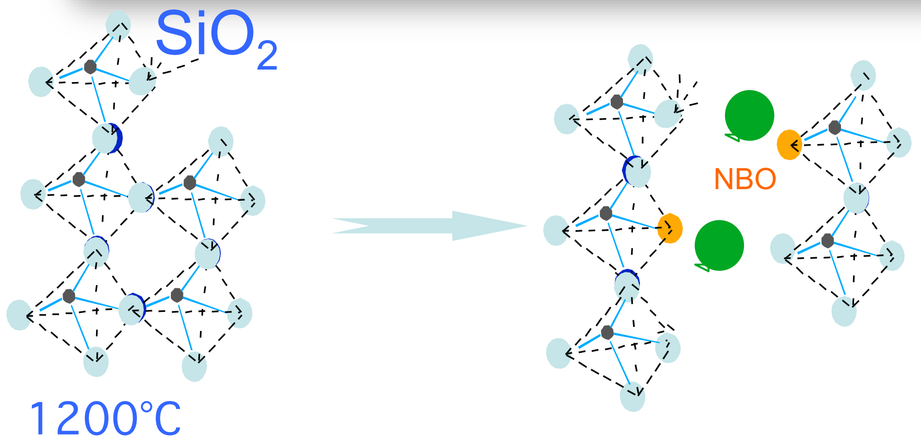
M^+, M^{++} : Network modifier => produce non-bridging oxygen,

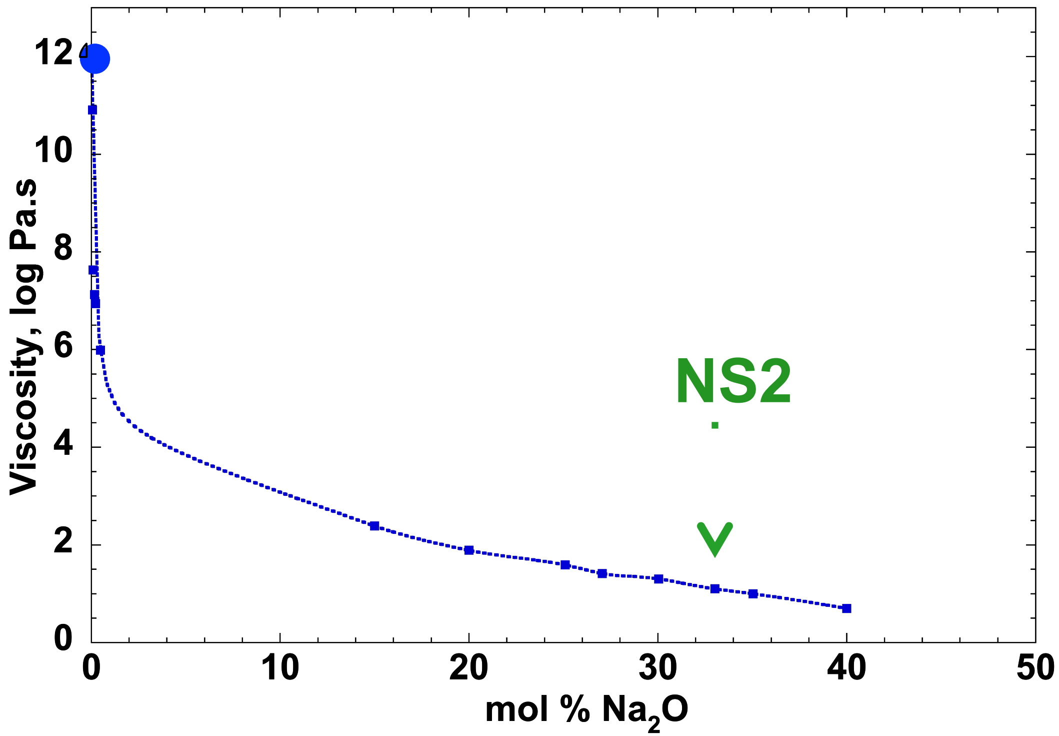
=> decrease viscosity, Tg, molar volume, ..

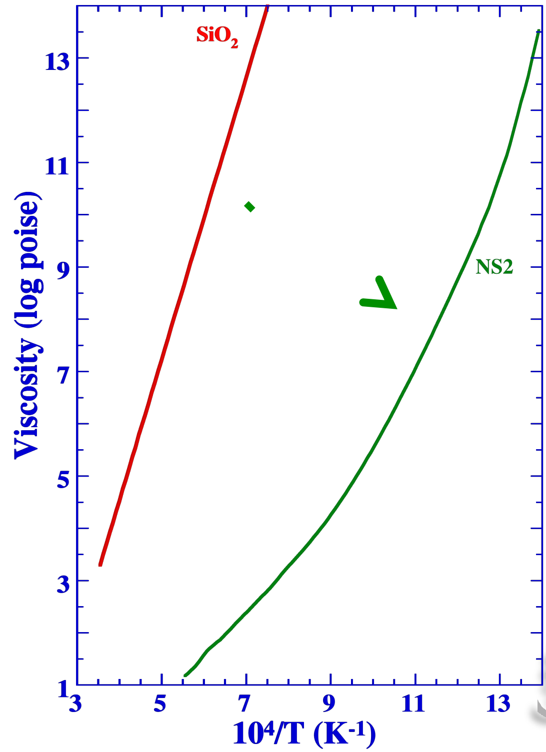
=> increase configurational entropy and disorder….

How can be change in charge compensator ?

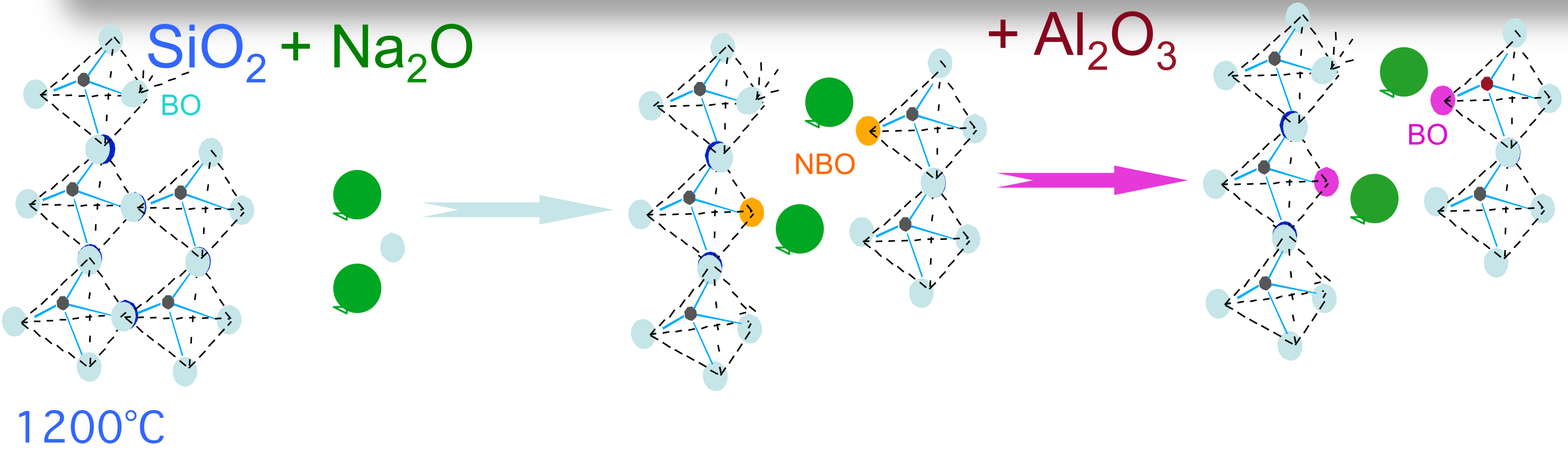
Structure versus properties of silicate melts

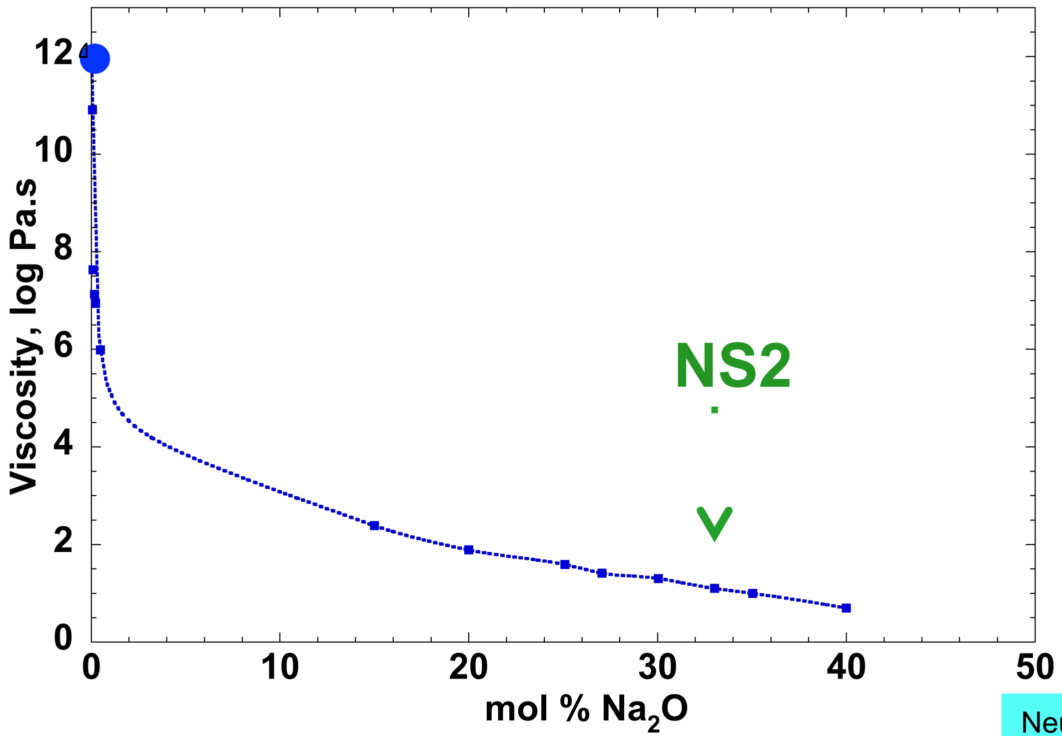


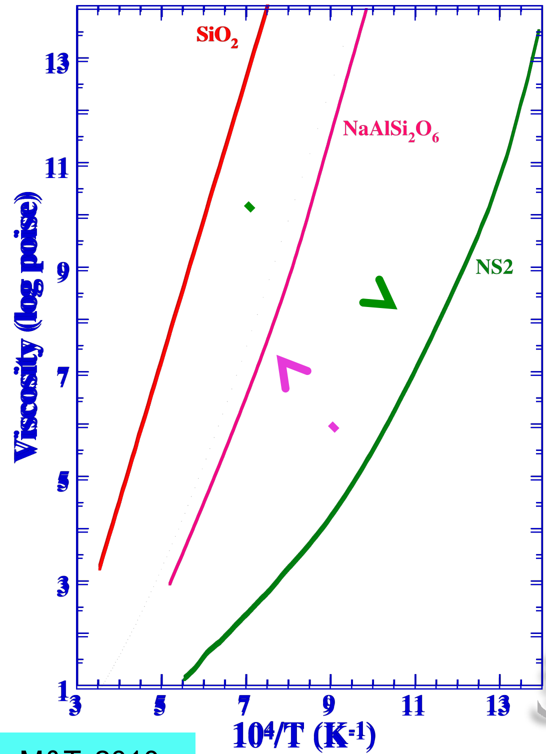




Structure versus properties of silicate melts



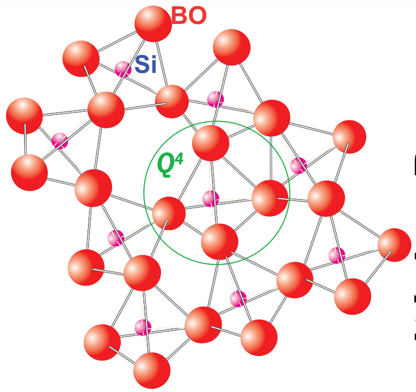


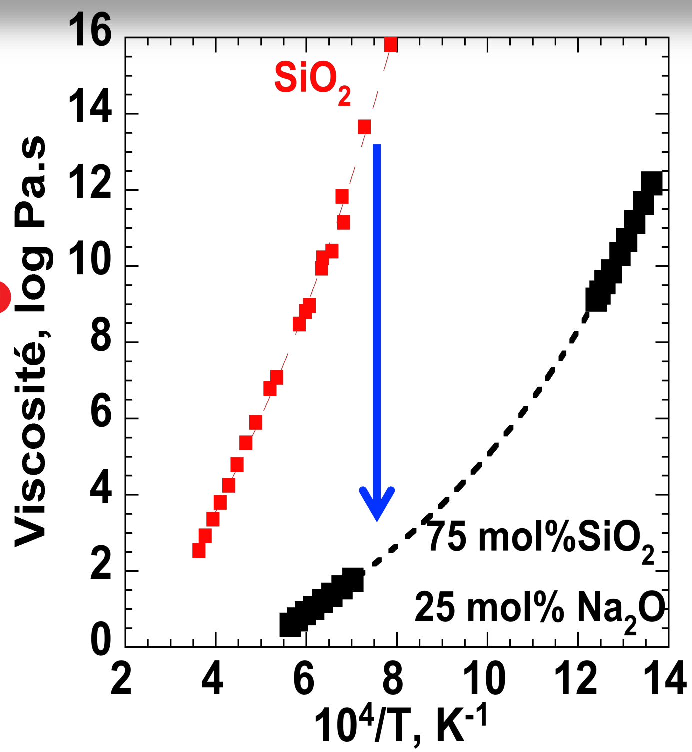


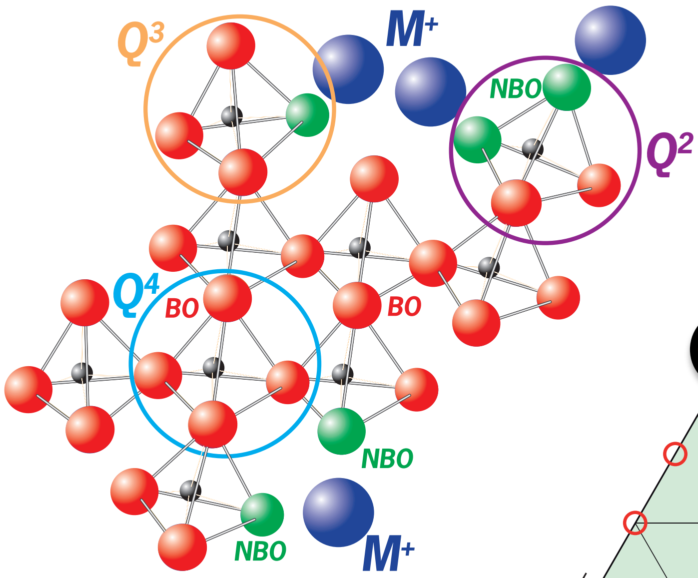
Neuville et al., M&T, 2010

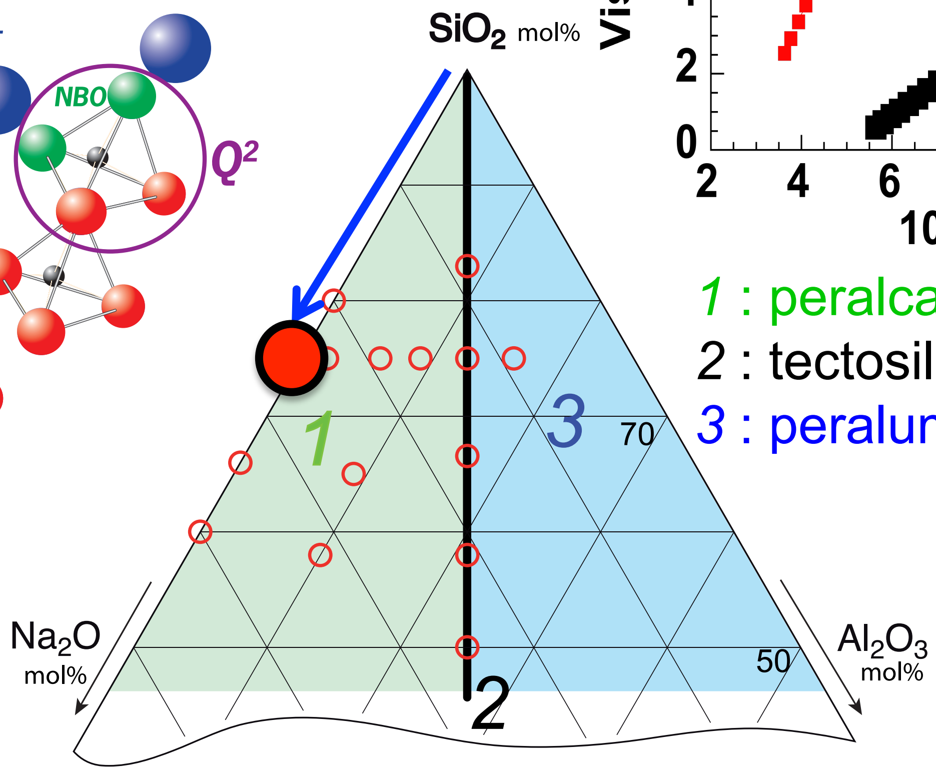
Adding Na_2O to SiO_2

⇒ Depolymerisation, formation of NBOs









1 : peralcalin: Na > Al

2 : tectosilicate: Na = Al

3 : peraluminous: Na < Al

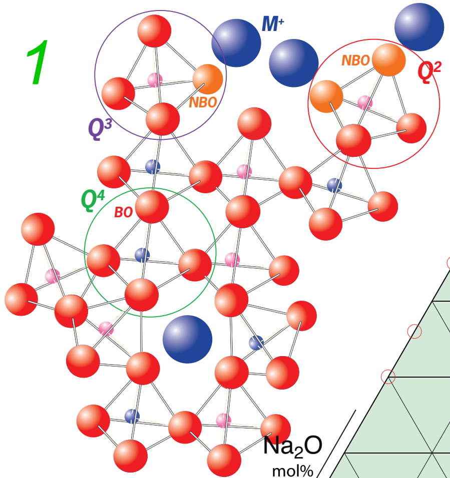
Aluminium effect

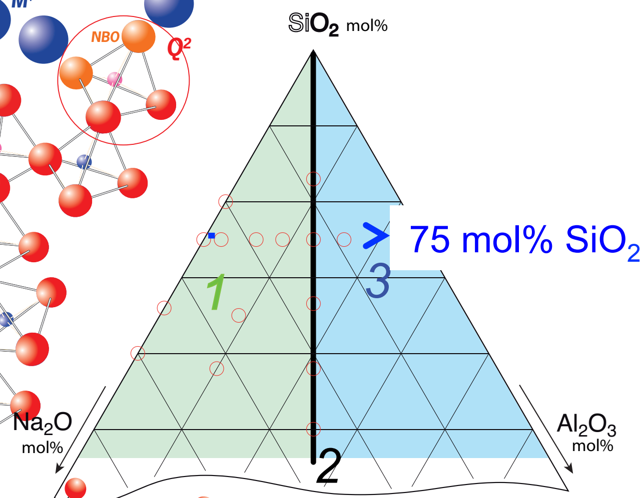
Na_2O substitution by Al_2O_3 :

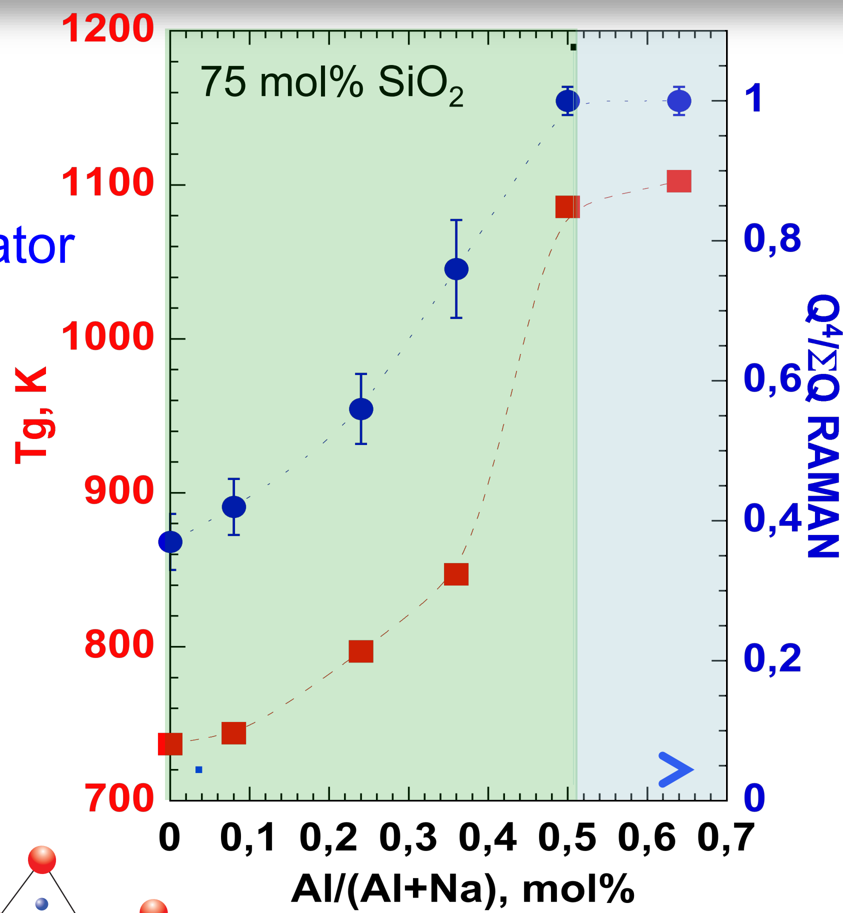
⇒ Polymerization

⇒ Change Q^3 in Q^4

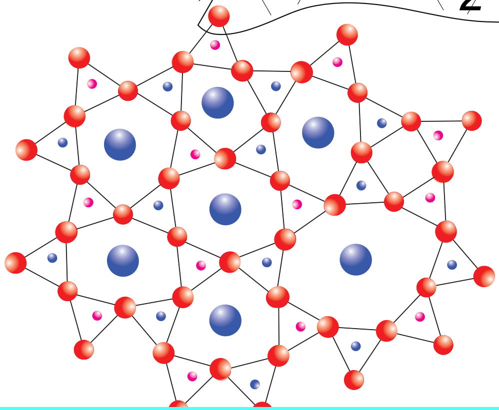
⇒ Al in Q^4 and Na charge compensator

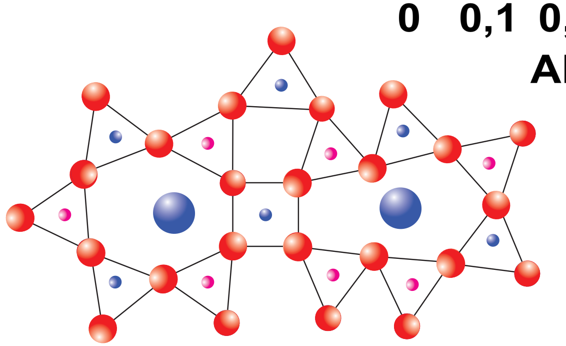






2





Al in CN 5 in peraluminous domain (3)

Le Losq Ch., Neuville D.R., Florian P., G.S. Henderson and Massiot D. (2014) Role of Al^{3+} on rheology and nano-structural changes of sodium silicate and aluminosilicate glasses and melts. Geochimica Cosmochimica Acta, 126, 495-517

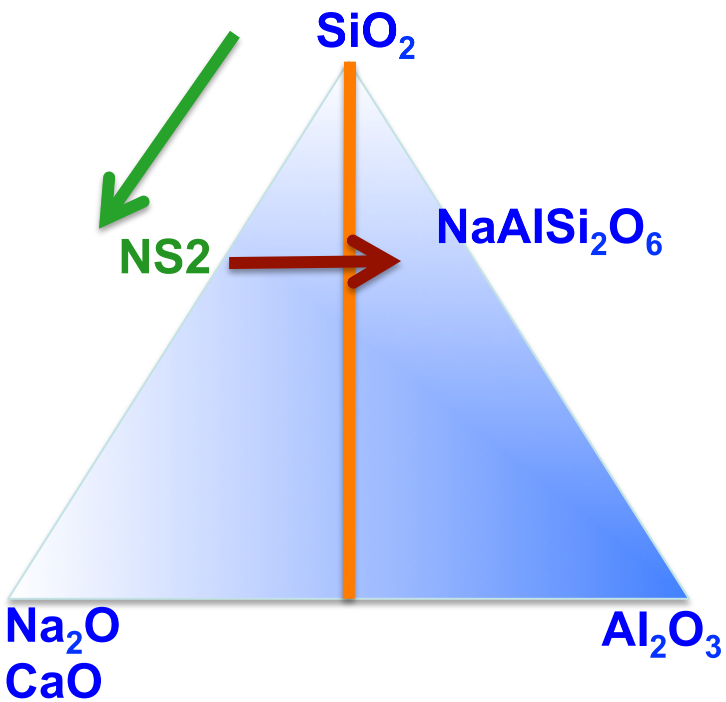
In summary:

Si^{4+}, Al^{3+} network former

O bridging or non-bridging oxygen

Na^{+}, Ca^{++}, network modifier

or charge compensator



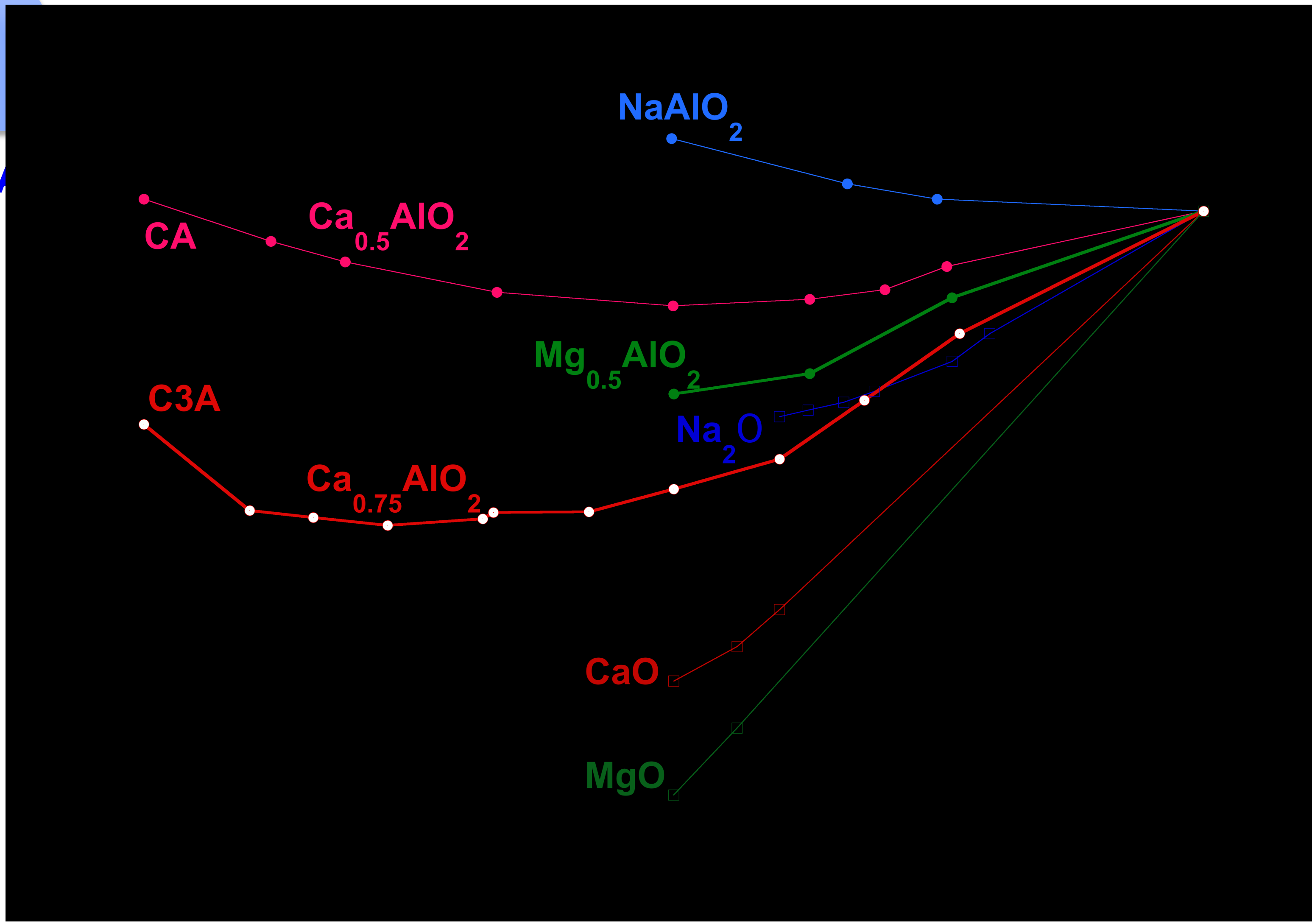
$MO-Al_2O_3-SiO_2$ Molar volume

SiO_2

Na_2O

CaO

MgO

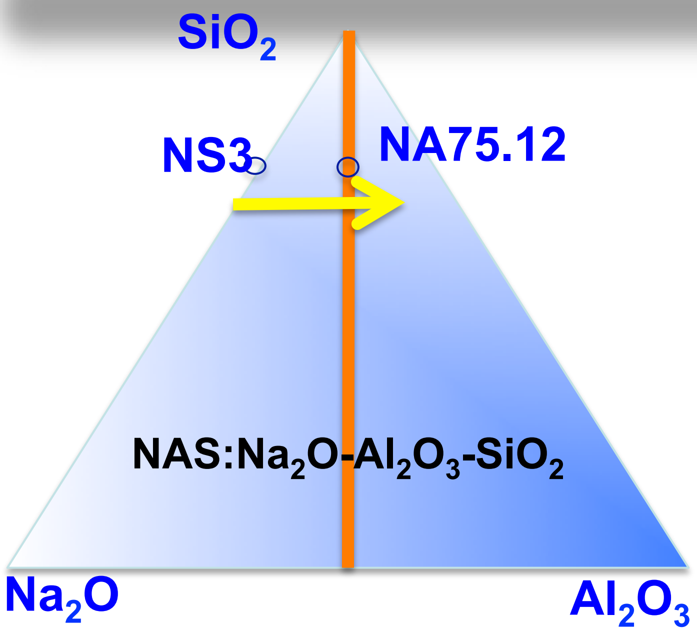


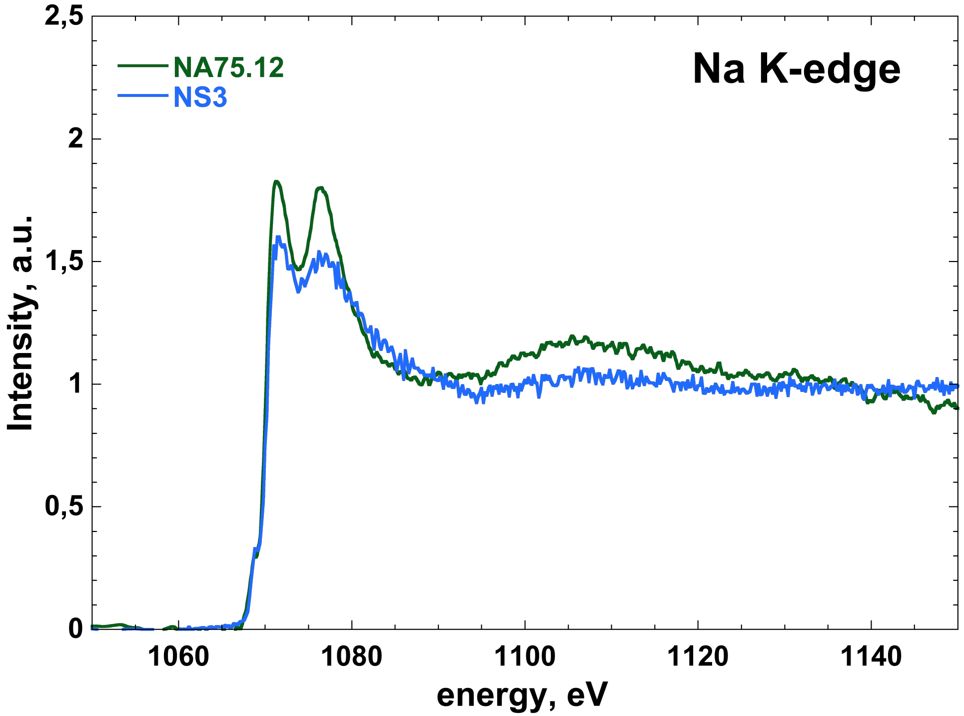
SiO_4

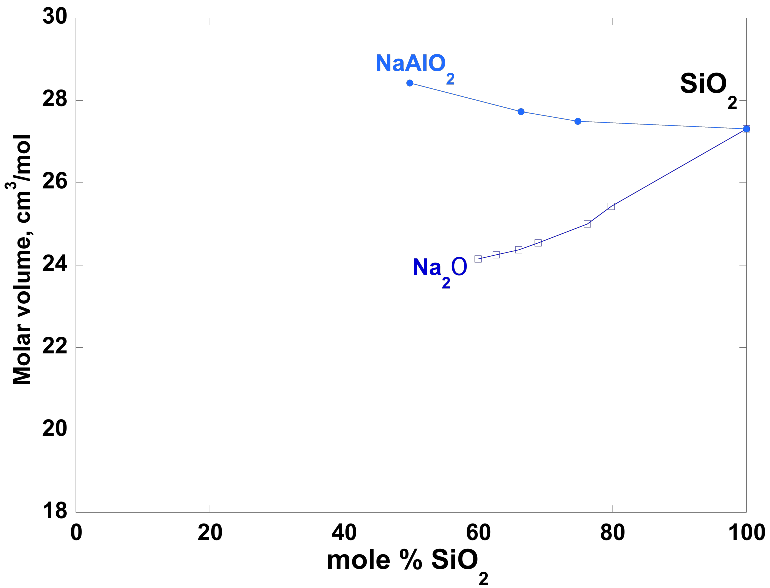
AlO_4^-

Na_2O-Al_2O_3-SiO_2

XANES at the Na K-edge







NS3 => [6]Na

NA75.12 => [9]Na

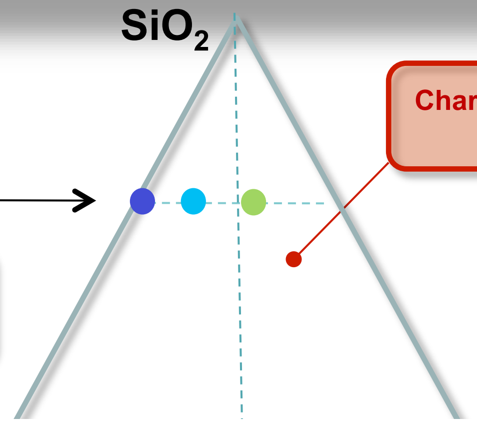
Neuville D.R., Cormier L, R., Flank A.M., Prado R.J. and Lagarde P. (2004) Na K-edge XANES spectra of minerals and glasses. Eur. J Mineral, 16, 809-816.

