Viscosité des verres d'oxydes
Lien entre structure et Propriétés

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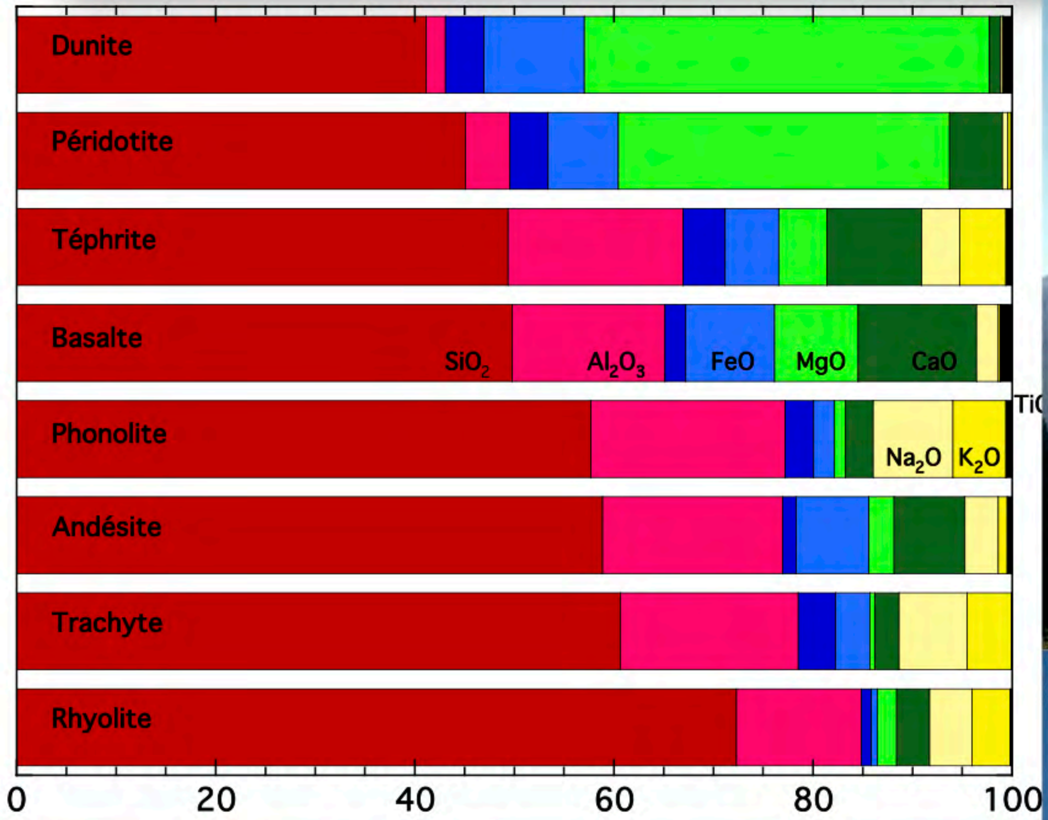
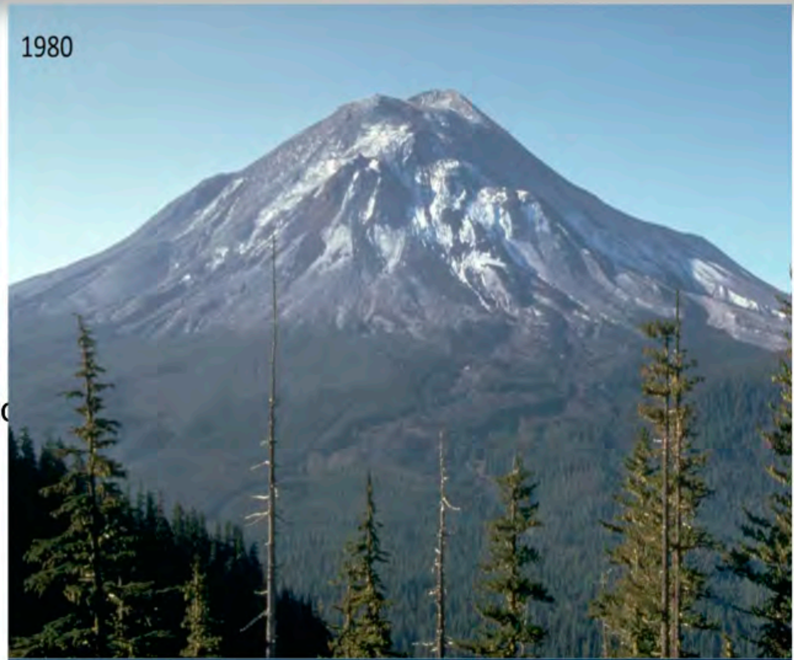
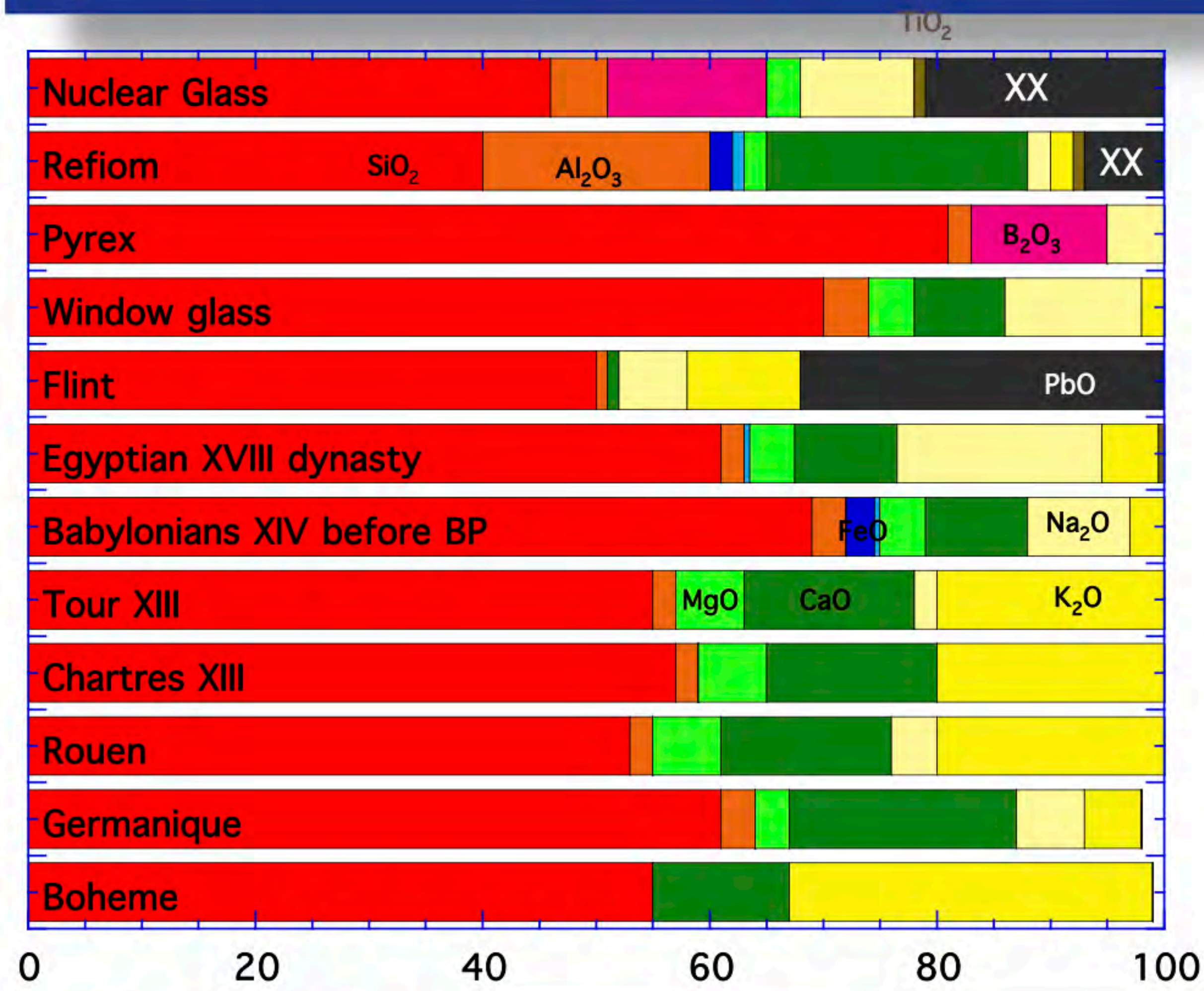

Dunite
Péridotite
Téphrite
Basalte
Phonolite
Andésite
Trachyte
Rhyolite
SiO_2
Al_2O_3
FeO
MgO
CaO
Na_2O
K_2O
0
20
40
60
80
100


1980

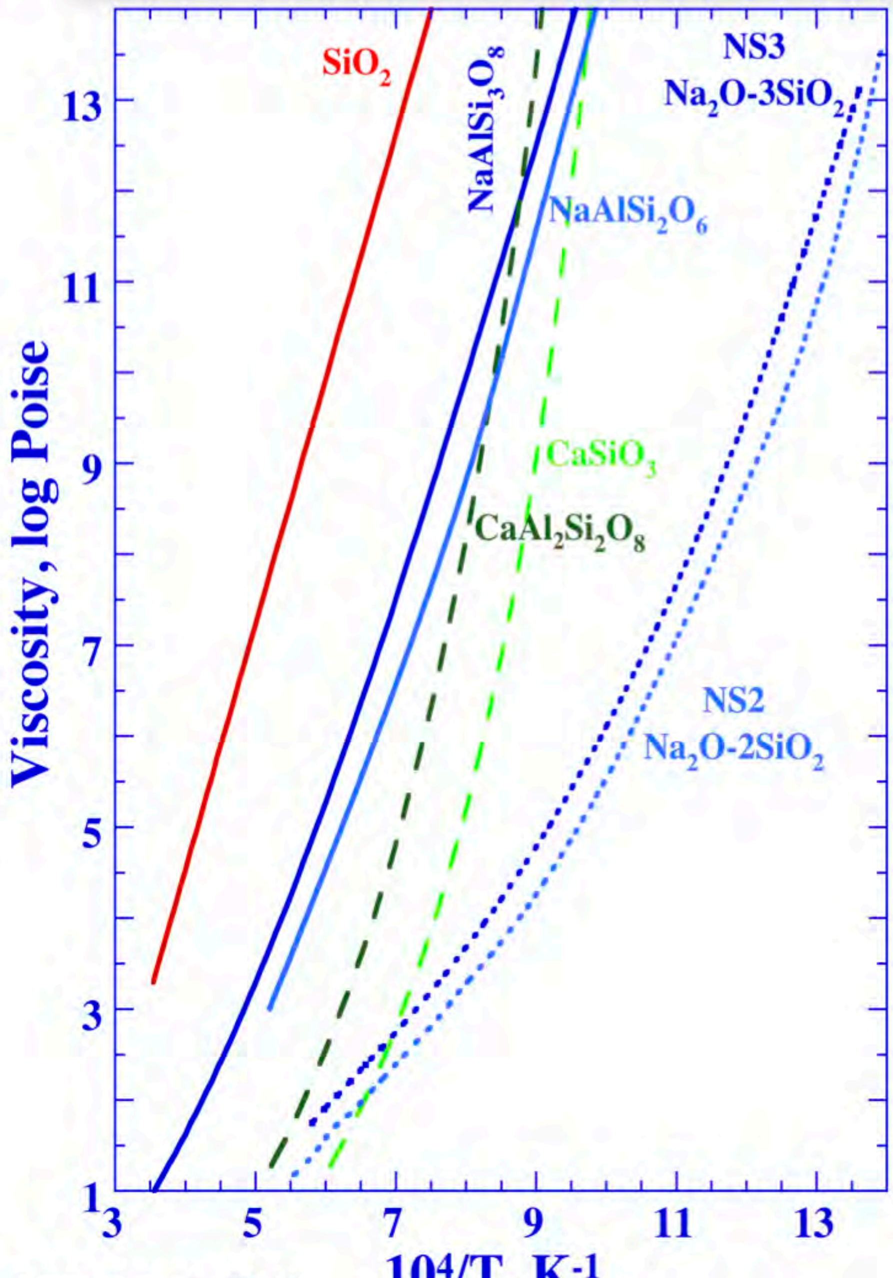

1982



TiO_2
Nuclear Glass
XX
Refiom
SiO_2
Al_2O_3
XX
Pyrex
B_2O_3
Window glass
Flint
PbO
Egyptian XVIII dynasty
Babylonians XIV before BP
FeO
Na_2O
Tour XIII
MgO
CaO
K_2O
Chartres XIII
Rouen
Germanique
Boheme
0
20
40
60
80
100

