TC03 of ICG
School Thermodynamic of Glass

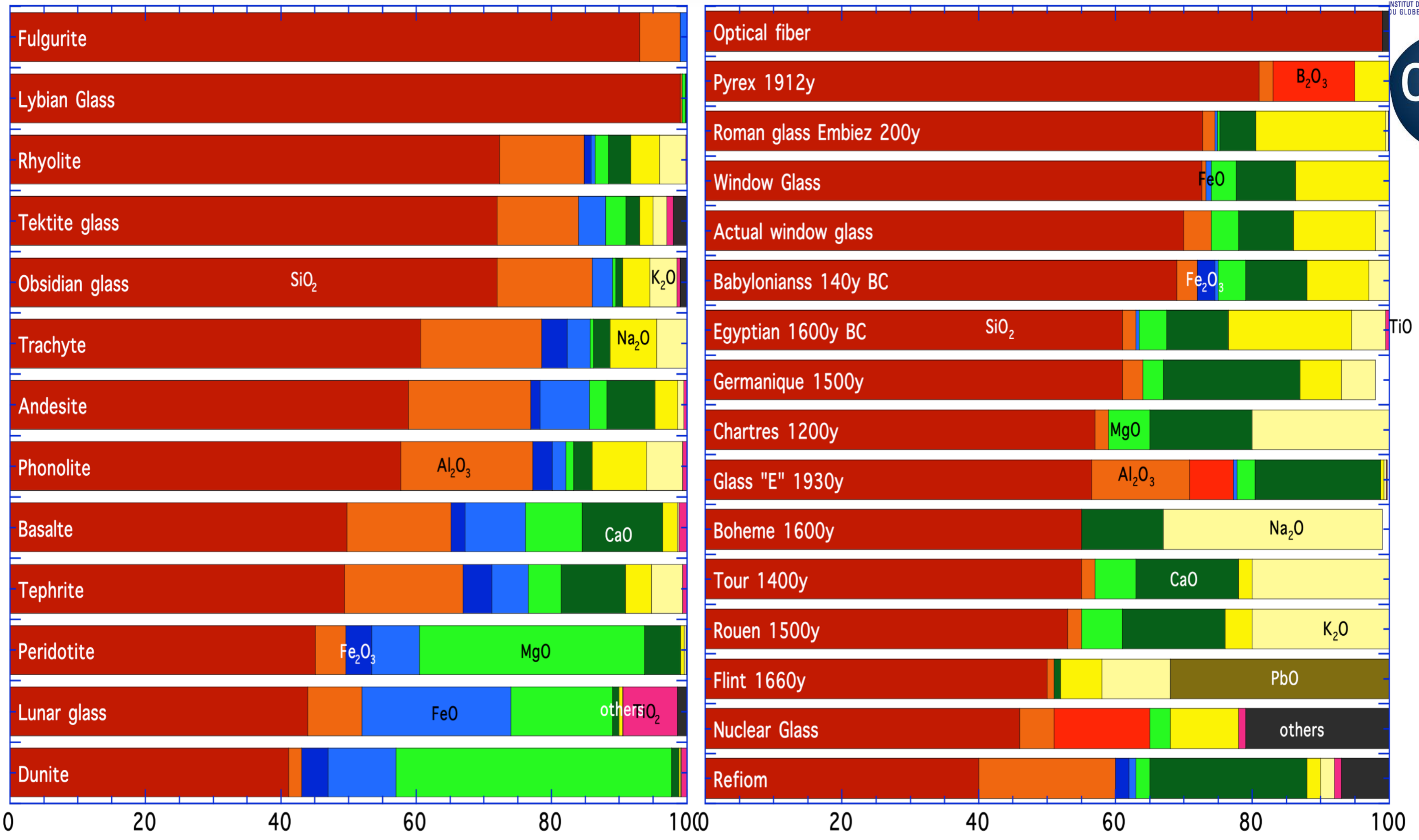
Entropy, viscosity and structure of glasses and melts

Daniel R. Neuville

Géomatériaux,
CNRS-Institut de physique du globe de Paris,
Université de Paris,
1 rue Jussieu, F-75238 Paris cedex 05, France

Huge similarities between natural glasses and human glasses….

Geomaterial



Phase equilibria between melts and crystal

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

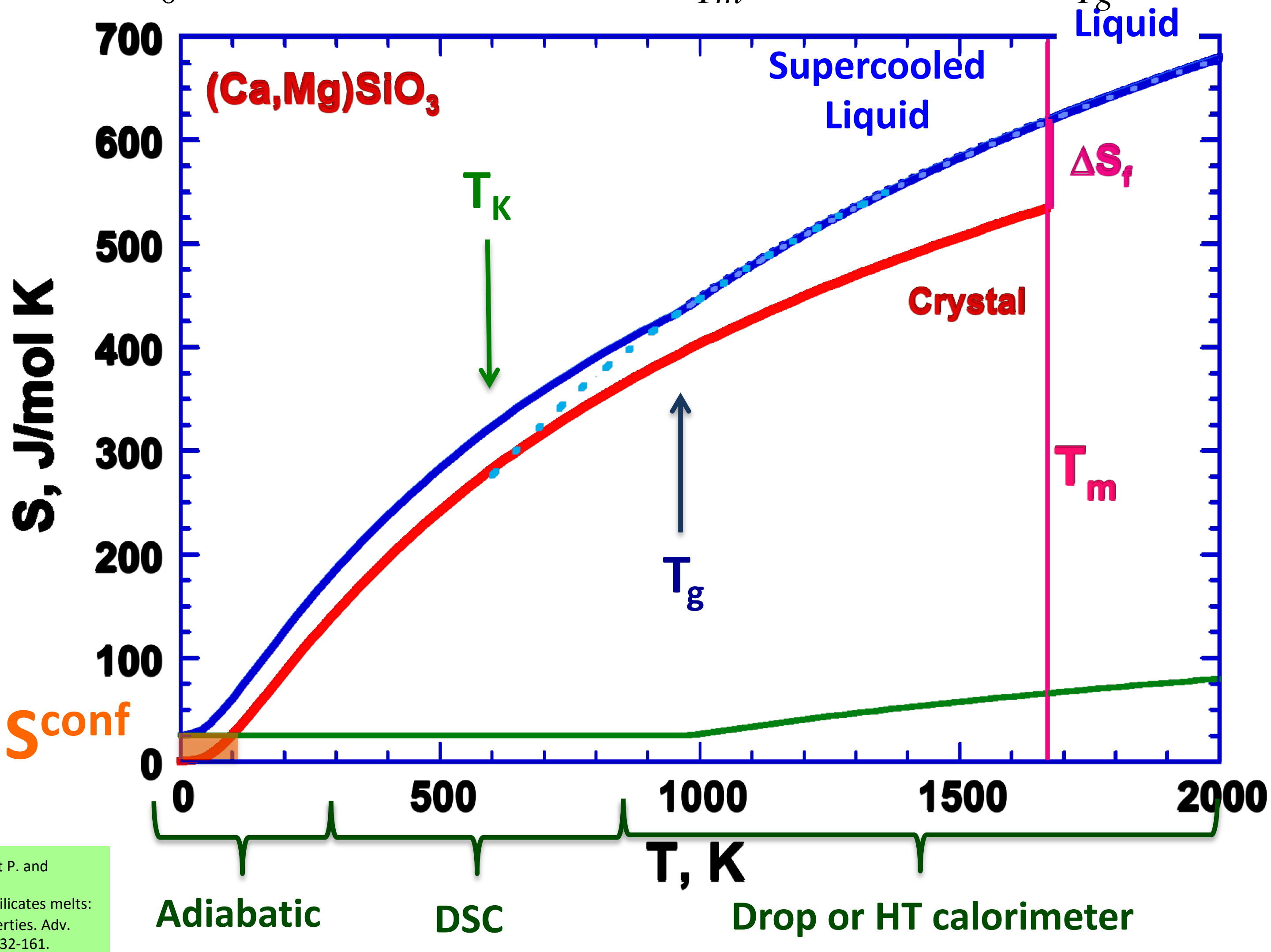
$$S^{conf}_{melts} => \Delta S_{mix} => \Delta S_{mi}$$

Diopside

$CaMgSi_2O_6$

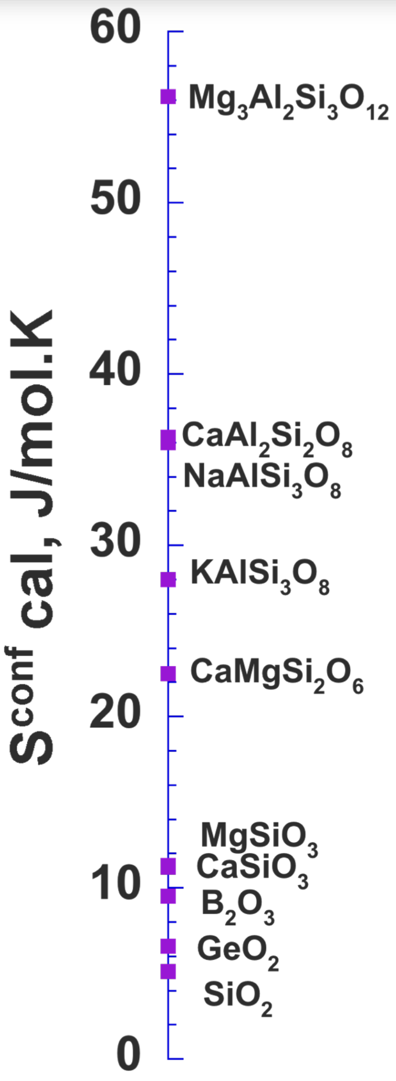
Thermodynamic cycle

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



Modifyed from Richet P. and Neuville D.R. (1992) Thermodynamics of silicates melts: Configurational properties. Adv. Phys. Geochim., 10, 132-161.

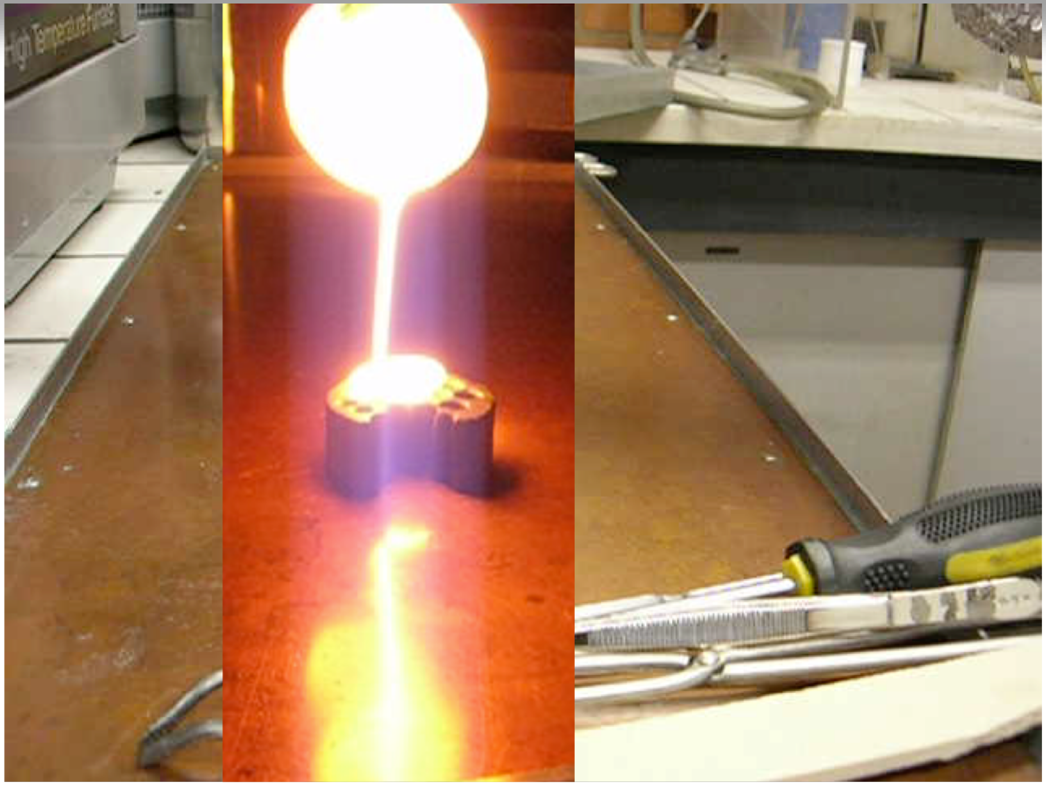
Configurational entropy



Diopside - $CaMgSi_2O_6$

Geomaterial

Crystal



Glass

Geomaterial


NEWEST MIRACLE IN GLASS ANNOUNCED BY CORNING GLASS WORKS—

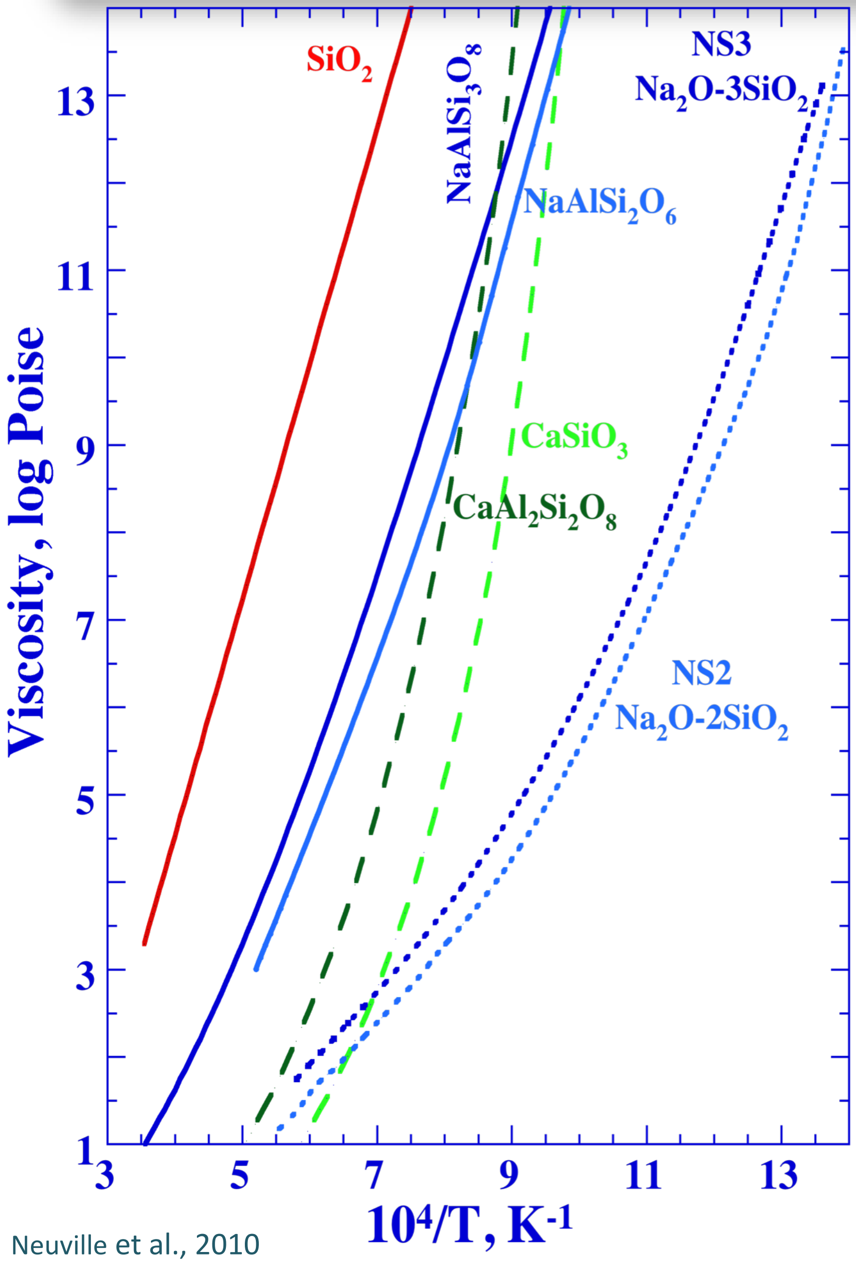
Now Cook in Glass on open-*Flame!*

Only "Pyrex" Top-of-Stove Ware brings you all these advantages!