$Na_2O-Al_2O_3-SiO_2$ NMR : IR RMN CEMHTI-CNRS, Orléans

$x SiO_2$: **(1-y)Na_2O** : **y**Al_2O_3

***x*=0.67**

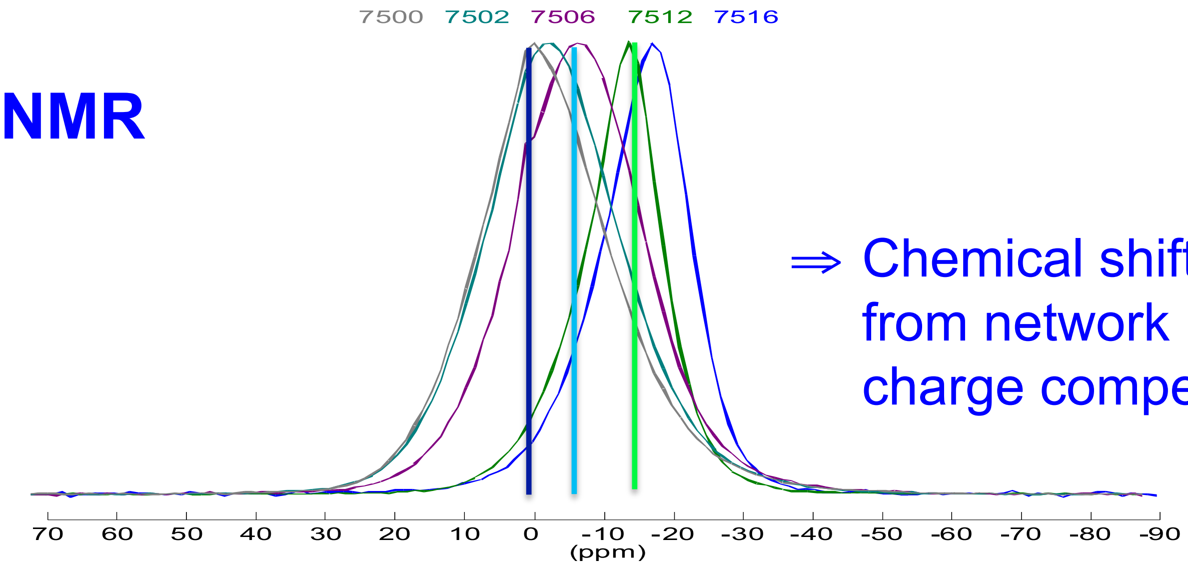
Na : Network modifier



Charge compensator region

NAS:$Na_2O-Al_2O_3-SiO_2$

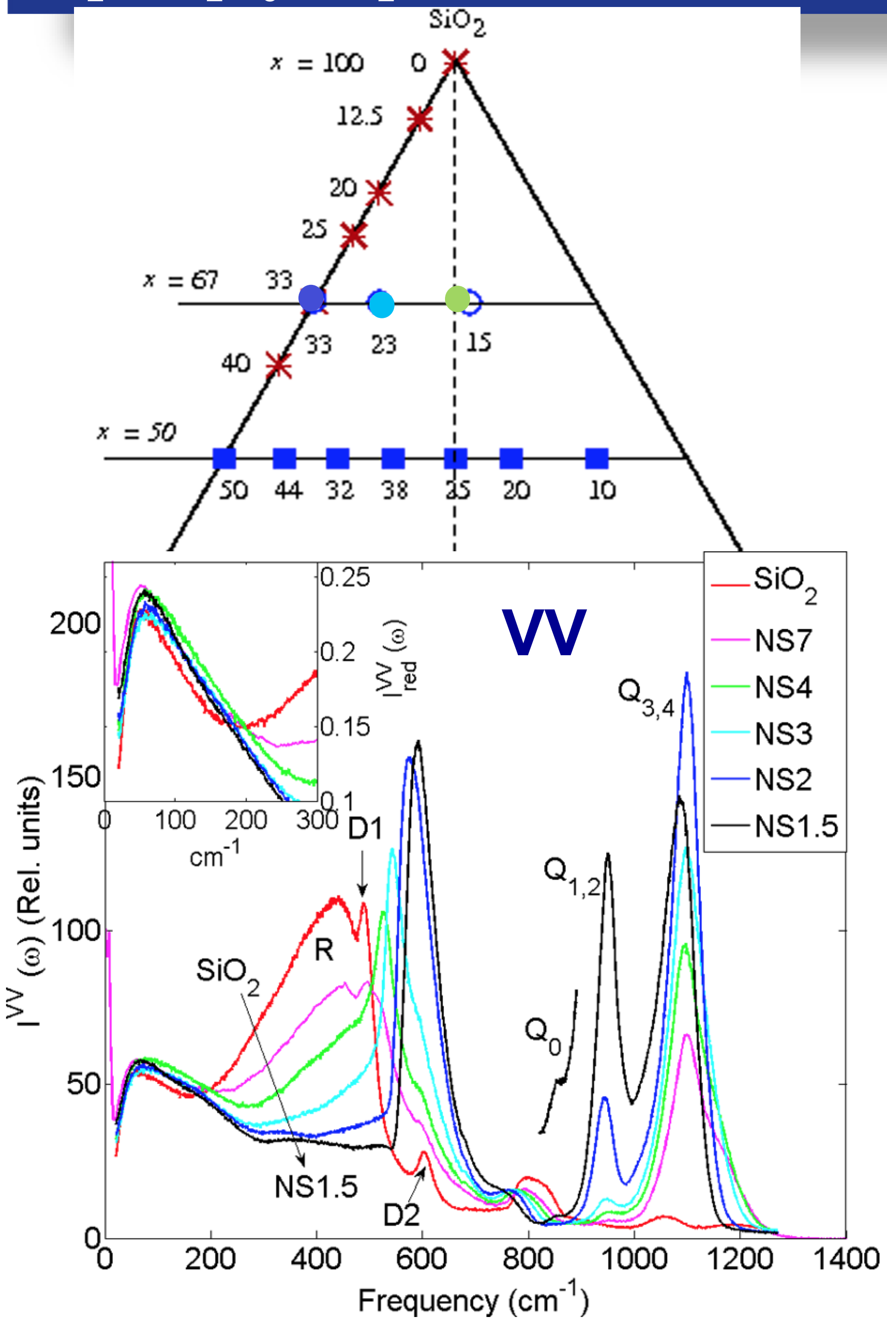
^{23}Na NMR

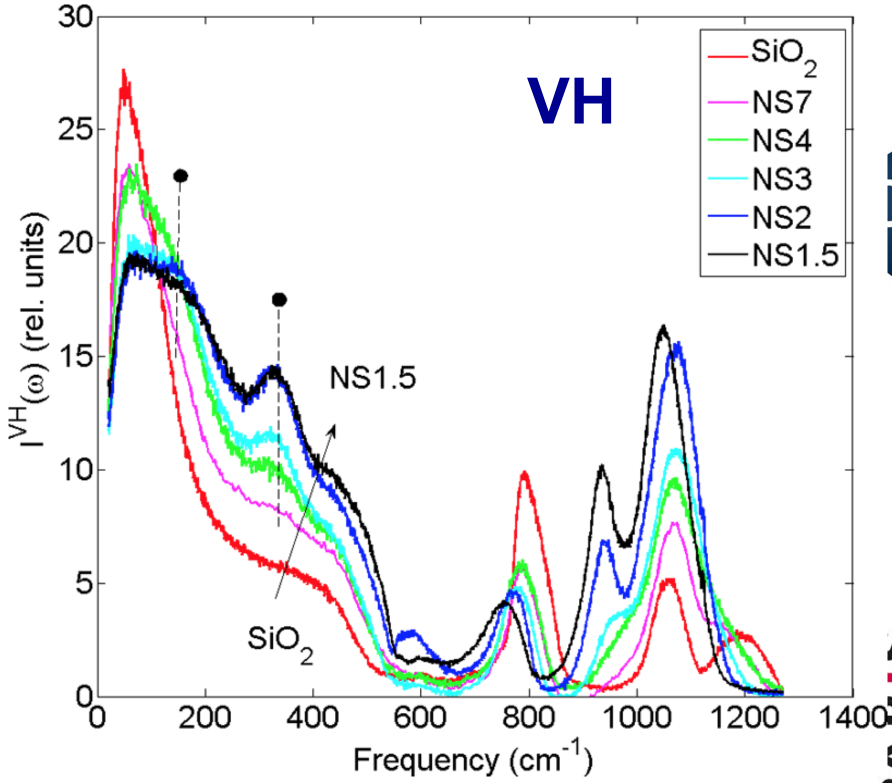


⇒ Chemical shift of 23Na, from network modifyer to charge compensator

Le Losq Ch., Neuville D.R., Florian P., G.S. Henderson and Massiot D. (2014) Role of Al3+ on rheology and nano-structural changes of sodium silicate and aluminosilicate glasses and melts. Geochimica Cosmochimica Acta, 126, 495-517.

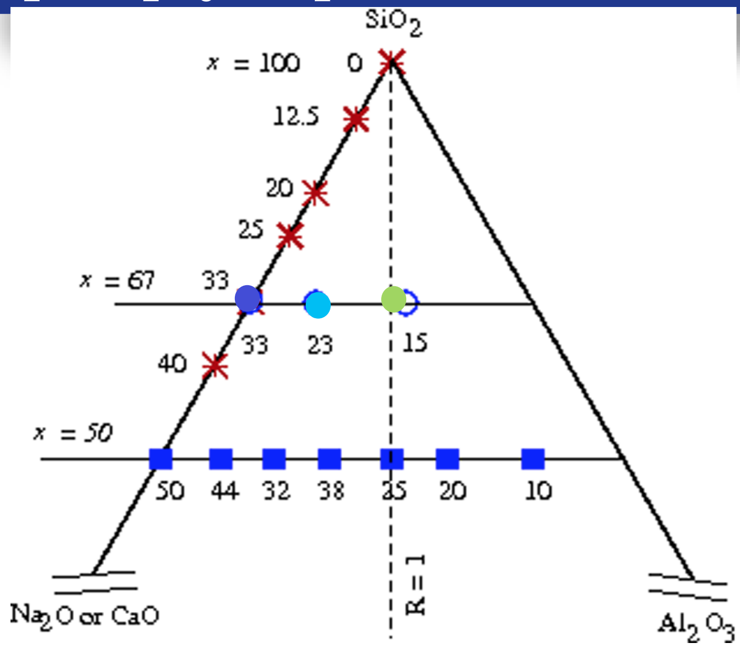
$Na_2O-Al_2O_3-SiO_2$ Raman spectrometry VV and VH



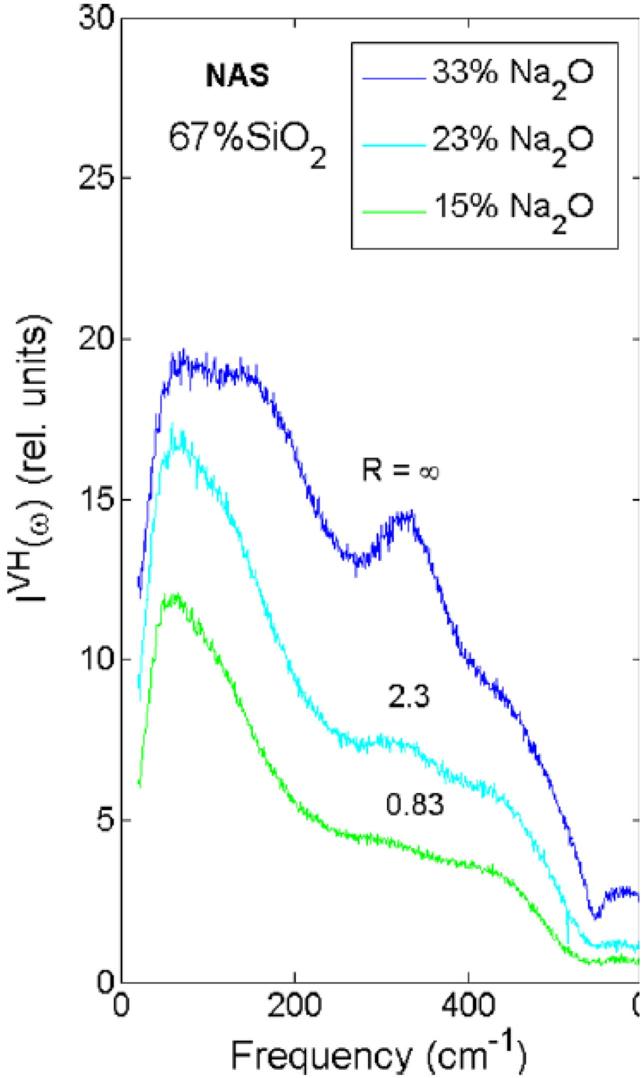


Hehlen B. and Neuville D.R. (2015) Raman response of network modifier cations in alumino-silicate glasses. The Journal of Physical Chemistry B. 119, 4093–4098.

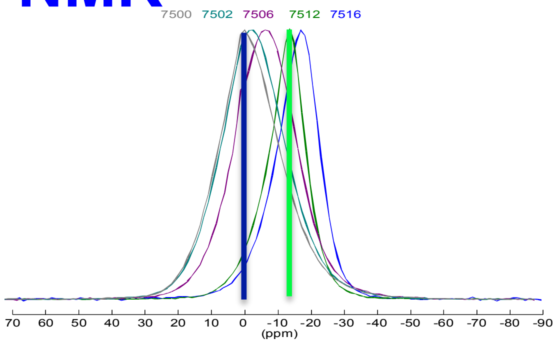
Na_2O-Al_2O_3-SiO_2 Raman spectrometry VV and VH



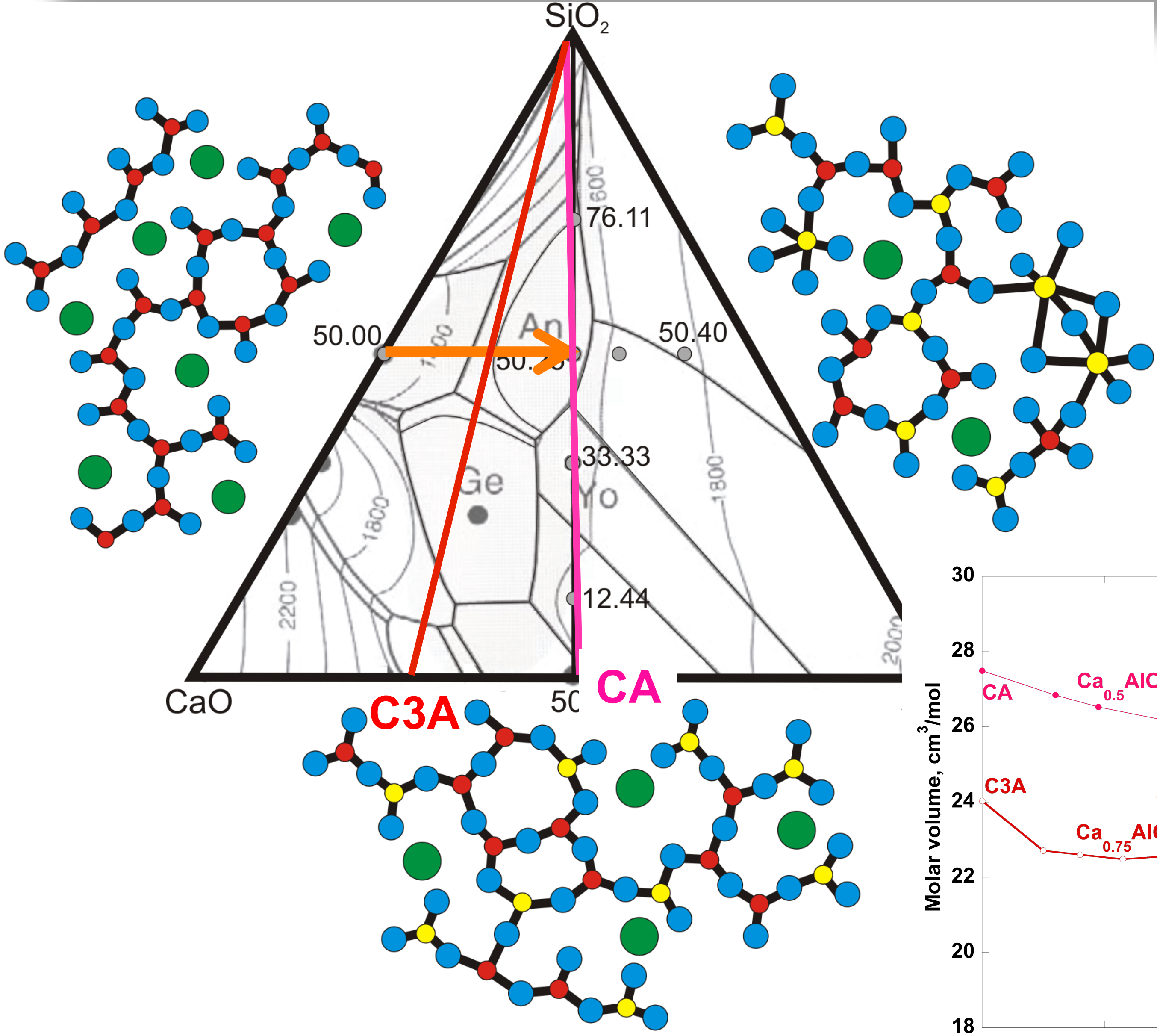
Hehlen B. and Neuville D.R. (2015) Raman response of network modifier cations in alumino-silicate glasses. The Journal of Physical Chemistry B. 119, 4093–4098.

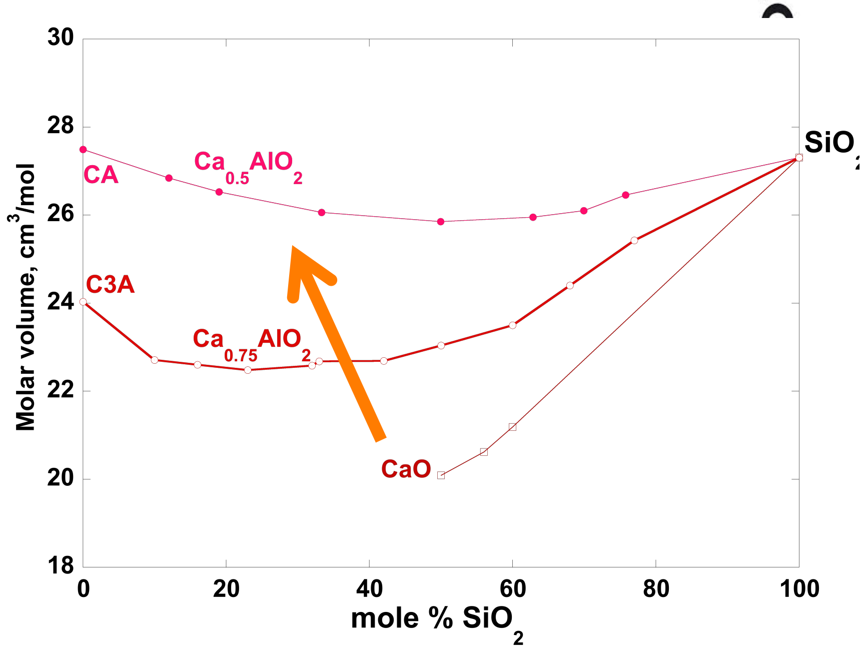


^{23}Na NMR



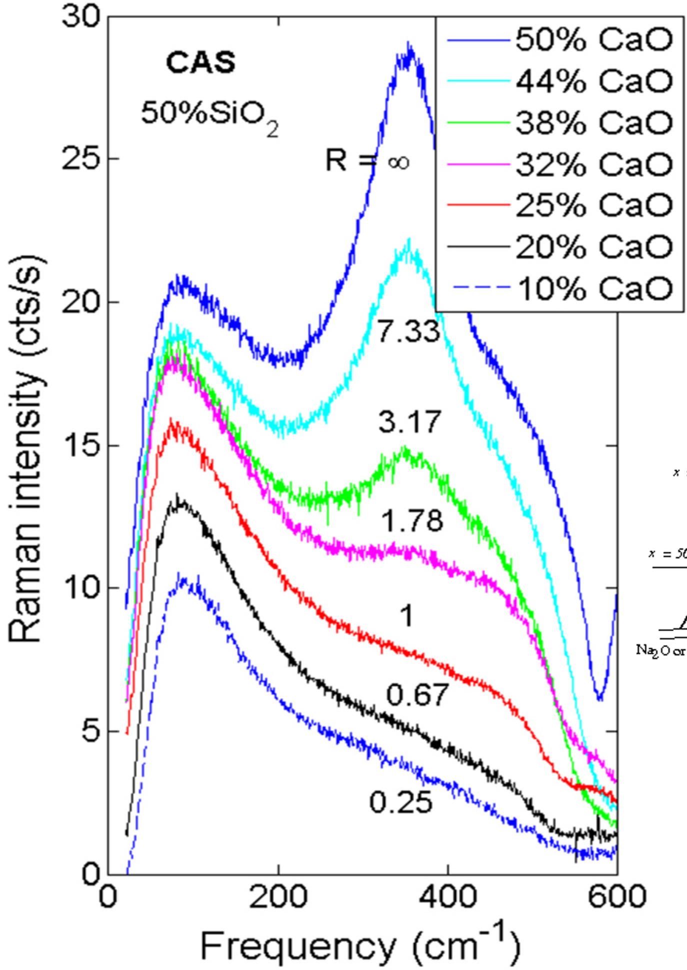
CAS glass system

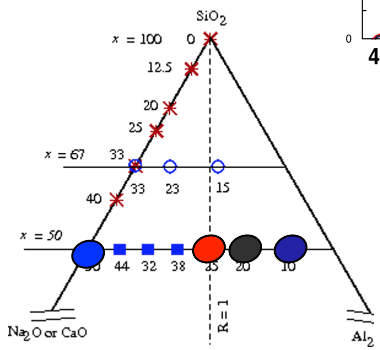


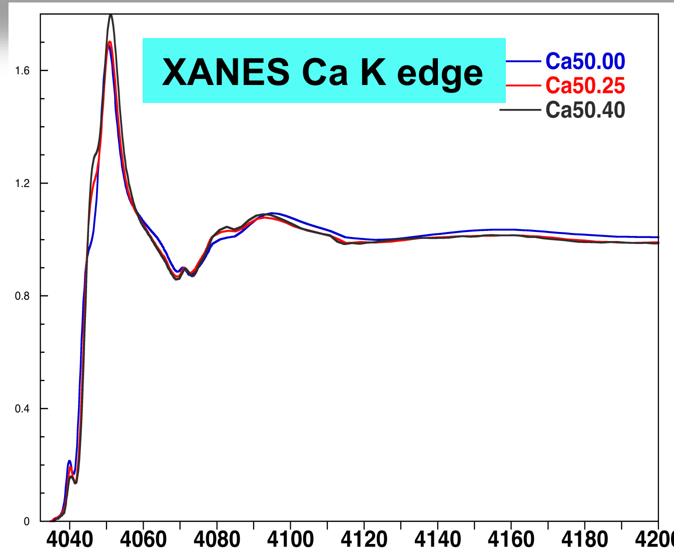


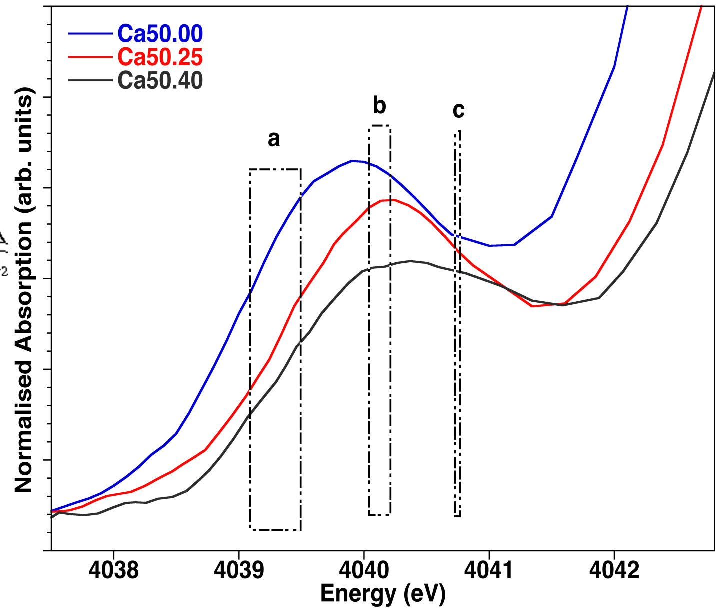
Modifier/compensator state of cations

Raman VH





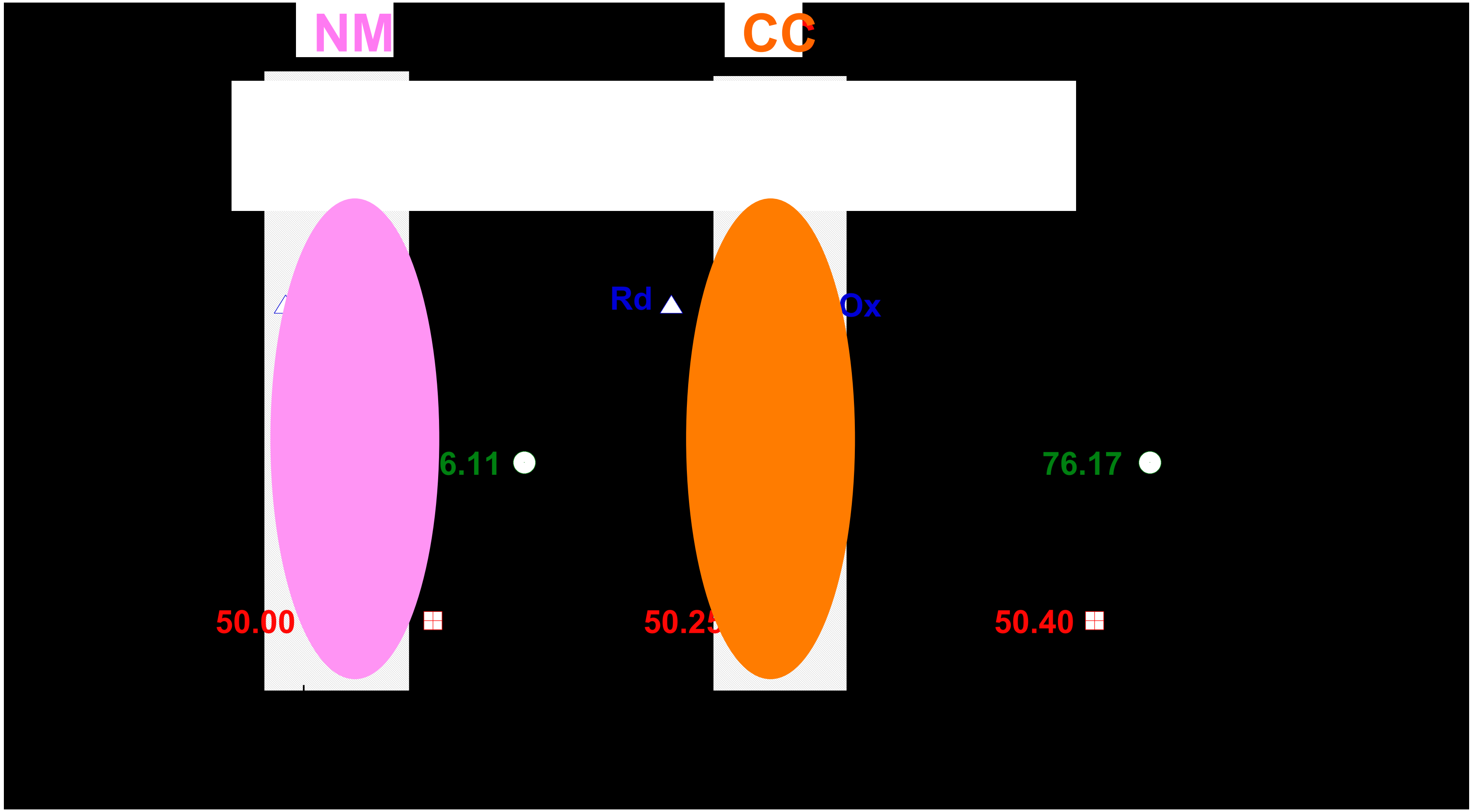




Hehlen B. and Neuville D.R. (2015) Raman response of network modifier cations in alumino-silicate glasses. The Journal of Physical Chemistry B. 119, 4093–4098.