Network former
M_2O
MO

IVème siècle



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

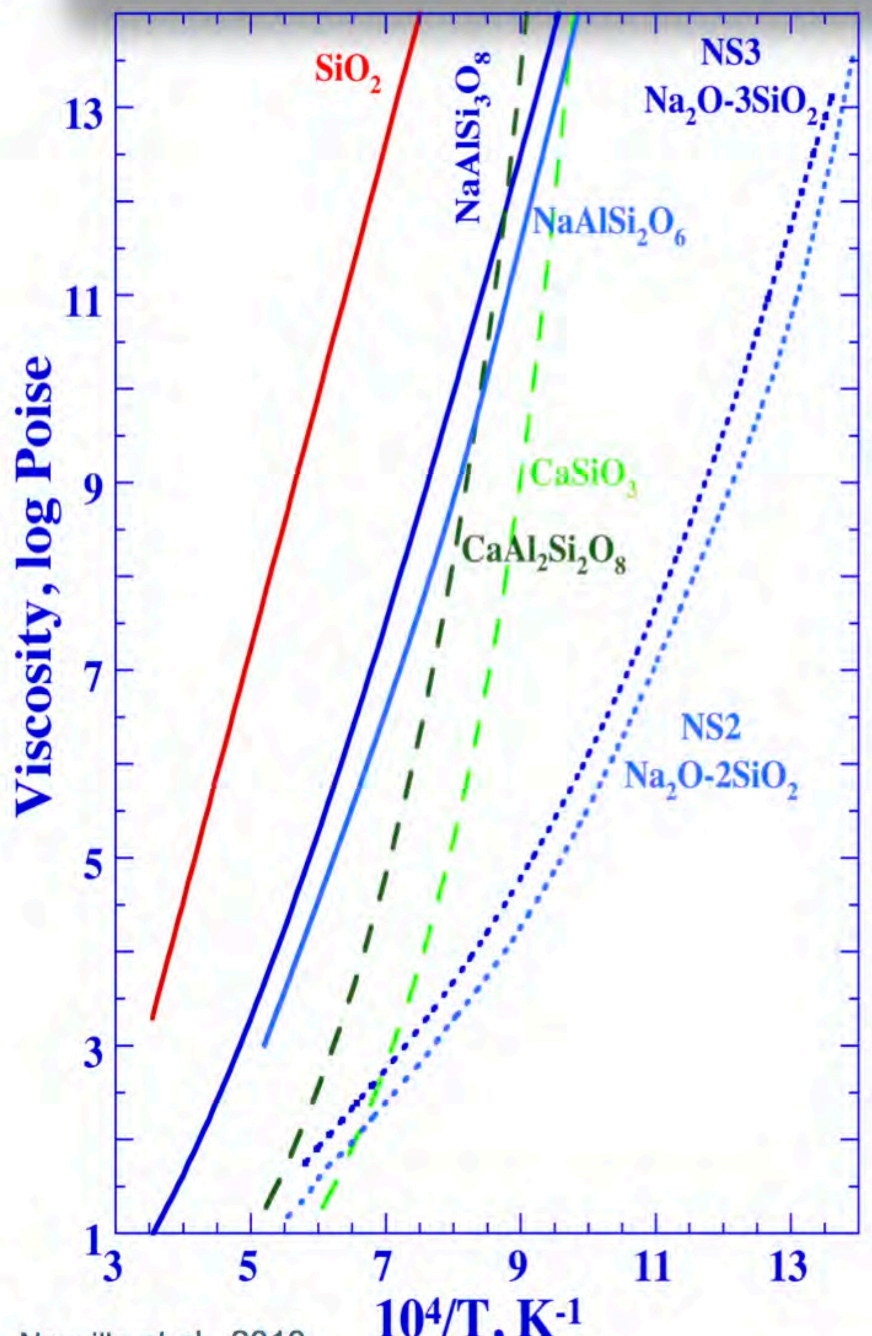
$$\log \eta = A_1 + B_1/(T-T_1)$$

But, just a fit …..

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

Proposed by Adam and Gibbs, 1964

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



Neuville et al., 2010

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

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

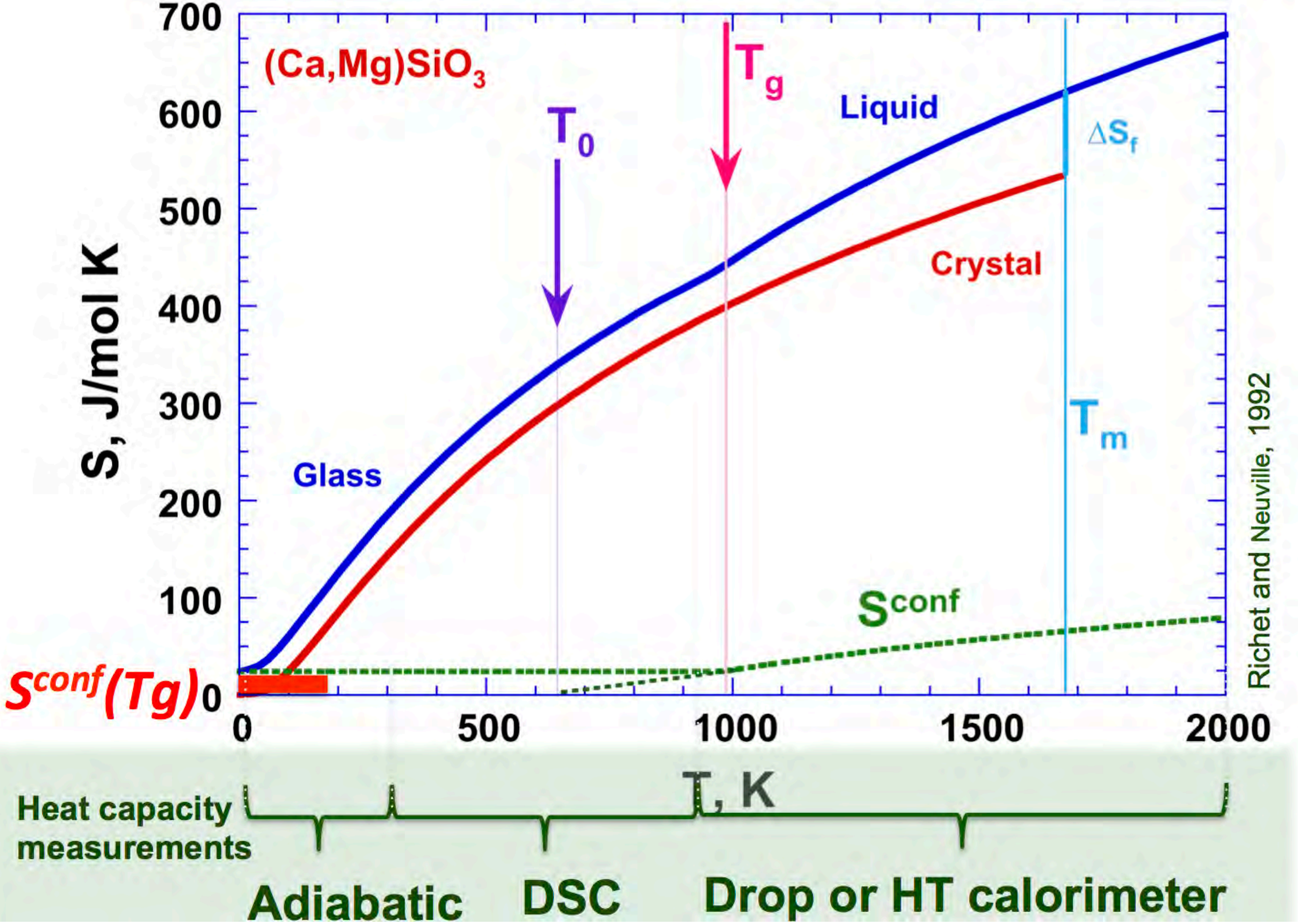
Calorimetry measurements

=> Easy

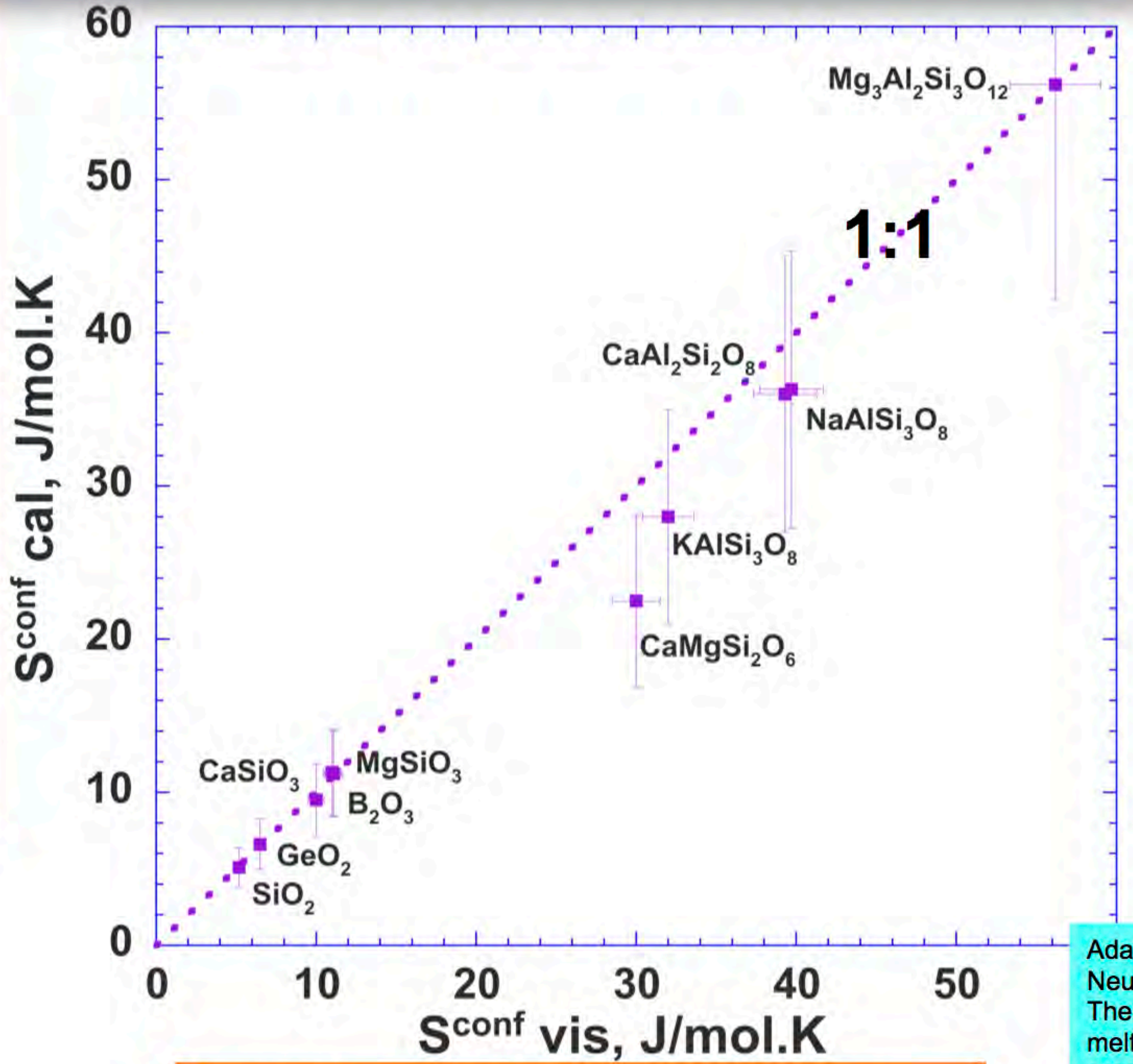
$S^{conf}(Tg)$

⇒ What is that ?