Extra Heat-Resistant "Pyrex" Top-of-Stove Ware Now Ready...

NEW PYREX TOP-OF-STOVE WARE

Where is the crystal?



Neuville et al., 2010

Arrhenius :

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

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

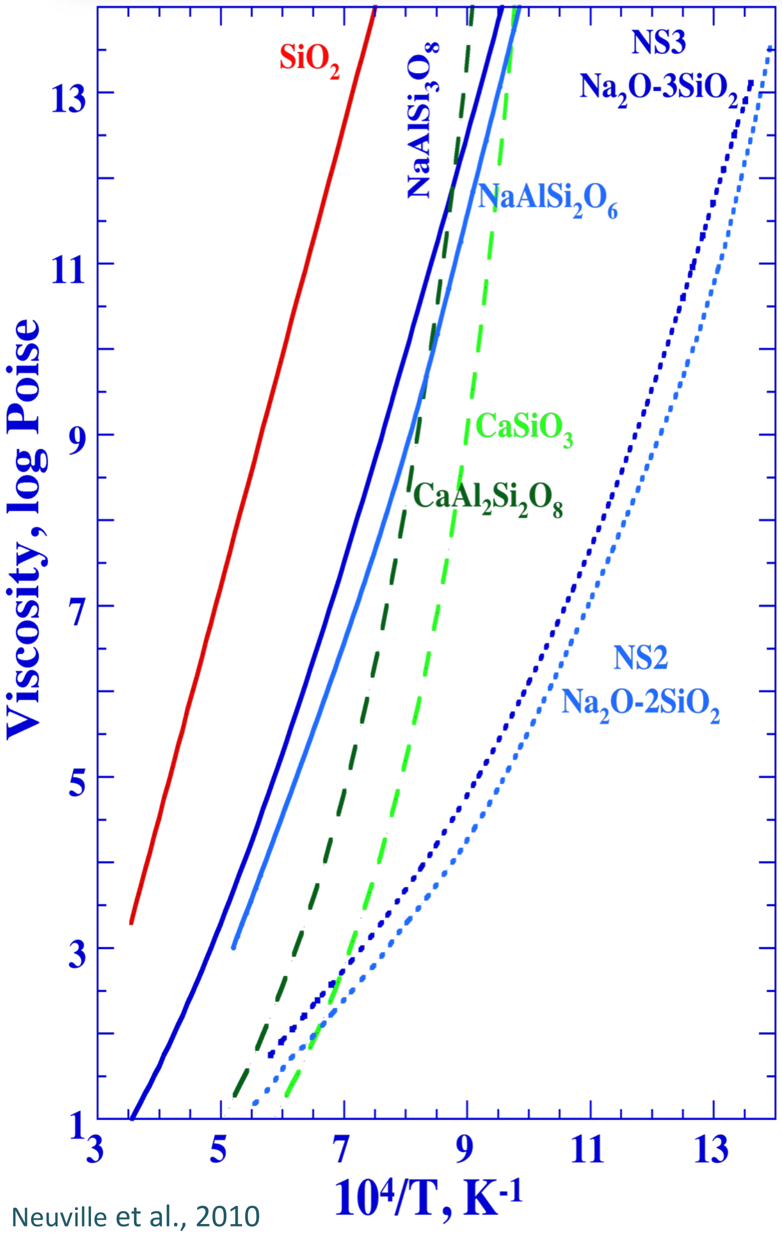
Yes but only for SiO_2, GeO_2, $NaAlSiO_8$, $KAlSiO_8$ because activation energy change from 2000kJ/mol at 1000K up down 300kJ/mol at 1800K for NS3.

Need TVF equation

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

But, just a fit …..

Viscosity equation ?



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,**

Wong and Angell 1976,

Scherer, 1984, Richet, 1984, …

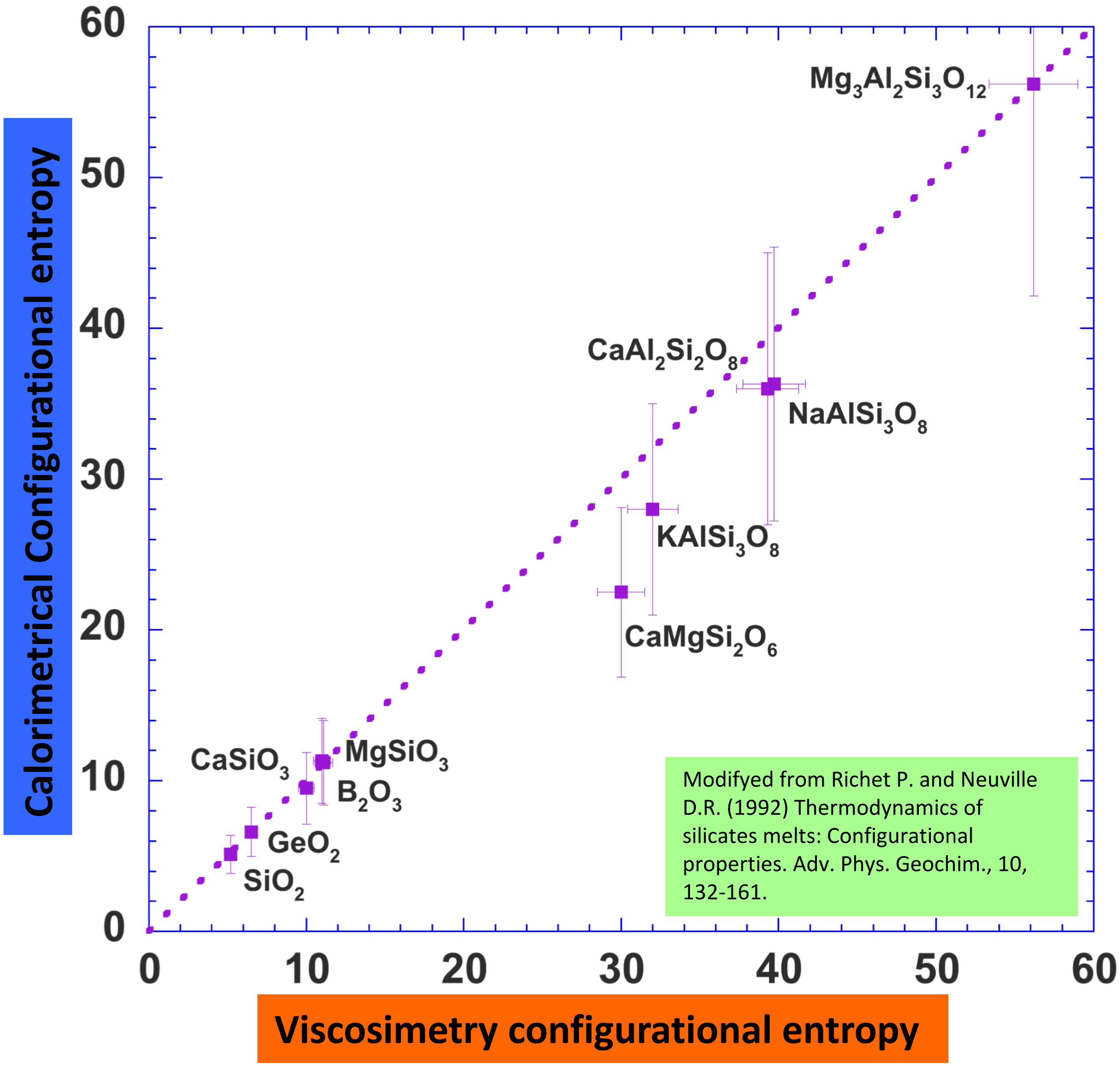
Neuville and Richet, 1991….

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

$$Cp^{conf}(T) = Cpg(Tg) – Cpl(T)$$

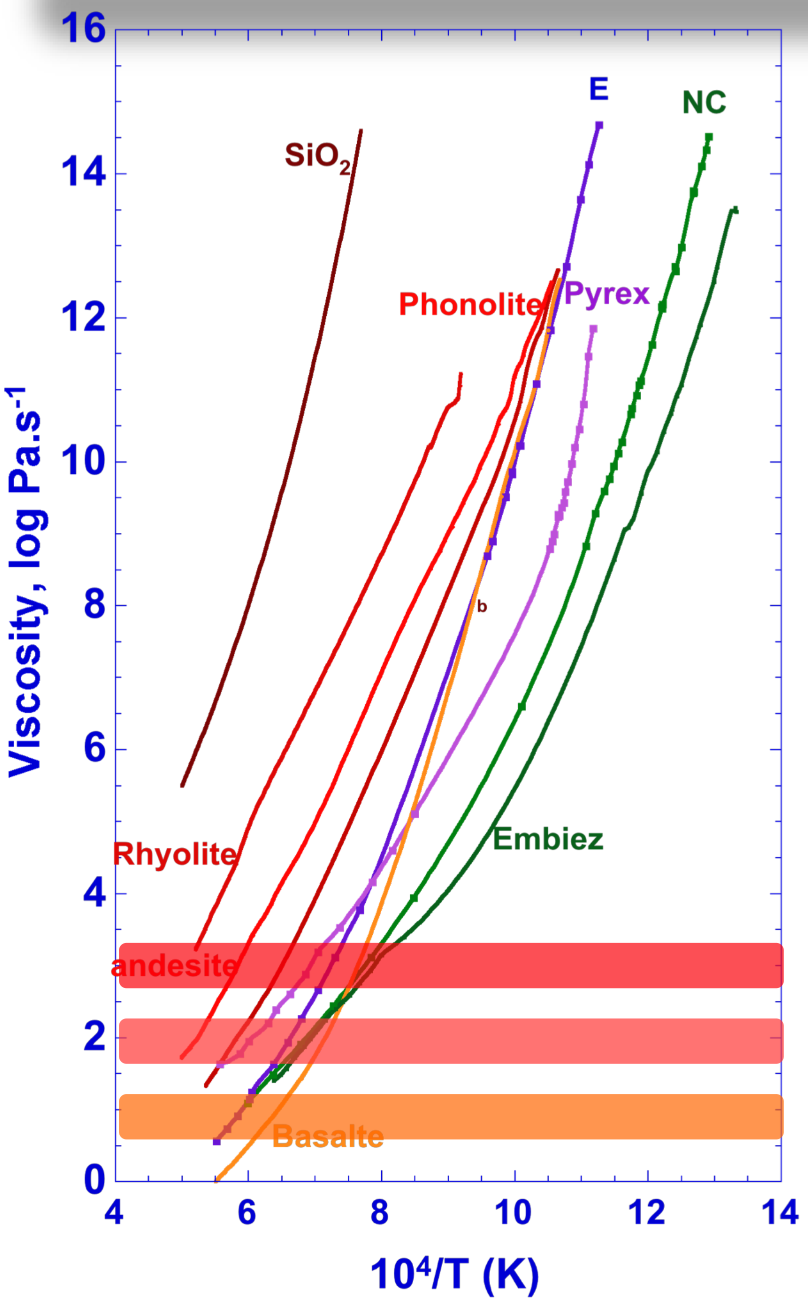
Calorimetry measurements
=> Easy

Configurational entropy



Modifyed from Richet P. and Neuville D.R. (1992) Thermodynamics of silicates melts: Configurational properties. Adv. Phys. Geochim., 10, 132-161.

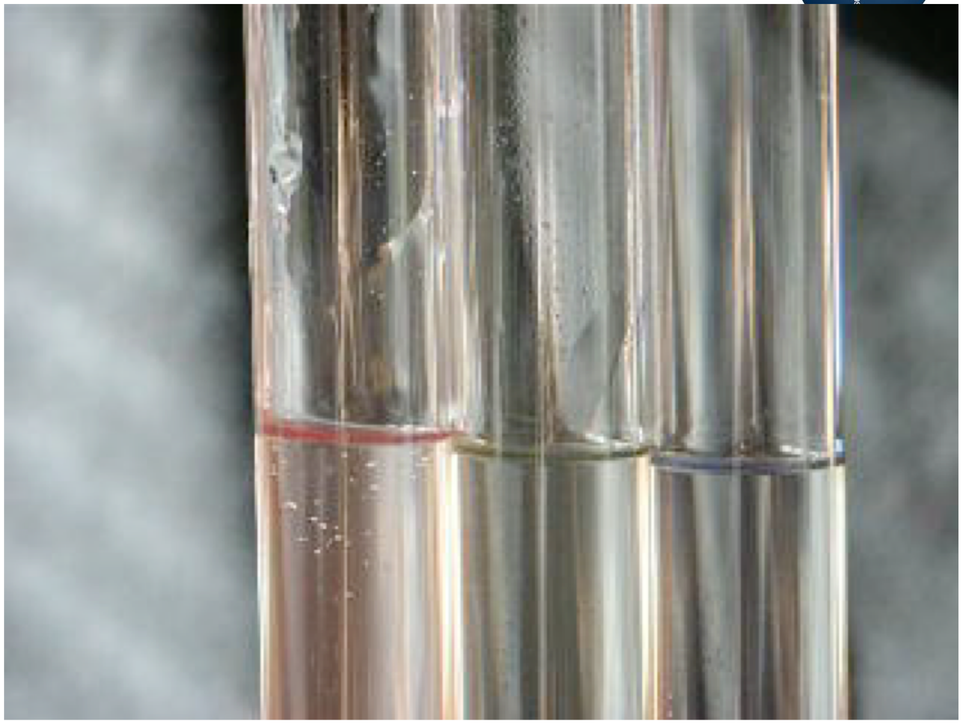
What is viscosity ?



