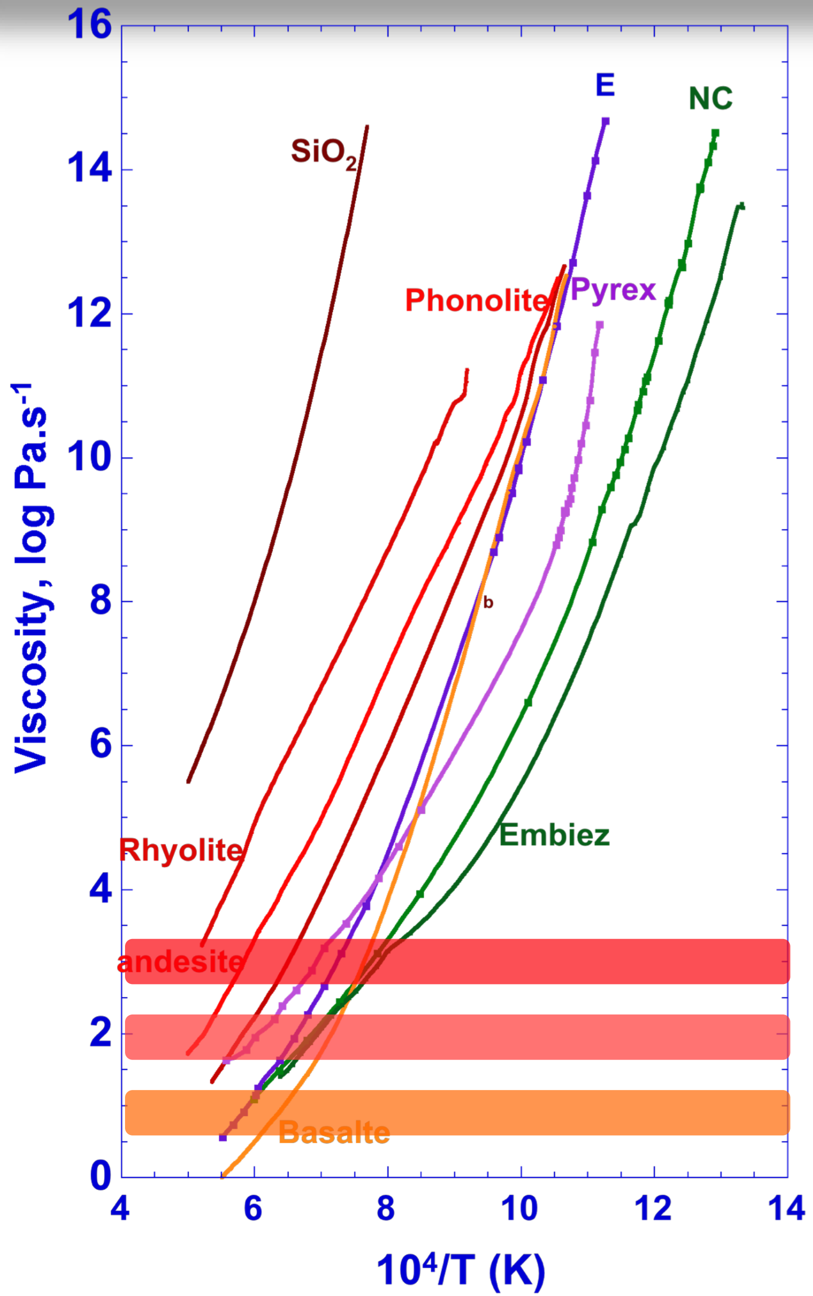
Structure "and properties" of glasses and melts

Daniel R. Neuville
Géomatériaux,
IPGP-CNRS-Université de Paris
neuville@ipgp.fr

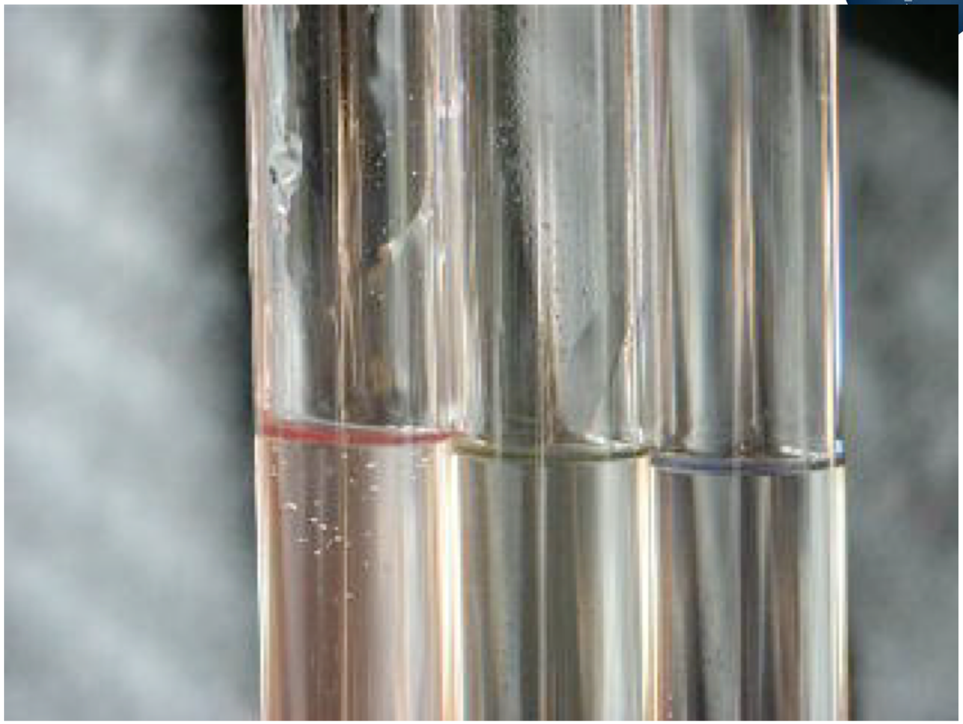
Thanks : C. Le Losq, IPGP
P. Florian, L. Hennet, D. Massiot -CEMHTI
L. Cormier - IMPMC
N. Trcera - SOLEIL

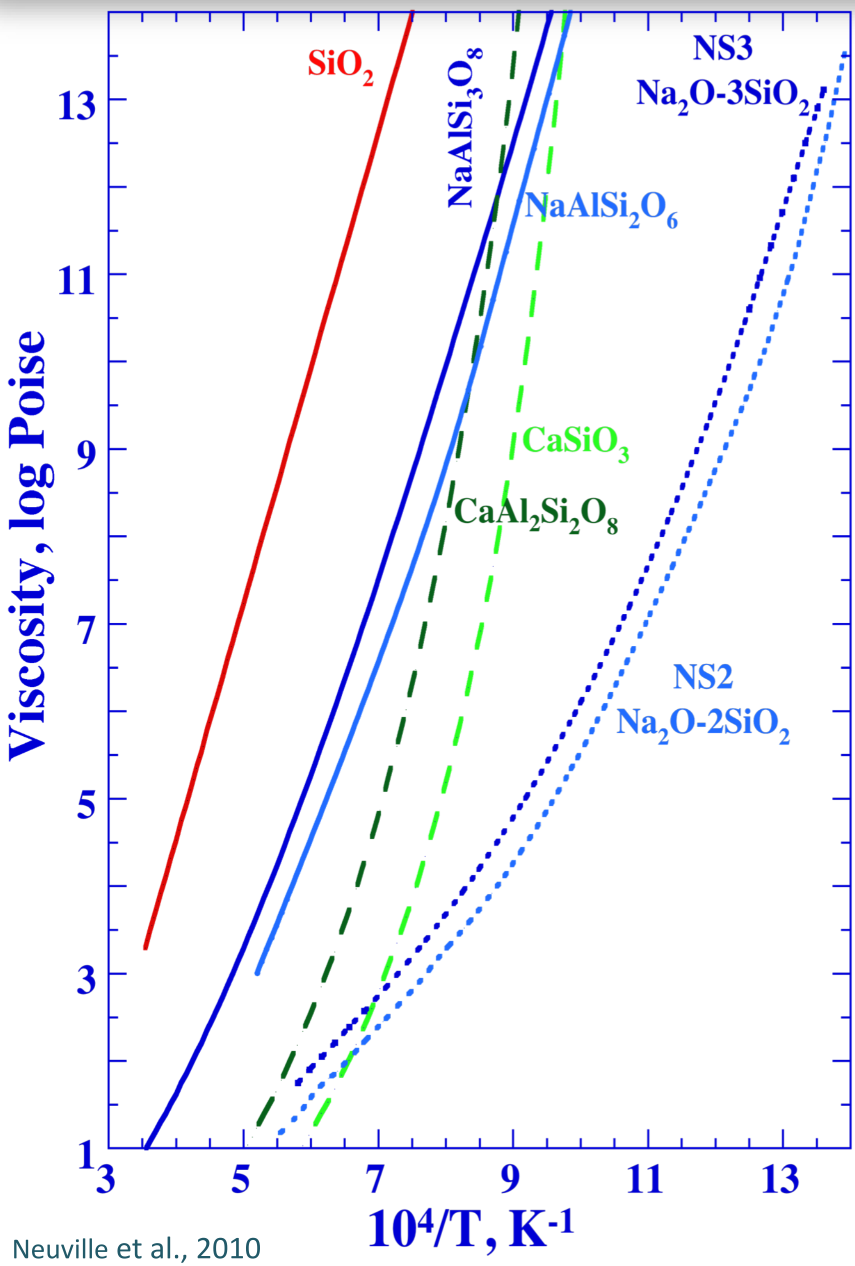

Viscosity, log Pa.s-1
10^4/T (K)
SiO2
E
NC
Phonolite
Pyrex
b
Rhyolite
Embiez
andesite
Basalte
0
2
4
6
8
10
12
14
16
4
6
8
10
12
14

1

2

3





Neuville et al., 2010

Arhenius :

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

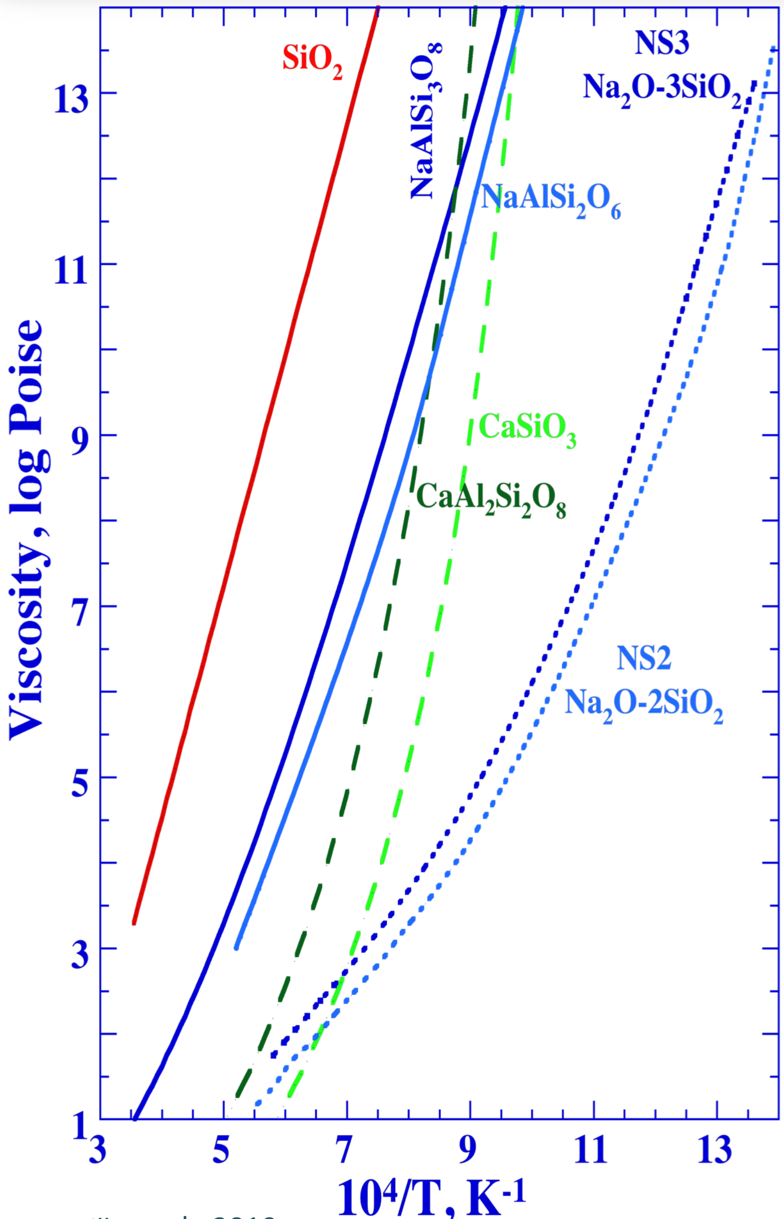
$$\Leftrightarrow \log \eta = A + B/T$$

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 …..