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



Calorimetrical Configurational entropy

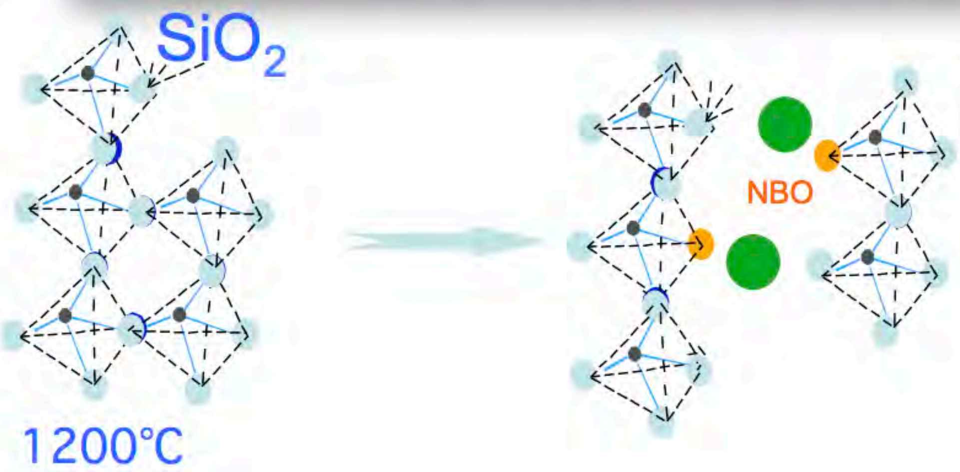


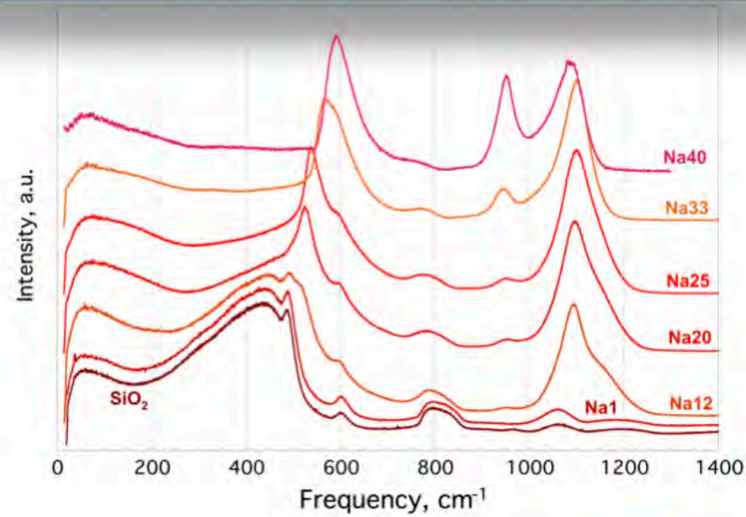
Viscosimetry configurational entropy

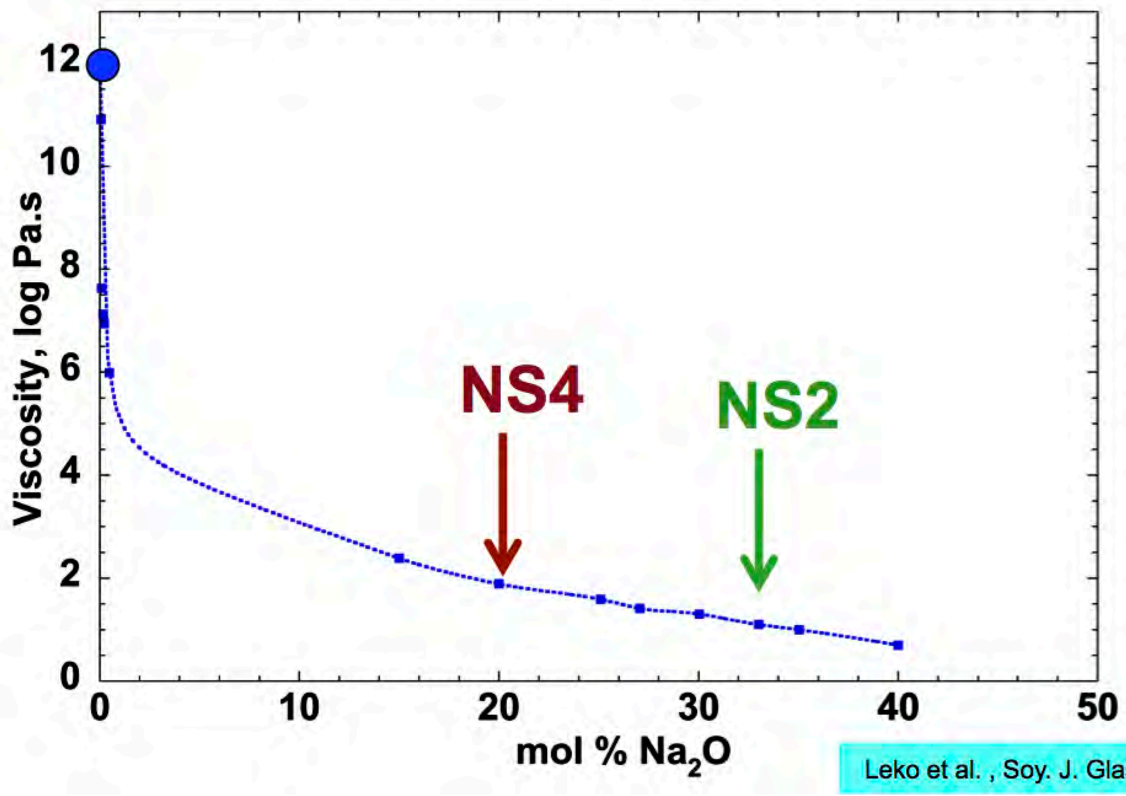
Adapted from : Richet P. and Neuville D.R. (1992) Thermodynamics of silicates melts: Configurational properties. Adv. Phys. Geochim., 10, 132-161.

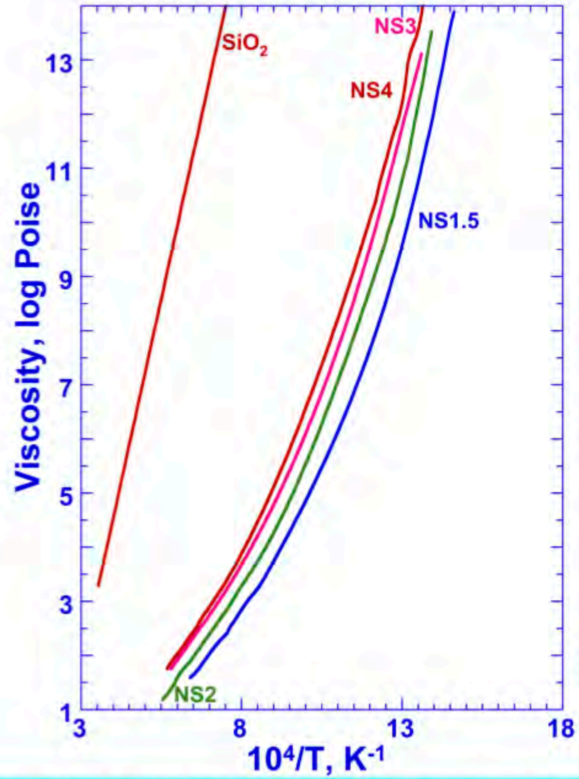
$S^{conf} \sim \eta$ *versus* structure

Structure versus properties of silicate melts



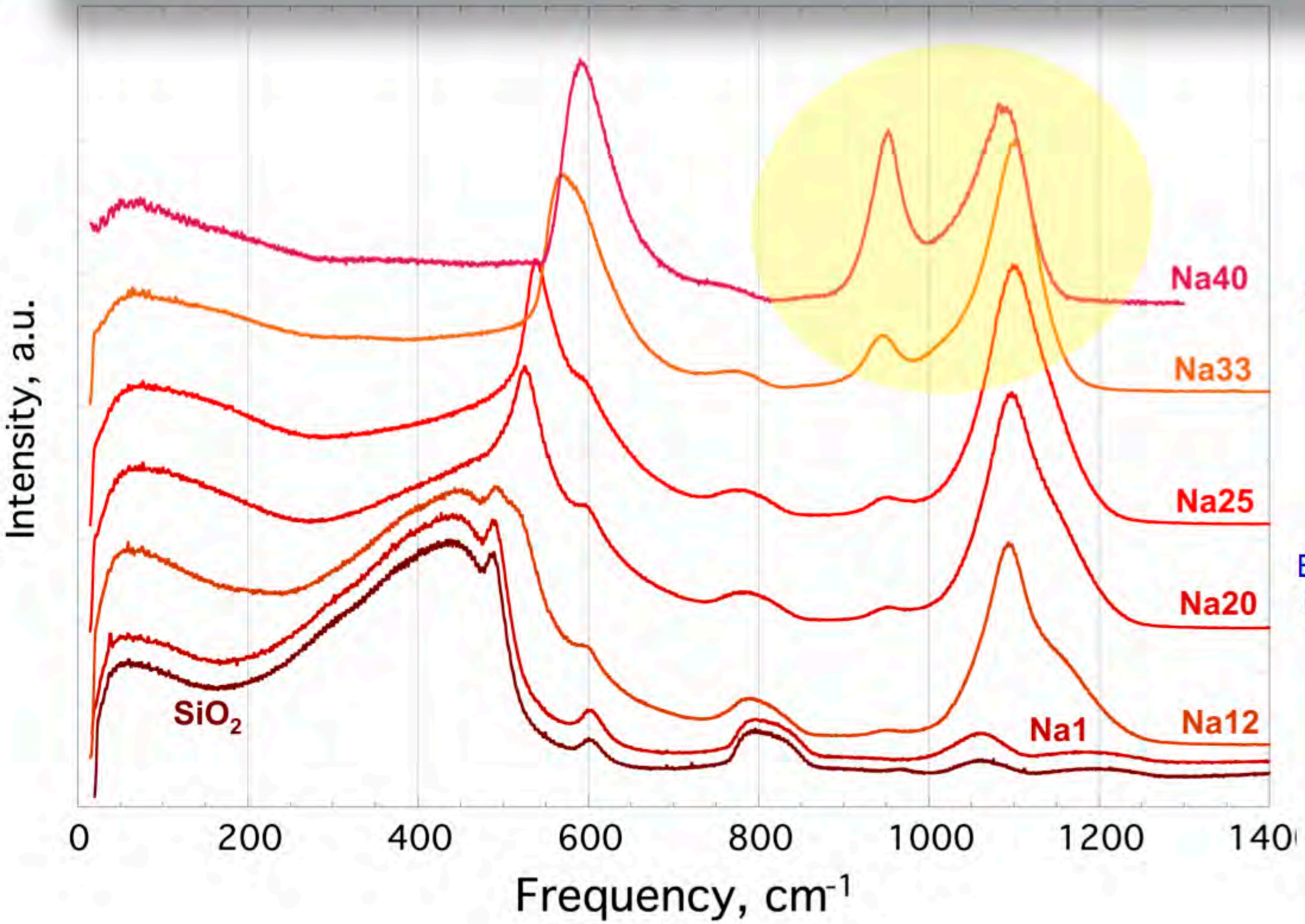


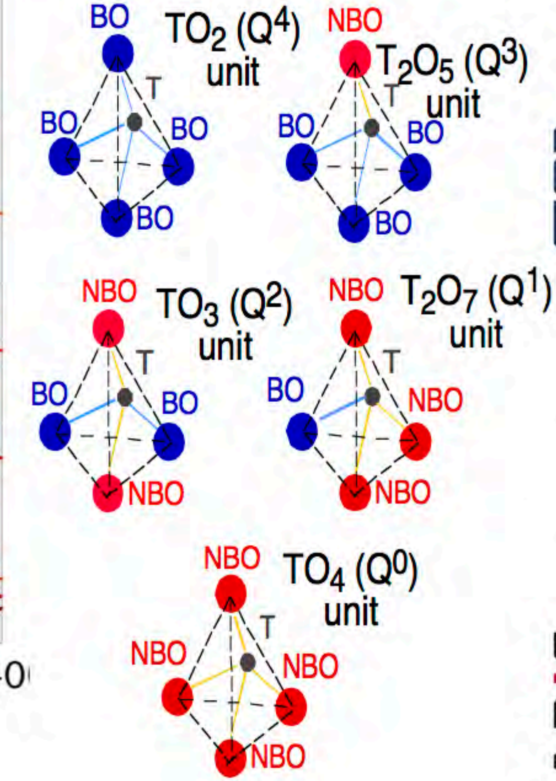


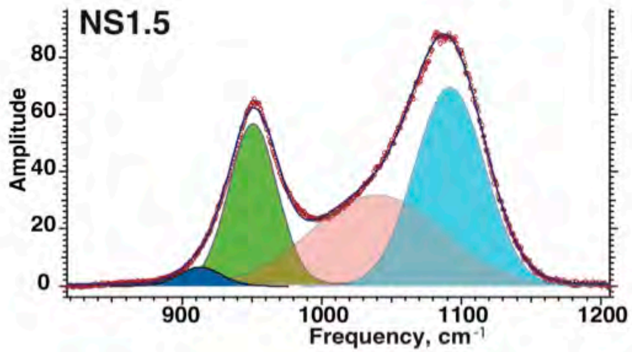


Leko et al. , Soy. J. Glass Phys. Chem., 1977, 3, 204-210 and Neuville, Chem Geol, 2006, 229, 28-42