1

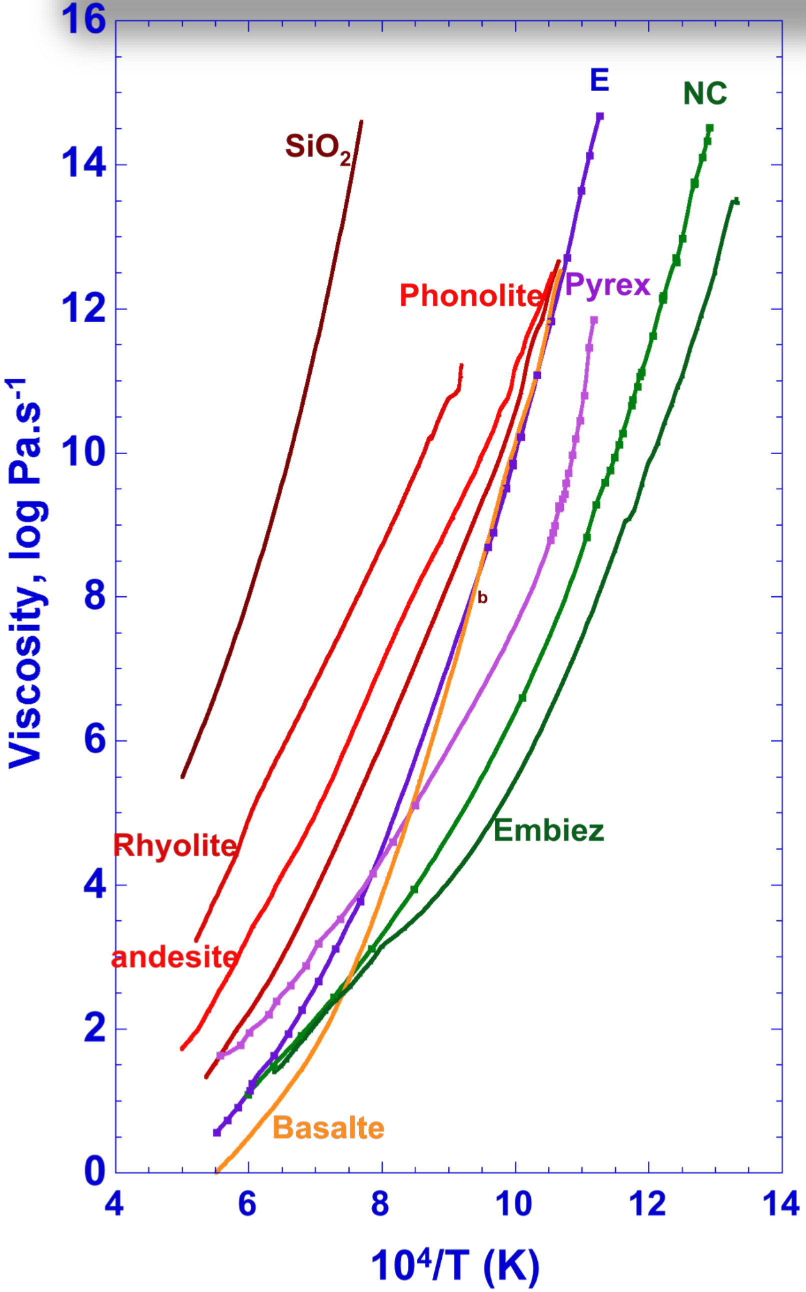
2

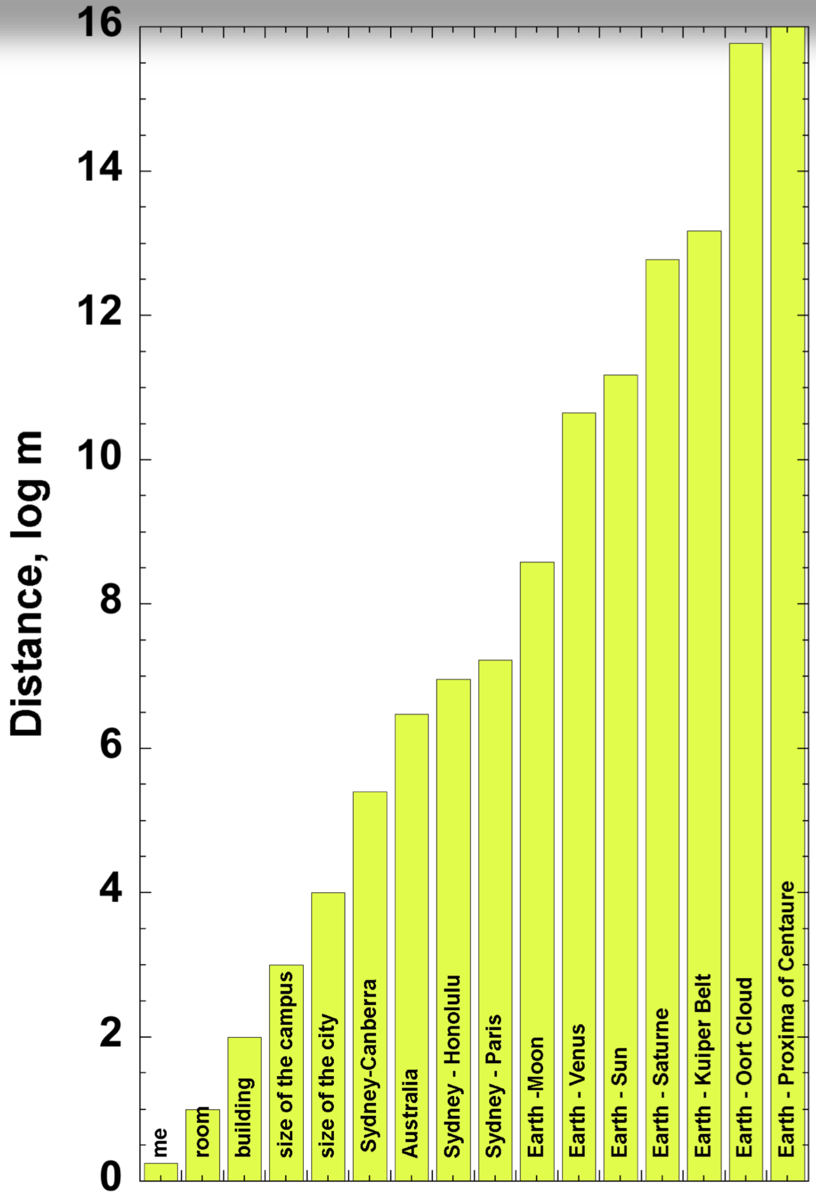
3



What is viscosity ?

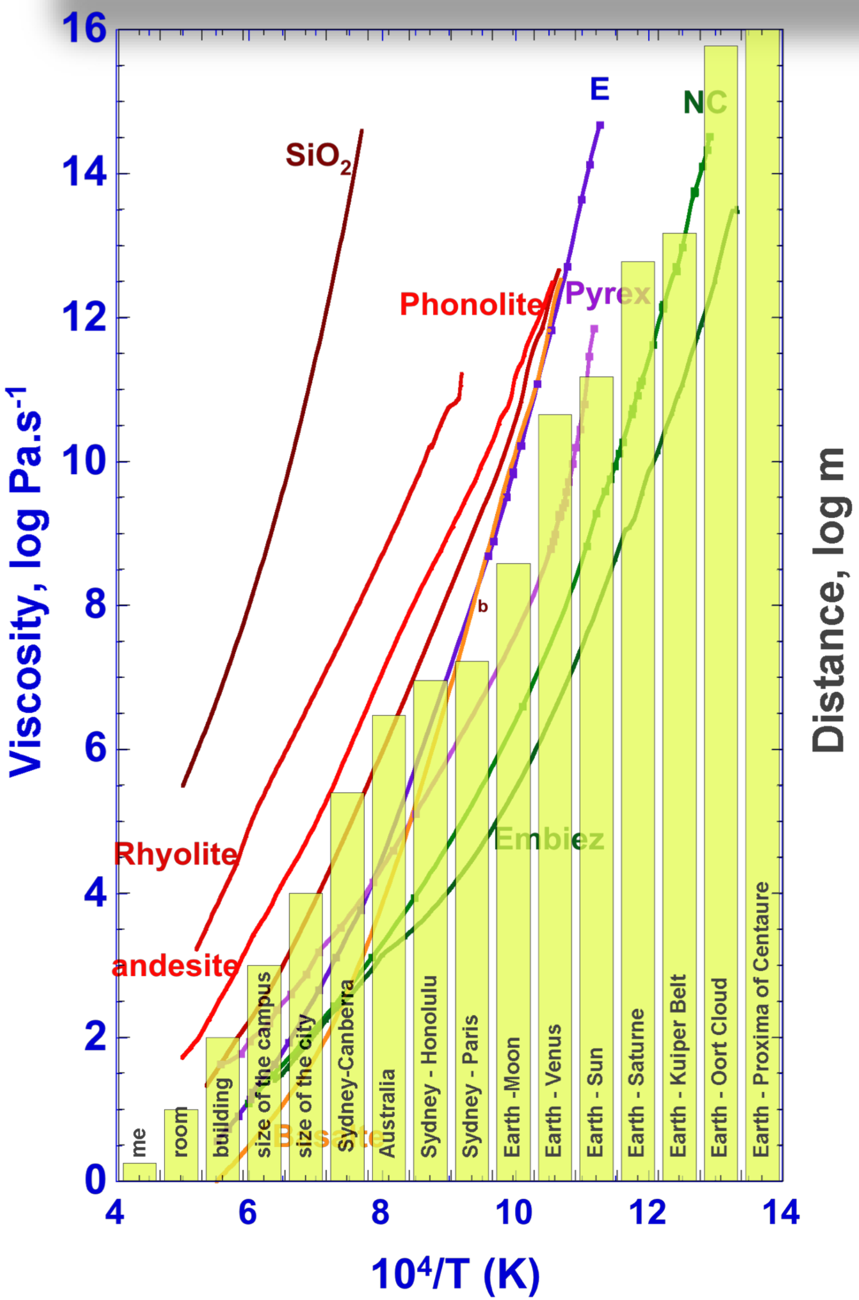
Geomaterial

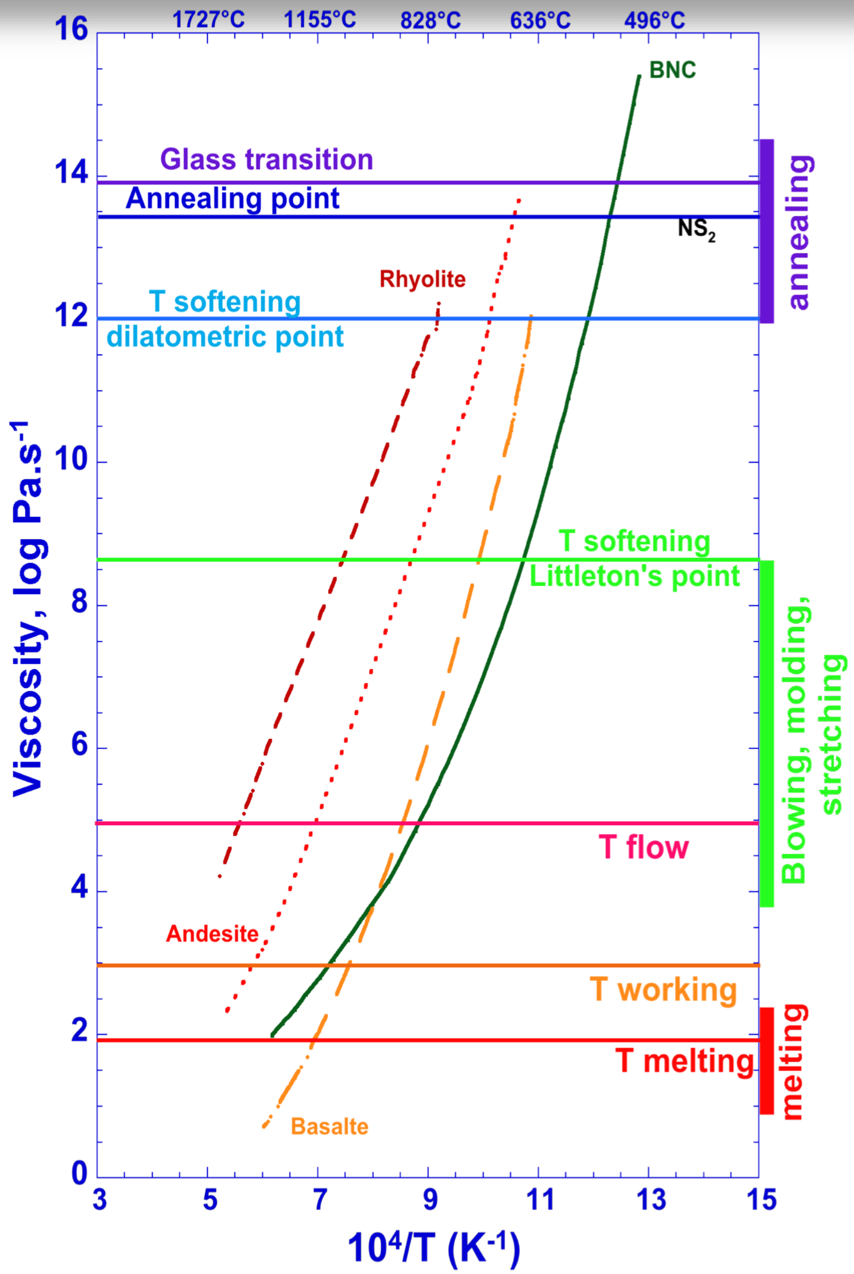




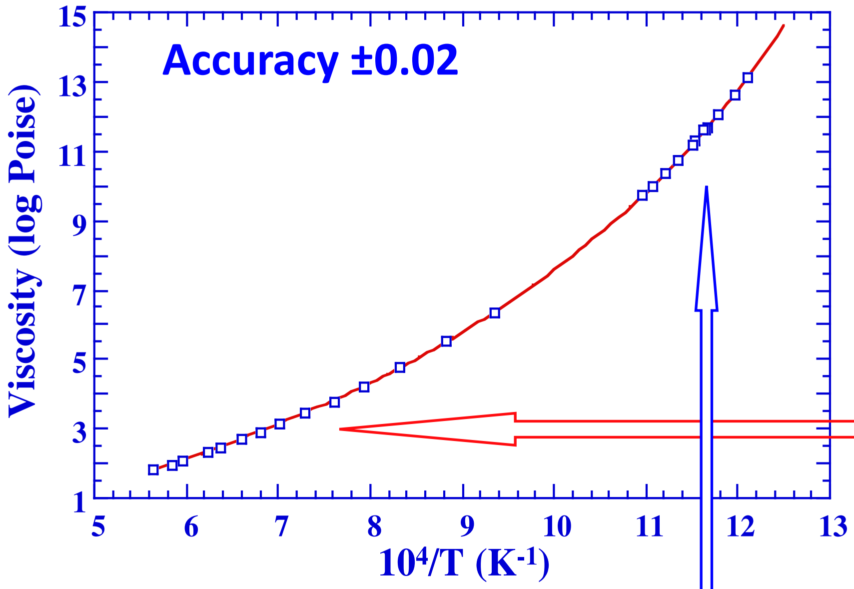
What is viscosity ?