Neuville et al., 2010

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

Proposed by Adam and Gibbs 1965

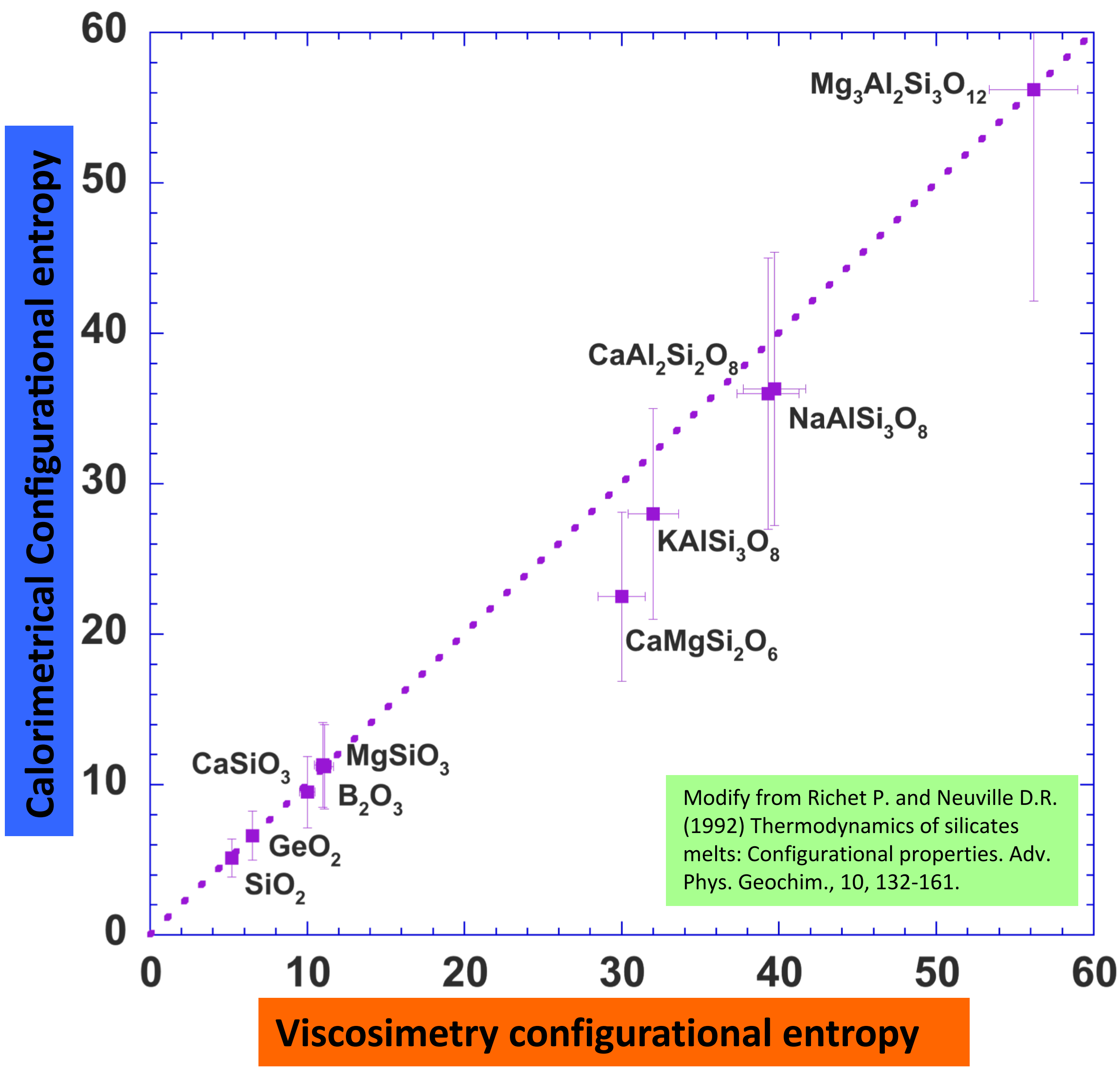
First used to silicate melts by Urbain 1972,

Wong and Angell 1976,
Scherer 1984, Richer 1984, Neuville and Richet 1991….

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

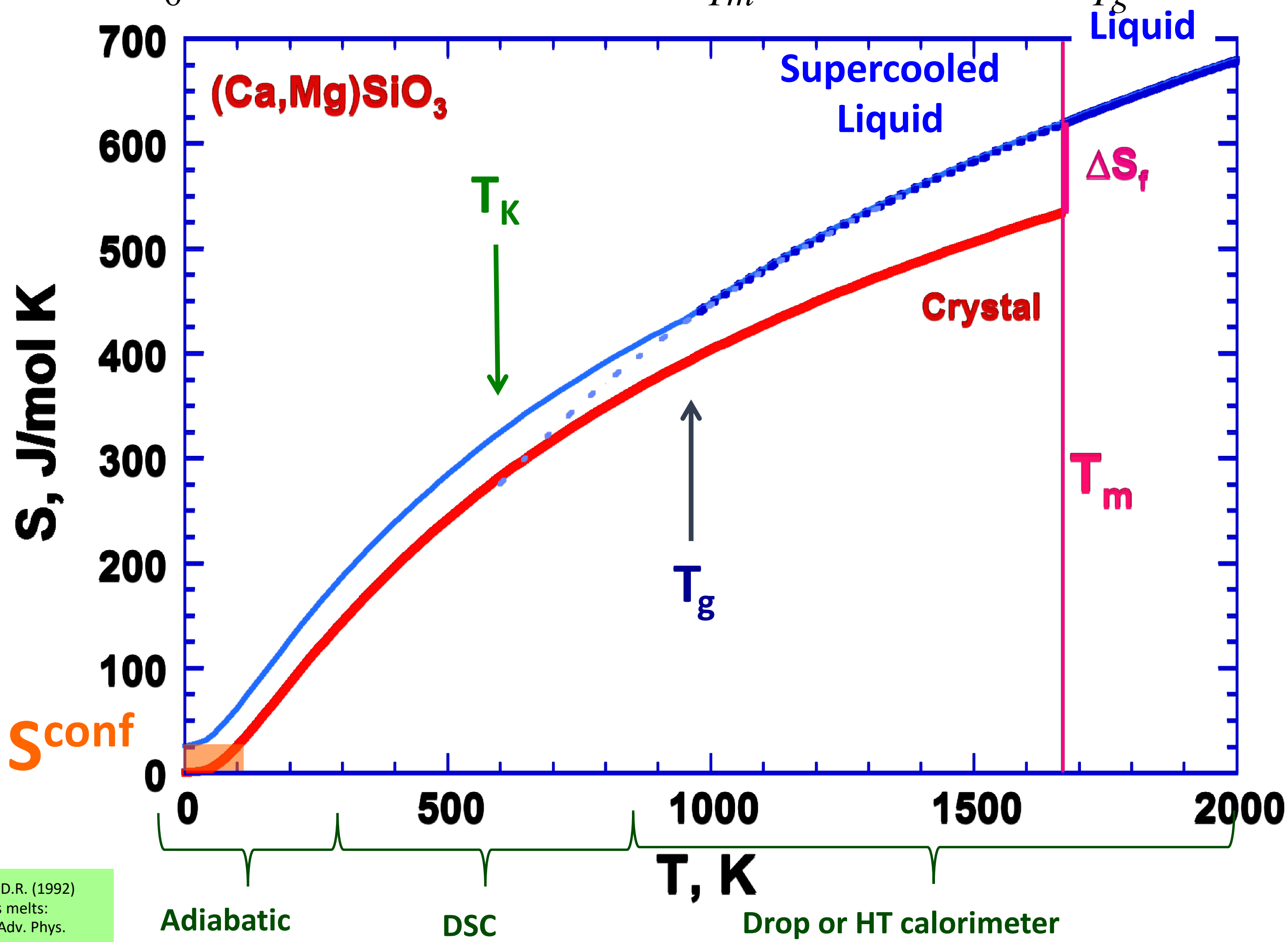
$$Cp^{conf}(T) = Cpg(Tg) - Cpl(T)$$

Calorimetry measurements
=> Easy

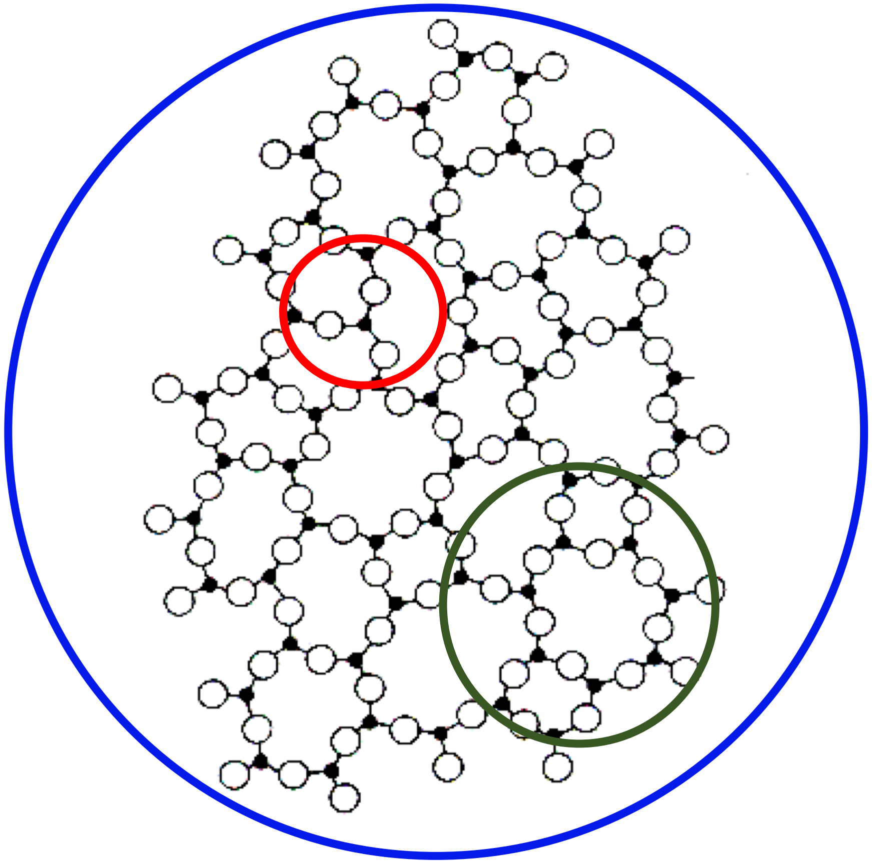


Modify from Richet P. and Neuville D.R. (1992) Thermodynamics of silicates melts: Configurational properties. Adv. Phys. Geochim., 10, 132-161.

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



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



Short range order <3 Å:

– Coordination, bond length, bond angle

– homopolar (-Se –Se, -C-C, -As-As) versus heteropolar (Si-O, B-O, Ge-S)

Medium (intermediate) range order (~3-10Å):

– angles between structural units

– connectivity between structural units (linkage by corner, edge, face)

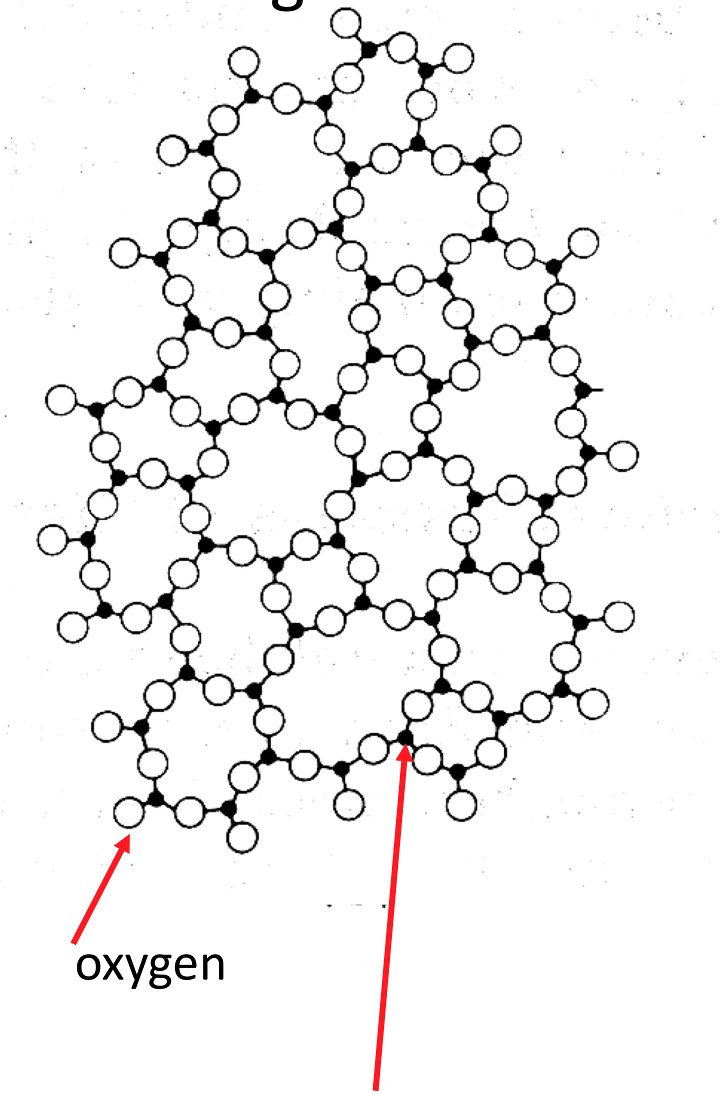
– dimensionnality, rings

Almost no long order (no periodicity !) :