Raman spectra of SiO_2-Na_2O glass

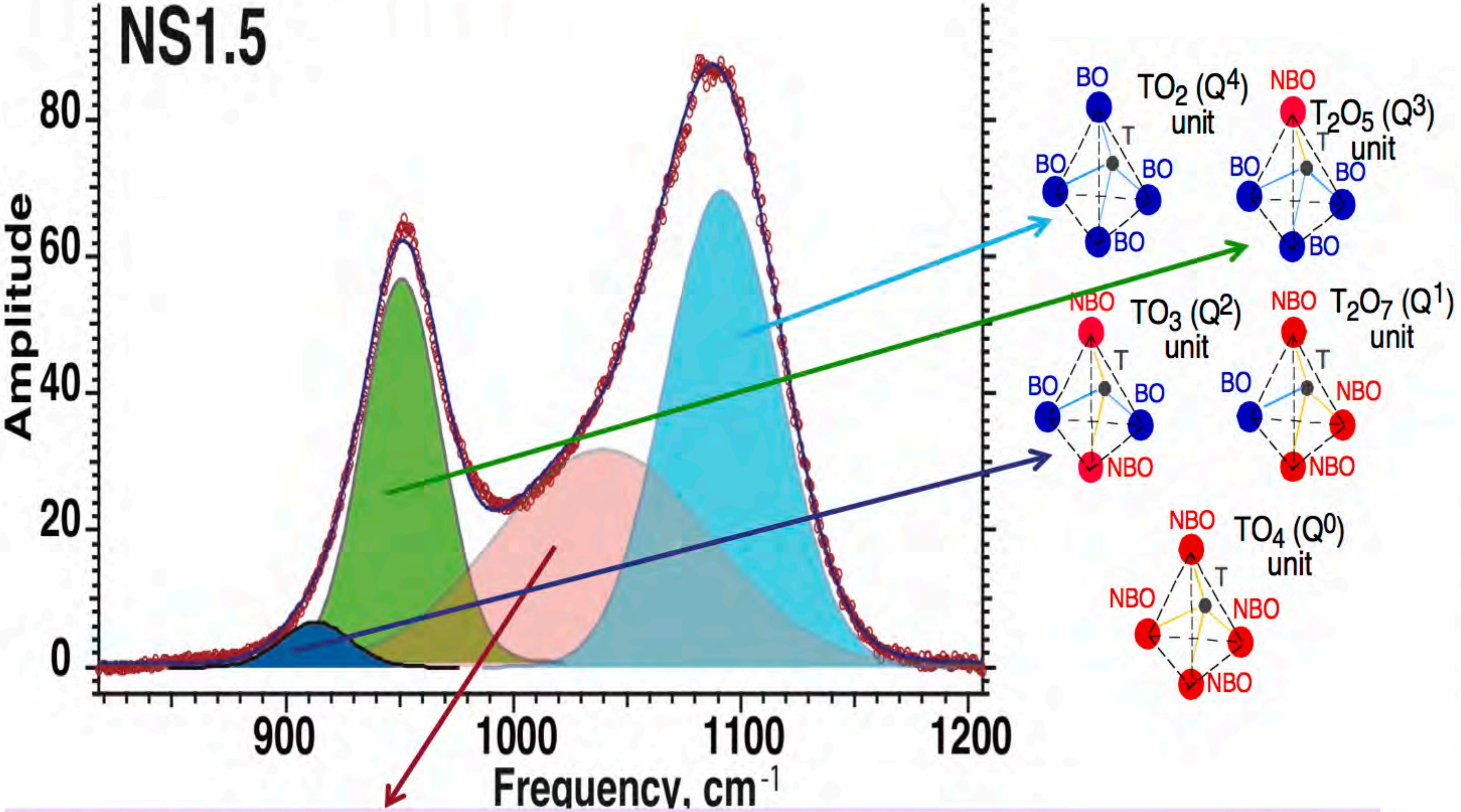






Raman spectra of SiO_2-Na_2O glass — Q^n species

T-O-T stretching vibration



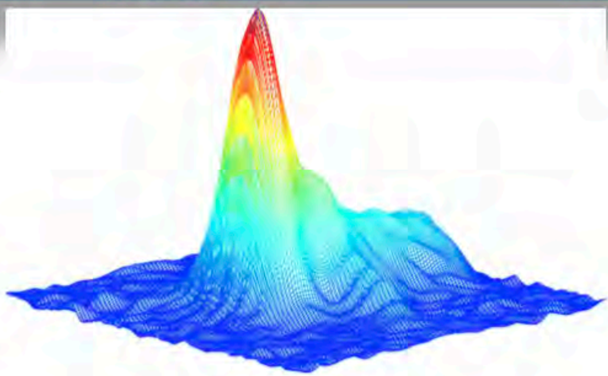
T_2 mode of TO^4 tetrahedra, Q^4, two oxygen atoms moving closer to the central Si atom while the two others oxygen atoms are moving away (Sarnthein et al. 1997; Taraskin and Elliott 1997; Pasquarello et al. 1998)

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

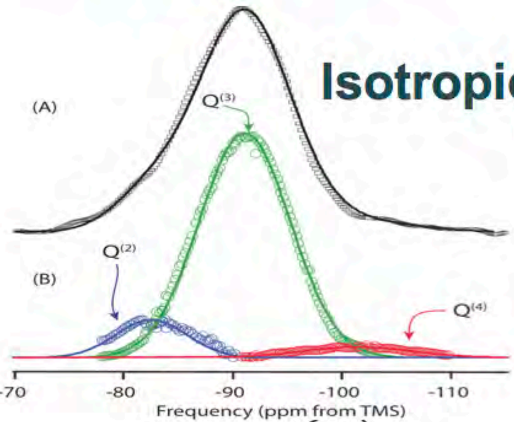
NMR — Q^n species — X-ray absorption

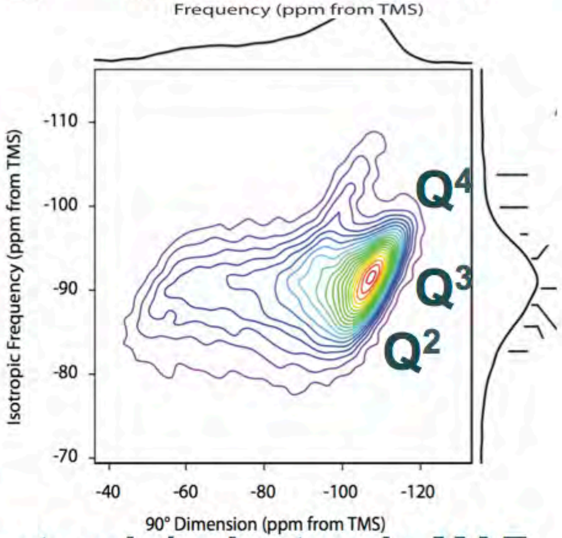
^{29}Si MAF Spectrum of K_2O-2SiO2 glass