Cicconi M.R., de Ligny D., Gallo T. M., Neuville D.R. (2016) Ca Neighbors from XANES spectroscopy: a tool to investigate structure, redox and nucleation processes in silicate glasses, melts and crystals. American Mineralogist, 101, 1232-1236.

XANES at the Ca K-edge

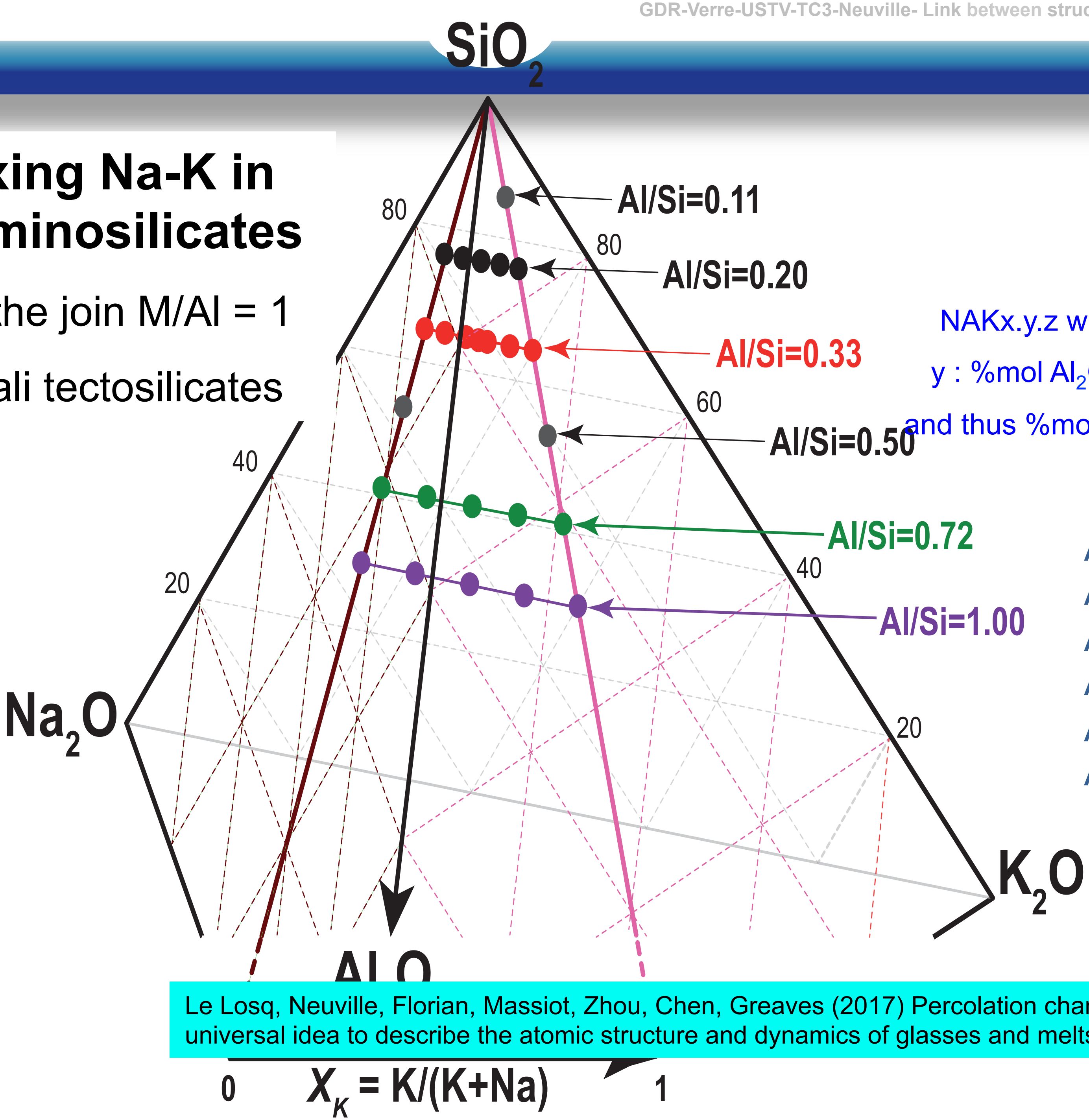


Cicconi M.R., de Ligny D., Gallo T. M., Neuville D.R. (2016) Ca Neighbors from XANES spectroscopy: a tool to investigate structure, redox and nucleation processes in silicate glasses, melts and crystals. American Mineralogist, 101, 1232-1236.

Mixing Na-K in aluminosilicates

On the join M/Al = 1

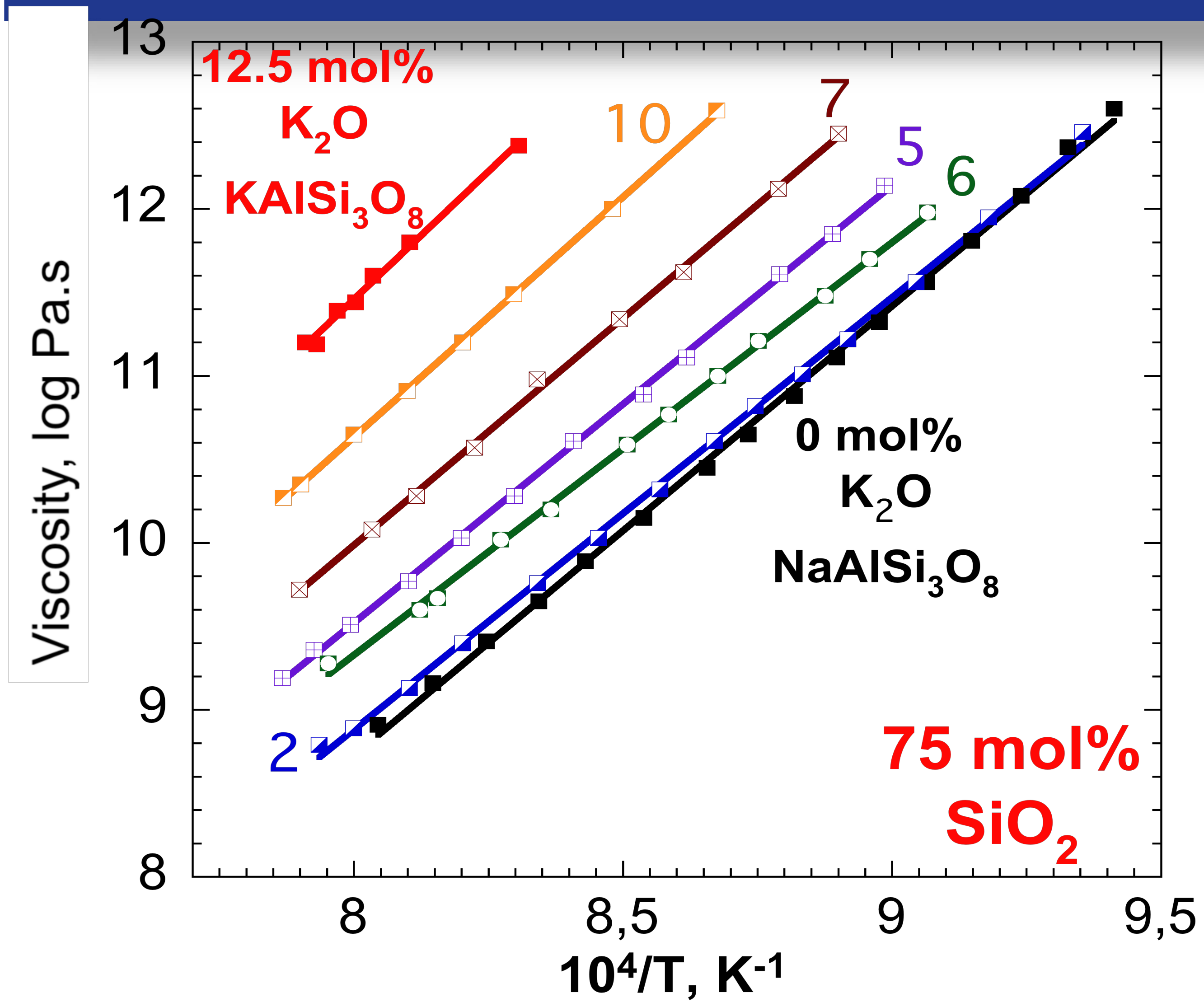
Alkali tectosilicates



NAKx.y.z with x : %mol SiO_2 ; y : %mol Al_2O_3 ; z : %mol K_2O ; and thus %mol Na_2O = 100-(x+y+z)

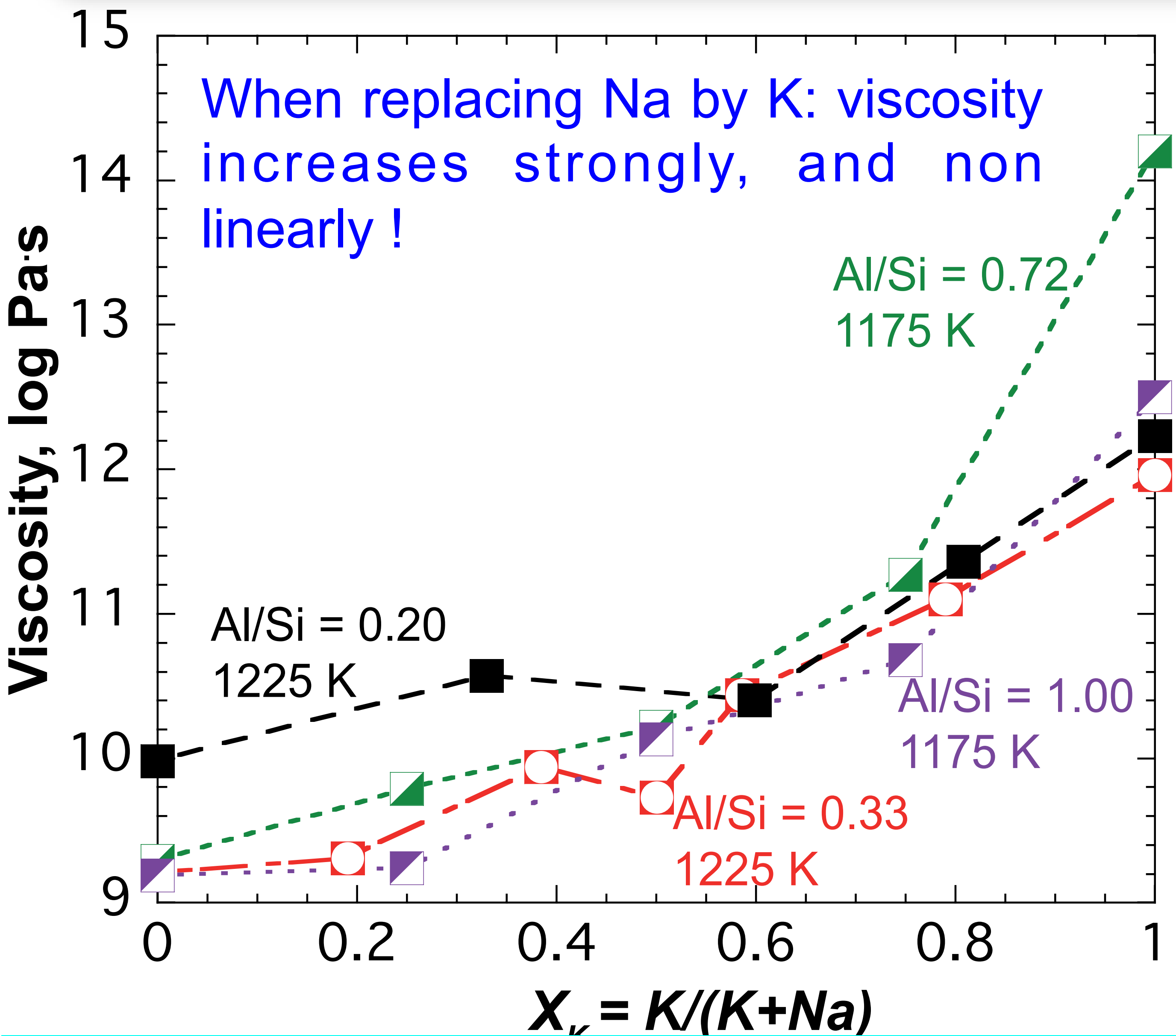
Al/Si=0.11 =90%S
Al/Si=0.20 =83%S
Al/Si=0.33 =75%S
Al/Si=0.50 =66%S
Al/Si=0.72 =58%S
Al/Si=1.00 =50%S

Le Losq, Neuville, Florian, Massiot, Zhou, Chen, Greaves (2017) Percolation channels: a universal idea to describe the atomic structure and dynamics of glasses and melts. PNAS



When replacing Na by K: viscosity increases strongly…

Losq C. and Neuville D.R. (2013) Effect of K/Na mixing on the structure and rheology of tectosilicate silica-rich melts. Chemical Geology, 346, 57-71.

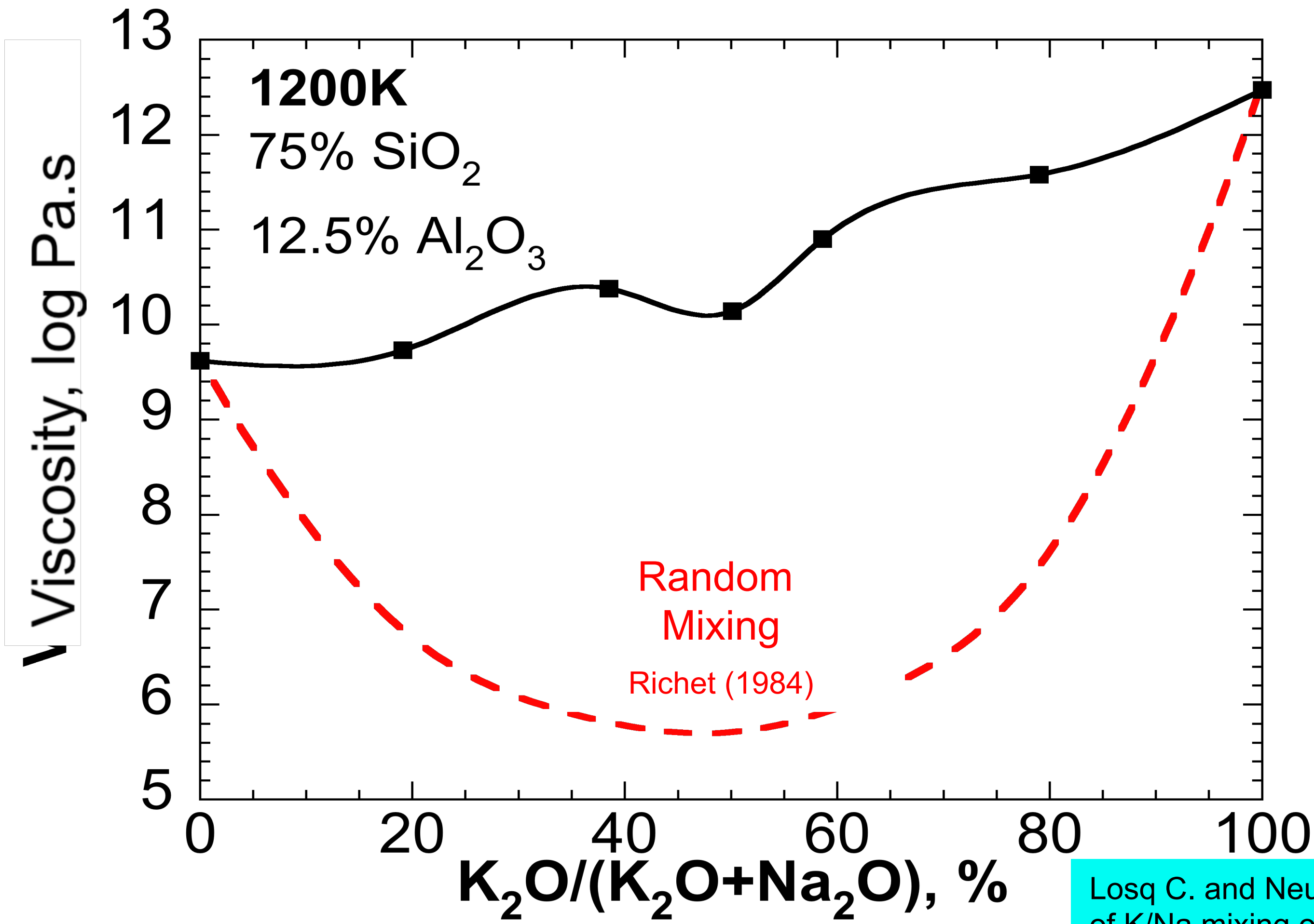


Al/Si=0.11 =90% SiO_2
Al/Si=0.20 =83% SiO_2
Al/Si=0.33 =75% SiO_2
Al/Si=0.50 =66% SiO_2
Al/Si=0.72 =58% SiO_2
Al/Si=1.00 =50% SiO_2

Le Losq, Neuville, Florian, Massiot, Zhou, Chen, Greaves (2017) Percolation channels: a universal idea to describe the atomic structure and dynamics of glasses and melts. PNAS

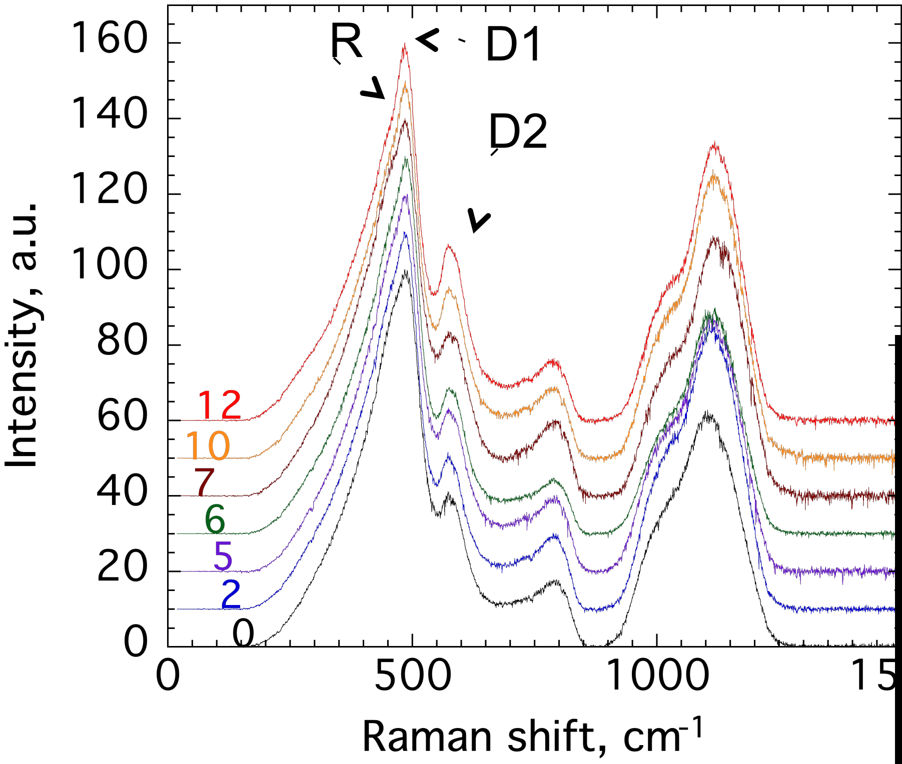
Mixed albite-orthoclase melts $NaAlSi_3O_8$-$KAlSi_3O_8$

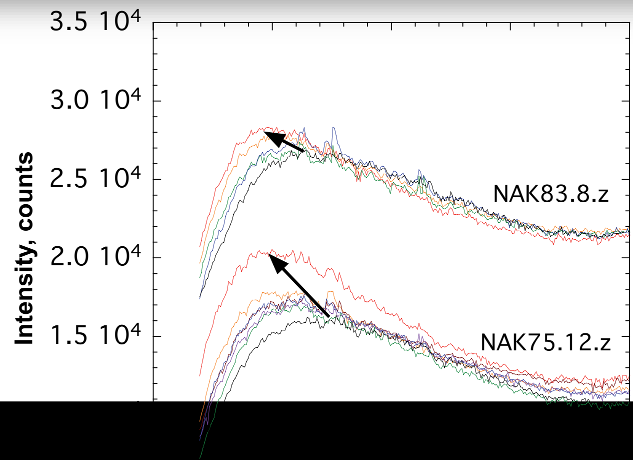
75 mol% SiO_2

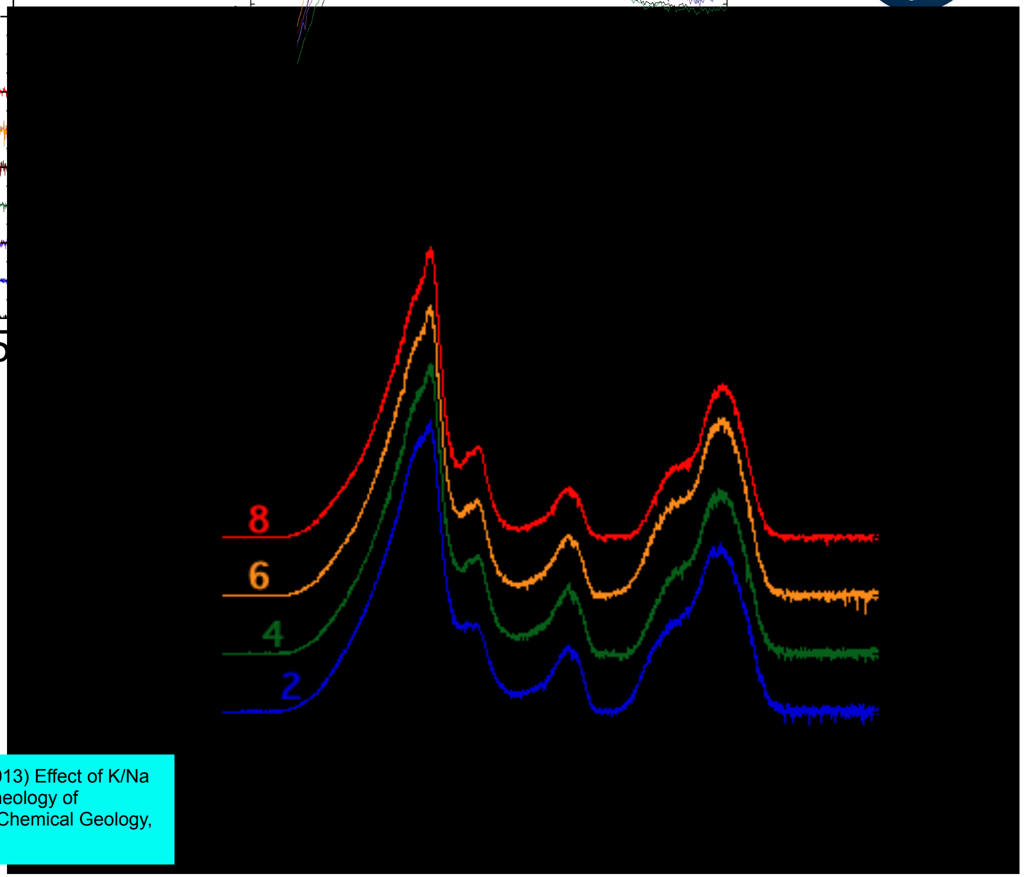


Na and K do not mix randomly
⇒ Viscosity, thermodynamics
⇒ Structure

Losq C. and Neuville D.R. (2013) Effect of K/Na mixing on the structure and rheology of tectosilicate silica-rich melts. Chemical Geology, 346, 57-71.

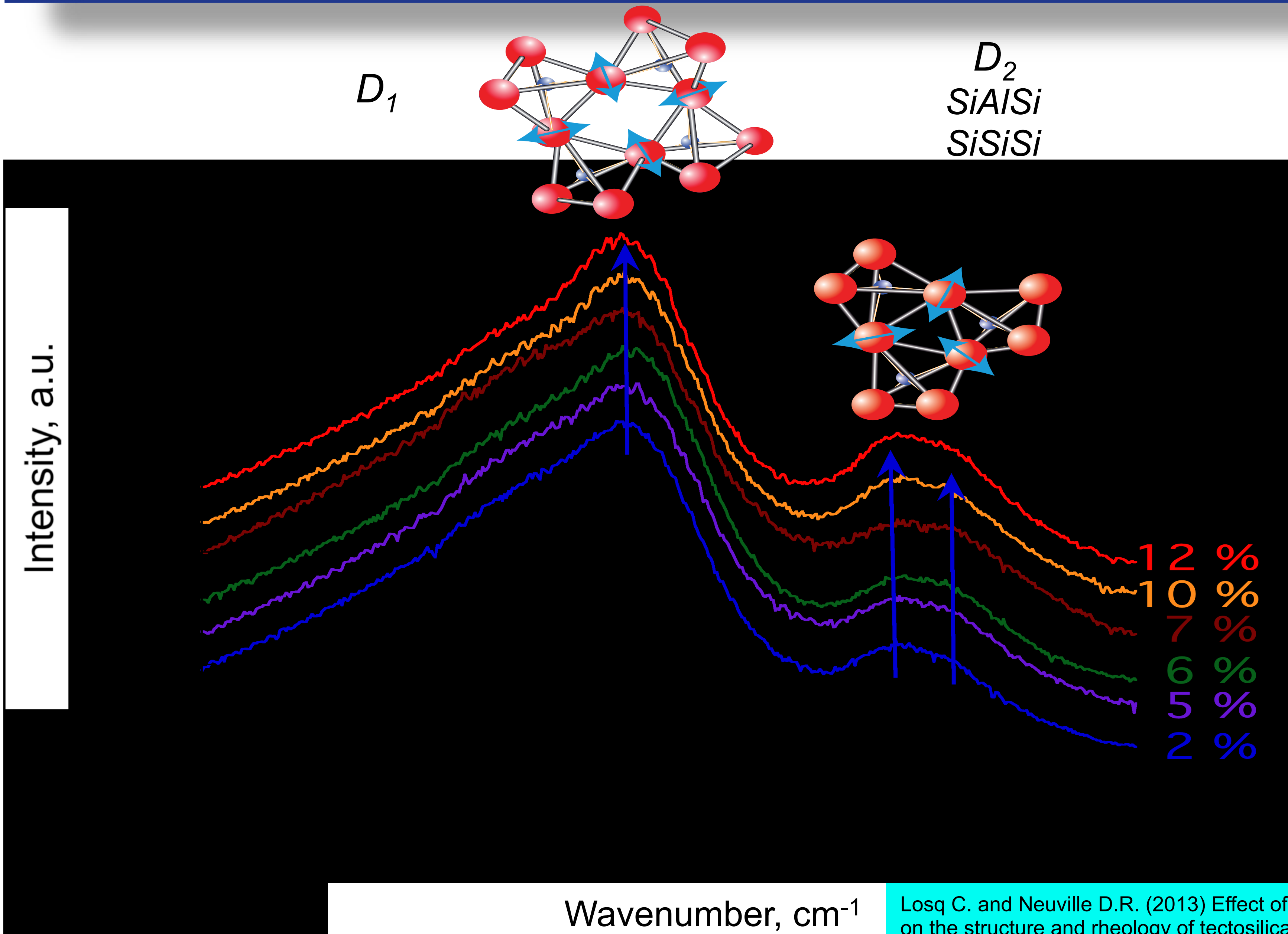




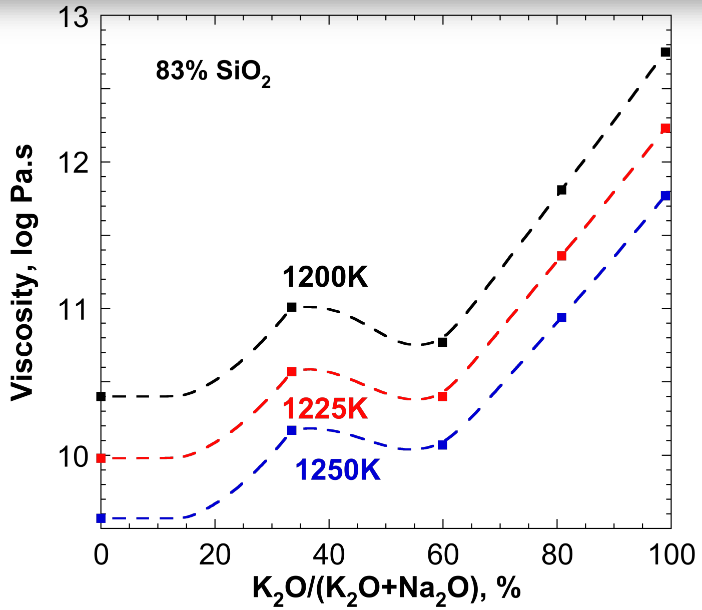


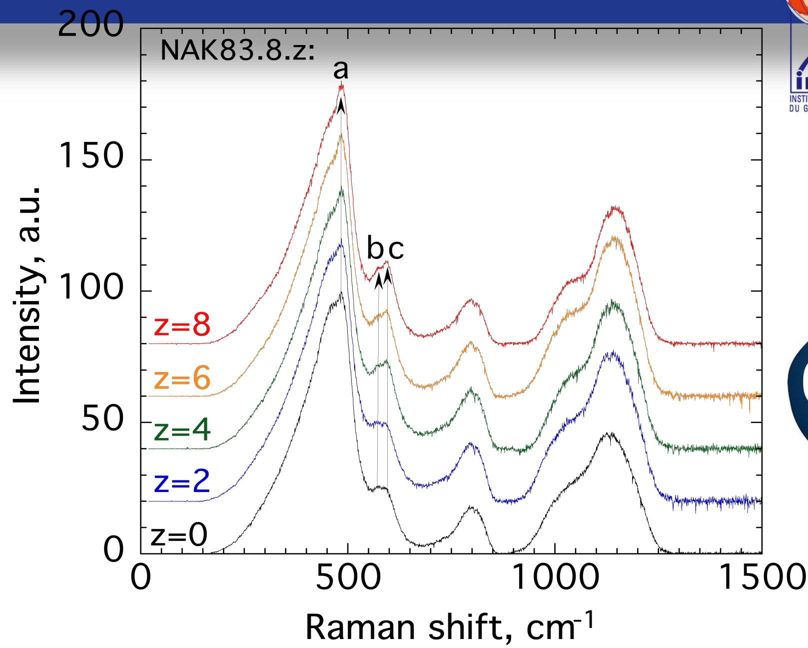
- Boson peak increase in I and decreases in frequency with K like close than SiO2
- D1 and D2 increase with K
- New D2 band

Losq C. and Neuville D.R. (2013) Effect of K/Na mixing on the structure and rheology of tectosilicate silica-rich melts. Chemical Geology, 346, 57-71.