Geomaterial





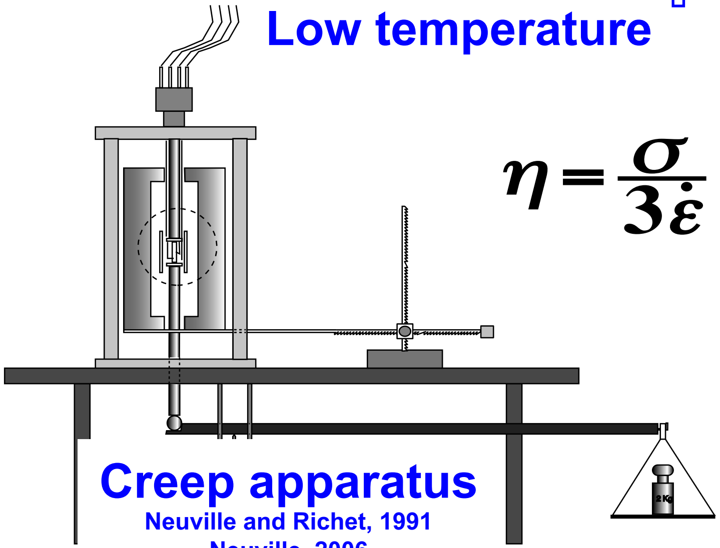
Viscosity measurements



High temperature

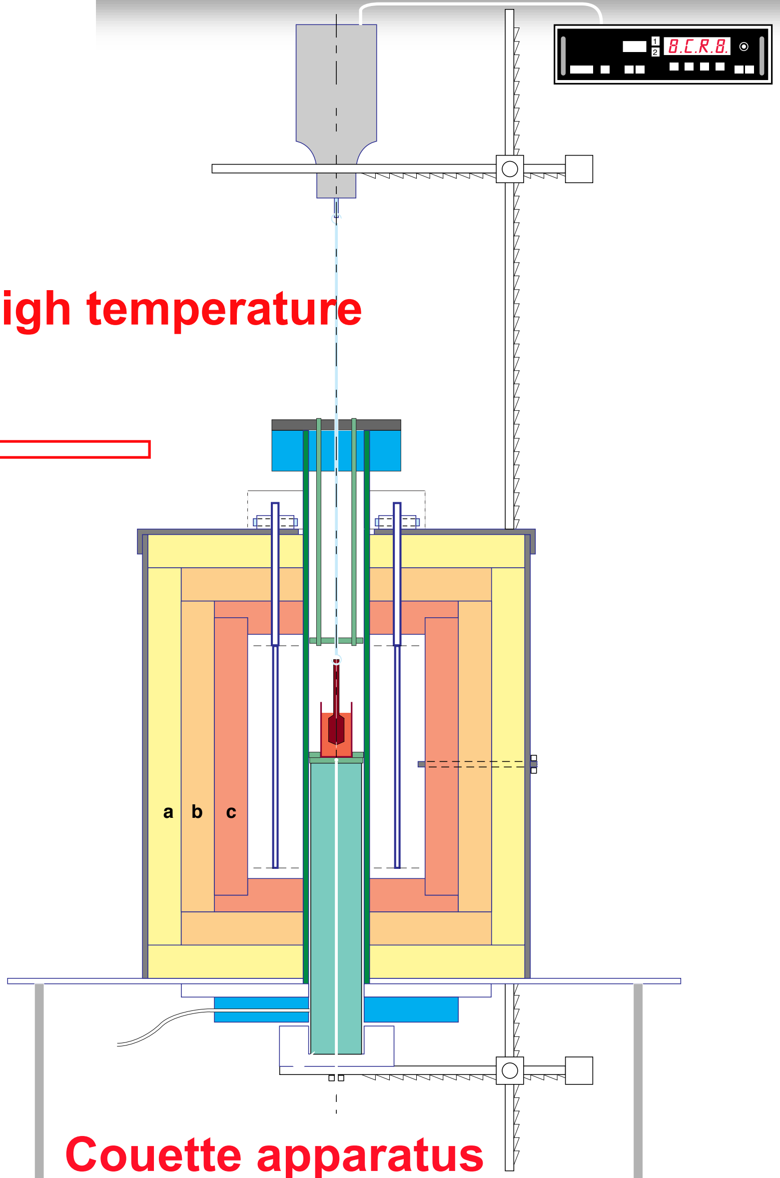
Low temperature

$$\eta = \frac{\sigma}{3\dot{\varepsilon}}$$



Creep apparatus

Neuville and Richet, 1991
Neuville, 2006

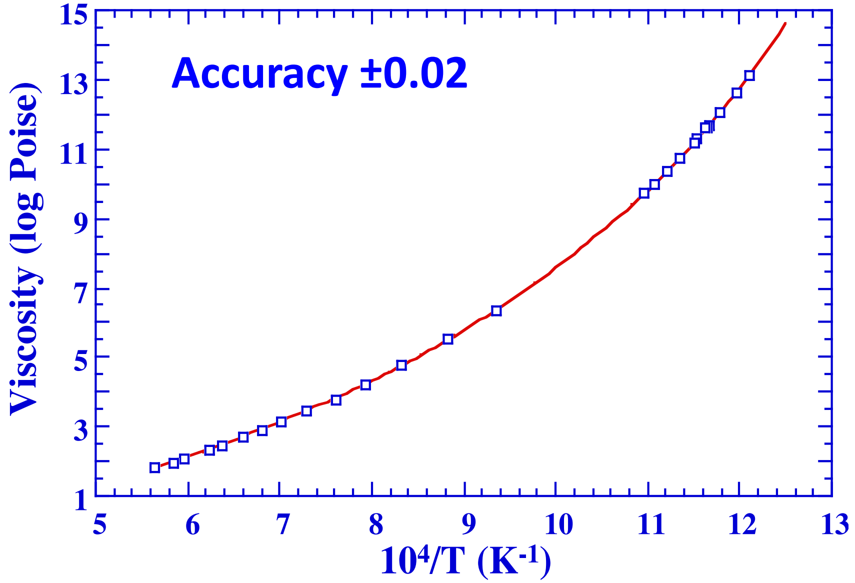


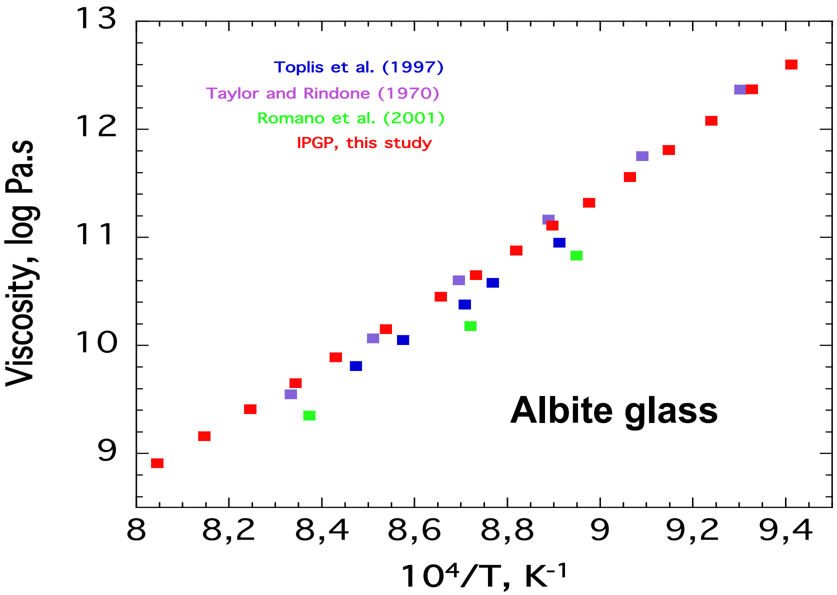
Couette apparatus

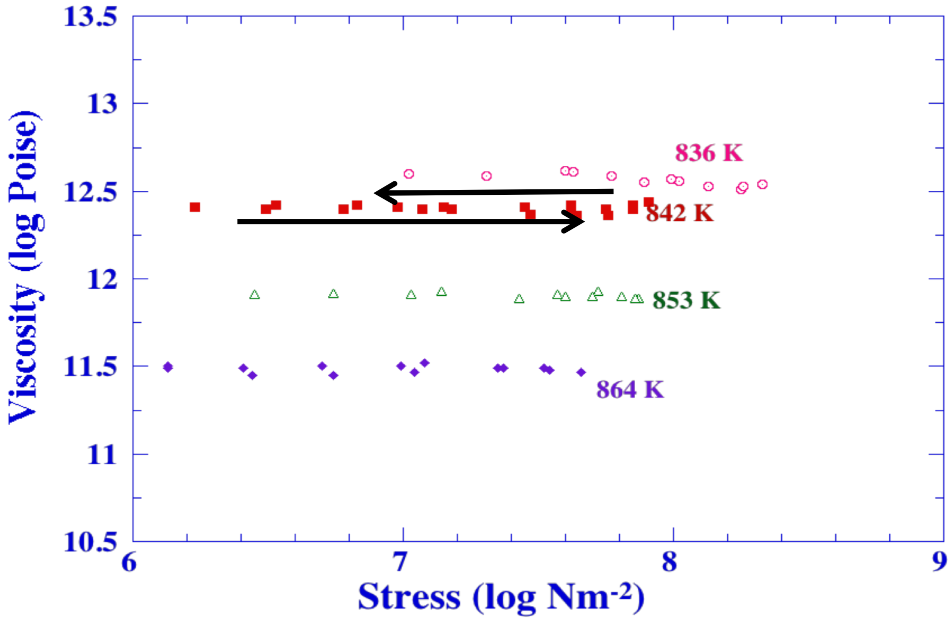
Neuville, 2006

Viscosity measurements

Geomaterial


Accuracy ±0.02

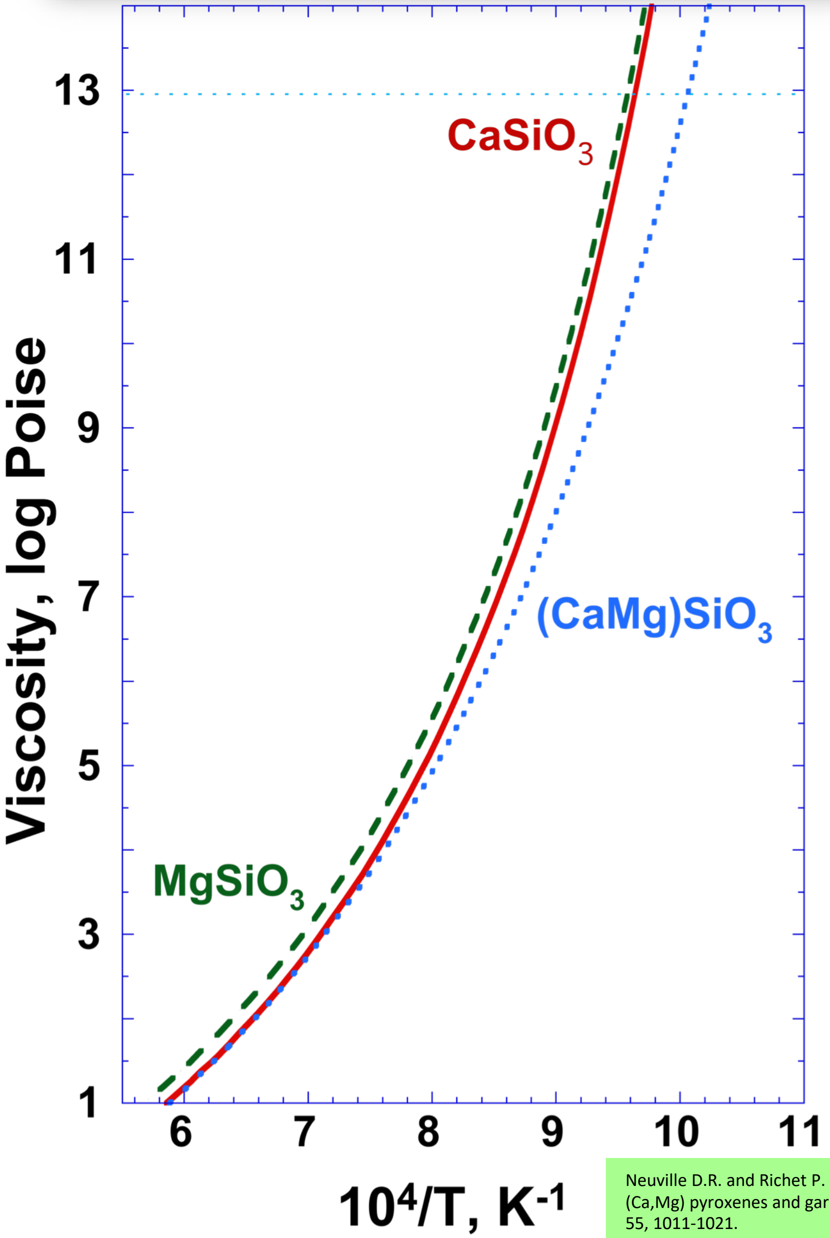

Albite glass

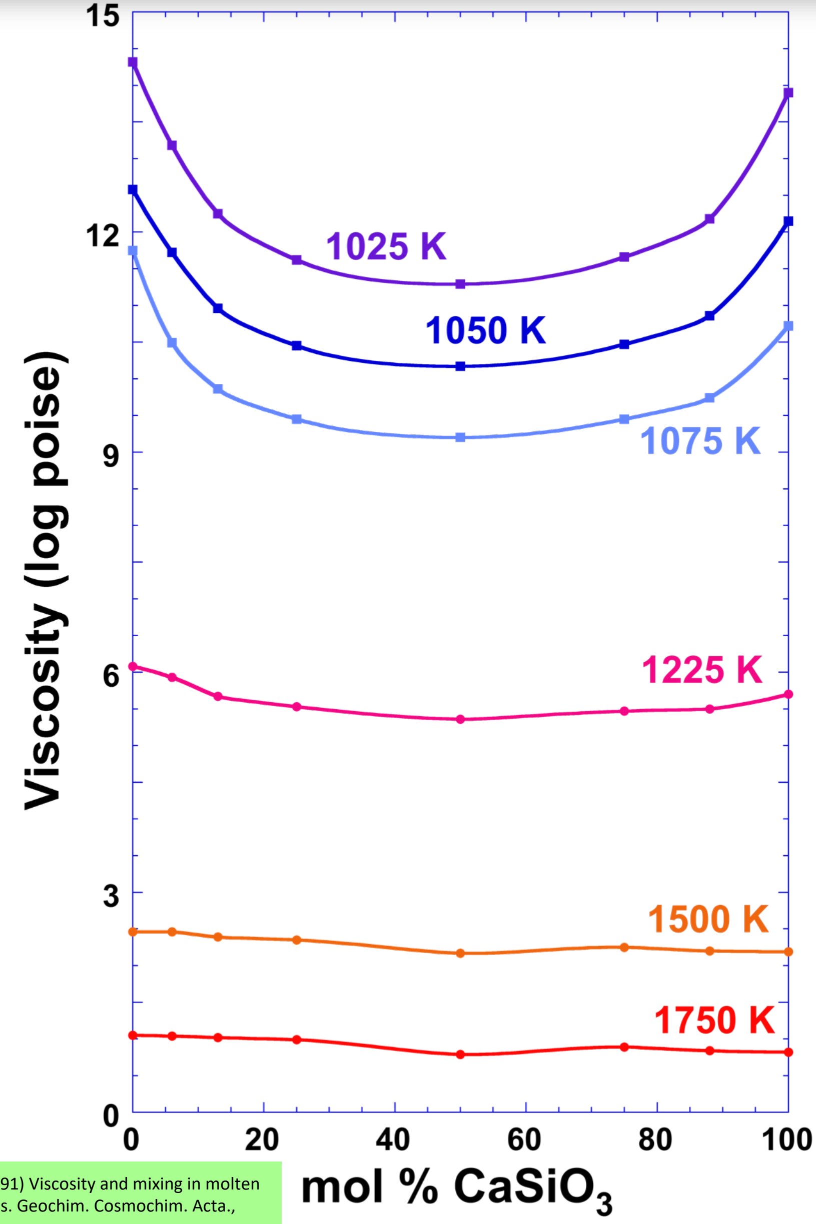


Liquid =>
Newtonian behavior

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

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

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

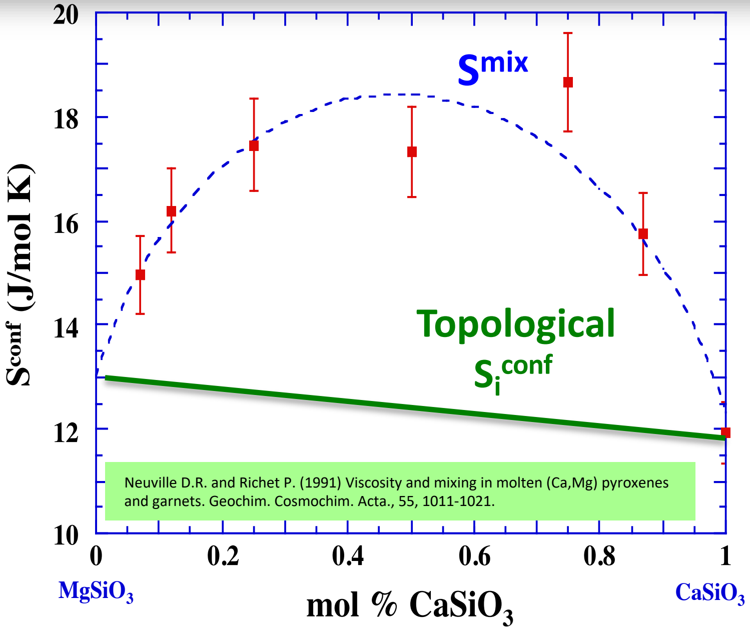
$$S^{conf}(T) = S^{conf}(Tg) + \int_{Tg}^{T} Cp^{conf} / T dt$$