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



Isotropic MAS





Isotropic/anisotropic MAF

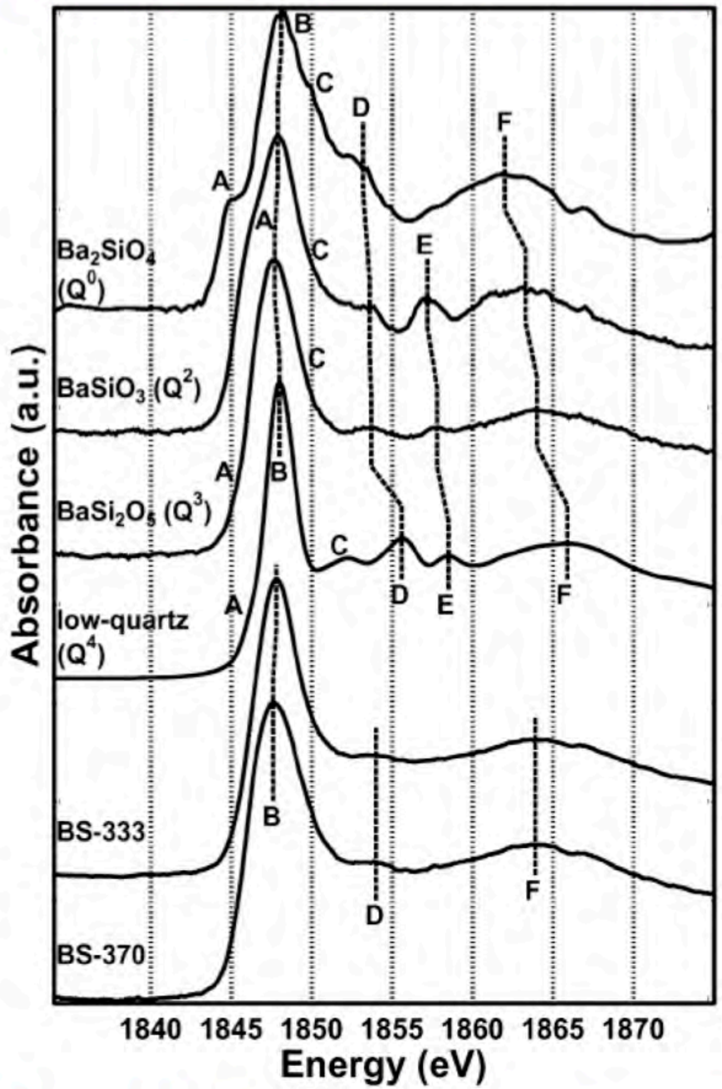
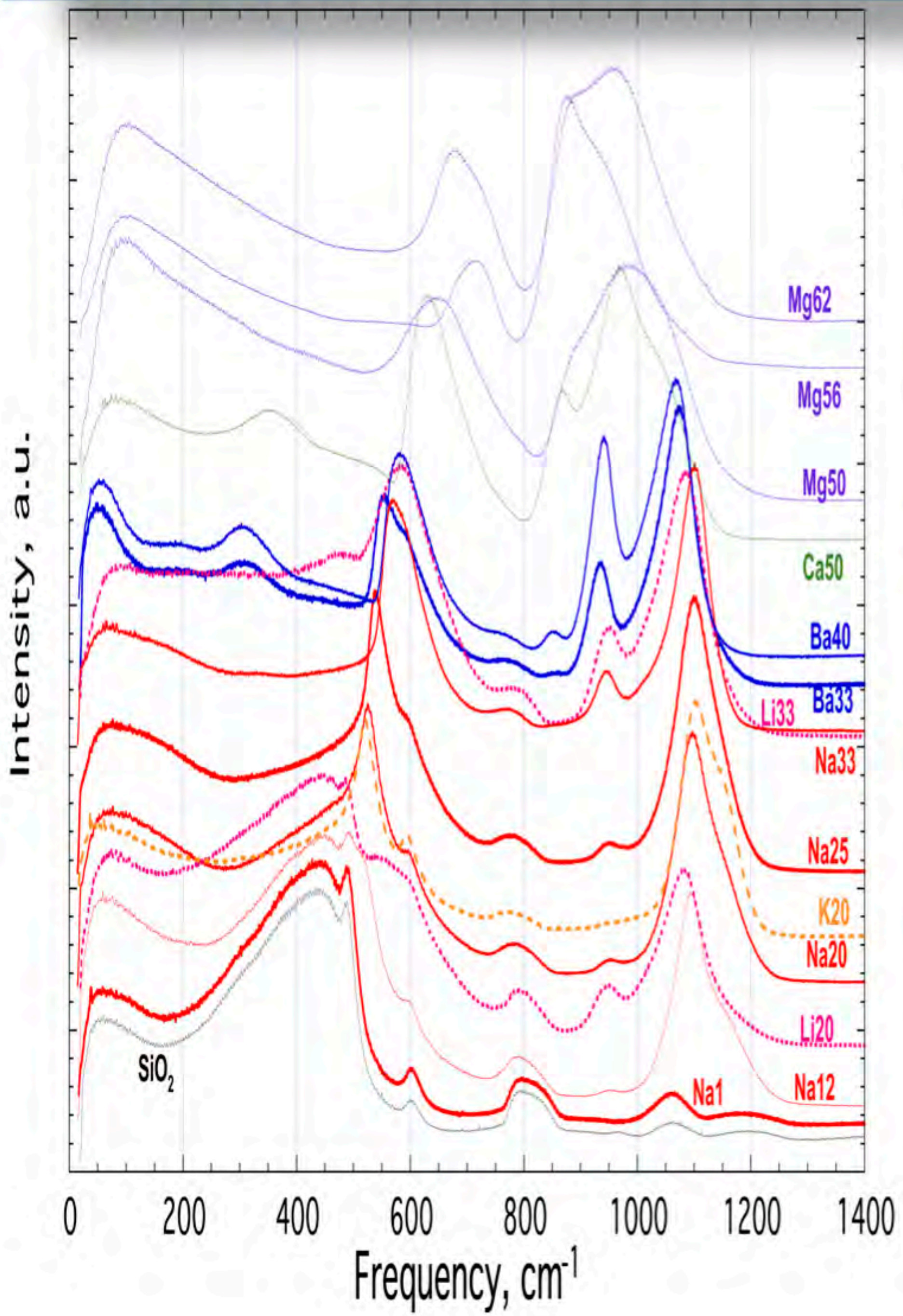
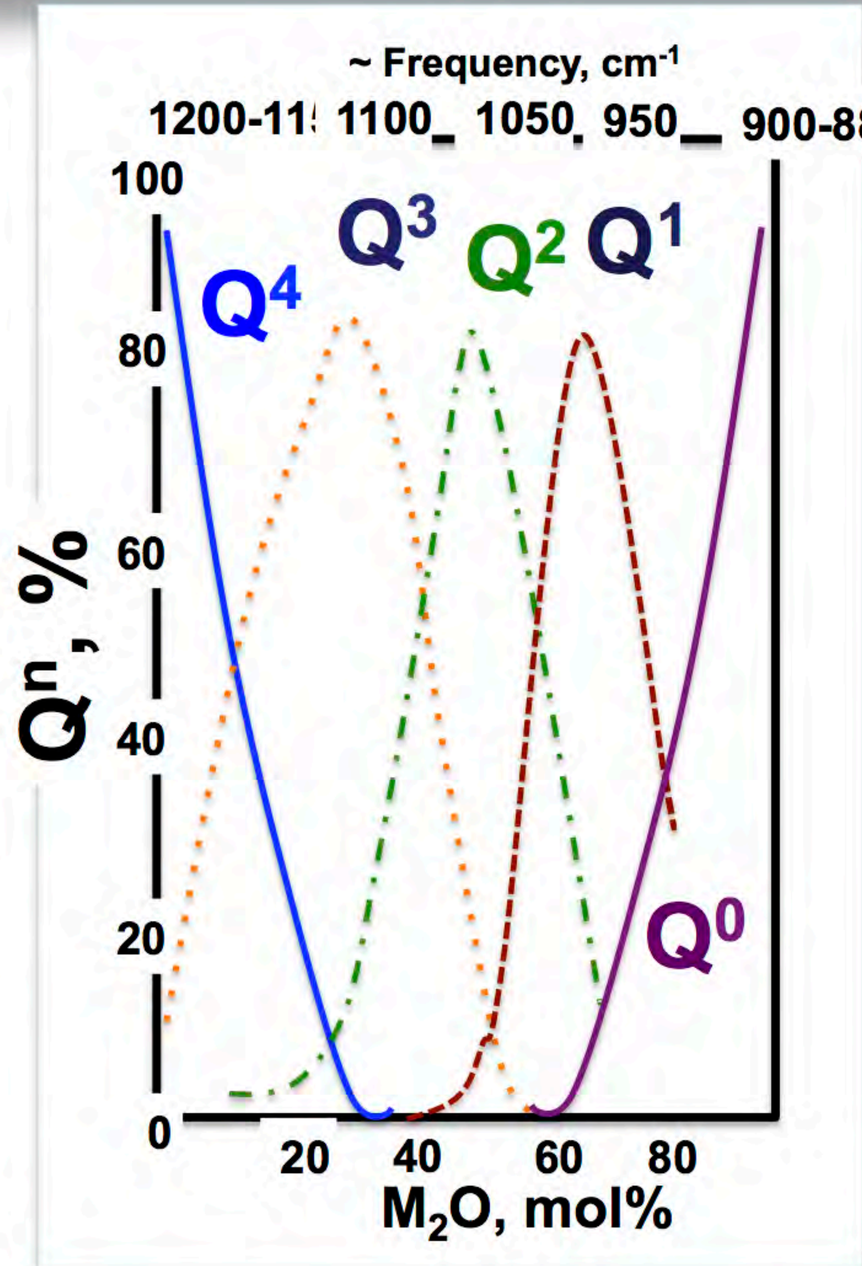


Fig. 1. Si K-XANES spectra of barium silicates, low quartz and the amorphous samples BS-333 and BS-370.

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

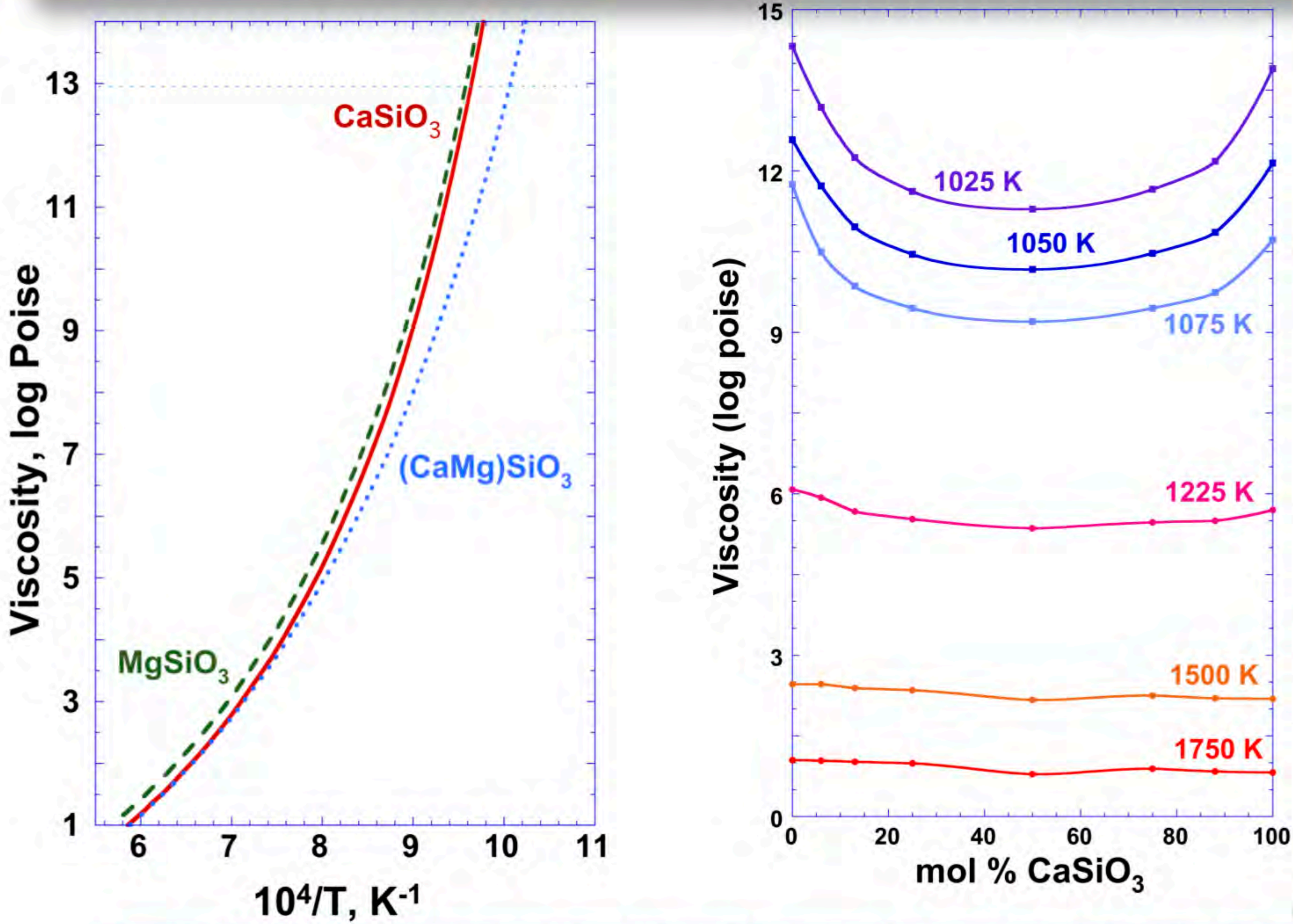
Qⁿ species





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

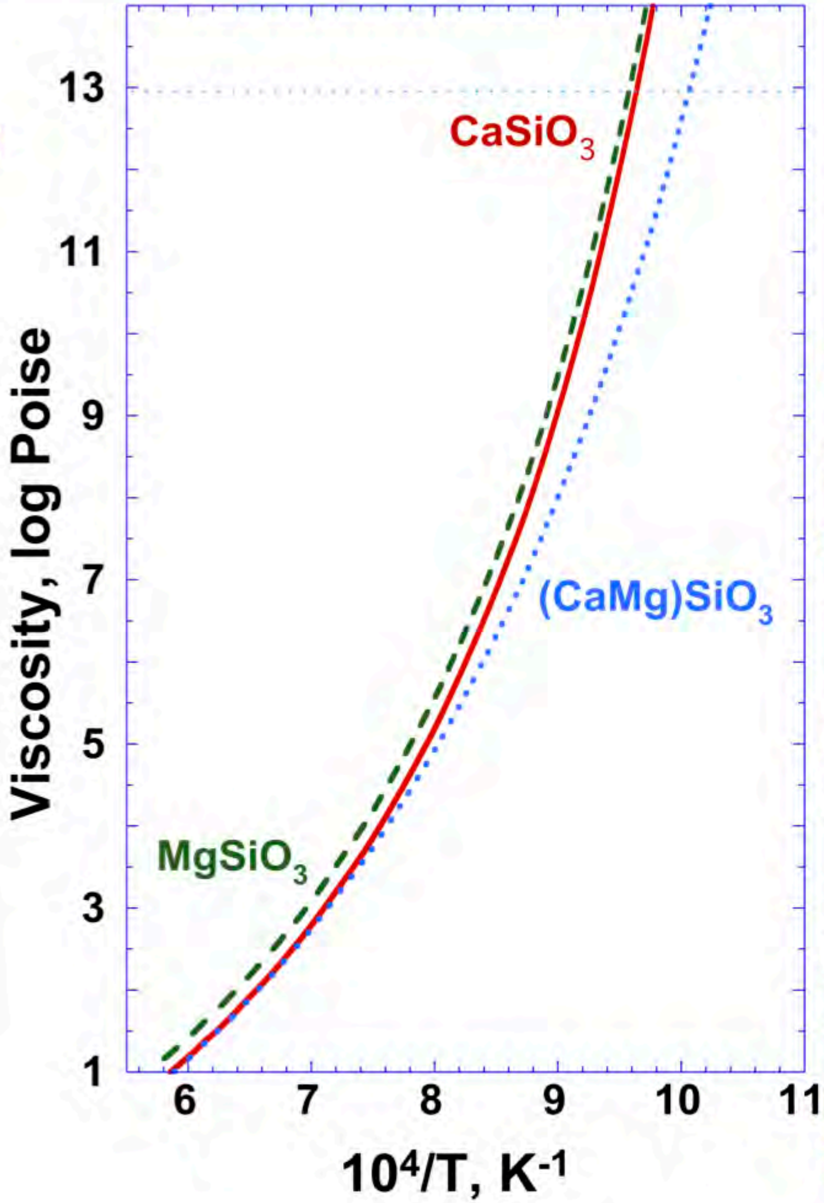
Ca/Mg Mixing ?