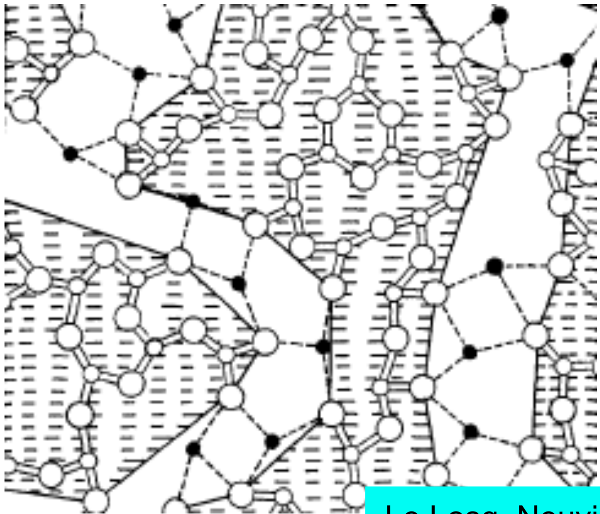


Losq C. and Neuville D.R. (2013) Effect of K/Na mixing on the structure and rheology of tectosilicate silica-rich melts. Chemical Geology, 346, 57-71.

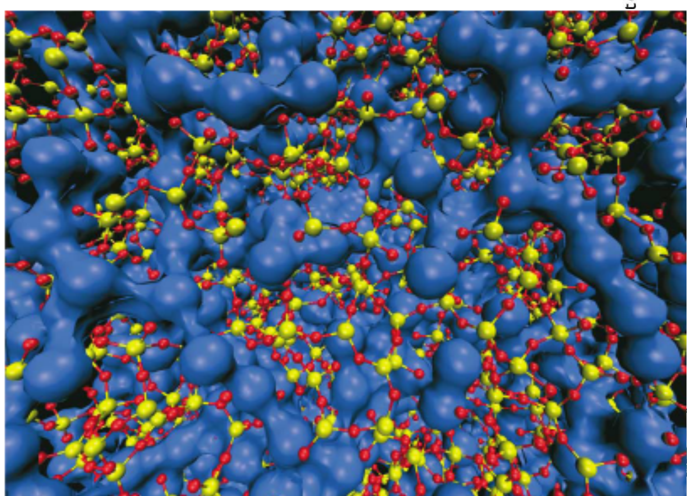




Greaves, 1985: MRN

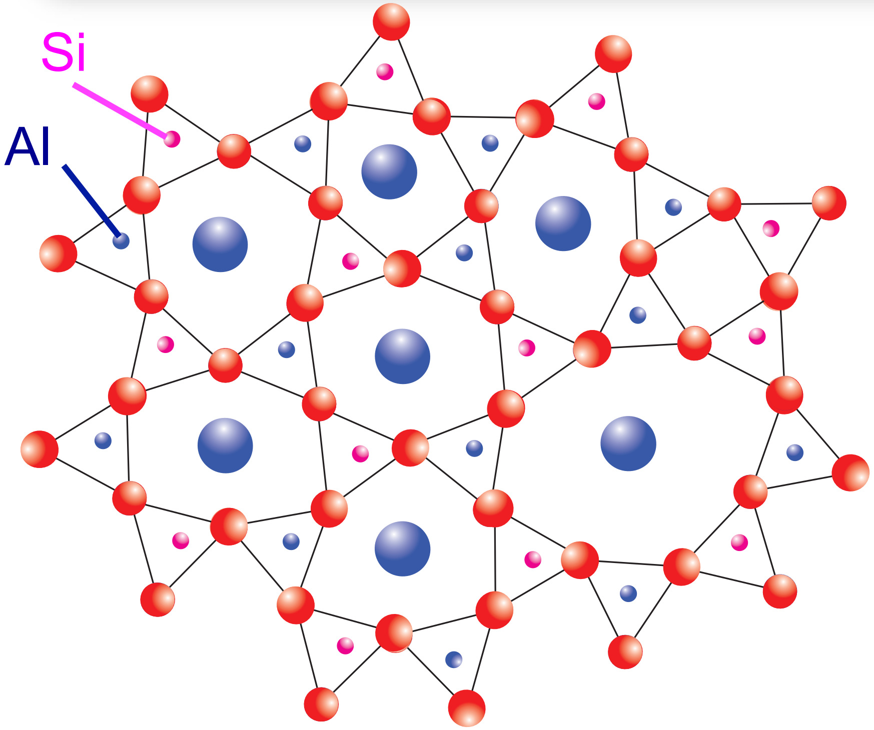


Meyer et al., 2004

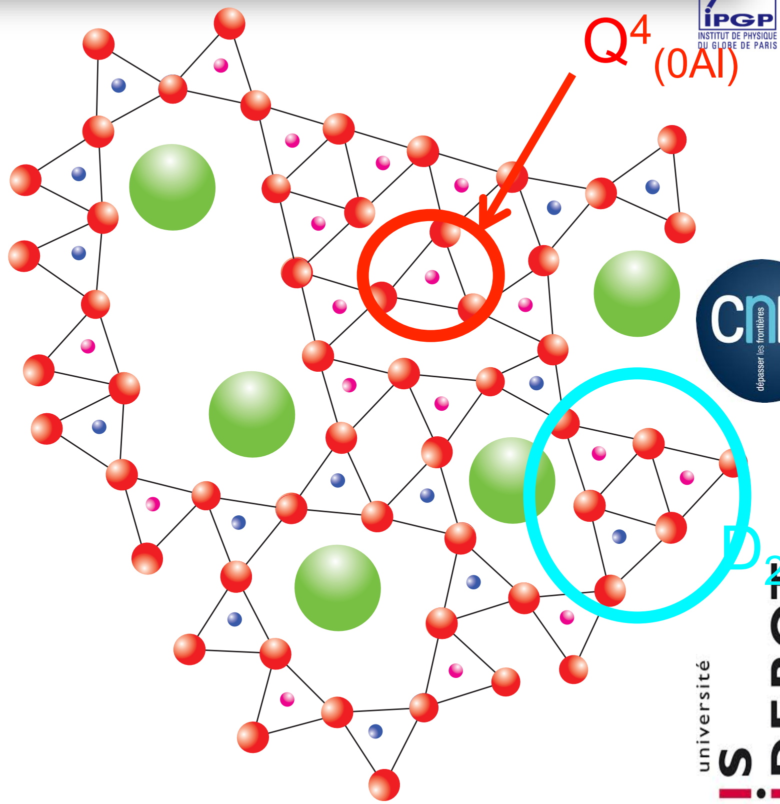


Le Losq, Neuville, Florian, Massiot, Zhou, Chen, Greaves (2017) Percolation channels: a universal idea to describe the atomic structure and dynamics of glasses and melts. PNAS

Na tectosilicates | K tectosilicates



Compensated Continuous Random Network
From Greaves and Ngai, 1995



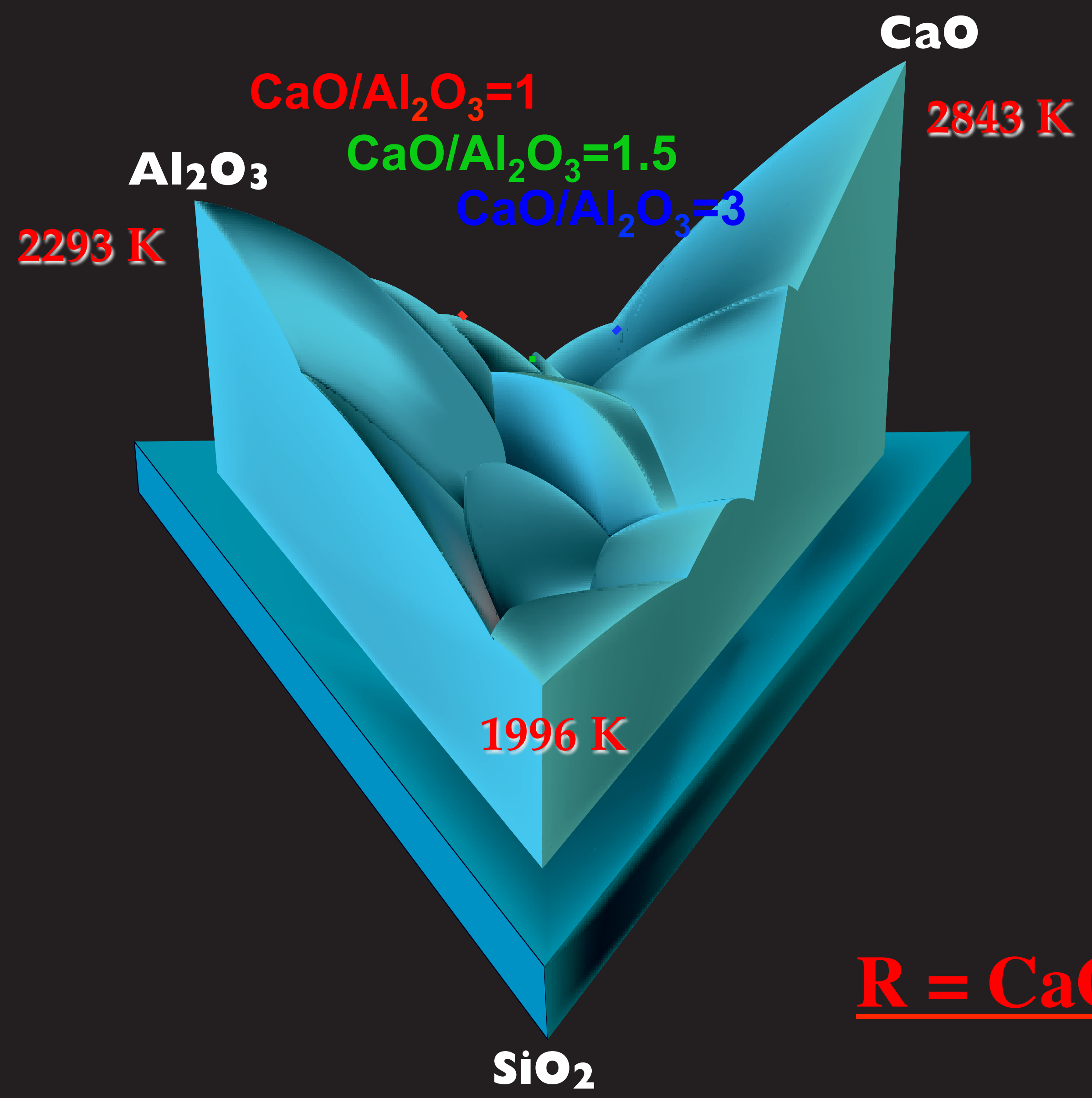
We propose a new version: Compensated Modified Random Network

Na and K are in different structural positions

⇒ Two different networks

⇒ Non random mixing

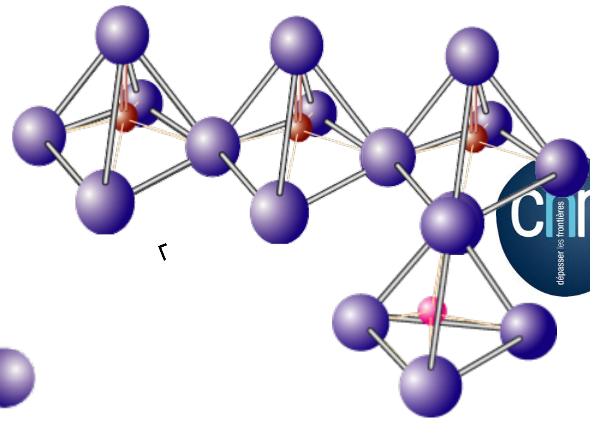
Al^{3+} in silicate glasses and melts

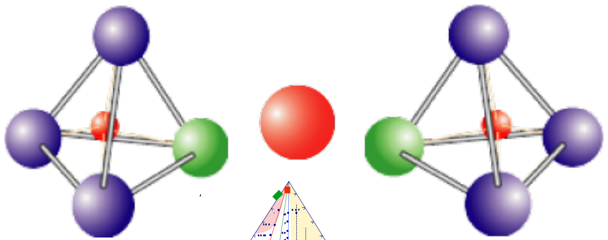


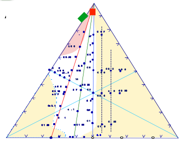
$R = CaO/Al_2O_3$

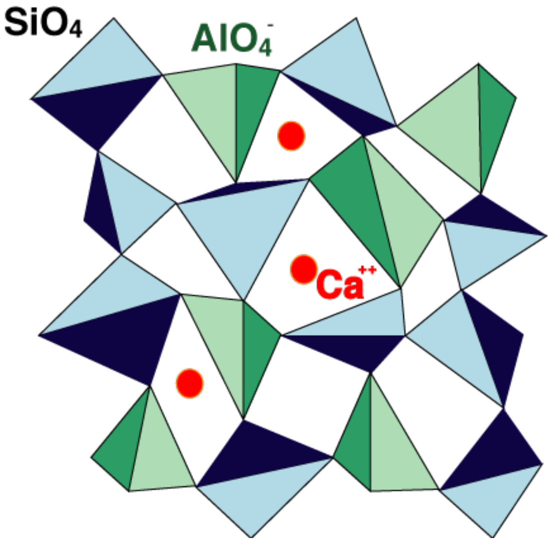
after Rankin, 1915

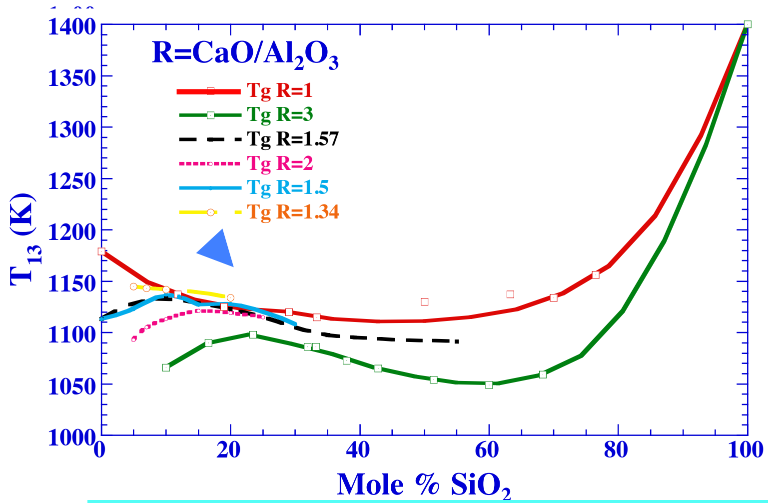
Glass transition temperature

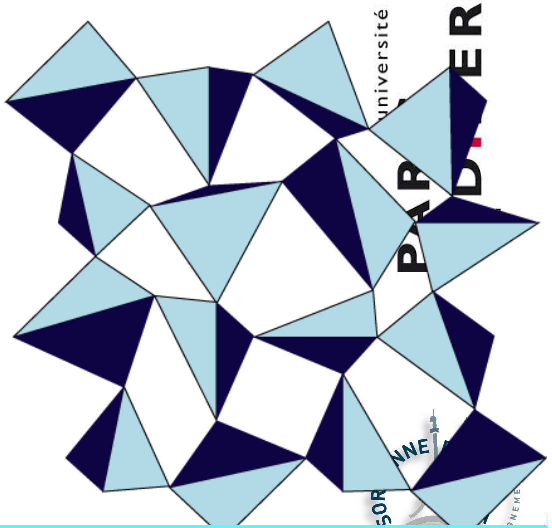


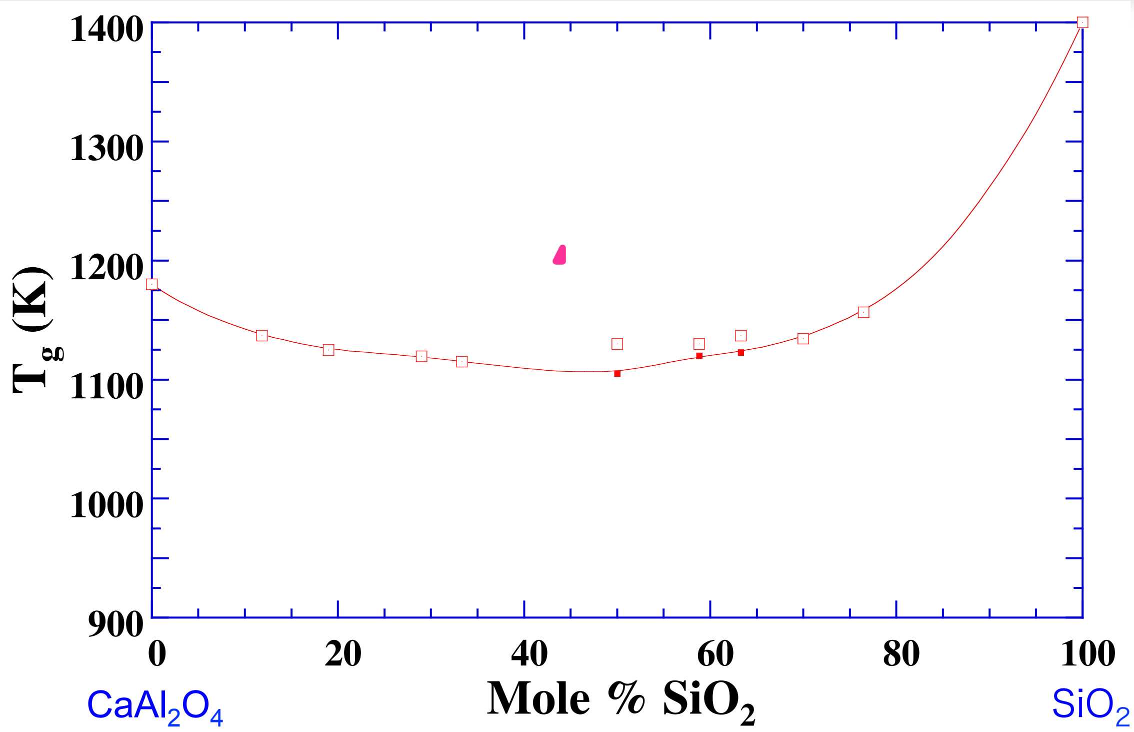




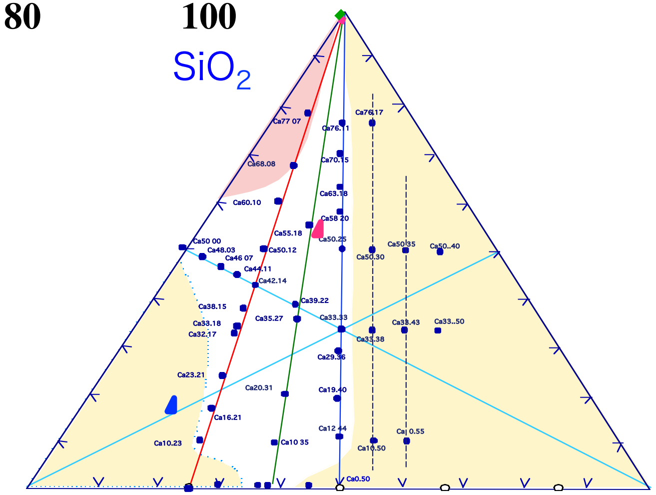




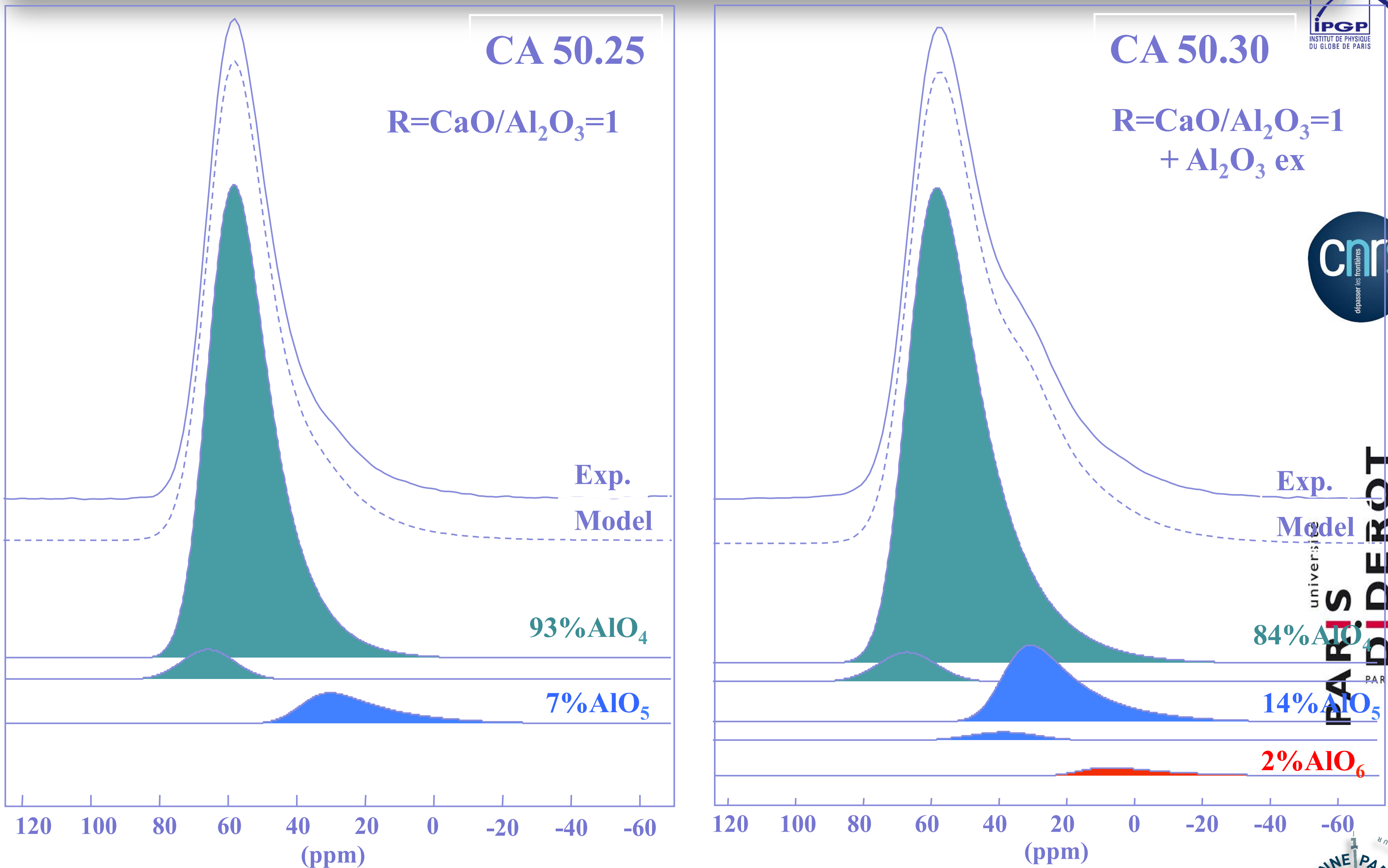




SiO_2
Tg=1400K



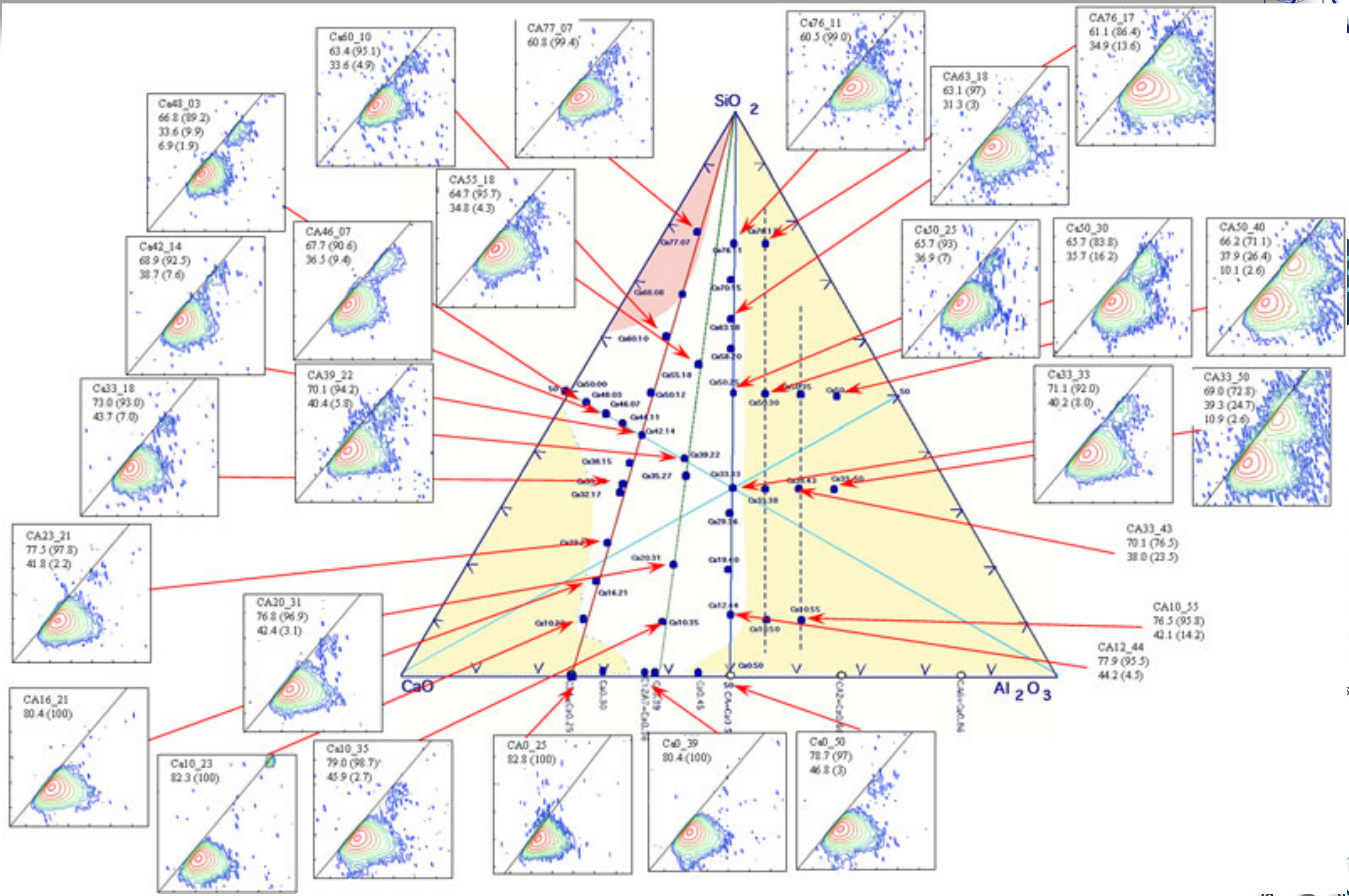
Al^{3+} in silicate glasses and melts



RMN 750MHz, CRMHT, Orléans, ^{27}Al 1D MAS

Neuville D.R., Cormier L. and Massiot D. (2004) Role of aluminium in peraluminous region in the CAS system. Geochim. Cosmochim. Acta., 68, 5071-5079

Al^{3+} in silicate glasses and melts



Neuville D.R., Cormier L., Massiot D. (2006) Al speciation in calcium aluminosilicate glasses: A NMR and Raman spectrocospie. Chem Geol., 229, 173-185.

Al^{3+} in silicate glasses and melts

CA 16_21
80.4 (100)

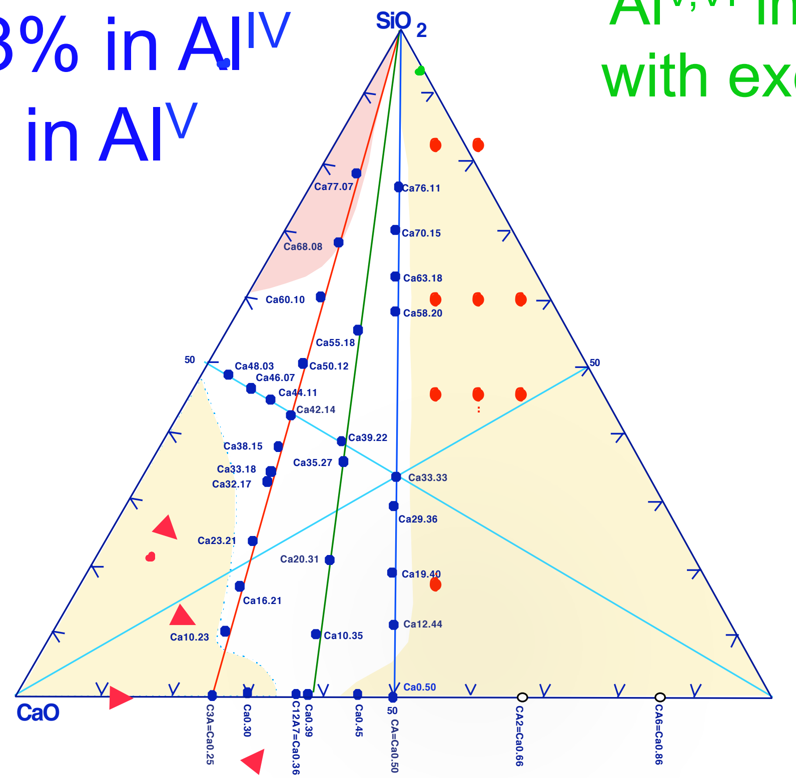
CA 10_23
82.3 (100)

CA 0_25
82 8 (100)

CA 0_39
80.4 (100)

1<R<+3
Al =>93% in Al^{IV}
~7% in Al^{V}

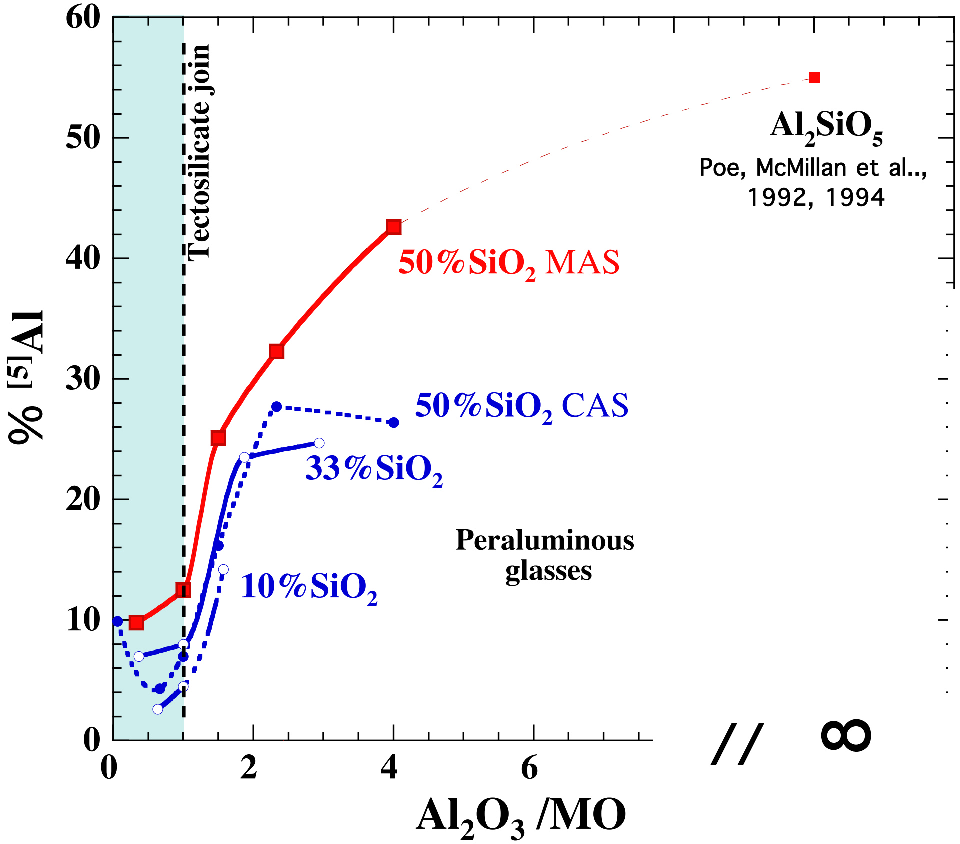
Peraluminous glasses
Al in Al^{IV},Al^{V},Al^{VI}
$Al^{V,VI}$ increase
with excess Al

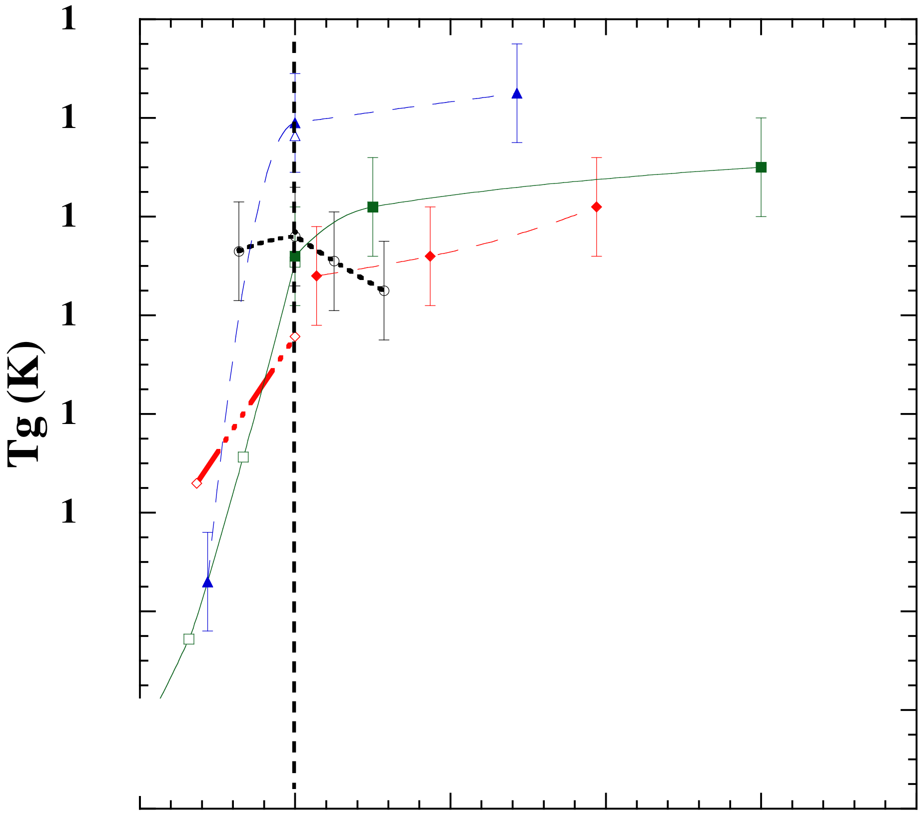


⇒Al 100% in Al^{IV}
Al in Q^2 and Q^3 species

Neuville D.R., Cormier L., Massiot D. (2006) Al speciation in calcium aluminosilicate glasses: A NMR and Raman spectrocospie. Chem Geol., 229, 173-185.