– phase separation

– inhomogeneities

Oxide glass



Zachariasen model (1932)

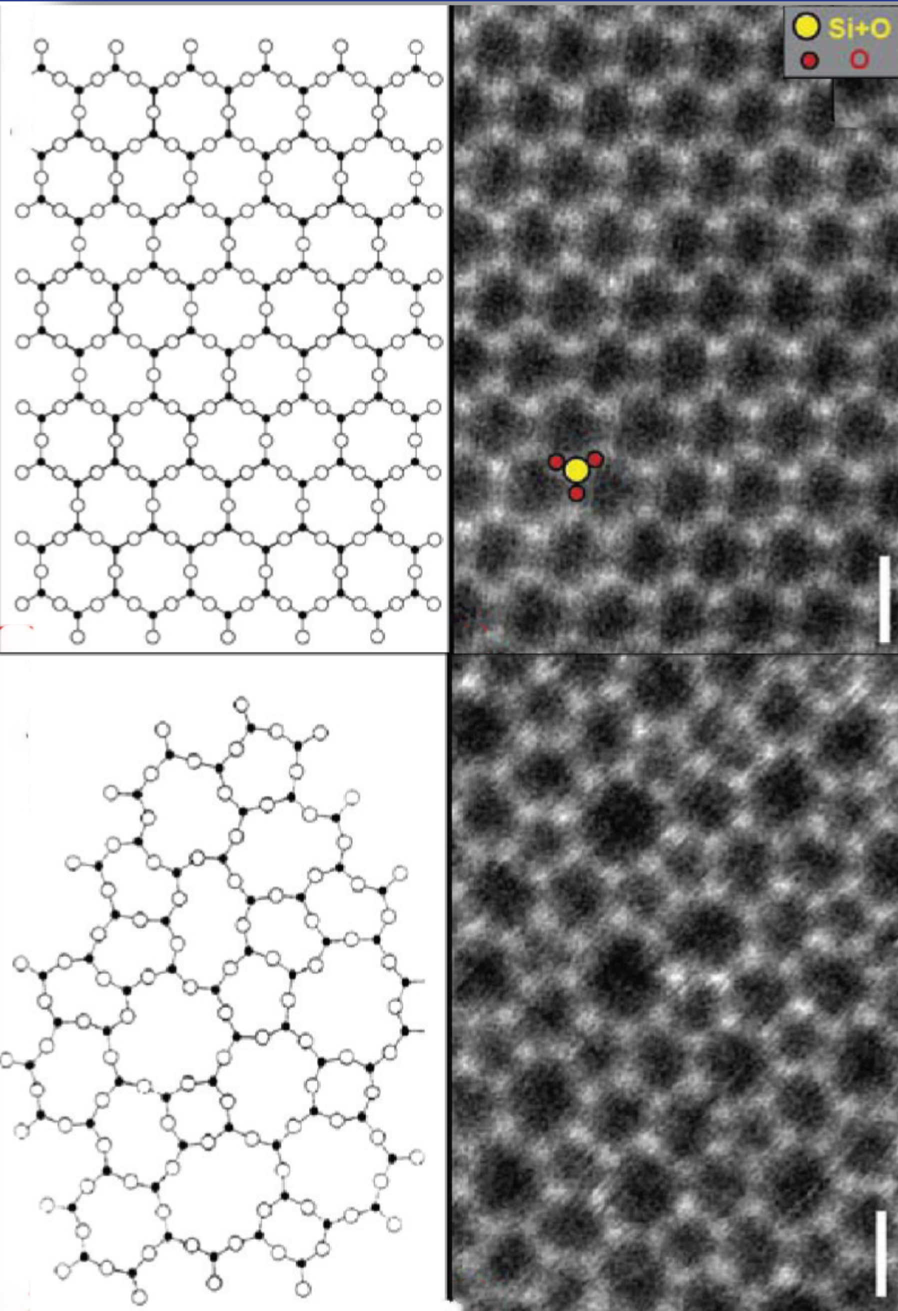
1. Each oxygen atom linked (bonded) to no more than two glass-forming cations (e.g. Si^{4+}).

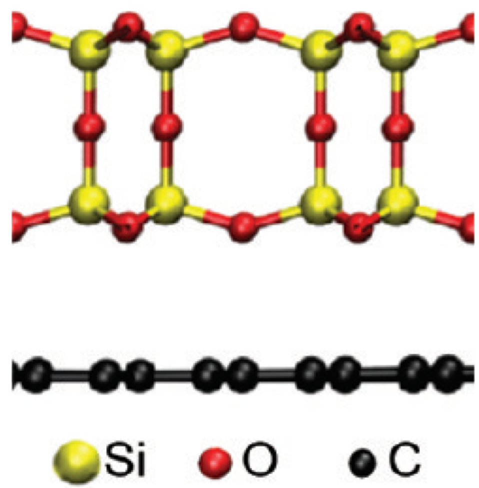
2. Oxygen coordination number (CN) around glass-forming cation is small: 3 or 4.

3. Cation polyhedra share corners, not edges or faces.

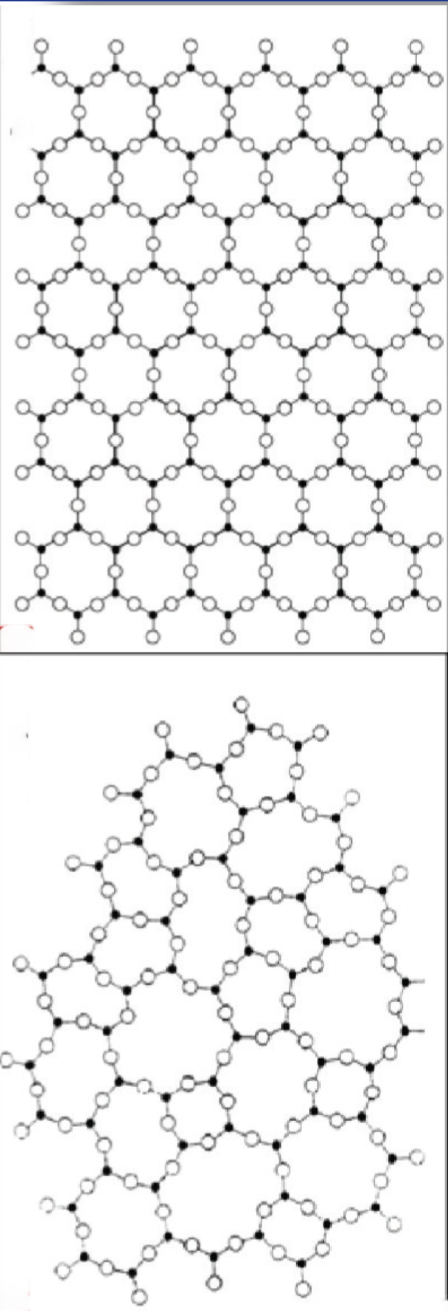
4. The polyhedral structural units form a **3-D continuous random network** in which every polyhedron shares at least 3 corners with its neighbors.

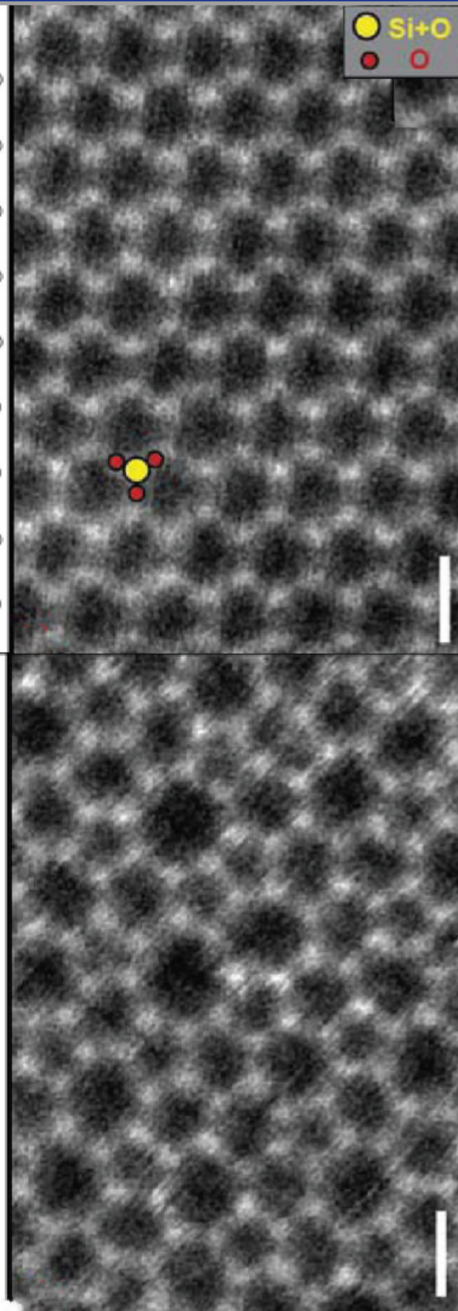
Zachariasen model (1932) STEM image Huang et al., (2012)

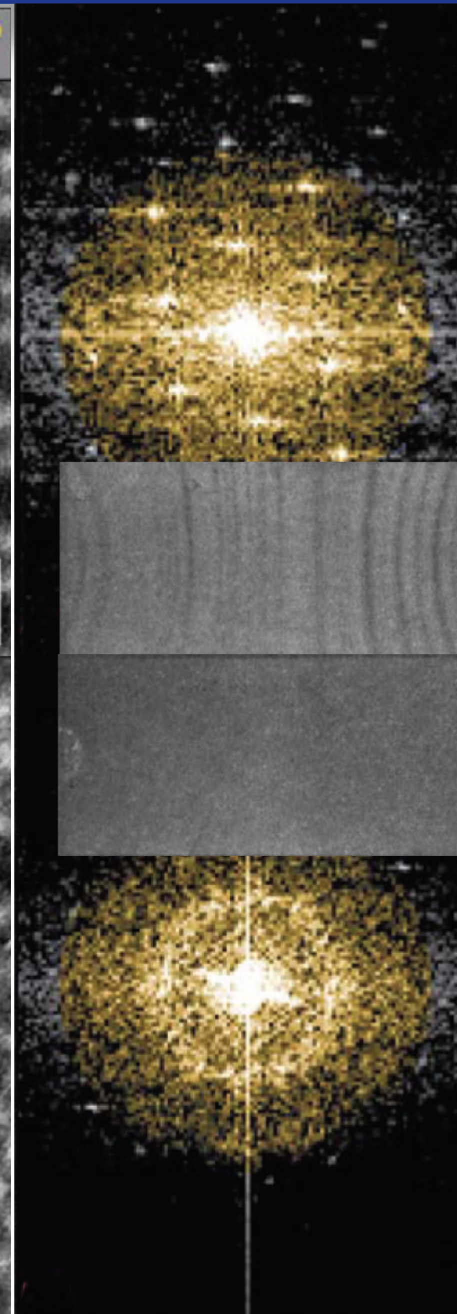


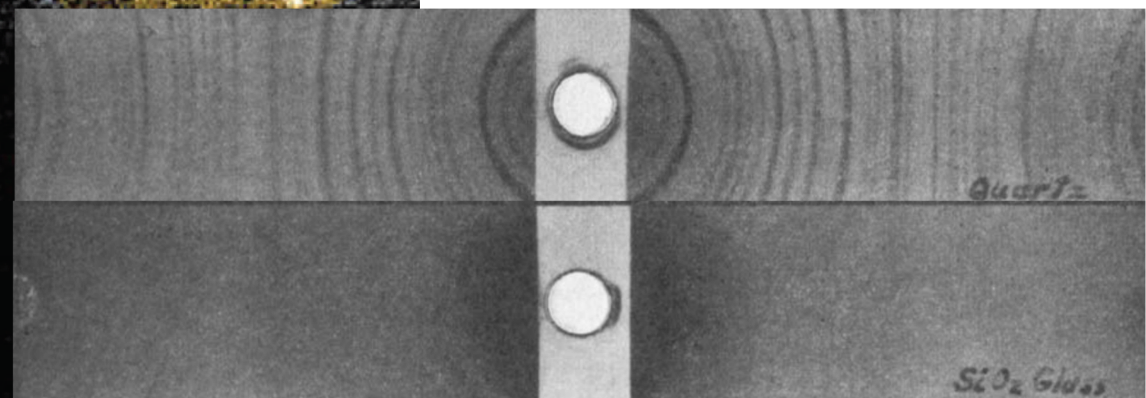


Zachariasen model (1932) STEM image Huang et al., (2012)