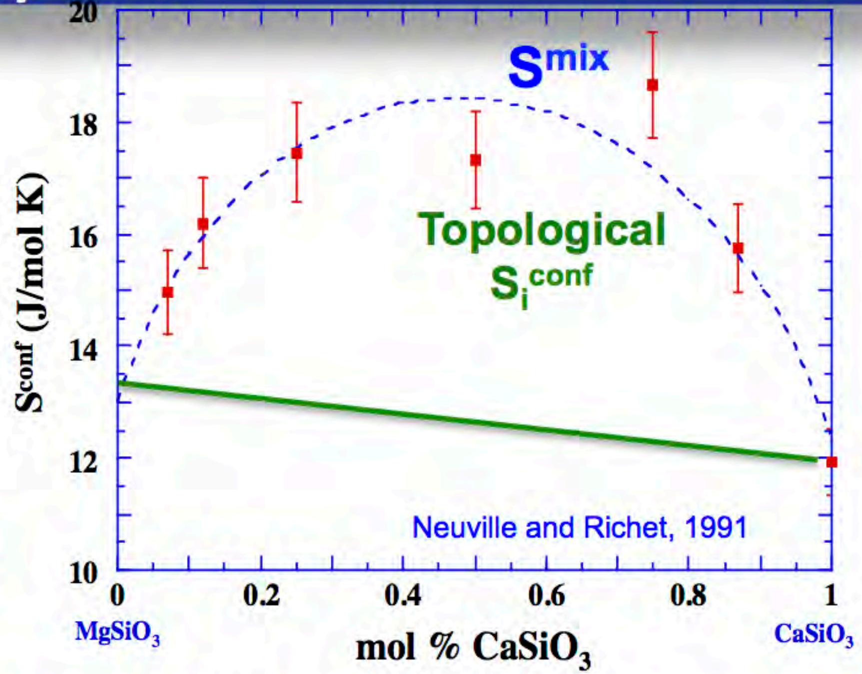


Neuville D.R. and Richet P. (1991) Viscosity and mixing in molten (Ca,Mg) pyroxenes and garnets. Geochim. Cosmochim. Acta., 55, 1011-1021.

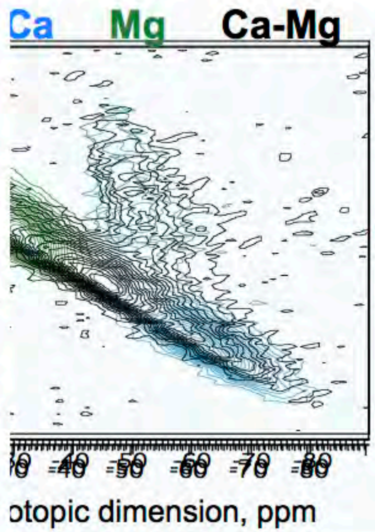
Entropy theory (Adam et Gibb, 1965)

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





/lg)



- 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

Morey and Bowen, (1925)

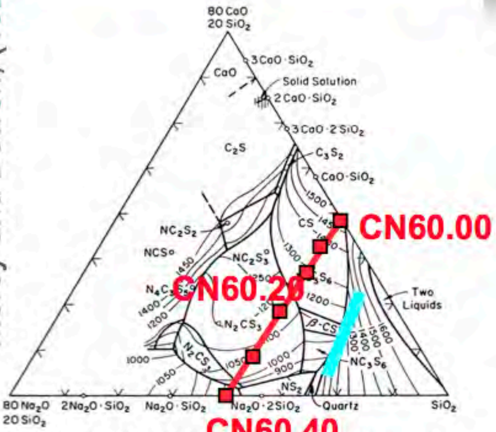
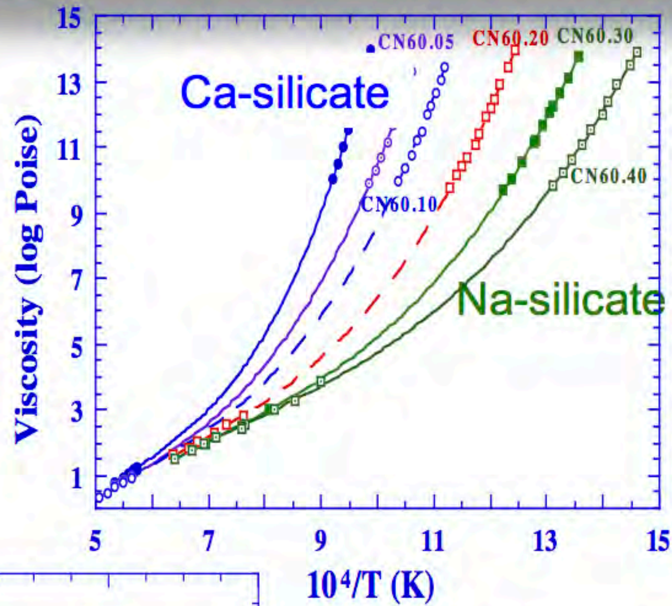
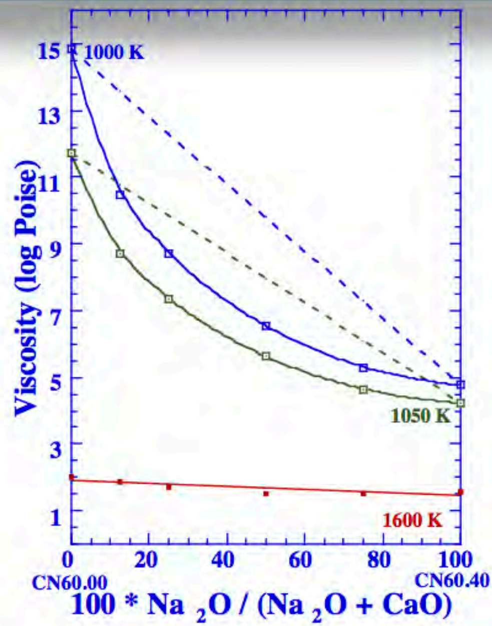
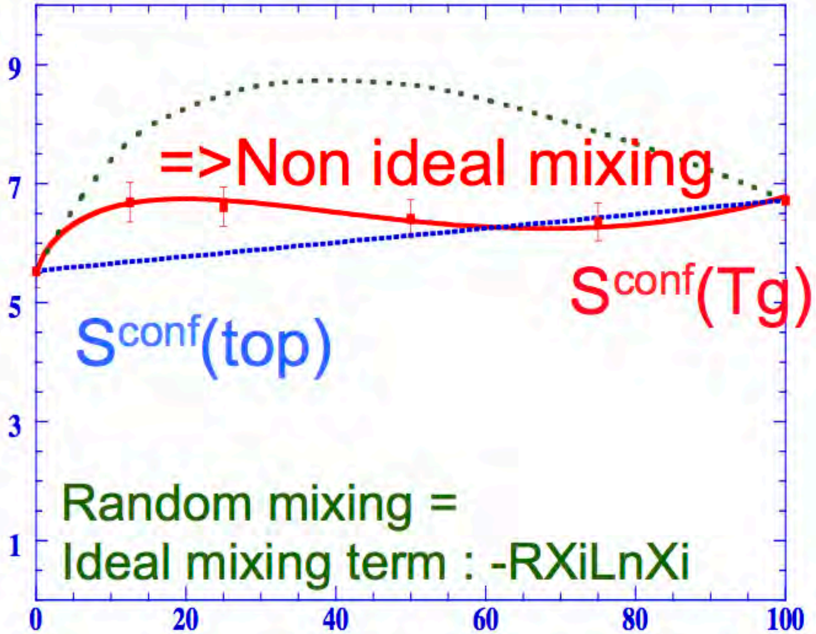


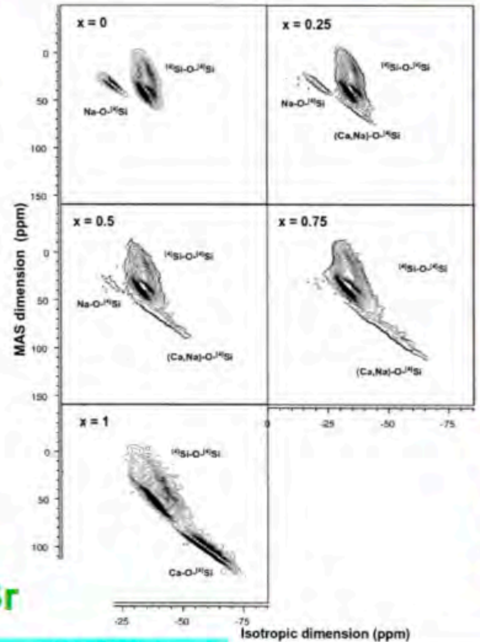
FIG. 481.—System Na_2O–CaO–SiO_2. N = Na_2O; C = CaO; S = SiO_2
The area NS-CS-SiO_2 after Morey and Bowen, Fig 482.
E. R. Segnit, Am. J. Sci., 251 [8] 590 (1953).







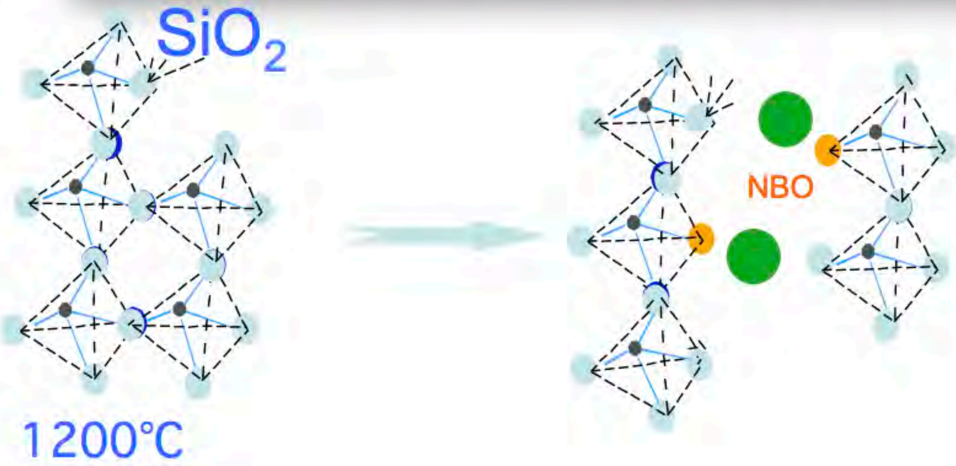
Ideal mixing does not work between Na/Ca and Na/Sr