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

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

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

Ideal mixing => random distribution

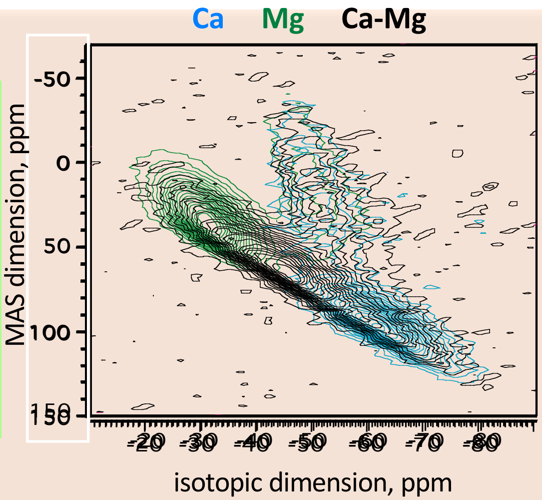


Neuville D.R. and Richet P. (1991) Viscosity and mixing in molten (Ca,Mg) pyroxenes and garnets. Geochim. Cosmochim. Acta., 55, 1011-1021.

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

Configurational entropy : image of the structure of the liquid

Ca/Na mixing

Geomaterial

Morey and Bowen, (1925)

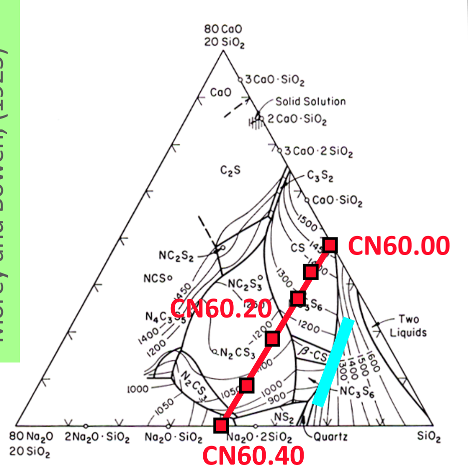
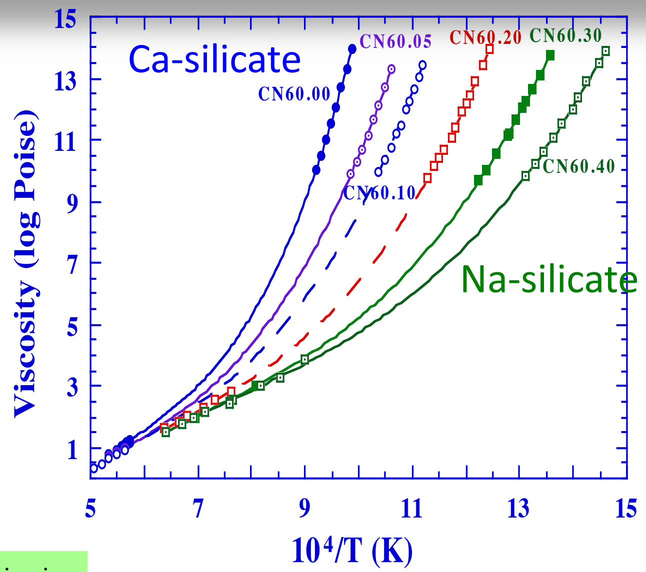
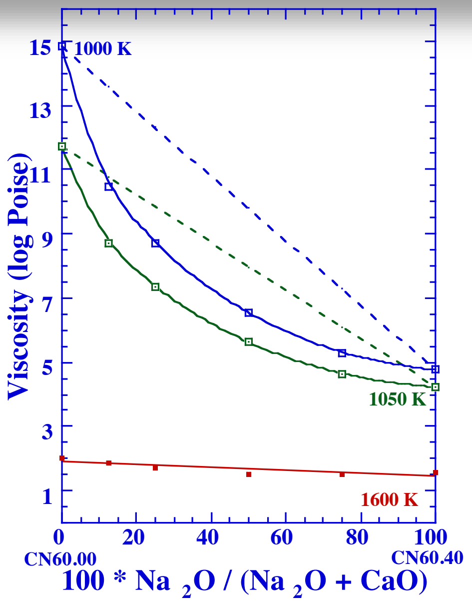


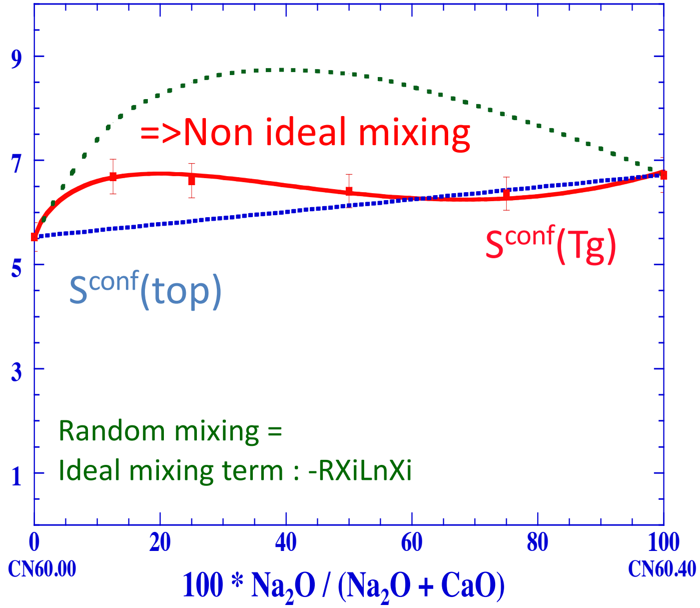
FIG. 481.—System Na_2O–CaO–SiO_2. N = Na_2O; C = CaO; S = SiO_2

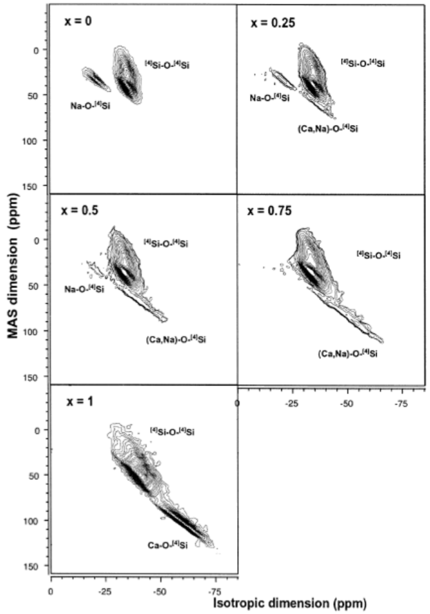
The area NS-CS-SiO$_2$ after Morey and Bowen, Fig 482.
E. R. Segnit, *Am. J. Sci.*, 251 [8] 590 (1953).





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.**

The Adam and Gibbs relaxation theory

*A*e pre-exponential term
Viscosity at “infinite” temperature

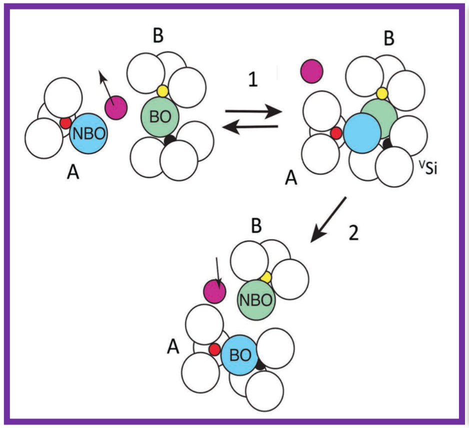
*B*e proportional to the energy barriers $\Delta\mu$ to viscous flow

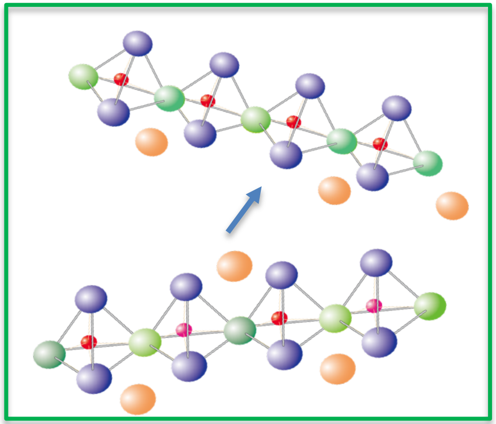
$$\log(\eta) = A_e + \frac{B_e}{T\,S^{conf}(T)}$$

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

Viscous flow occurs through cooperative rearrangements of subunits

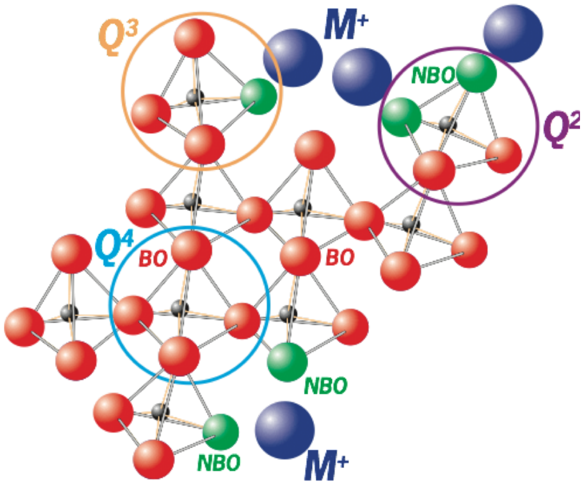
In silicate melts,viscous flow is related to exchange of oxygen by and interactions between high coordinated units (Farnan and Stebbins, 1992) or depolymerized species (Neuville et al., 2008)





Na_2O - K_2O - SiO_2 melts → extensive dataset

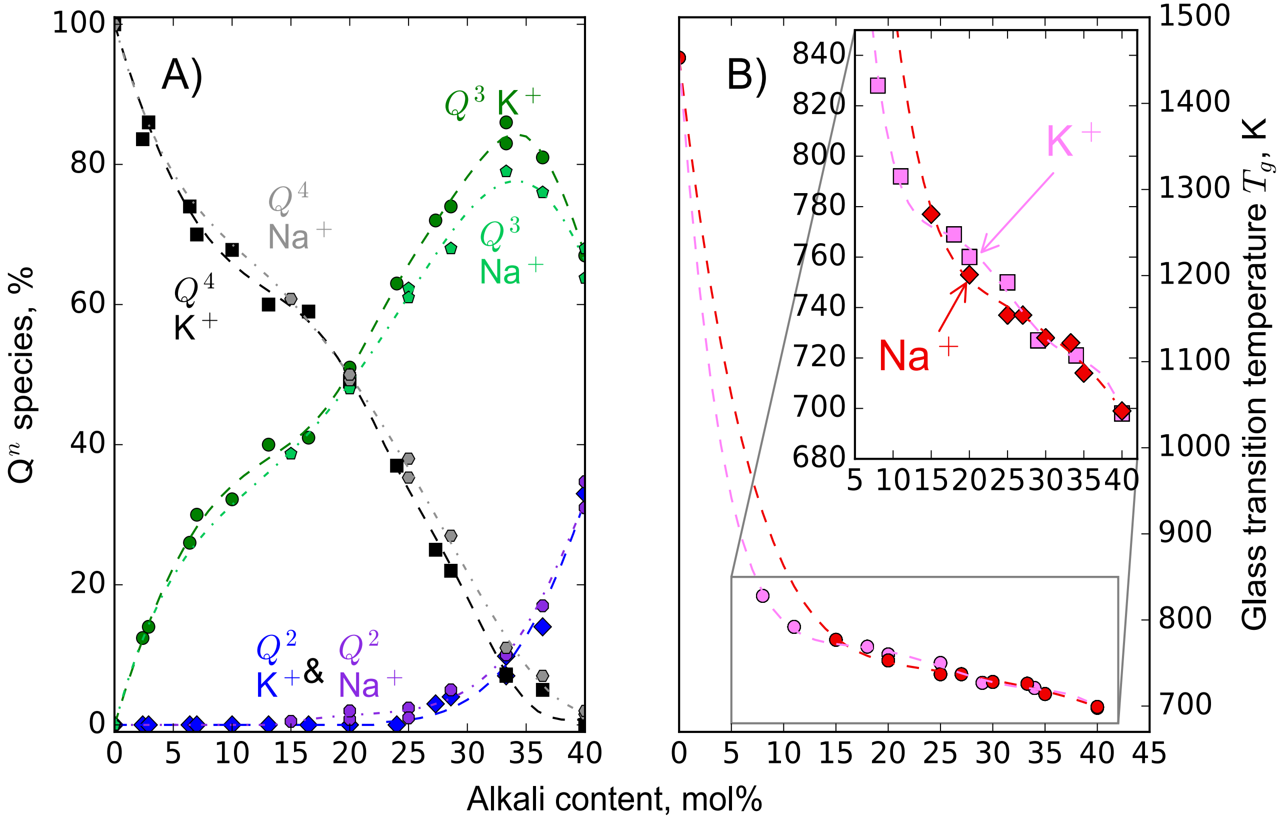
- glass and liquid heat capacity (e.g., Richet and Bottinga 1985, Richet 1987)
- glass molecular structure (e.g. from ^{29}Si NMR: Maekawa et al. 1991, Sen and Yougman 2003)
- liquid viscosity (e.g., Bockris 1954, Poole 1949, Neuville 1992, Neuville 2006)



BO:bridging oxygen

NBO: non-bridging ox

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:

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

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 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