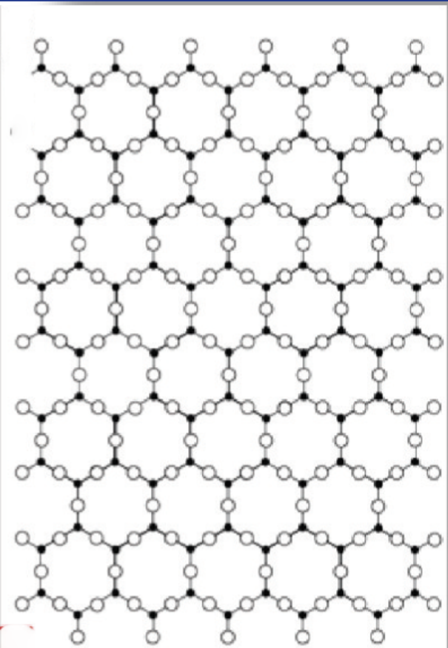


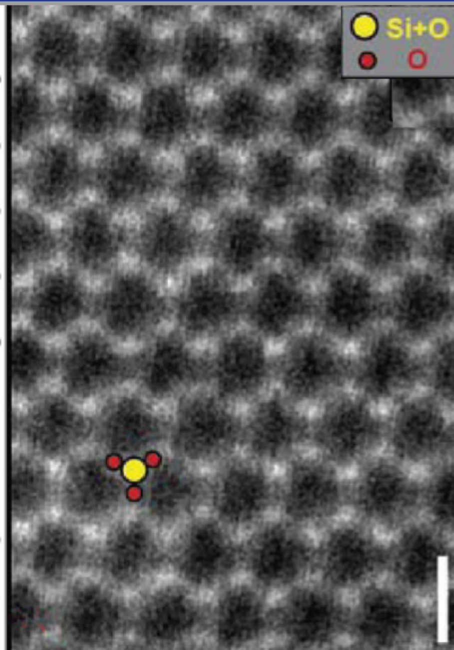


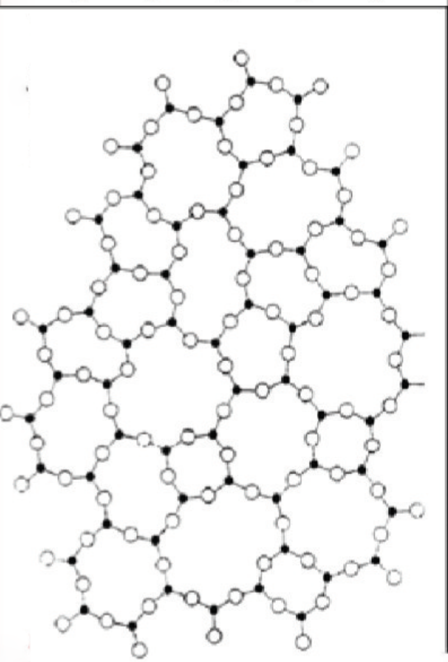


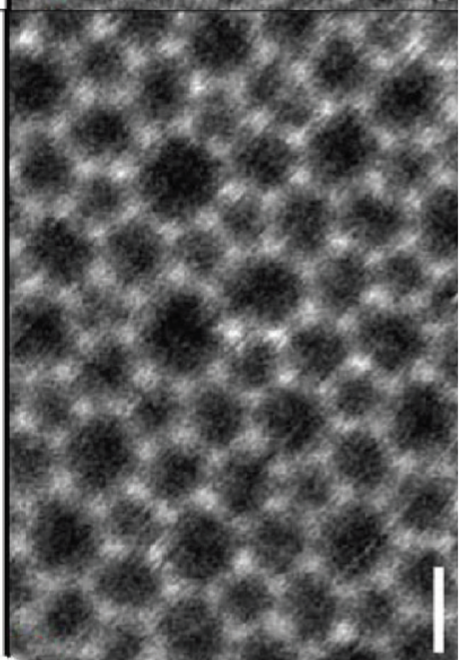
Warren, 1934

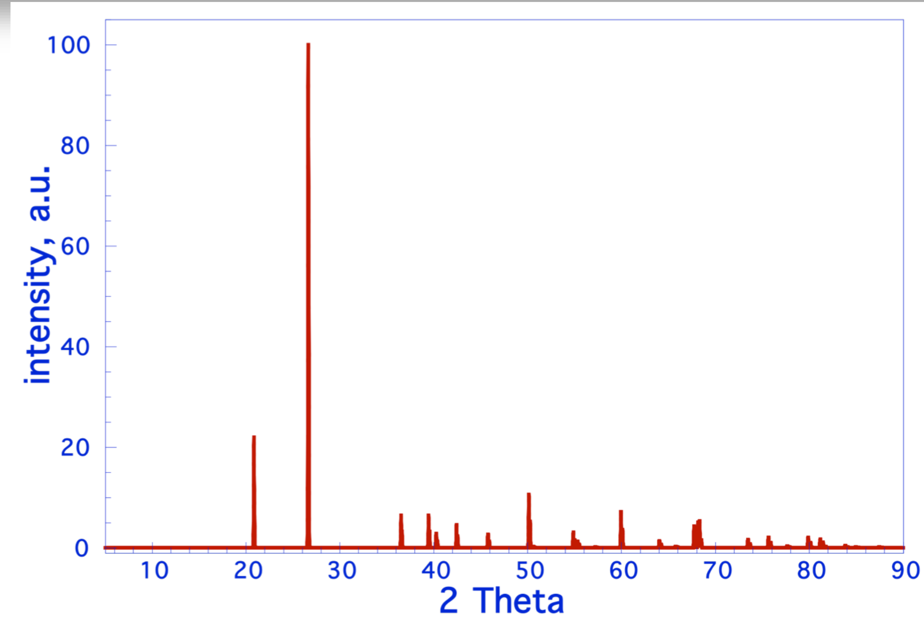
Zachariasen model (1932) STEM image Huang et al., (2012)