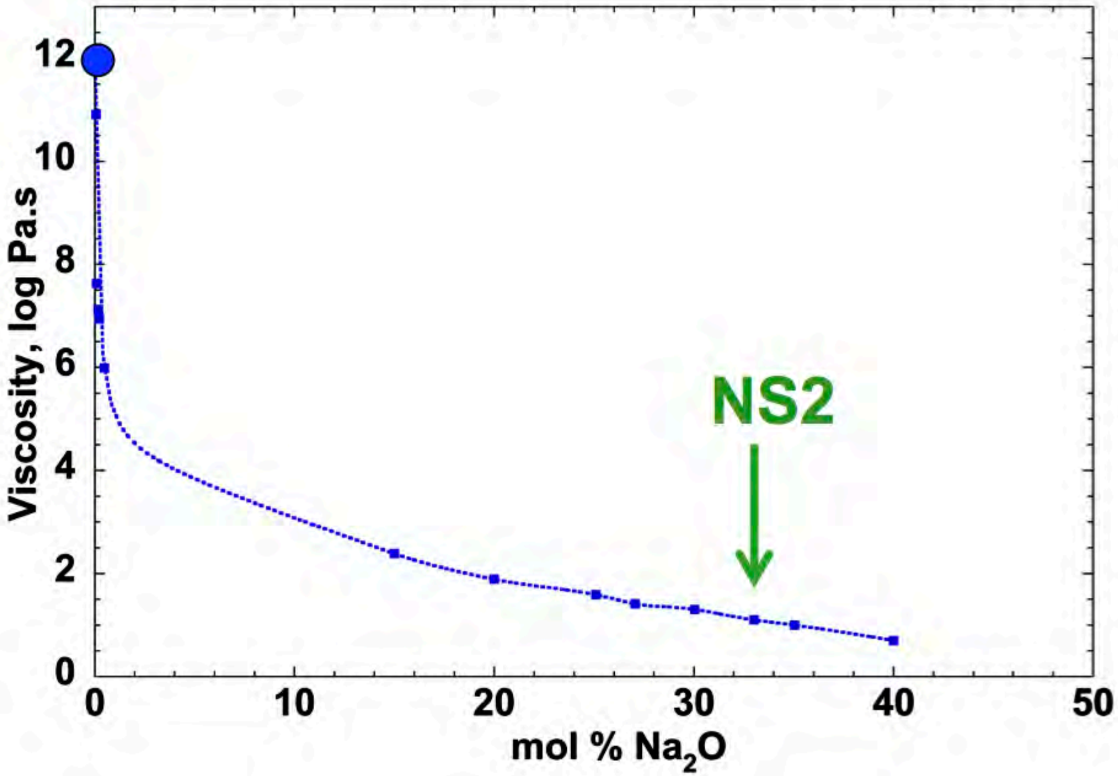


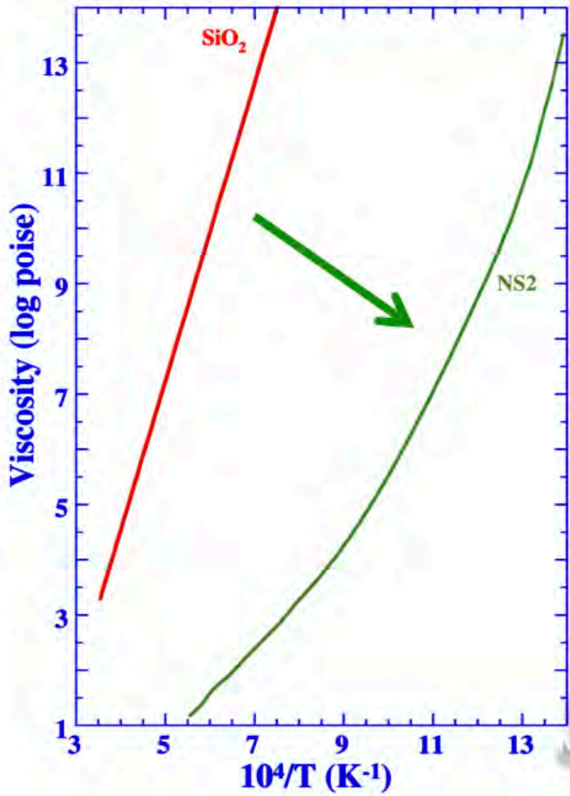
Raman spectrocopy (Neuville, 2006) and ^{17}O NMR (Lee and Stebbins, 2003) show a **non random distribution of Na and Ca.**

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

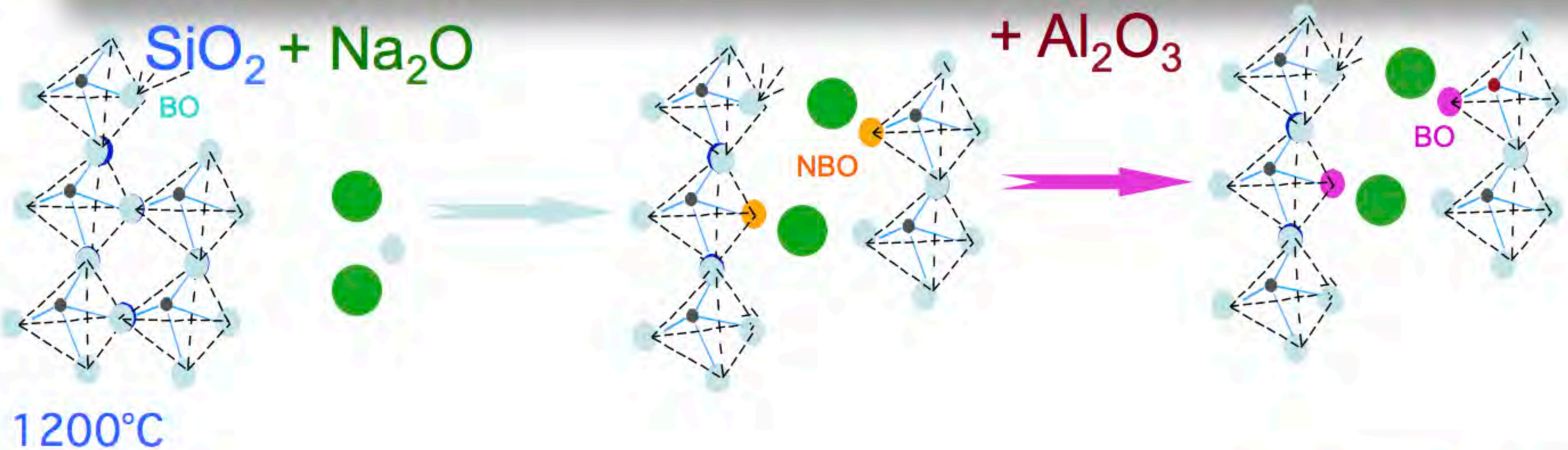
Structure versus properties of silicate melts