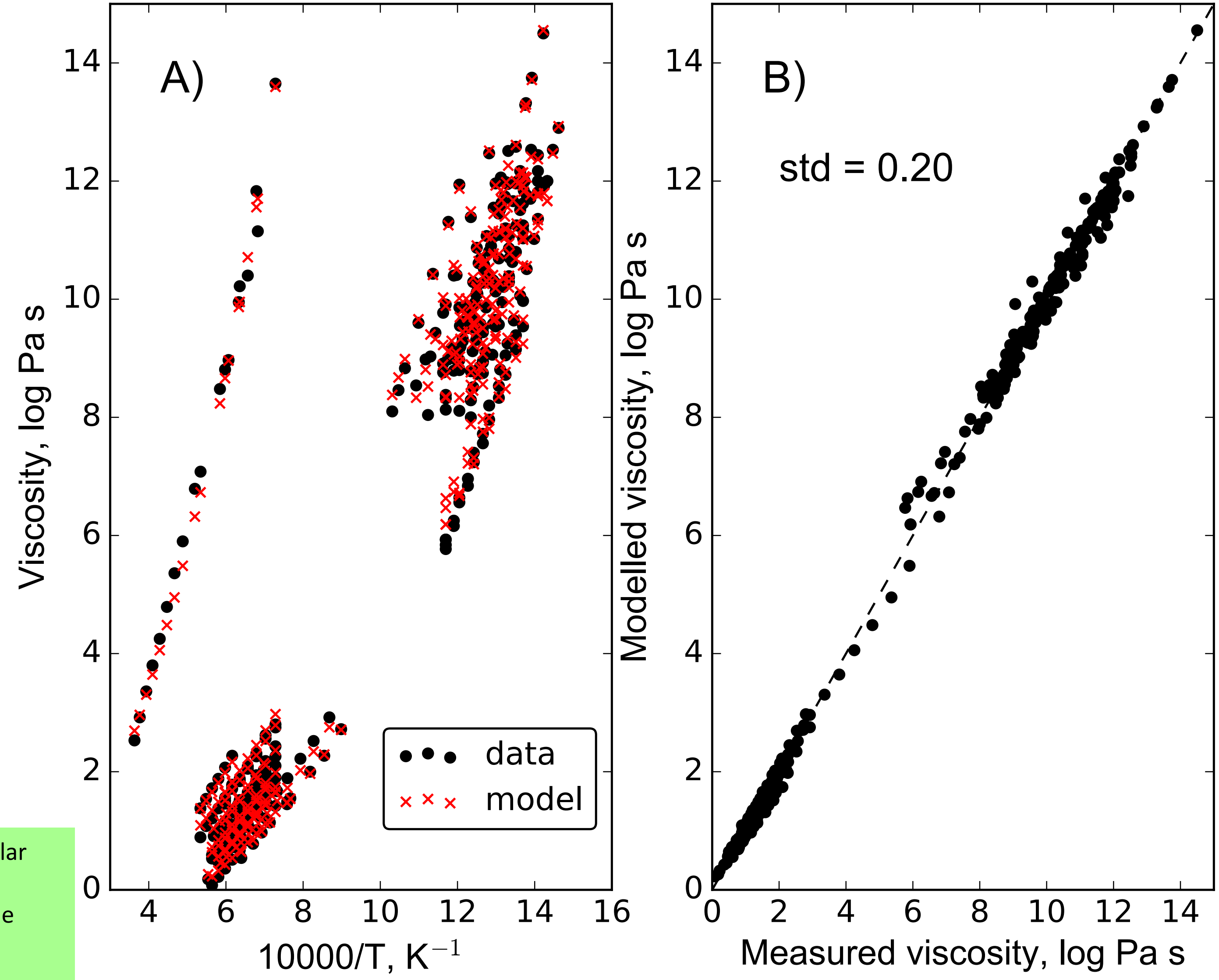
- 13 parameters, 326 data points, from 60 to 100 mol% SiO_2
- Minimisation of the least-square criterion using the Ipopt (Wächter and Biegler 2006) and Knitro (Byrd et al. 2006) solvers, and error calculation via non-parametric bootstrapping (20 000 re-sampling done)

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]

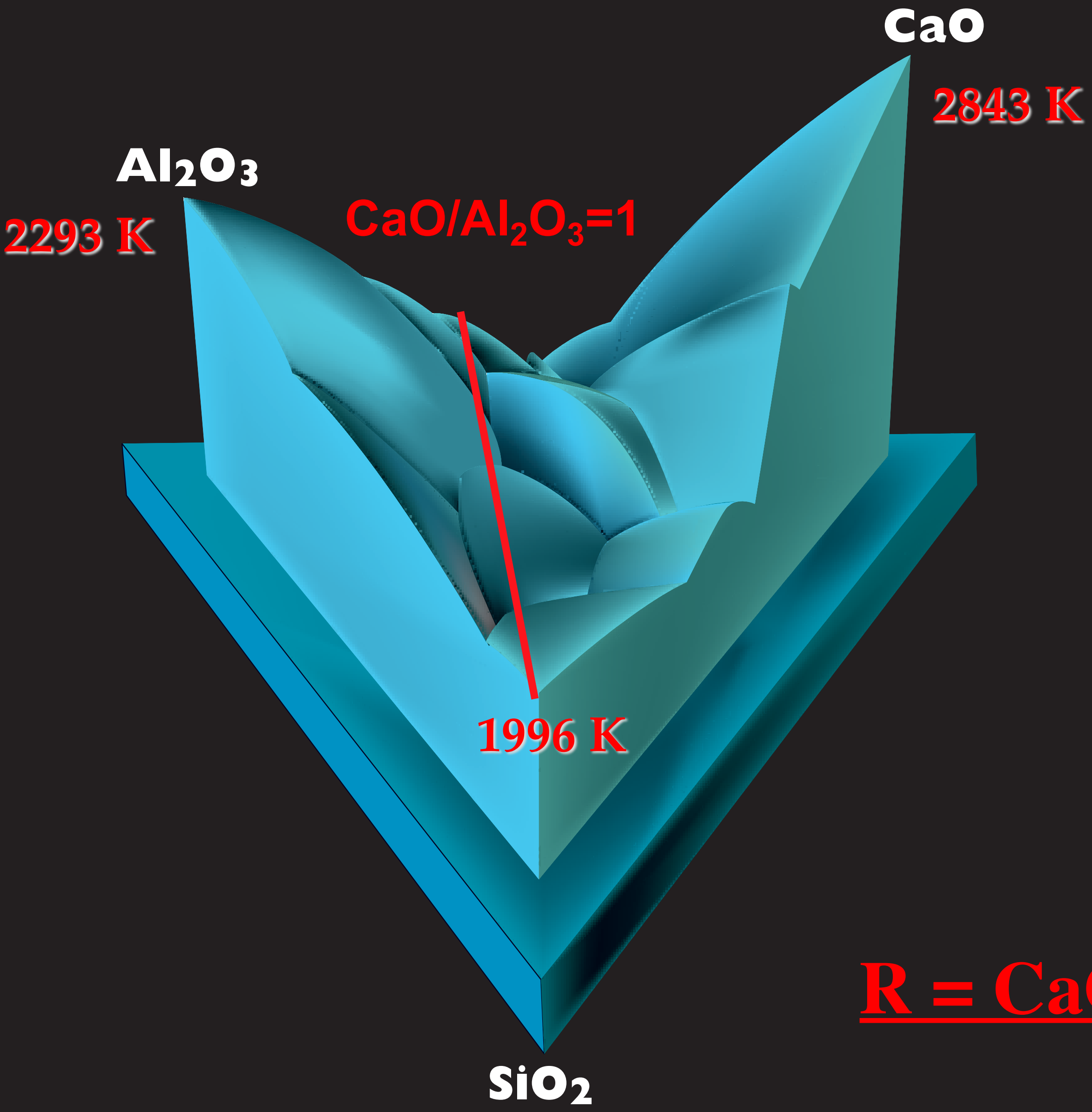
K-Q^2: 12.0 [6.8 - 20.4]
K-Q^3: 4.4 [3.3 - 5.4]

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

Al^{3+} in silicate glasses and melts



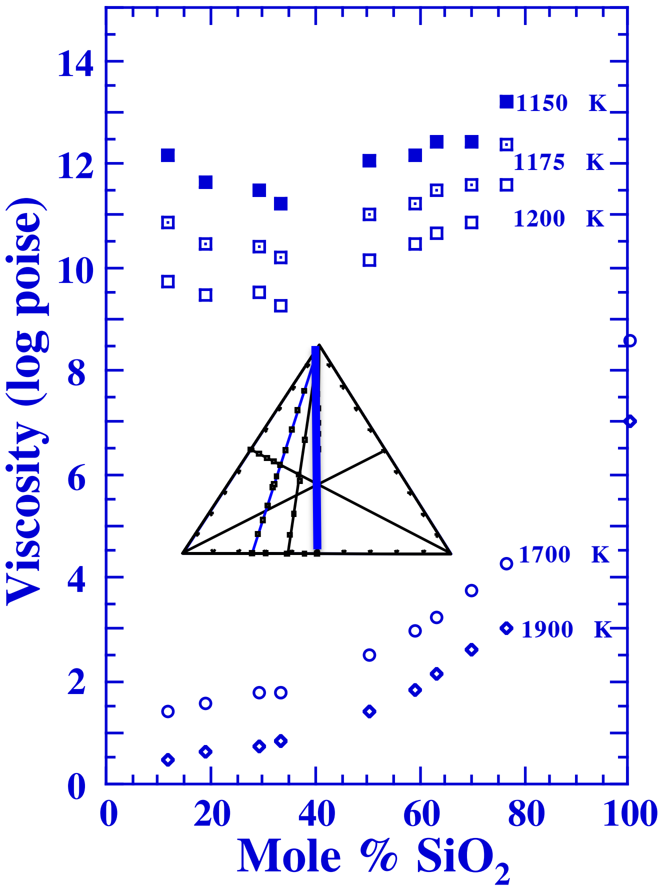
$R = CaO/Al_2O_3$

after Rankin, 1915

Configuration Entropy Theory

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

R = 1



R = CaO/Al_2O_3

$S^{conf}(Tg) = S^{mix} + S^{conf}top$

$S^{conf}top = \Sigma x_i S_i^{conf}(Tg)$.

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

$X_i = Al/(Al+Si)$

Ideal mixing => random distribution

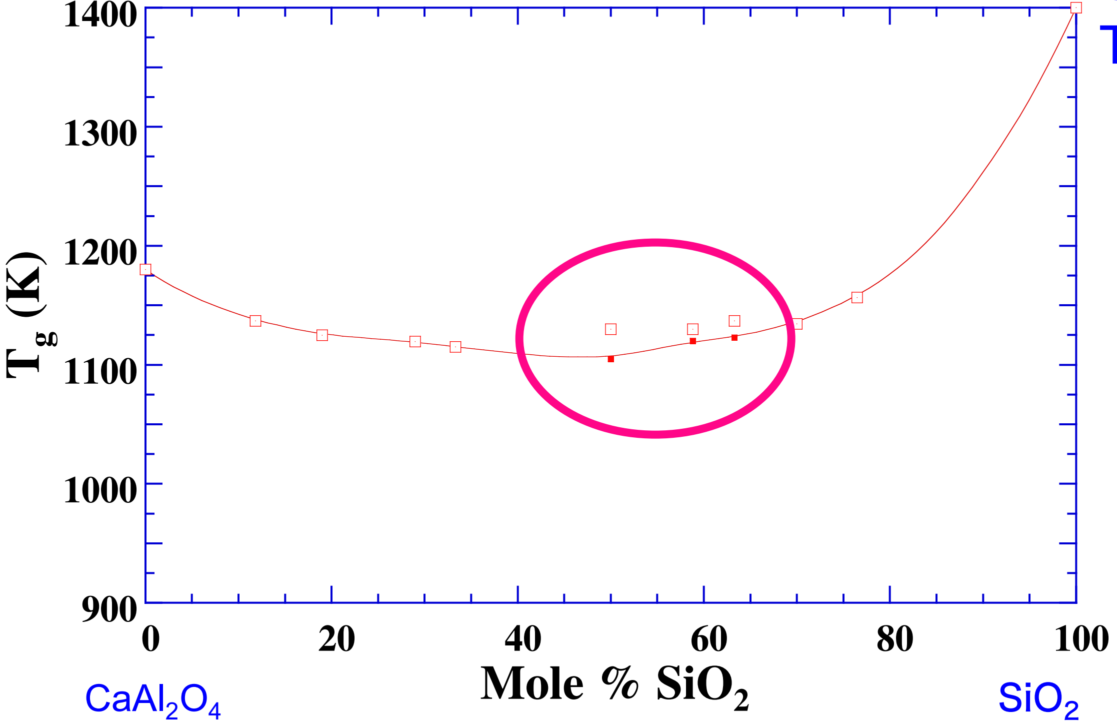
$$S^{conf}(T) = S^{conf}(T_g) + \int_{T_g}^{T} C_p^{conf}/T \, dT$$

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

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

$CaO-Al_2O_3-SiO_2$ system

Geomaterial

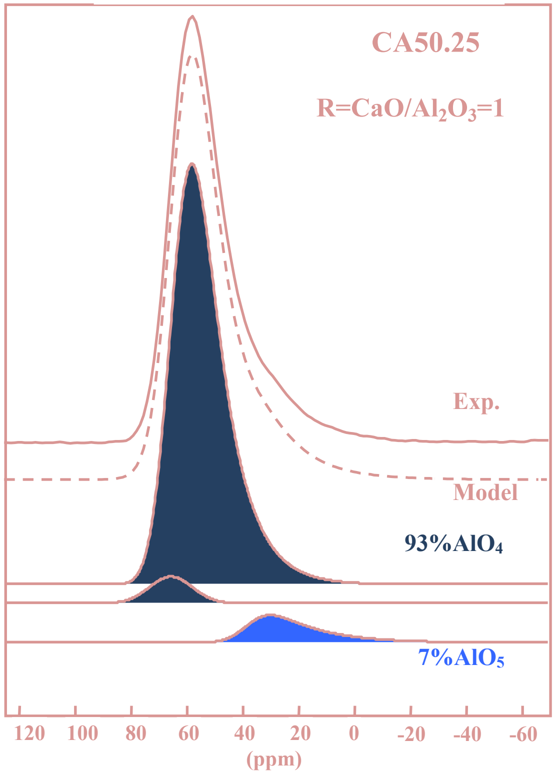


SiO_2
Tg=1400K

SiO_2 => Tetrahedra SiO_4

$CaAl_2O_4$ => Tetrahedra AlO_4
substitution of 1 Si by 1 Al and
Ca charge compensator

