Basic data on glass structure and its influence on viscosity

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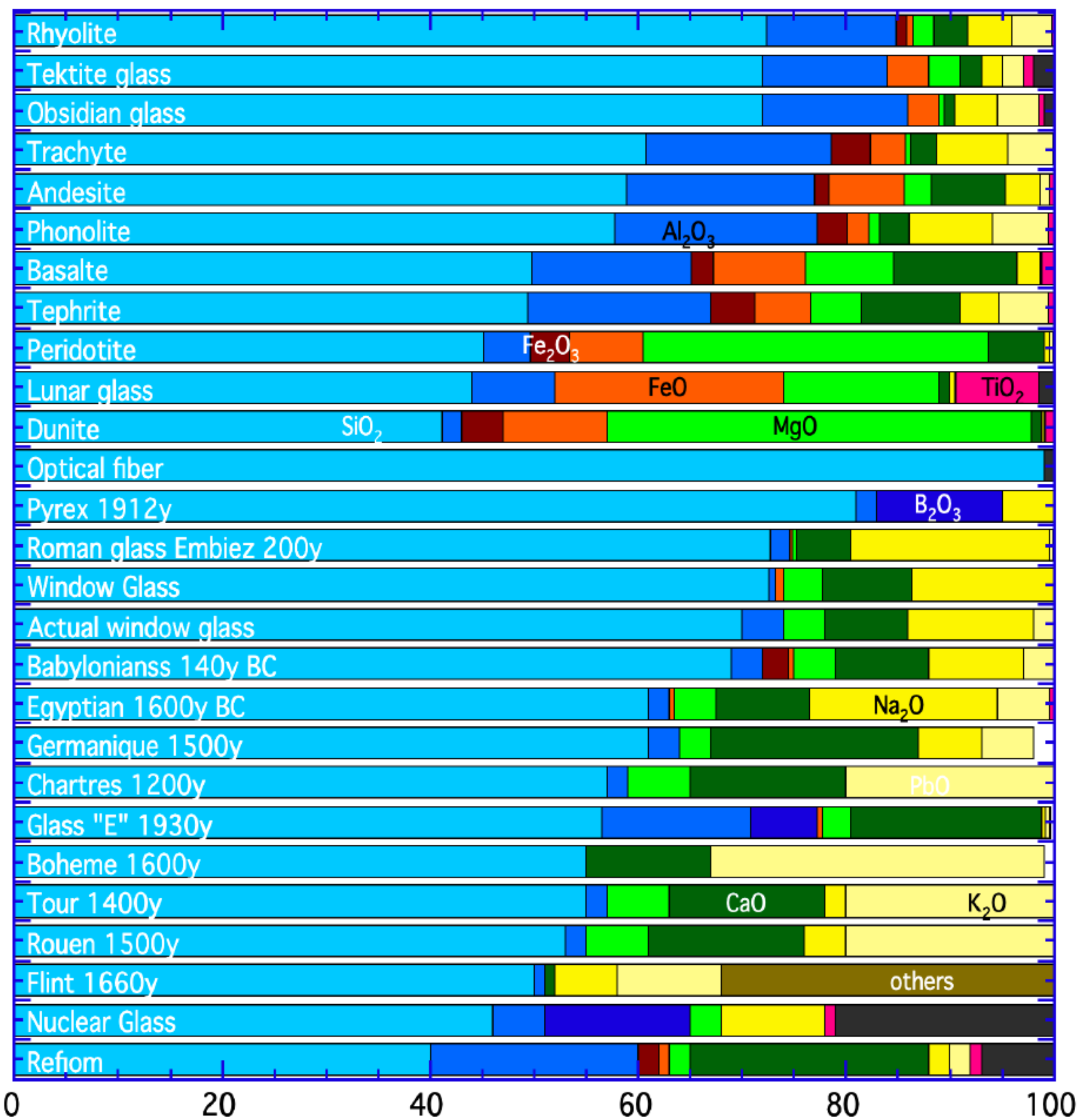
TO_2-MO-M'_2O, with T= Si, Al, Fe^{3+}, M=Mg, Ca, Fe^{2+}, M'=Li, Na, K



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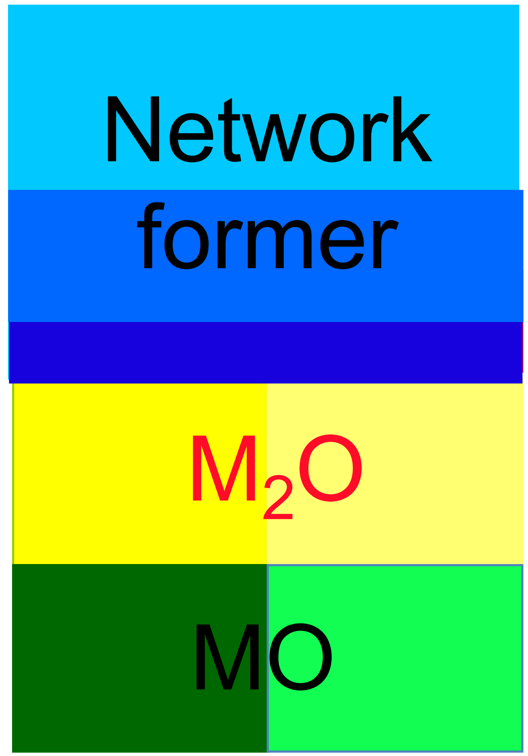


Properties versus Structure ?

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?

Redox talk tomorrow

How network former can be mixed?

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?

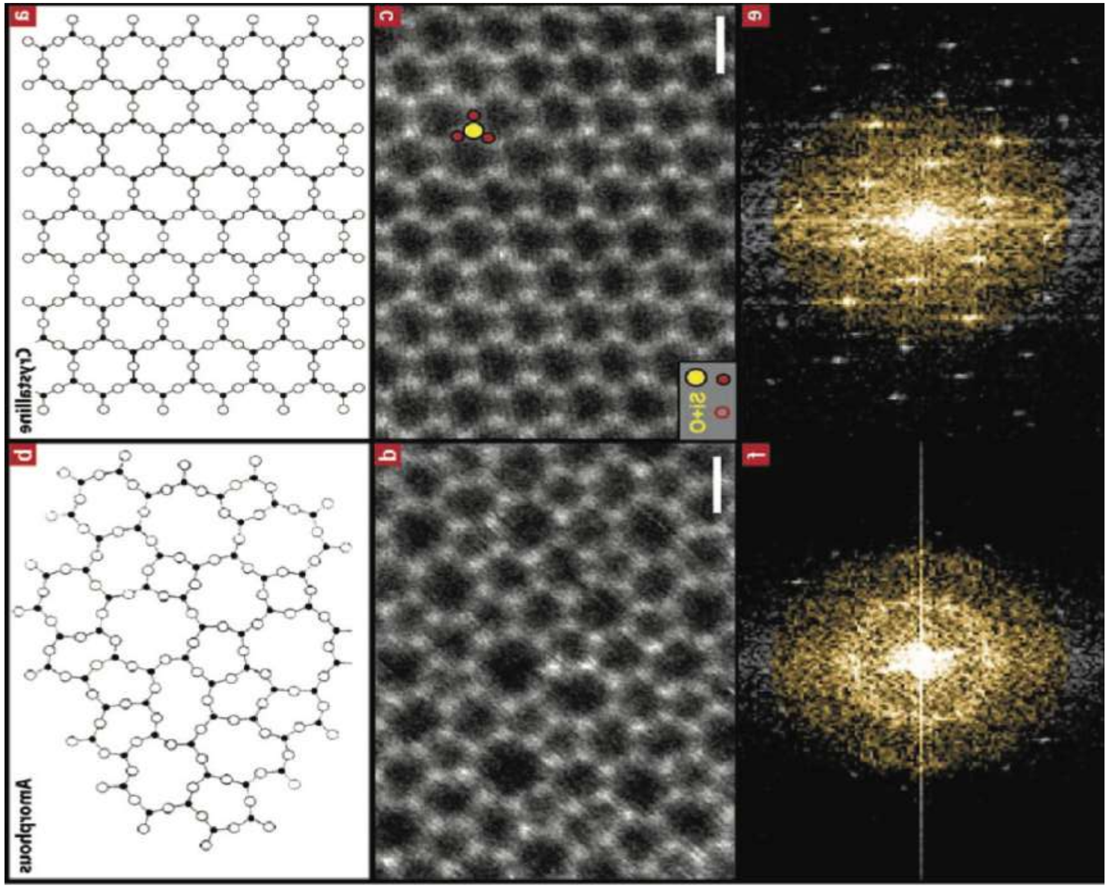
Is there and universal definition of glass former?

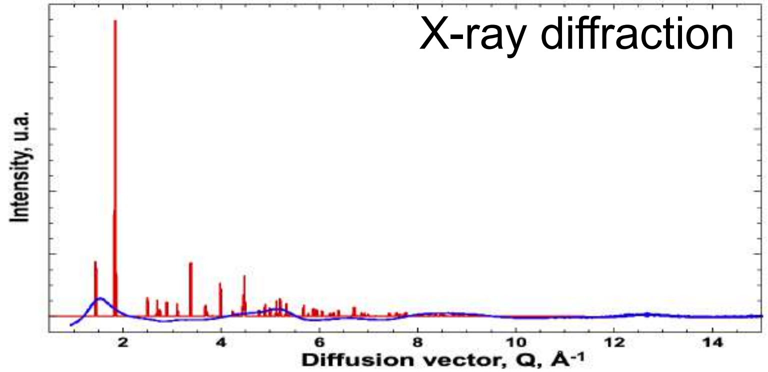
Does the definition of glass formers depends on the type of glass systems?

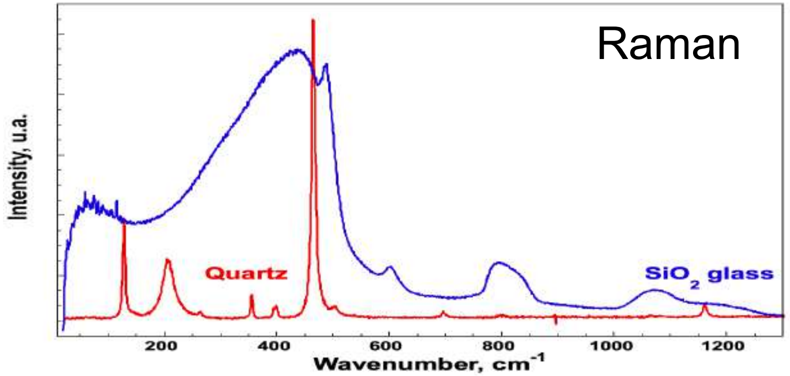
Does the definition of glass formers evaluate with new analytical tools?

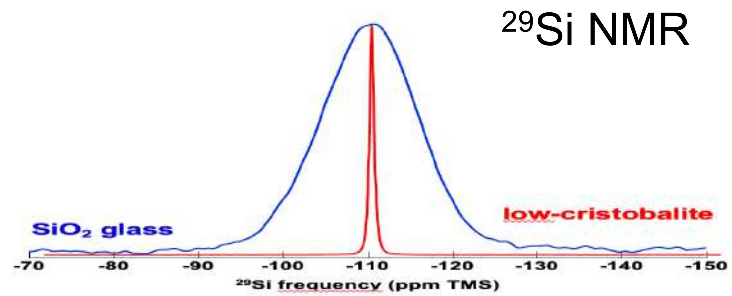
Does modelisation enable to get a different view of glass forming effect?

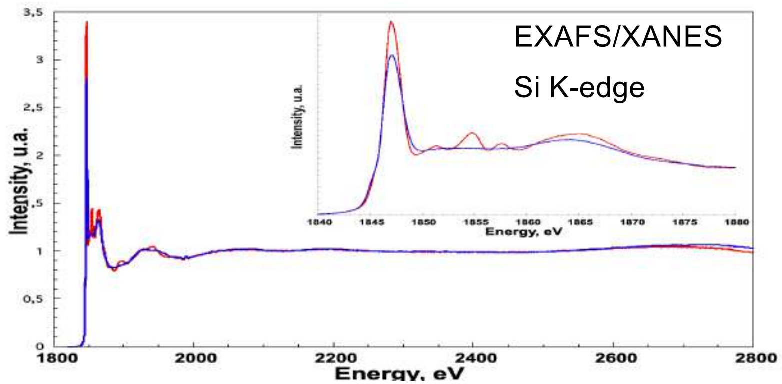
Crystal versus glass ?







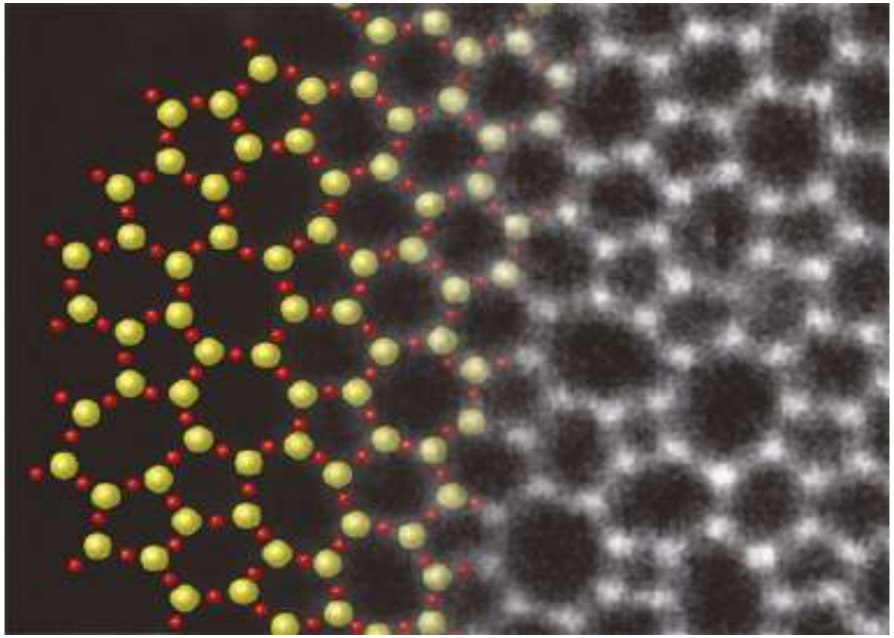




Huang et al., (2012) Direct Imaging of a Two-Dimensional Silica Glass on Graphene Nano Lett. 2012, 12, 1081−1086

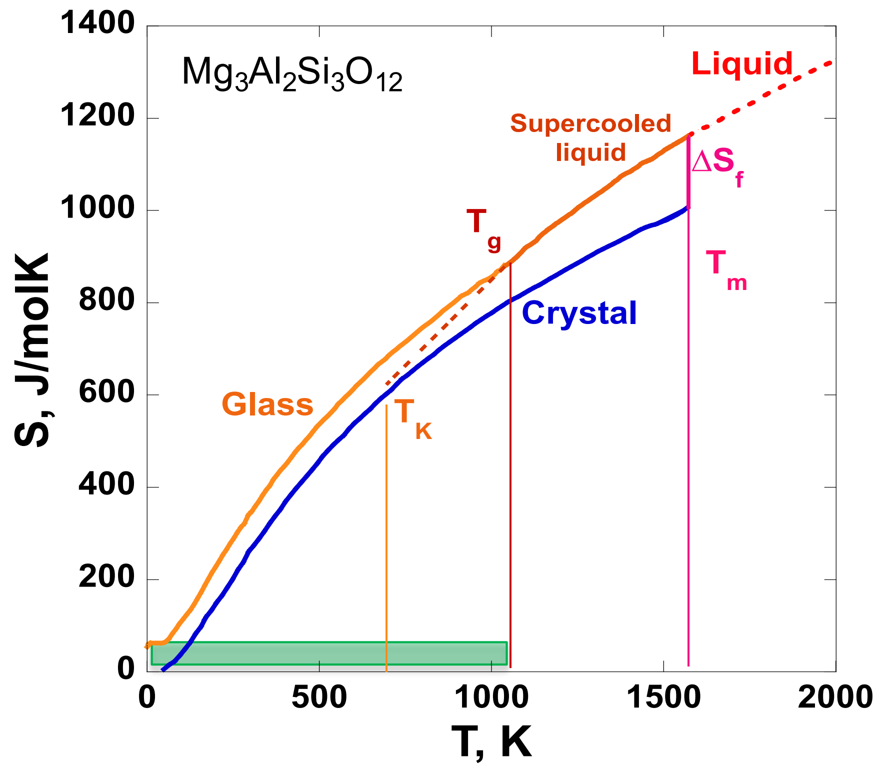
Neuville D.R., Cormier L. (2022) Le verre : un matériau d’hier, d’aujourd’hui et de demain. Matériaux & Techniques 110, 404. DOI- 10.1051/mattech/2022037

A disordered state



Huang et al., (2012) Direct Imaging of a Two-Dimensional Silica Glass on Graphene Nano Lett. 2012, 12, 1081−1086

A glass transition temperature



Neuville D.R., Henderson G.S, Dingwell D. B. (2022) "Geological melts" Review in Mineralogy and Geochemistry. DOI : 10.2138/rmg.2022.87.02

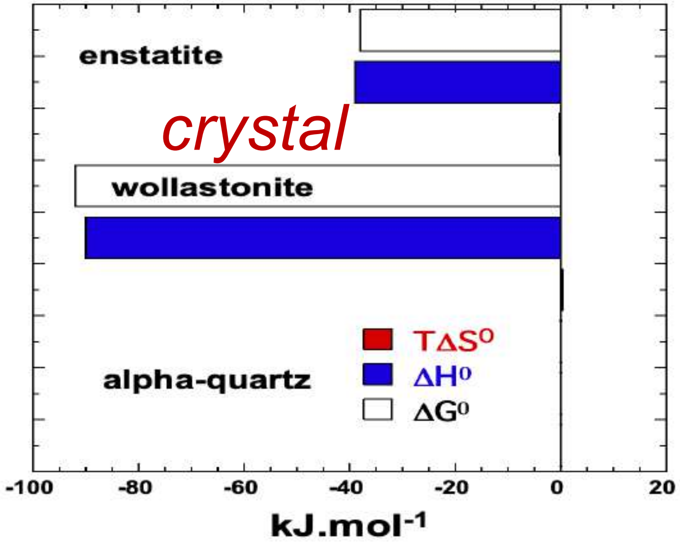
Residual entropy = configurational entropy
=> image of the glass structure

Phase equilibria between melts and crystal

Phase equilibria between melts and crystal

$$\mu_i = \Delta H_i - T\Delta S_{mi}$$

$$S^{conf}{}_{melts} \Rightarrow \Delta S_{mix} \Rightarrow \Delta S_{mi}$$

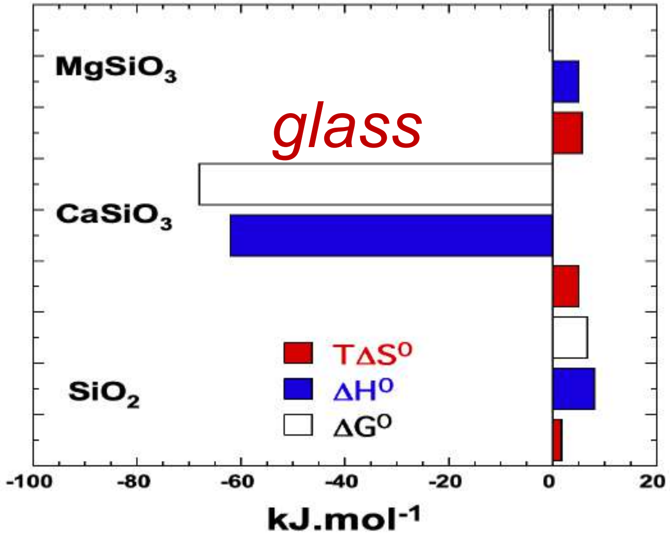


free enthalpy of formation with respect to oxides

$$\Delta G_f^0(T) = \left[\sum_i n_i \Delta H_{s_i}(T) - \Delta H_s(T)\right] - T\left[S(0) + \int_0^T C_p\, dT/T - \sum_i n_i \left(S_i(0) + \int_0^T C_{p_i}\, dT/T\right)\right]$$

$$\Delta G^0{}_f(T) = \Delta H^0{}_f(T) - T\Delta S^0{}_f(T)$$

$$S(0) = S^{conf}\ (Tg)$$



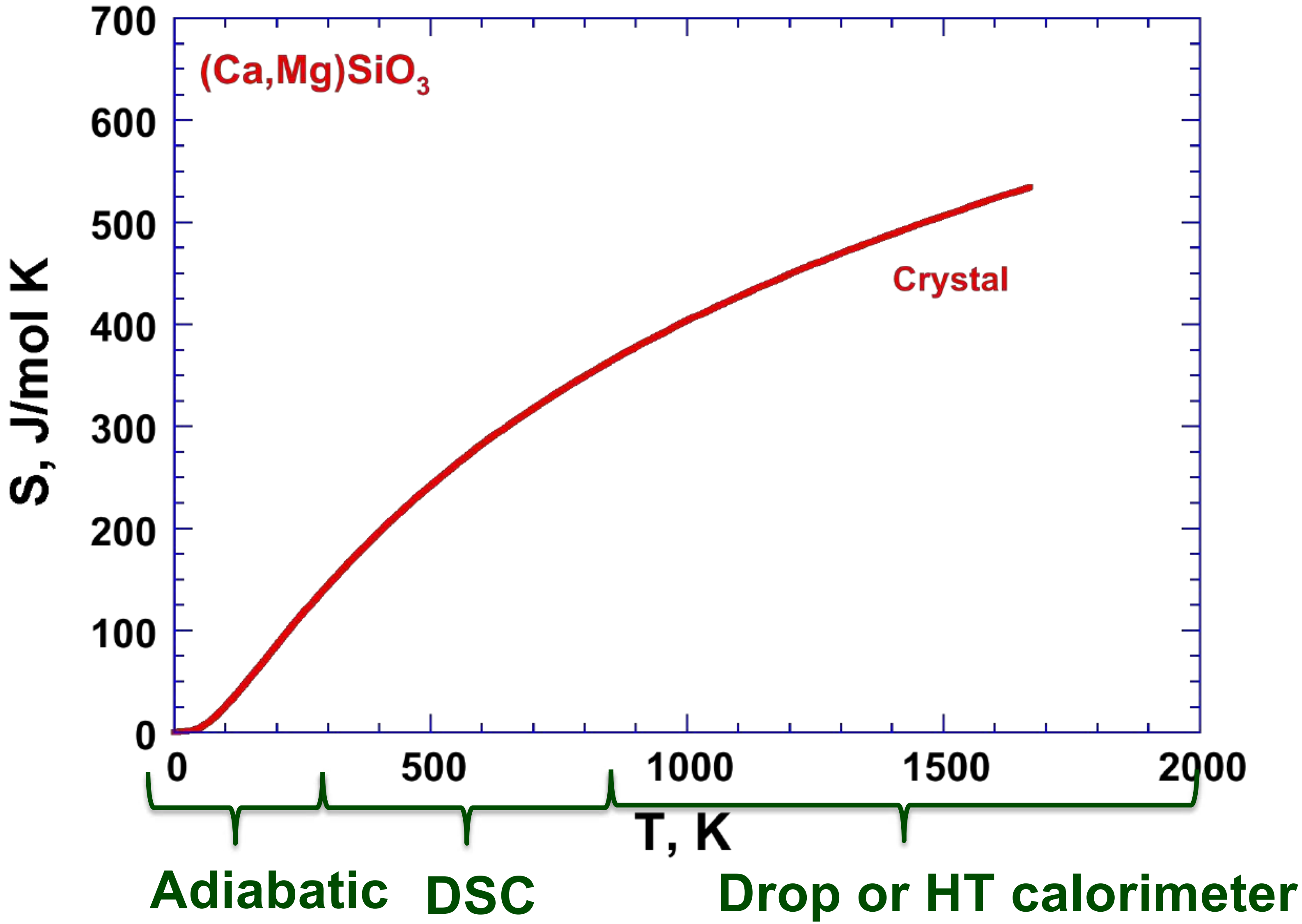
At room temperature S^{conf} can be up to 30% of total entropy of glass

Linard, Neuville, Richet (1997) Thermochimie des verres de stockage de dechets nucleaires: Une nouvelle approche. https://www.researchgate.net/publication/343852518 liquid

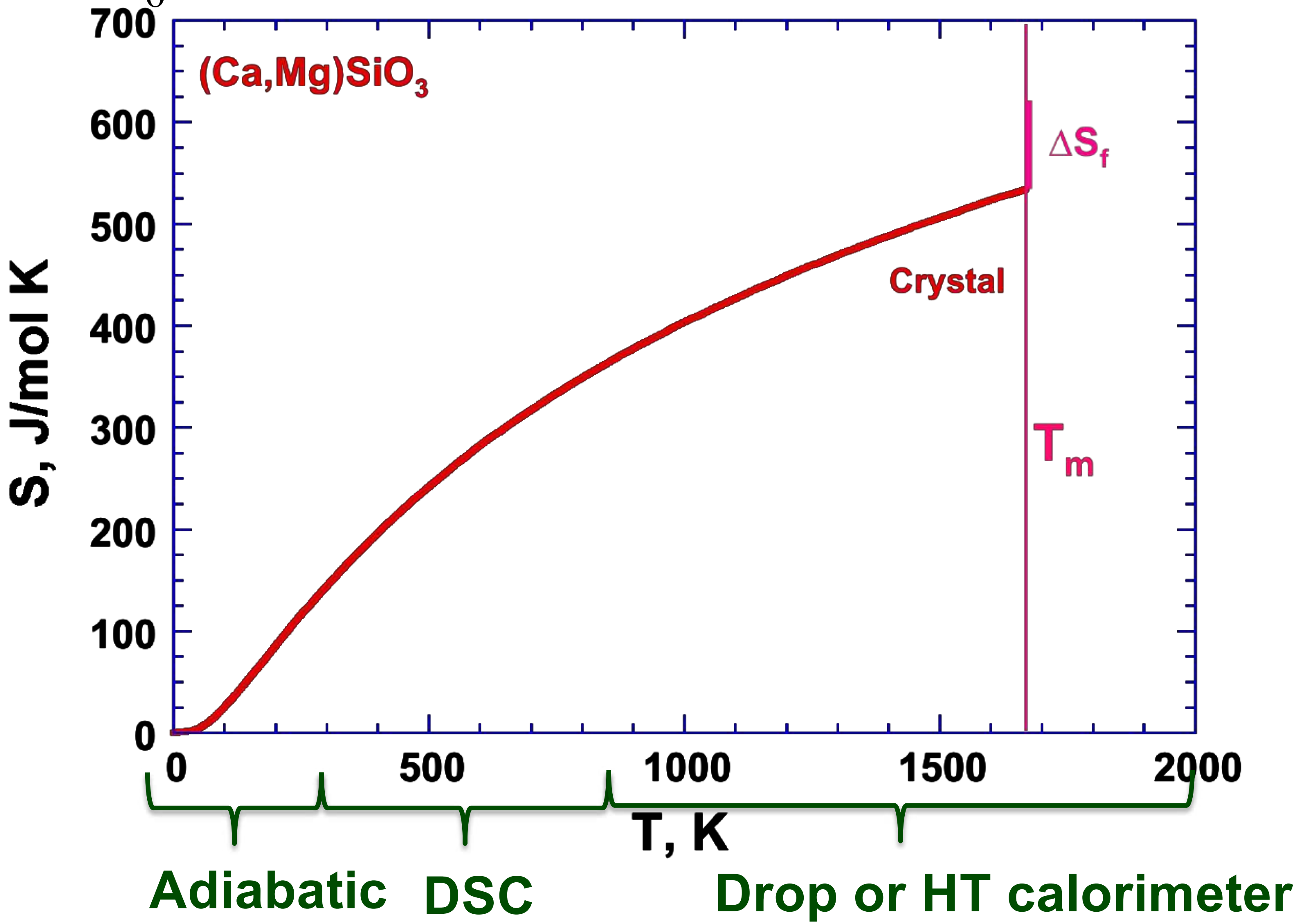
Diopside
$CaMgSi_2O_6$

Glass

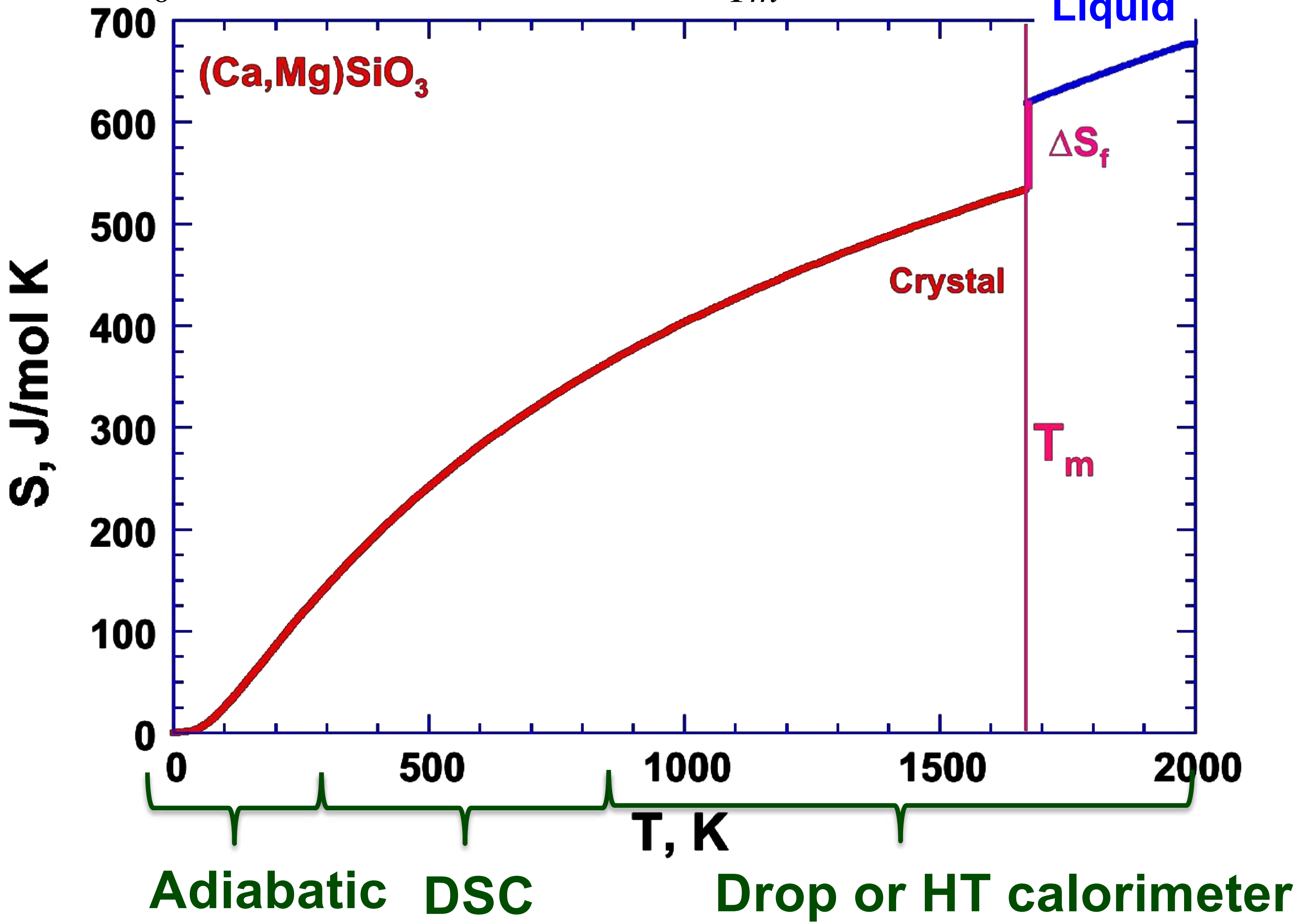
$$\int_0^{Tm} \frac{Cp^{Crystal}}{T}.dT$$



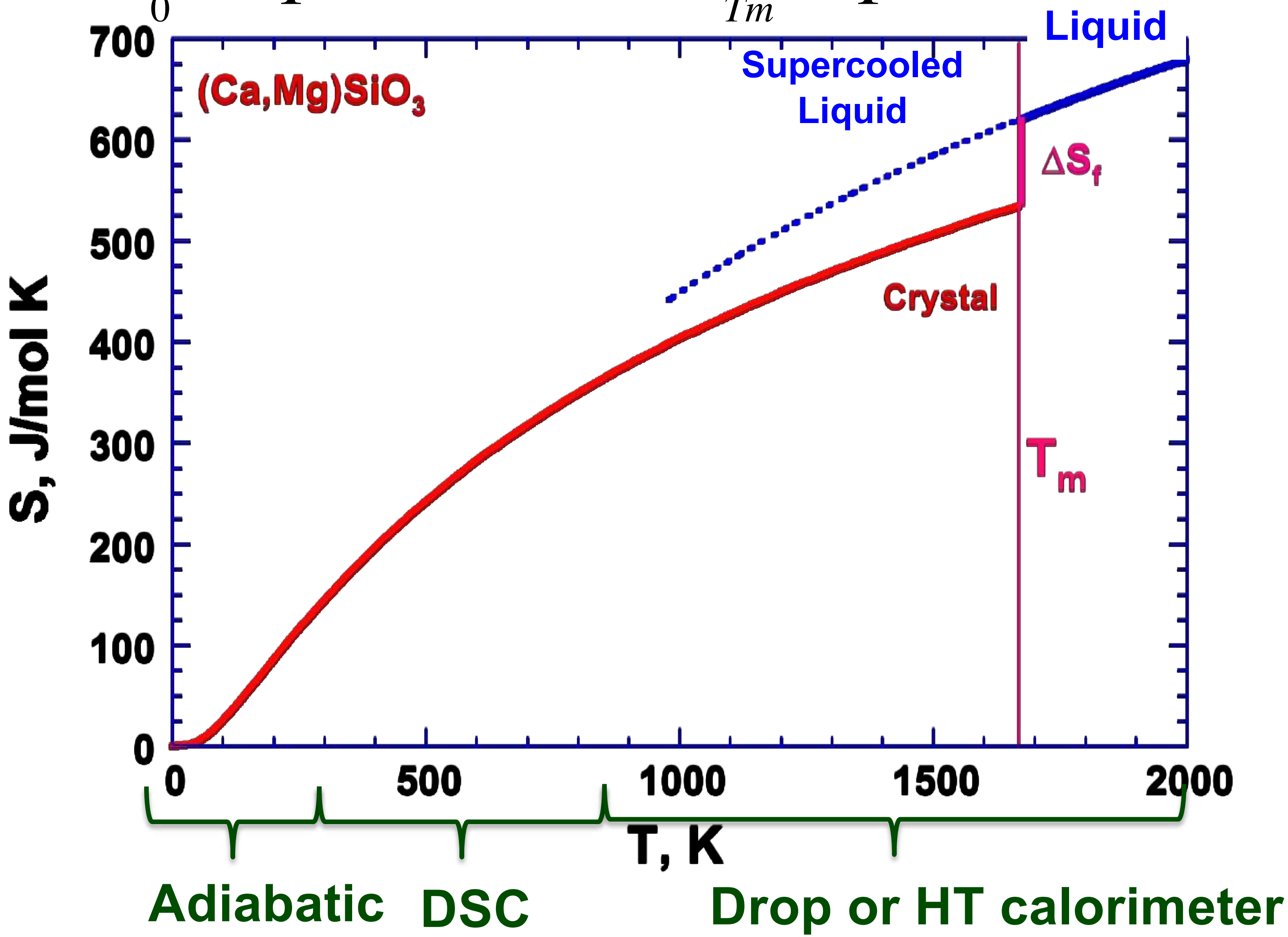
$$\int_0^{Tm} \frac{Cp^{Crystal}}{T}.dT + \Delta S_f$$



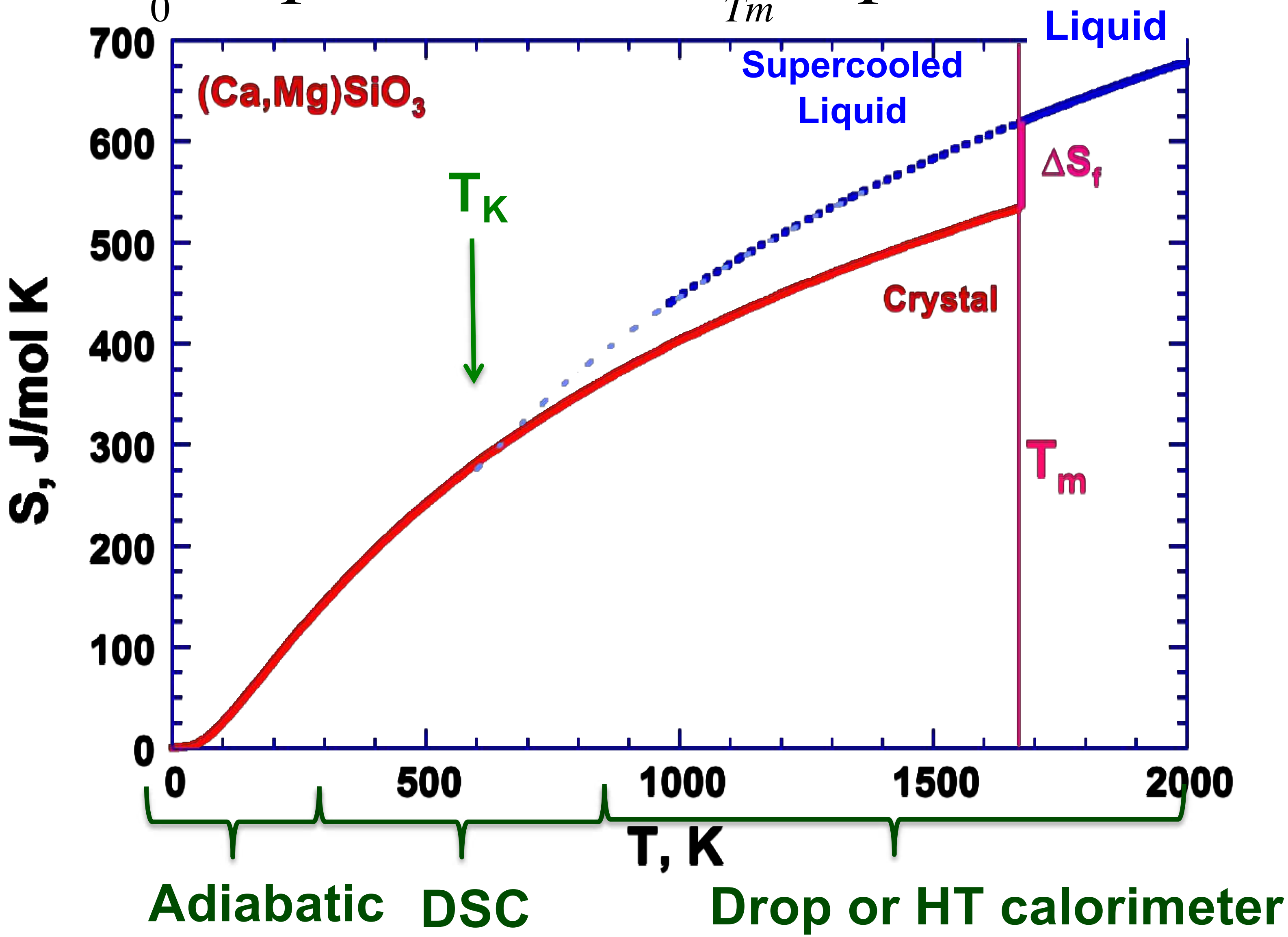
$$\int_0^{Tm} \frac{Cp^{Crystal}}{T}.dT + \Delta S_f + \int_{Tm}^{Tg} \frac{Cp^{liquid}}{T}.dT$$



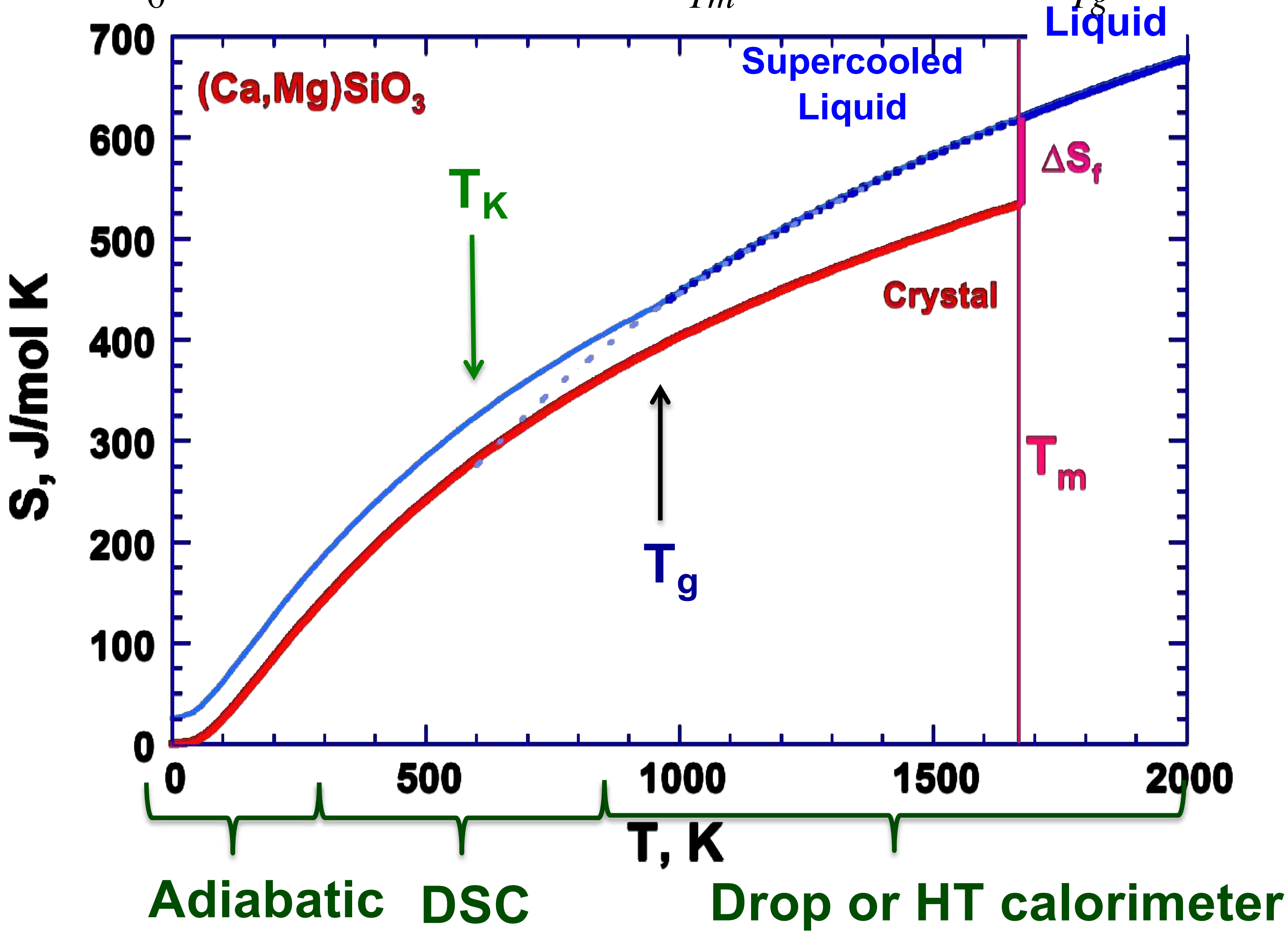
$$\int_0^{Tm} \frac{Cp^{Crystal}}{T}.dT + \Delta S_f + \int_{Tm}^{Tg} \frac{Cp^{liquid}}{T}.dT$$