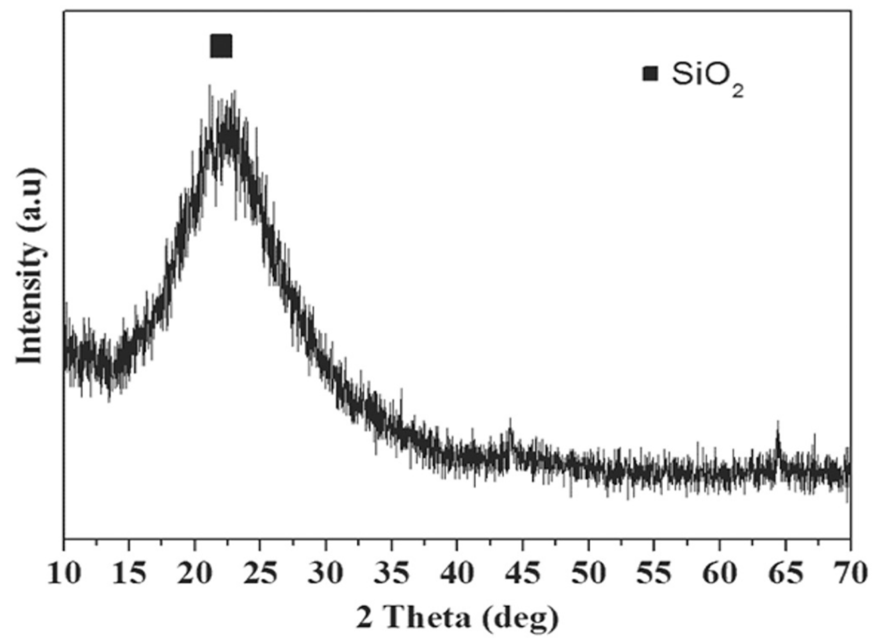




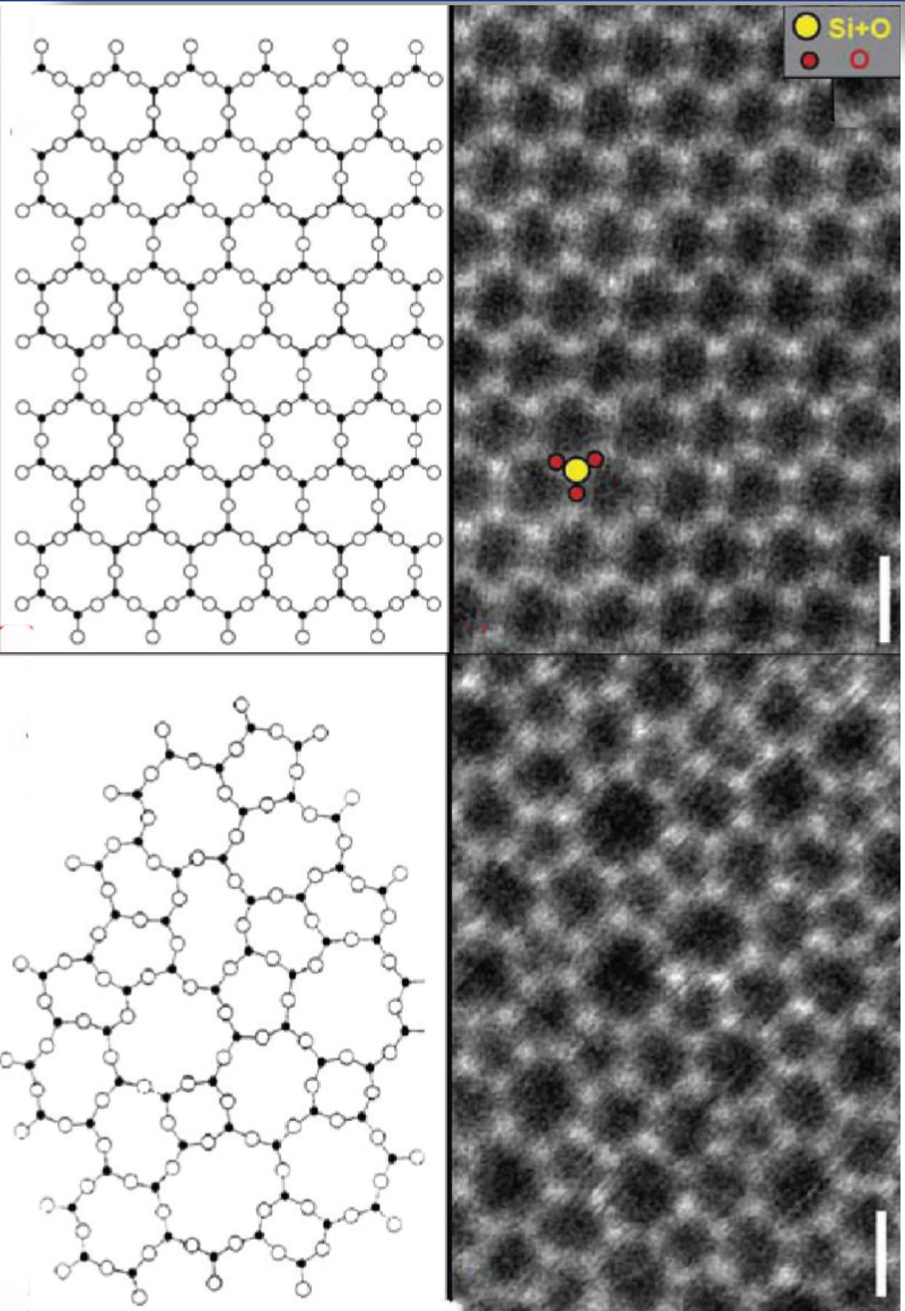


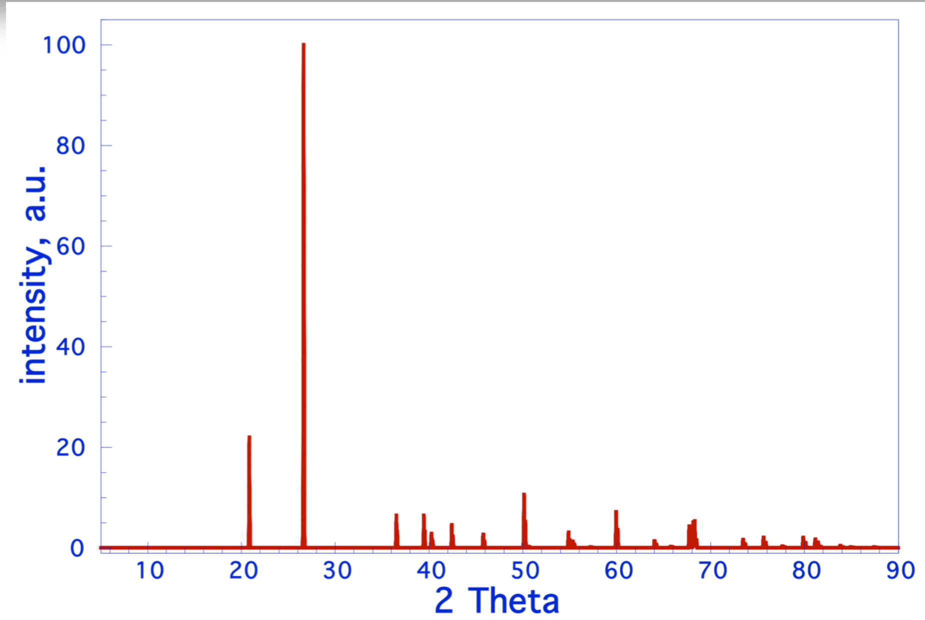


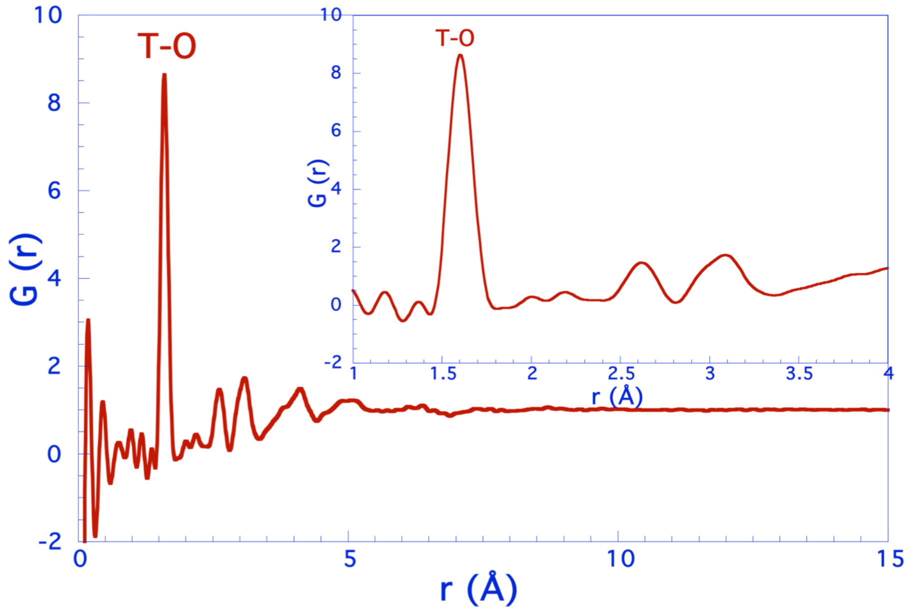


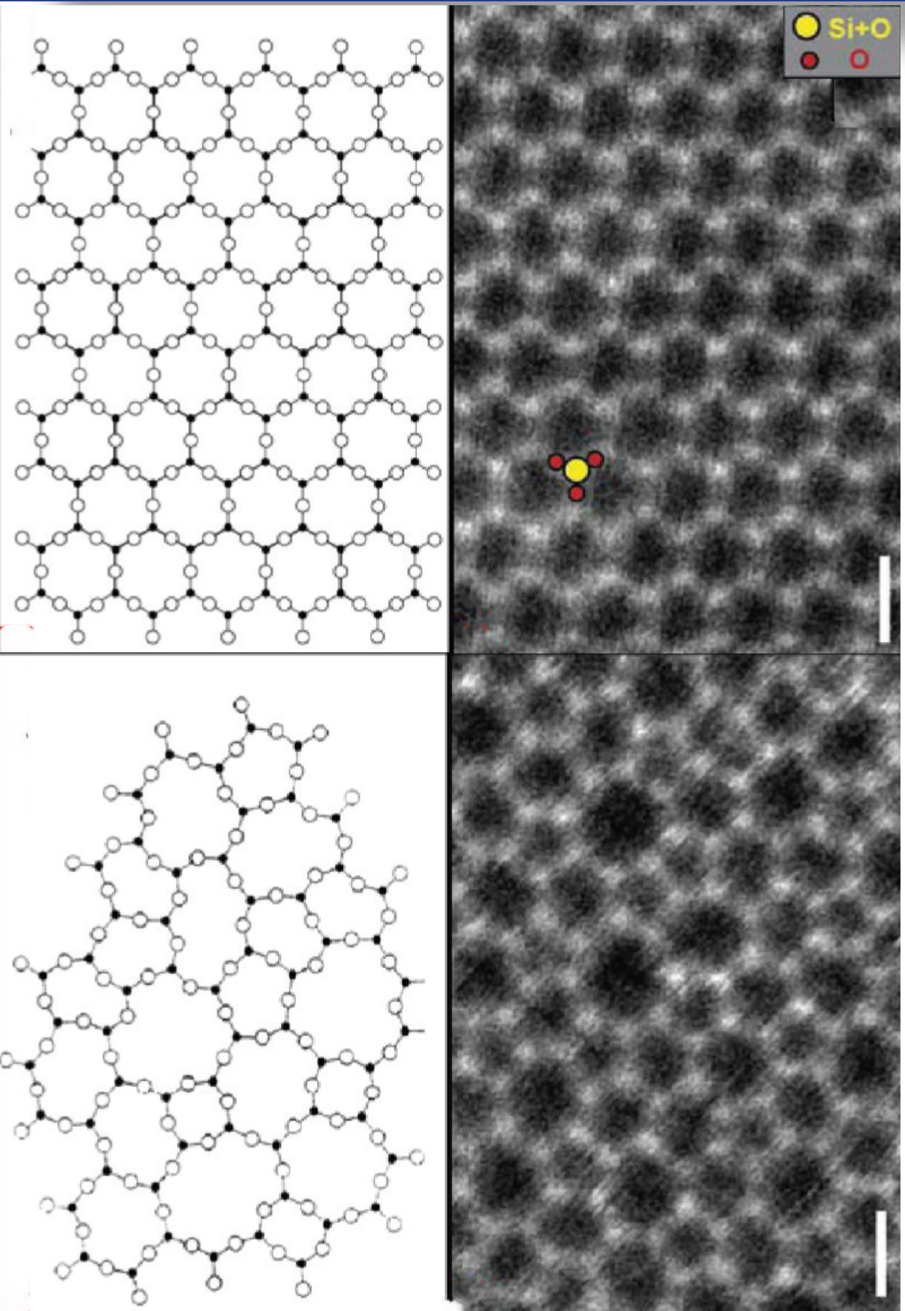


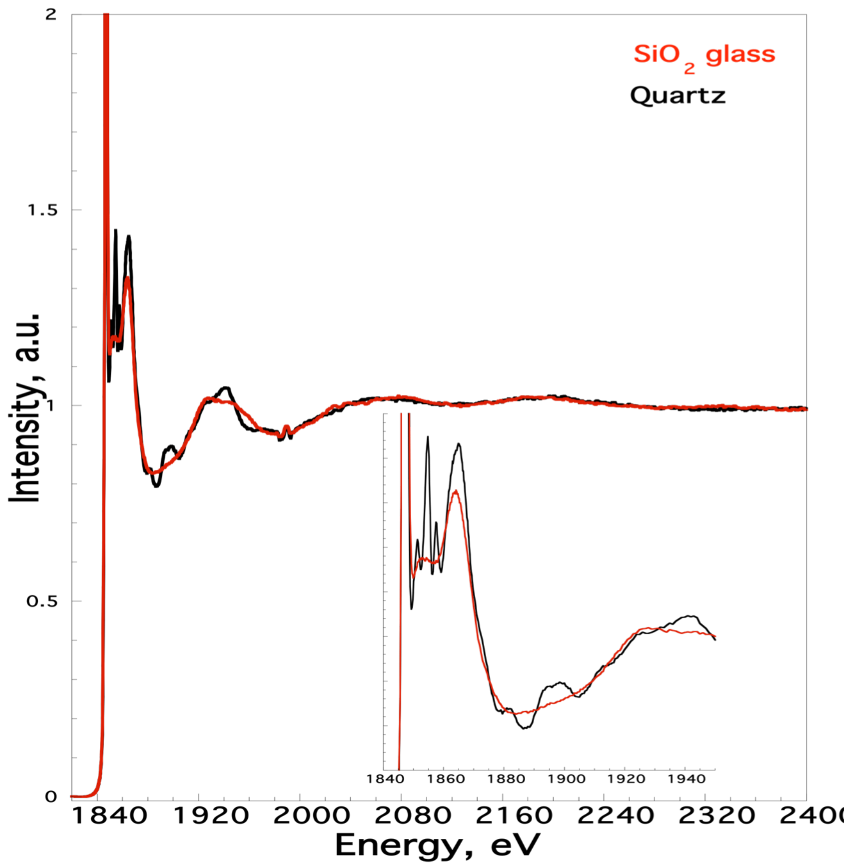
Zachariasen model (1932) STEM image Huang et al., (2012)