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



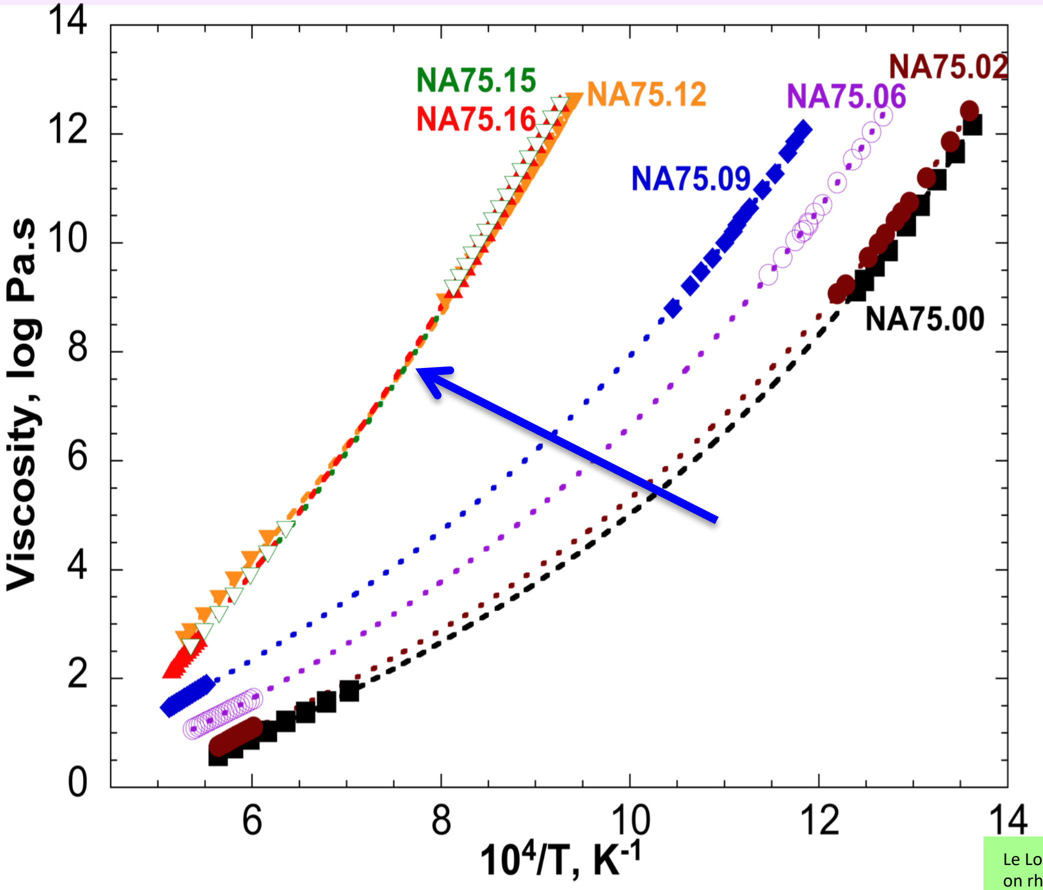
Neuville D.R., Cormier L. and Massiot D. (2004) Role of aluminium in peraluminous region in the CAS system. Geochim. Cosmochim. Acta., 68, 5071-5079

Na_2O-Al_2O_3-SiO_2 system

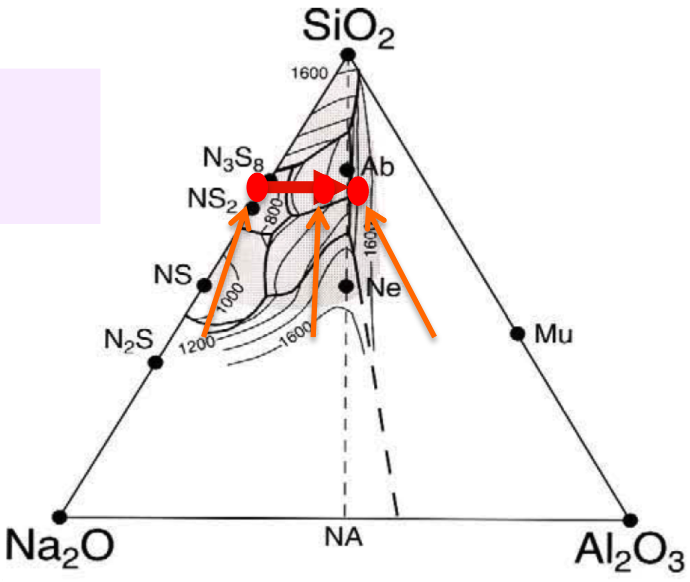
Geomaterial

NA75.X : 75% SiO_2
X=%Al_2O_3
Na_2O=100-(75+X)

High-viscosity measurements **10^8-10^{14}Pa.s ±0.02**: Creep apparatus (Neuville and Richet, 1991, Neuville 2006)
Low-viscosity measurements **1-10^5Pa.s ±0.04**: (Neuville,2006)



NS3 -> Albite -> NA75.16



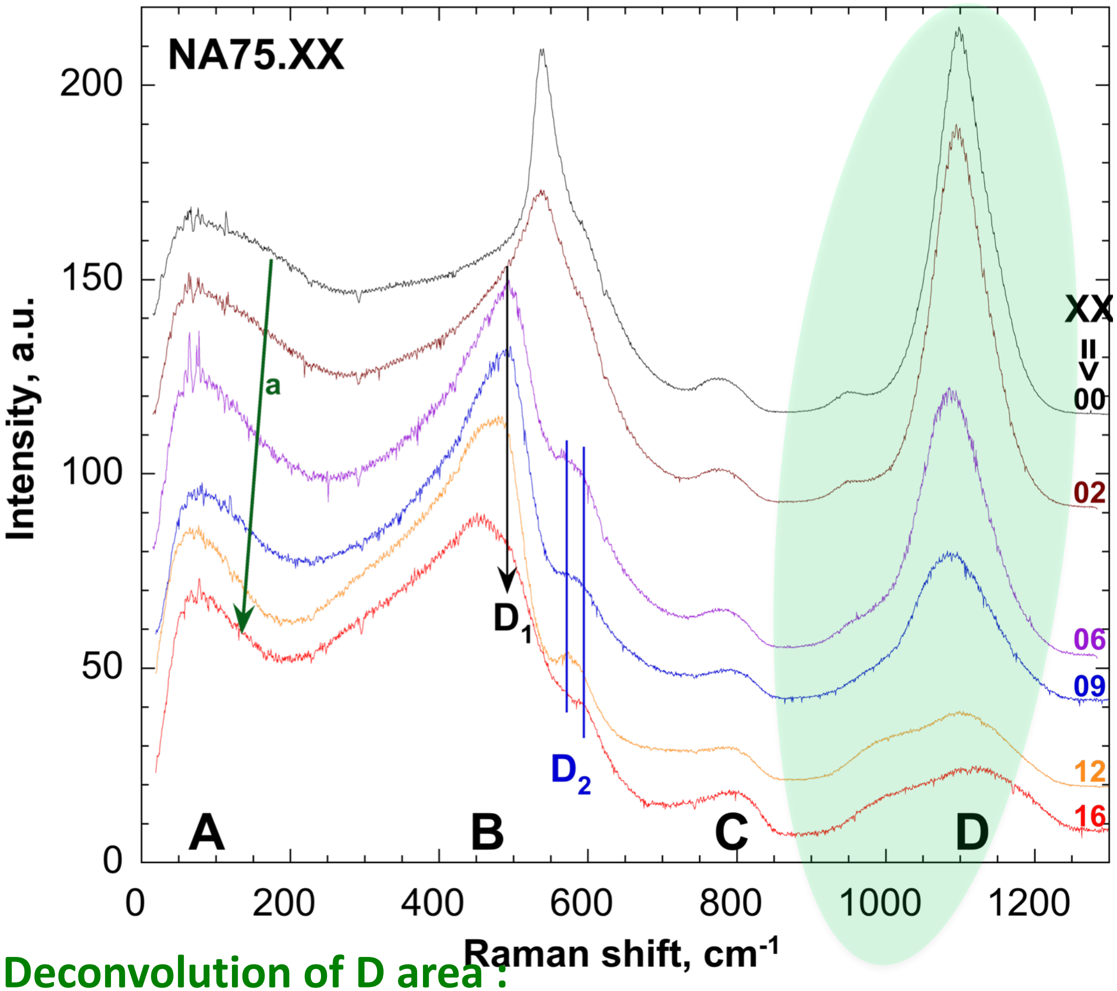
η increases with
Al/Na≤1 and Al/Na≥1

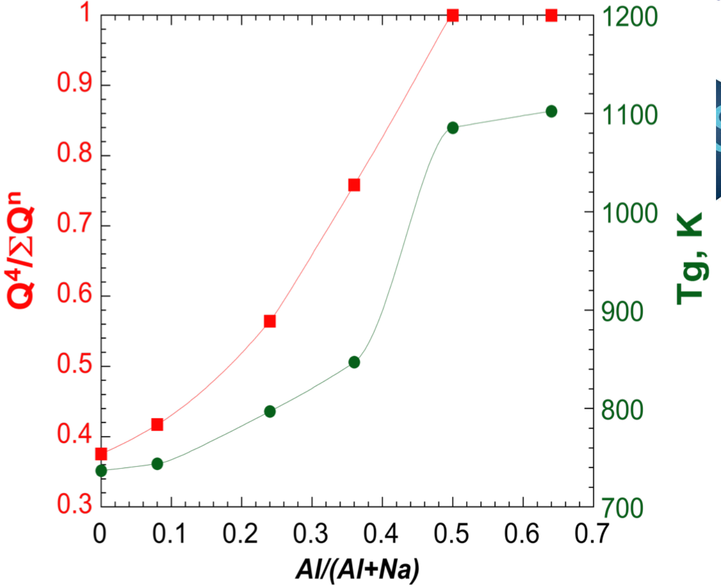
Le Losq Ch., Neuville D.R., Florian P., G.S. Henderson and Massiot D. (2014) Role of Al3+ on rheology and nano-structural changes of sodium silicate and aluminosilicate glasses and melts. Geochimica Cosmochimica Acta, 126, 495-517

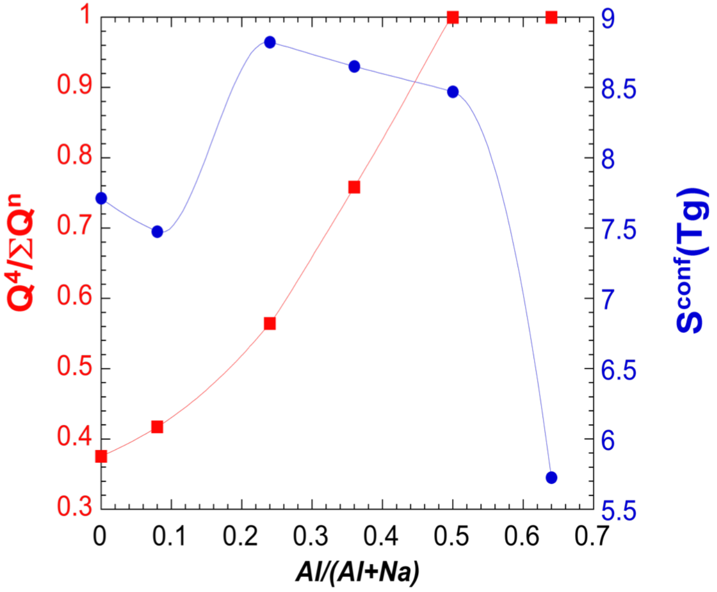
Na_2O-Al_2O_3-SiO_2 Raman spectroscopy

Geomaterial

T64000, Jobin-Yvon-Horiba, 488nm







Deconvolution of D area :

Q^{4II}, Q^{4II}, Q^3, Q^2, T^{2s}

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

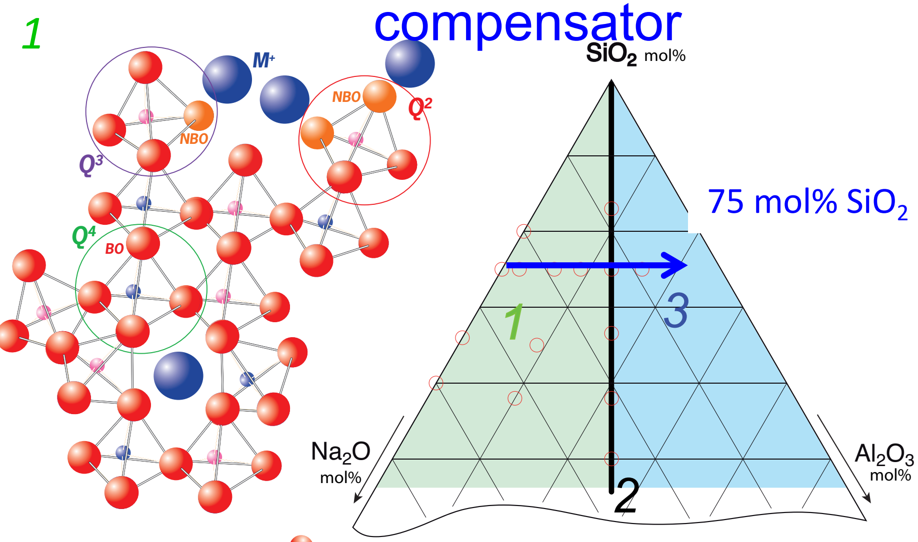
Summary Al effect 75 mol% SiO_2

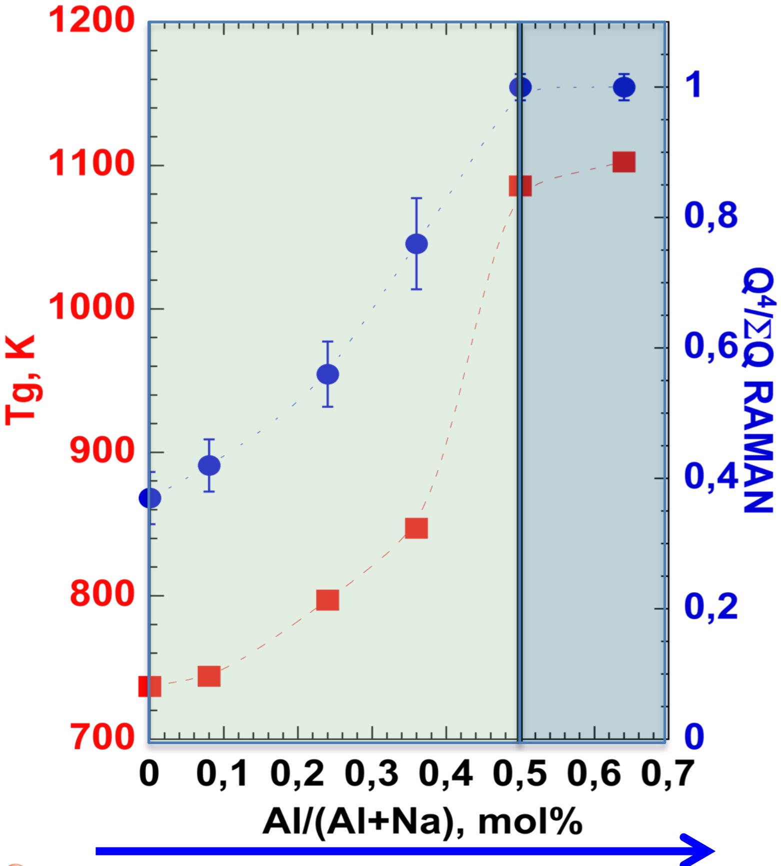
Na_2O substitution by Al_2O_3 :

$\Rightarrow$ Polymerization

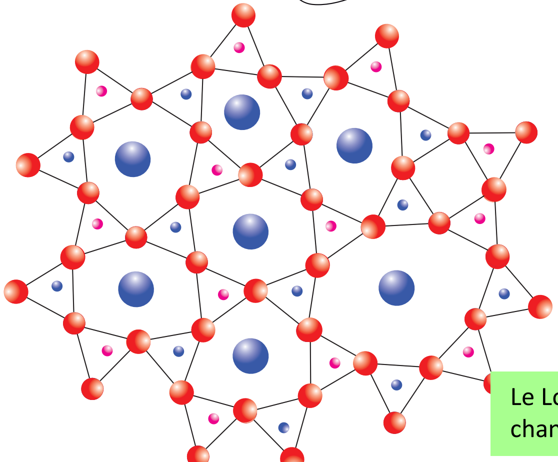
$\Rightarrow$ Change Q^3 in Q^4

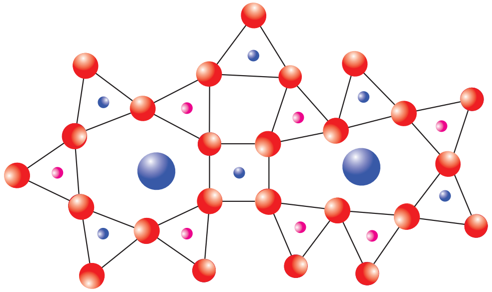
$\Rightarrow$ Al in Q^4 and Na charge compensator