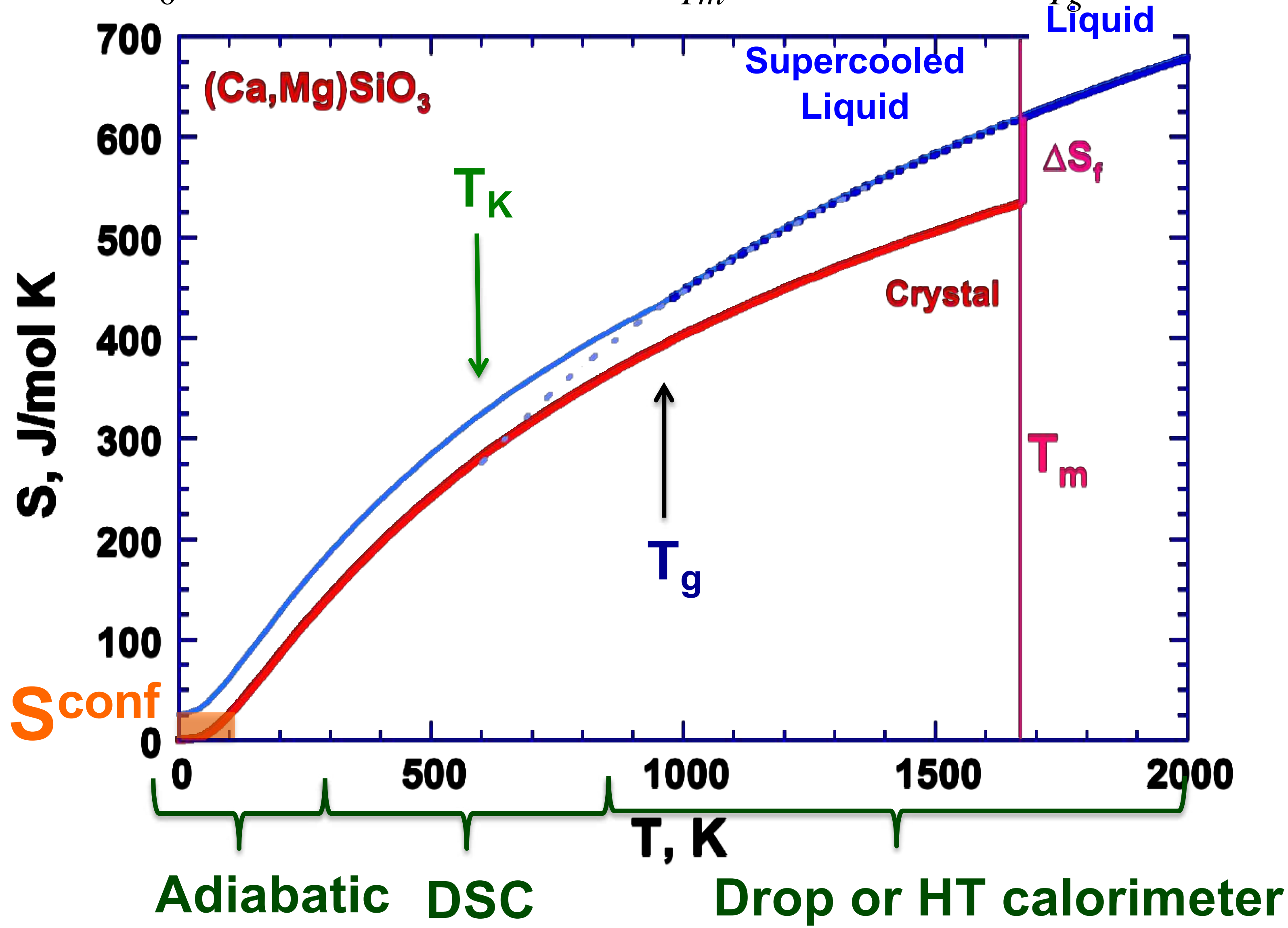
$$\int_0^{Tm} \frac{Cp^{Crystal}}{T}.dT + \Delta S_f + \int_{Tm}^{Tg} \frac{Cp^{liquid}}{T}.dT$$

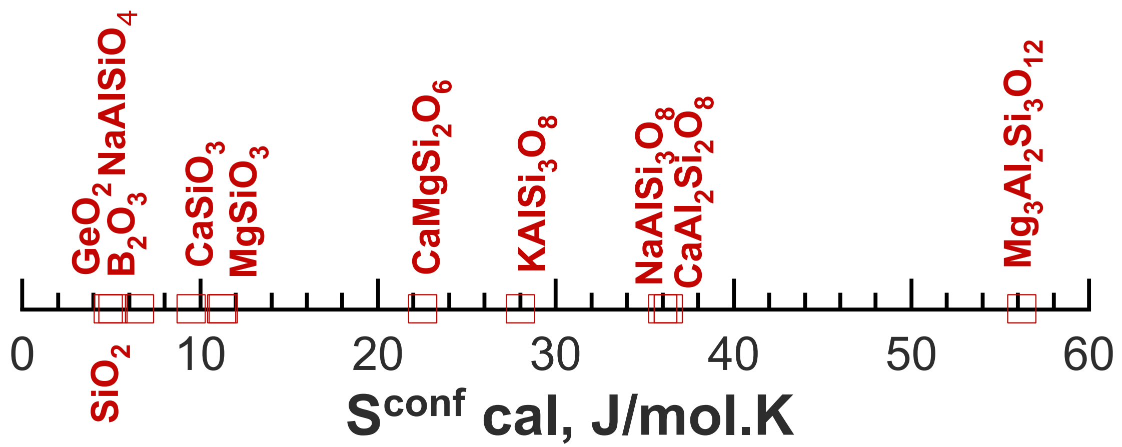


$$\int_0^{Tm} \frac{Cp^{Crystal}}{T}.dT + \Delta S_f + \int_{Tm}^{Tg} \frac{Cp^{liquid}}{T}.dT + \int_{Tg}^{0} \frac{Cp^{glass}}{T}.dT$$

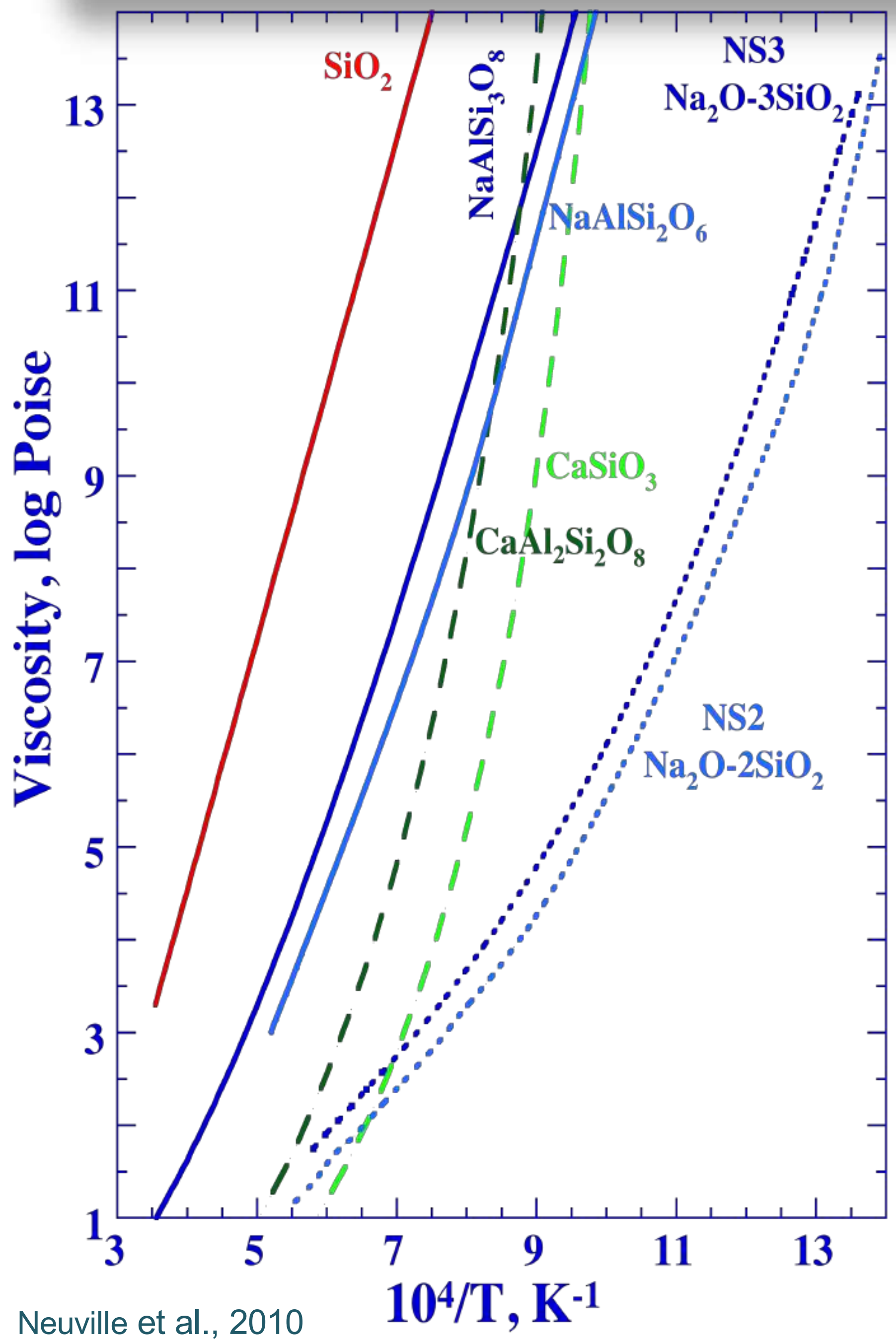


$$S^{conf}(Tg) = \int_0^{Tm} \frac{Cp^{Crystal}}{T}.dT + \Delta S_f + \int_{Tm}^{Tg} \frac{Cp^{liquid}}{T}.dT + \int_{Tg}^{0} \frac{Cp^{glass}}{T}.dT$$





Calorimetrical Configurational entropy



Neuville et al., 2010

Arrhenius :

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

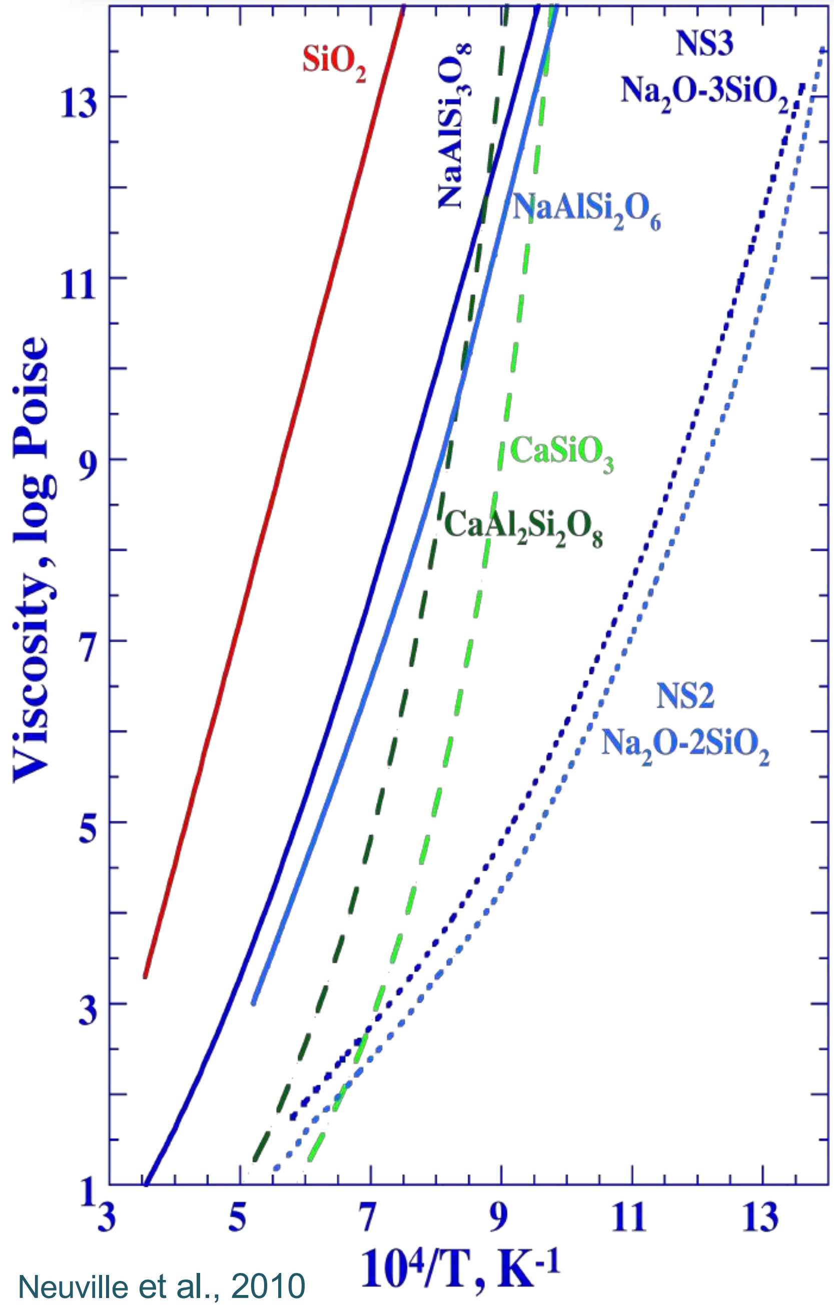
⇔ $\log \eta = A + B/T$

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 …..



Neuville et al., 2010

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

Proposed by Adam and Gibbs, 1965

First used to silicate melts by Urbain, 1972,
Wong and Angell 1976,
Scherer, 1984, Richet, 1984, …
Neuville and Richet, 1991….

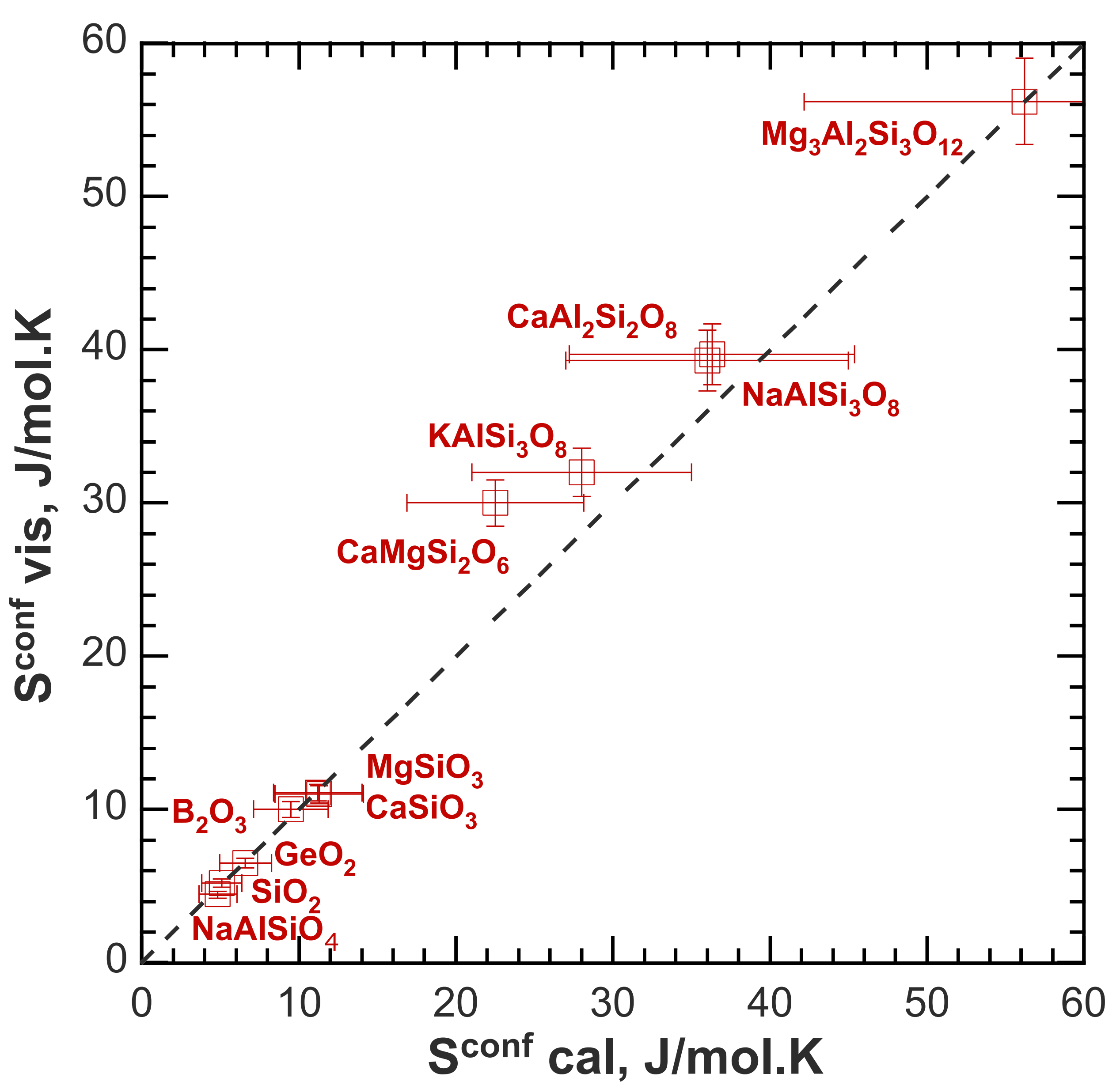
$$S^{conf}(T) = S^{conf}(Tg) + \int_{Tg}^{T} Cp^{conf} / T dt$$

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

Calorimetry measurements
=> Easy

Configurational entropy

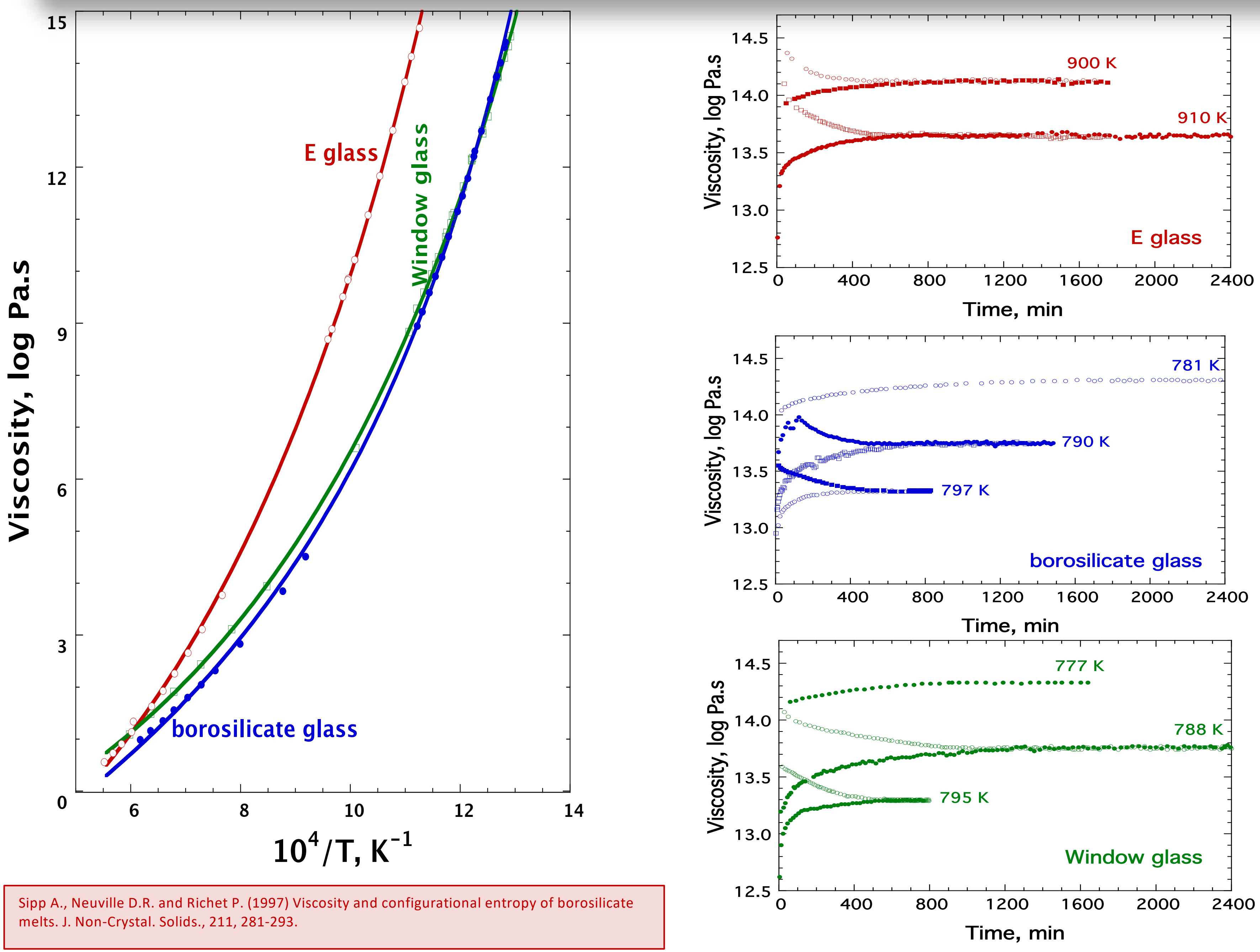
Viscosimetry configurational entropy



Calorimetrical Configurational entropy

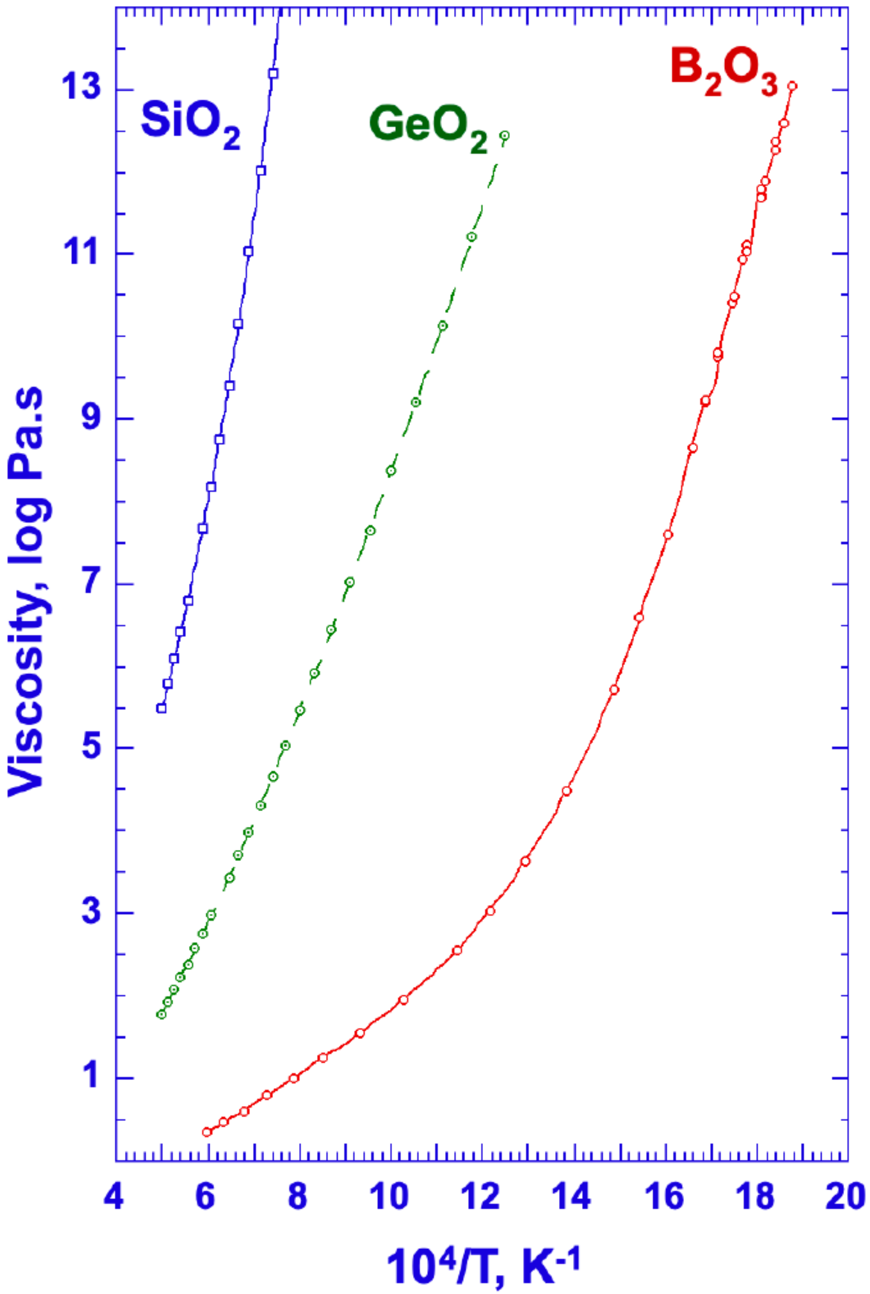
In Neuville D.R., Henderson G.S, Dingwell D. B. (2022) "Magmas, melts, liquids and glasses: Experimental insights " Review in Mineralogy and Geochemistry. DOI : 10.2138/rmg.2022.87.03

Non-Newtonian behavior, relaxation problem?



Sipp A., Neuville D.R. and Richet P. (1997) Viscosity and configurational entropy of borosilicate melts. J. Non-Crystal. Solids., 211, 281-293.

Network former



SiO_2 covalent bond

SiO_4 tetrahedra

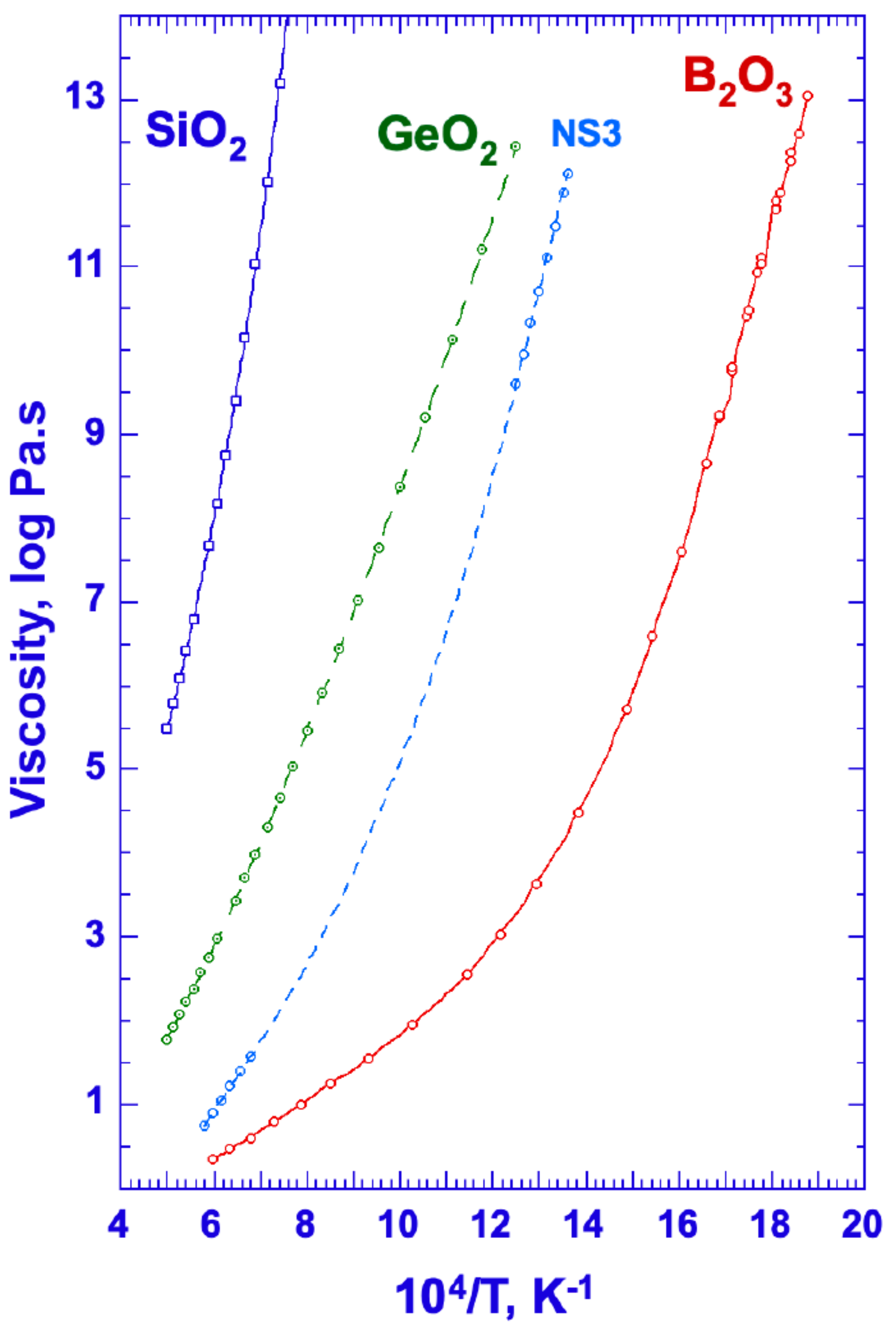
GeO_2 covalent bond

GeO_4 tetrahedra

B_2O_3 covalent bond

BO_3 triangle and BO_4 tetrahedra

Network former



SiO_2 covalent bond

- SiO_4 tetrahedra
- Na_2O breaks the network
- Viscosity decreases

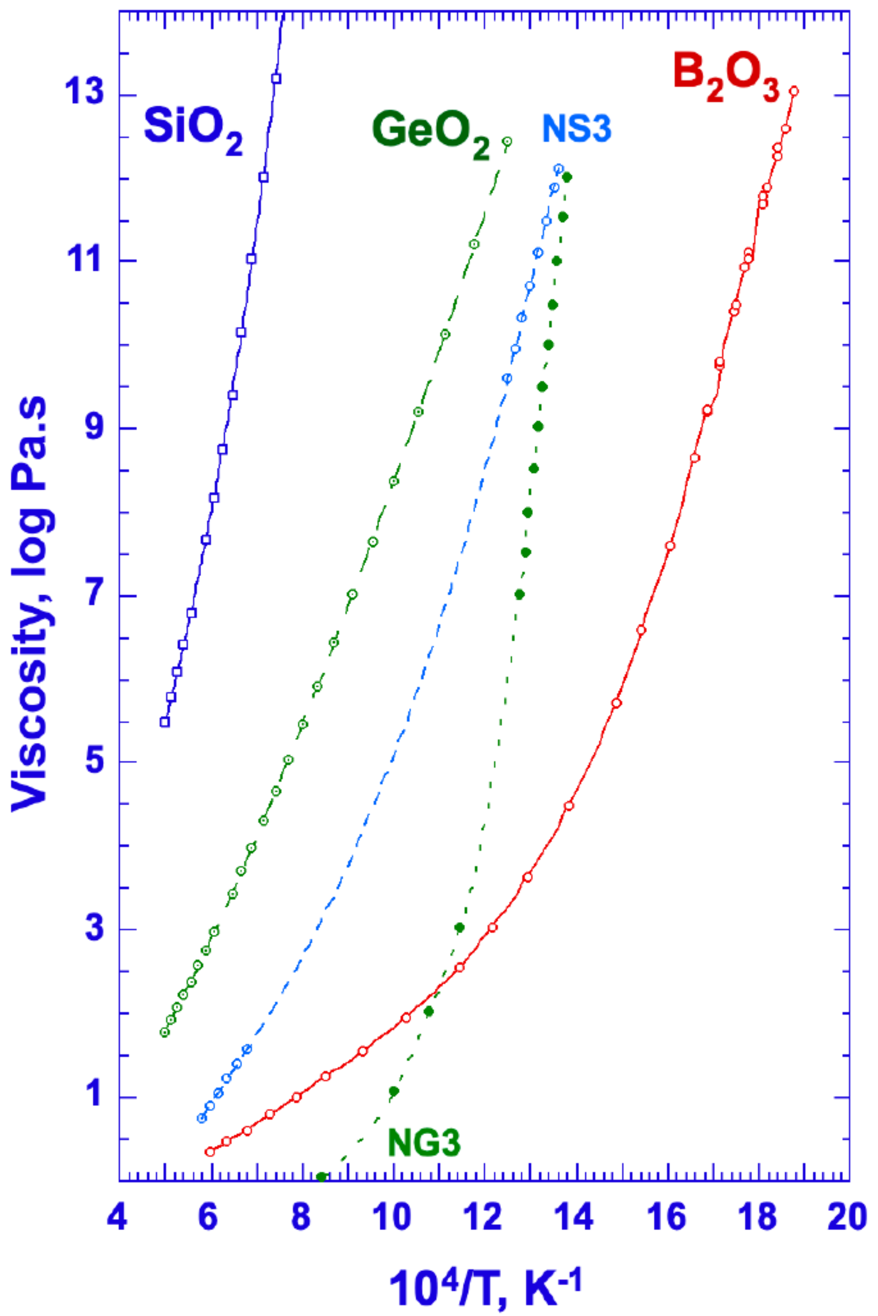
GeO_2 covalent bond

- GeO_4 tetrahedra

B_2O_3 covalent bond

- BO_3 triangle and BO_4 tetrahedra

Network former



SiO_2 covalent bond

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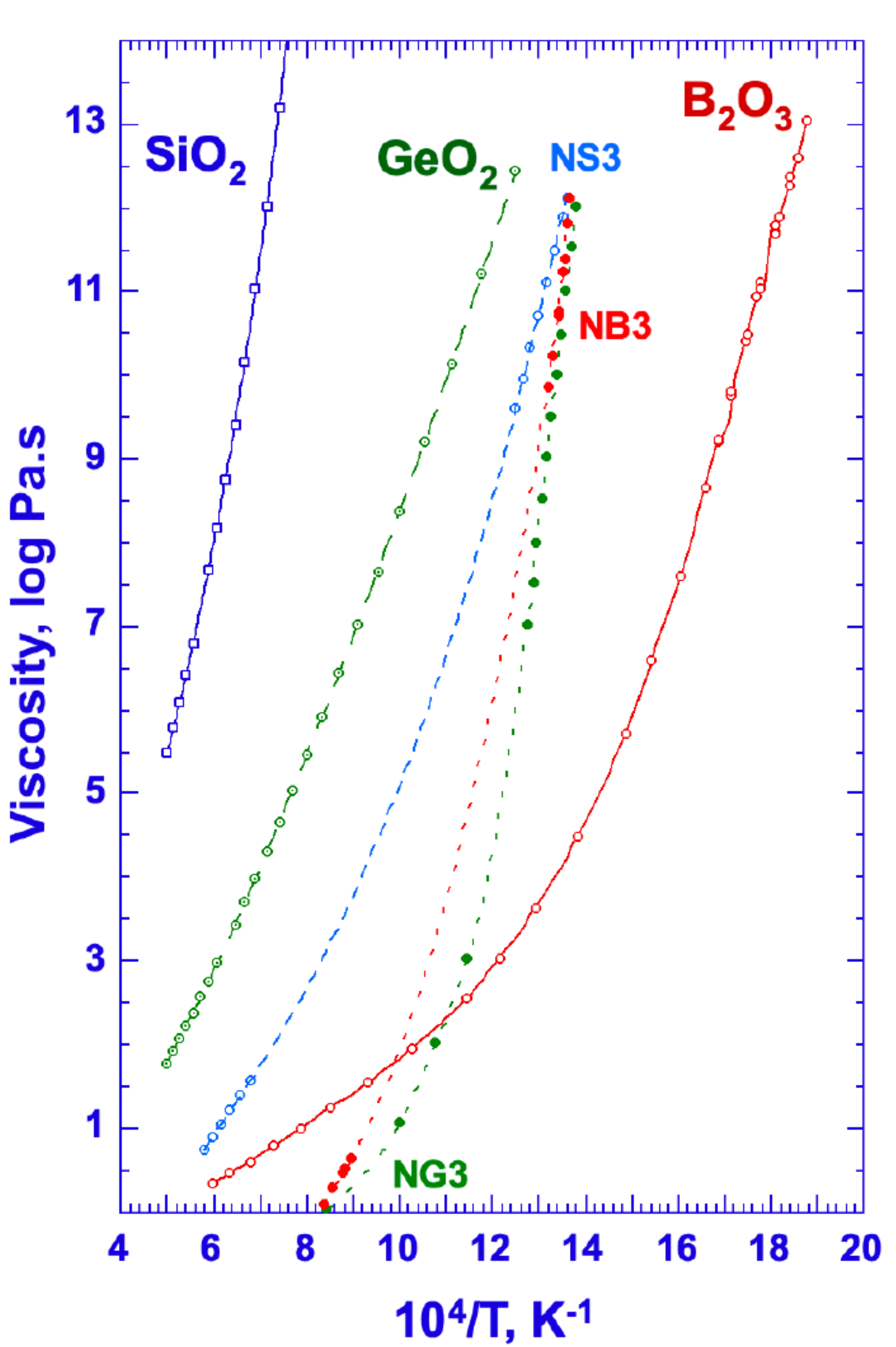
GeO_2 covalent bond

- GeO_4 tetrahedra
- Na_2O breaks the network
- Viscosity decreases

B_2O_3 covalent bond

- BO_3 triangle and BO_4 tetrahedra

Network former



SiO_2 covalent bond

- SiO_4 tetrahedra
- Na_2O breaks the network
- Viscosity decreases

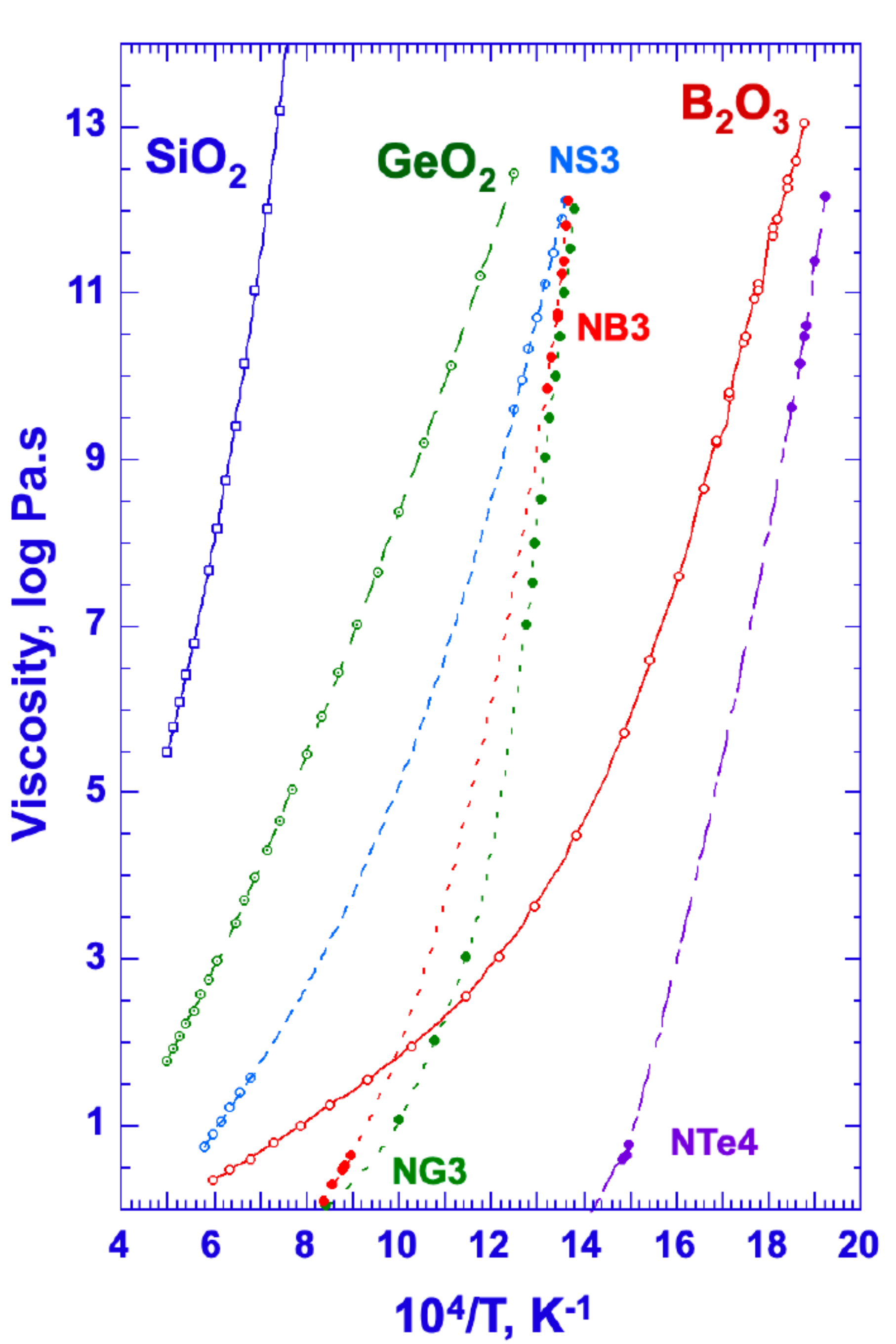
GeO_2 covalent bond

- GeO_4 tetrahedra
- Na_2O breaks the network
- Viscosity decreases

B_2O_3 covalent bond

- BO_3 triangle and BO_4 tetrahedra
- Na increases BO_4 content
- Viscosity increases

Network former



SiO_2 covalent bond
- SiO_4 tetrahedra
- Na_2O breaks the network
- Viscosity decreases

GeO_2 covalent bond
- GeO_4 tetrahedra
- Na_2O breaks the network
- Viscosity decreases

B_2O_3 covalent bond
- BO_3 triangle and BO_4 tetrahedra
- Na increases BO_4 content
- Viscosity increases

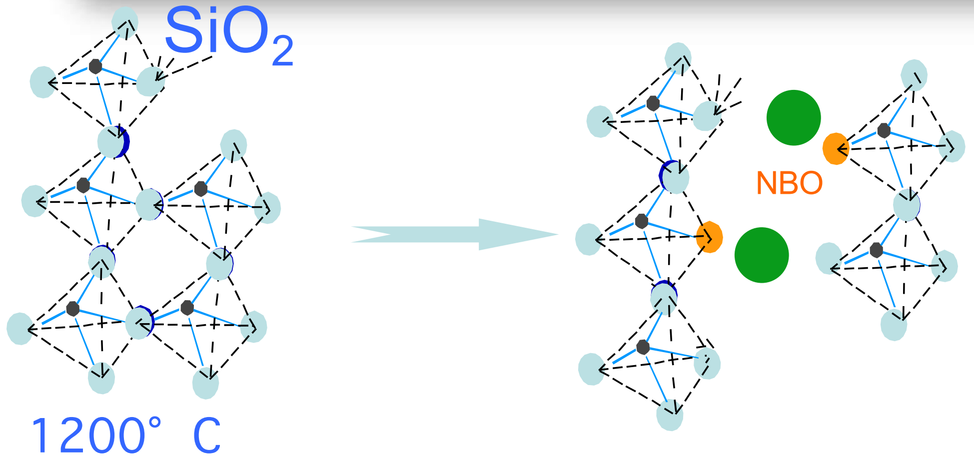
TeO_2 ionic bonding

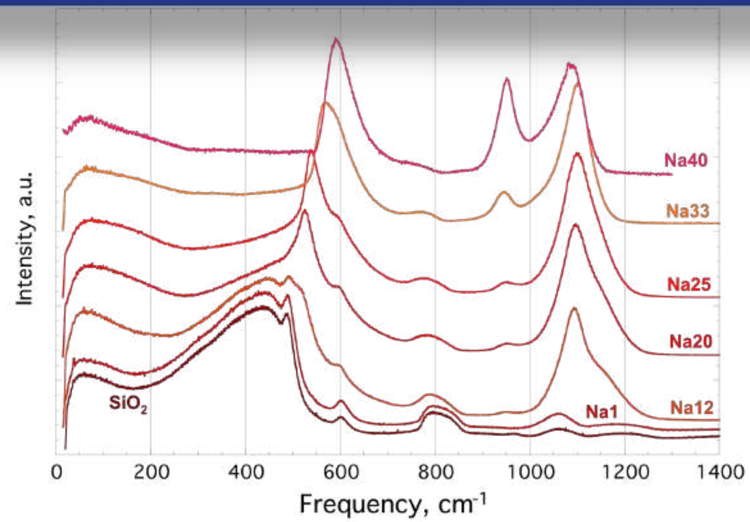
SiO_2 : SiO_4 tetrahedra, 3D network, high connectivity
=> strong liquid
Alkali broke network, viscosity decreases, Tg…..