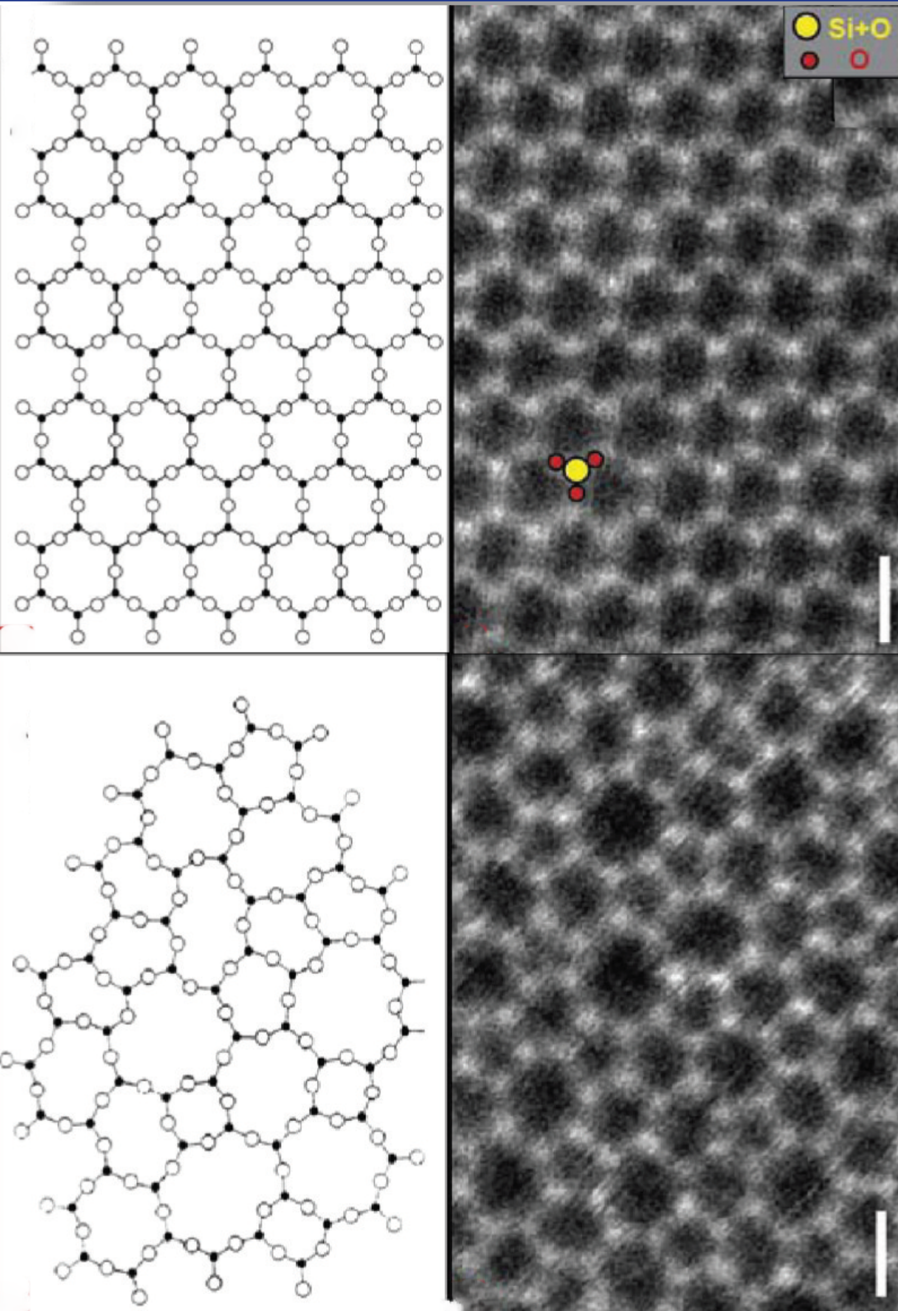


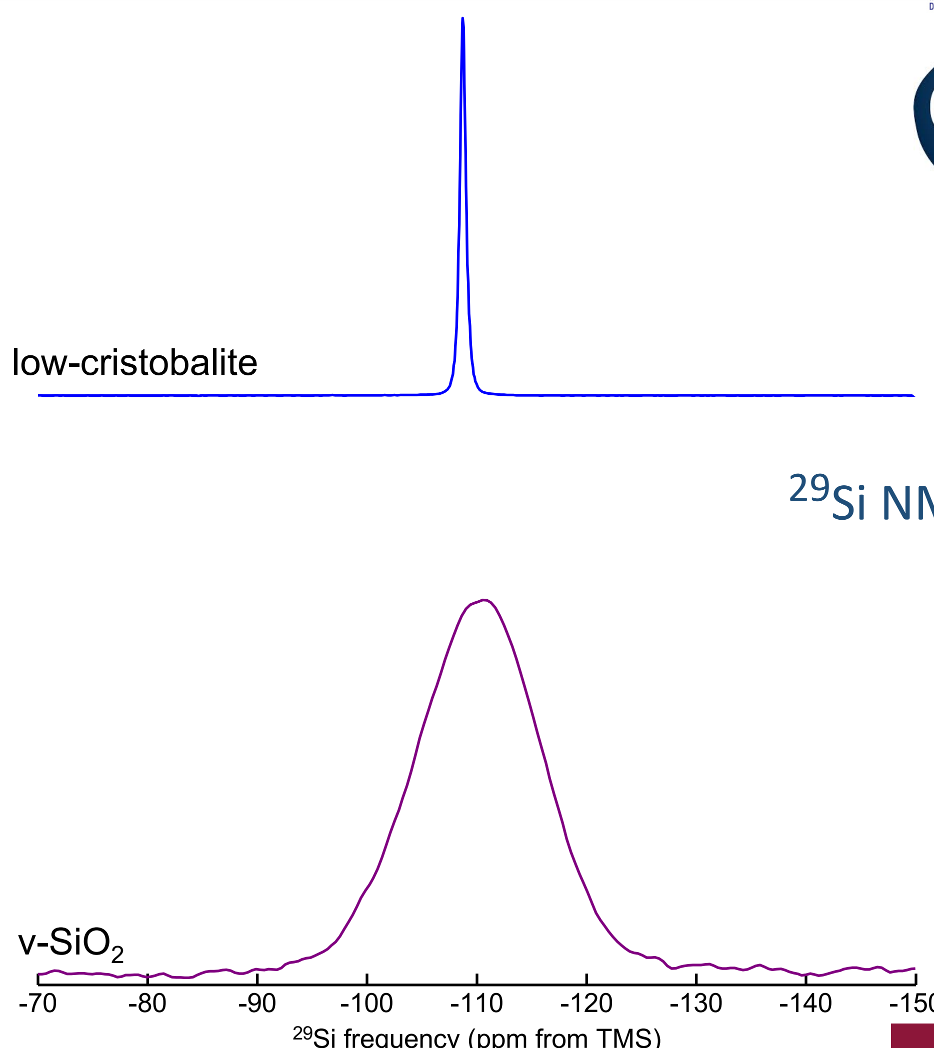


XANES at the Si K-edge

N. Trcera, SOLEIL

Zachariasen model (1932) STEM image Huang et al., (2012)

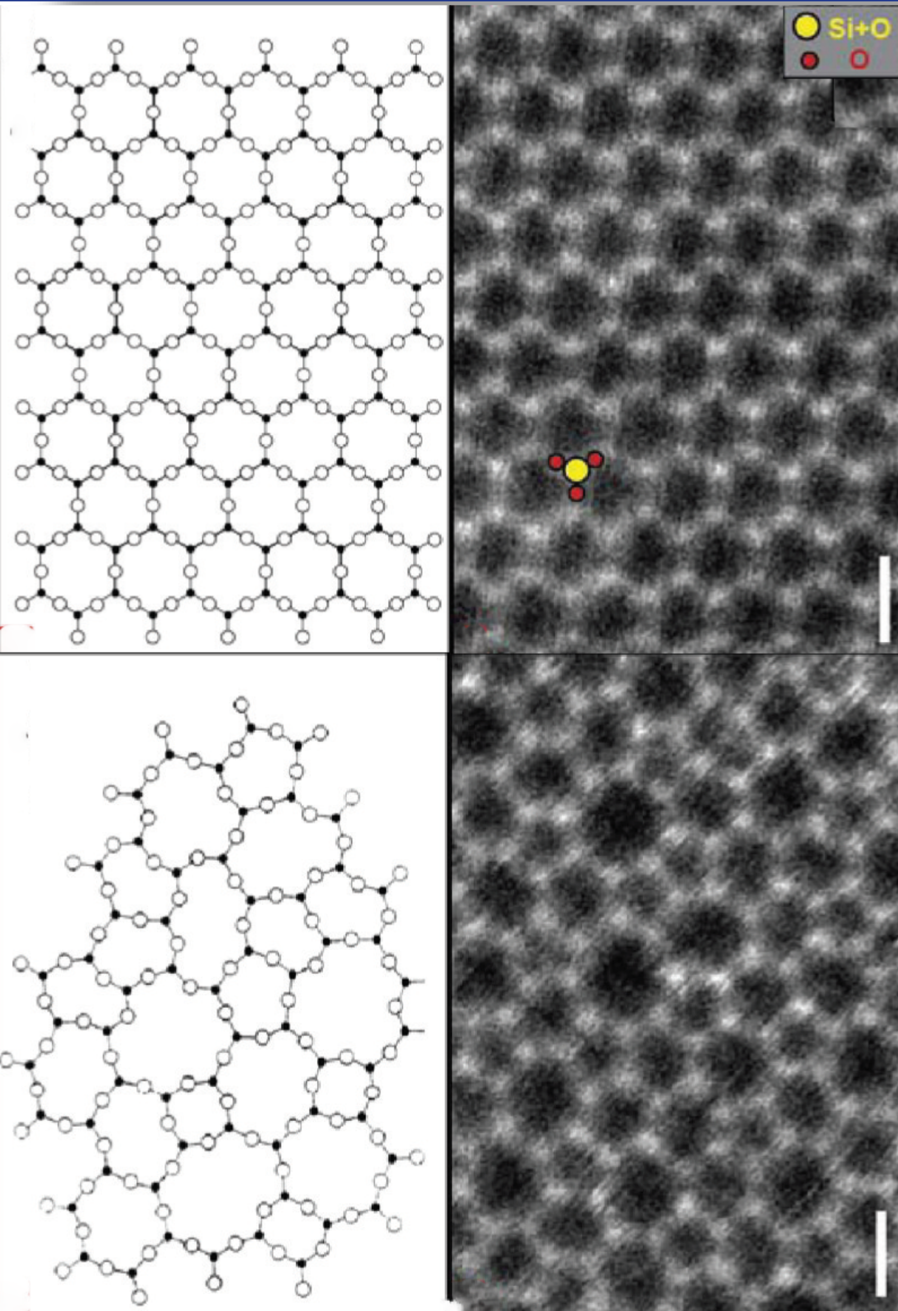


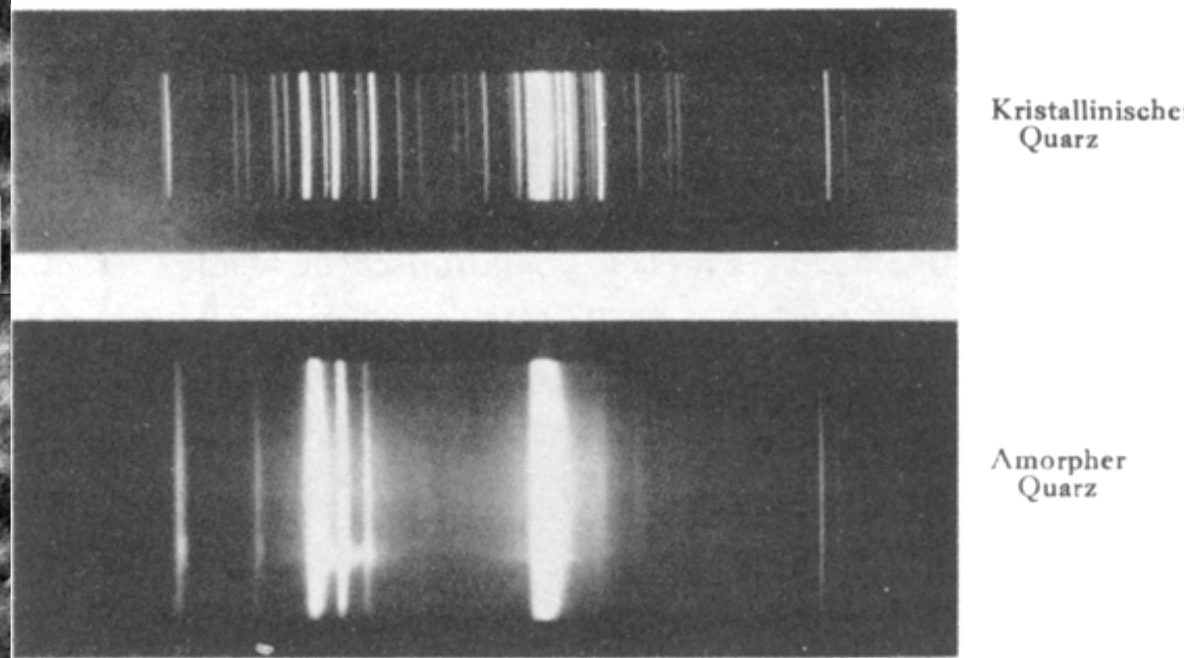


^{29}Si NMR

Florian et al.,

Zachariasen model (1932) STEM image Huang et al., (2012)