2

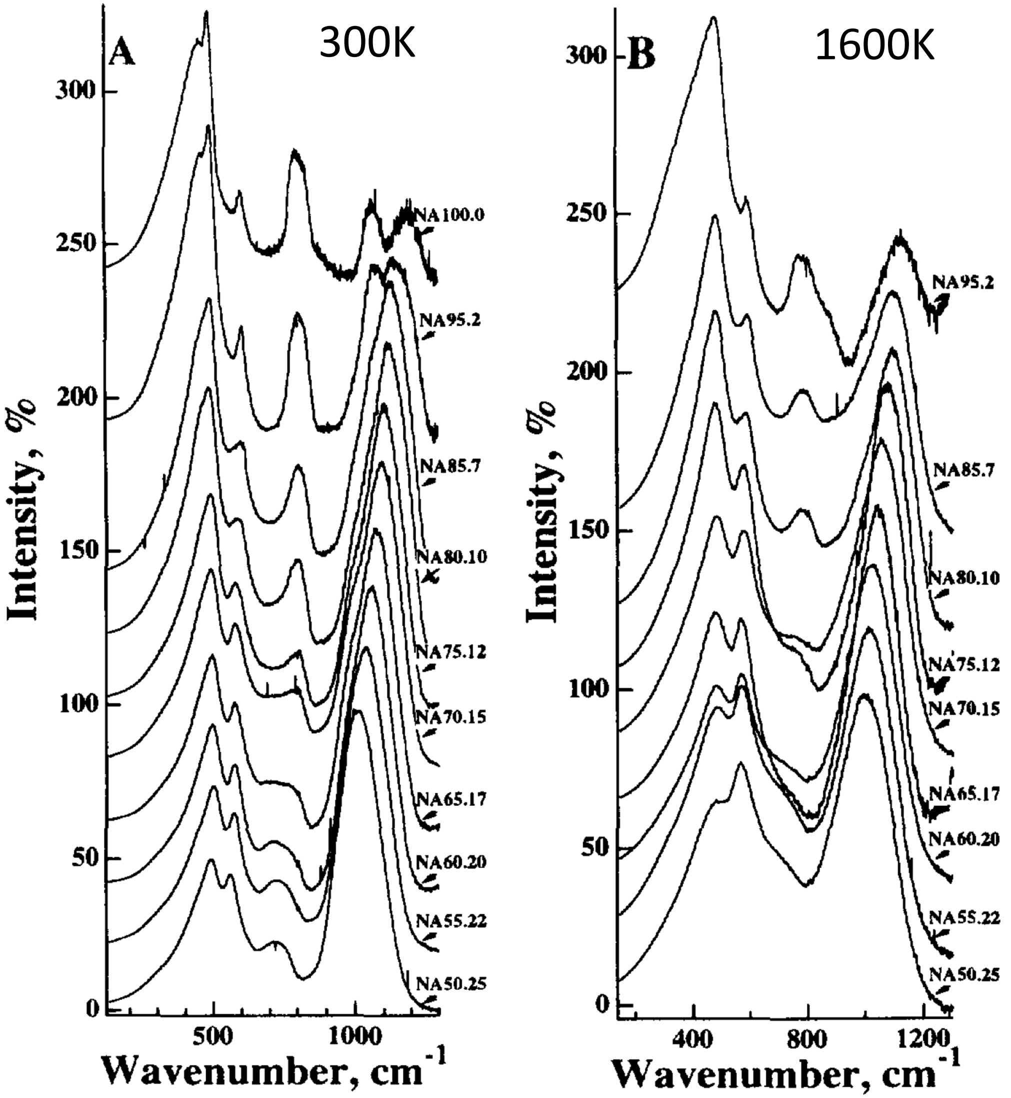


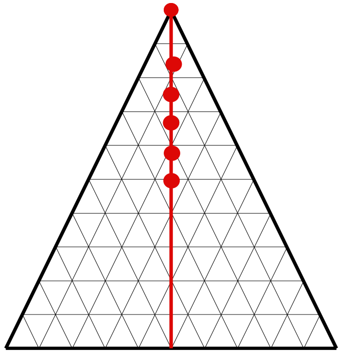


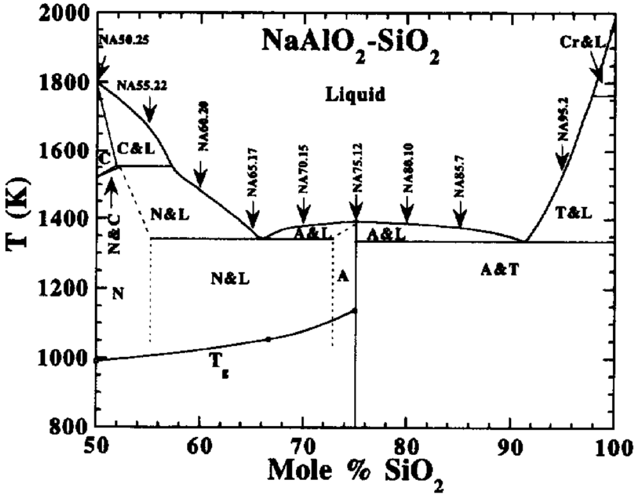
Al in CN 5 in peraluminous domain (*3*)

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

SiO_2-$Na_2Al_2O_4$

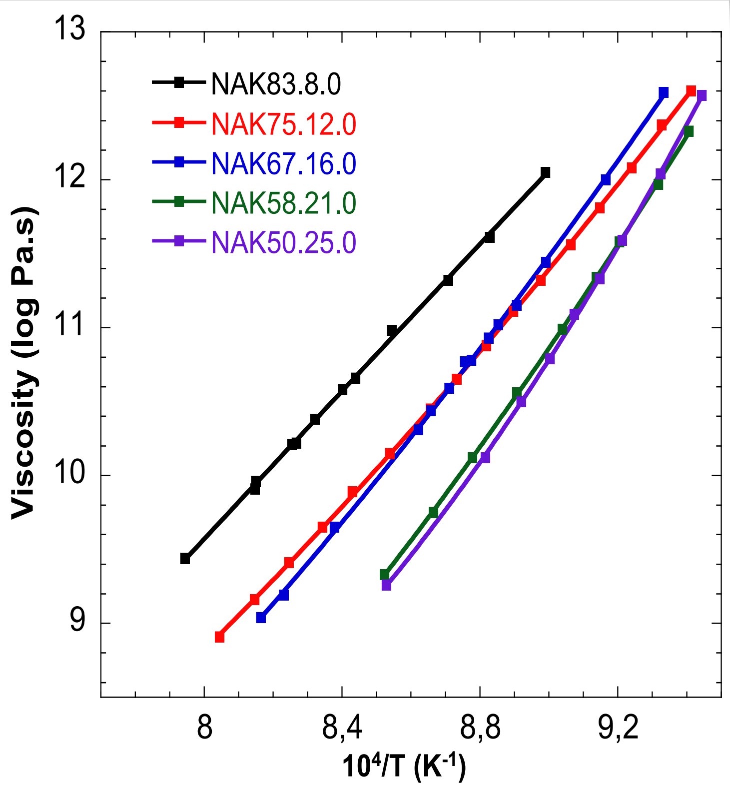


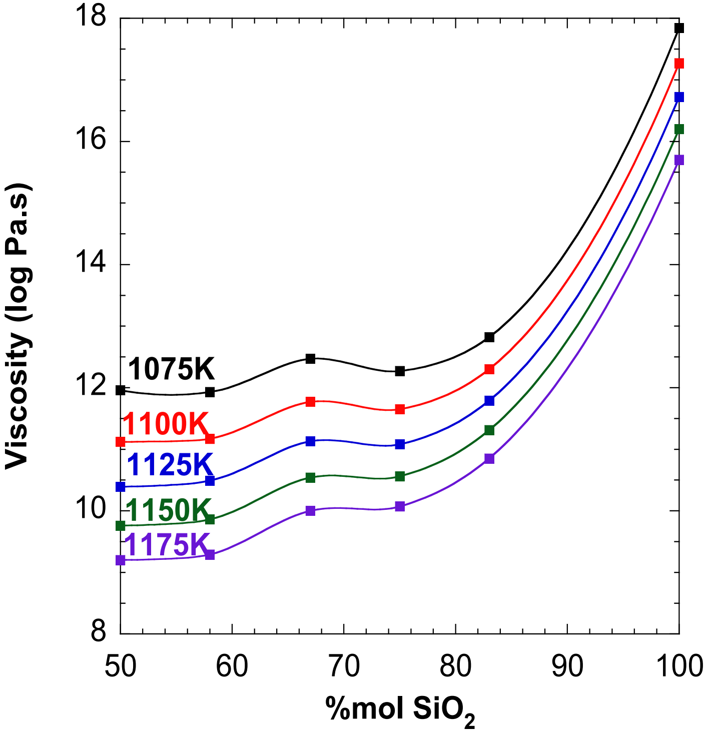


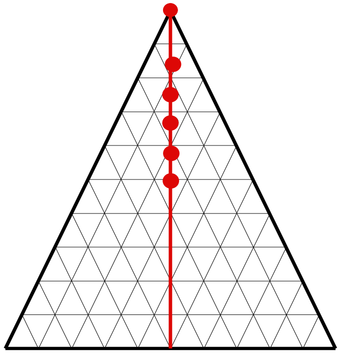


Neuville D.R. and Mysen B.O (1996) Role of aluminiun in the silicate network: in situ, high-temperature study of glasses and melts on the join SiO2-NaAlO2. Geochimica Cosmochimica Acta., 60, 1727-1737

NAS tectosilicate join



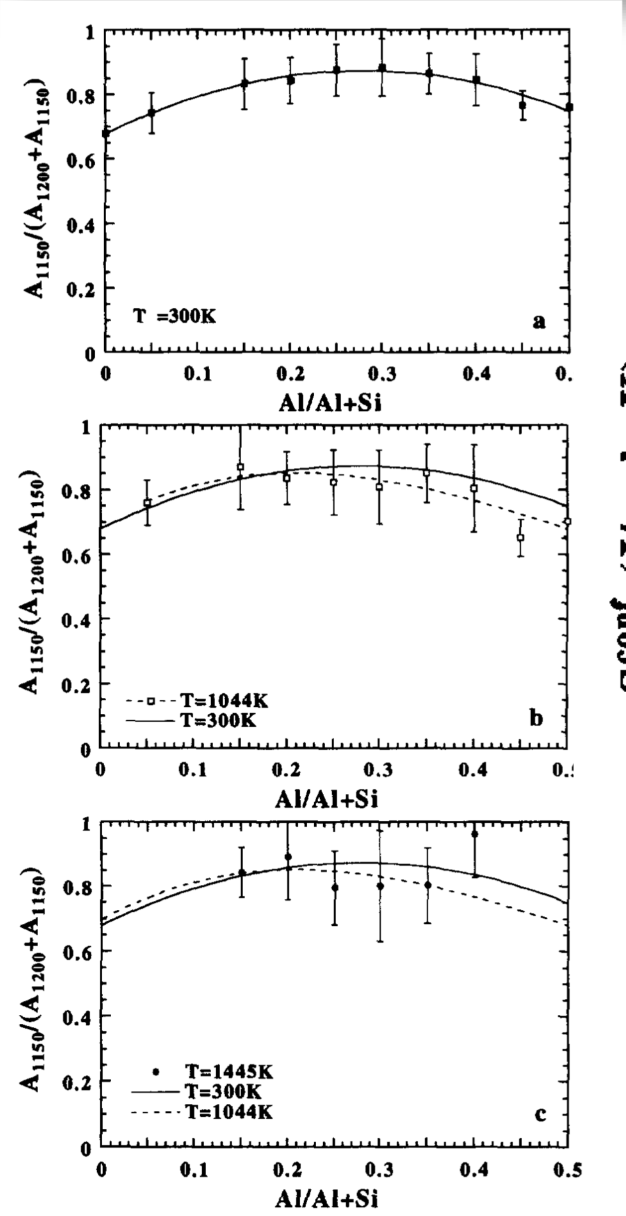


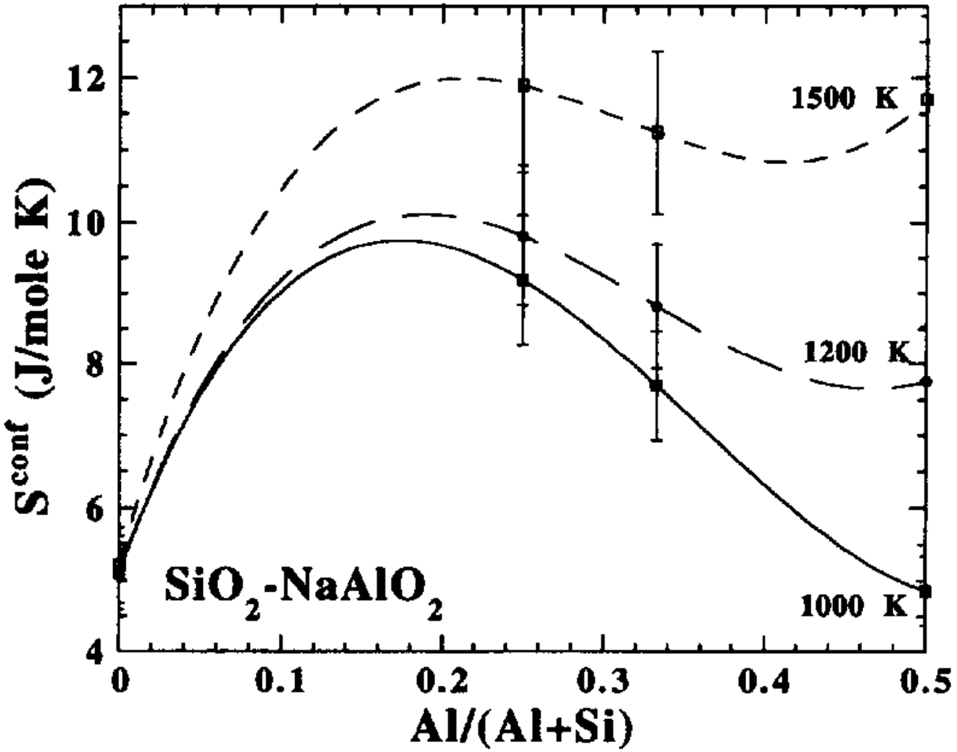


$\Rightarrow$**Variation of viscosity : not a linear function of SiO_2**

$\Rightarrow$**Near the Tg : importance of the configurational entropy**

SiO_2-$Na_2Al_2O_4$





Neuville D.R. and Mysen B.O (1996) Role of aluminiun in the silicate network: in situ, high-temperature study of glasses and melts on the join SiO2-NaAlO2. Geochimica Cosmochimica Acta., 60, 1727-1737

Conclusion

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 and aluminosilicate glasses and melts

Na/Ca and Na/Sr or Na/M^{2+} are not mixed randomly in silicate and aluminosilicate glasses and melts.

Na/K are mixed randomly in silicate and non randomly aluminosilicate glasses and melts. It is possible to determine viscosity from Q species.

Si/Al are mixed randomly in tectosilicate glasses and melts.

Coming soon : a general model between Q species and viscosity