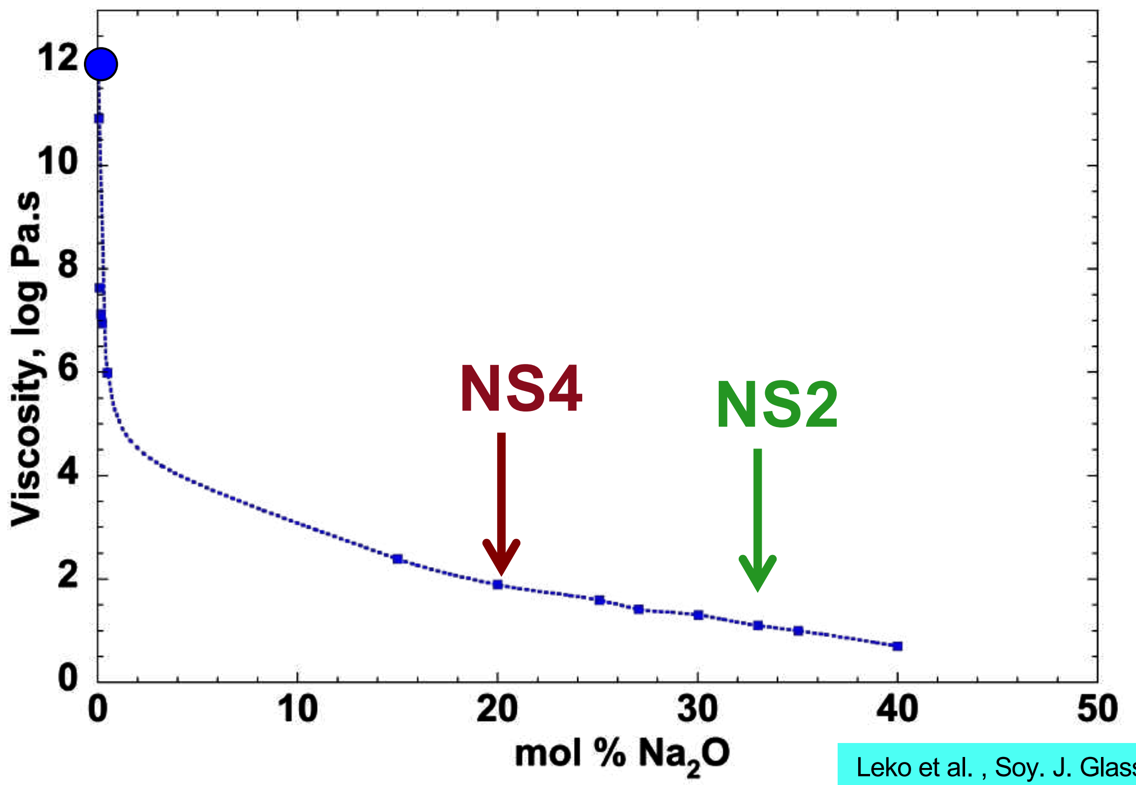
GeO_2 : GeO_4 tetrahedra, 3D network, high connectivity
=> strong liquid
Alkali broke network, viscosity decreases, Tg…..

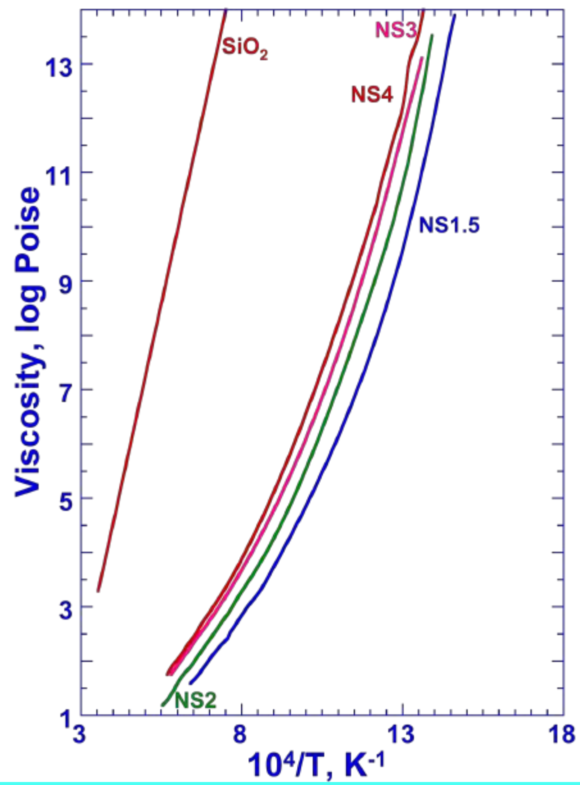
B_2O_3 : BO3 triangle, 2D network, low connectivity,
=> fragile liquid
With alkali : M_2O + BO3 => BO4 : 3D network

Structure versus properties of silicate melts



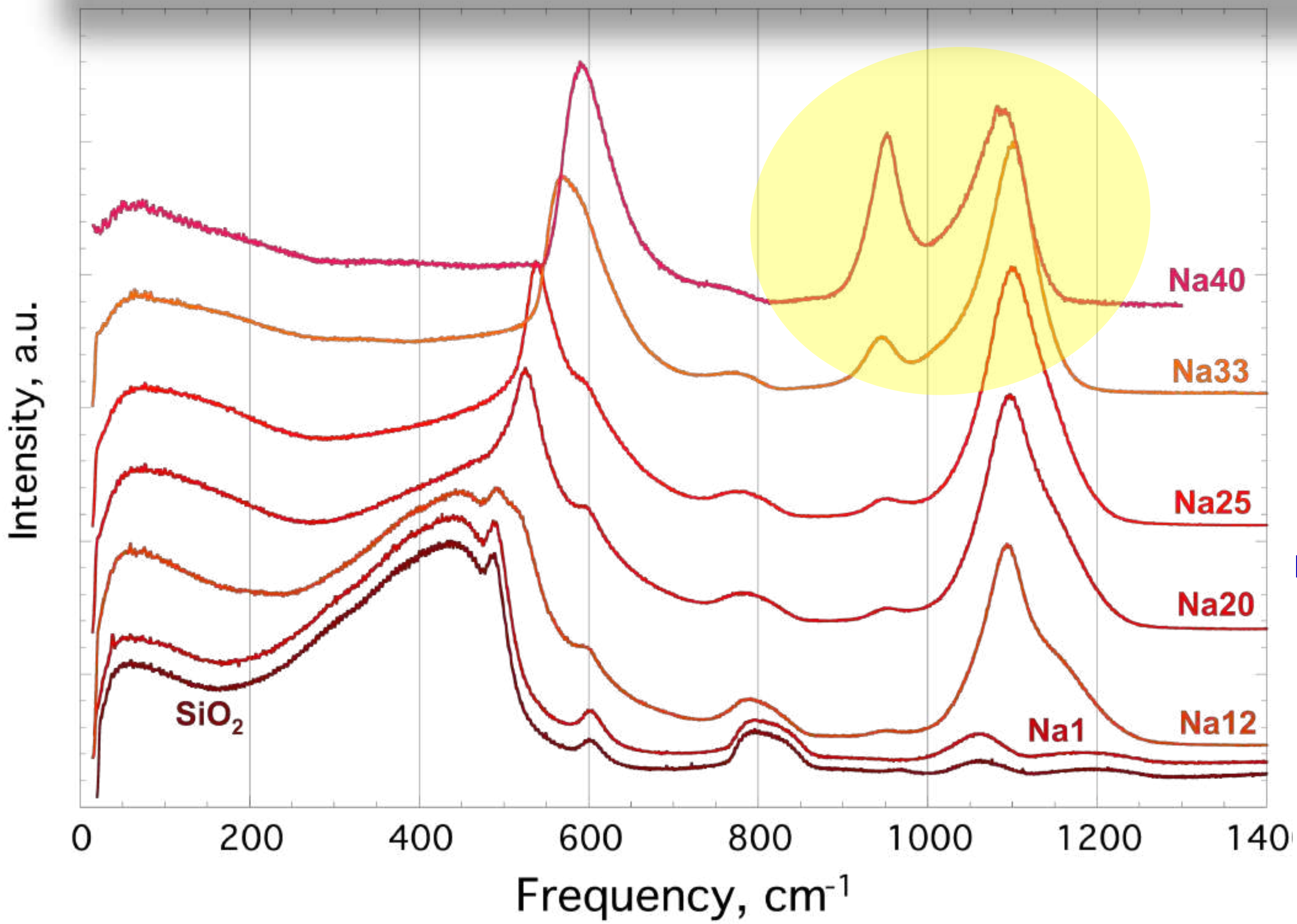


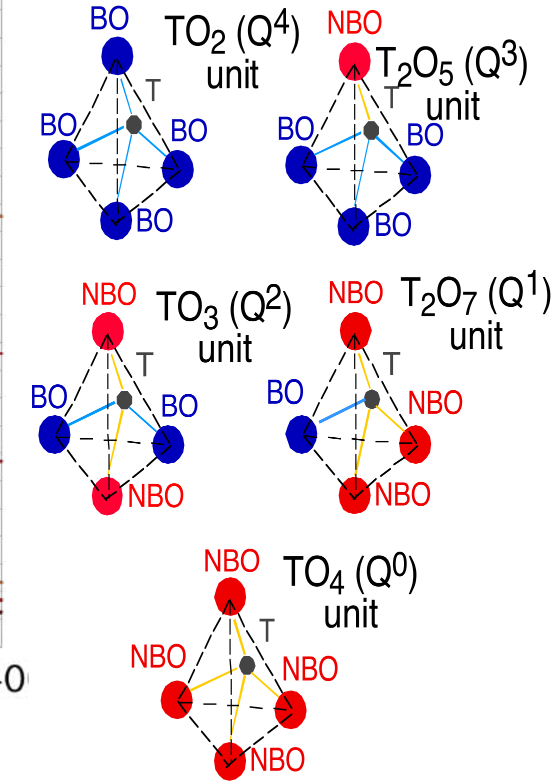


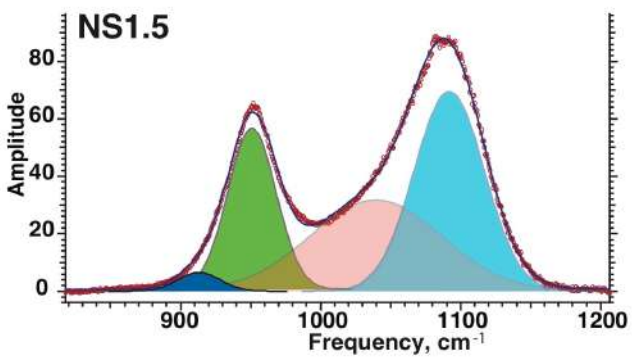


Leko et al. , Soy. J. Glass Phys. Chem., 1977, 3, 204-210 and Neuville, Chem Geol, 2006, 229, 28-42

Raman spectra of SiO_2-Na_2O glass



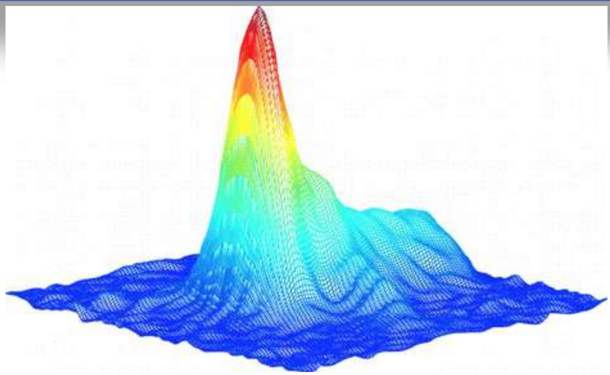


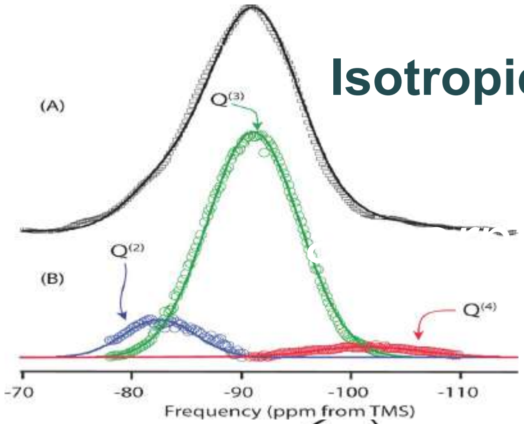


NMR — Q^n *species* — *X-ray absorption*

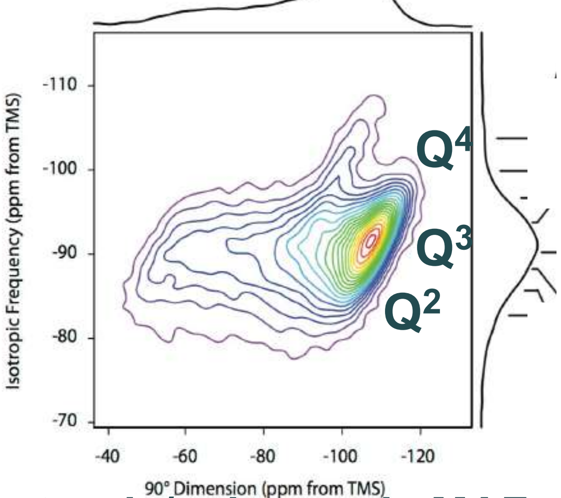
^{29}Si MAF Spectrum of K_2O-2SiO2 glass

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





Isotropic MAS



Isotropic/anisotropic MAF

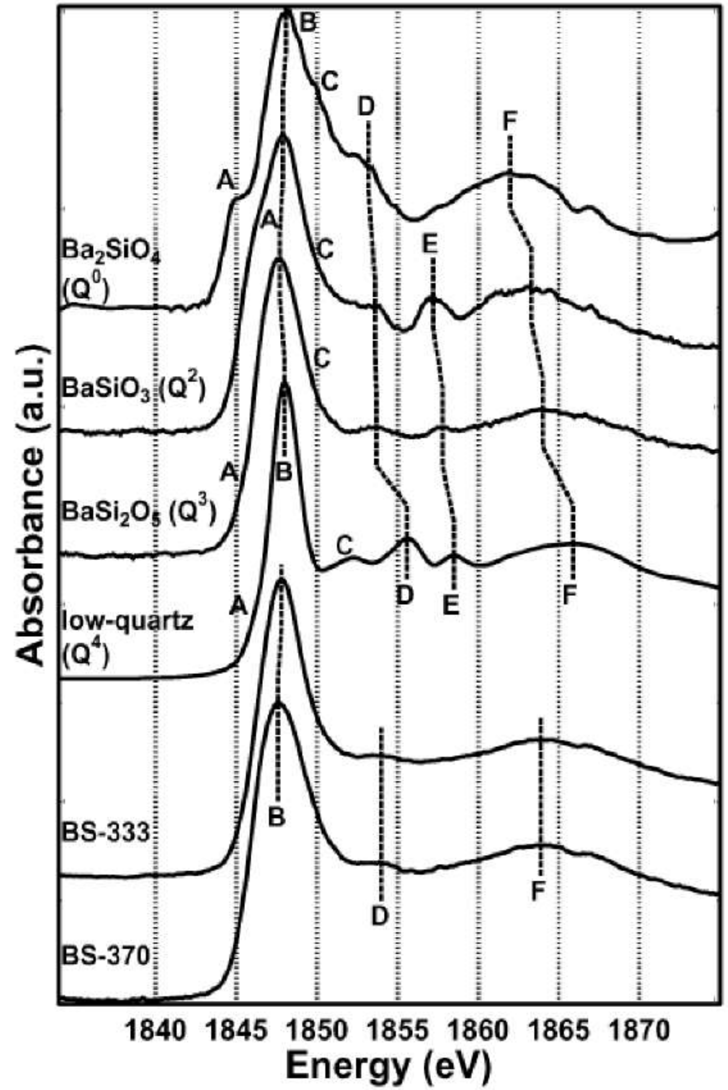
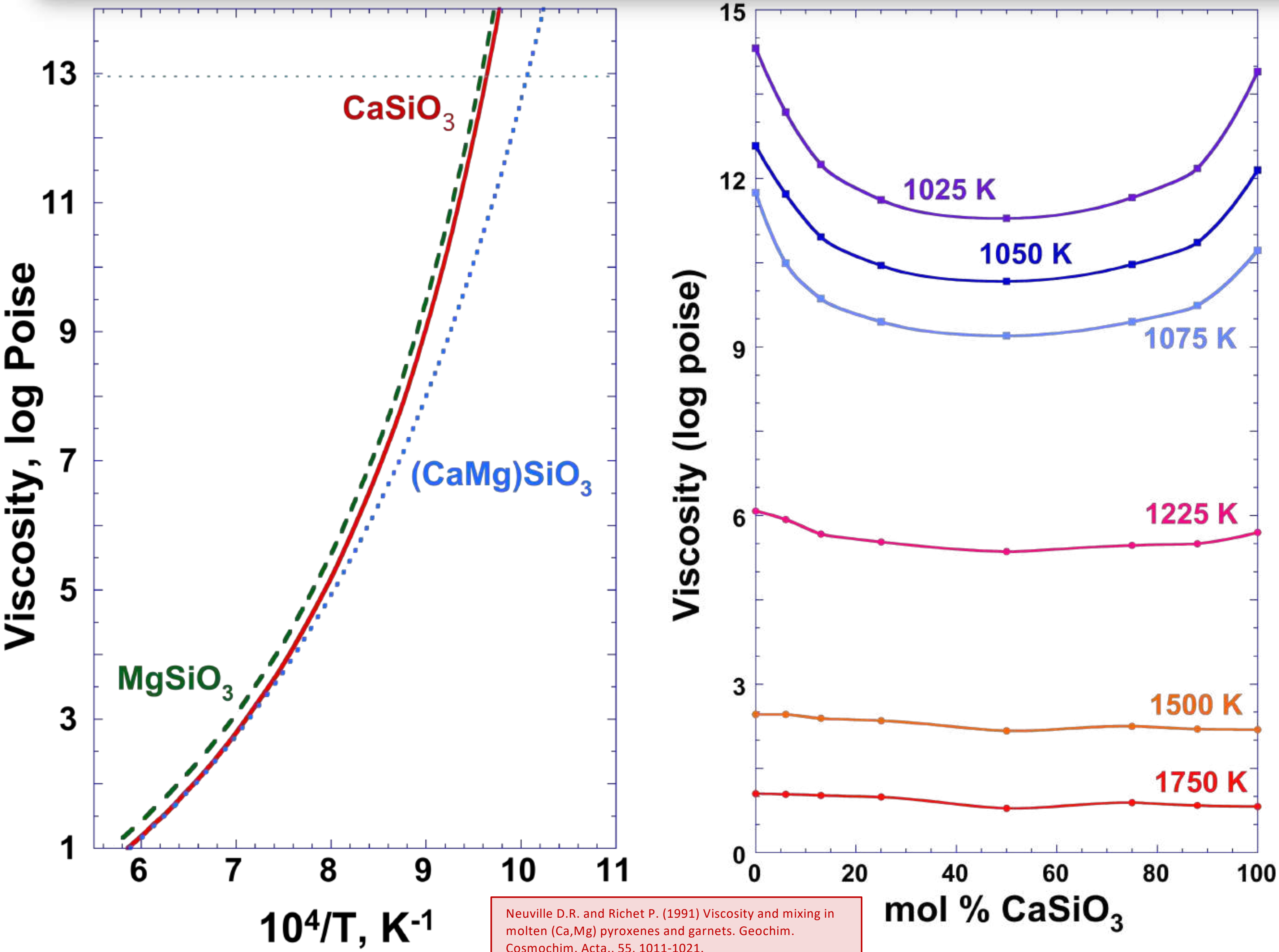


Fig. 1. Si K-XANES spectra of barium silicates, low quartz and the amorphous samples BS-333 and BS-370.

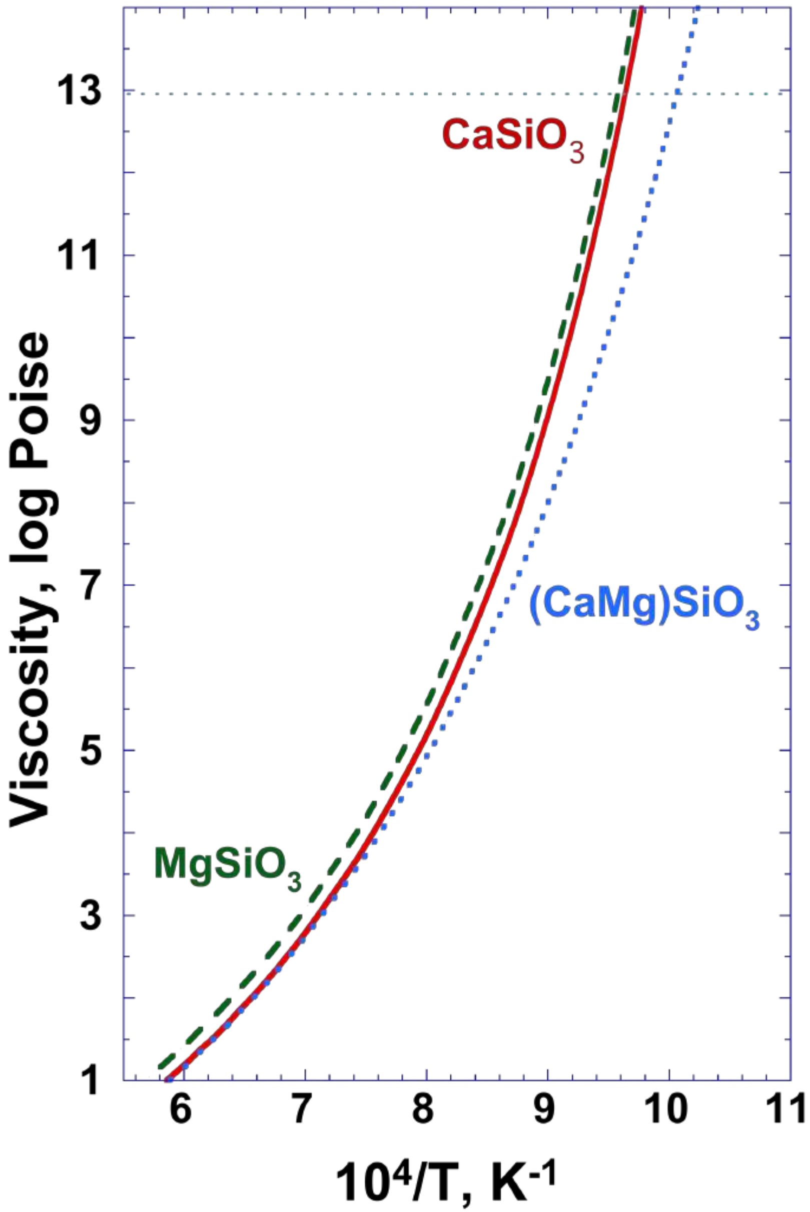
Si K-edge of BaO-SiO_2 glass
Bender et al., JNCS, 2002, 298, 99-108

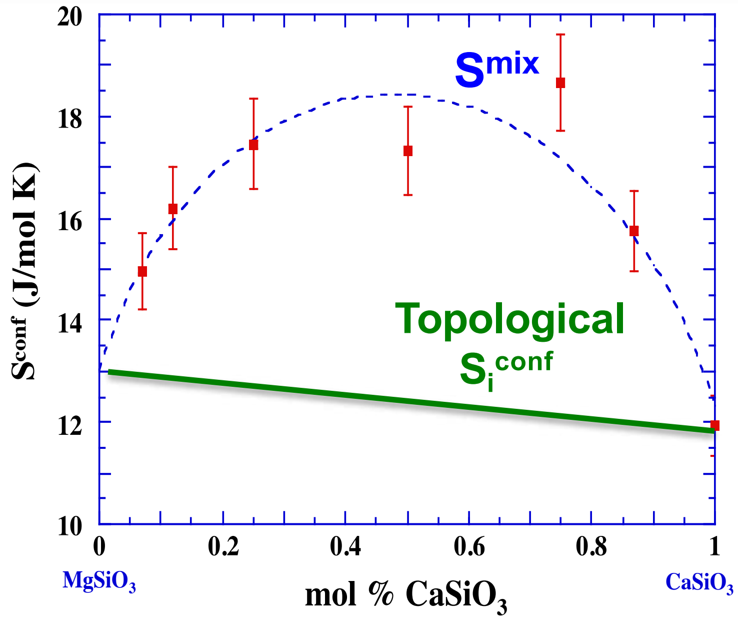
Ca/Mg Mixing



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

Ca/Mg Mixing





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

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

$C_p^{conf} = C_p^{l} - C_{pg}(T_g)$

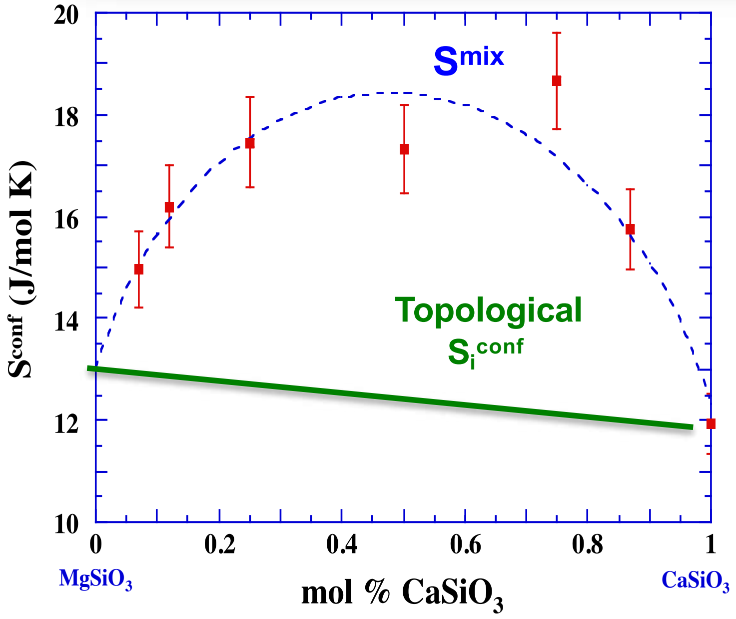
$$S^{conf}(Tg) = S^{mix} + \Sigma x_i S_i^{conf}(Tg)$$

$S^{mix} = - nR\Sigma X_i \ln X_i$ with X_i=Ca/(Ca+Mg)

Ideal mixing => random distribution

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

Ca/Mg Mixing



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Ideal mixing => random distribution

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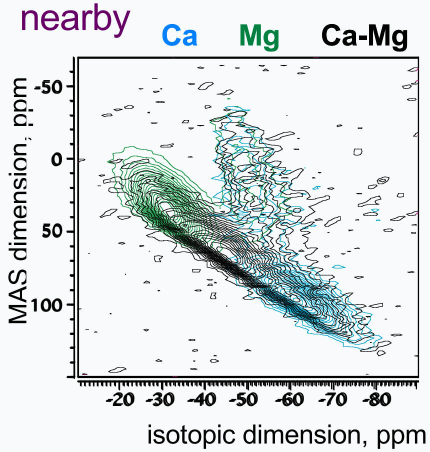
O-NMR

Allwardt and Stebbins 2004

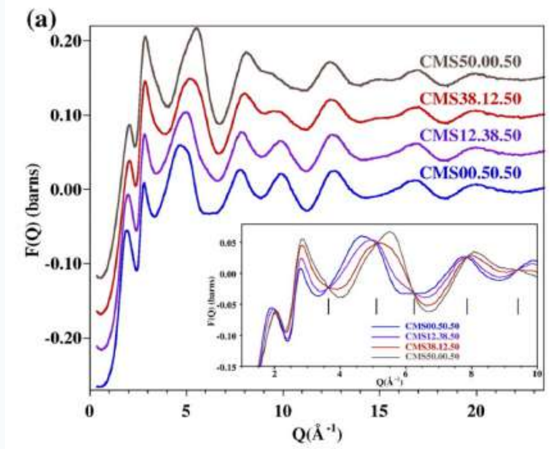
- "viewpoint" of the NBO
- ^{17}O chemical shifts depend strongly on which cations are nearby

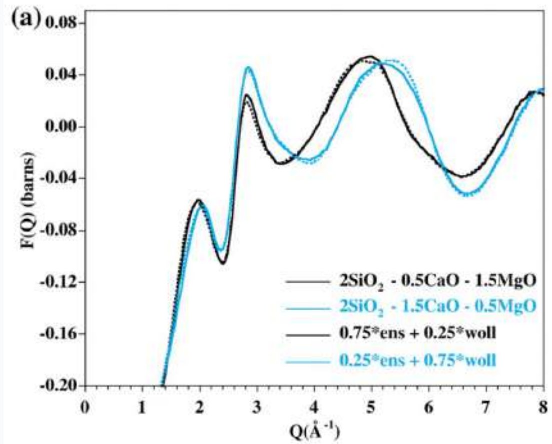


- **detailed analyses of spectra support almost random distribution of Ca + Mg around NBO**
- **size difference of Ca^{2+} and Mg^{2+} is insufficient to cause ordering**

Allwardt and Stebbins (2004) Ca-Mg and K-Mg mixing around non-bridging O atoms in silicate glasses: An investigation using 17O MAS and 3QMAS NMR. American Mineralogist, 89, 777–784

total neutron structure factors

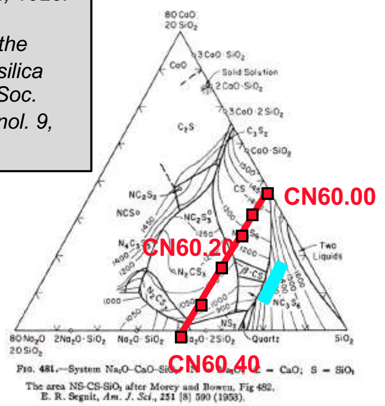


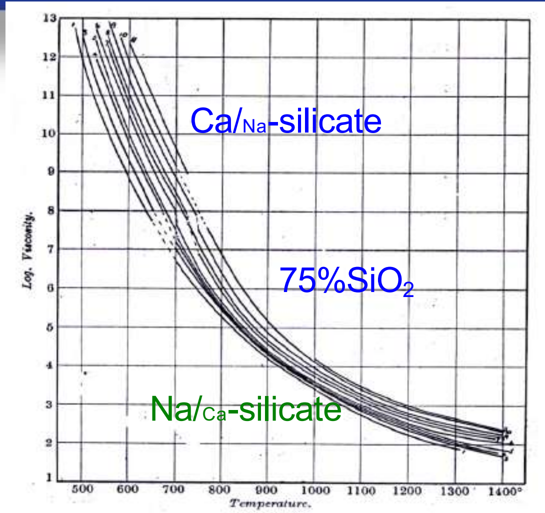


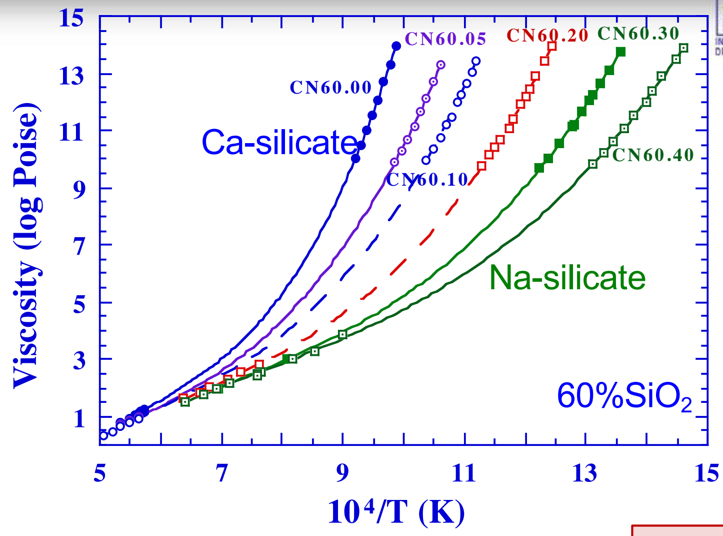
Cormier L., Calas G., Cuello G. (2010) Structural study of Ca–Mg and K–Mg mixing in silicate glasses by neutron diffraction. Journal of Non-Crystalline Solids 356, 2327.

Ca/Na Mixing

Morey, G.W., Bowen, N.L., 1925. The melting relations of the soda–lime–silica glasses. J. Soc. Glass Technol. 9, 226–264.

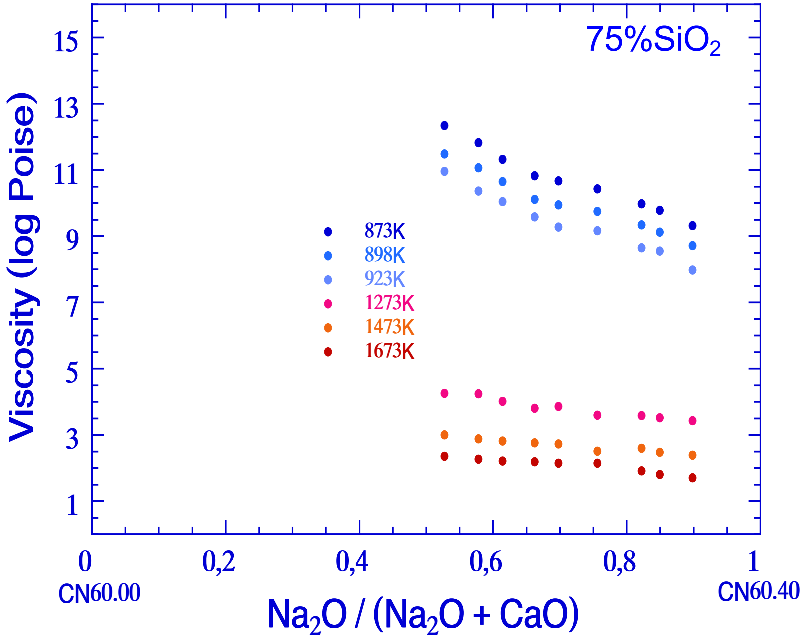


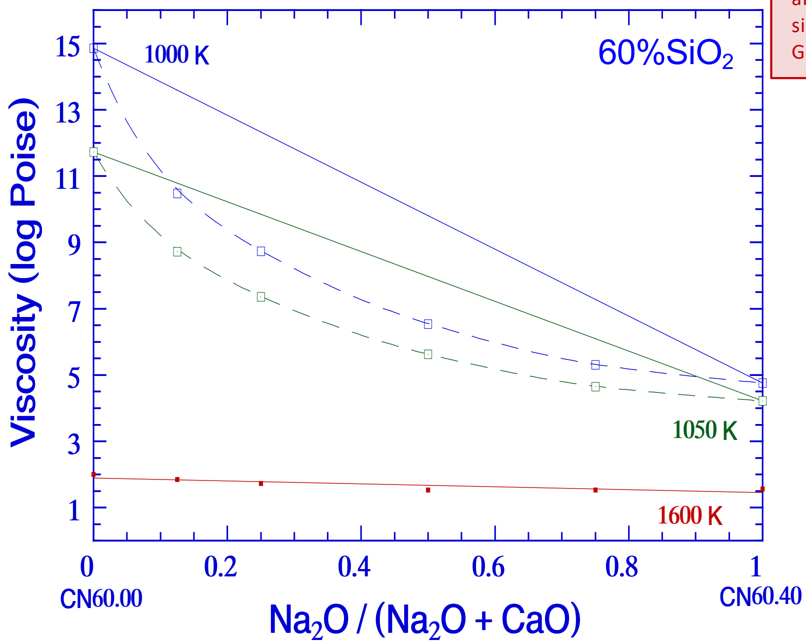




English, S., 1923. The effect of composition on the viscosity of glass: Part II. J. Soc. Glass Technol. 8, 205–251.

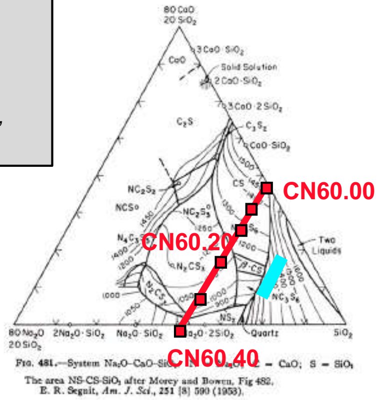
Neuville D.R. (2006) Viscosity, structure and mixing in (Ca, Na) silicate melts. Chem. Geol., 229, 28-42.





Ca/Na Mixing

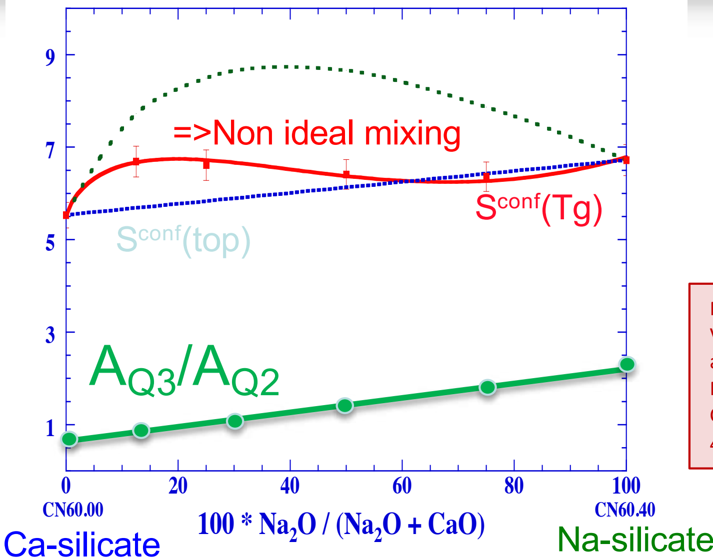
Morey, G.W., Bowen, N.L., 1925. The melting relations of the soda–lime–silica glasses. J. Soc. Glass Technol. 9, 226–264.



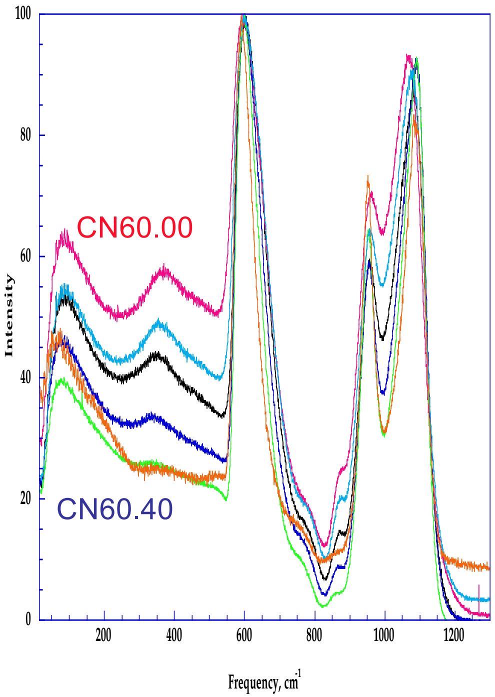
$$\log \eta = A_e + B_e / TS^{conf}(T)$$

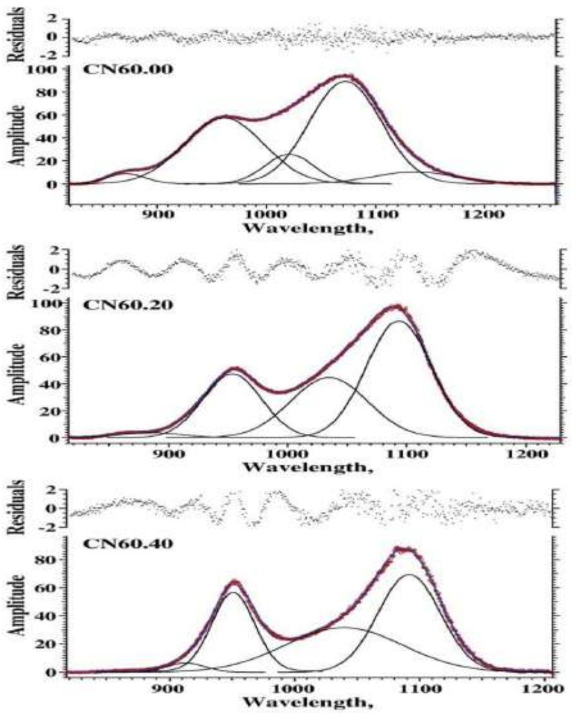
$$S^{conf}(Tg) = S^{mix} + \Sigma x_i S_i^{conf}(Tg)$$

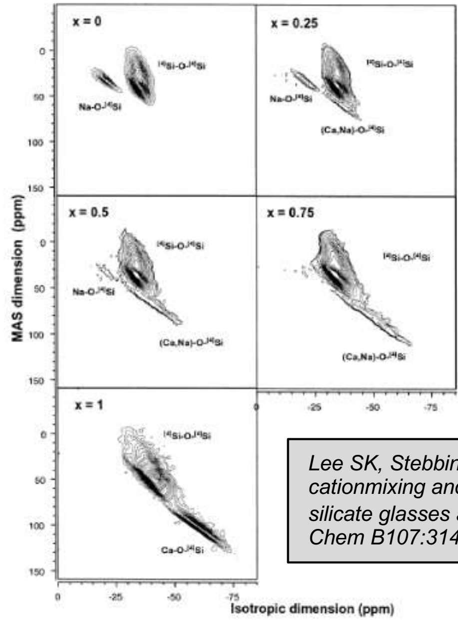
Random mixing =
Ideal mixing term : -RXiLnXi



Neuville D.R. (2006) Viscosity, structure and mixing in (Ca, Na) silicate melts. Chem. Geol., 229, 28-42.