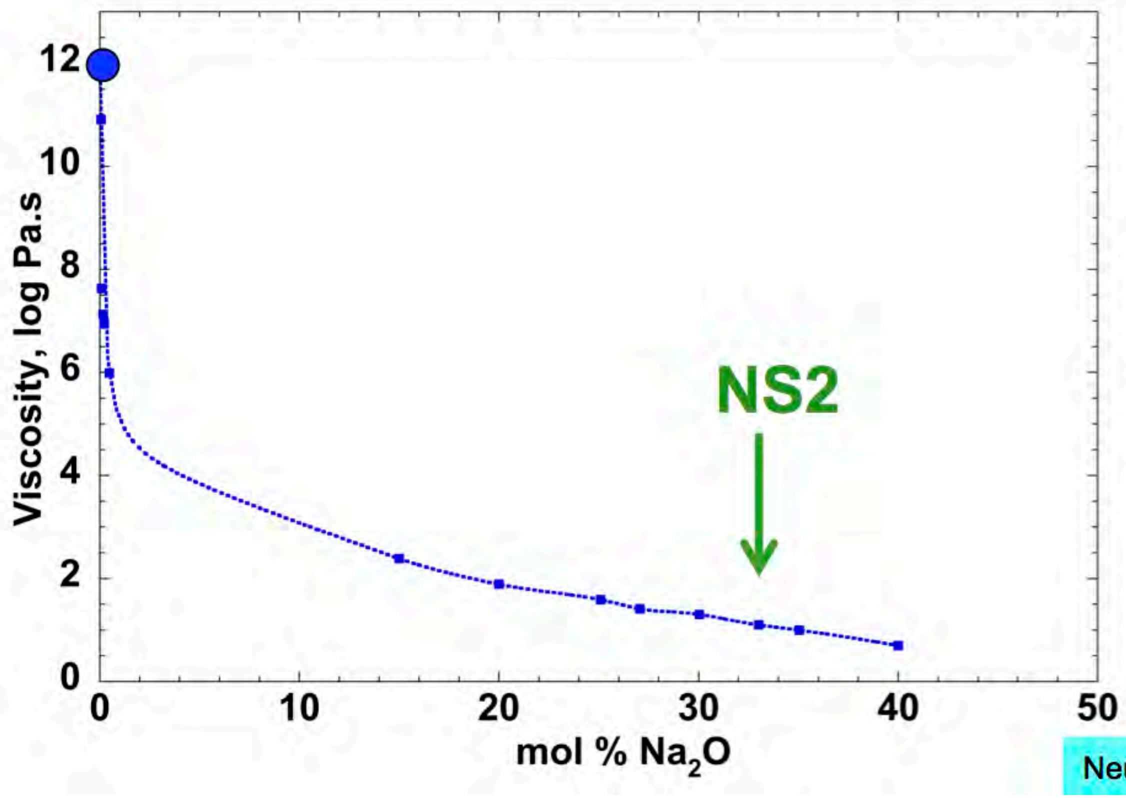


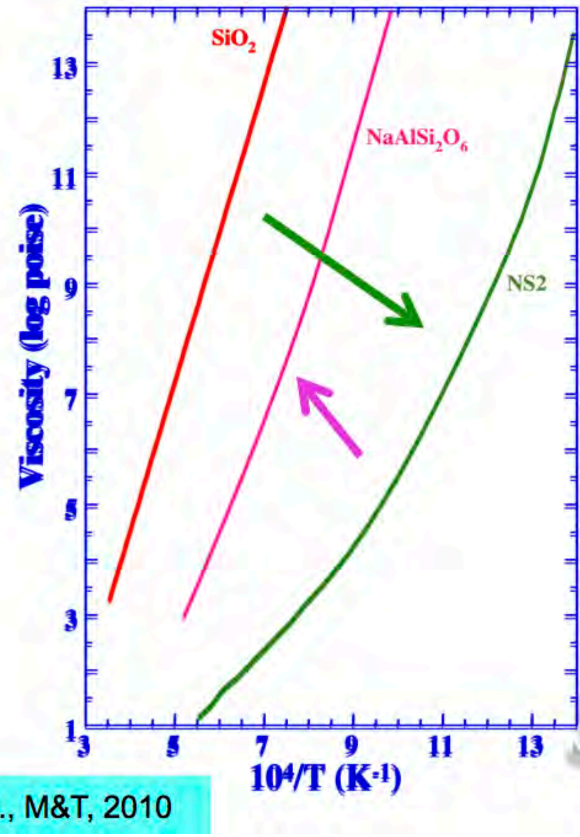




Structure versus properties of silicate melts



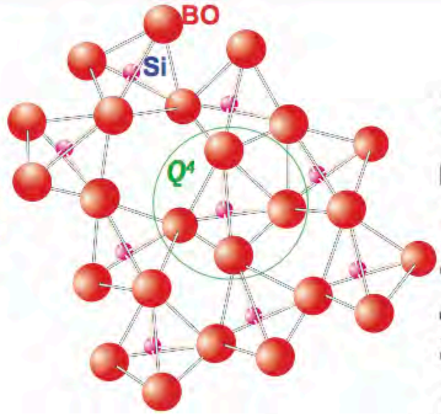


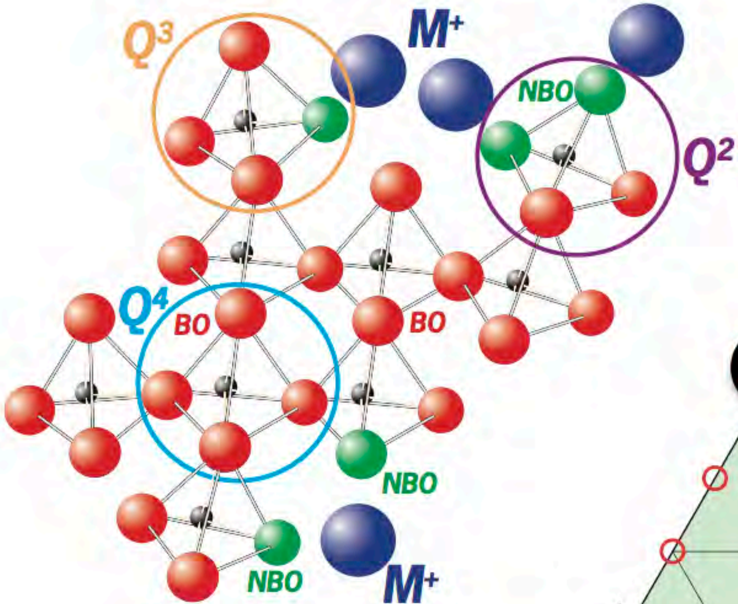


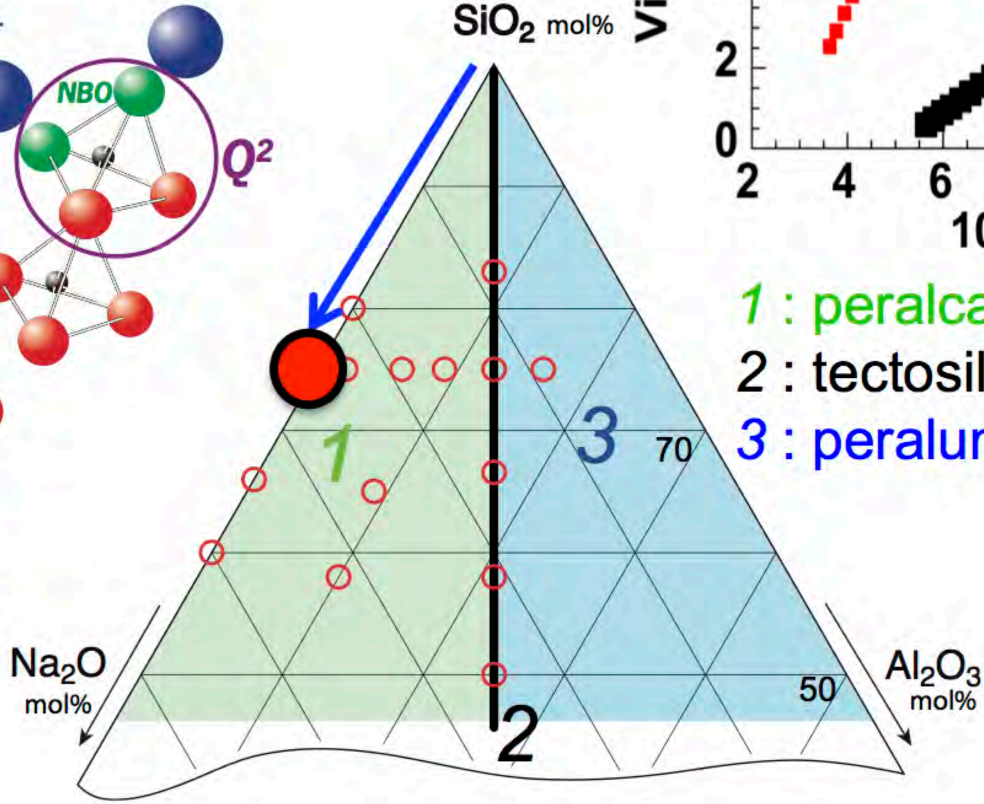
Neuville et al., M&T, 2010

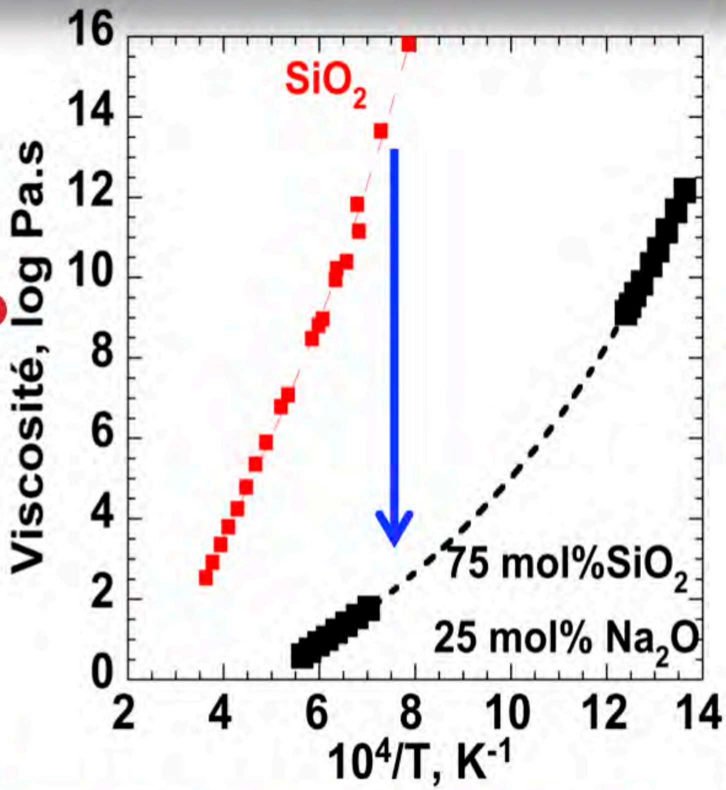
Adding Na_2O to SiO_2

⇒ Depolymerisation, formation of NBOs









1 : peralcalin: Na > Al

2 : tectosilicate: Na = Al

3 : peraluminous: Na < Al

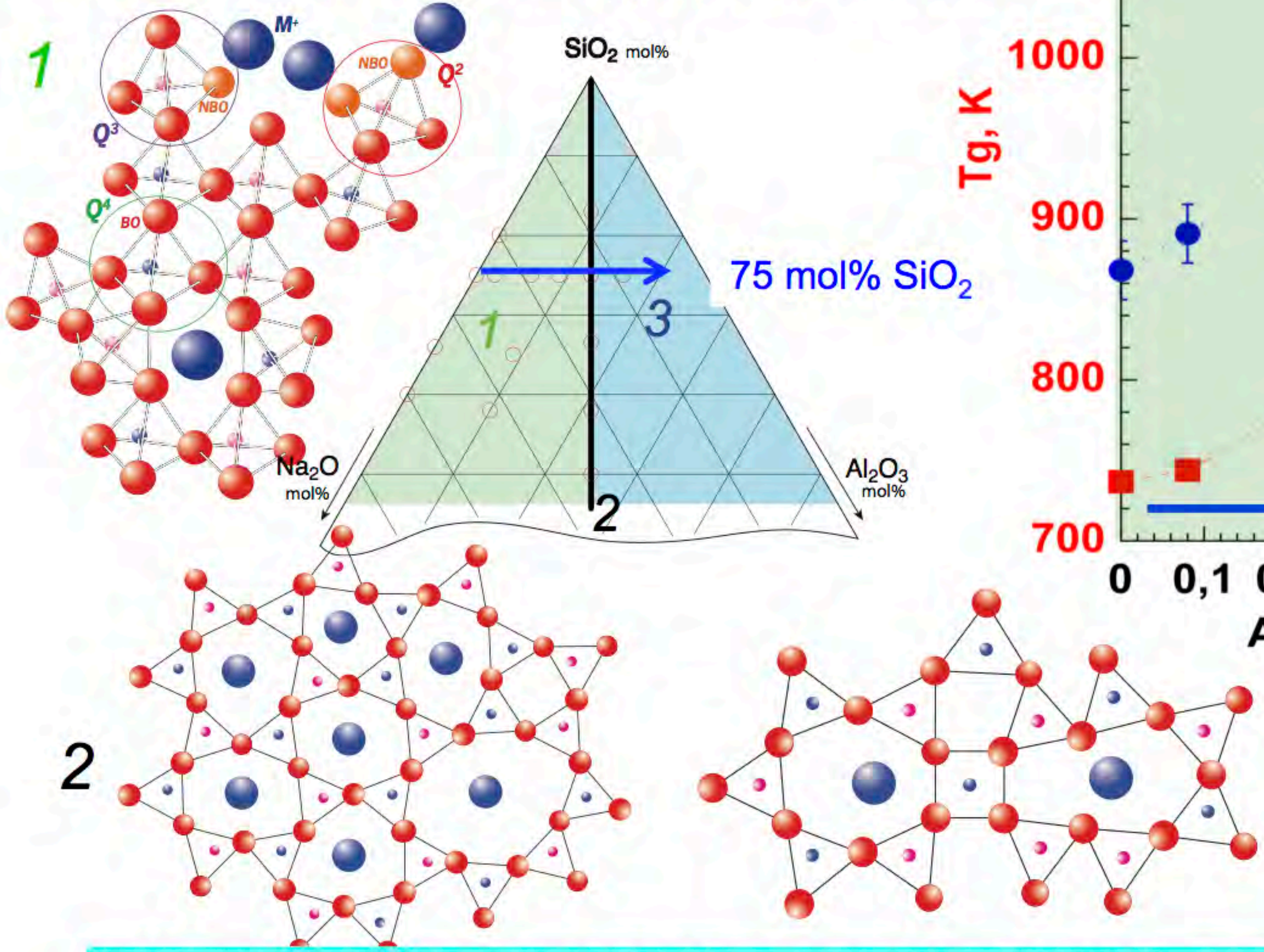
Aluminium effect

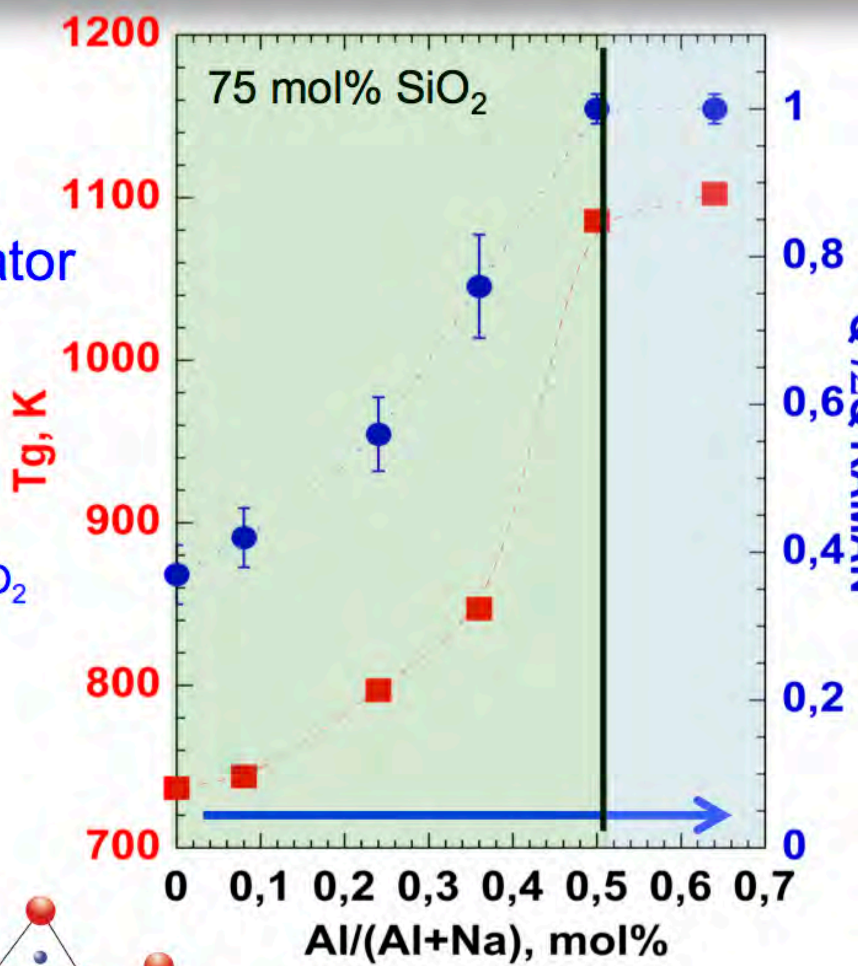
Na_2O substitution by Al_2O_3 :

⇒ Polymerization

⇒ Change Q^3 in Q^4

⇒ Al in Q^4 and Na charge compensator





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