$^{[5]}Al$ increases with Al_2O_3 content for $R=CaO/Al_2O_3<1$

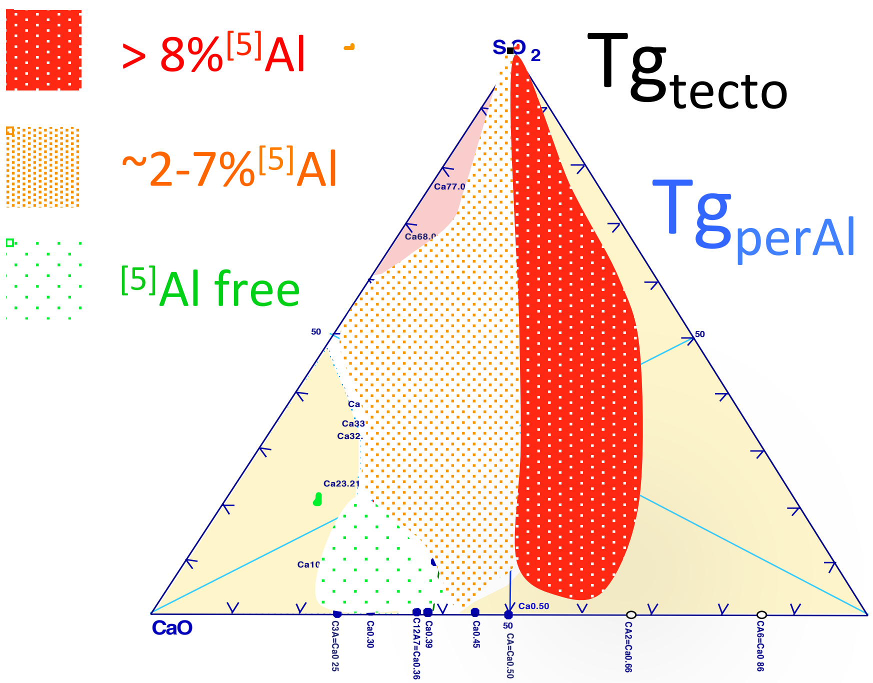


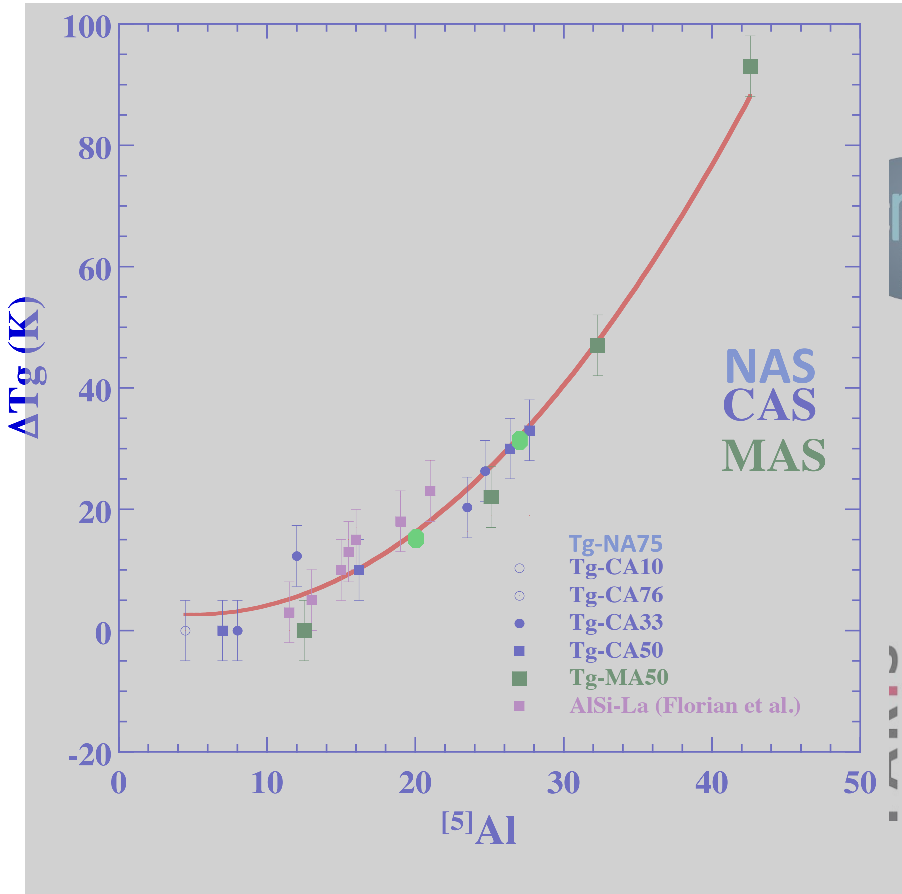


Neuville et al. Chem Geol., 2006, 229, 173

$^{[5]}$Al proportion and role in CAS, MAS and NAS ?

$\Delta Tg = Tg_{perAl} - Tg_{tecto}$





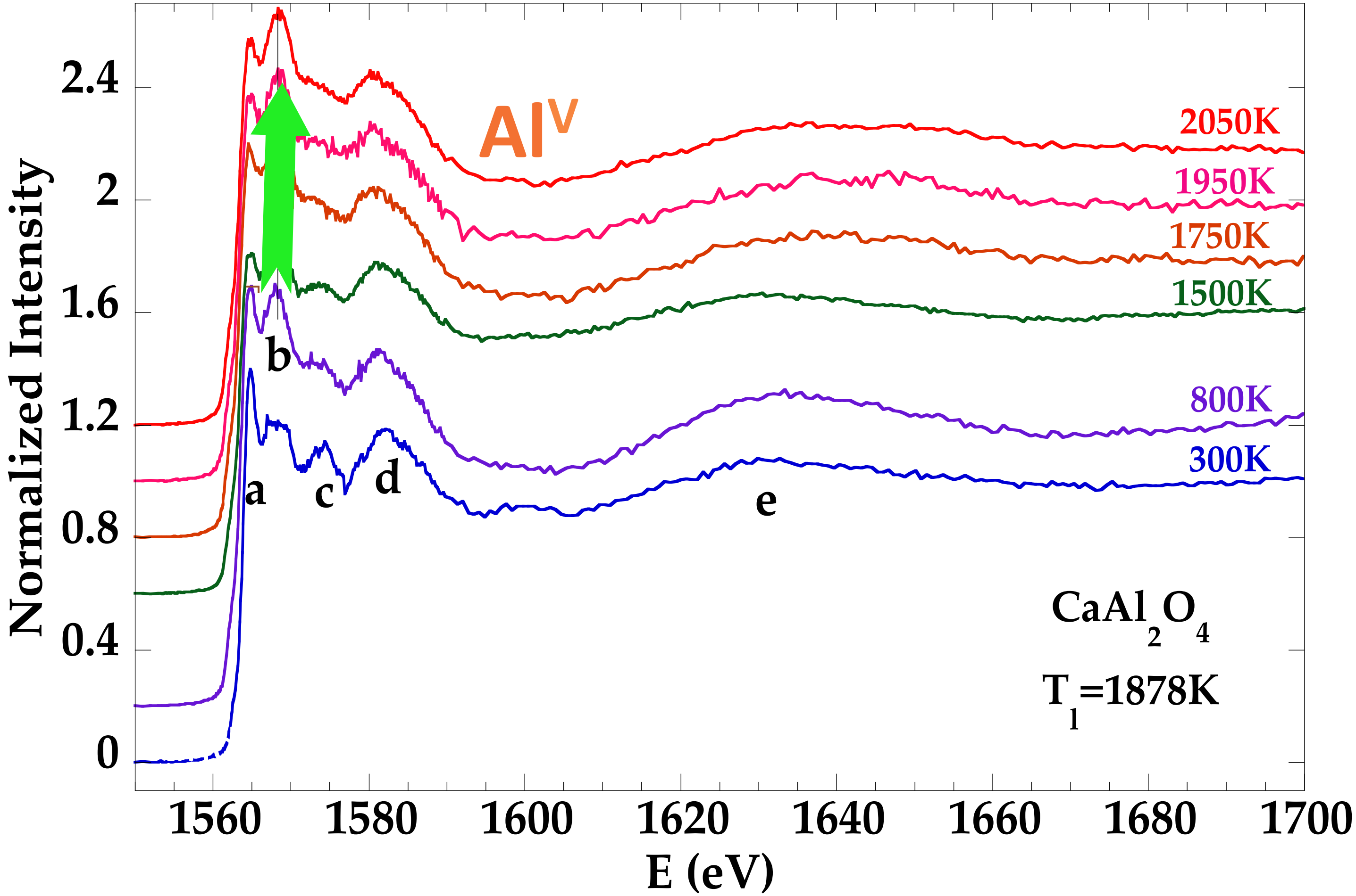
⇒ $^{[5]}$Al increases Tg at all SiO_2 content and for CAS, NAS and MAS glass systems.

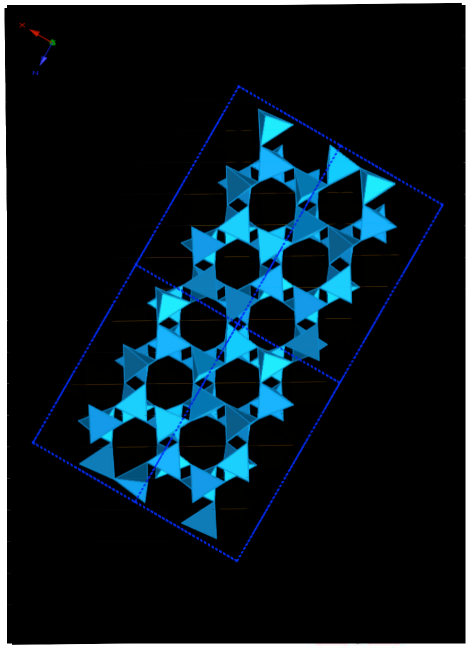
⇒ $^{[5]}$Al can be a strong network former !

Neuville (2017) role of aluminum in five fold coordination, JNCS

Al in tectosilicate melt ?

Al K

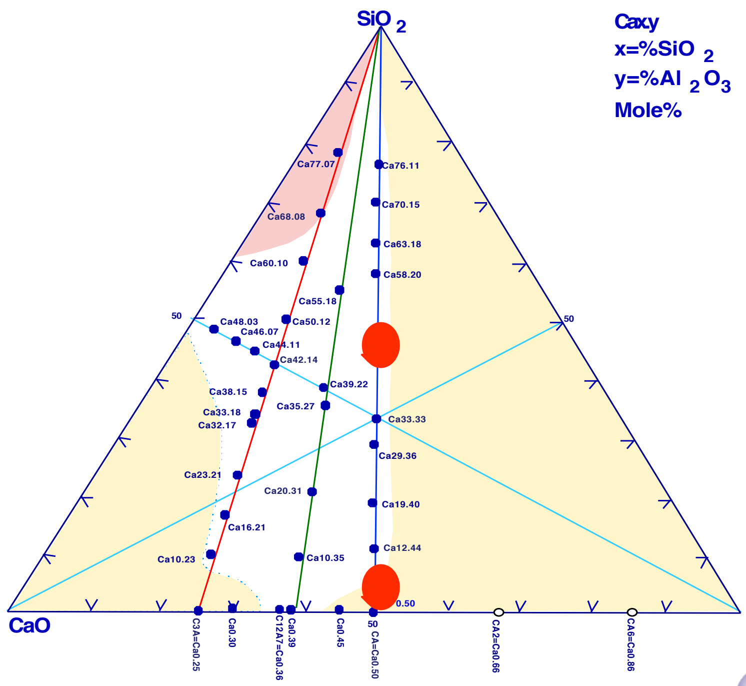


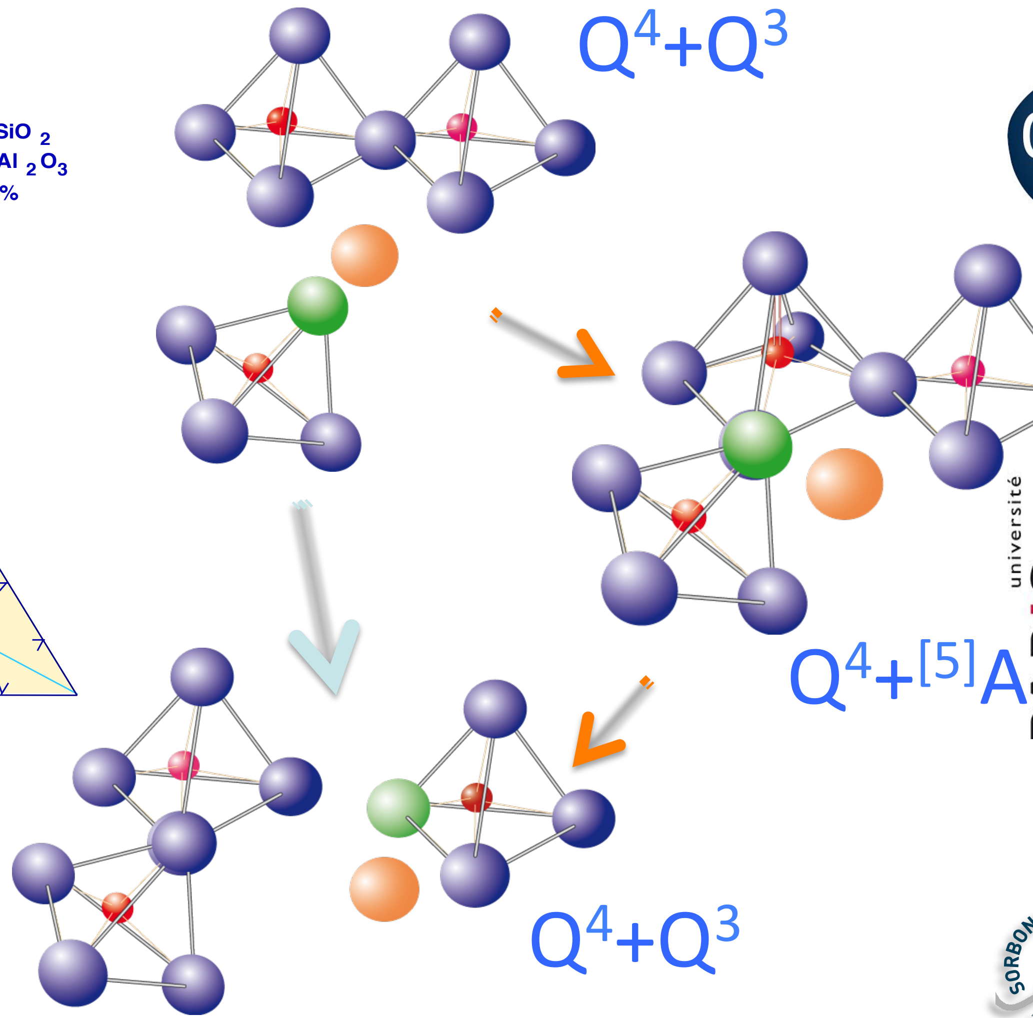


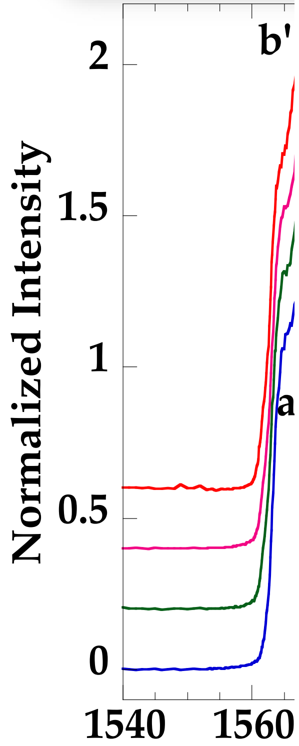
Role of [5]Al ?

Why $^{[5]}$Al ?

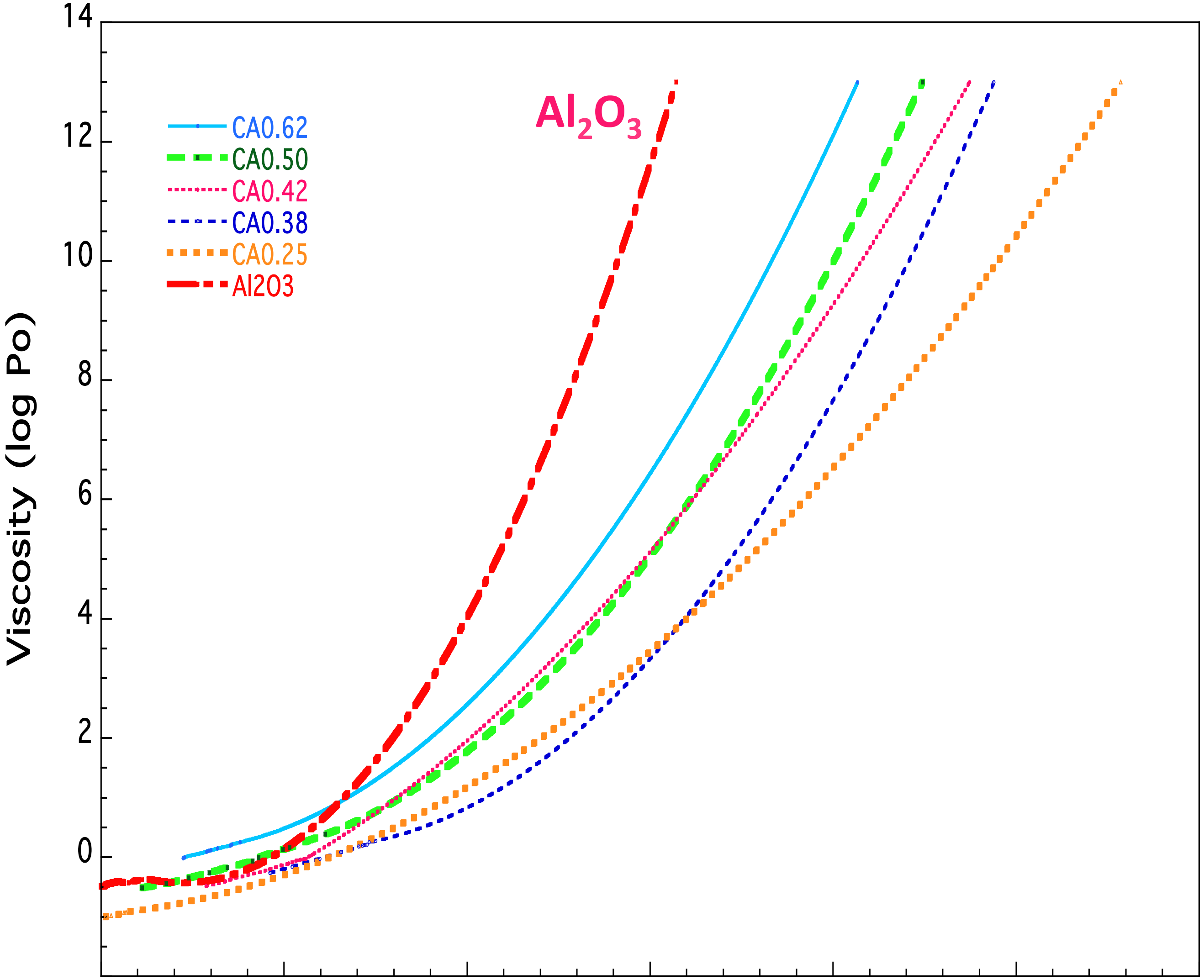
Need to ensure cationnic mobility, according at those observed on Si by Stebbins et Farnan (1992) using NMR.





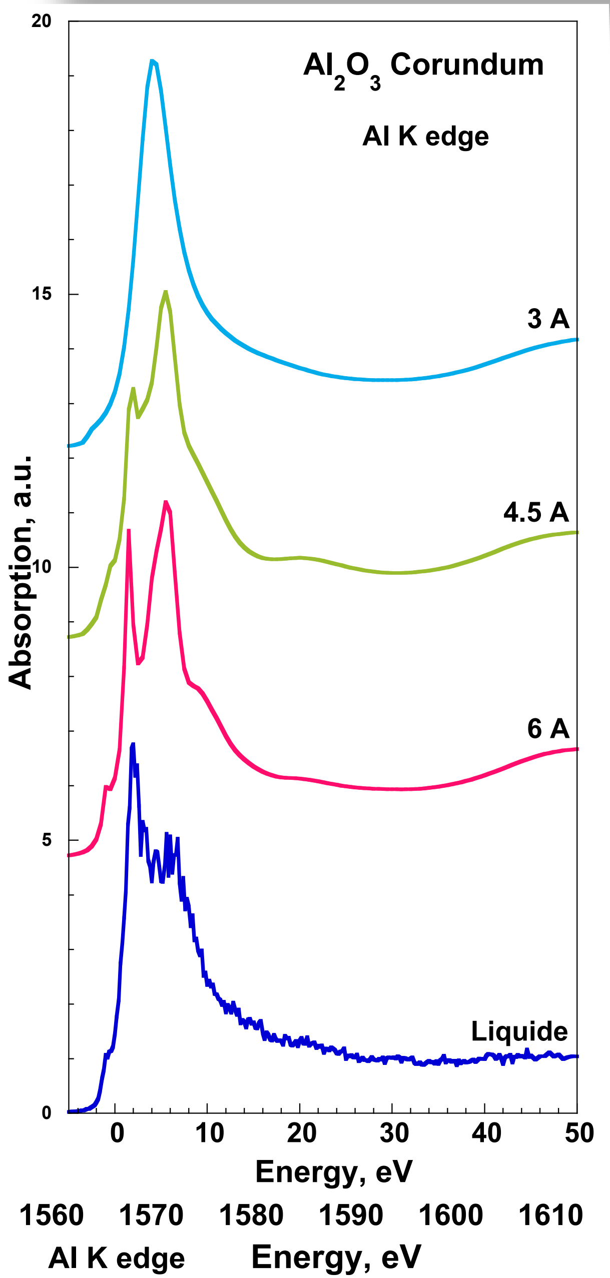


Normalized Intensity
b'
a
2
1.5
1
0.5
0
1540
1560



Viscosity (log Po)
14
12
10
8
6
4
2
0
CA0.62
CA0.50
CA0.42
CA0.38
CA0.25
Al2O3
Al_2O_3

Al_2O_3 corundum 300K => Al^{VI}



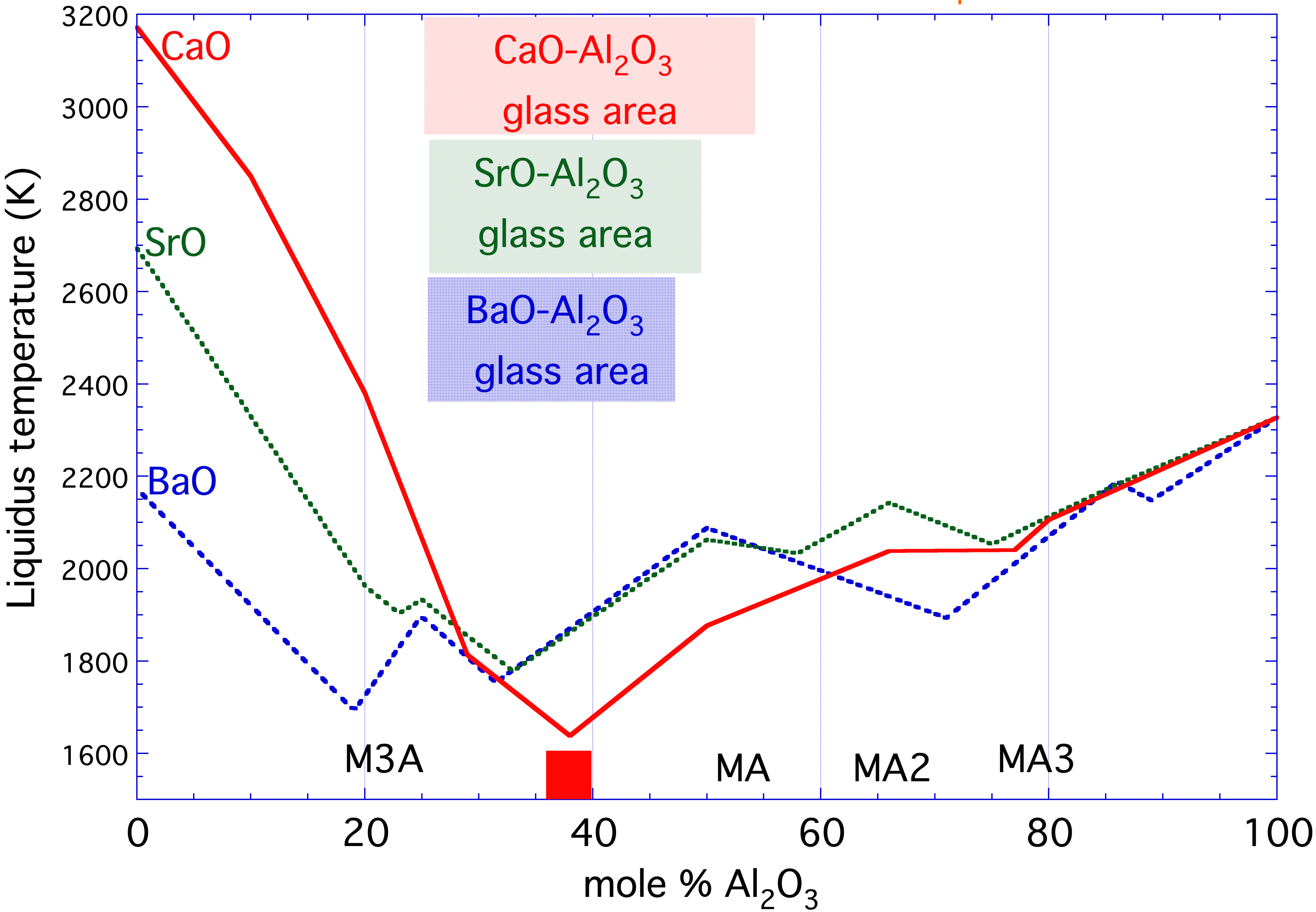
Similar to NMR-HT
(Florian et al., 1996)

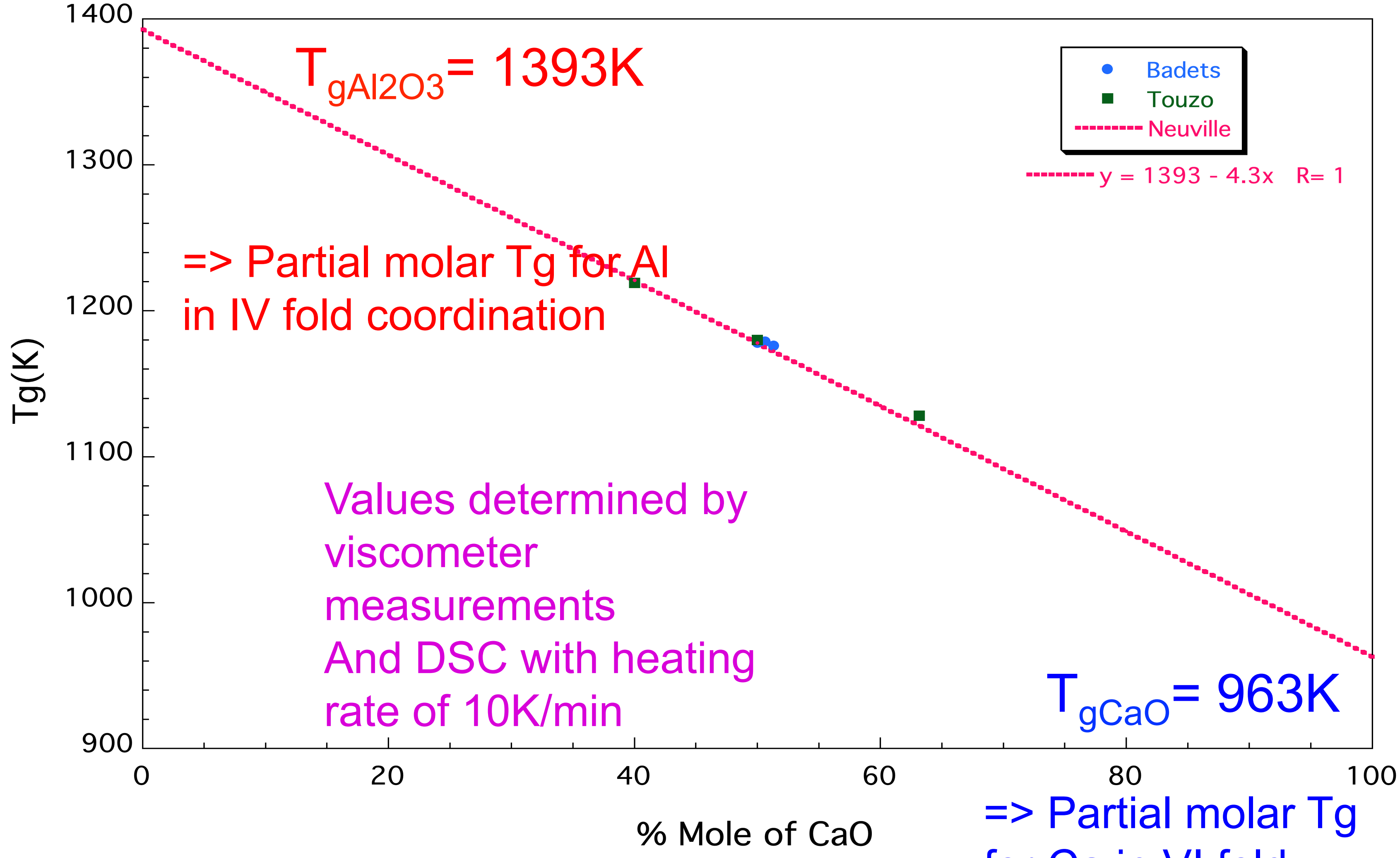
Liquid Al_2O_3

9.4 T
2 lasers
67 mg
2320°C
Experimental (blue) & simulation (red)

85 80 75 70 65 60 55 50 45 40 35 30
(ppm from $Al(NO_3)_3$ 1M)