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

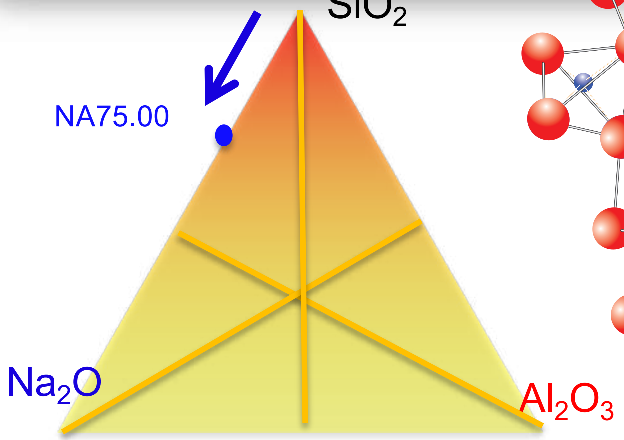
Lee SK, Stebbins JF (2003) Nature of cationmixing and ordering in Na-Ca silicate glasses and melts. J Phys Chem B107:3141–3148

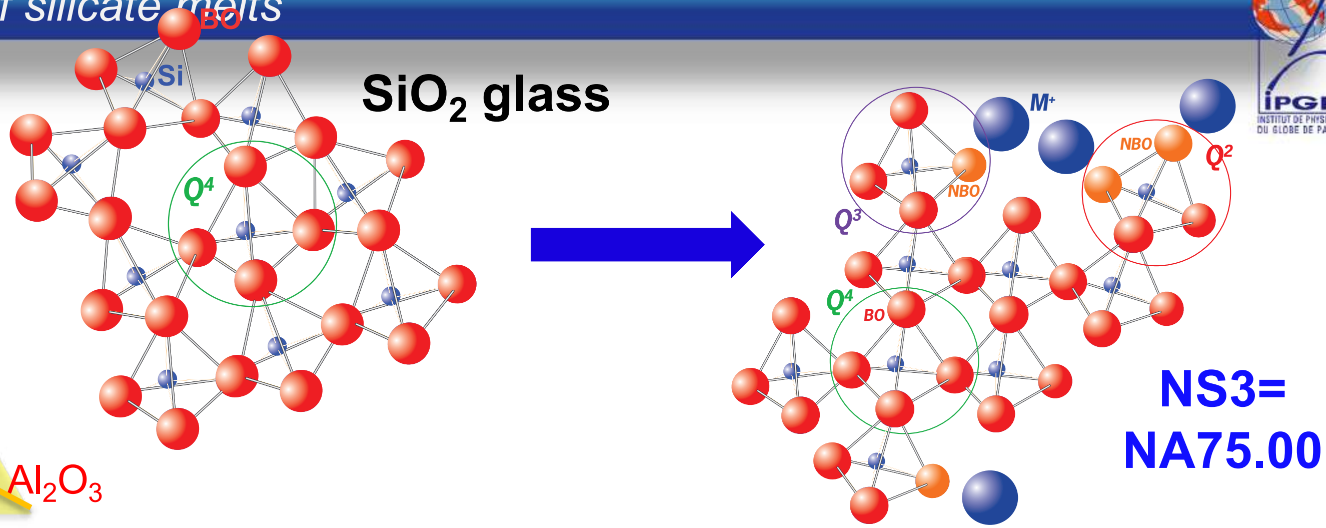
M^+, M^{++} : Network modifier => produce non-bridging oxygen,

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

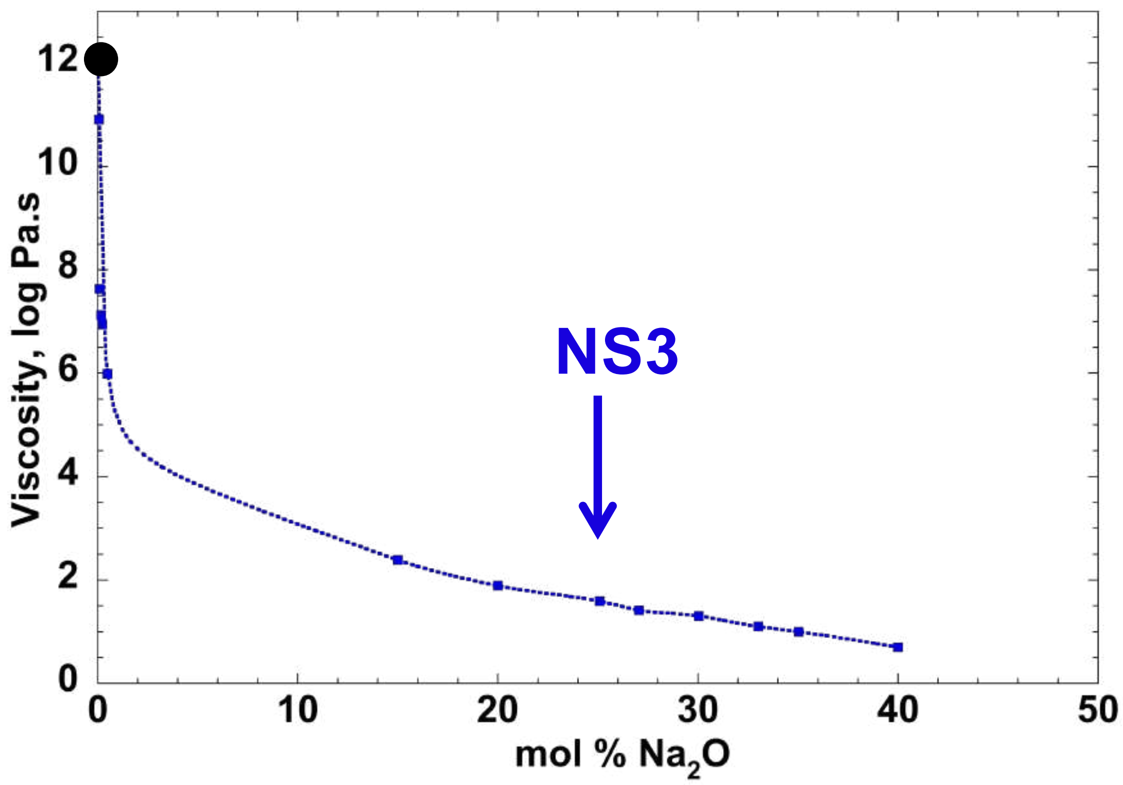
=> increase configurational entropy and disorder….

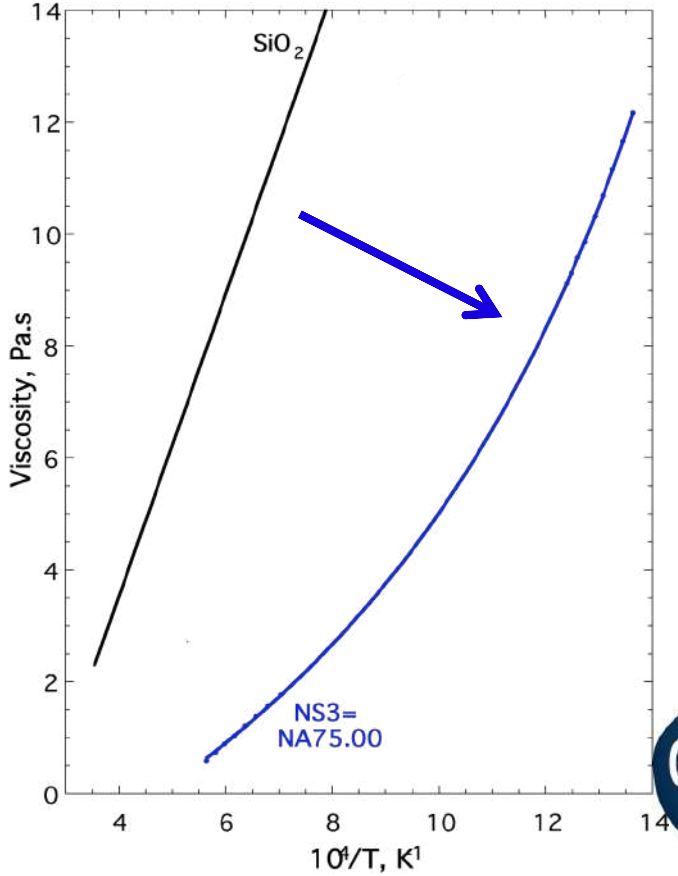
How can be change in charge compensator ?

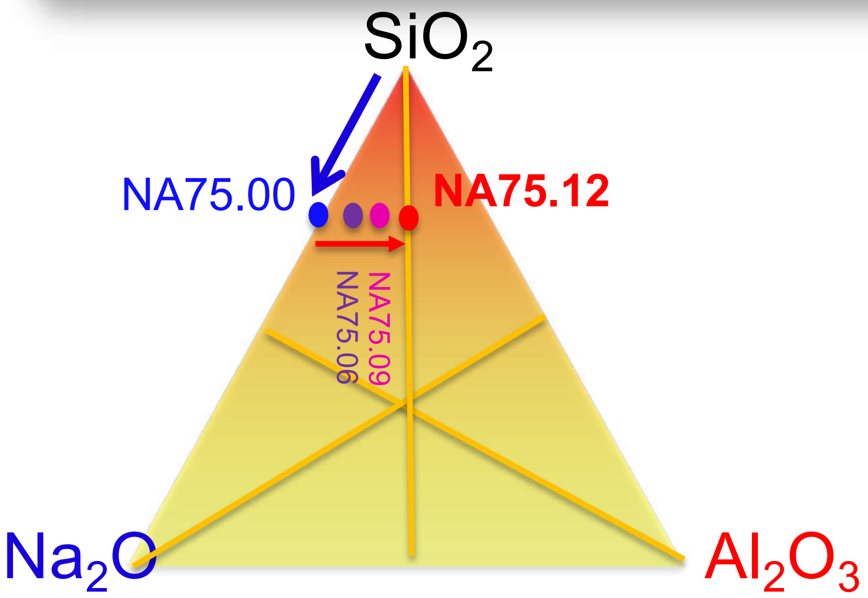

SiO2
NA75.00
Na2O
Al2O3

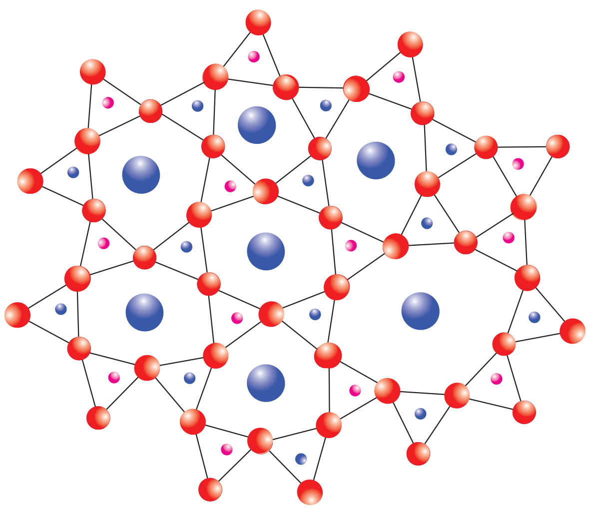

BO
Si
Q4
SiO2 glass
M+
NBO
Q2
NBO
Q3
Q4
BO
NS3=
NA75.00

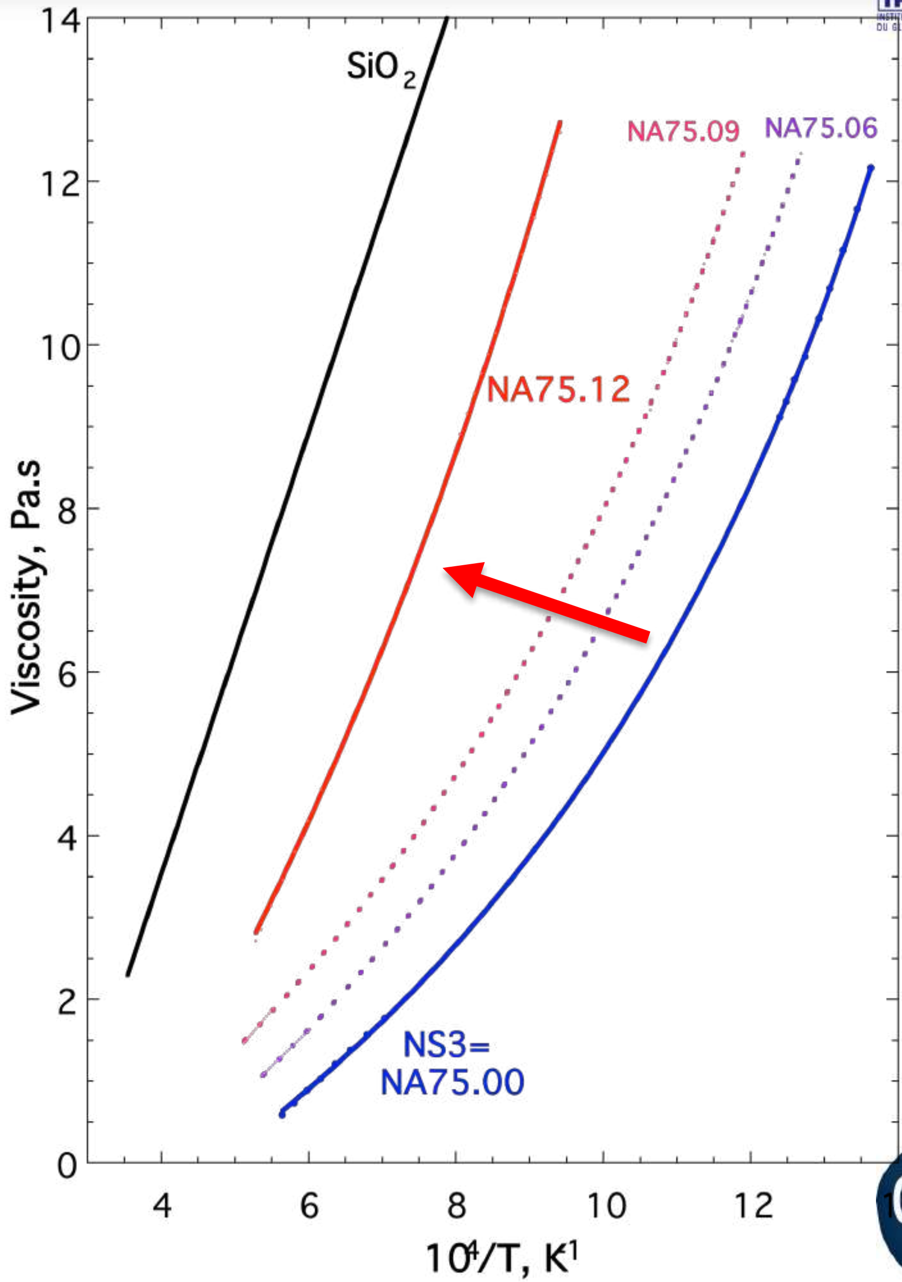
1200° C


12
10
8
6
4
2
0
Viscosity, log Pa.s
NS3
0
10
20
30
40
50
mol % Na2O


14
12
10
8
6
4
2
0
Viscosity, Pa.s
SiO2
NS3=
NA75.00
4
6
8
10
12
14
10^4/T, K^-1

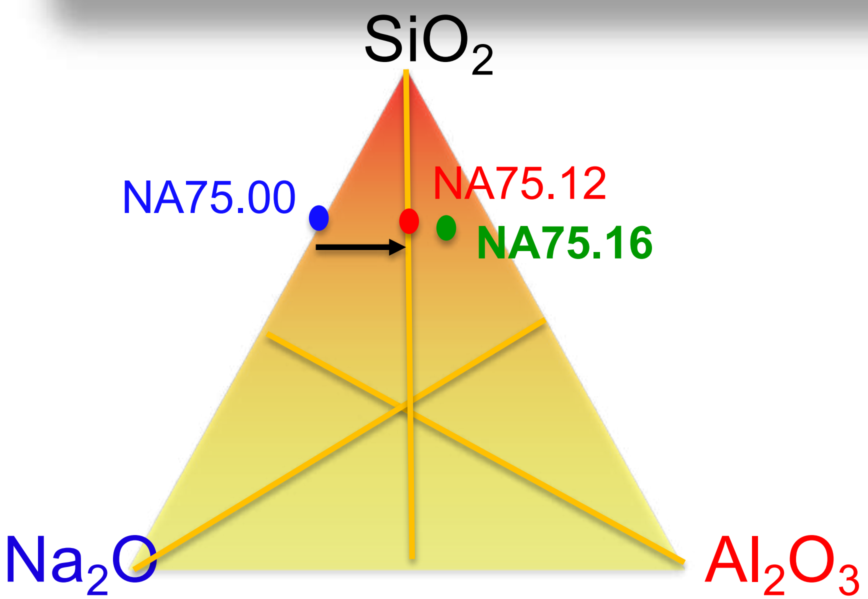


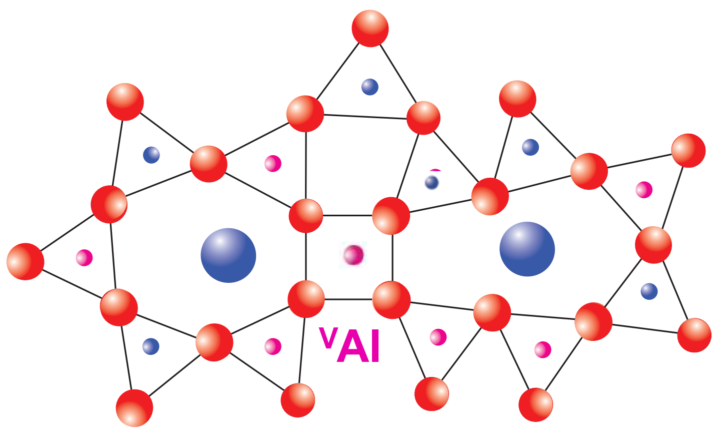




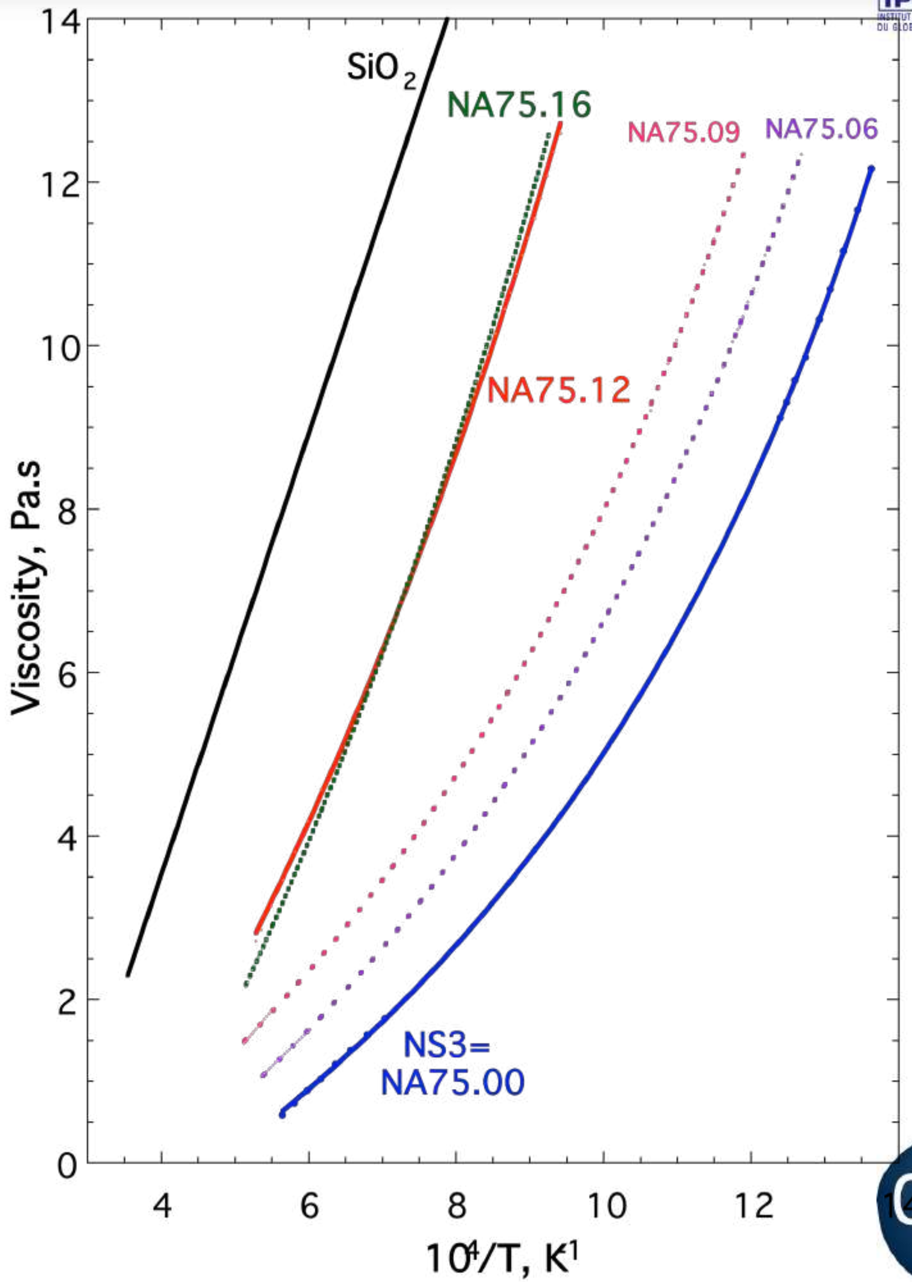
NA75.00 -> **NA75.12**

Network modifier versus charge compensator?

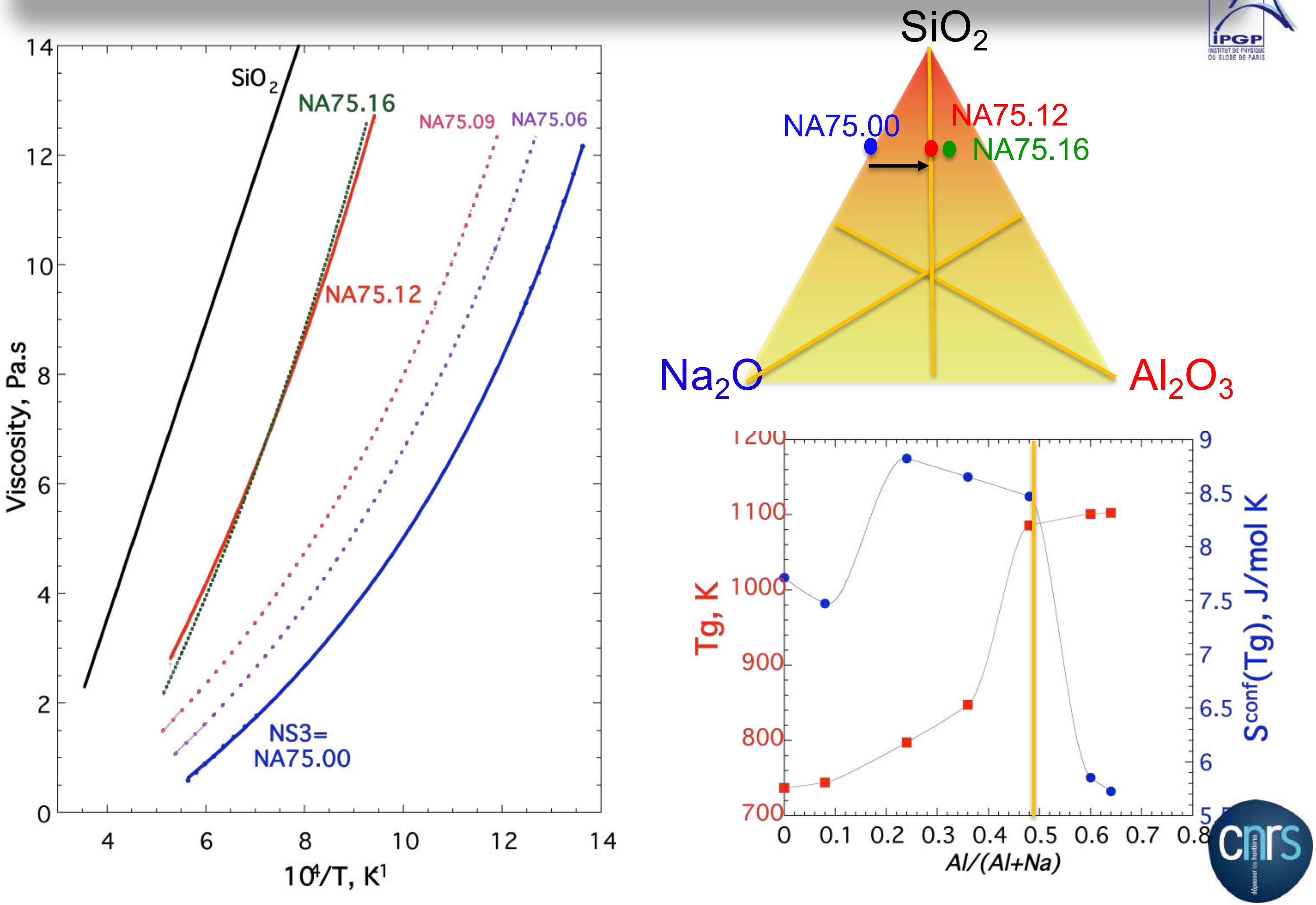




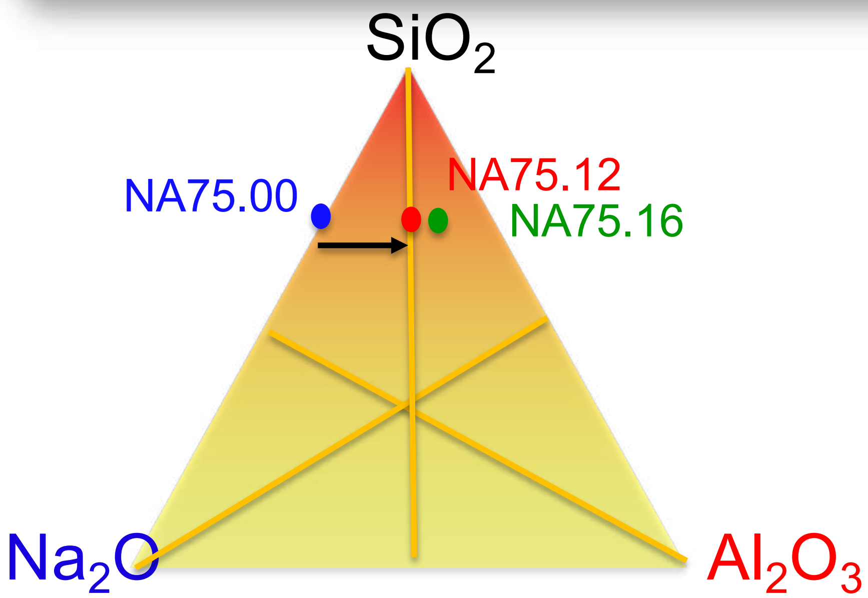
NA75.16
peraluminous composition

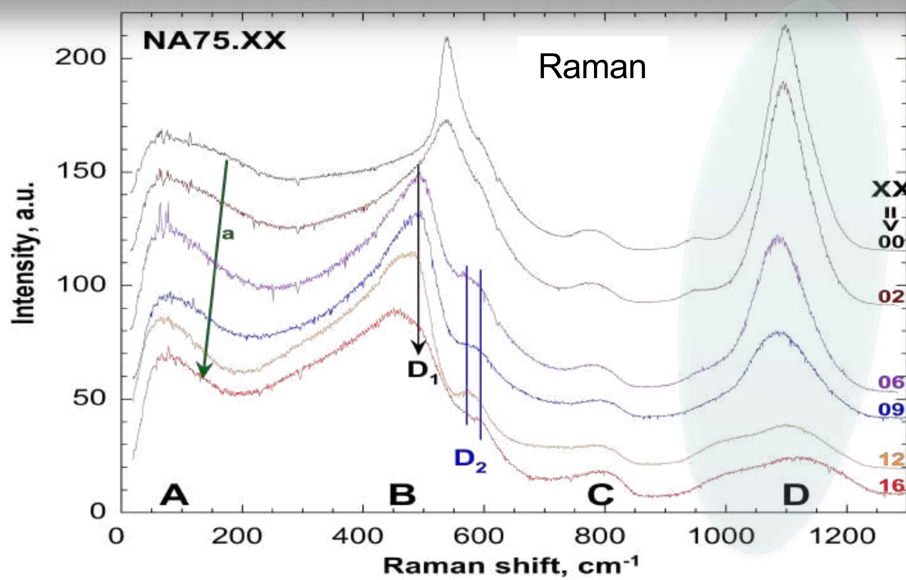


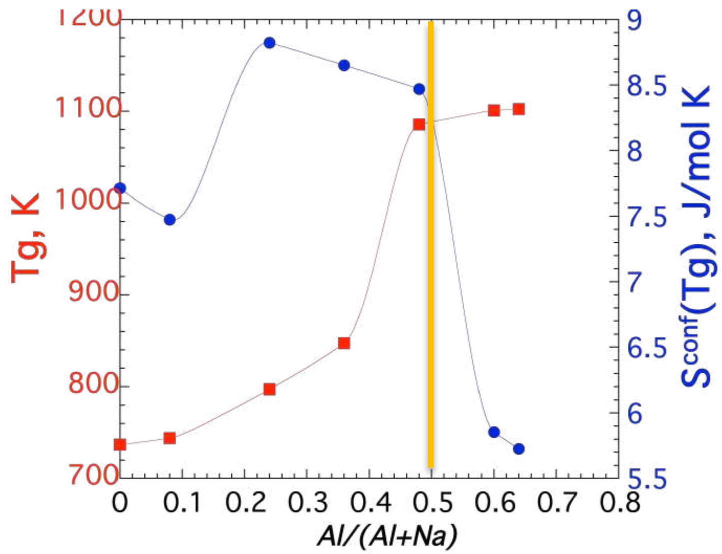
Network modifier versus charge compensator?

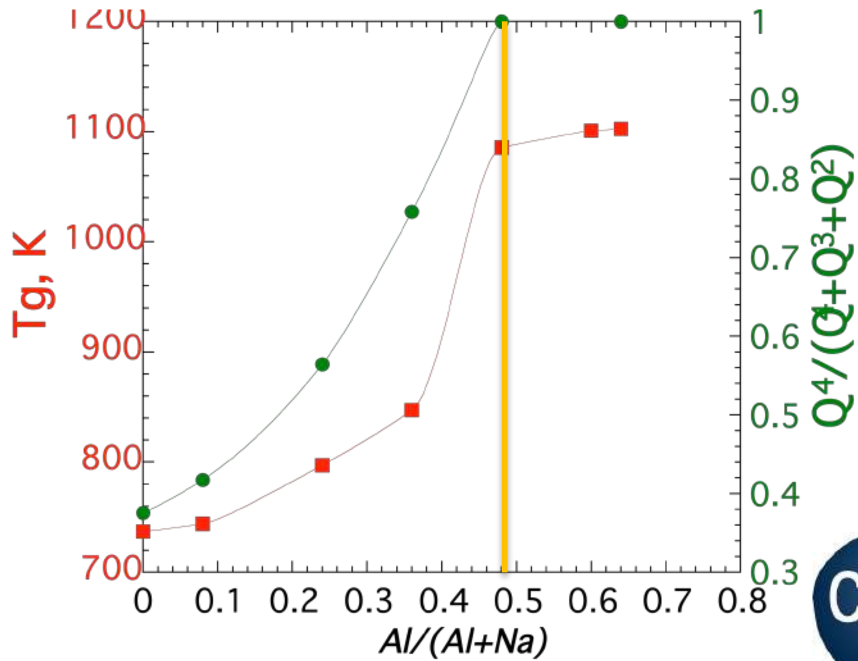


Network modifier versus charge compensator?



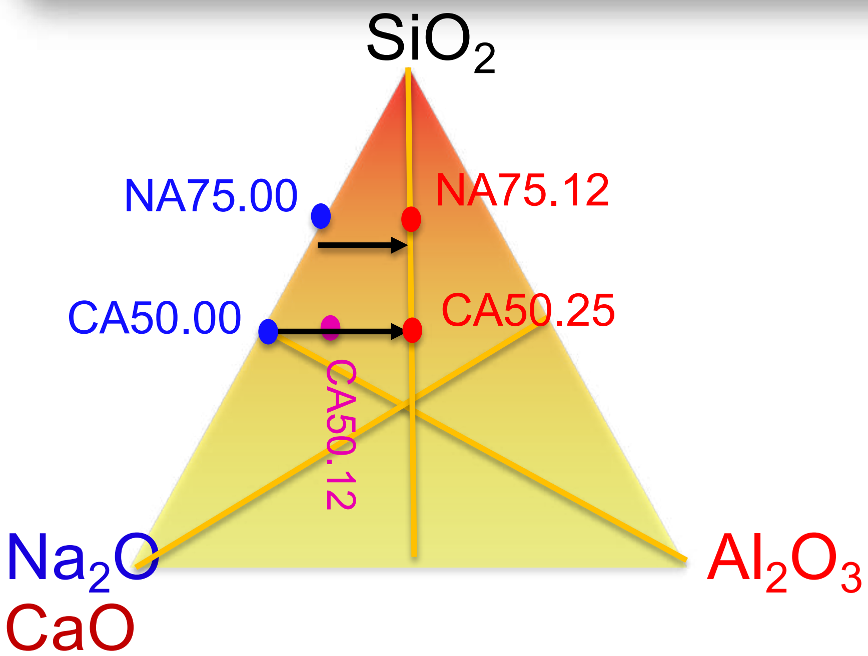


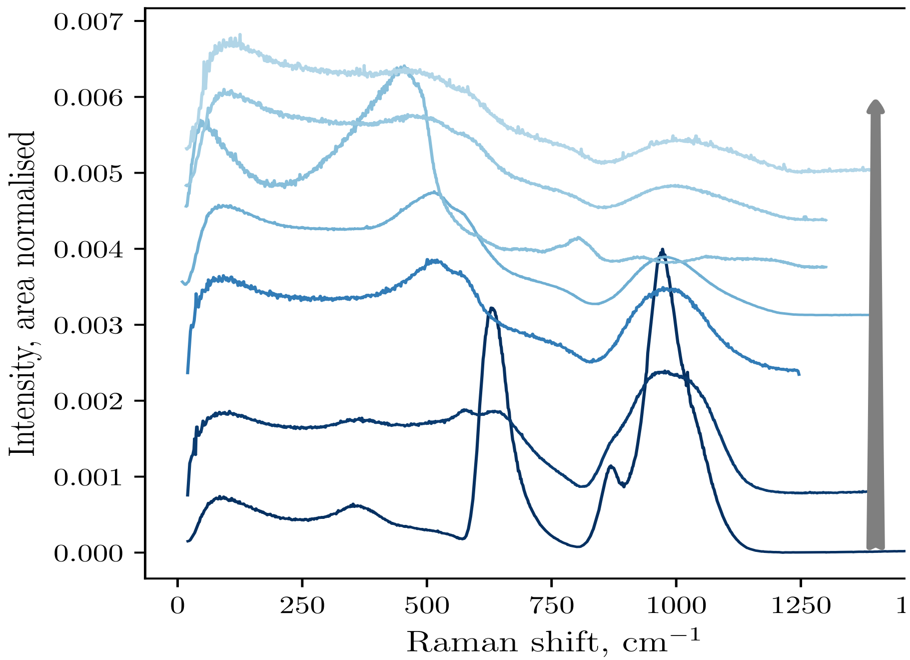


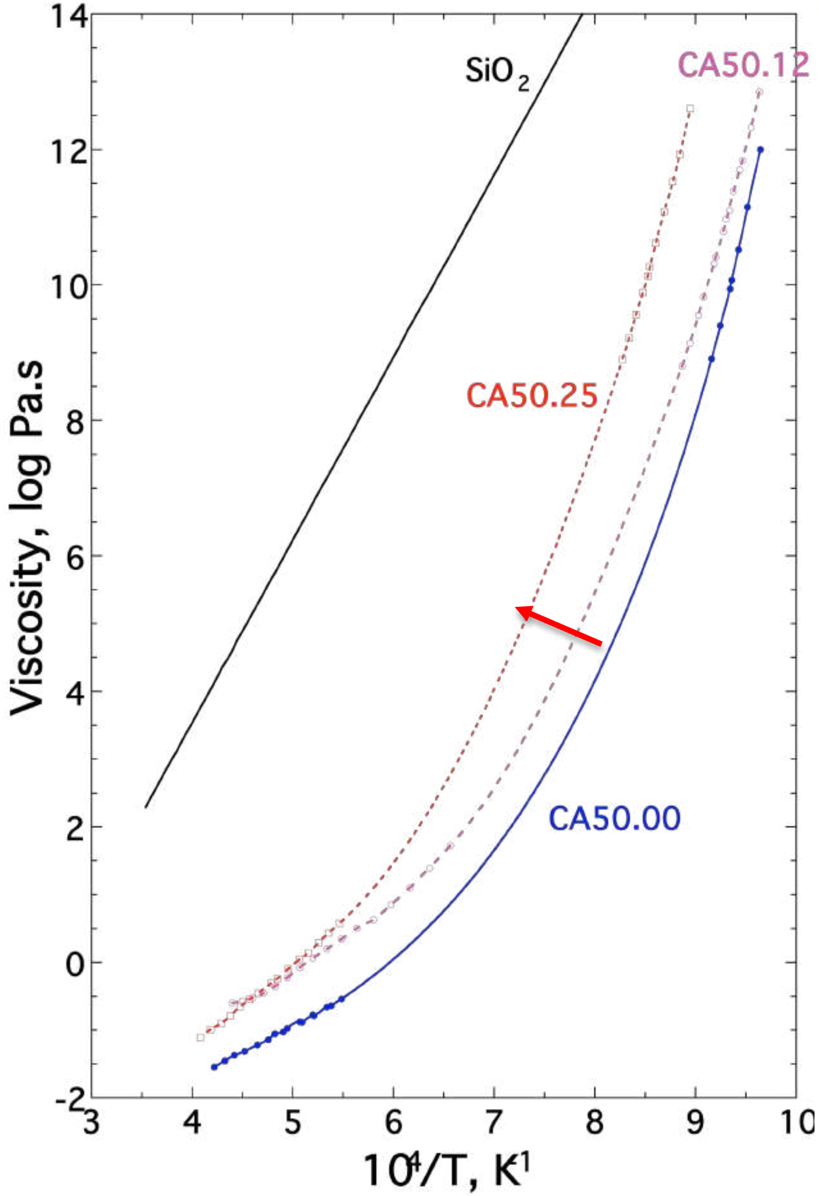


Na_2O-Al_2O_3-SiO_2

Network modifier versus charge compensator?

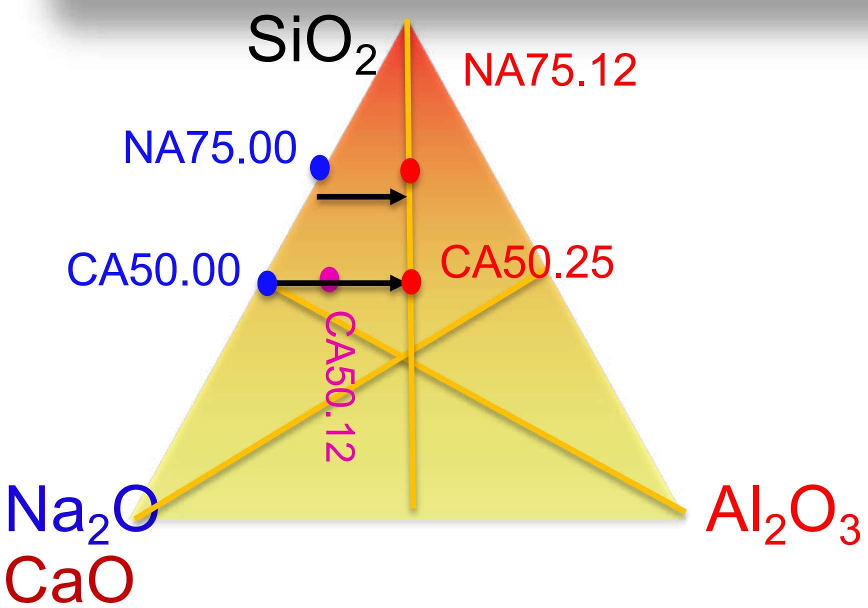


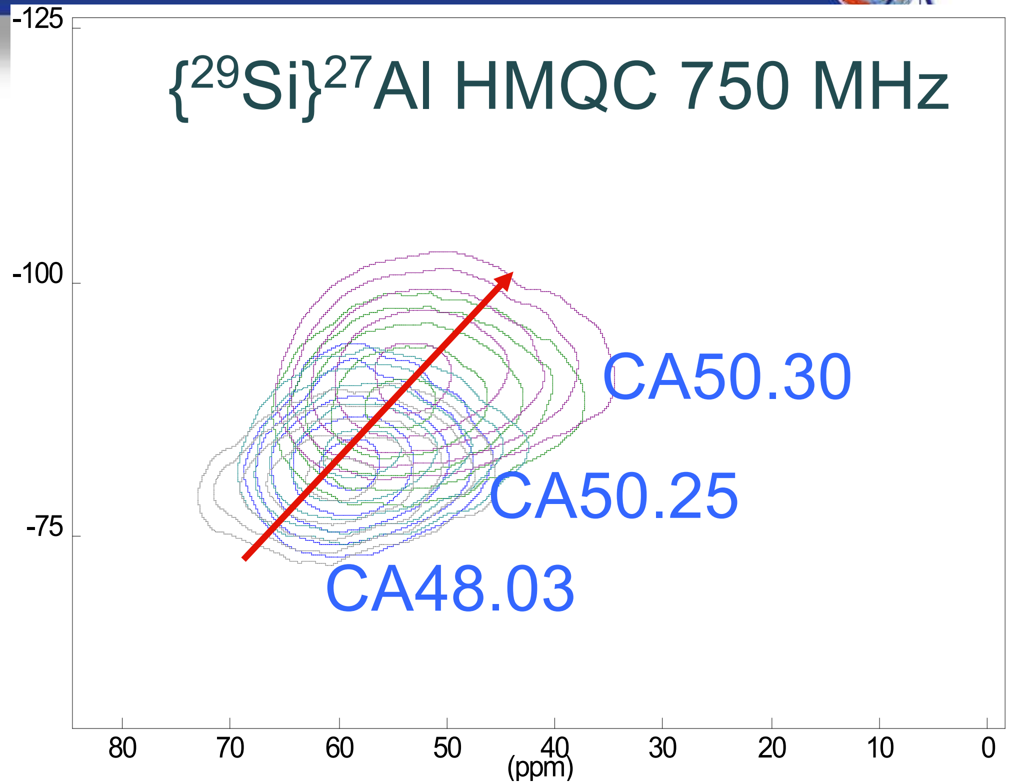


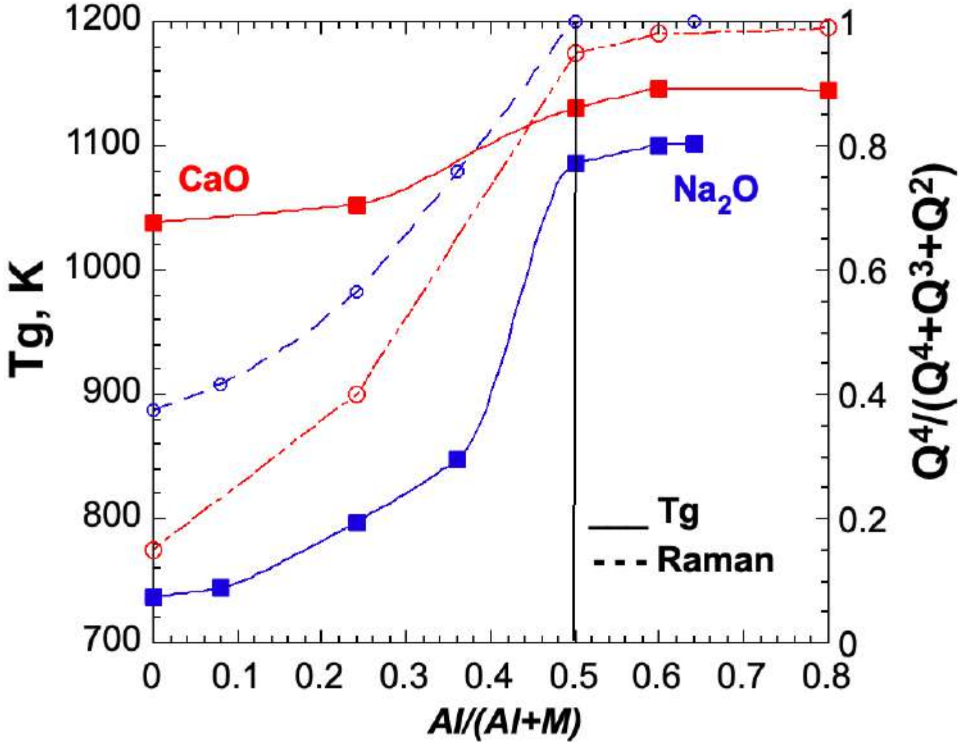


$CaO-Al_2O_3-SiO_2$

Network modifier versus charge compensator?