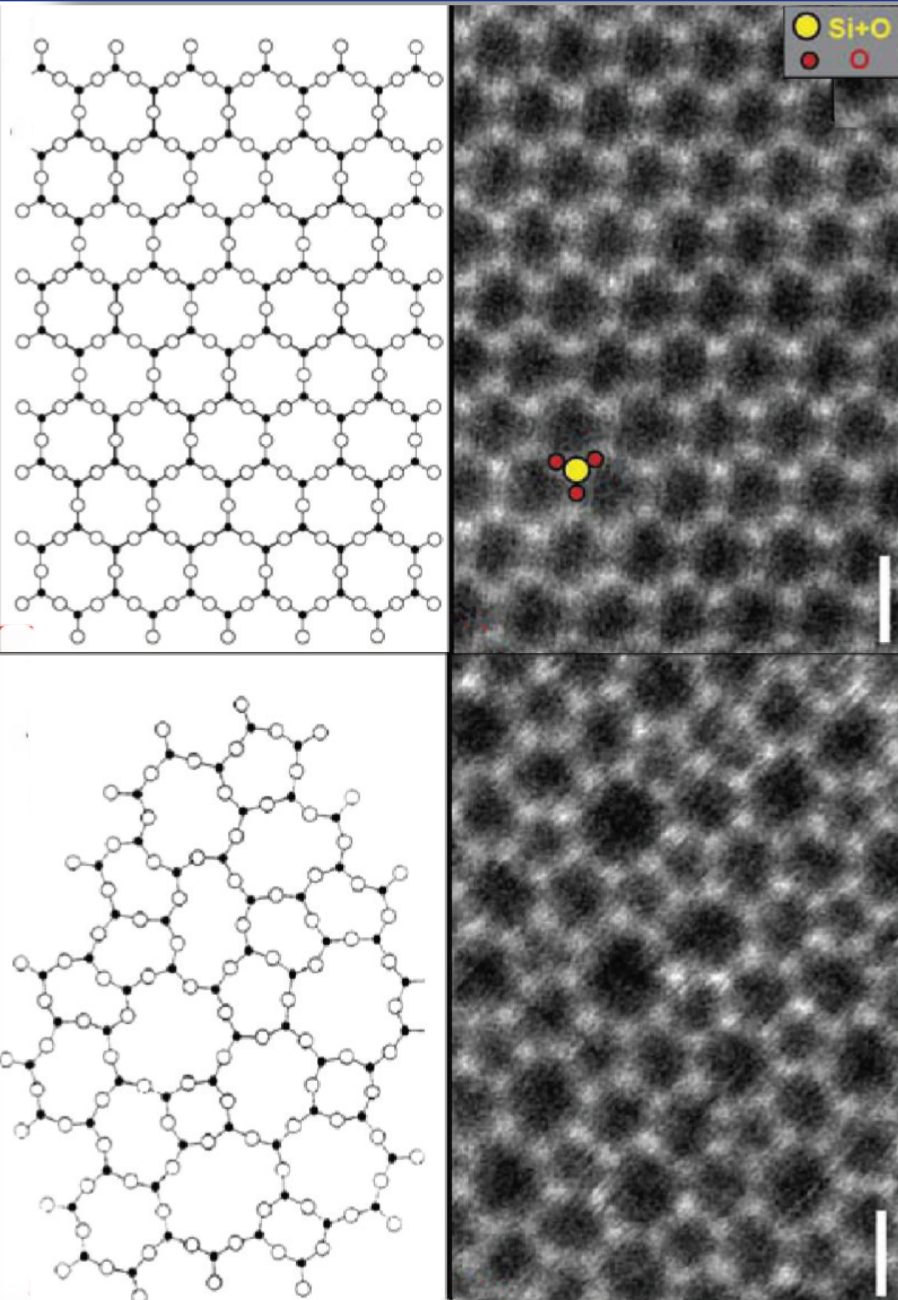


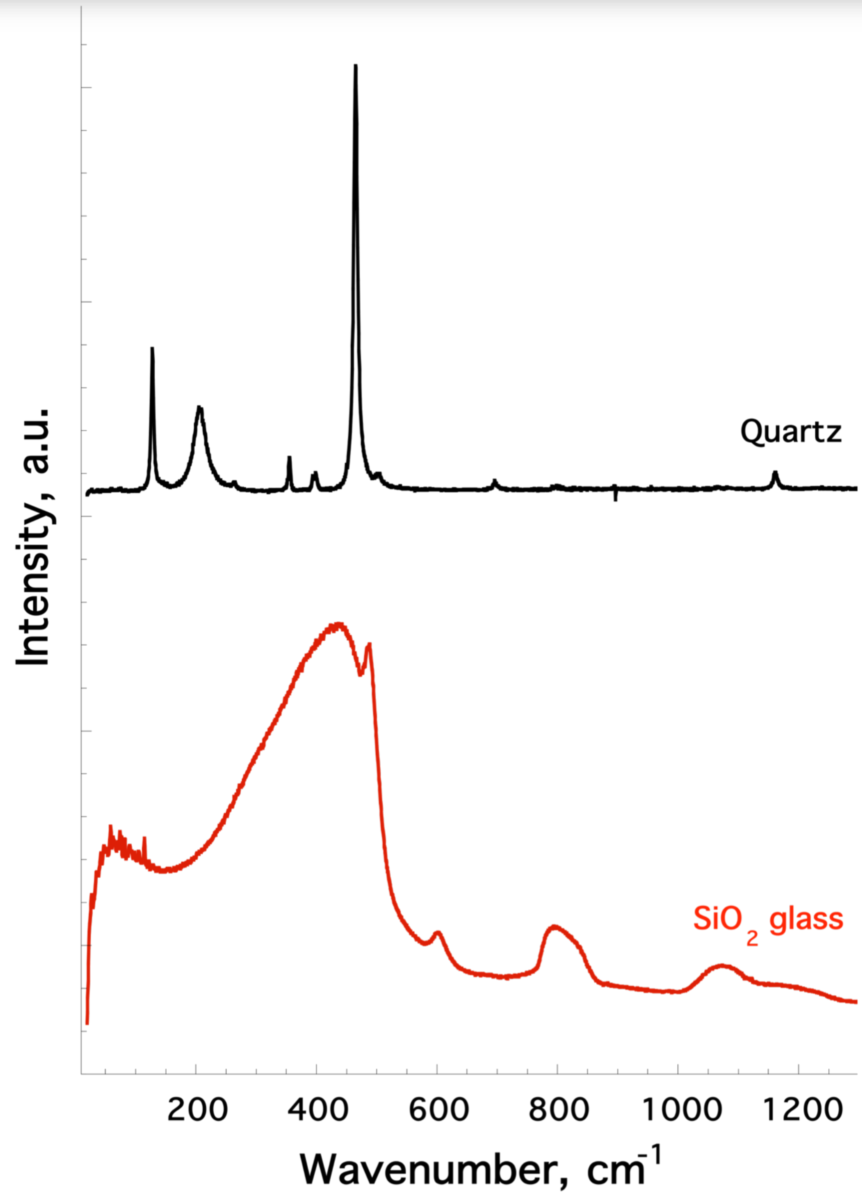


Gross and Ramanova, 1929

Zachariasen model (1932) STEM image Huang et al., (2012)