Voir exposé L. Hennet

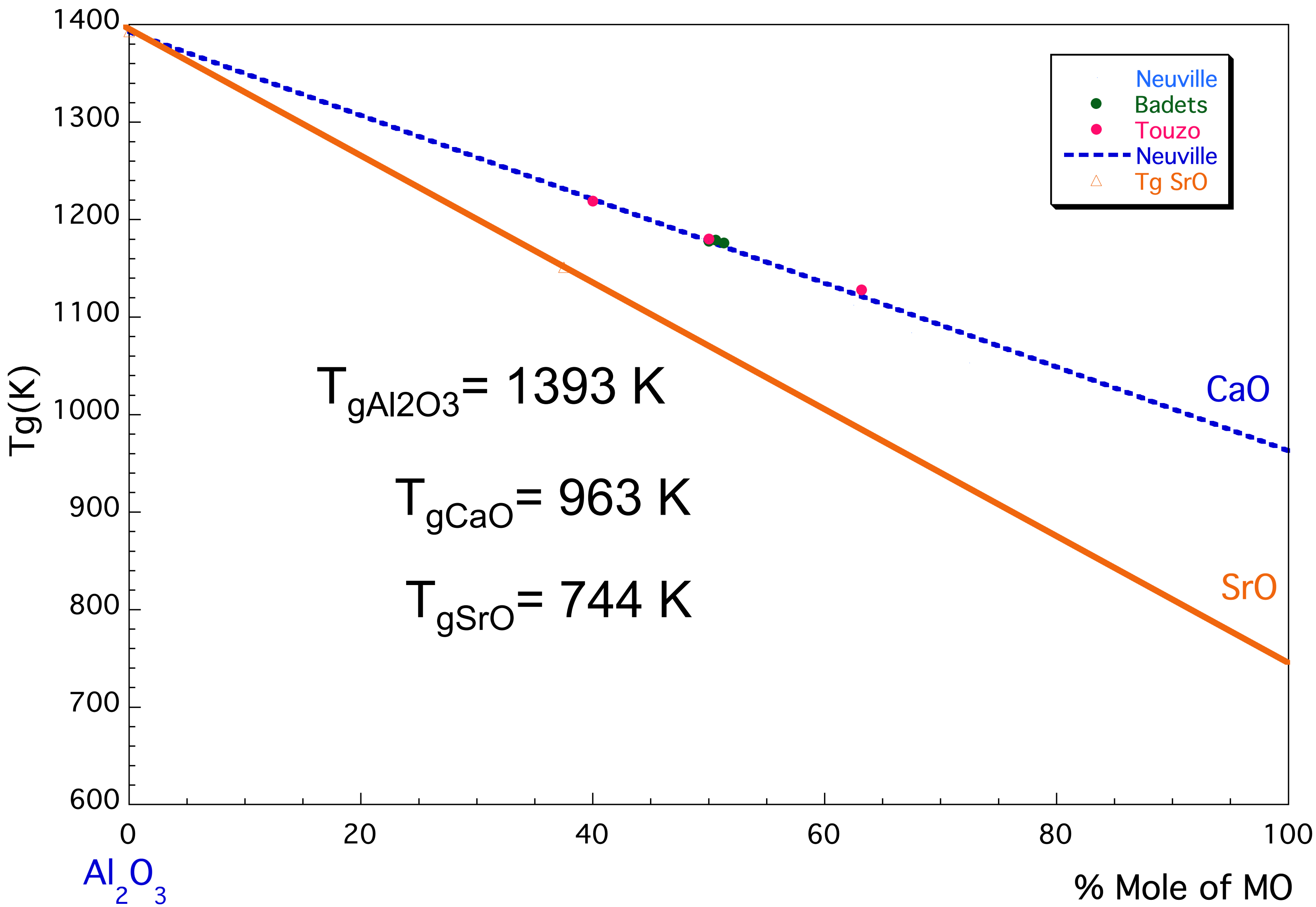




=> Partial molar Tg for Ca in VI fold coordination

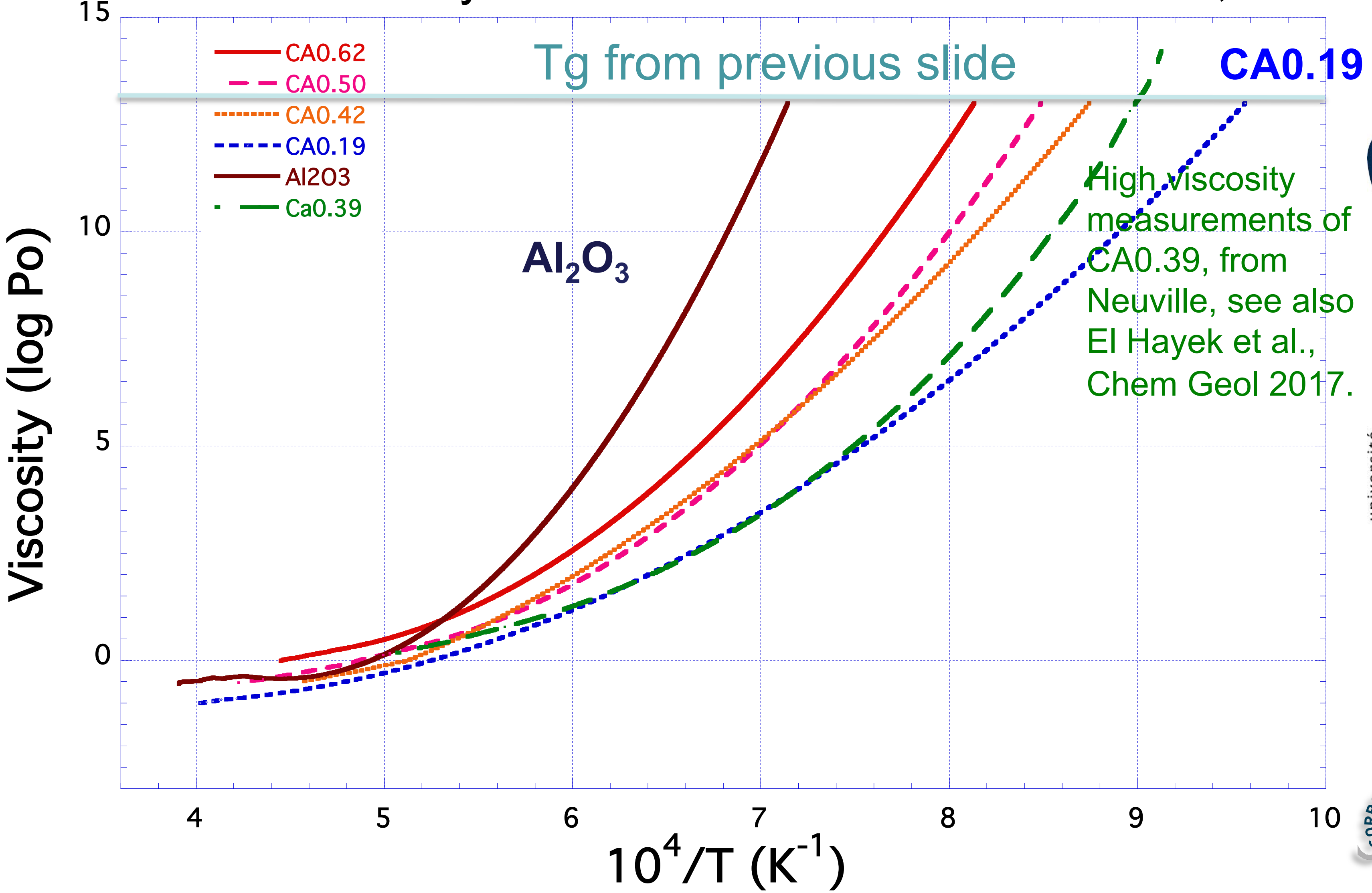
Determination T_{gi} (partial molar)

Voir exposé L. Hennet



1400
1300
1200
1100
1000
900
800
700
600
Tg(K)
0
20
40
60
80
100
Al_2O_3
% Mole of MO
Neuville
Badets
Touzo
Neuville
Tg SrO
CaO
SrO
T_{gAl2O3}= 1393 K
T_{gCaO}= 963 K
T_{gSrO}= 744 K

Low viscosity measurements from Urbain 1970, 1974



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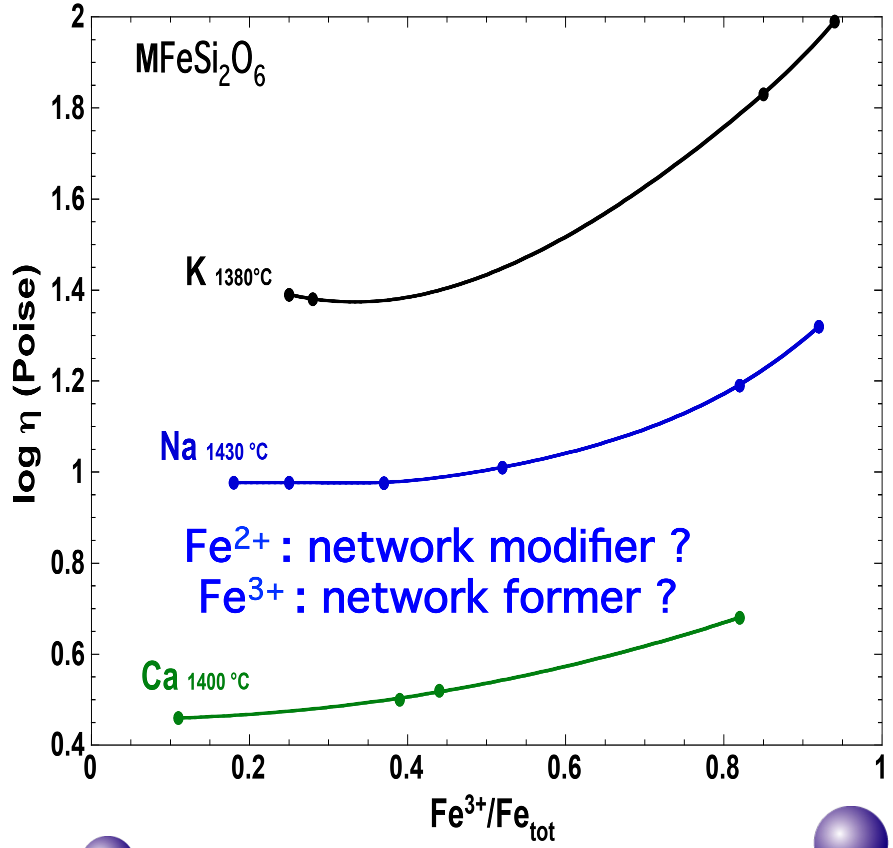
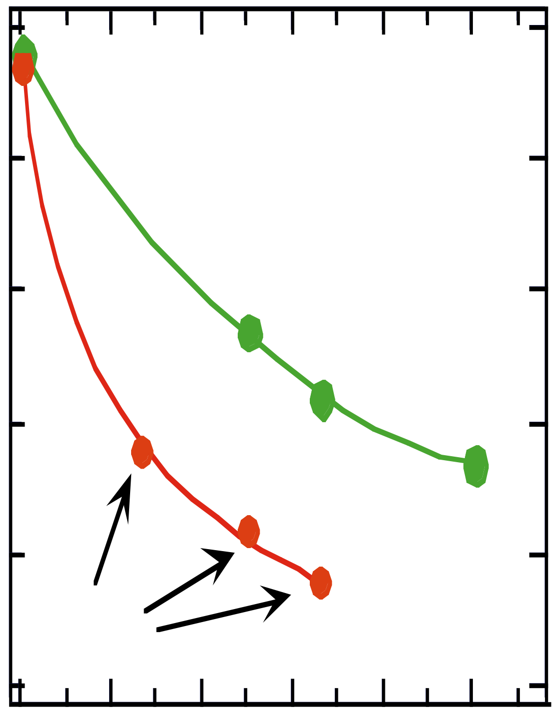
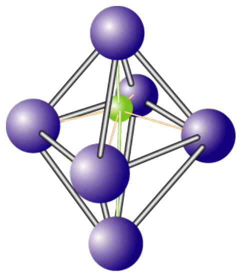
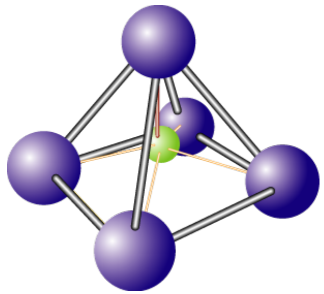


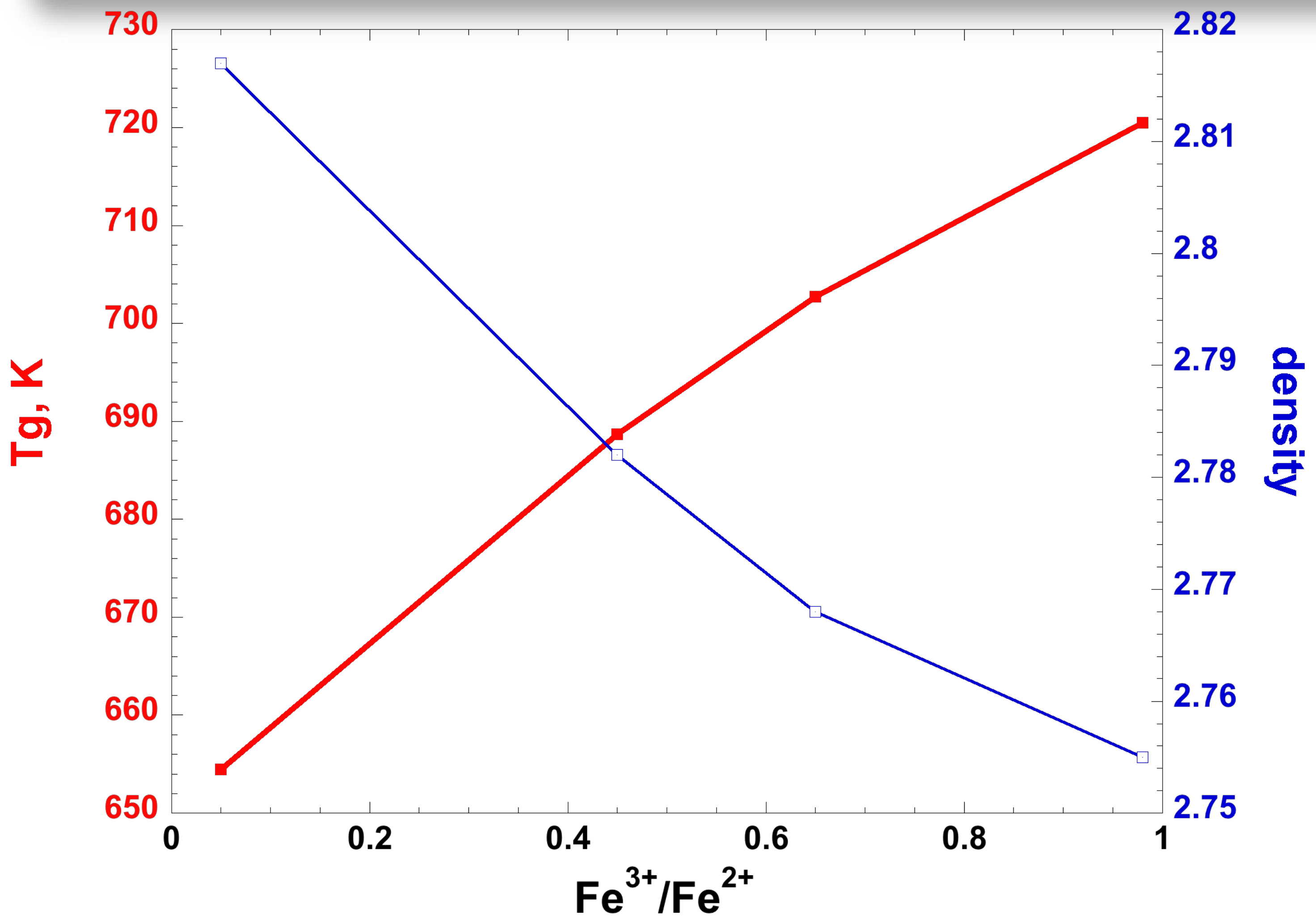
Fe²⁺ : network modifier ?
Fe³⁺ : network former ?







Fe^{2+}/Fe^{3+}

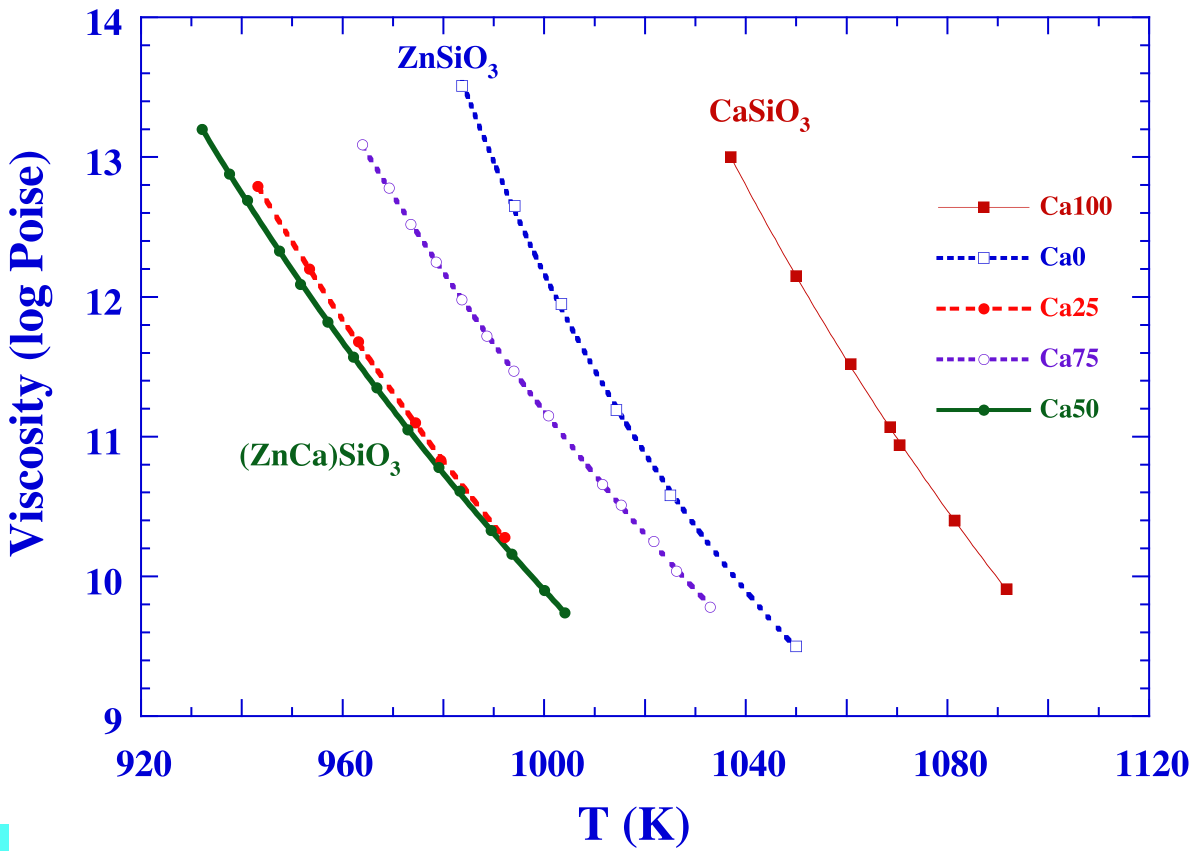


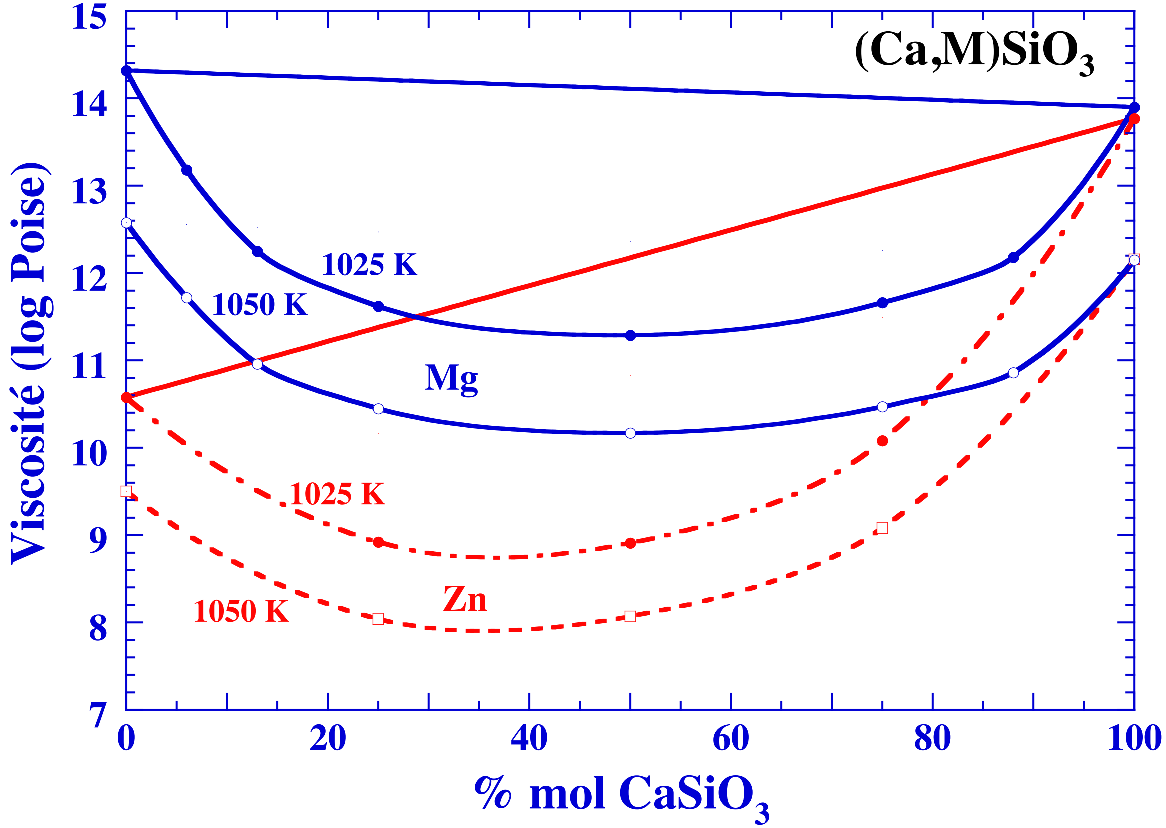
Fe^{2+} : network modifier
Fe^{3+} : network former

Ca/Mg mixing => ideal mixing

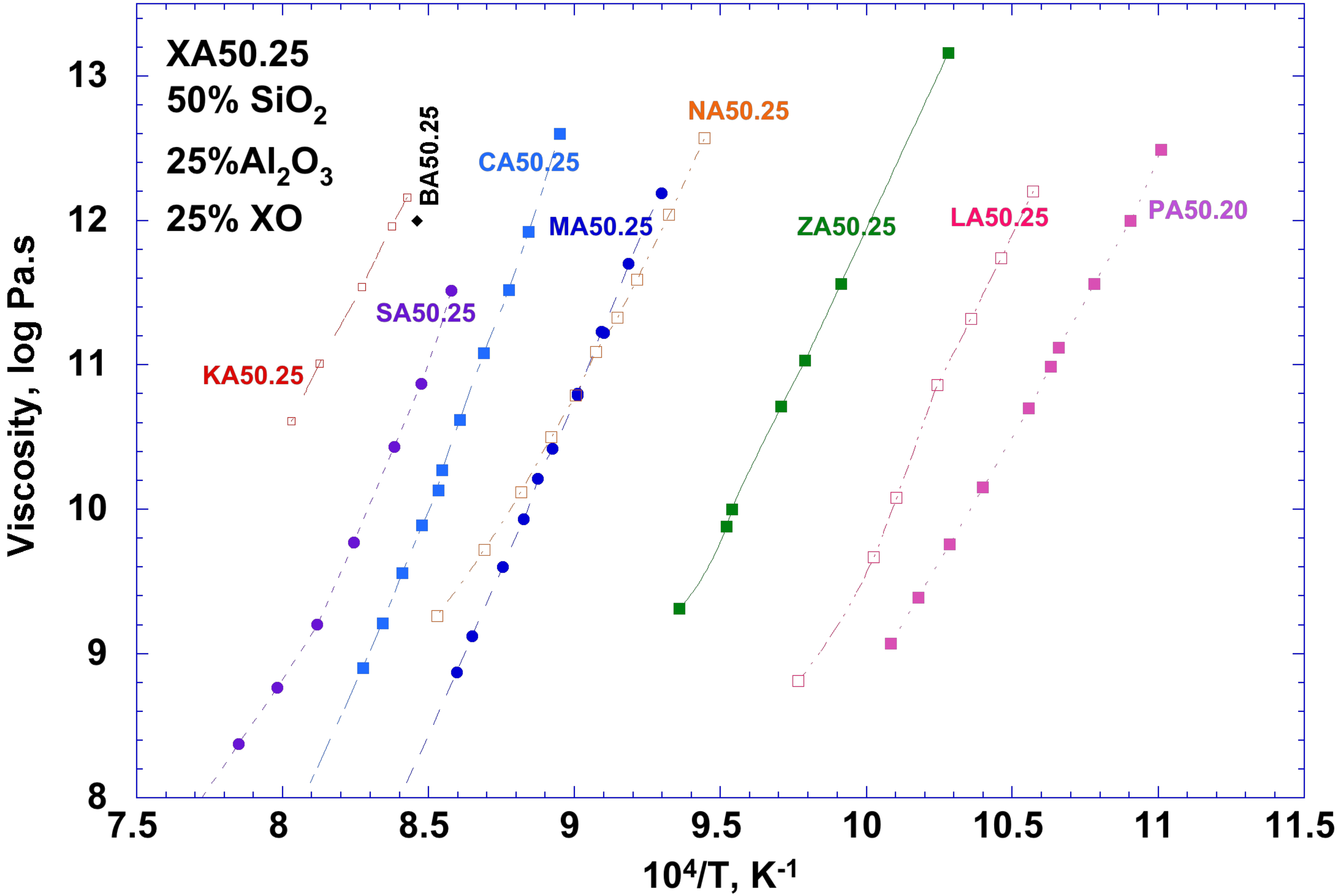
Other systems ?

Ca/Zn Substitution? $(CaZn)SiO_3$




(Ca,M)SiO3
Viscosité (log Poise)
15
14
13
12
11
10
9
8
7
1025 K
1050 K
Mg
1025 K
Zn
1050 K
0
20
40
60
80
100
% mol CaSiO3

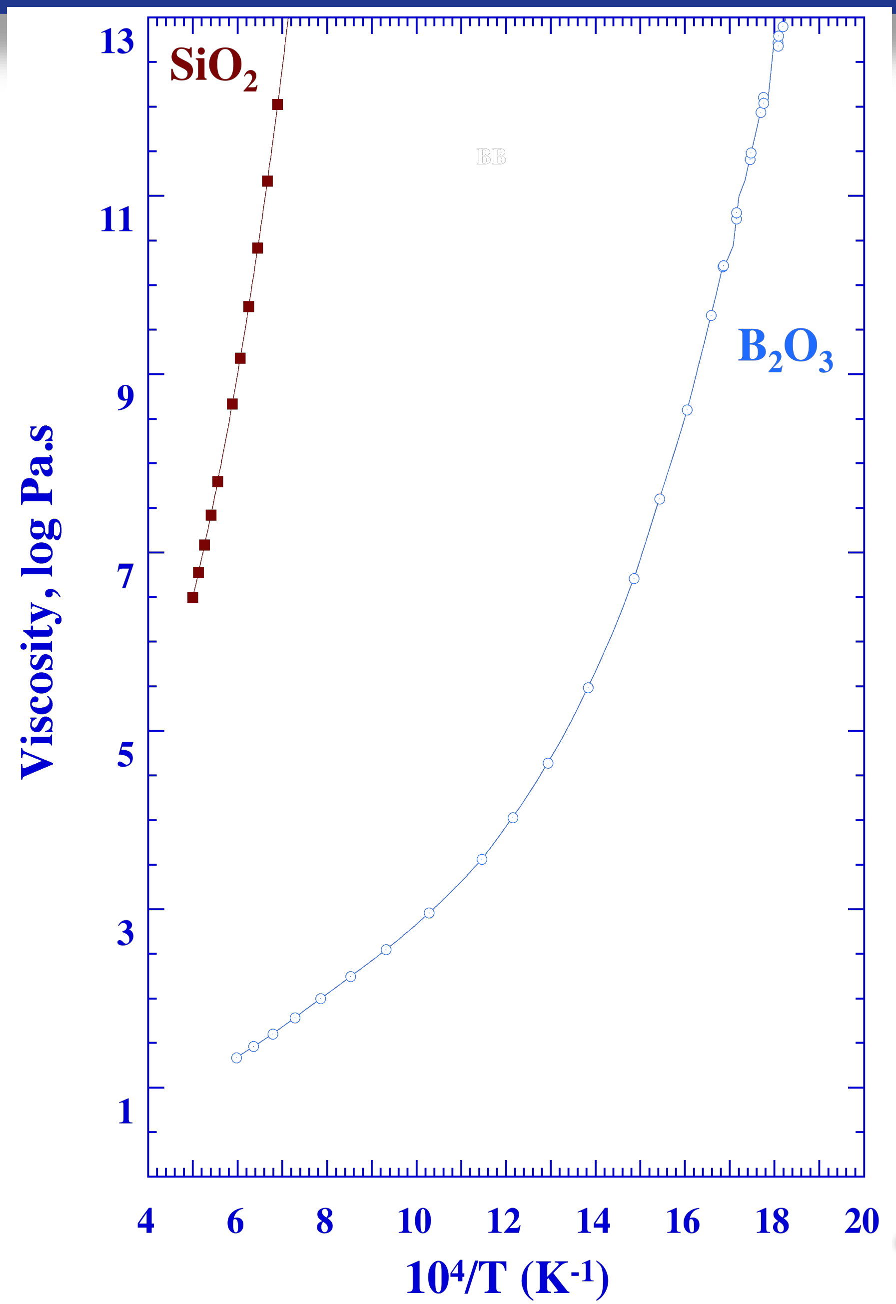
Zn and Pb with Al…



B2O3….