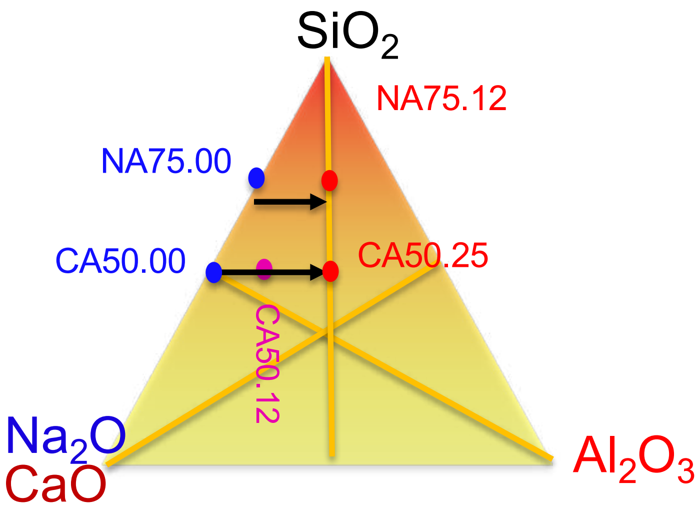


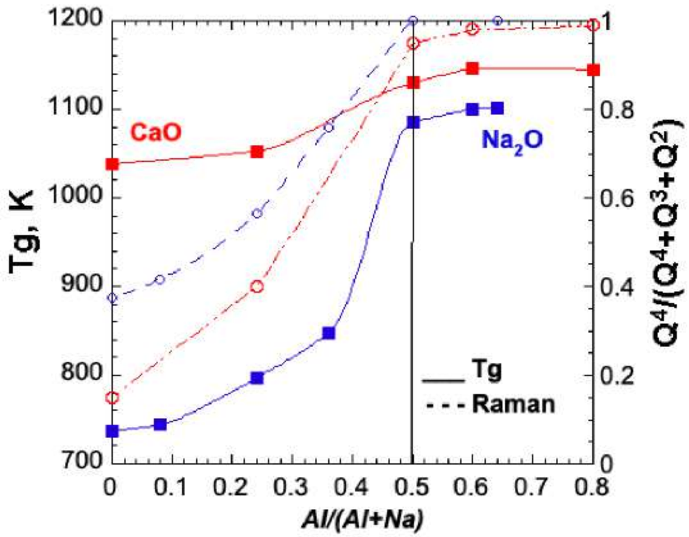
Good correlation between Tg and Q^n species

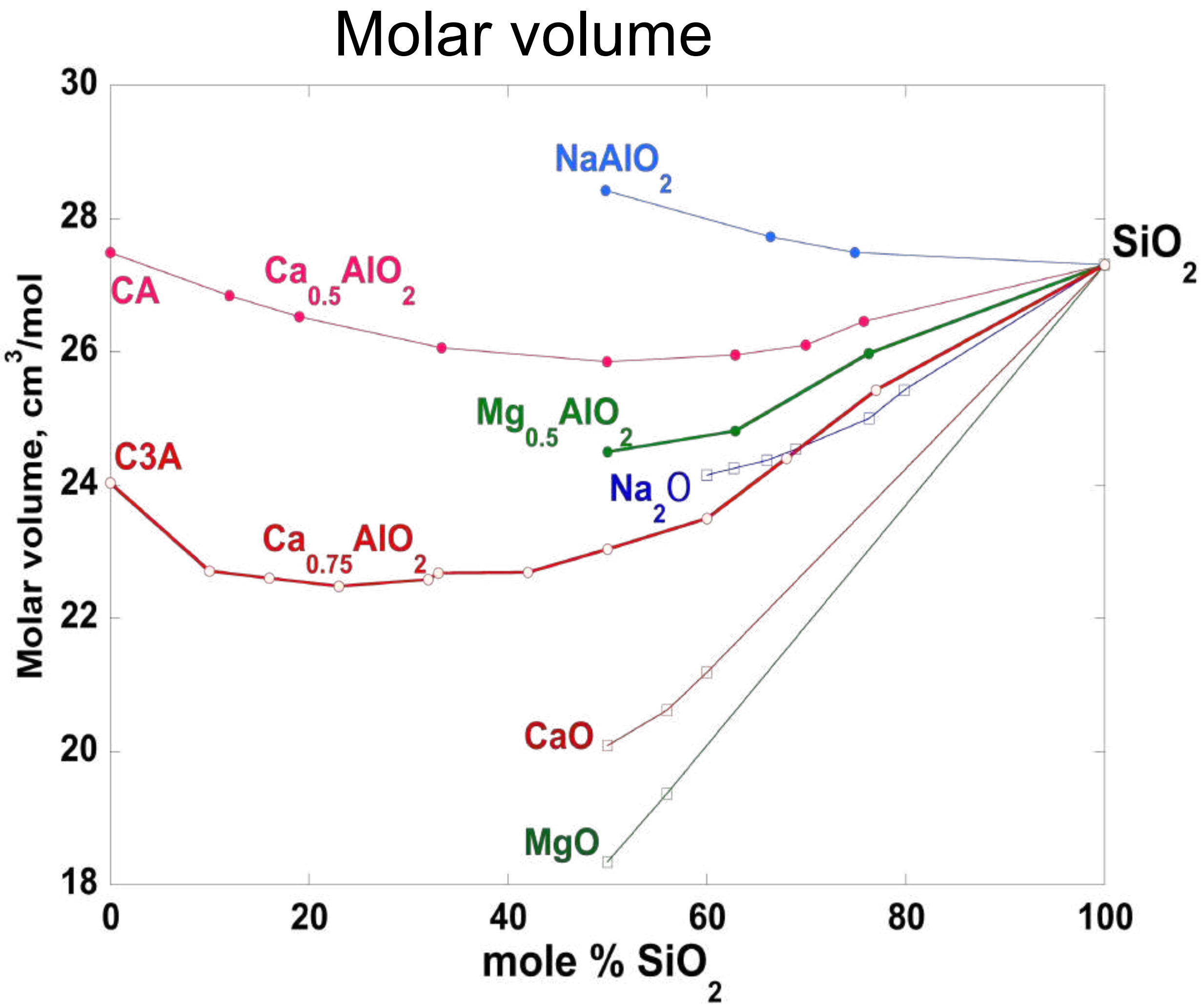
Na_2O and CaO depolymerase's the network and reduce the viscosity of silicates melts, while Al_2O_3 increases the viscosity of silicates to tectosilicate glasses ($R=MO/Al_2O_3=1$).

$^{[5]}Al$ and $^{[4]}Al$ are connected preferentially with Si in high Q species

Network modifier versus charge compensator?

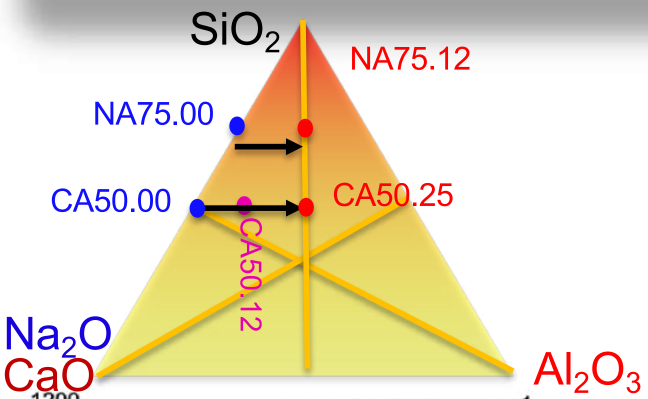


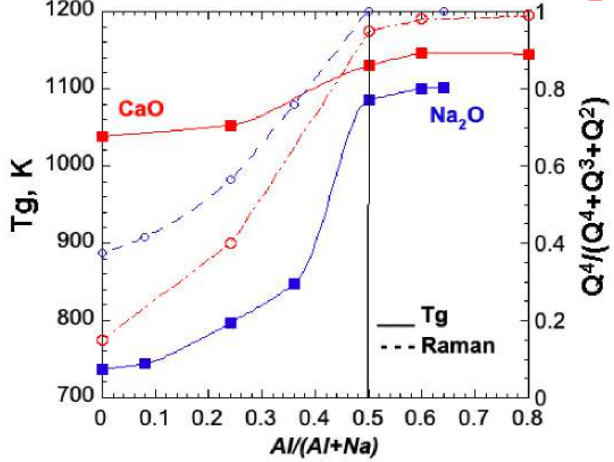


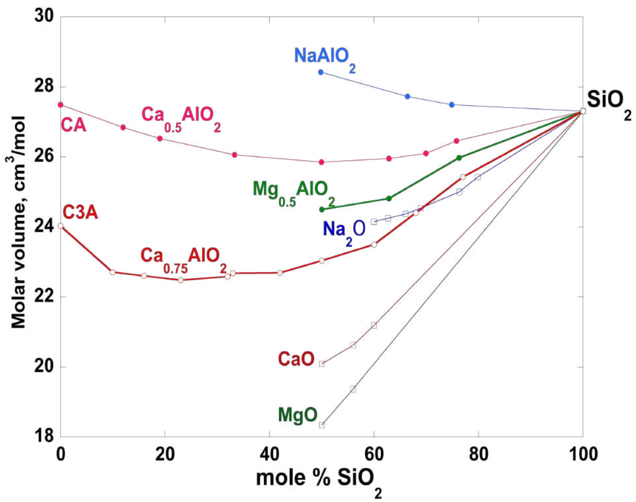


In Neuville D.R., Henderson G.S, Dingwell D. B. (2022) "Magmas, melts, liquids and glasses: Experimental insights " Review in Mineralogy and Geochemistry.
DOI : 10.2138/rmg.2022.87.03

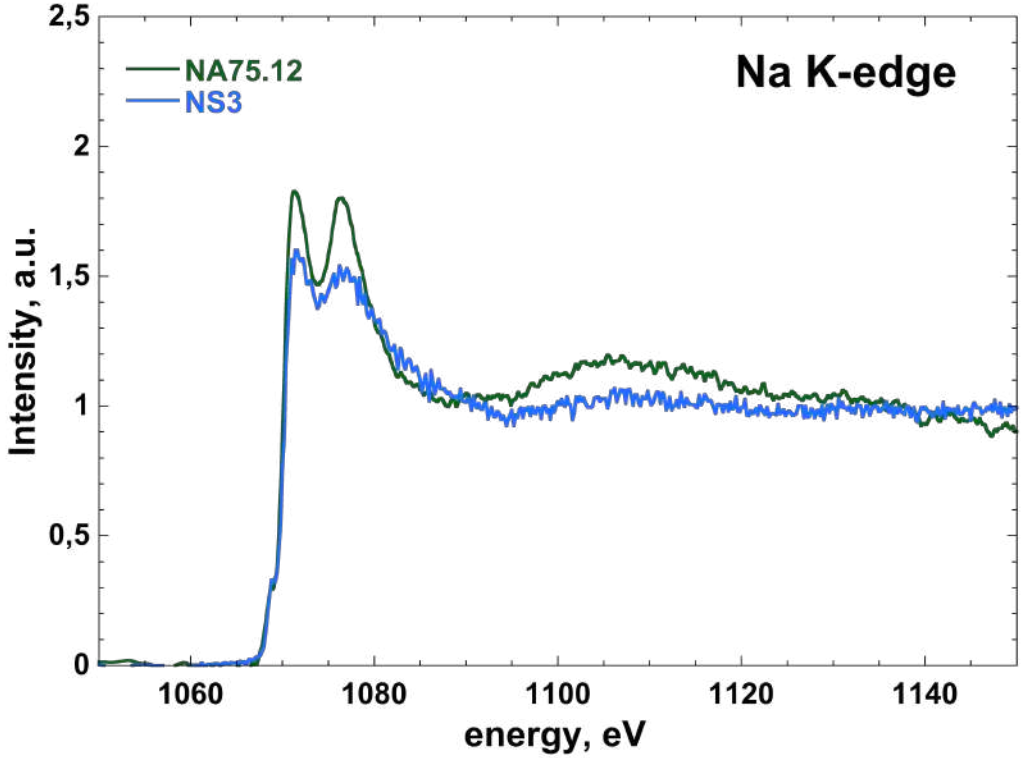
Network modifier versus charge compensator?







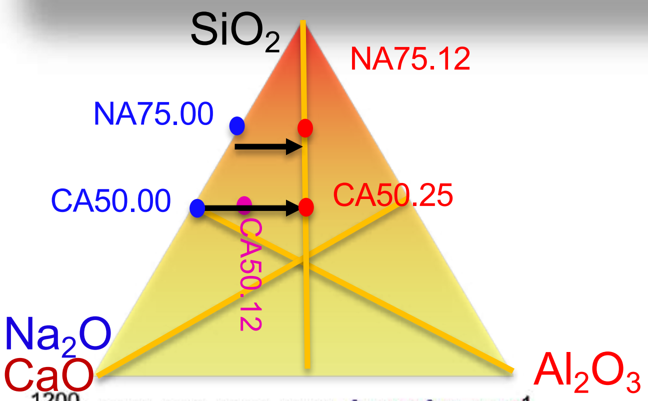
XANES

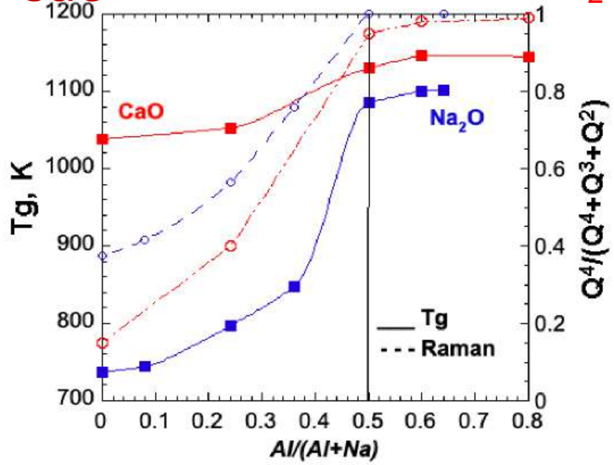


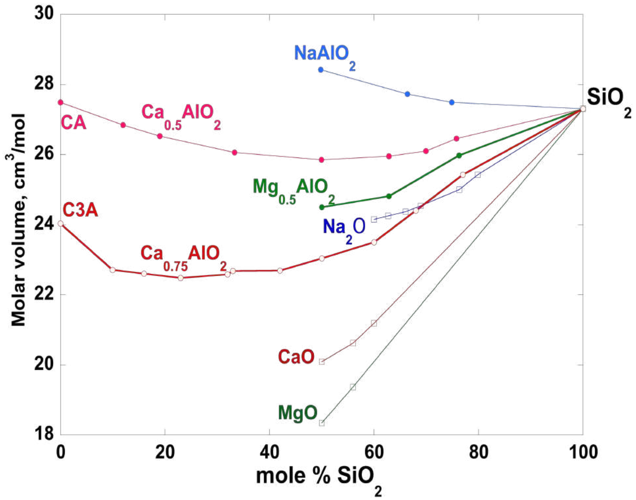
NS3 => [6]Na

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.

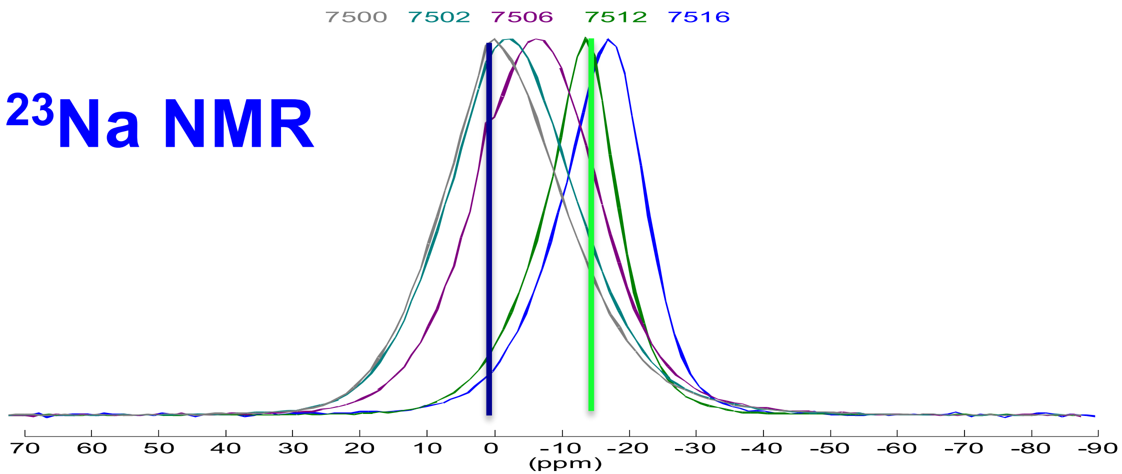






NMR

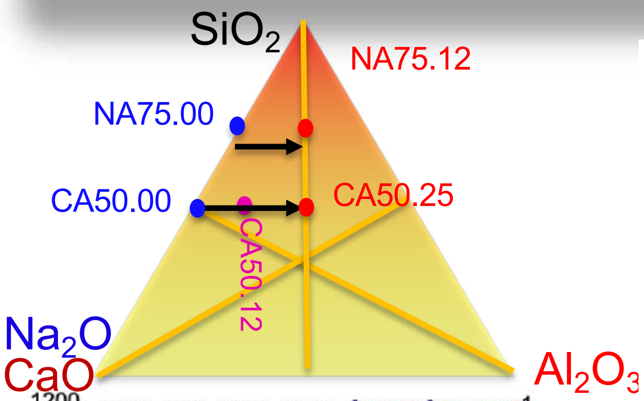
^{23}Na NMR

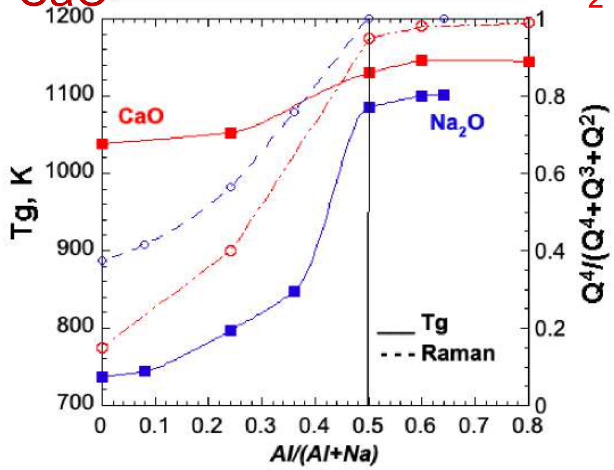


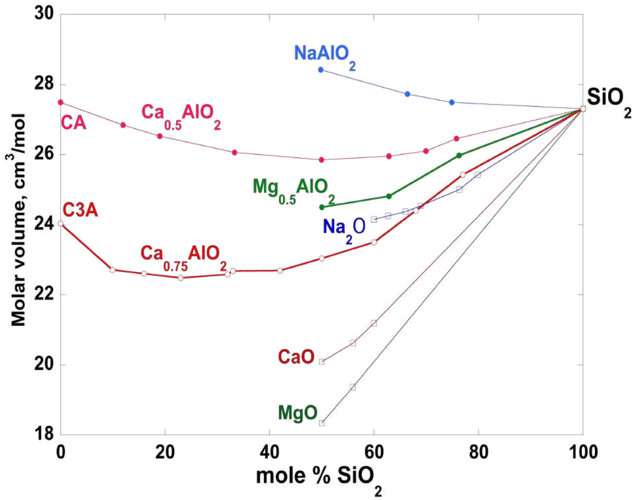
⇒ Chemical shift of 23Na, from network modifyer to charge compensator

Losq, 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.

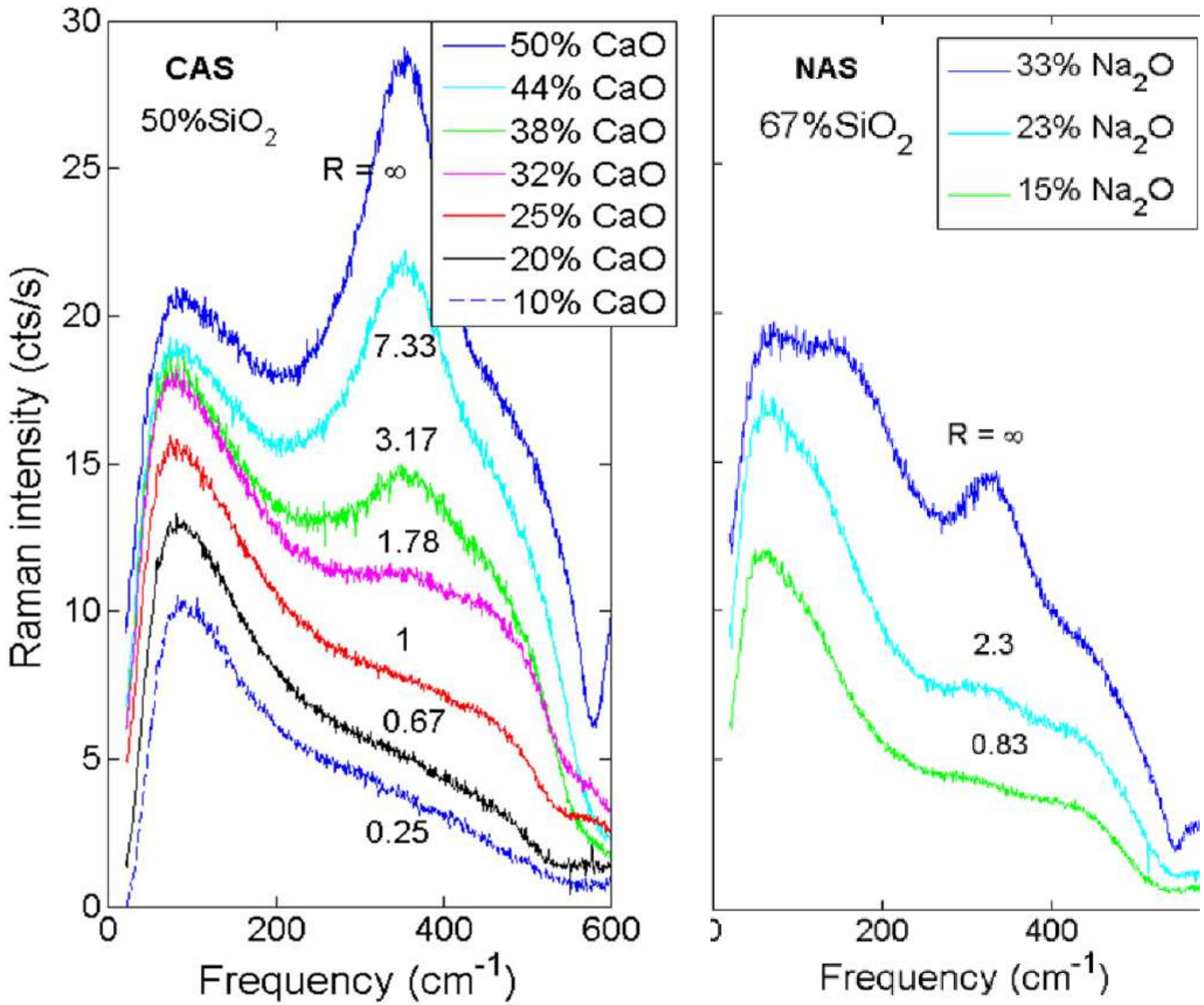
Network modifier versus charge compensator?





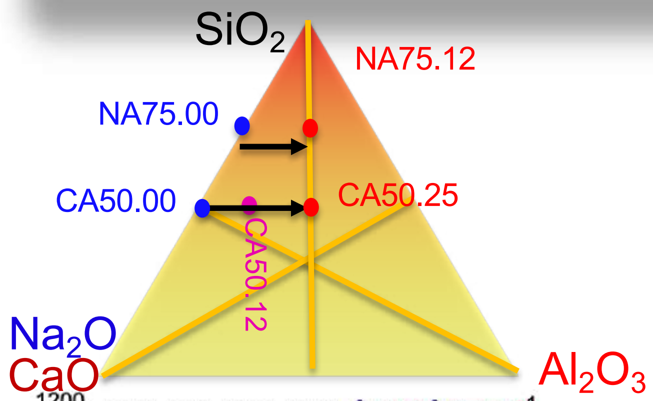


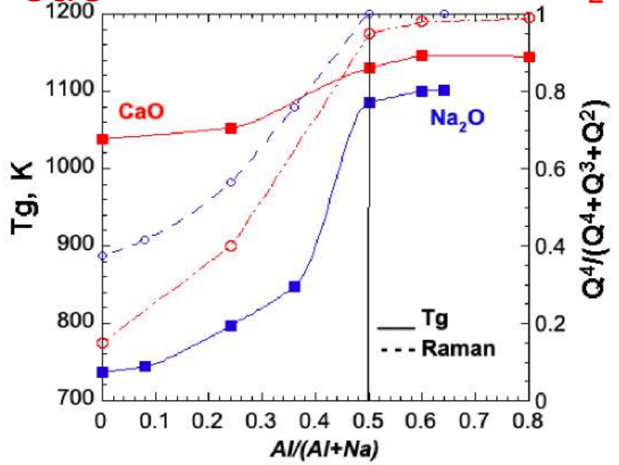
Raman VH

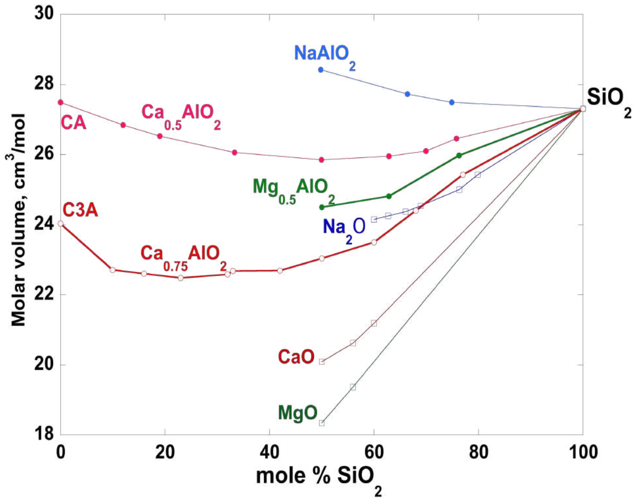


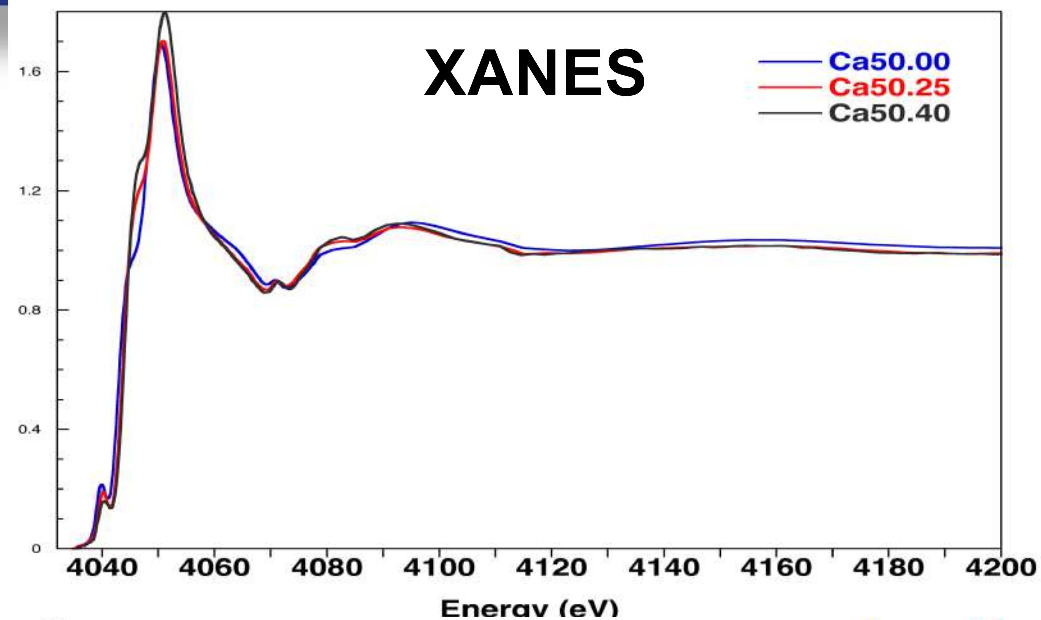
Hehlen B. and Neuville D.R. (2015) Raman response of network modifier cations in alumino-silicate glasses. The Journal of Physical Chemistry B. 119, 4093–4098.

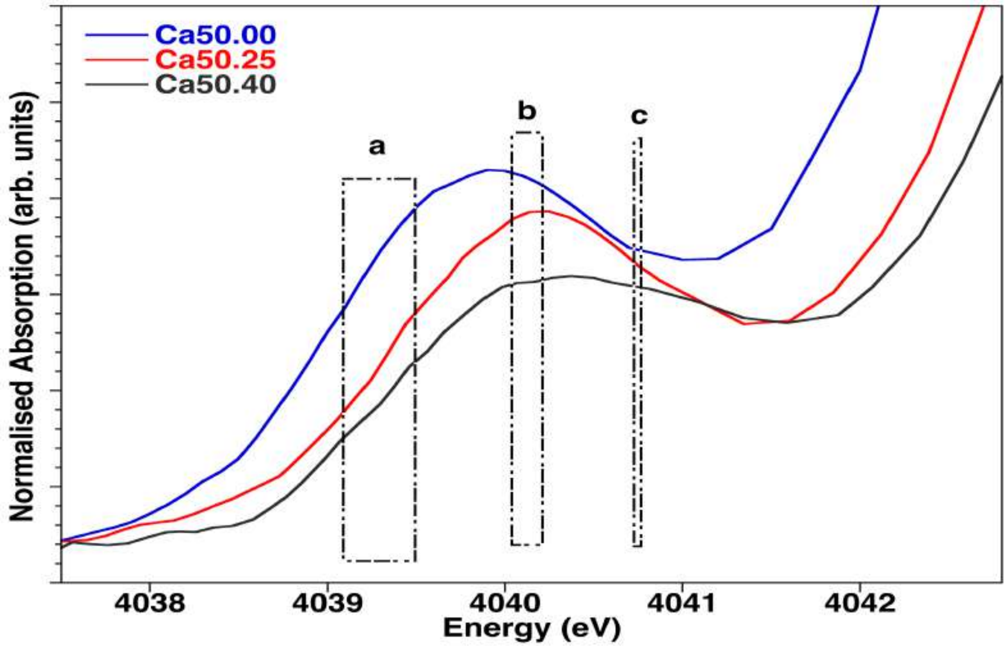
Network modifier versus charge compensator?





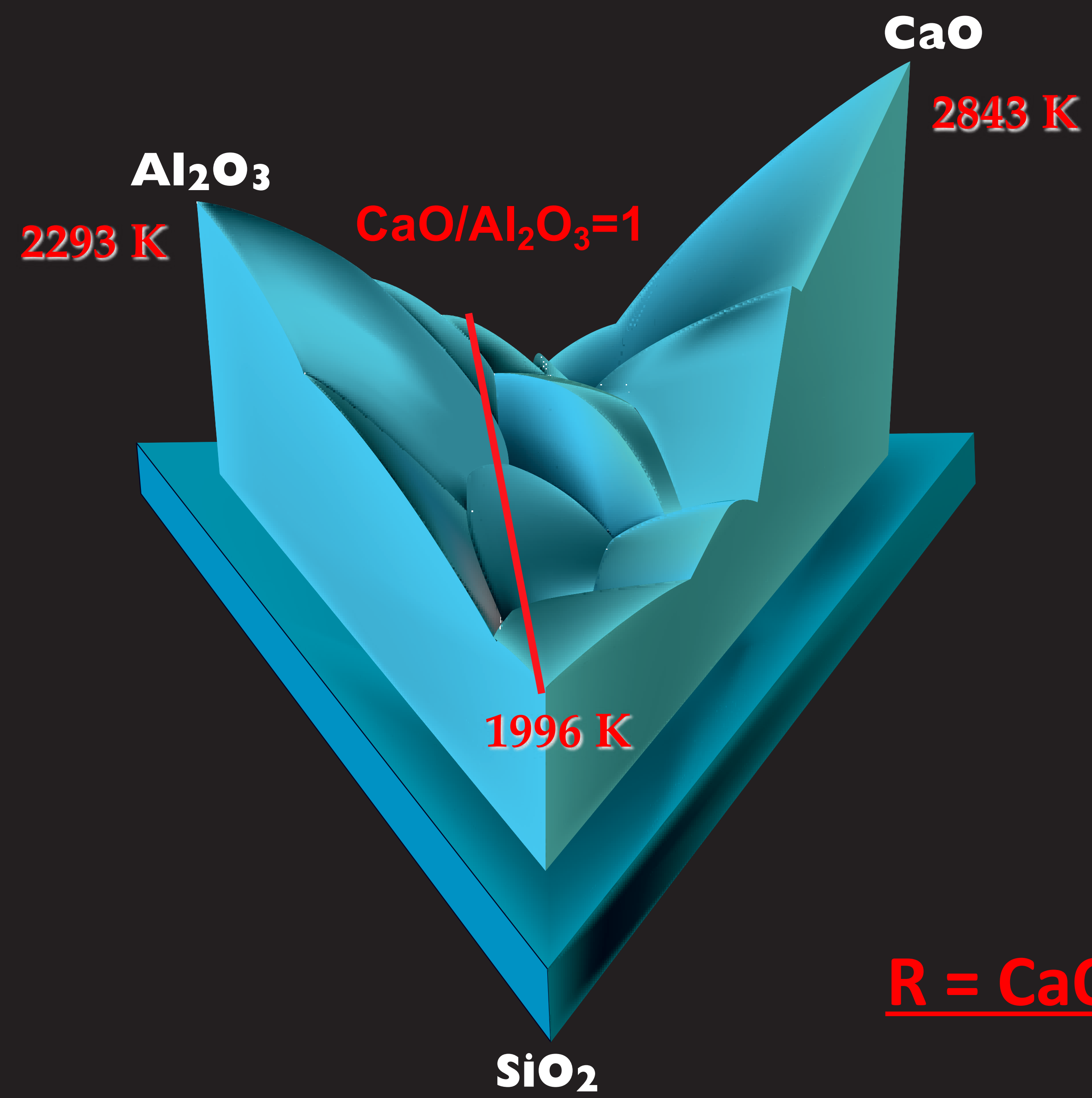






Cicconi M.R., d Ligny D., Gallo T. M., Neuville D.R. (2016) Ca Neighbors from XANES spectroscopy: a tool to investigate structure, redox and nucleation processes in silicate glasses, melts and crystals. American Mineralogist, 101, 1232-1236.

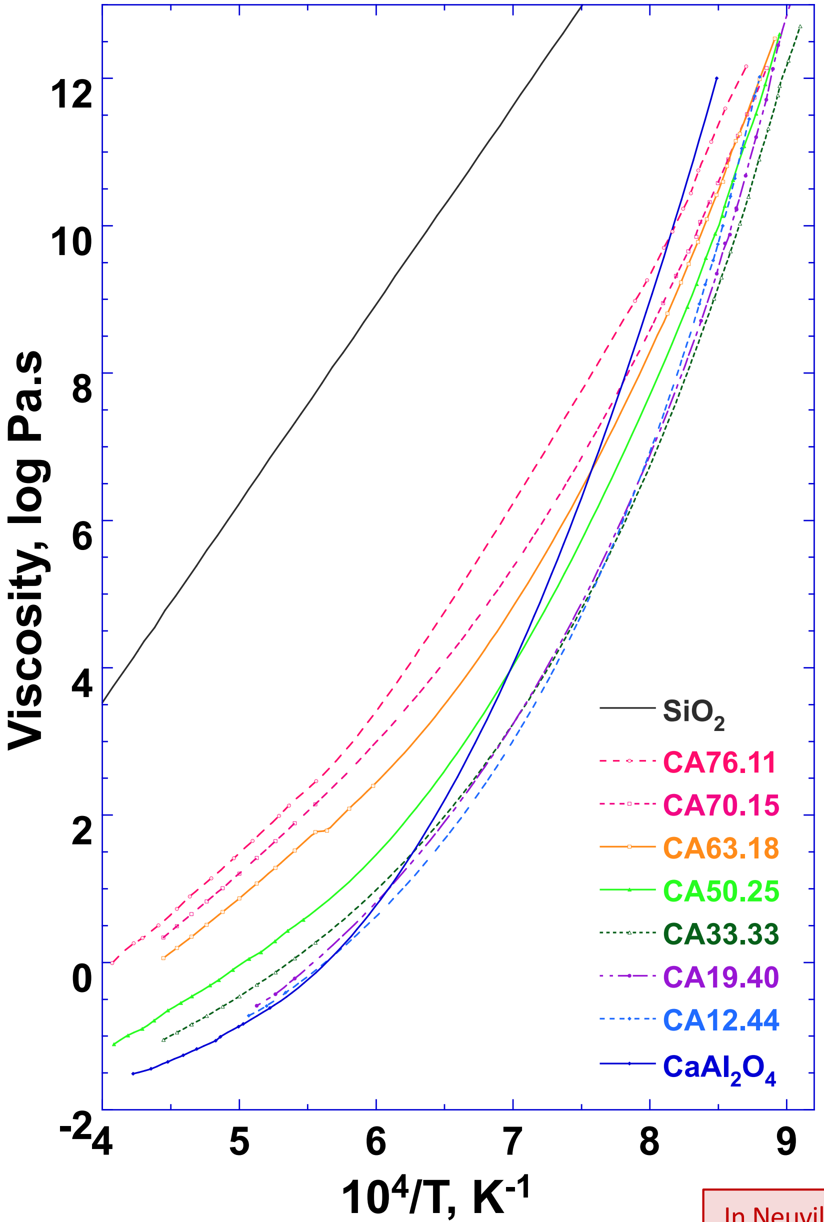
Al^{3+} in silicate glasses and melts

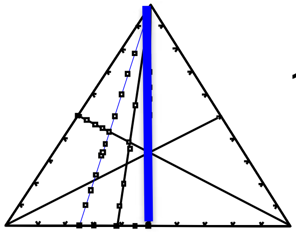


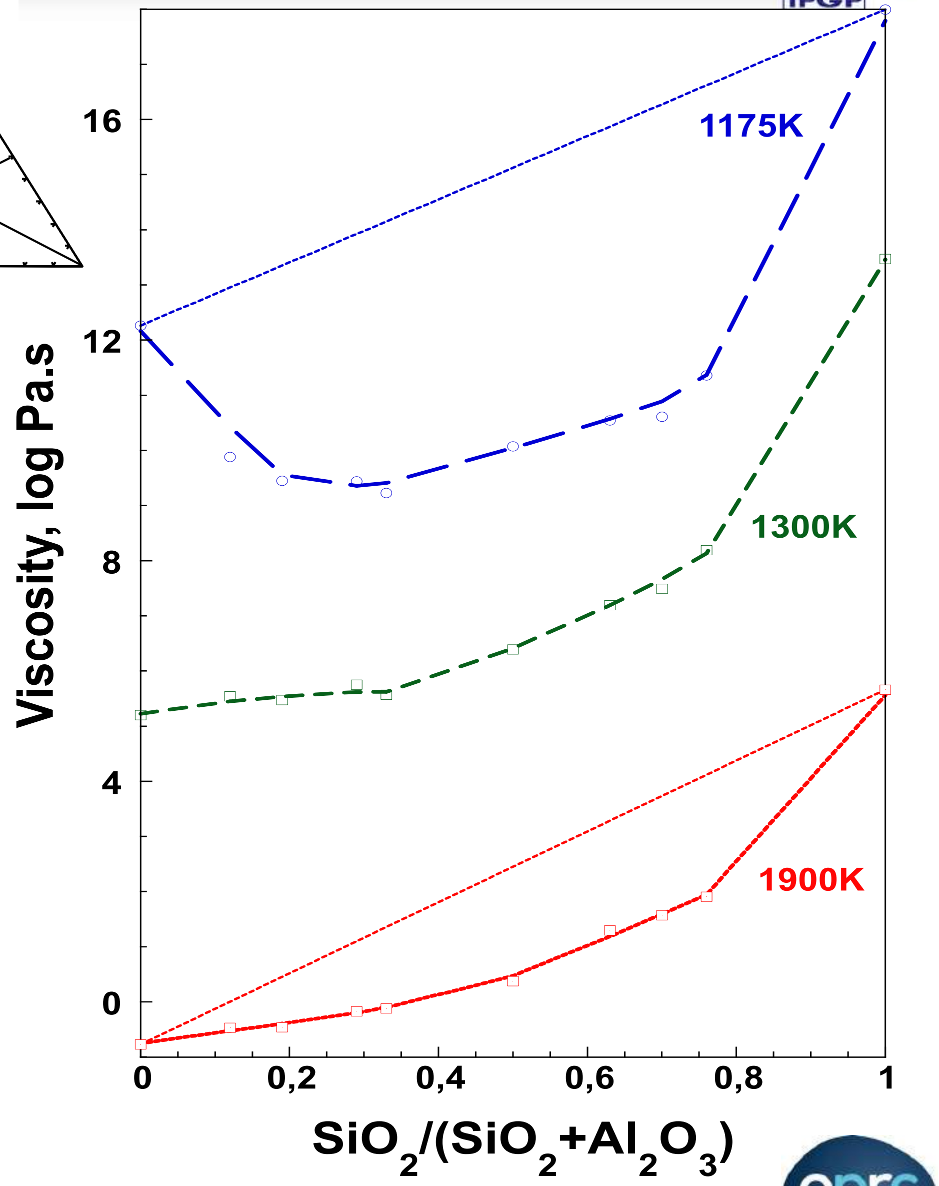
$R = CaO/Al_2O_3$

after Rankin, 1915

R = $CaO/Al_2O_3=1$



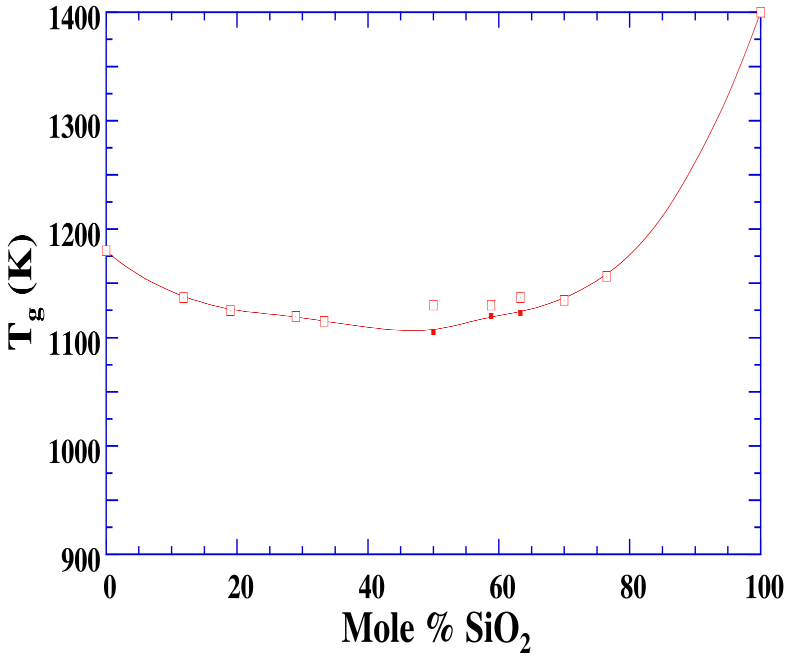




In Neuville D.R., Henderson G.S, Dingwell D. B. (2022) "Magmas, melts, liquids and glasses: Experimental insights " Review in Mineralogy and Geochemistry. DOI : 10.2138/rmg.2022.87.03

Configuration Entropy Theory

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



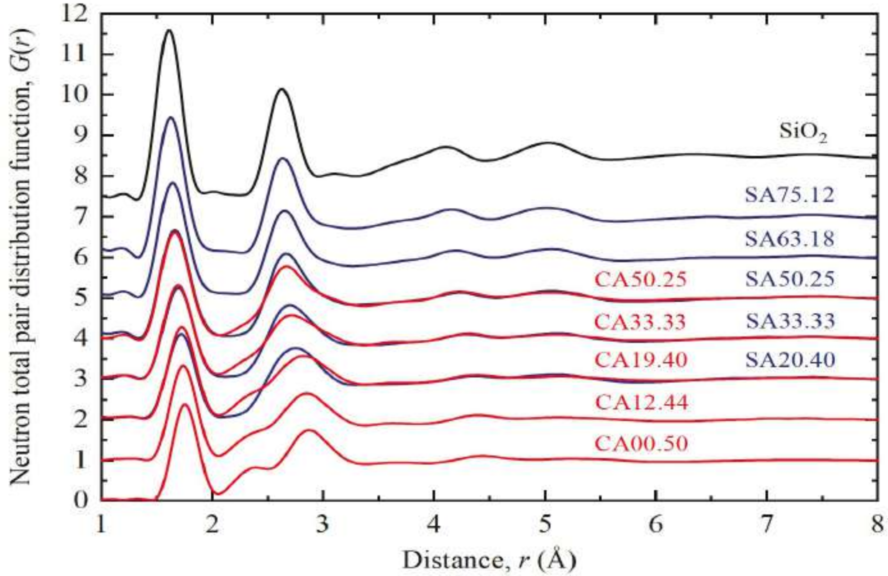
$S^{mix} = -\,nR\,X_i \ln X_i$

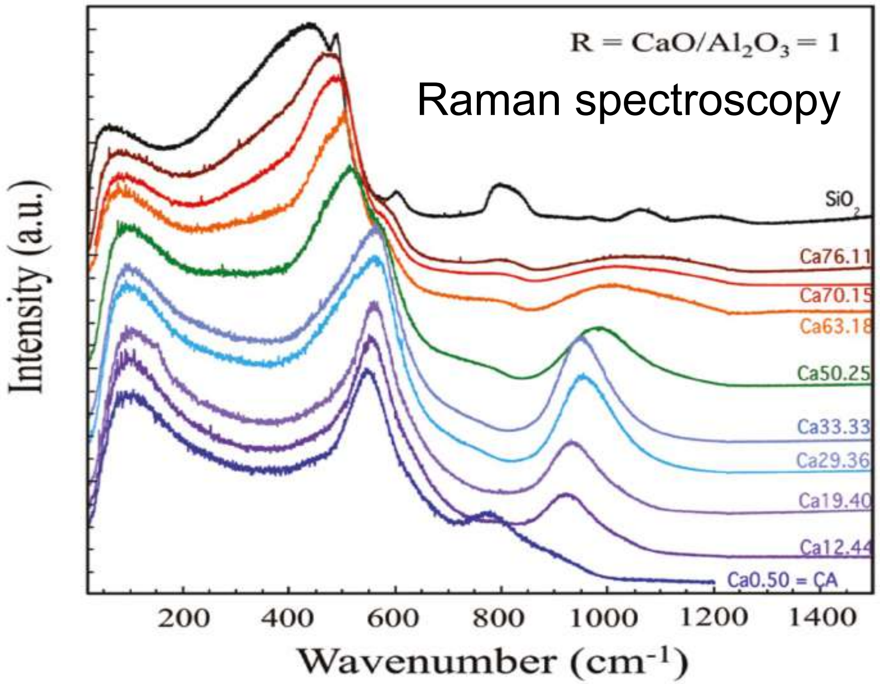
$X_i = Al/(Al+Si)$

Ideal mixing => random distribution

In Neuville D.R., Henderson G.S, Dingwell D. B. (2022) "Magmas, melts, liquids and glasses: Experimental insights " Review in Mineralogy and Geochemistry. DOI : 10.2138/rmg.2022.87.03

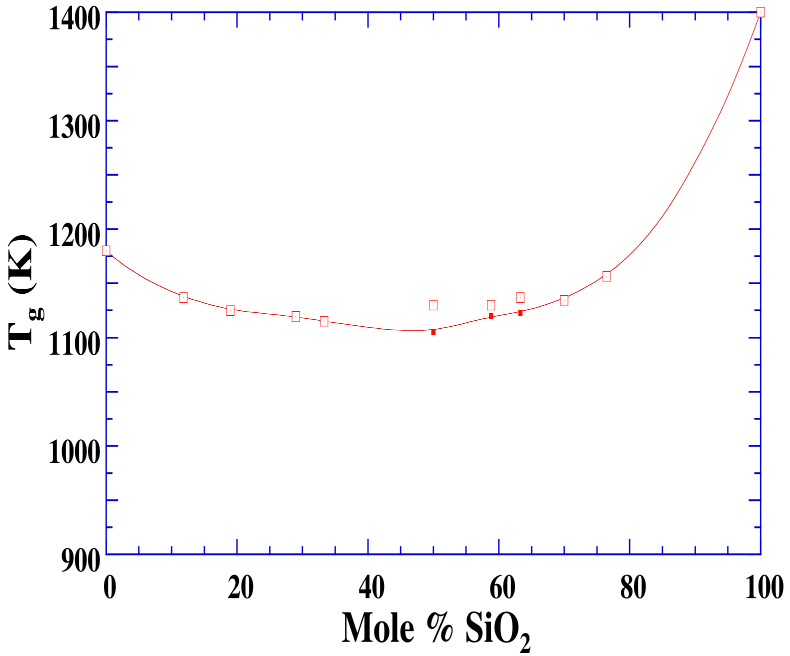
Neutron total pair distribution functions





Configuration Entropy Theory

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



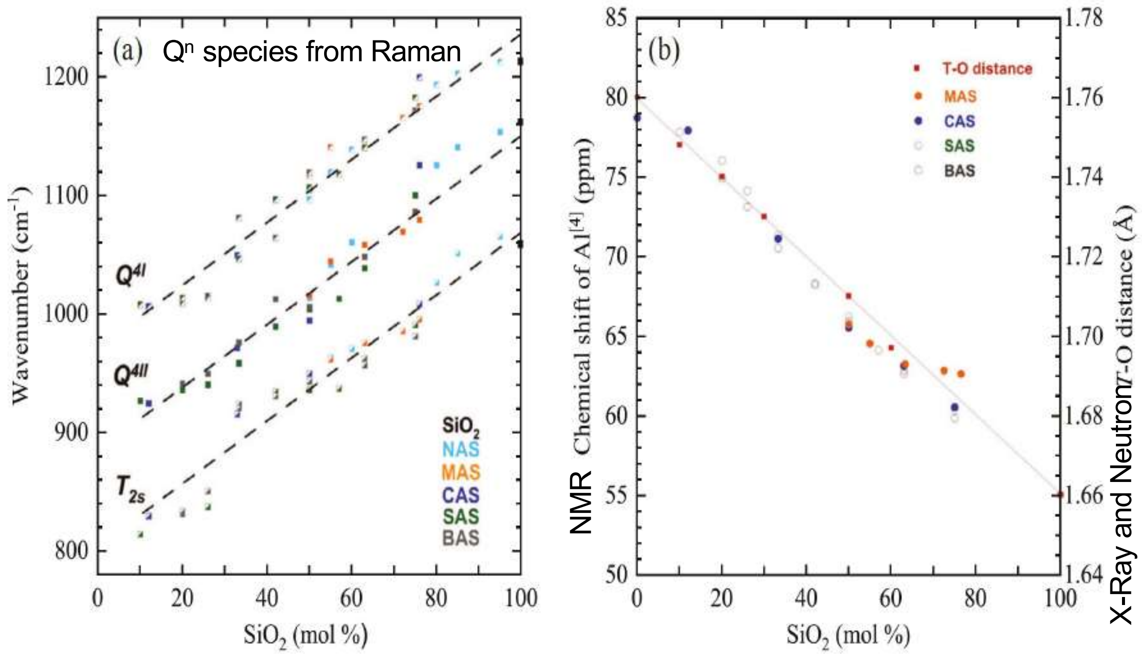
$S^{mix} = - nR\, X_i \ln X_i$

$X_i = Al/(Al+Si)$

Ideal mixing => random distribution

In Neuville D.R., Henderson G.S, Dingwell D. B. (2022) "Magmas, melts, liquids and glasses: Experimental insights " Review in Mineralogy and Geochemistry. DOI : 10.2138/rmg.2022.87.03

Substitution of Si by Al in Q^4 species along the join R=1



SiO_2 => Tetrahedra SiO_4

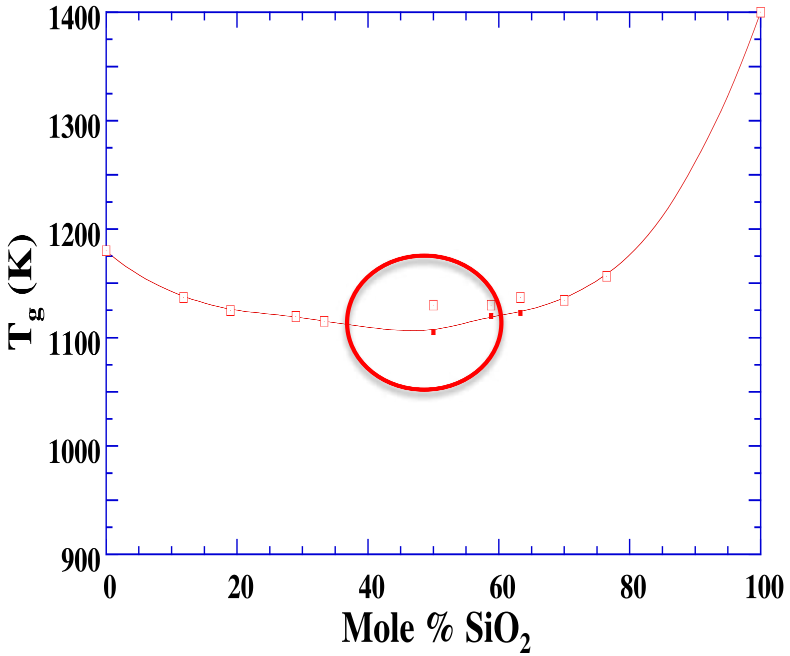
$CaAl_2O_4$ => Tetrahedra AlO_4

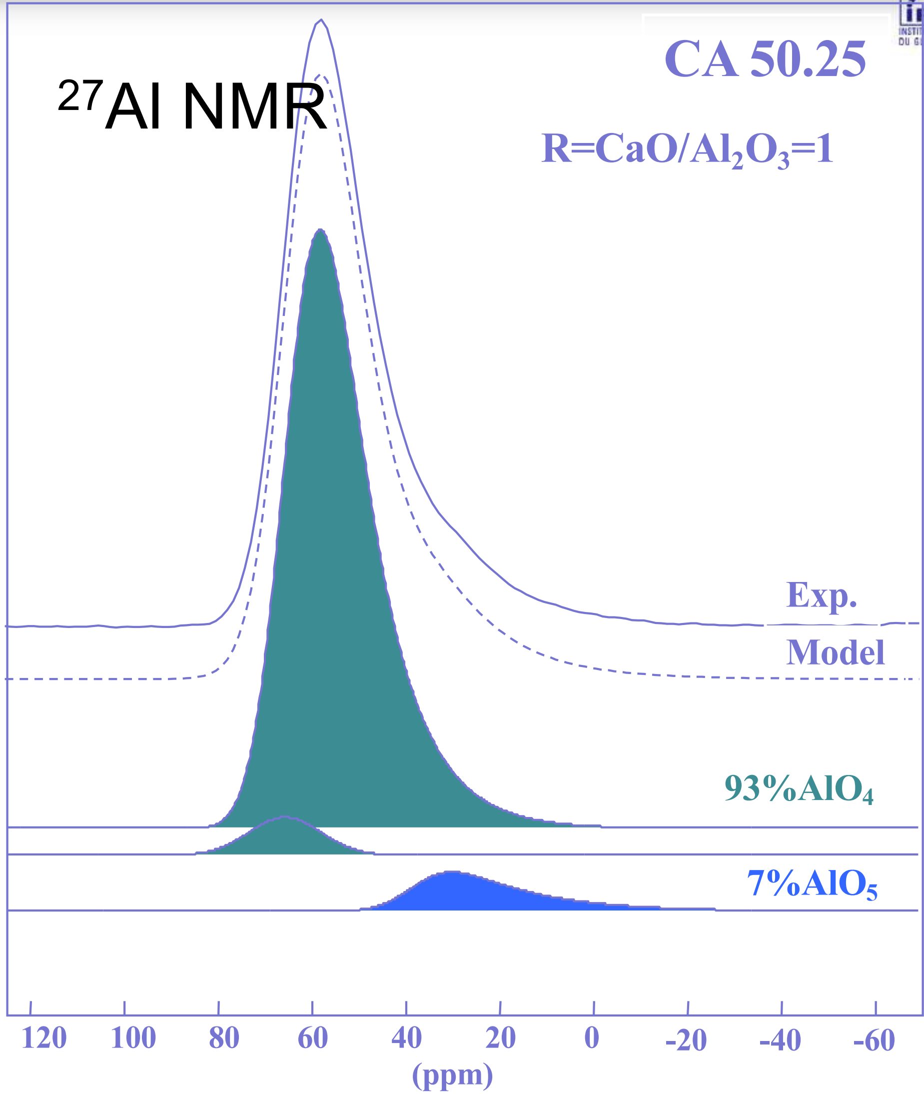
substitution of 1 Si by 1 Al and Ca or M as charge compensator

In Neuville D.R., Henderson G.S, Dingwell D. B. (2022) "Magmas, melts, liquids and glasses: Experimental insights " Review in Mineralogy and Geochemistry. DOI : 10.2138/rmg.2022.87.02

Configuration Entropy Theory

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

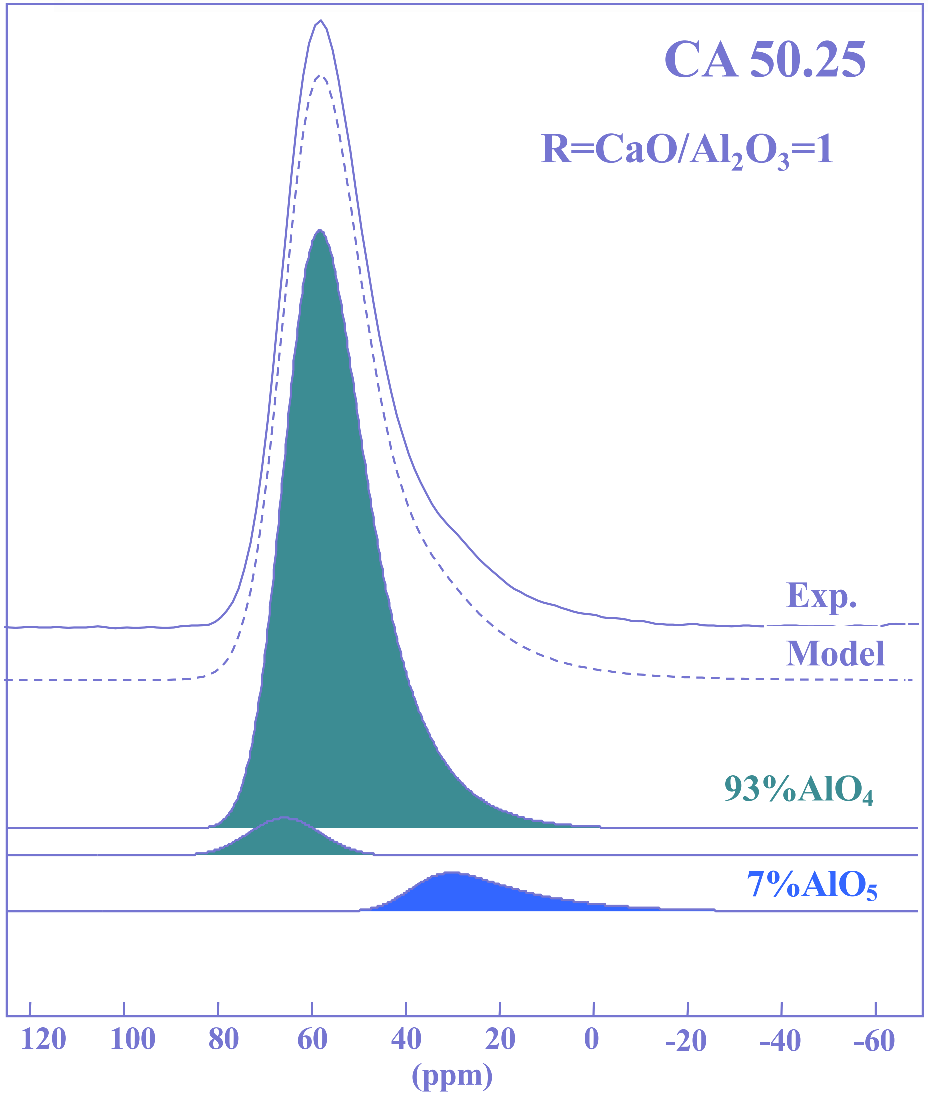


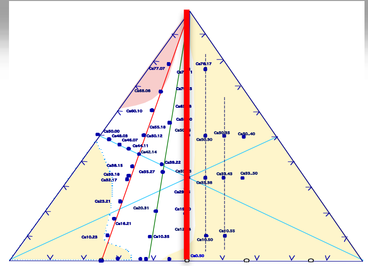


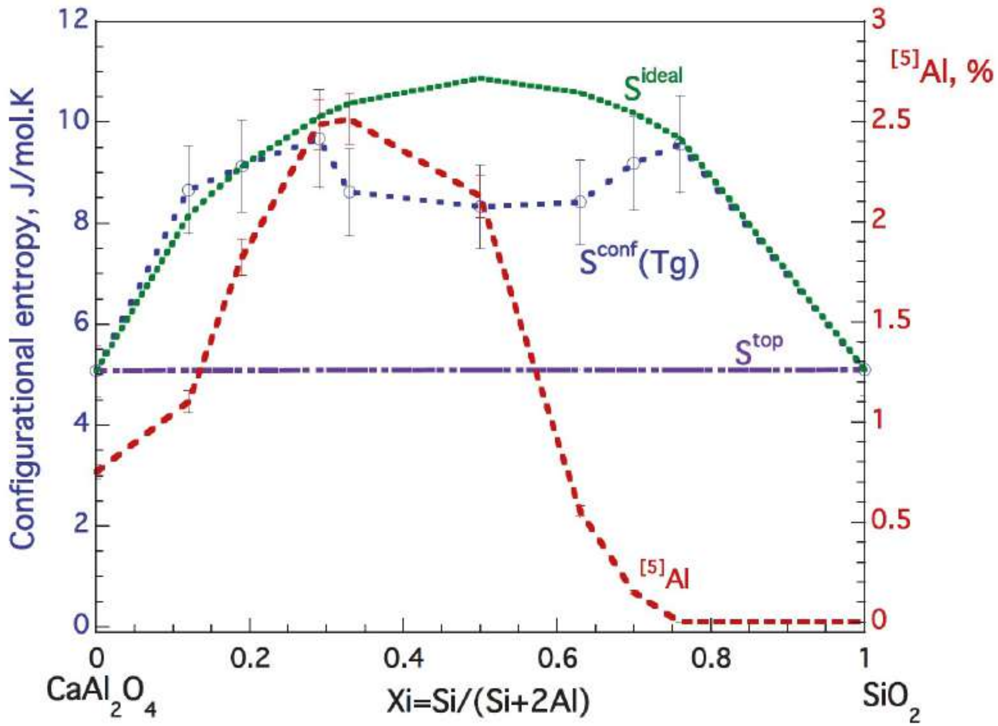
Neuville D.R., Cormier L. and Massiot D. (2004) Role of aluminium in peraluminous region in the CAS system. Geochim. Cosmochim. Acta., 68, 5071-5079

CaO-Al2O3-SiO2 system

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



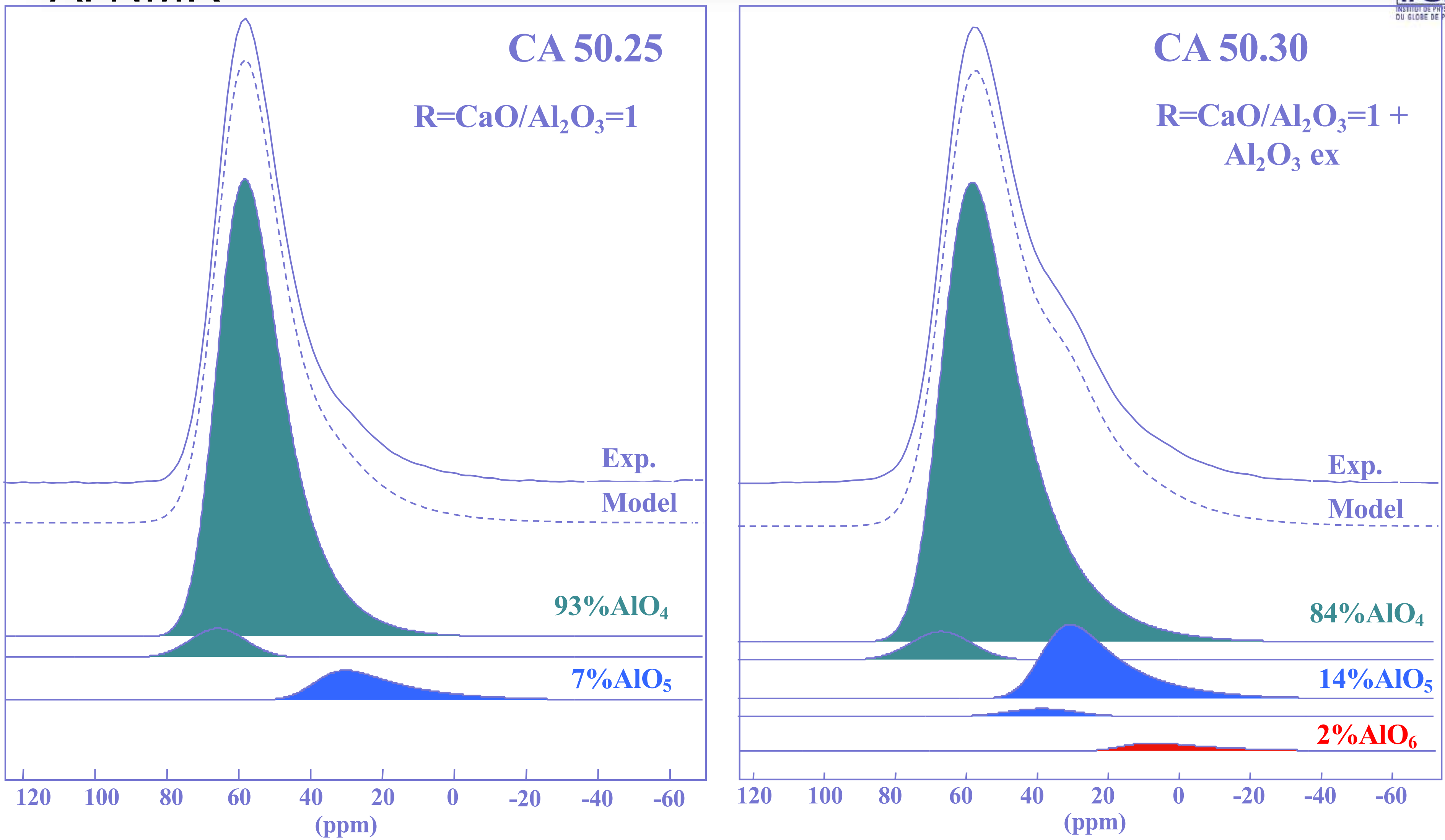




In Neuville D.R., Henderson G.S, Dingwell D. B. (2022) "Magmas, melts, liquids and glasses: Experimental insights " Review in Mineralogy and Geochemistry. DOI : 10.2138/rmg.2022.87.03

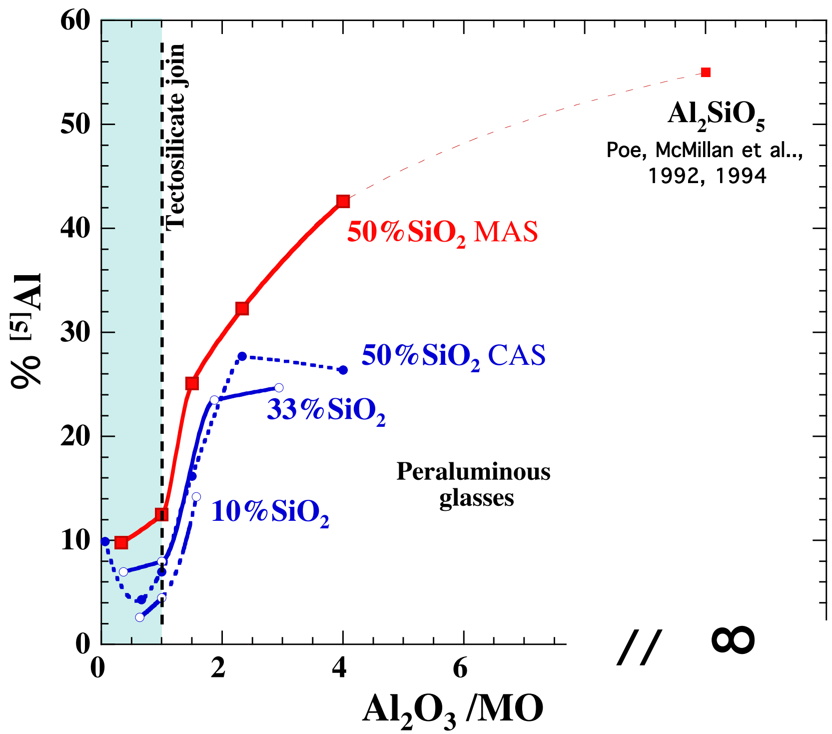
Neuville D.R., Cormier L. and Massiot D. (2004) Role of aluminium in peraluminous region in the CAS system. Geochim. Cosmochim. Acta., 68, 5071-5079

^{27}Al NMR



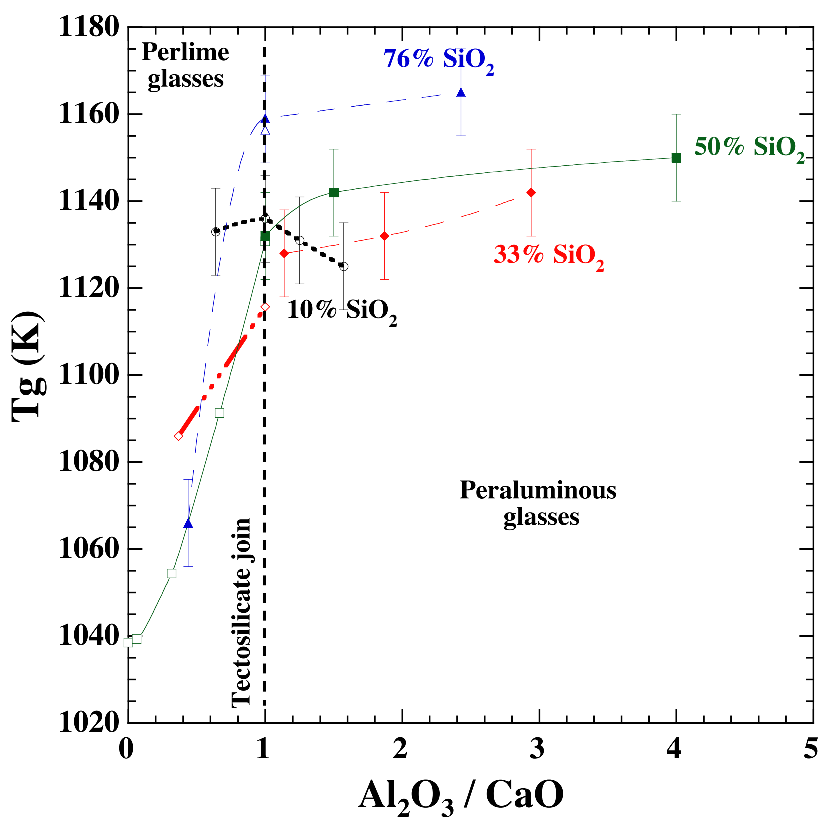
RMN 750MHz, CRMHT, Orléans, ^{27}Al 1D MAS

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

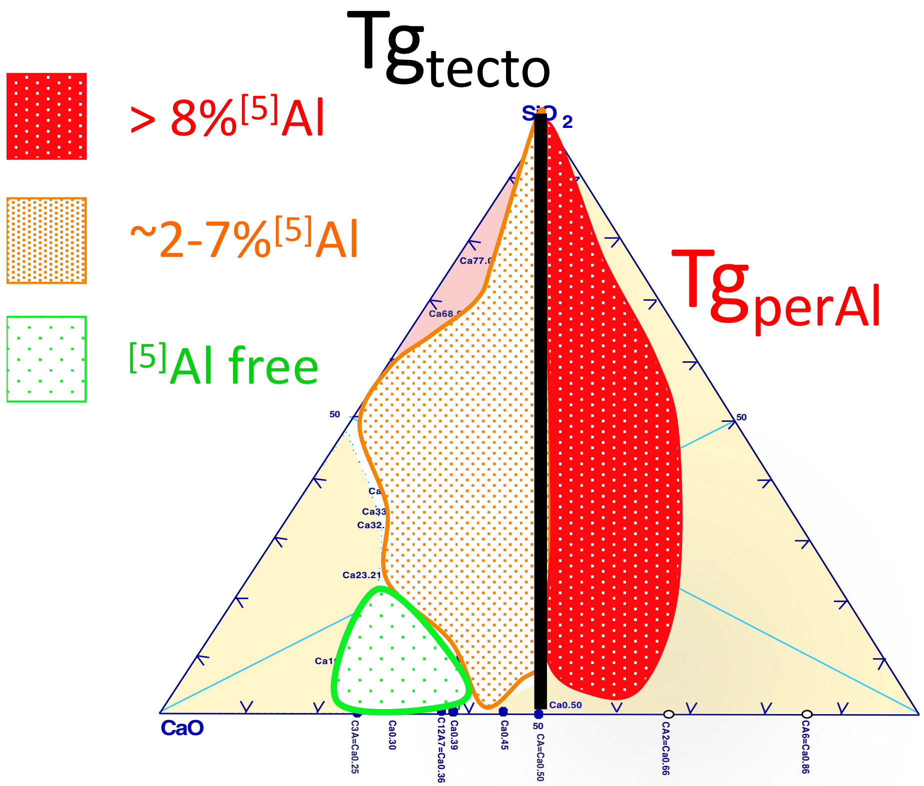


[5]Al increases with Al_2O_3 content for $R=CaO/Al_2O_3<1$

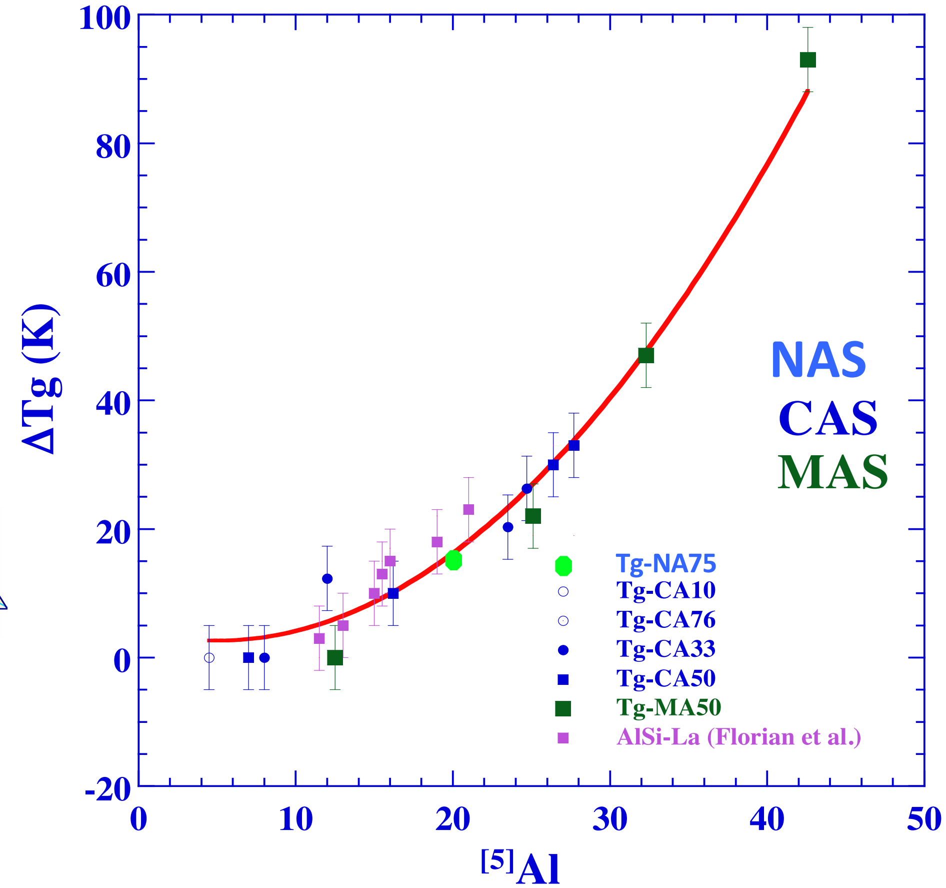
Tg from DSC, Heating rate 5K/min



Neuville D.R., Florian P., Le Losq Ch. et Massiot D. (2010) Structure et propriété des verres: le rôle de l'aluminium. Matériaux et Techniques. 98, 395-402.



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



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

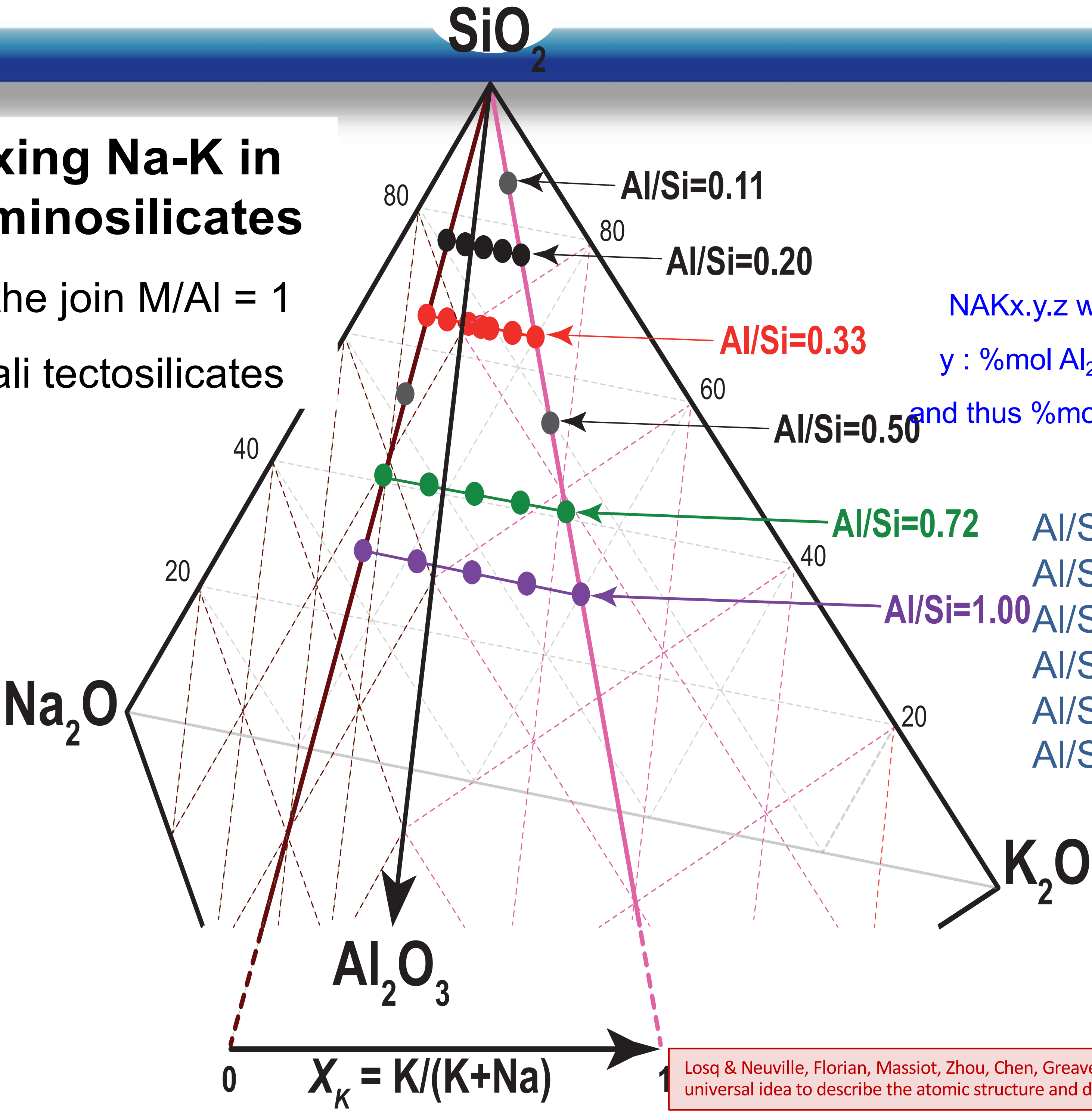
⇒ [5]Al can be a strong network former !

Neuville et al. 2024

Mixing Na-K in aluminosilicates

On the join M/Al = 1

Alkali tectosilicates



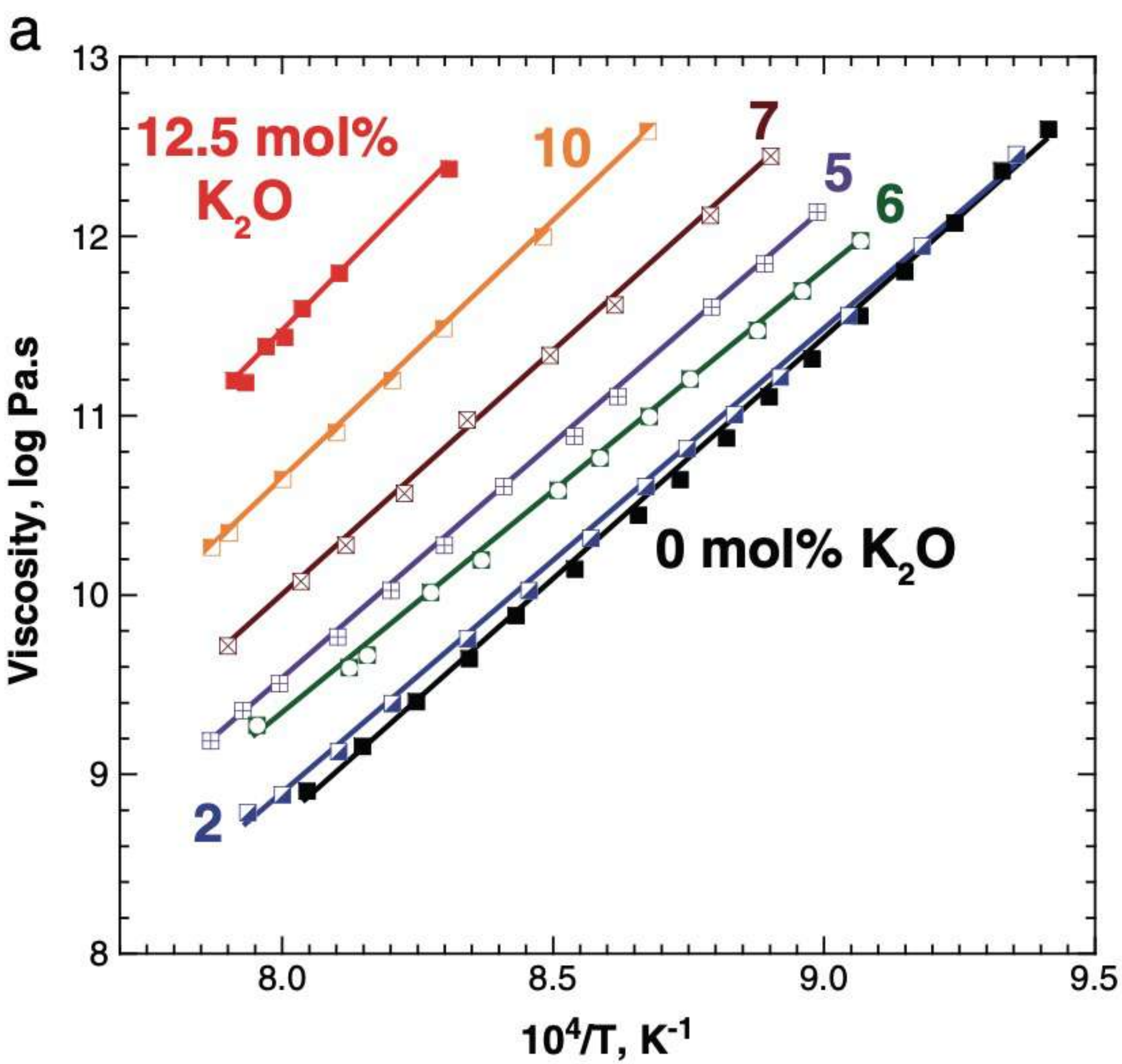
NAKx.y.z with x : %mol SiO_2 ;

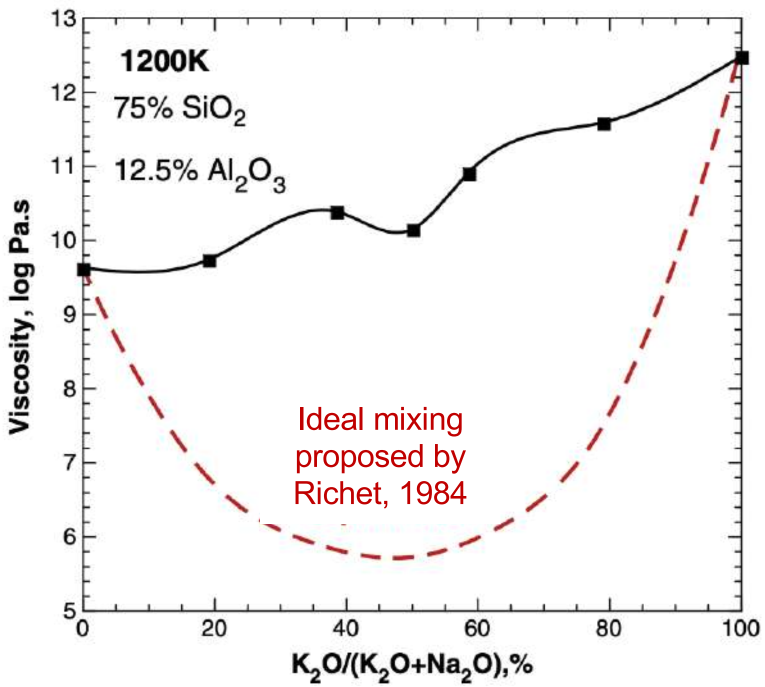
y : %mol Al_2O_3 ; z : %mol K_2O ;

and thus %mol Na_2O = 100-(x+y+z)