B2O3….

- SiO_4 tetrahedra => strong network former
- BO3 triangle => soft network former

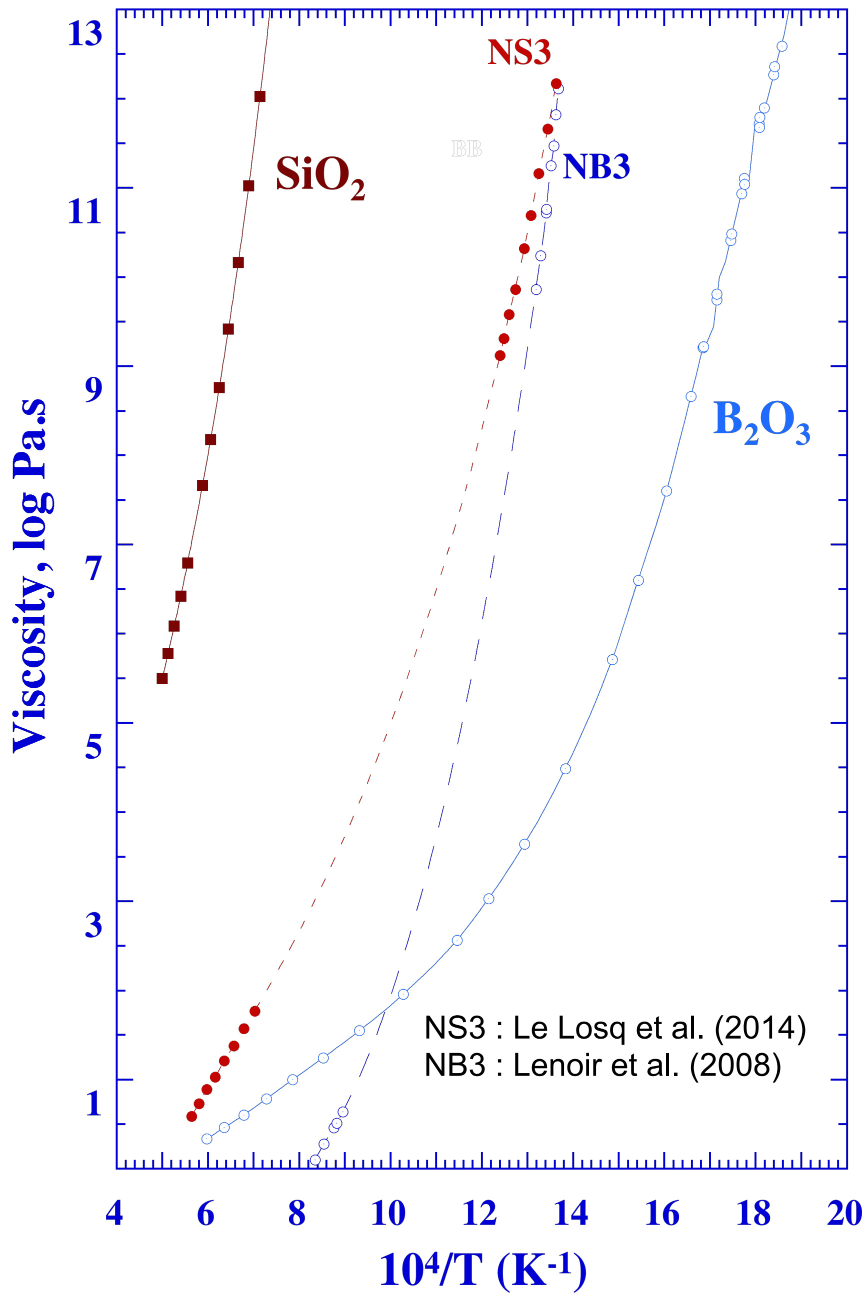


B2O3….

- SiO_4 tetrahedra => strong network former
- BO3 triangle => soft network former

+ Na^+

- BO4 tetrahedra => network former with M^+

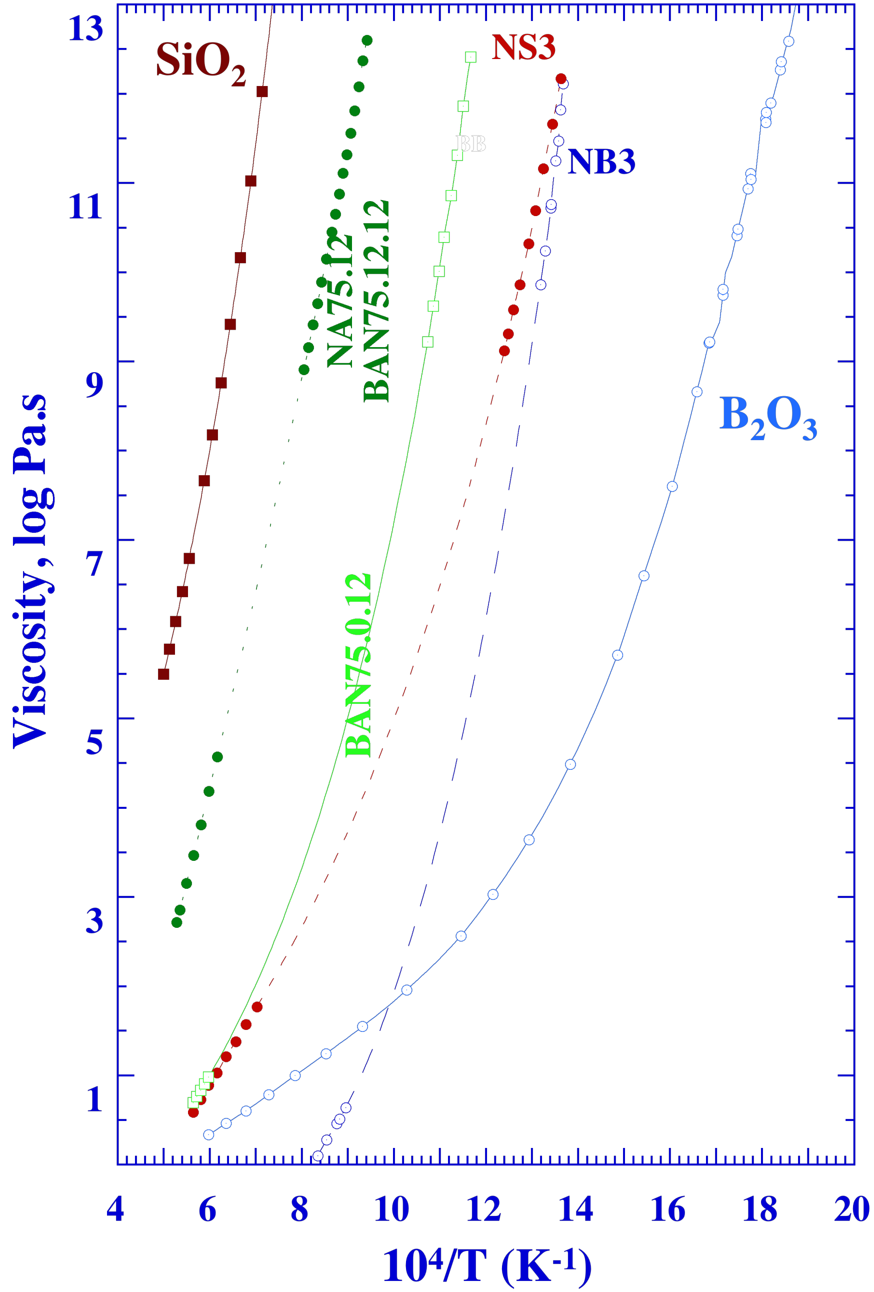


B2O3….

- SiO_4 tetrahedra => strong network former
- BO3 triangle => soft network former

- BO4 tetrahedra => network former with M^+

- AlO_4 tetrahedra => network former with M^+

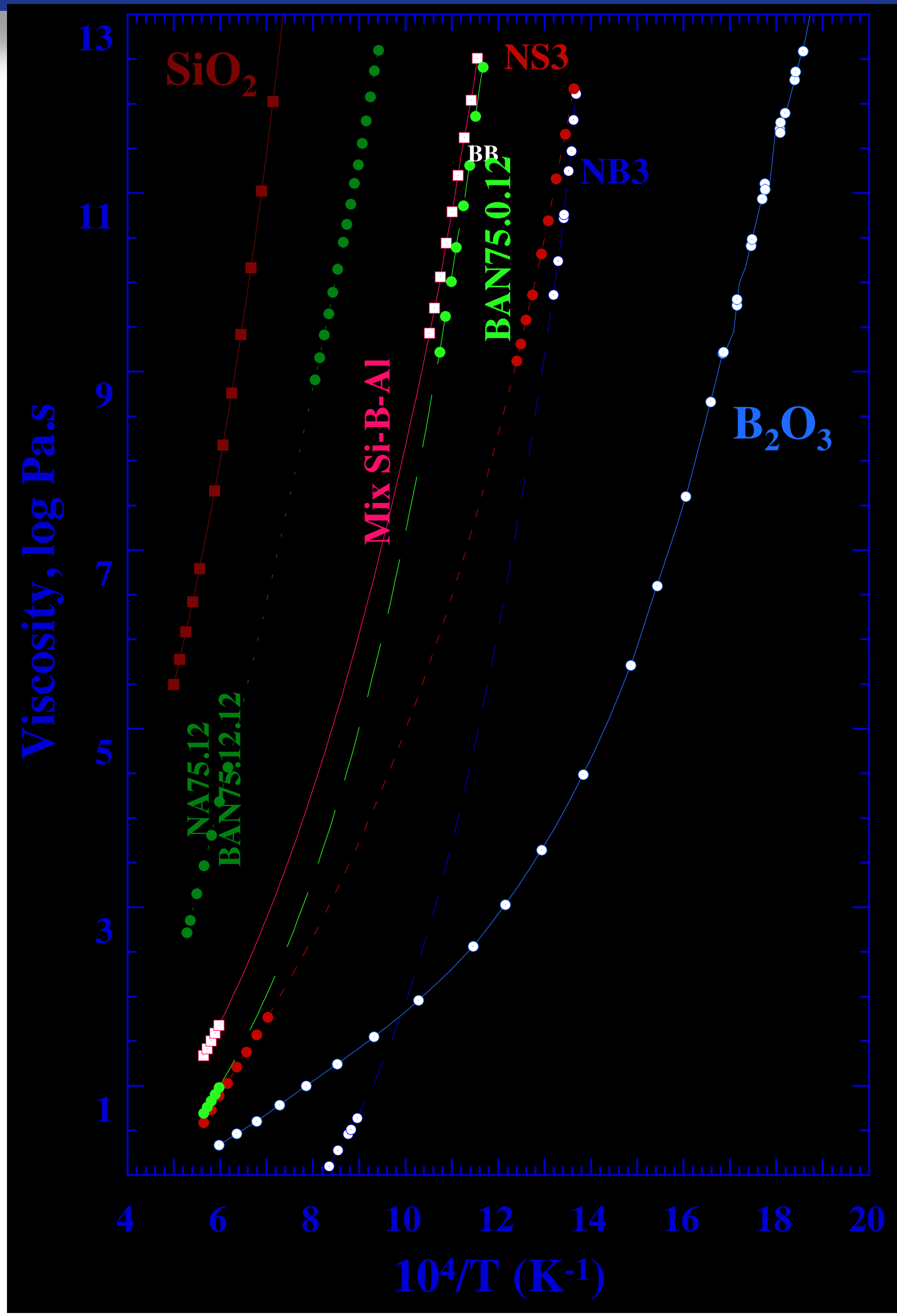


B2O3….

- SiO_4 tetrahedra => strong network former
- BO3 triangle => soft network former

- BO4 tetrahedra => network former with M^+

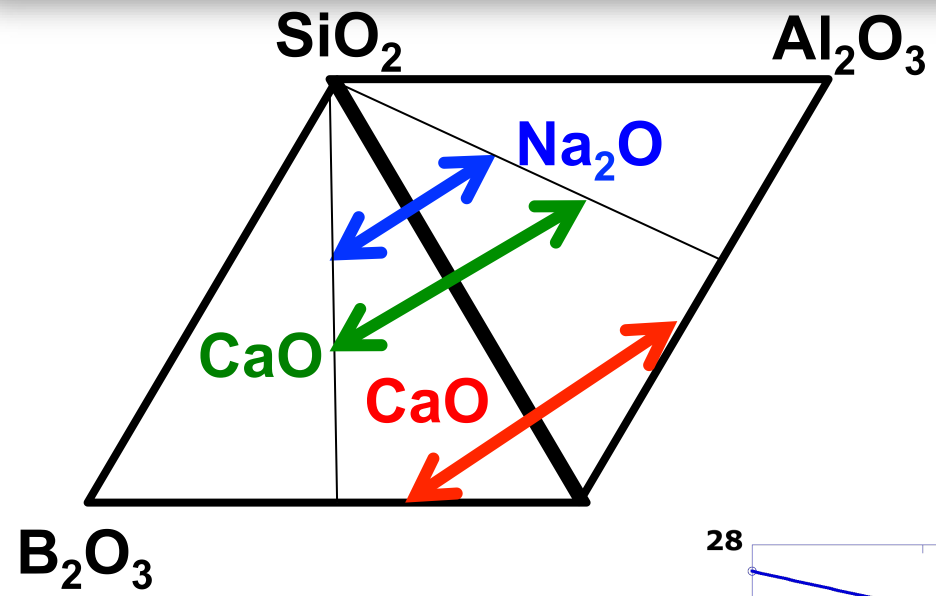
- AlO_4 tetrahedra => network former with M^+



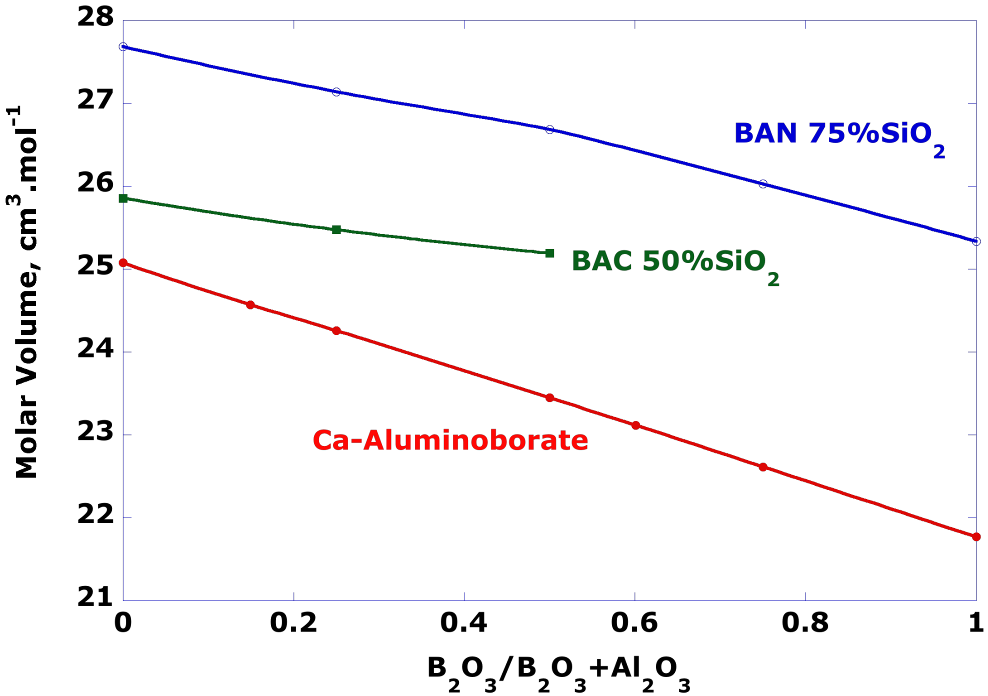
- SiO_4
- AlO_4 tetrahedra,
- BO4 tetrahedra,
- BO3 triangle

=> and only one M^+

B2O3….

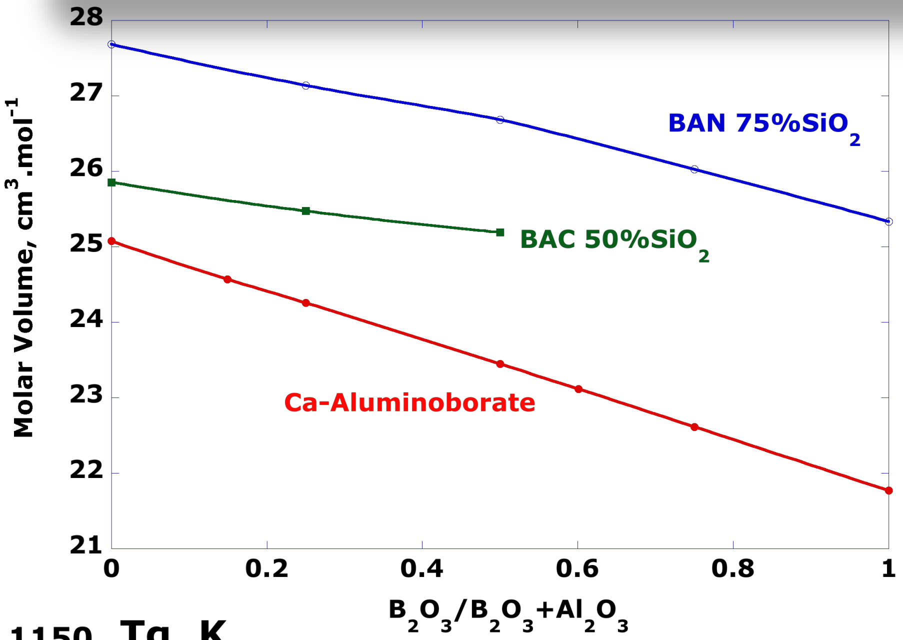


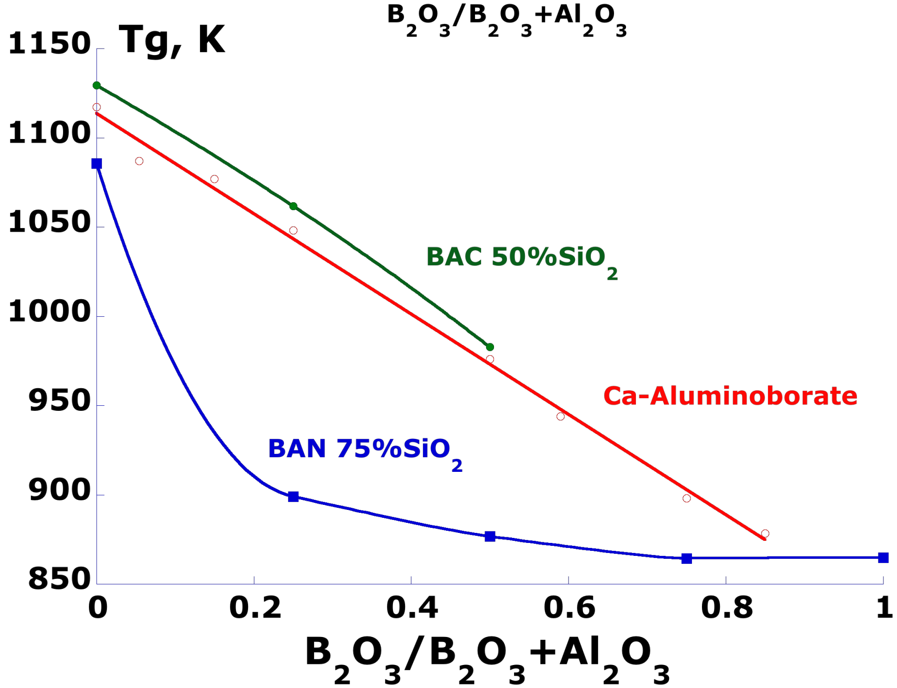
SiO2
Al2O3
Na2O
CaO
CaO
B2O3

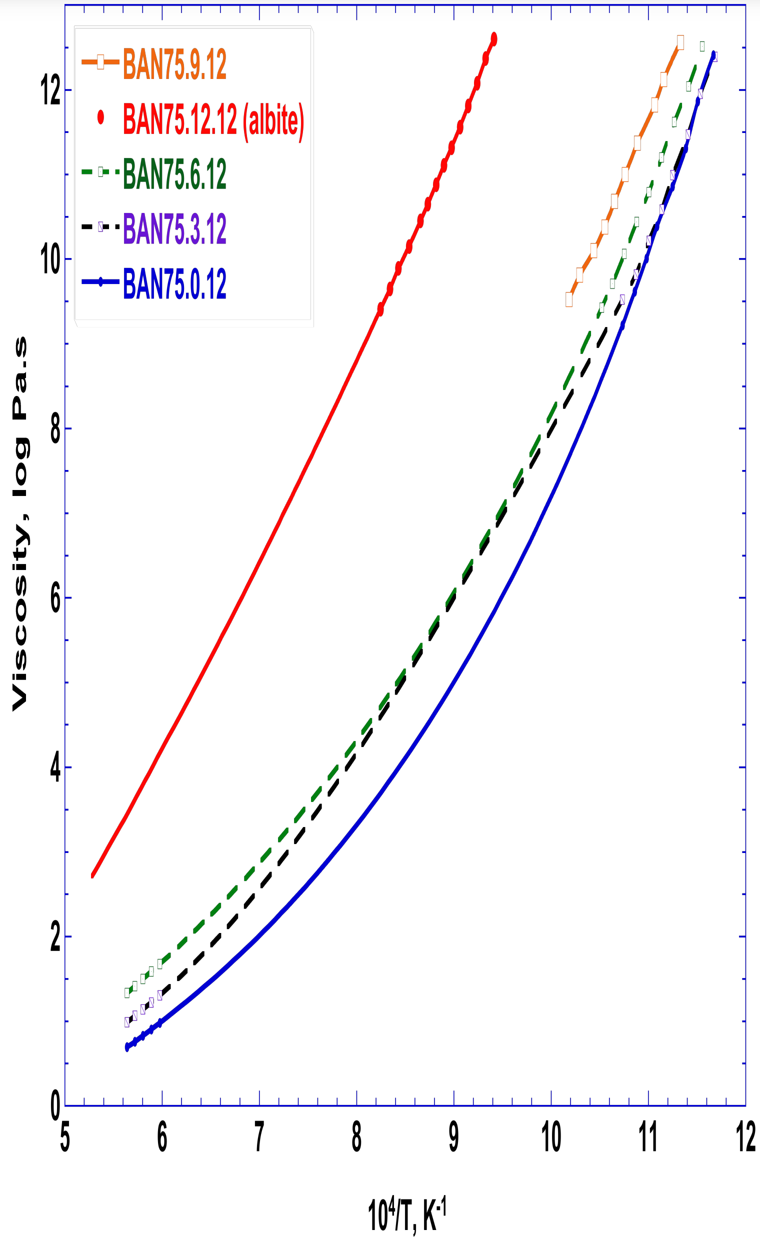


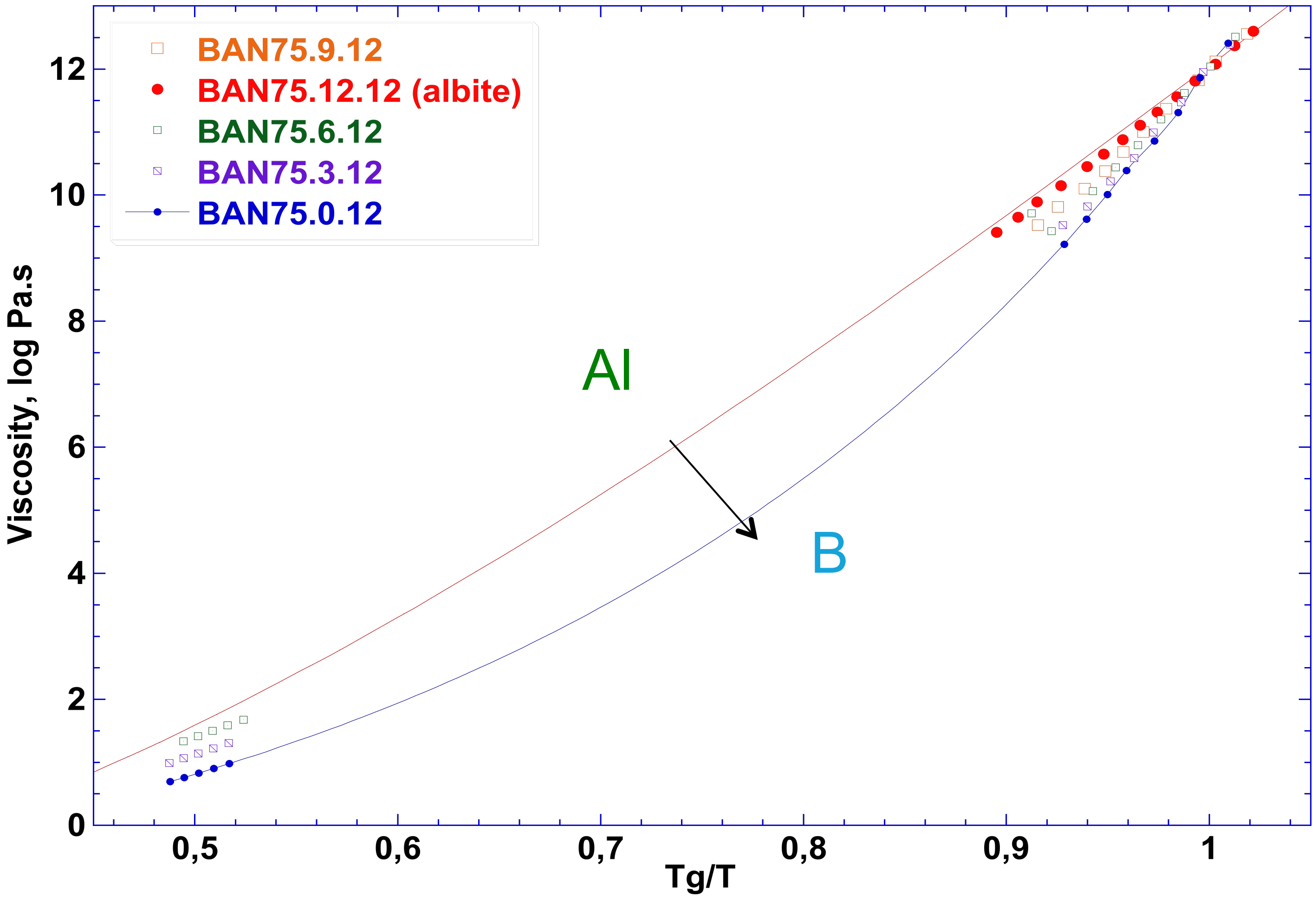
Molar Volume, cm3.mol-1
28
27
26
25
24
23
22
21
0
0.2
0.4
0.6
0.8
1
B2O3/B2O3+Al2O3
BAN 75%SiO2
BAC 50%SiO2
Ca-Aluminoborate

B2O3…. Vm, Viscosity, Tg





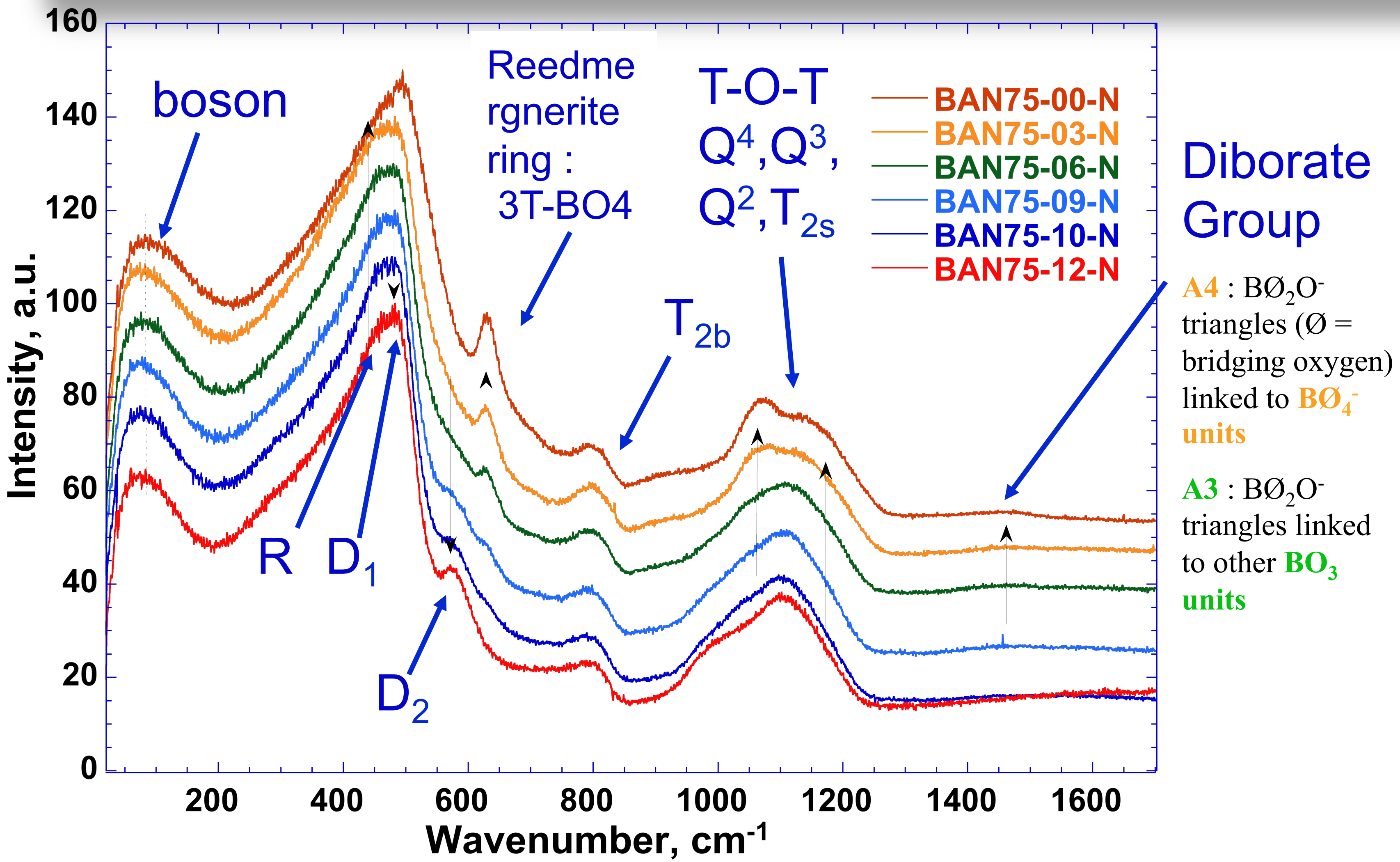




Very strong decrease of Vm, viscosity, Tg and fragility increases with Al/B substitution and using link between viscosity and configurational entropy :