Al/Si=0.11 =90%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

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





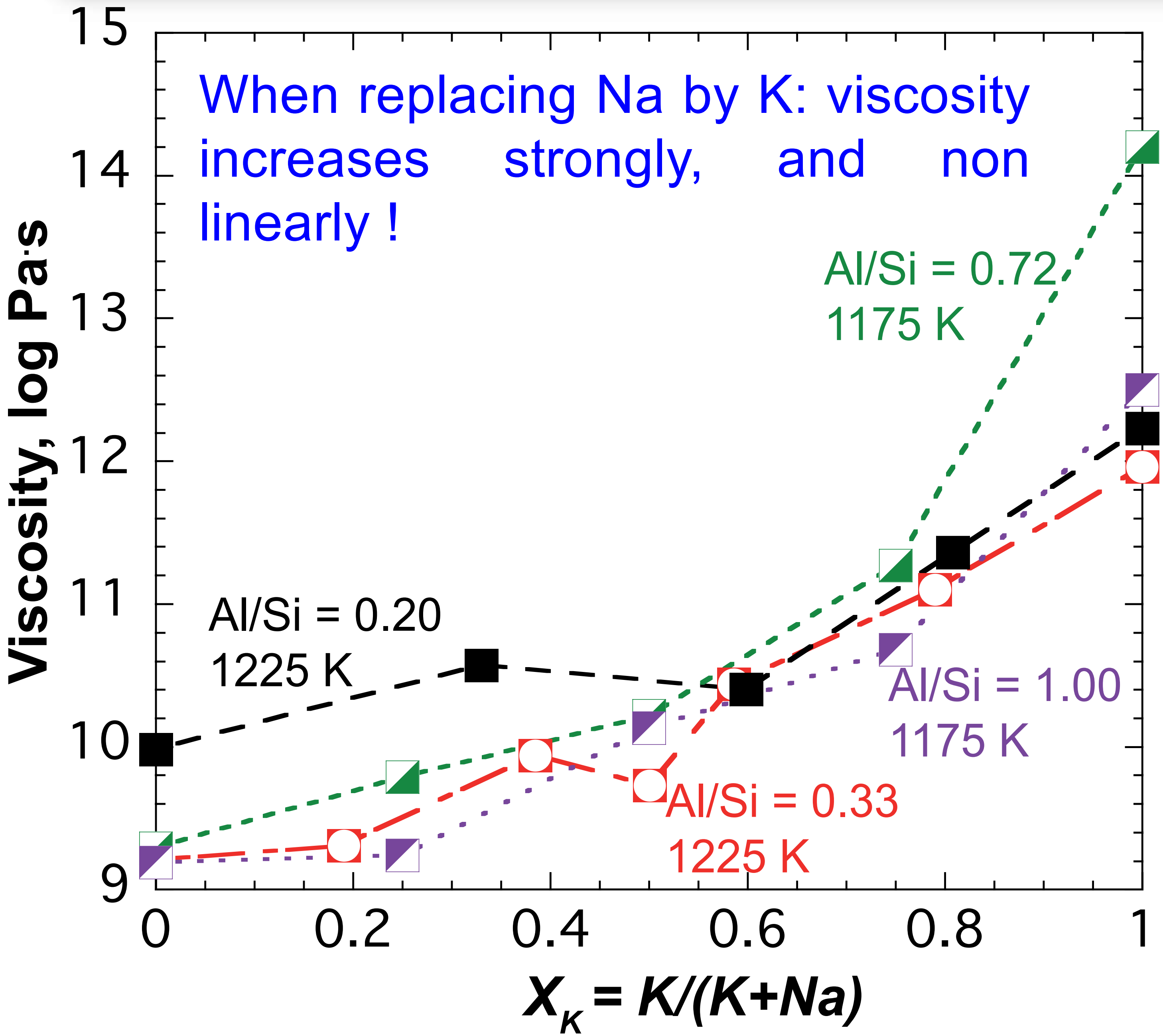
Na and K do not mix randomly

⇒ Viscosity, thermodynamics

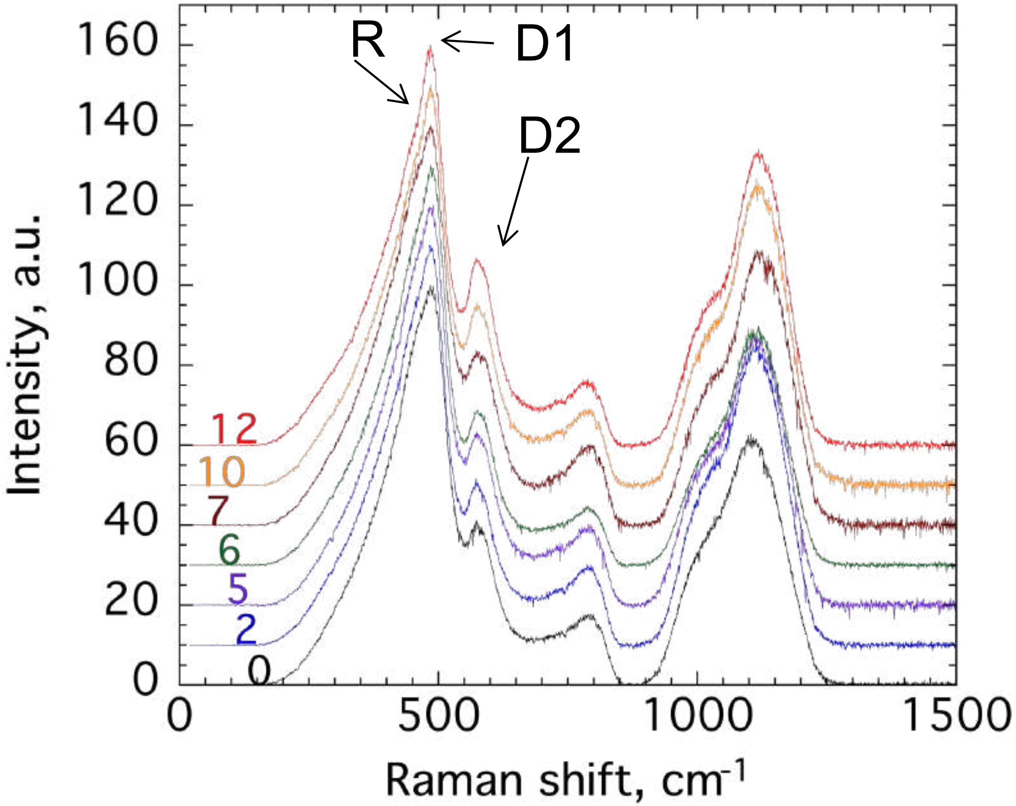
⇒ Structure

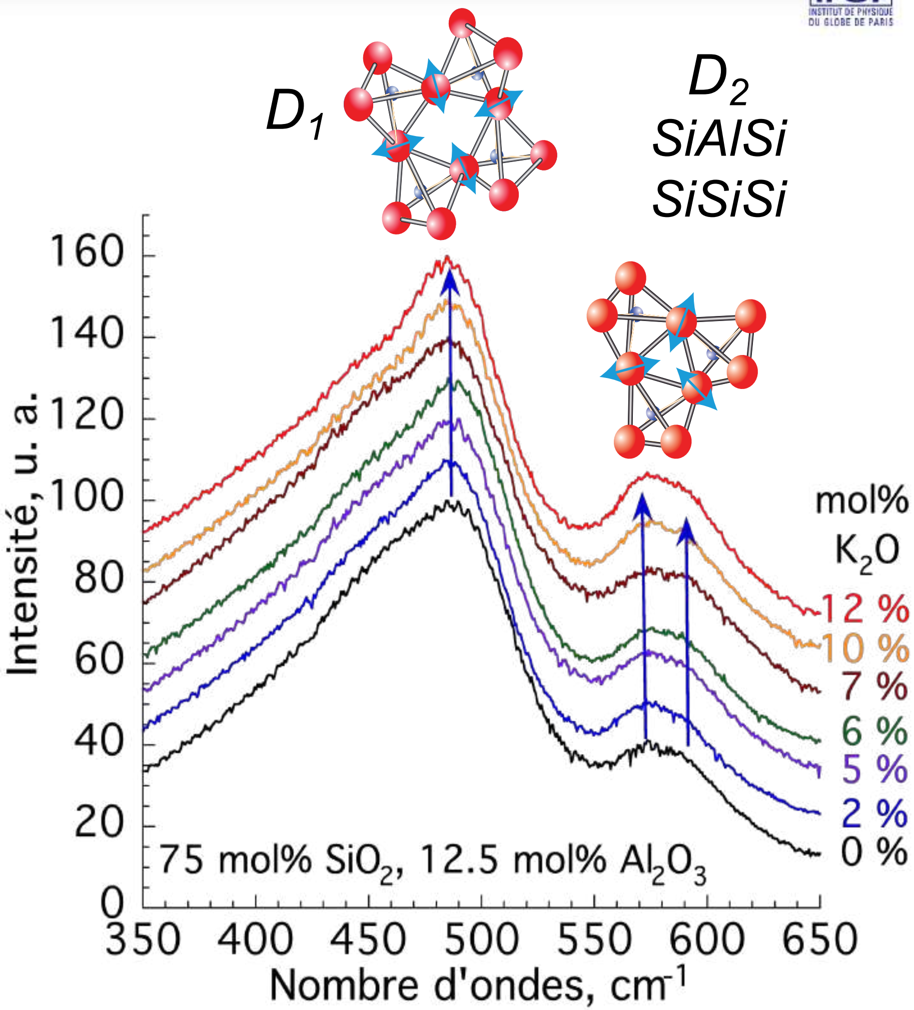
When replacing Na by K: viscosity increases strongly…

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



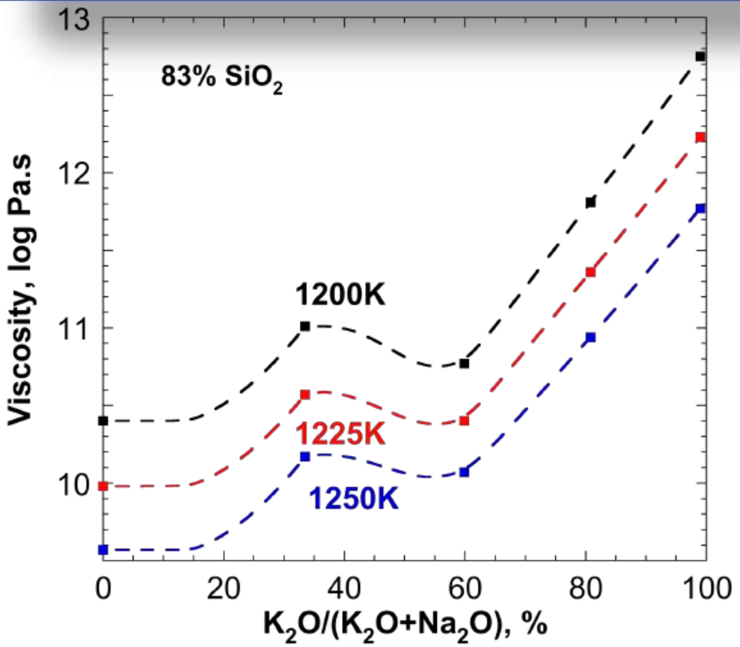
Al/Si=0.11 =90%SiO_2
Al/Si=0.20 =83%SiO_2
Al/Si=0.33 =75%SiO_2
Al/Si=0.50 =66%SiO_2
Al/Si=0.72 =58%SiO_2
Al/Si=1.00 =50%SiO_2

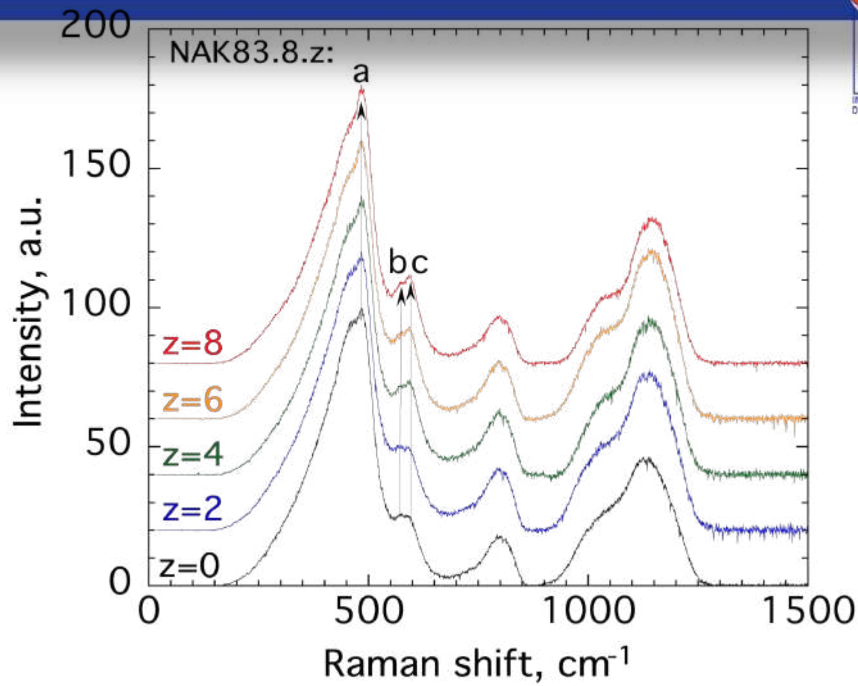




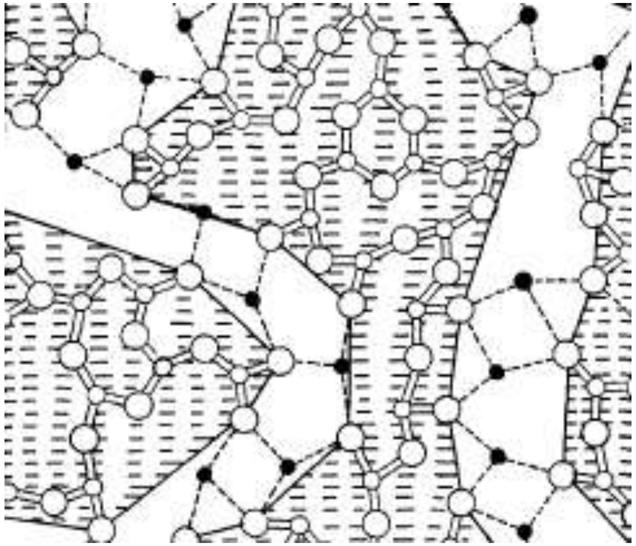
- Boson peak increase in I and decreases in frequency with K like close than SiO2
- D1 and D2 increase with K
- New D2 band

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

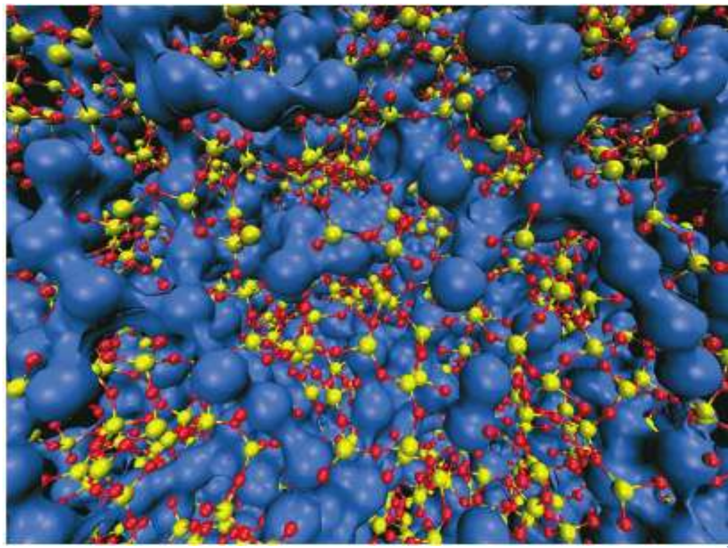




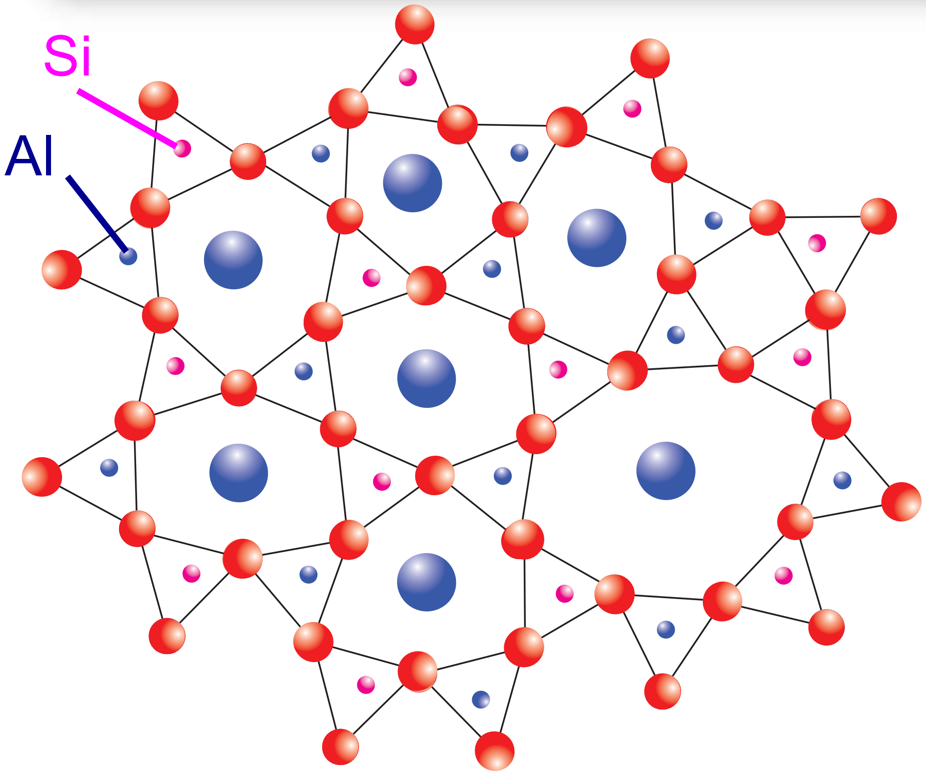
Greaves, 1985: MRN



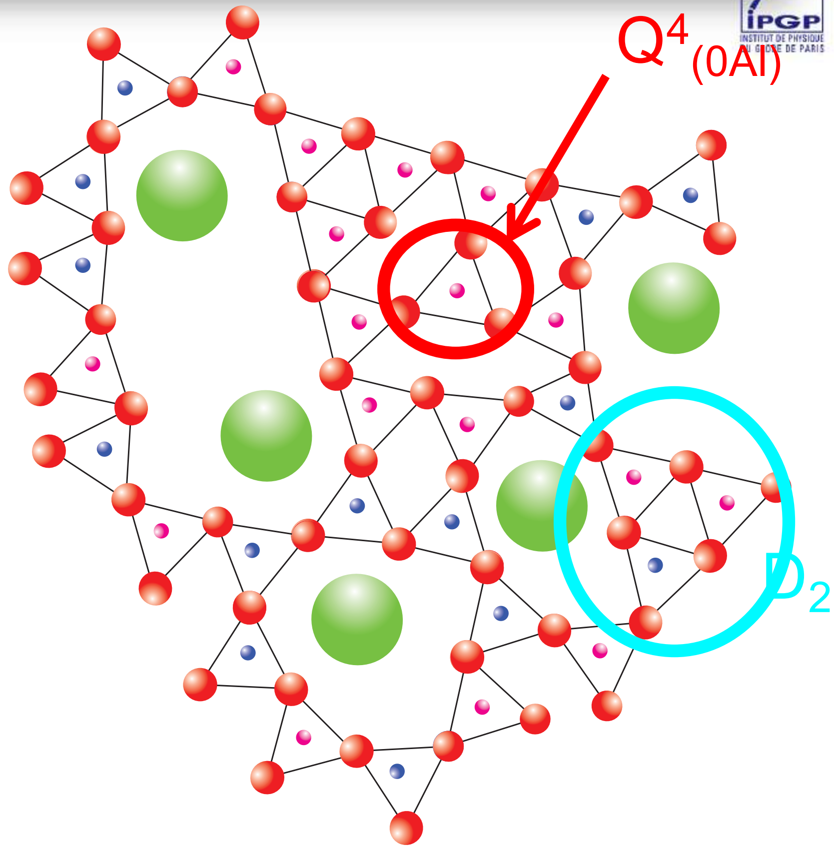
Meyer et al., 2004



Na tectosilicates | *K tectosilicates*



Compensated Continuous
Random Network
From Greaves and Ngai, 1995



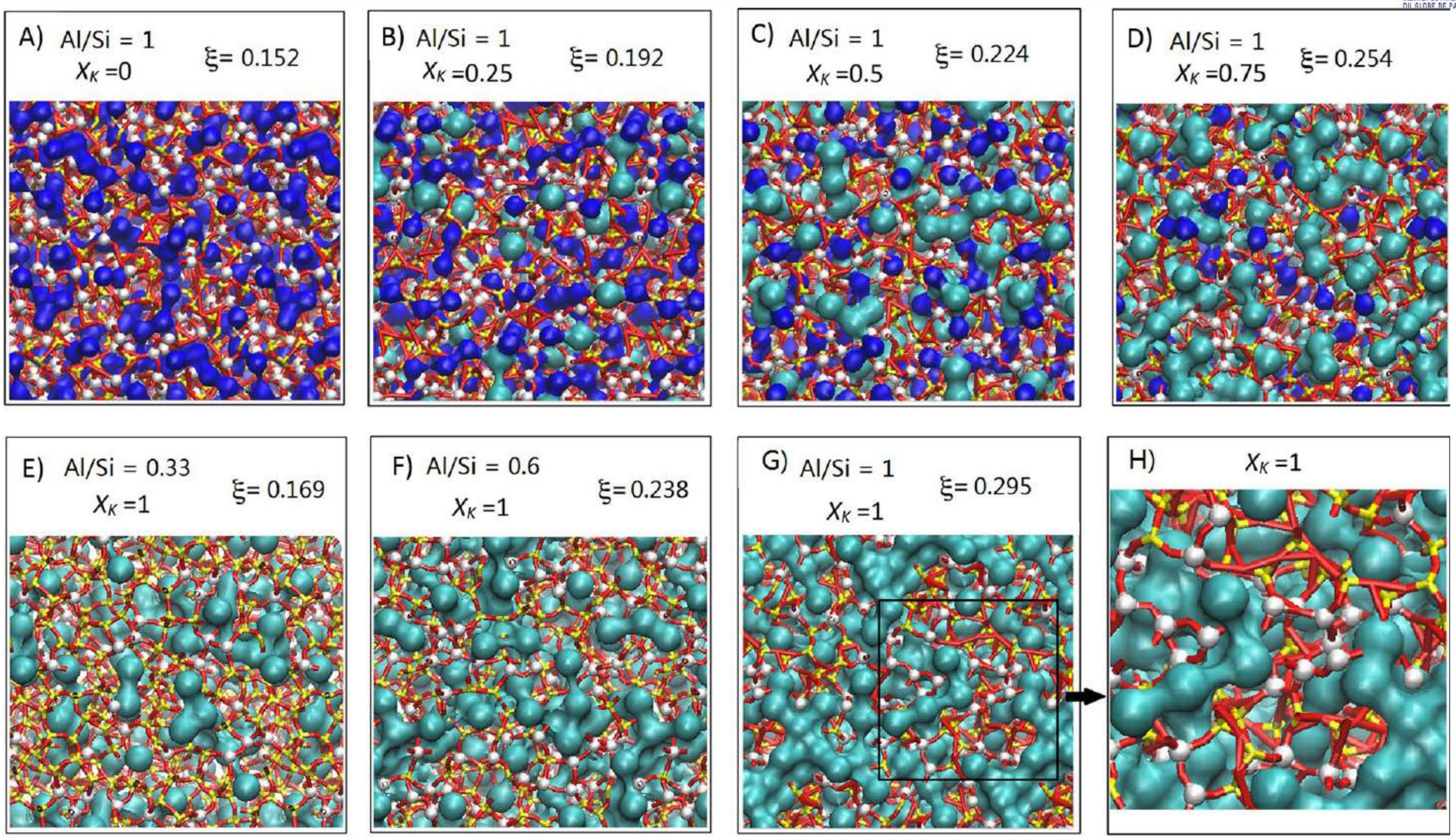
We propose a new version:
Compensated Modified
Random Network

Na and K are in different structural positions

$\Rightarrow$ Two different networks

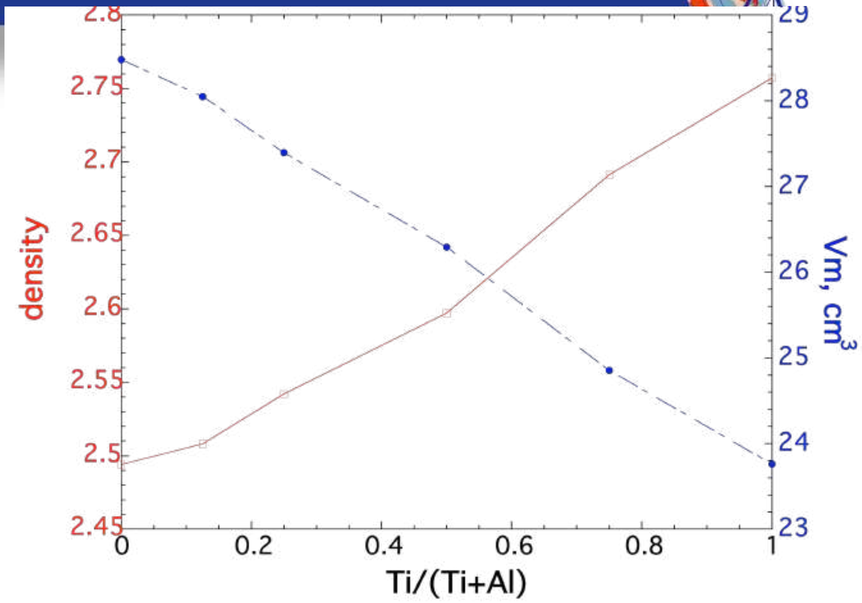
$\Rightarrow$ Non random mixing

Percolation channel !

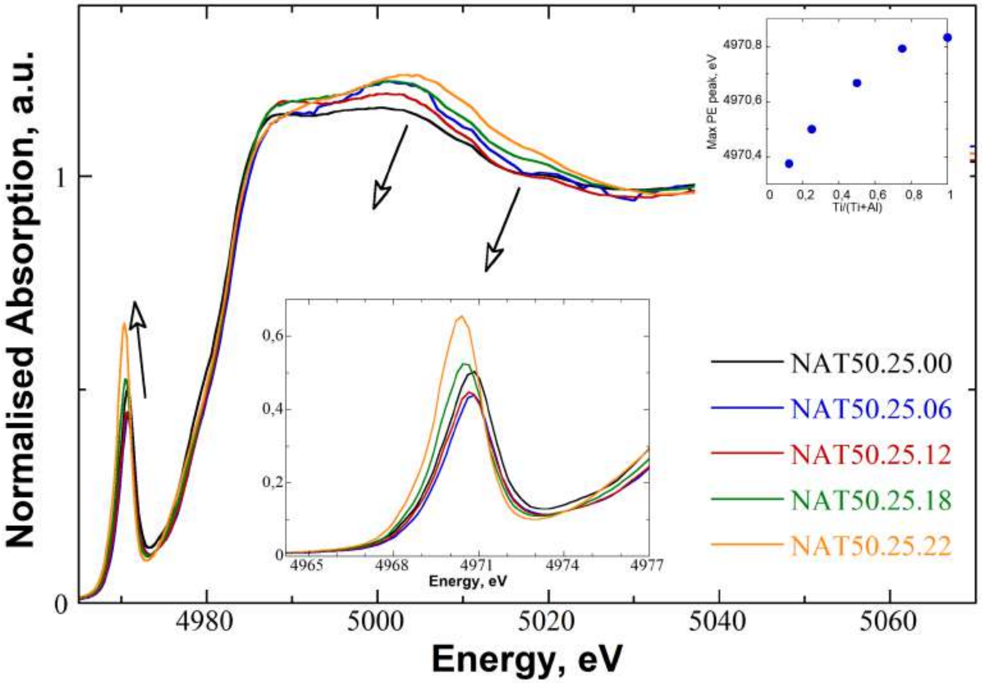


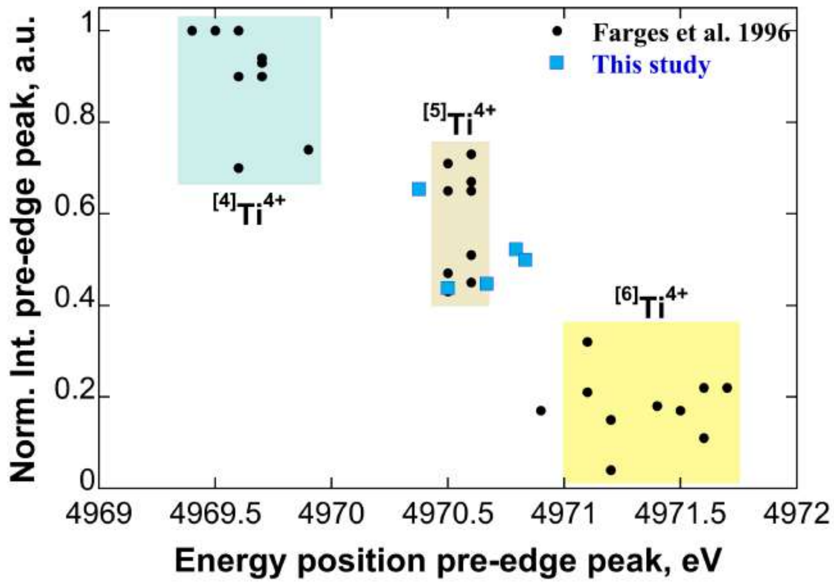
Losq, Neuville D.R., Florian P., Massiot D., Zhou Z., Chen W., Greaves N. (2017) **Percolation channels: a universal idea to describe the atomic structure of glasses and melts**. Scientific Reports, 7, Article number: 16490, doi:10.1038/s41598-017-16741-3

Composition (mol%)	SiO_2	Na_2O	Al_2O_3	TiO_2	Ti/Ti+Al
NAT 50.25.00	50	25	0	25	1
NAT 50.25.06	50	25	6,25	18,75	0,75
NAT 50.25.12	50	25	12,5	12,5	0,5
NAT 50.25.18	50	25	18,75	6,25	0,25
NAT 50.25.22	50	25	21,88	3,12	0,125
NAT 50.25.25	50	25	25	0	0



Ti replace Al in $NaAlSiO_4$

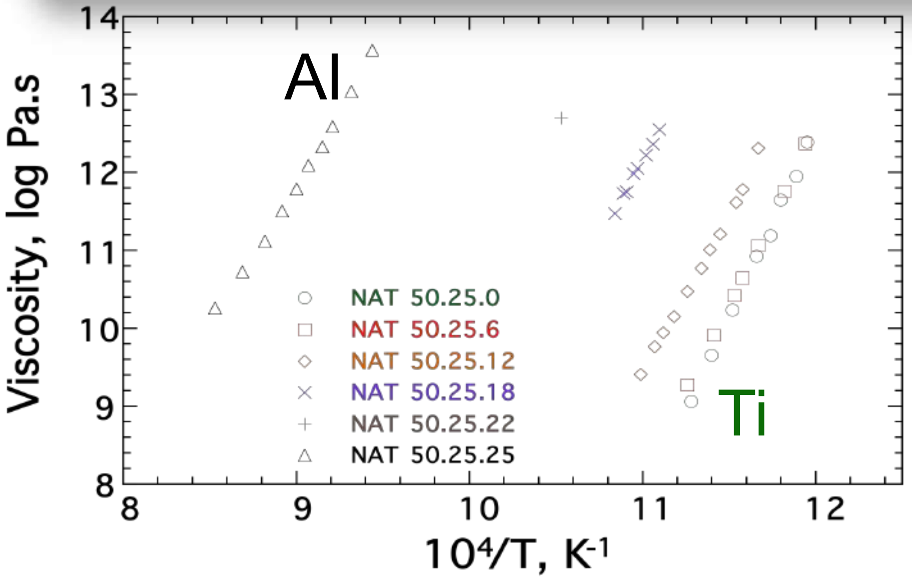


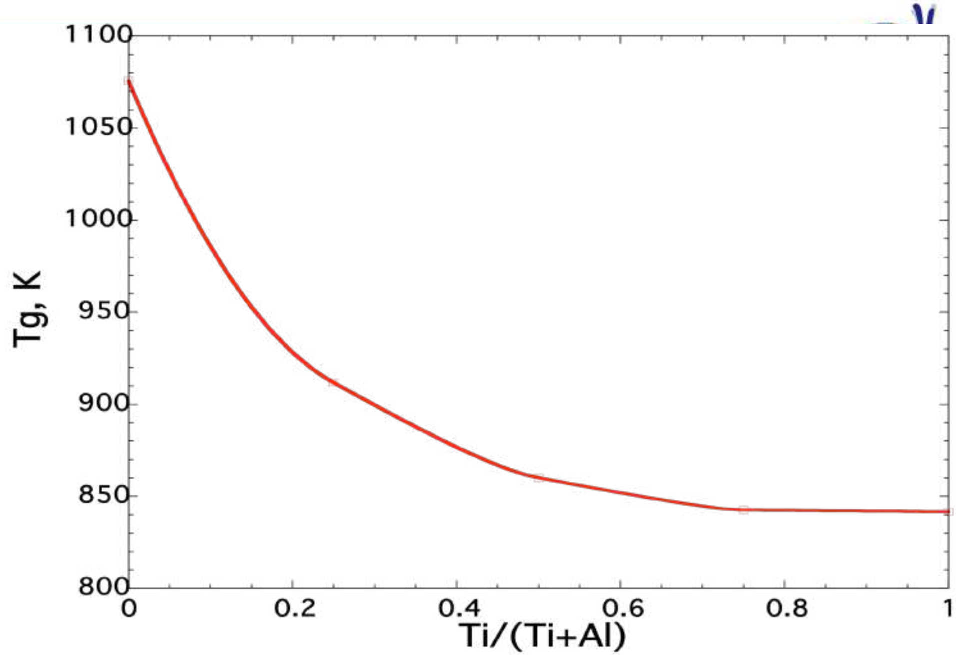


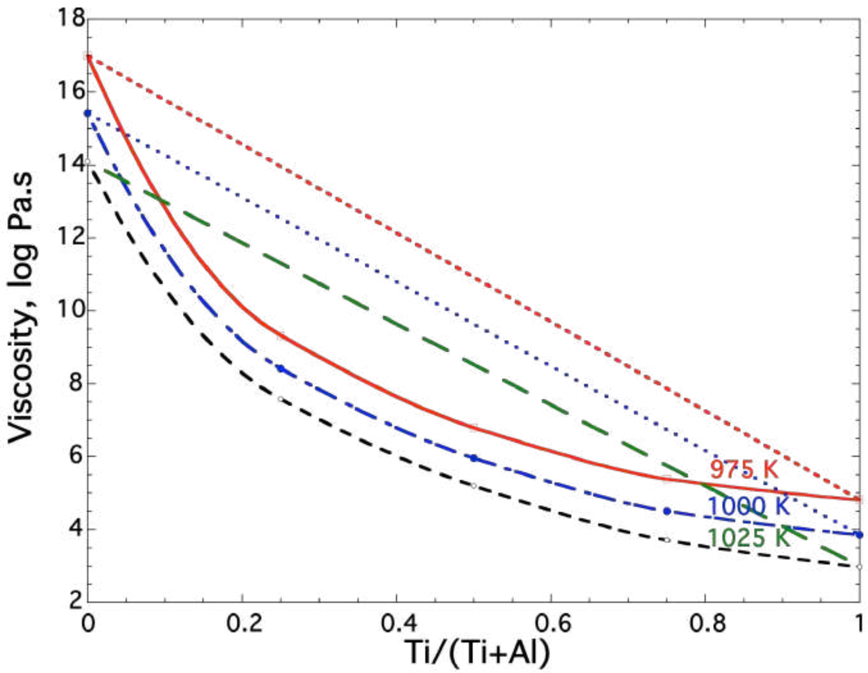
Ti^{4+} in 5-fold coordination

Robine, Cicconi, Neuville, in prep

replacement of Al by Ti







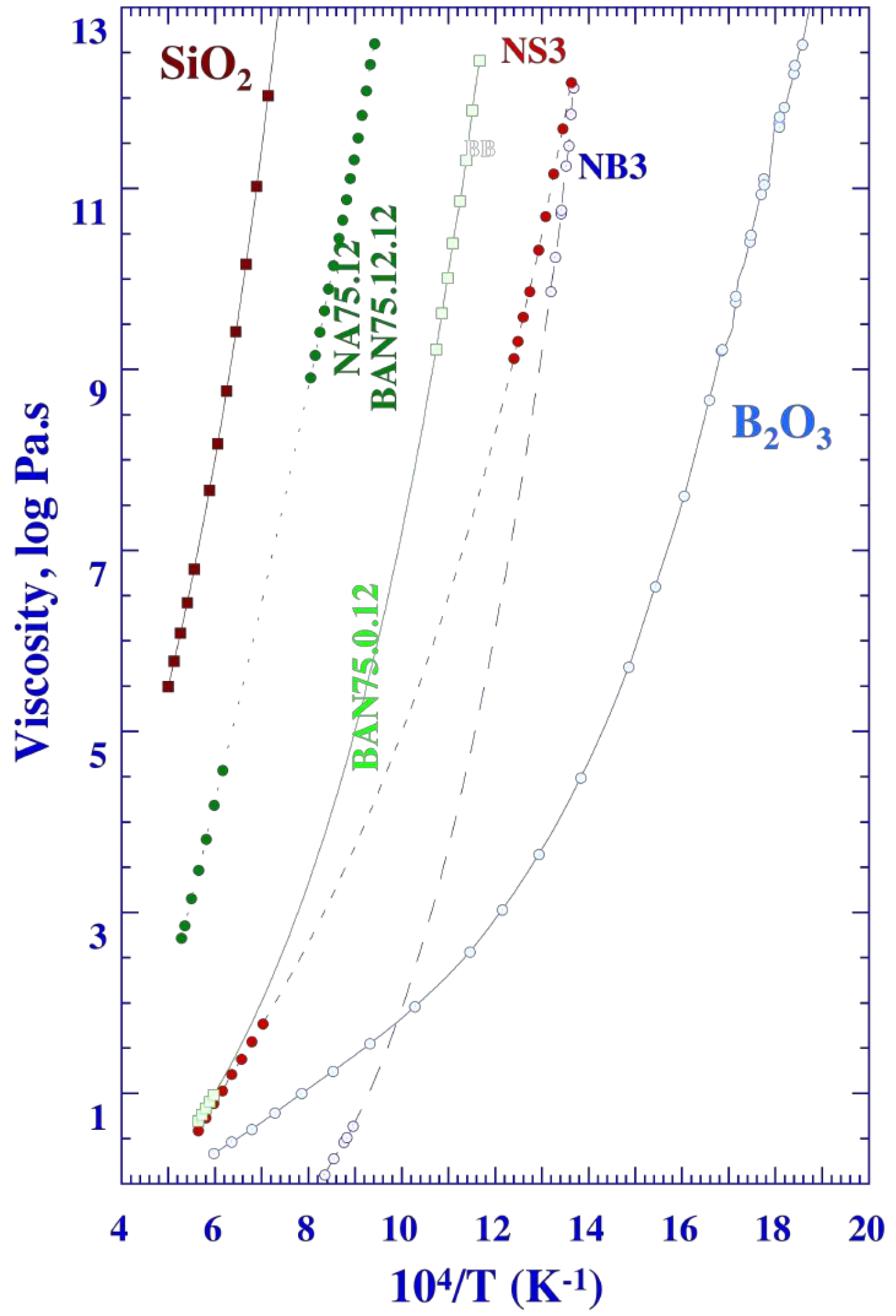
Viscosity as a function of Ti/(Ti+Al) shows a non linear variation at all temperatures => possible ideal mixing?