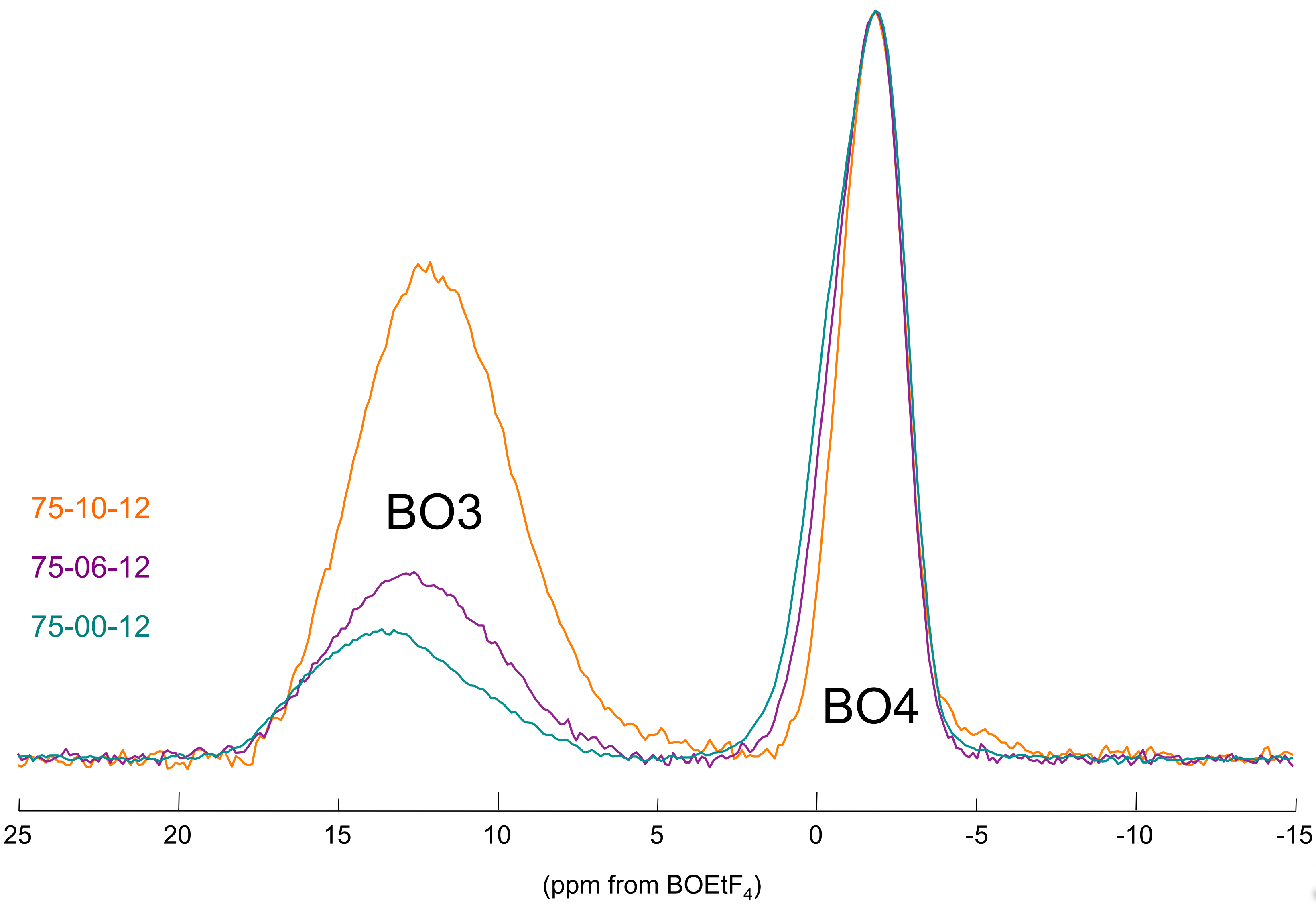
Log η= Ae + BeT/S^{conf}(T), we can calculte S^{conf} which goes from 8J/mol.K for up to 14.5J/mol.K with Al/B substitution

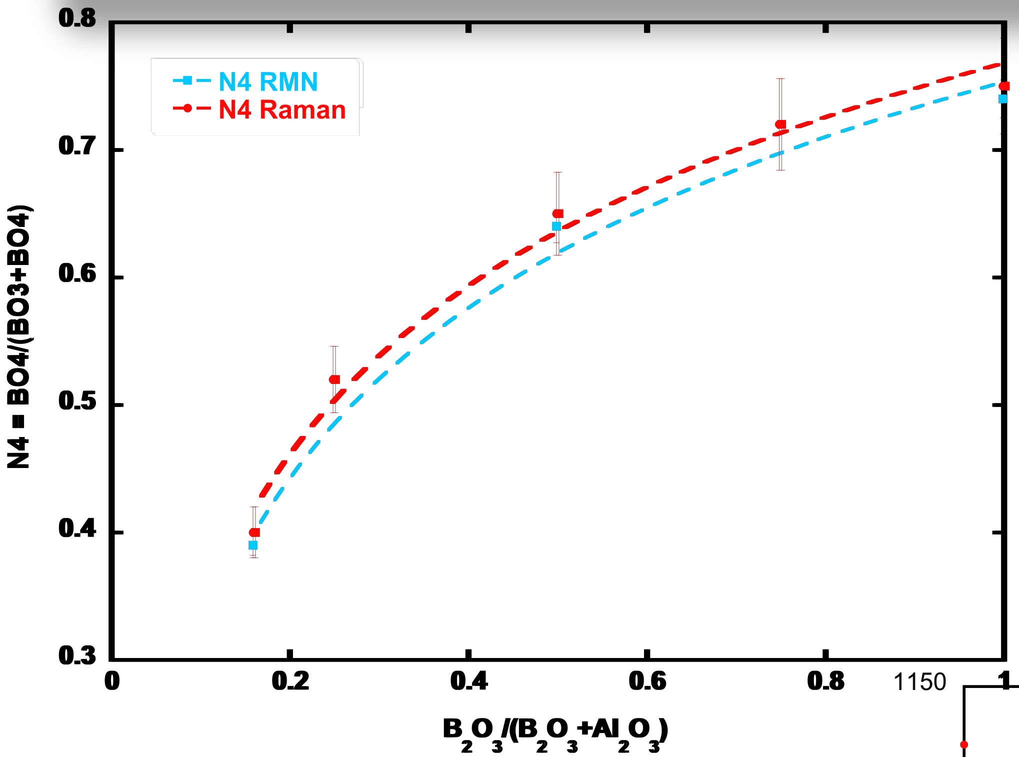
Raman Spectrometry



- With Al/B substitution => New band appear at 615, 920, 1200, 1450 cm^{-1}
- Important change in the T-O-T band vibrations
- No change in the boson peak and D1 and D2 decrease

^{11}B MAS (Echo) NMR in BAN

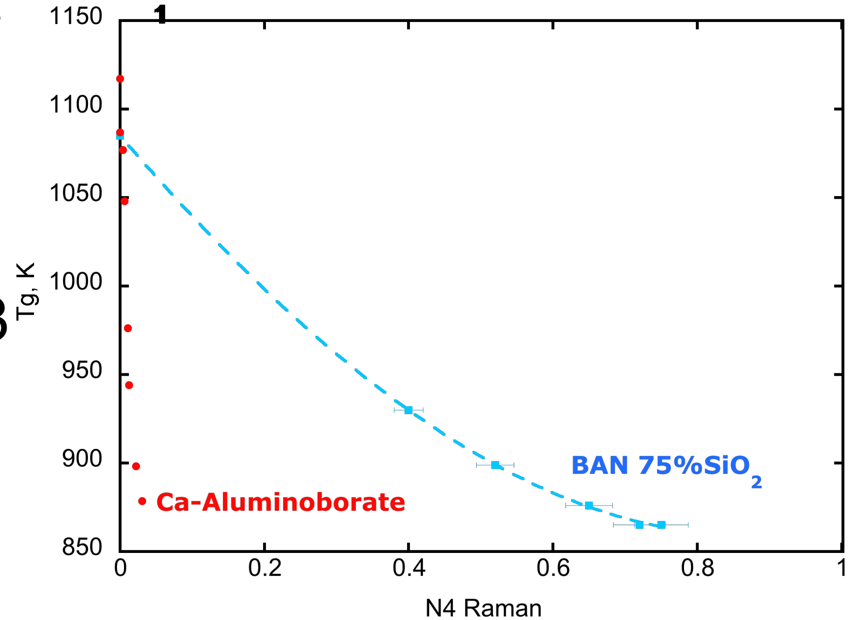




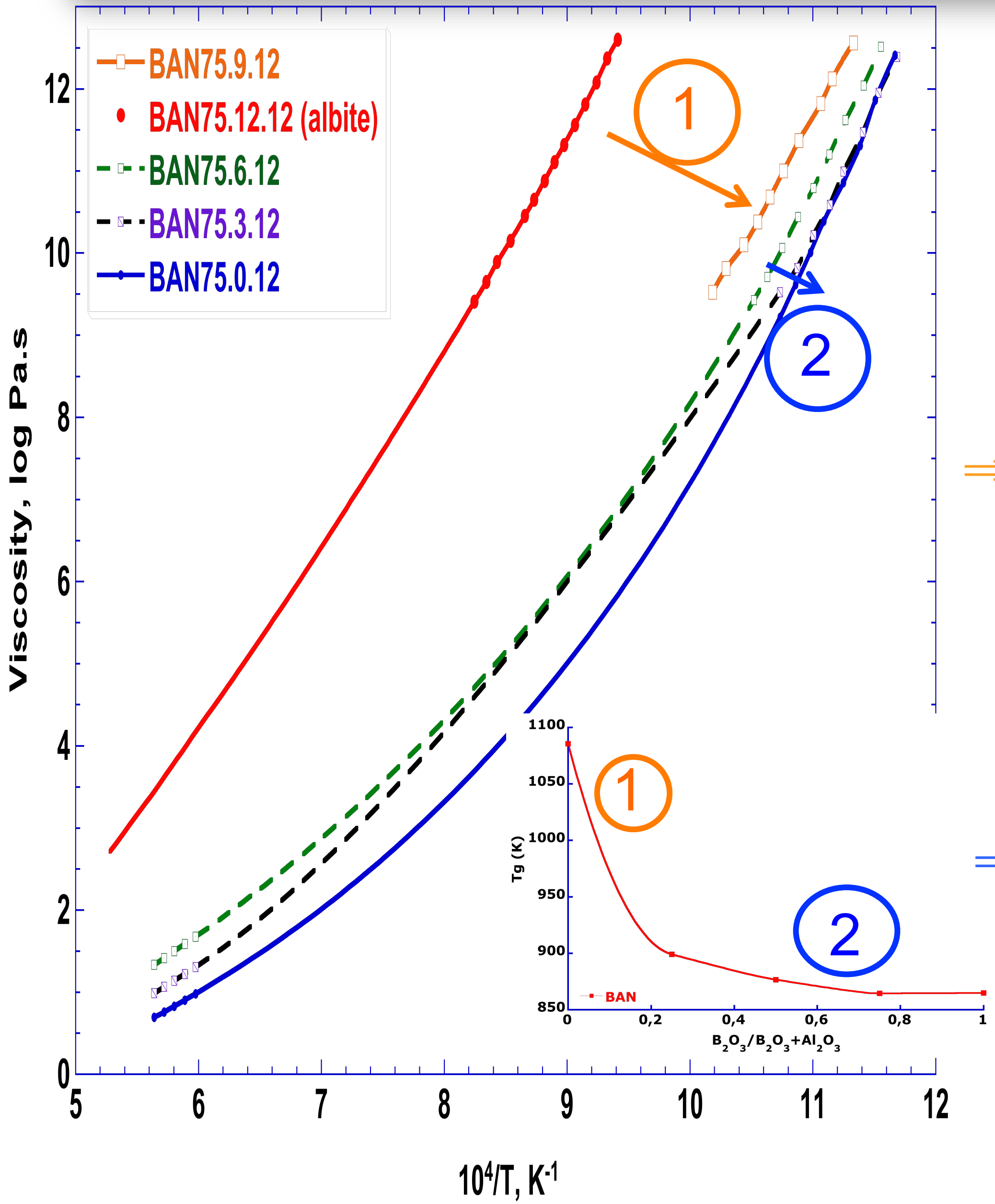
N4= BO4/(BO4+BO3)

Similar evolution than Geisinger et al., GCA 1988

Huge decrease of Tg with BO3



Assumption for Al/B substitution mechanism ?



But with Al/B substitution BO3 decreases and 2BO4 are present
⇒ BO3 decrease with B_2O_3 increases

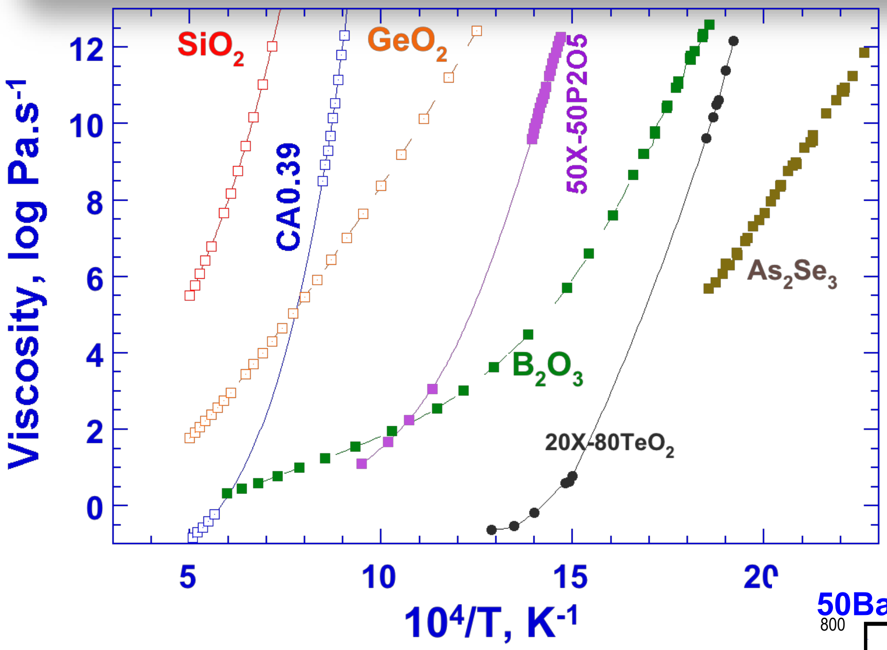
⇒ 1) by substitution Al by B => B is essentially in BO3 because Al used Na as a charge compensator and BO3 decreases a lot the viscosity

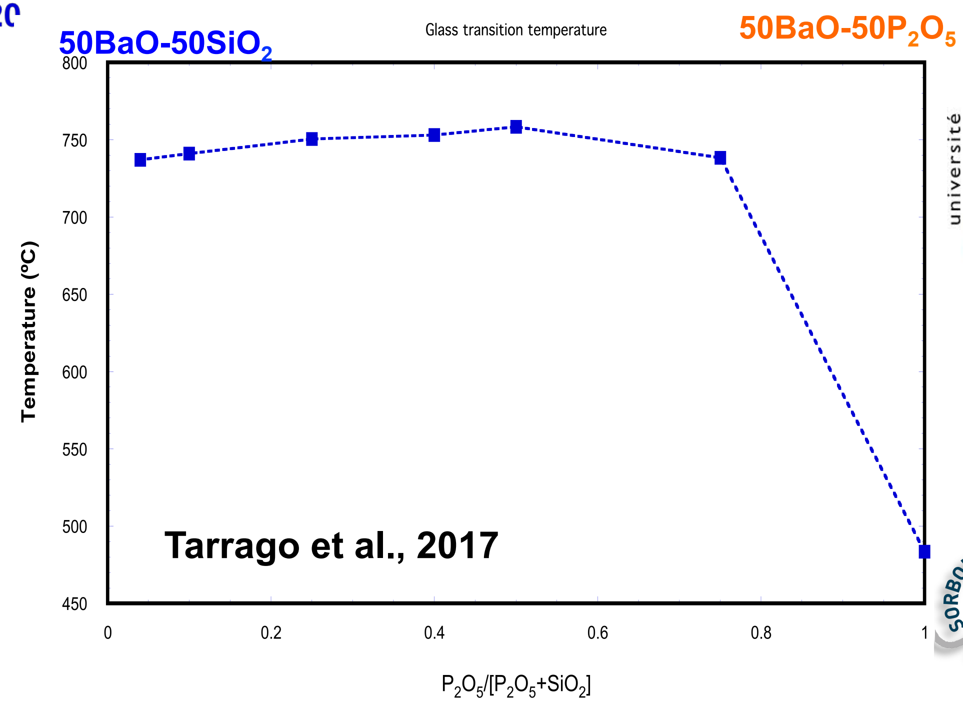
⇒ 2) With increasing B content => BO4 increases and used Na as a charge compensator => viscosity decreases slowly

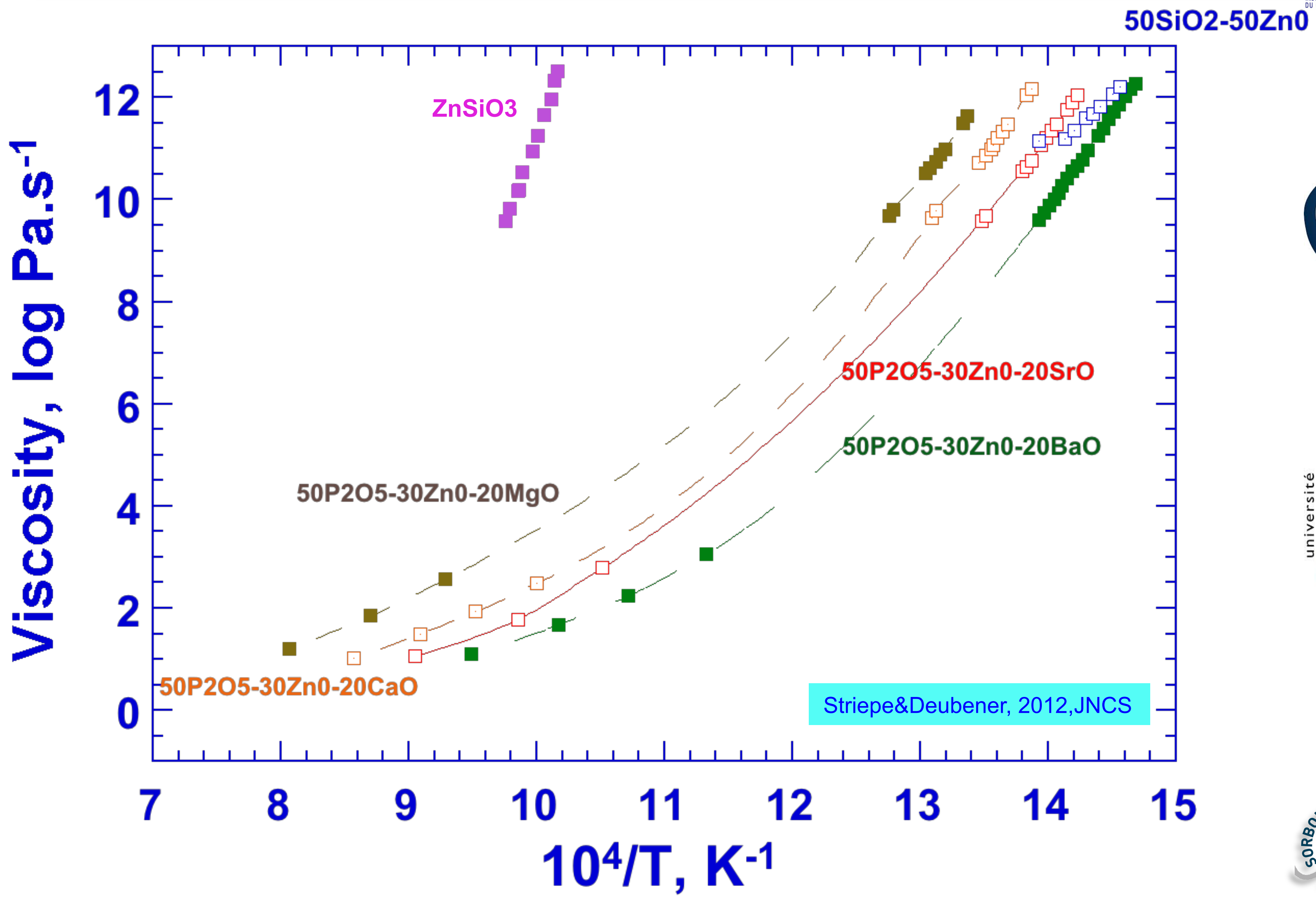
El Hayek et al., 2017 Chem Geol

P2O5....

SiO_2-P_2O_5


Viscosity, log Pa.s-1
10⁴/T, K-1
SiO2
CA0.39
GeO2
50X-50P2O5
B2O3
20X-80TeO2
As2Se3
0
2
4
6
8
10
12
5
10
15
20


50BaO-50SiO2
Glass transition temperature
50BaO-50P2O5
Temperature (°C)
P2O5/[P2O5+SiO2]
Tarrago et al., 2017
800
750
700
650
600
550
500
450
0
0.2
0.4
0.6
0.8
1


50SiO2-50Zn0
ZnSiO3
50P2O5-30Zn0-20SrO
50P2O5-30Zn0-20BaO
50P2O5-30Zn0-20MgO
50P2O5-30Zn0-20CaO
Striepe&Deubener, 2012,JNCS
Viscosity, log Pa.s-1
10^4/T, K-1
0
2
4
6
8
10
12
7
8
9
10
11
12
13
14
15

TeO_2….

TeO_2....

Références

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Impact of tellurite-based glass structure on Raman gain

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ABSTRACT

Raman gain efficiency and structure of tellurite glasses in the TeO_2–$TaO_{5/2}$–ZnO system have been investigated by Raman and IR spectroscopies. It has been found that replacement of $TaO_{5/2}$ by ZnO does not significantly modify the respective proportion of TeO_4, TeO_3 and TeO_{3+1} entities but induces an important decrease of the TeO_4 structural units Raman cross section. Change of the glass structure at the middle range length scale is proposed to be at the origin of the large decrease of the Raman cross section of the TeO_4 units.

Table 1

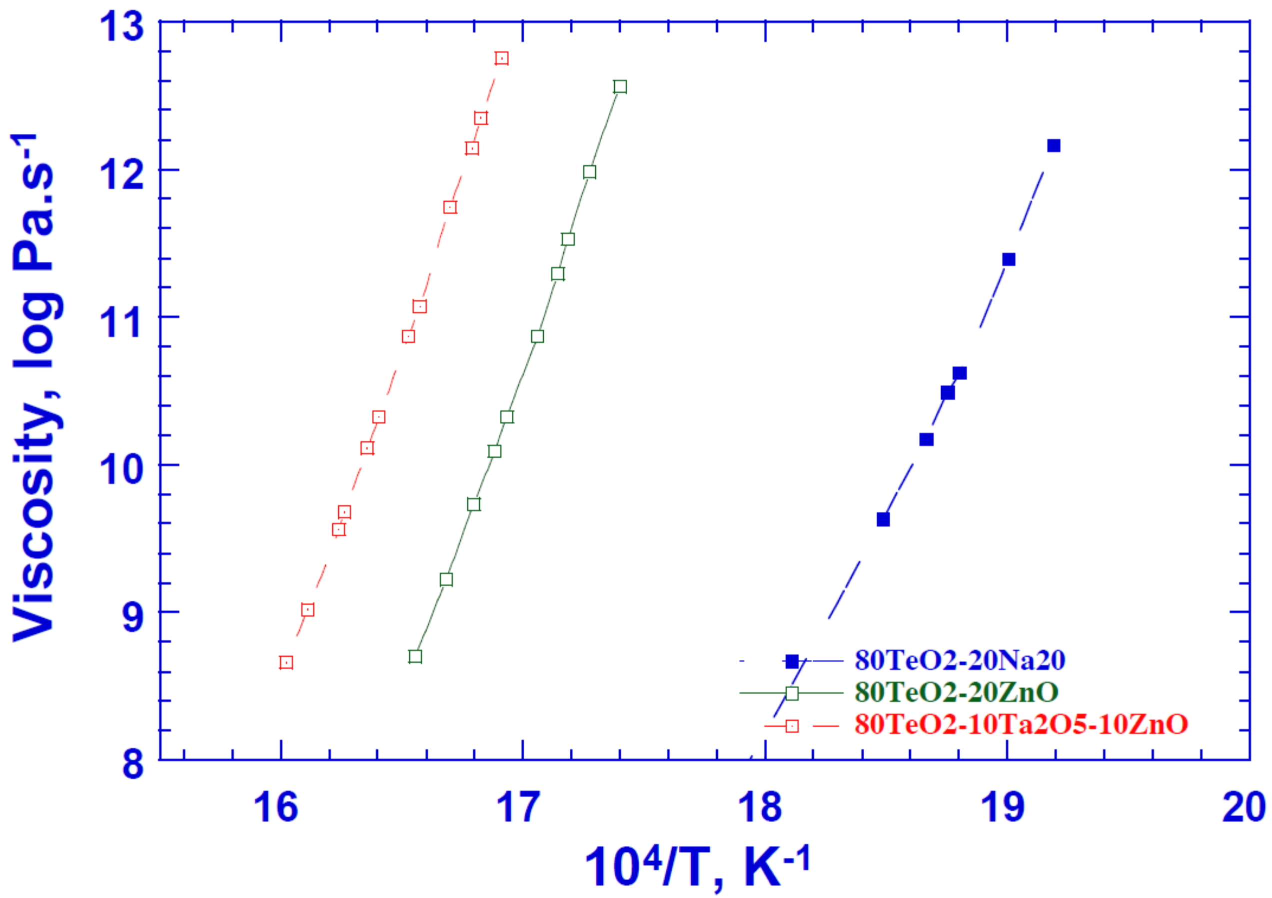
T_g glass transition temperature, T_x onset of the crystallization peak, T_p maximum of the crystallization peak, ΔT glass stability and volumetric weight.

Glass composition	T_g (±2 °C)	T_x (±2 °C)	T_p (±2 °C)	$\Delta T = T_x - T_g$	Volumetric weight (±0.3% g/cm^3)
$90TeO_2$–$10TaO_{5/2}$	351	430	465	79	5.81
$85TeO_2$–$15TaO_{5/2}$	370	489	516	119	5.91
$80TeO_2$–$20TaO_{5/2}$	387	502	505	115	5.99
$80TeO_2$–$15TaO_{5/2}$–5ZnO	360	496	537	136	5.89
$80TeO_2$–$10TaO_{5/2}$–10ZnO	350	478	526	128	5.78
$80TeO_2$–$5TaO_{5/2}$–15ZnO	335	468	498	133	5.67

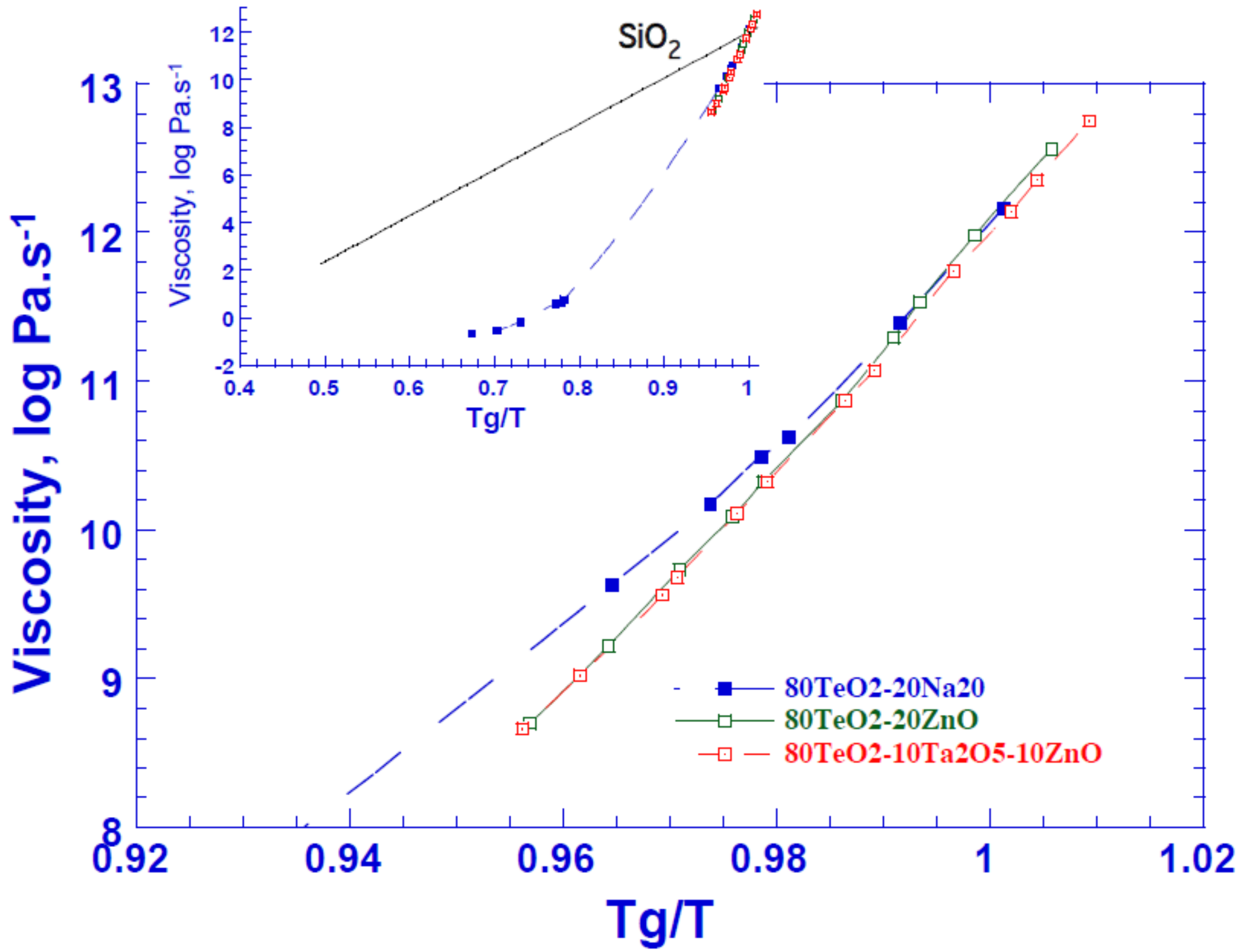
80% TeO_2 – 20% ZnO	Tg = 323°C	Tx >400°C	[I.Savelli 2012]
80% TeO_2 – 20% Na_2O	Tg = 256°C	Tx = 383°C	[A.Santic 2008]

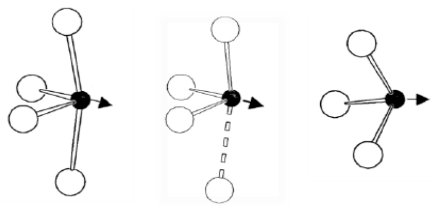
TeO_2....

Viscosity



Fragility


SiO2
Viscosity, log Pa.s-1
Tg/T
80TeO2-20Na20
80TeO2-20ZnO
80TeO2-10Ta2O5-10ZnO
13
12
11
10
9
8
0.92
0.94
0.96
0.98
1
1.02
12
10
8
6
4
2
0
-2
0.4
0.5
0.6
0.7
0.8
0.9
1



Summarize Oxide glasses

SiO_2, GeO_2 => strong network former

B_2O_3 (BO3,BO4), P_2O_5, V_2O_5, TeO_2 => soft network former

Al_2O_3, Ta_2O_3: mix… ?

Al^{IV} => network former

Al^{V}=> reticulator, need to ensure dynamics at HT

Al^{VI}=> generaly network modifier… but with P?

Fe2O3 => network former

As_2Se_3 : similar than B_2O_3

Li_2O, Na_2O, K_2O, MgO, CaO, SrO, BaO, ZnO, FeO =>network modifier or charge compensator in Si, Ge, P, B, V systems

PbO : probably network modifier…..

O BO, NBO, free? Other systems ?