Robine, Cicconi, Neuville, in prep

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

- BO4 tetrahedra => network former with M^+

- AlO_4 tetrahedra => network former with M^+



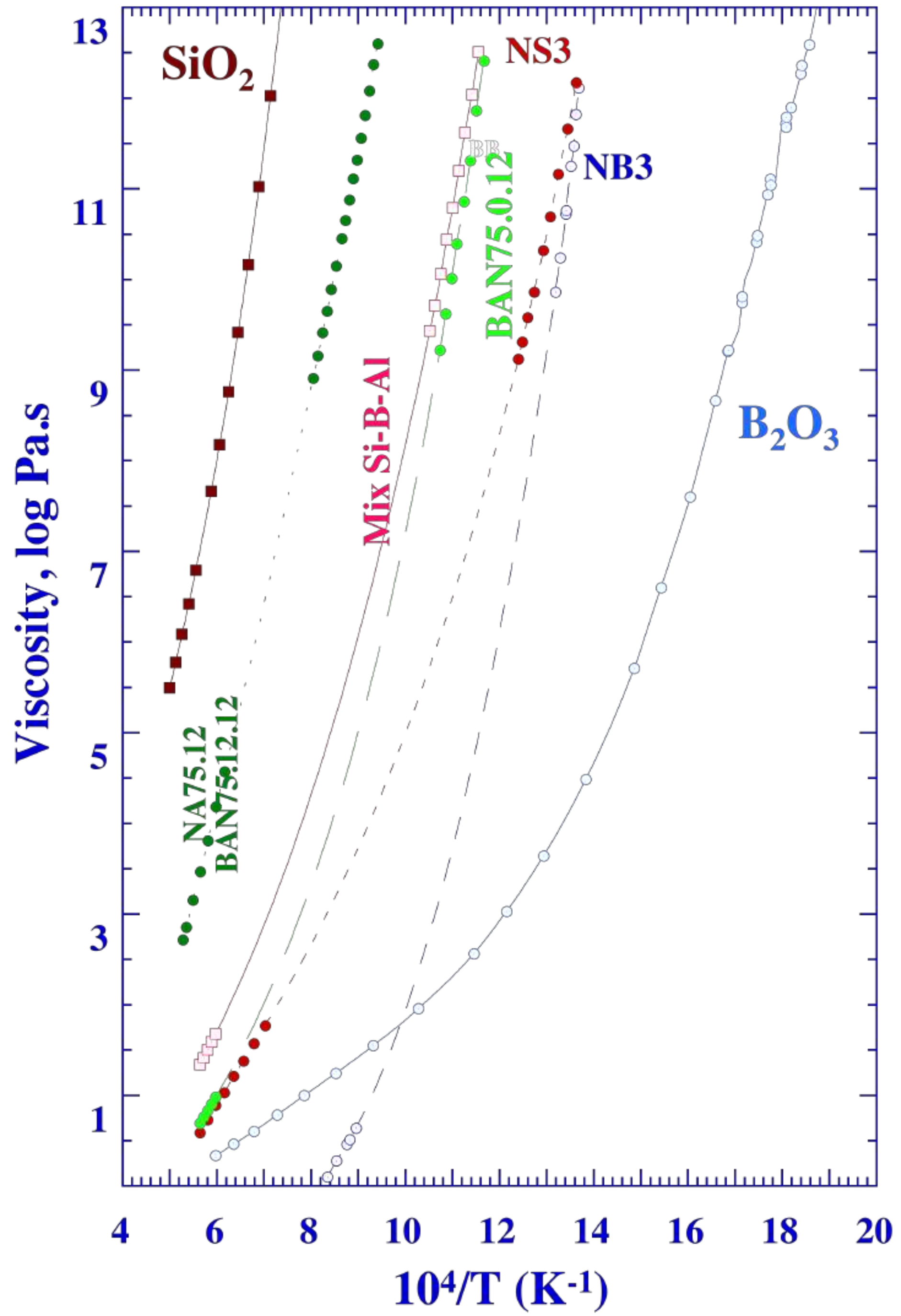
- SiO_4 tetrahedra => strong network former
- BO3 triangle => soft network former

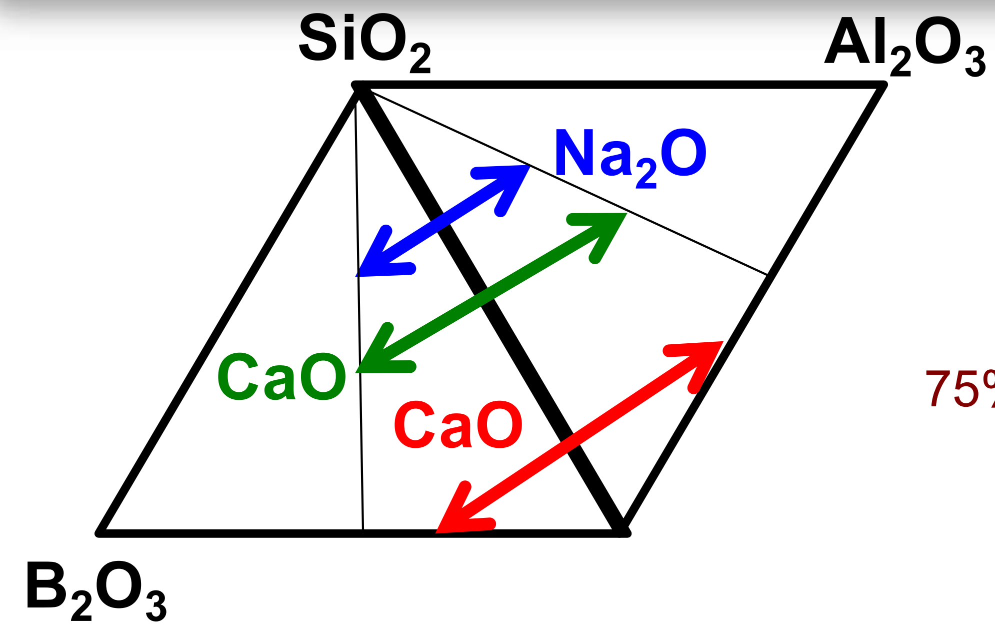
- BO4 tetrahedra => network former with M^+

- AlO_4 tetrahedra => network former with M^+

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

=> and only one M^+



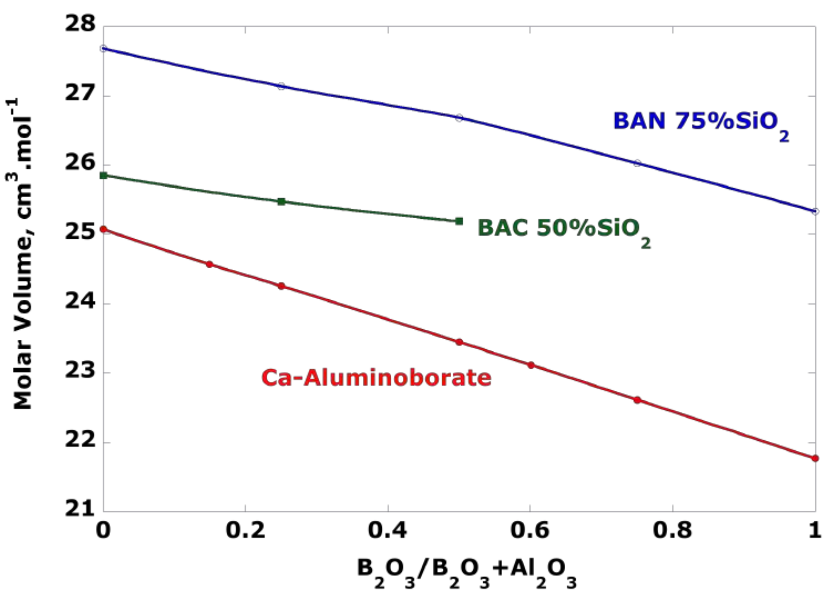


BAN75-X-12 compositions

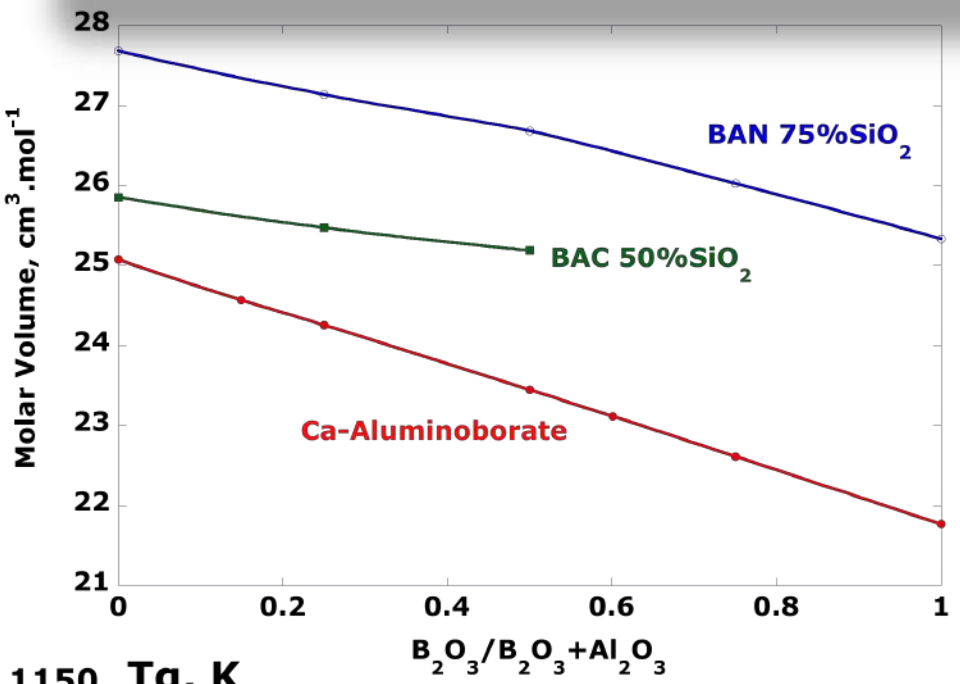
75%SiO_2-(12.5-X)Al_2O_3-XB_2O_3-12.5%Na_2O

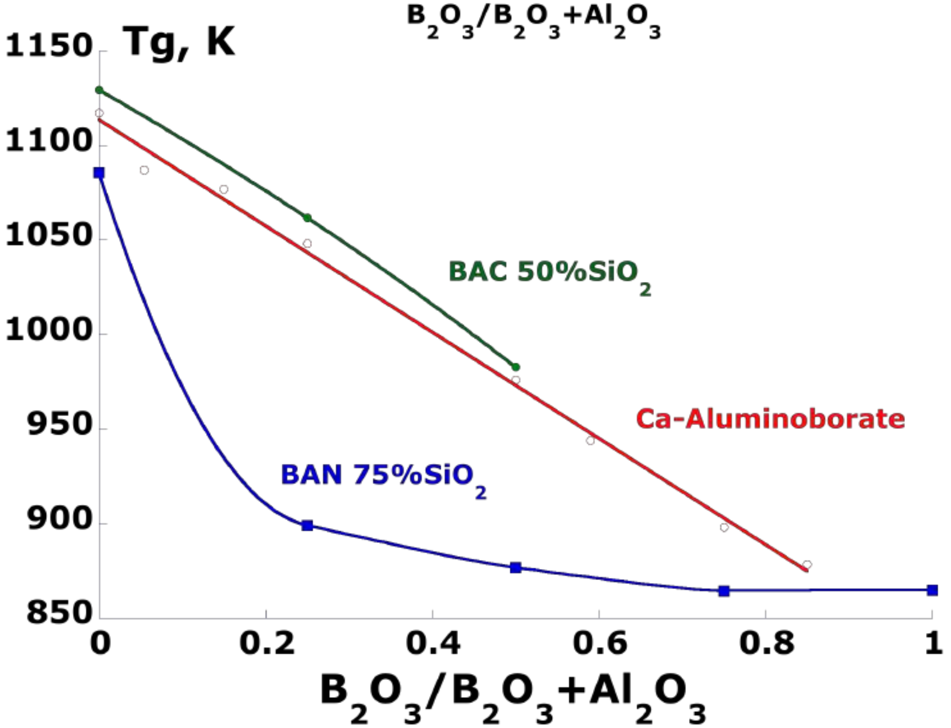
Incolored and clear glasses

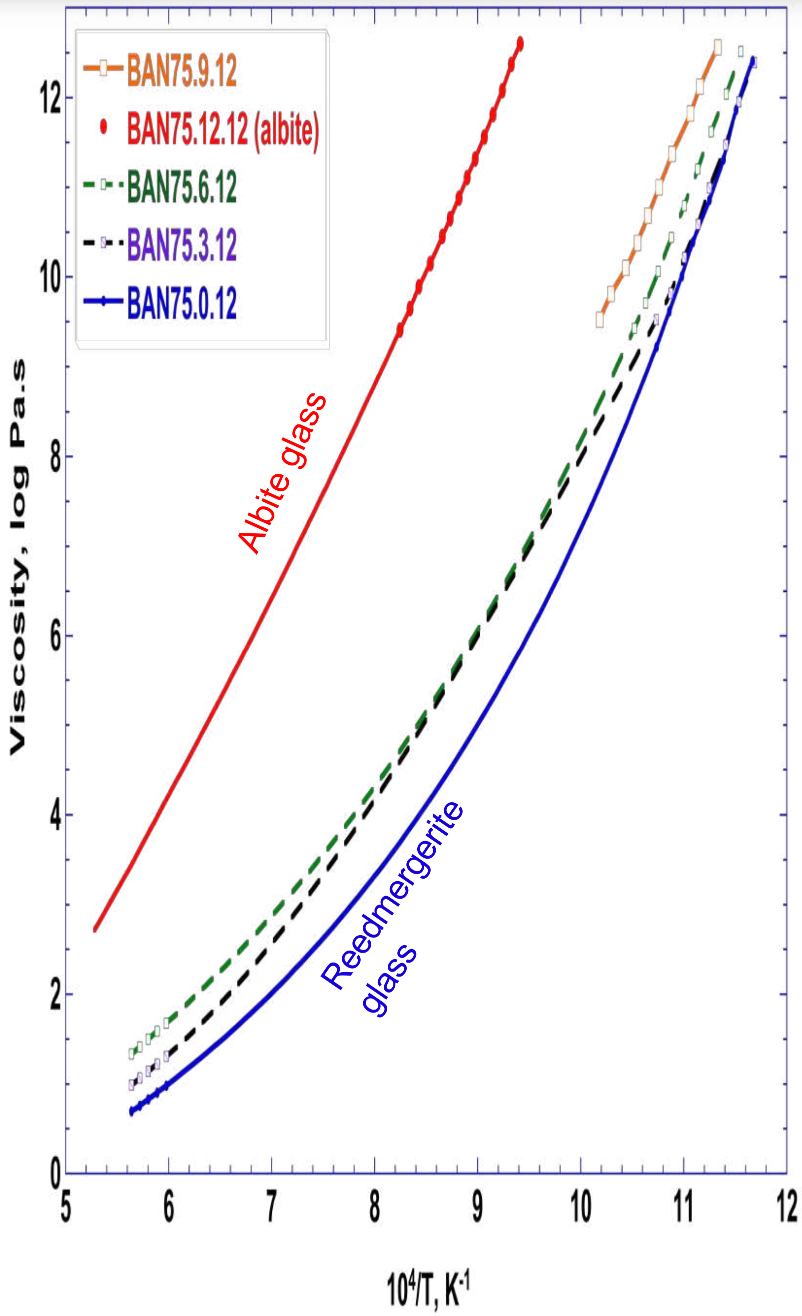
	SiO2	Al2O3	B2O3	Na20	
BAN75.12.12	75	12,5	0	12,5	Albite
BAN75.10.12	75	10,5	2	12,5	
BAN75.9.12	75	9,38	3,12	12,5	
BAN75.6.12	75	6,25	6,25	12,5	
BAN75.3.12	75	3,13	9,37	12,5	
BAN75.0.12	75	0	12,5	12,5	Reedmergnerit e



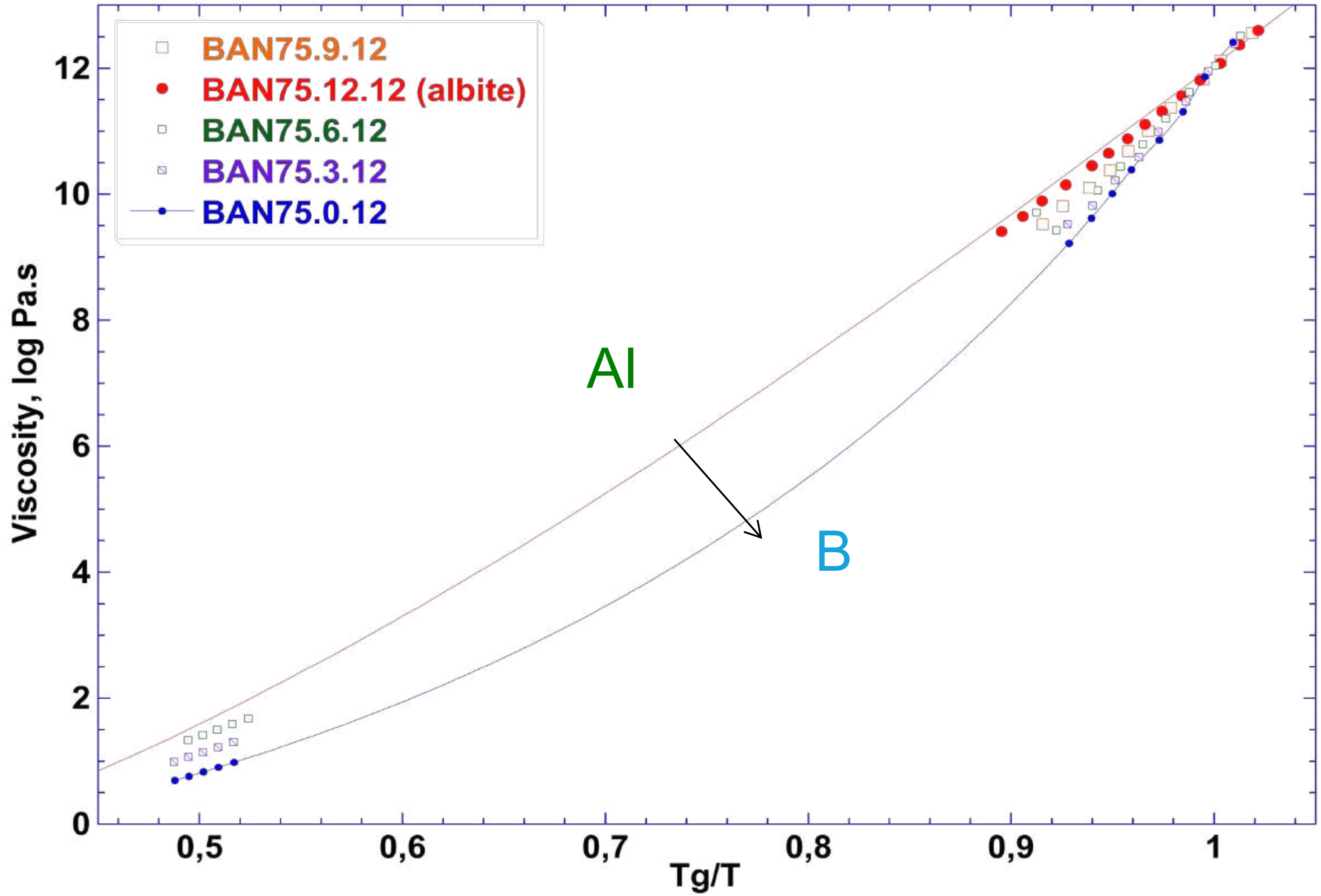
Borosilicate compositions *Vm, Viscosity, Tg*





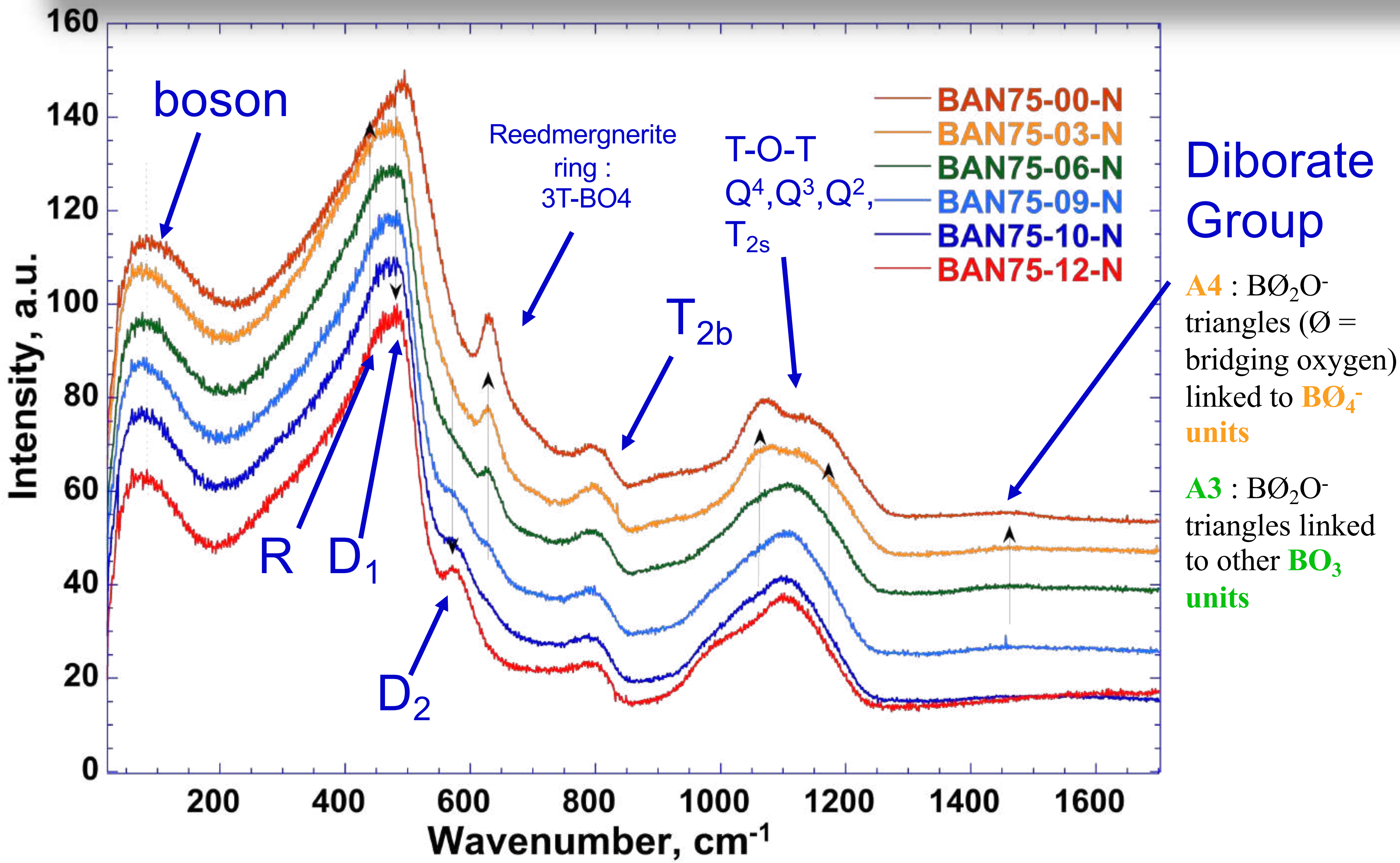


Borosilicate compositions



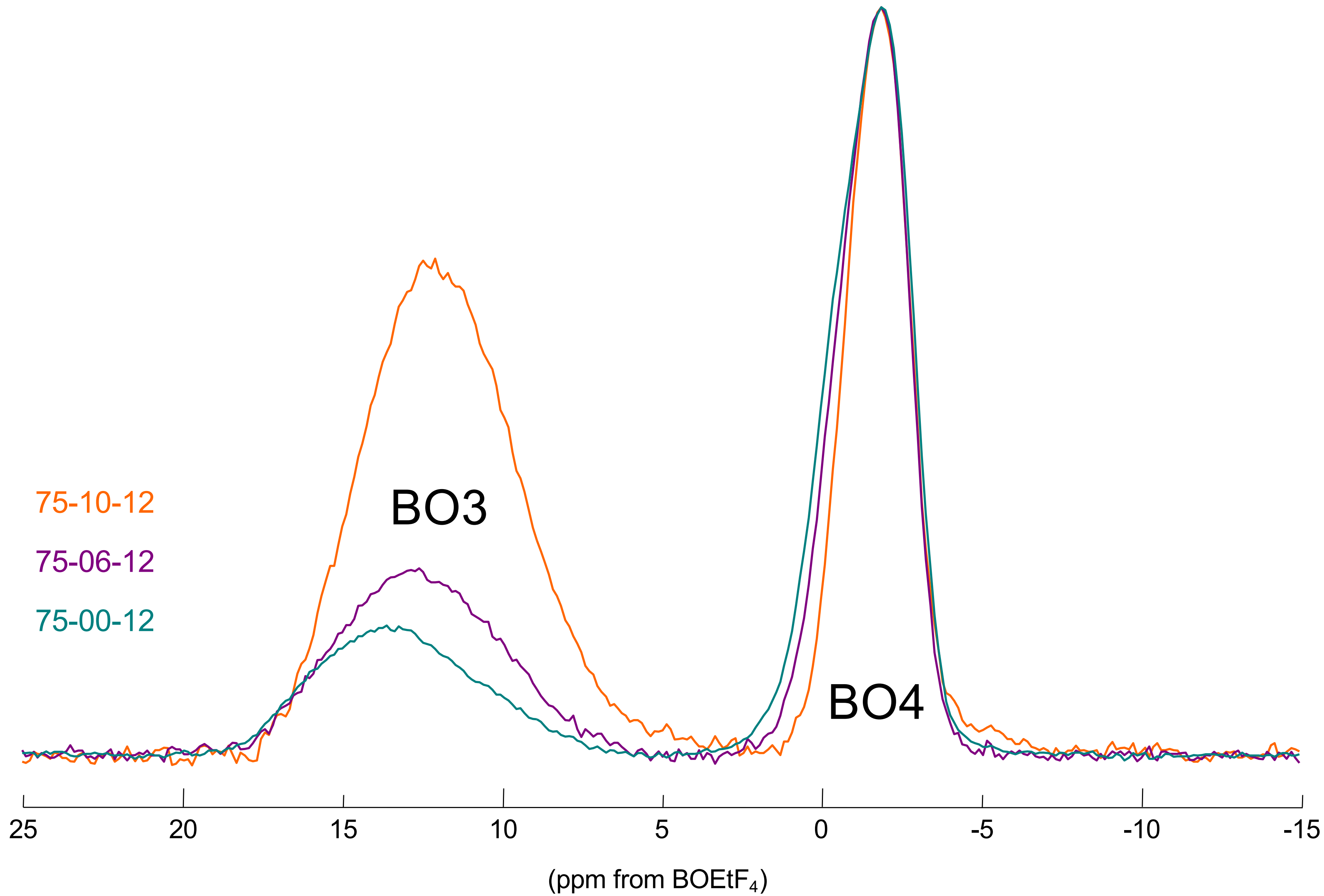
Very strong decrease of Vm, viscosity, Tg and fragility increases with Al/B substitution and using link between viscosity and configurational entropy :

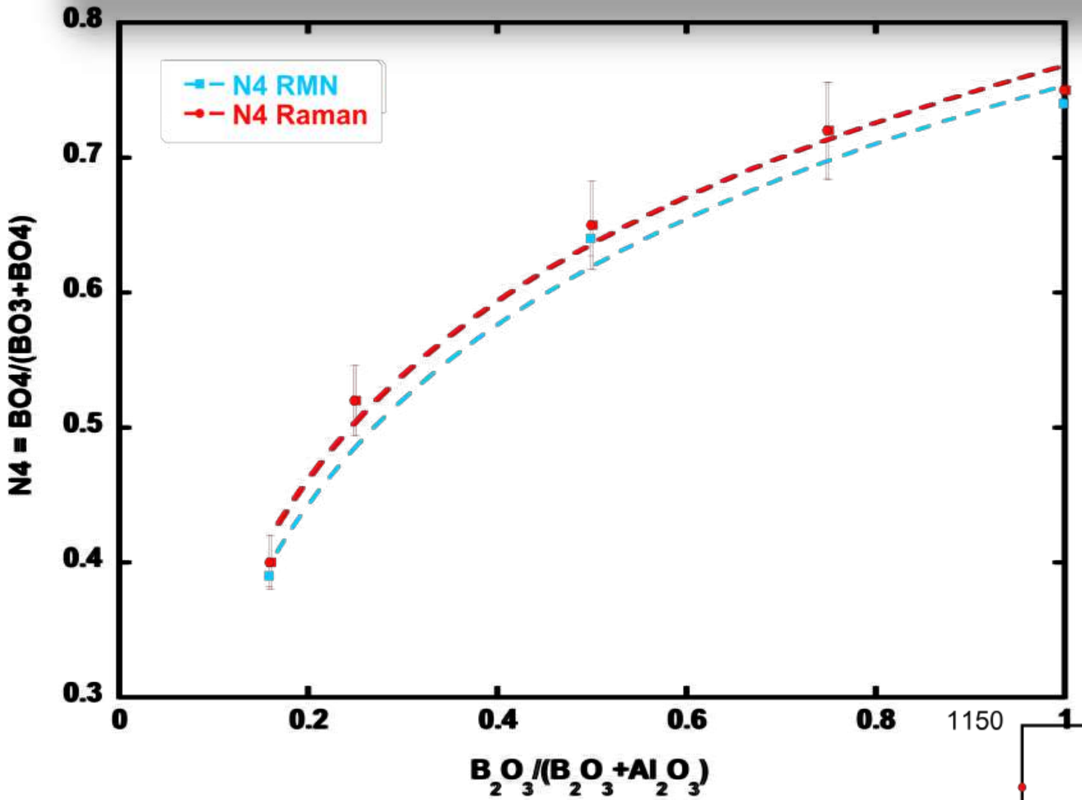
Log η= Ae + BeT/S^{conf}(T), we can calculte S^{conf} which goes from 8J/mol.K for up to 14.5J/mol.K with Al/B substitution



- 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

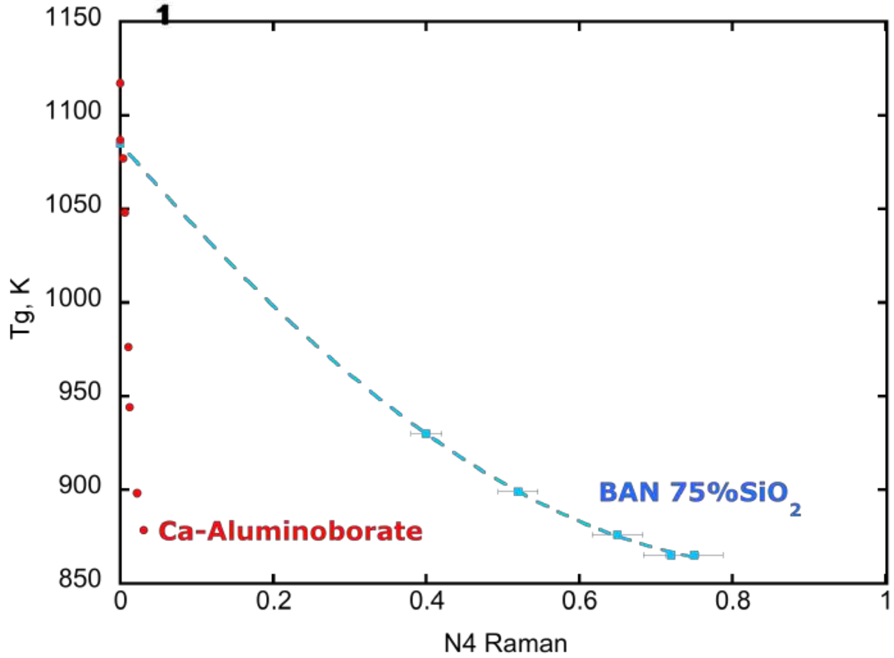




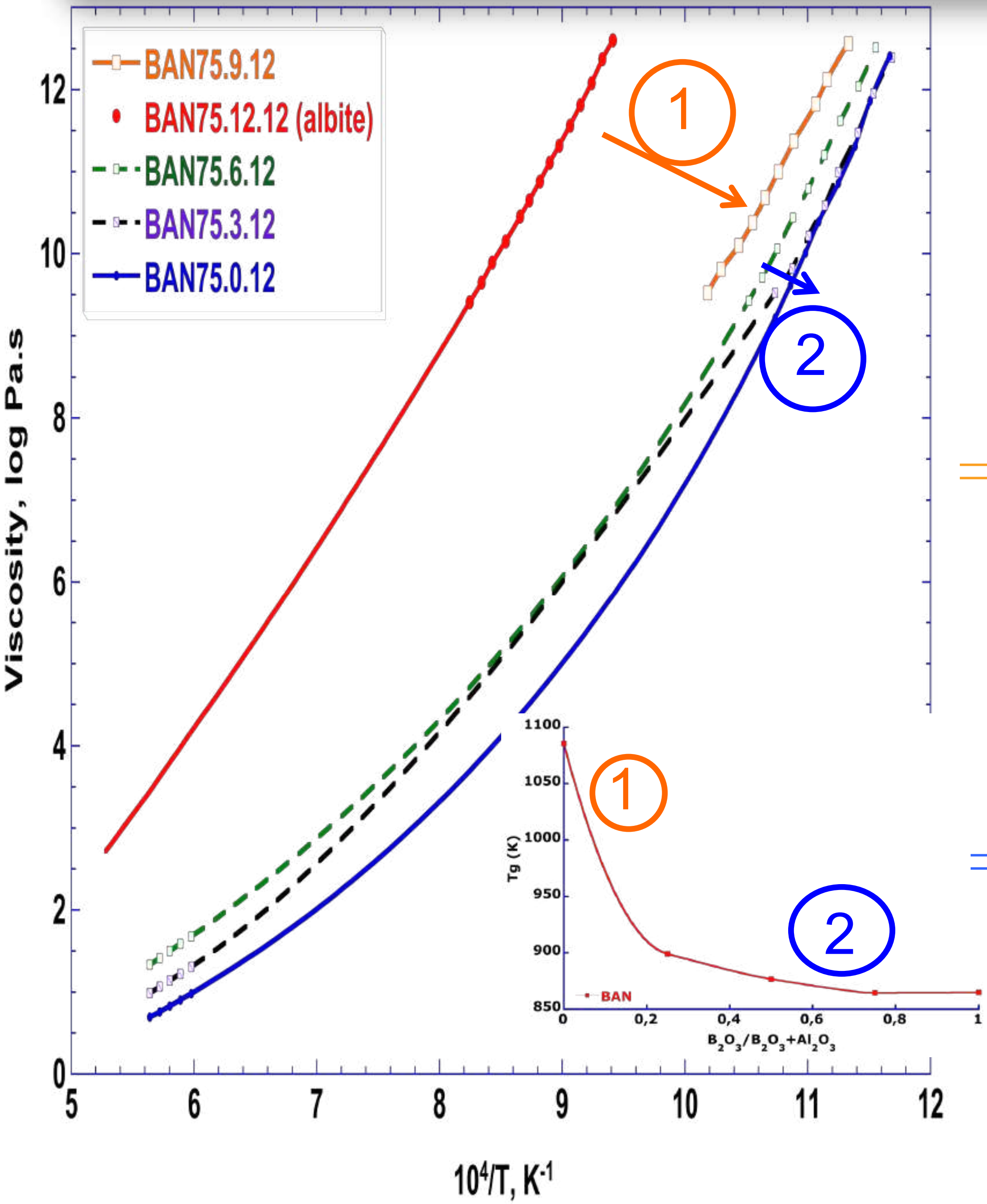
N4= BO4/(BO4+BO3)

Similar evolution than
Geisinger et al., GCA 1988

Huge decrease of Tg with BO3



Assumption for Al/B substitution mechanism ?



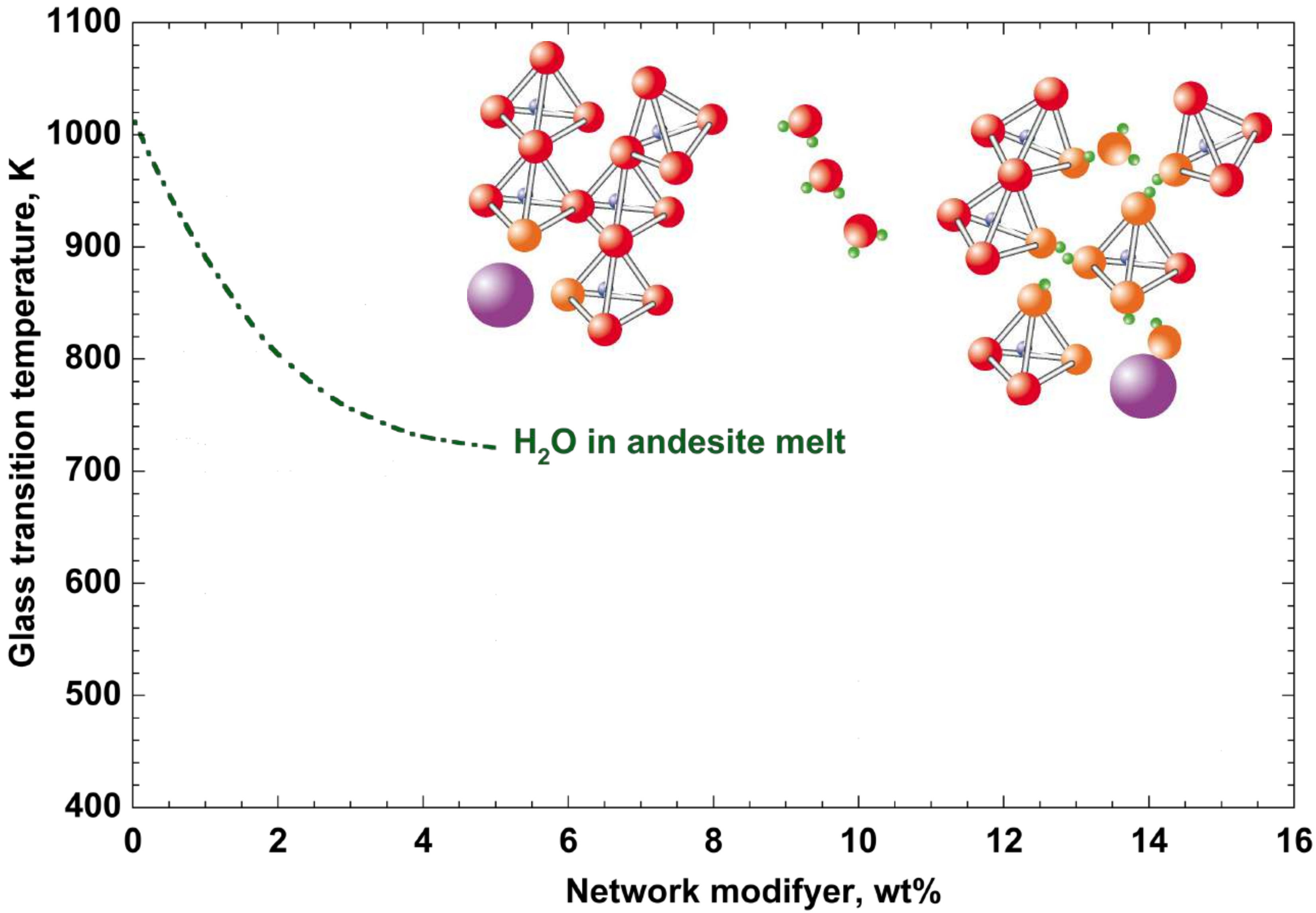
But with Al/B substitution BO3 decreases and 2BO4 are present

⇒ BO3 decrease with B_2O_3 increases

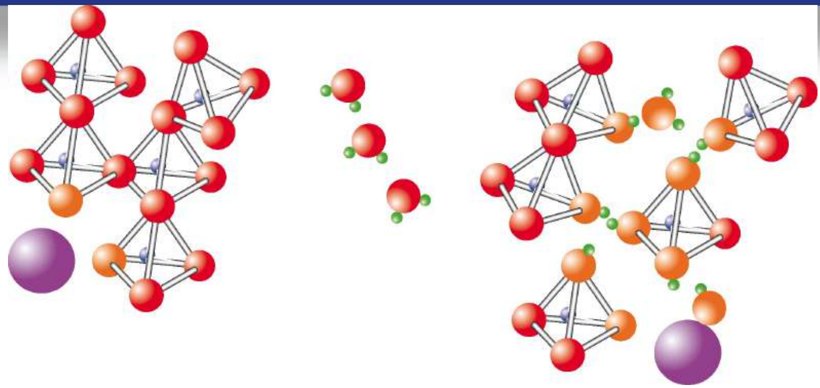
⇒ 1) by substitution Al by B => B is essentially in BO3 because Al used Na as a charge compensator and BO3 decreases a lot the viscosity

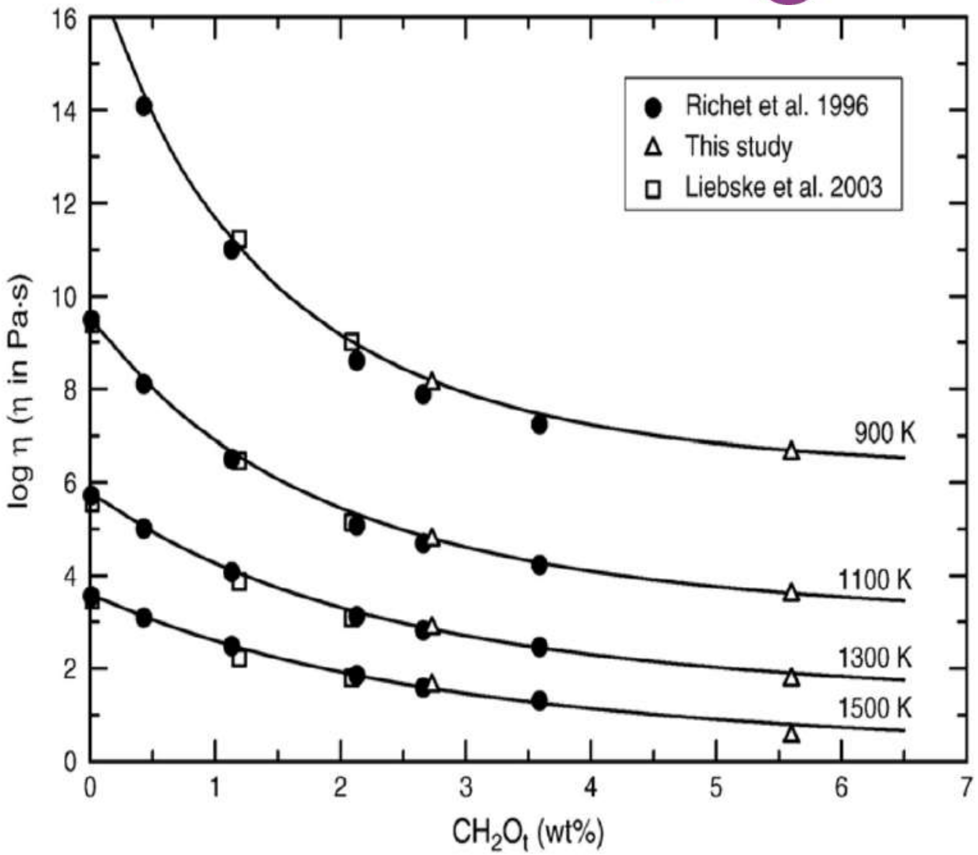
⇒ 2) With increasing B content => BO4 increases and used Na as a charge compensator => viscosity decreases slowly

Tg measured by DSC with heating rate 10K/min
or Tg taken for log η =12 Pa.s

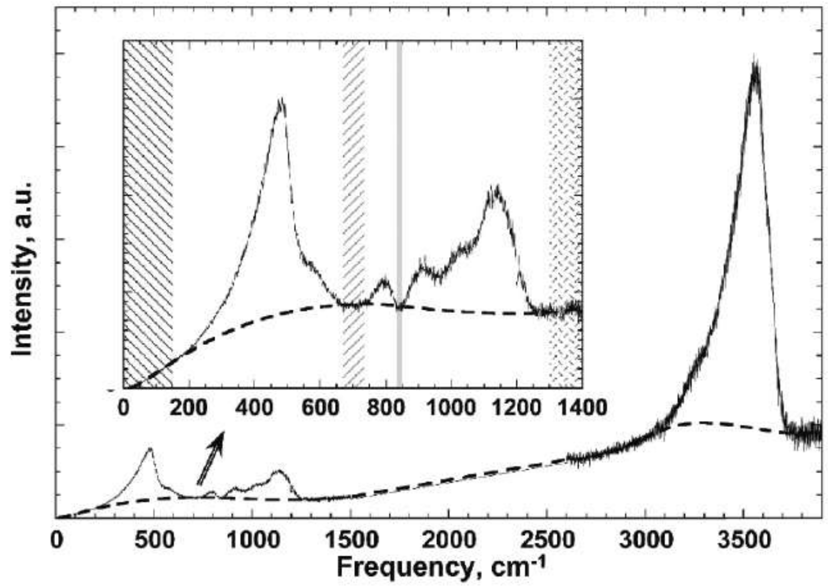


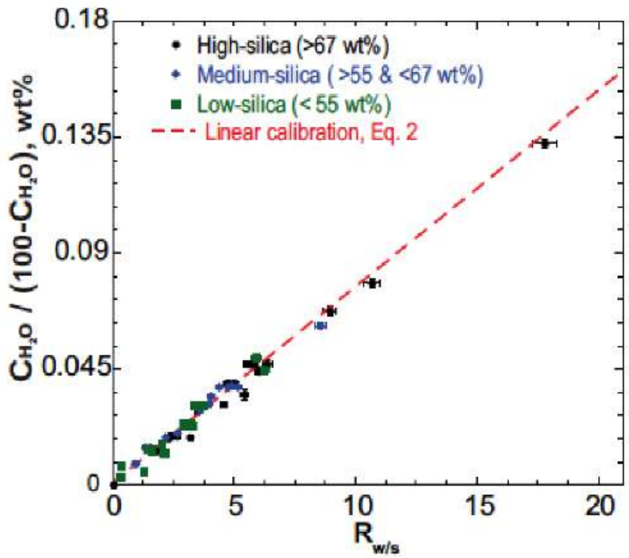
Effect of H_2O on properties





Vetere F., Behrens H., Holtz F., Neuville D.R. (2006) Viscosity of andesitic melts – new experimental data and a revised calculation model. Chem. Geol., 228, 233-245.





Neuville D.R., Cicconi M.R., Blanc W., Lancry M. (2021) Application of Raman spectroscopy on glass and glass fiber. Fiberglass Science and Technology edt H. Li, Springer ISBN 978-3-030-71199-2.

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, : mix… ?

Al^{IV} => network former

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

Al^{VI}=> generaly network modifier…

Li_2O, Na_2O, K_2O, MgO, CaO, SrO, BaO, ZnO, FeO

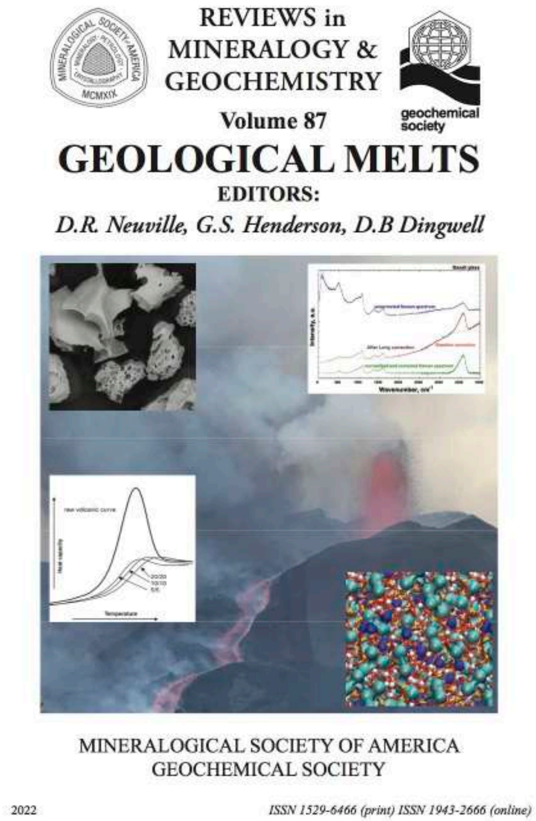
=>network modifier or charge compensator with T

The configurational properties of melts and glasses provide fundamental information needed to characterize magmatic and industrial processes.

The configurational entropy gives a strong idea about glass structure.

It is possible to link the "macroscopic" configurational entropy with the structure of melts determine by NMR or Raman spectroscopy.

- *Ca/Mg can be mixed randomly in silicate glasses and melts*
- *Na^+/Ca^{2+} and Na^+/Sr^{2+} or Na^+/M^{2+} are not mixed randomly in silicate and aluminosilicate glasses and melts.*
- *Na/K are non randomly mixed aluminosilicate glasses and melts.*
- *Si/Al are mixed randomly in tectosilicate glasses and melts.*
- ***$^{[5]}$Al is probably a good network former or reticulator***



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