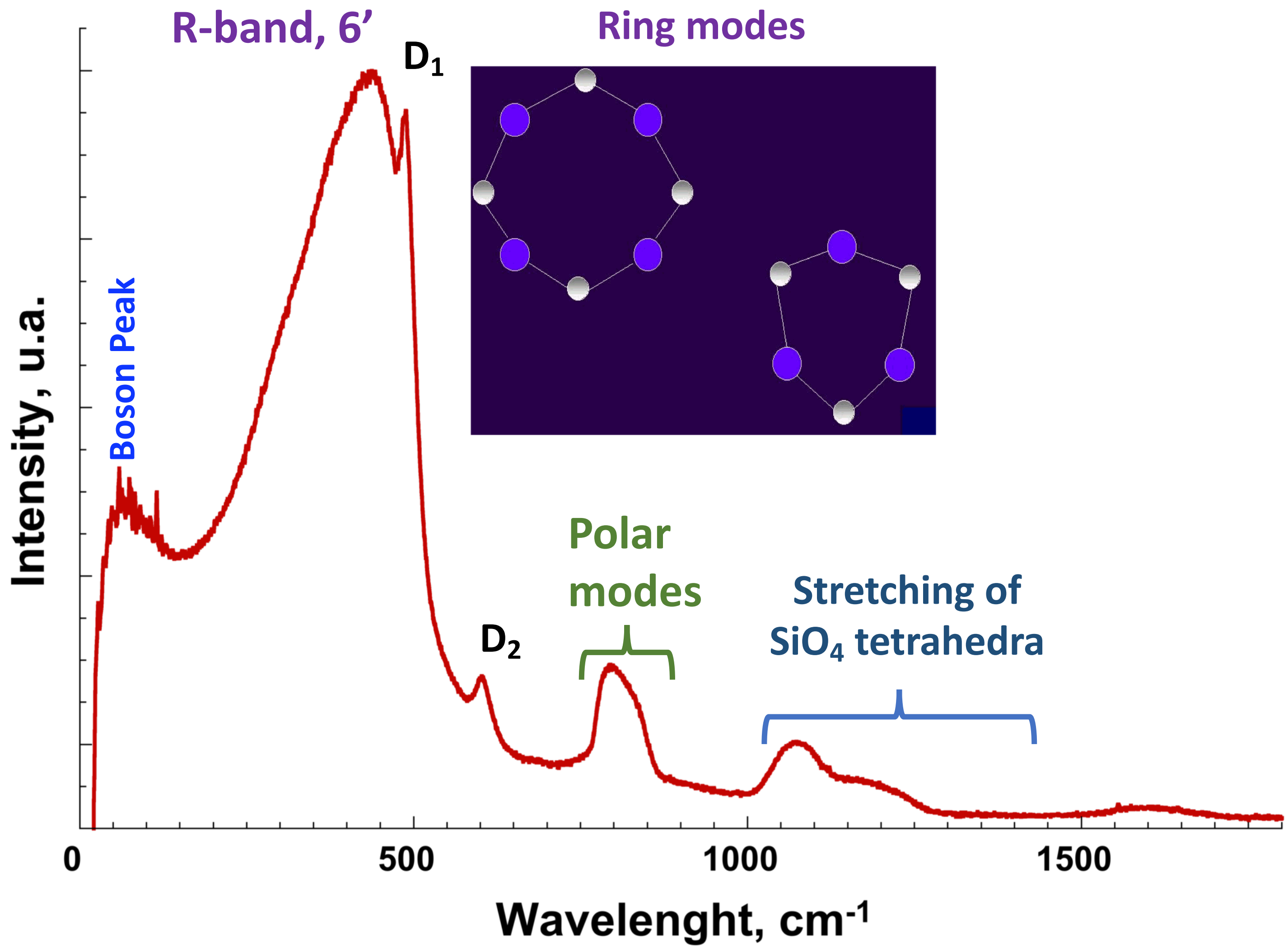
Géomatériaux

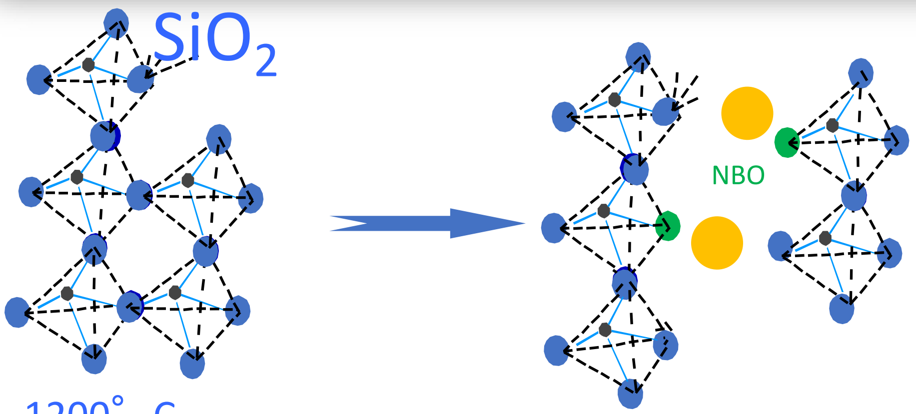


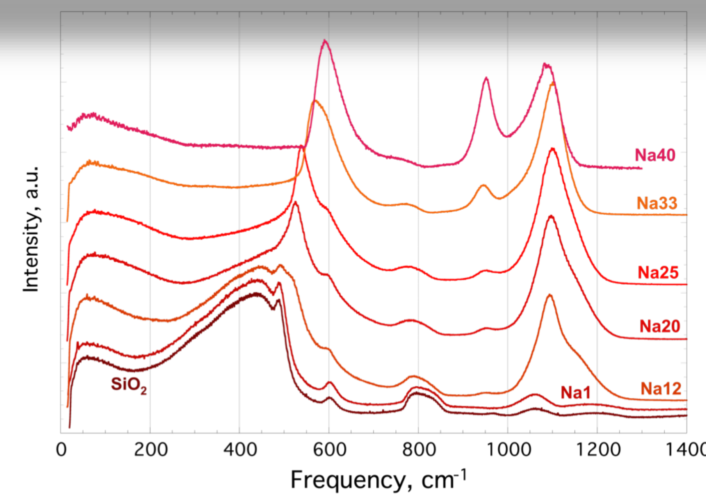


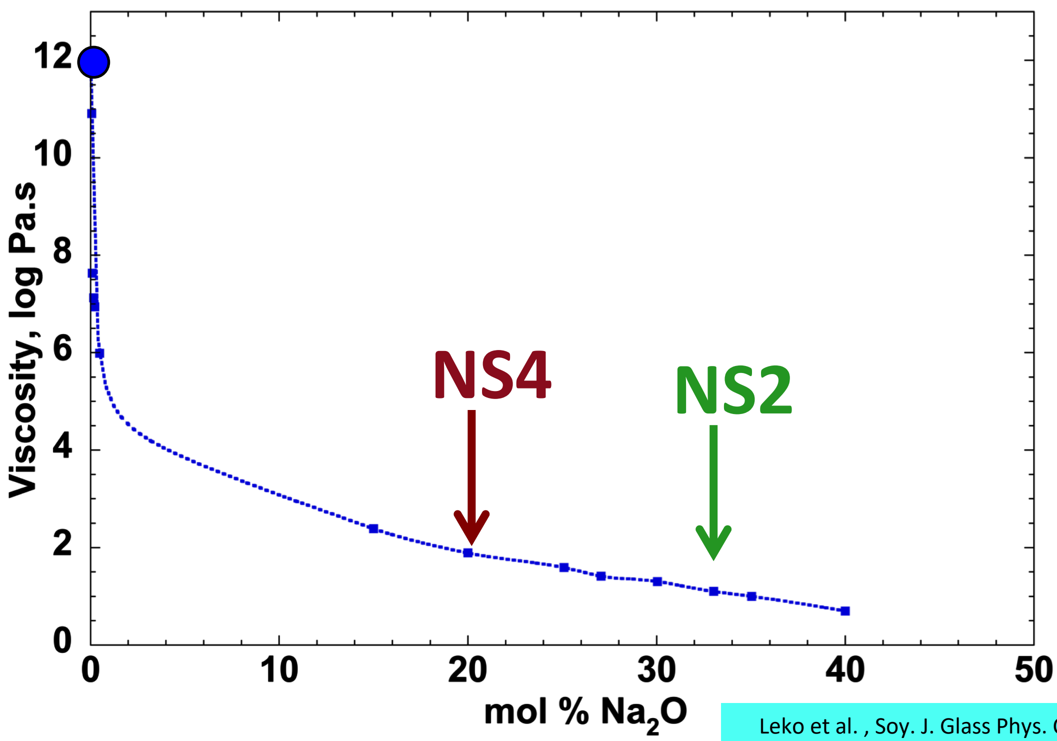
Neuville, Drewitt, Hennet, 2020, RIMG

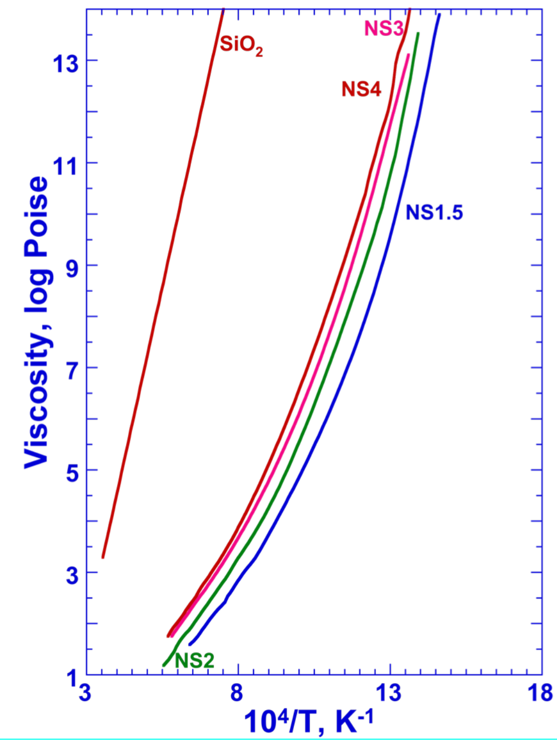
Raman : vibrations of v-SiO_2



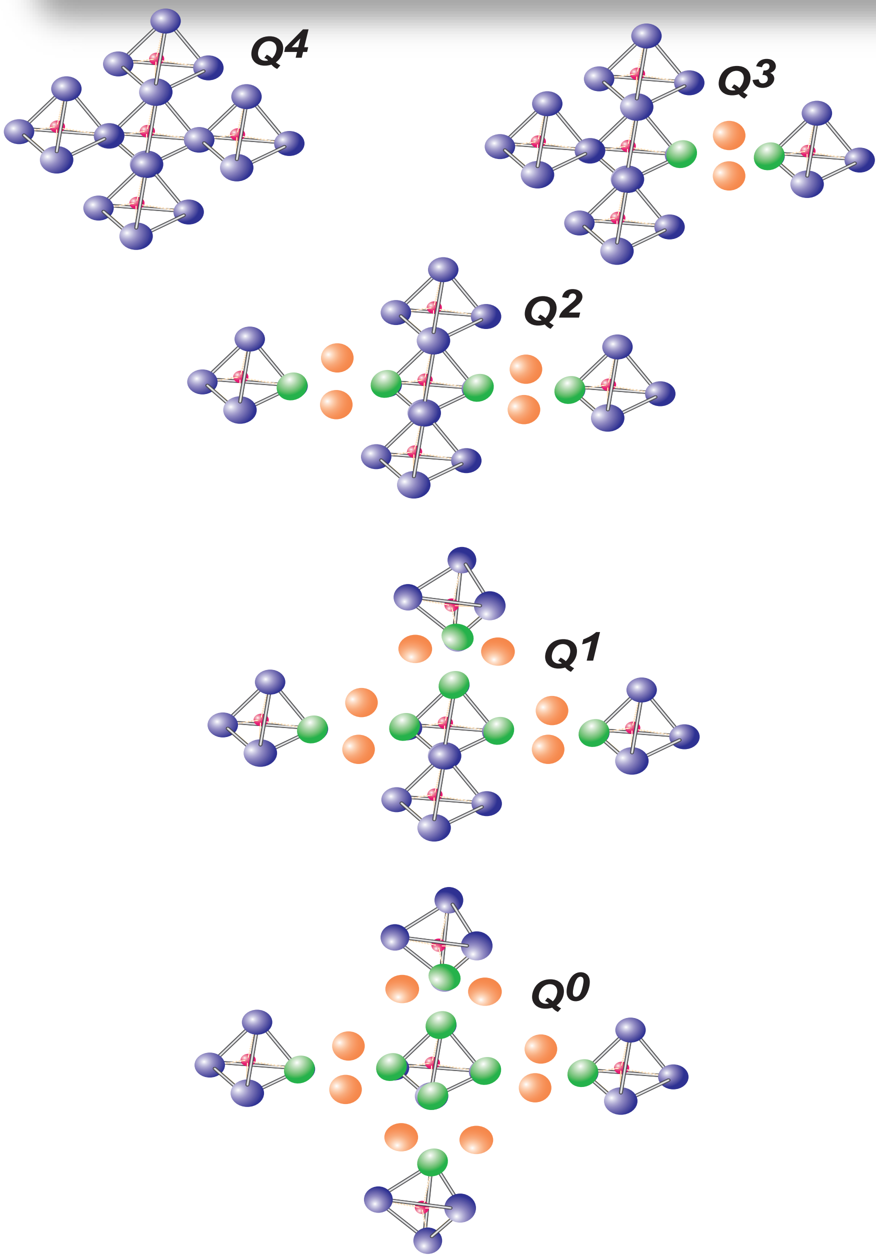








Leko et al. , Soy. J. Glass Phys. Chem., 1977, 3, 204-210 and Neuville, Chem Geol, 2006, 229, 28-42

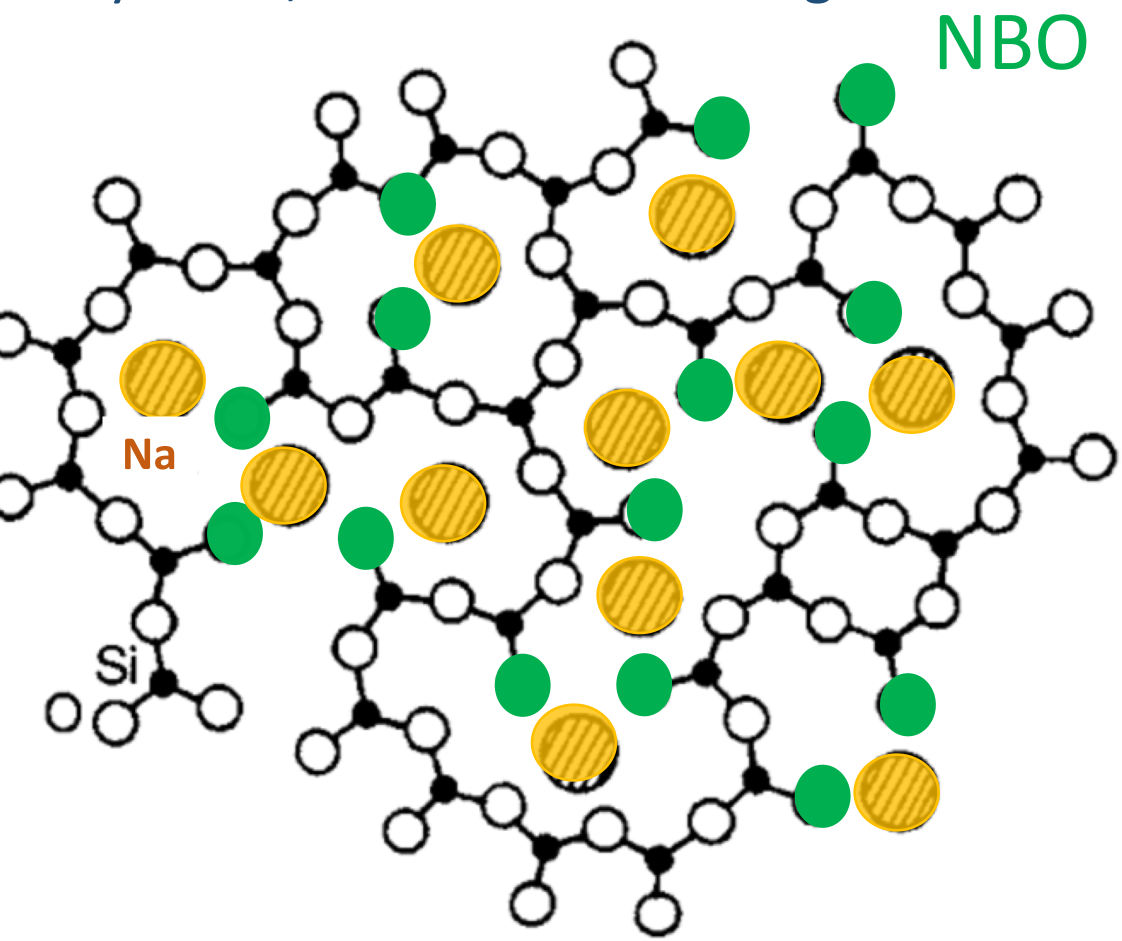


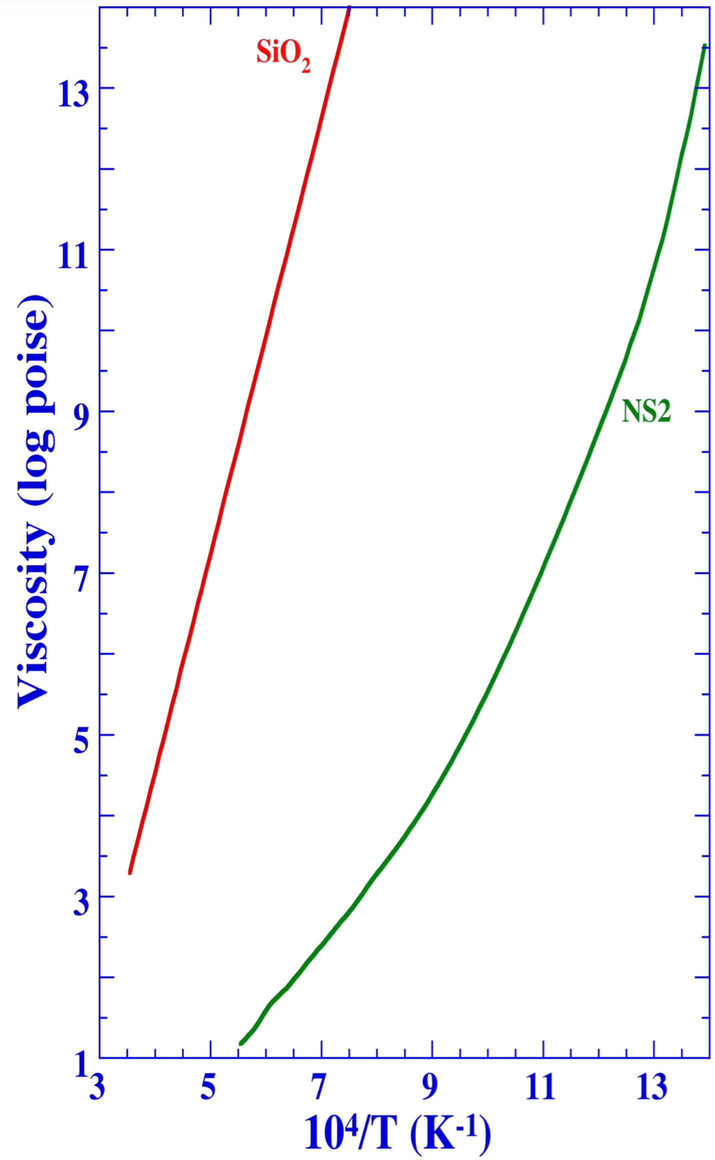
Non-network formers (alkali, alkaline-earth, transition elements) decrease the network connectivity, Tg, η by forming **non-bridging oxygens (NBO)** (≠**bridging oxygens BO**)

=>Network modifier

***Q^n* species *n* = number of bridging oxygens by tetrahedra**

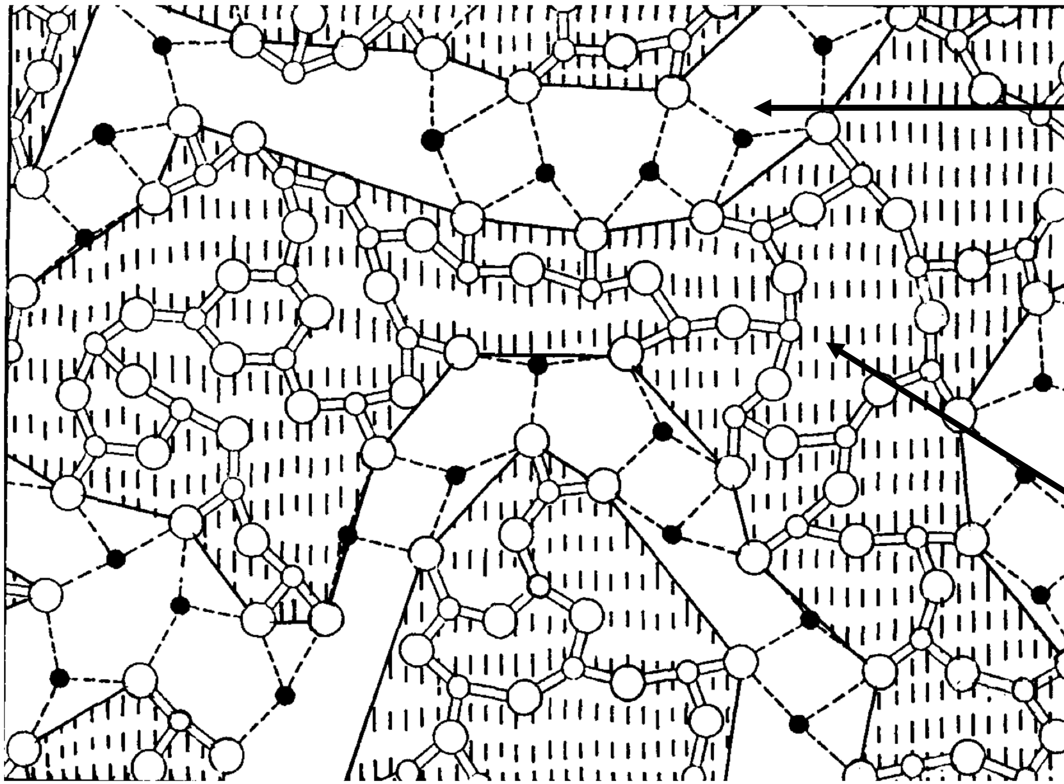
Zachariasen's rules do not consider at all modified oxides or multicomponent systems, or even non-oxide glasses





Zachariasen–Warren network theory

Modified random network - MRN (Greaves, 1985)



Zones rich with network modifiers

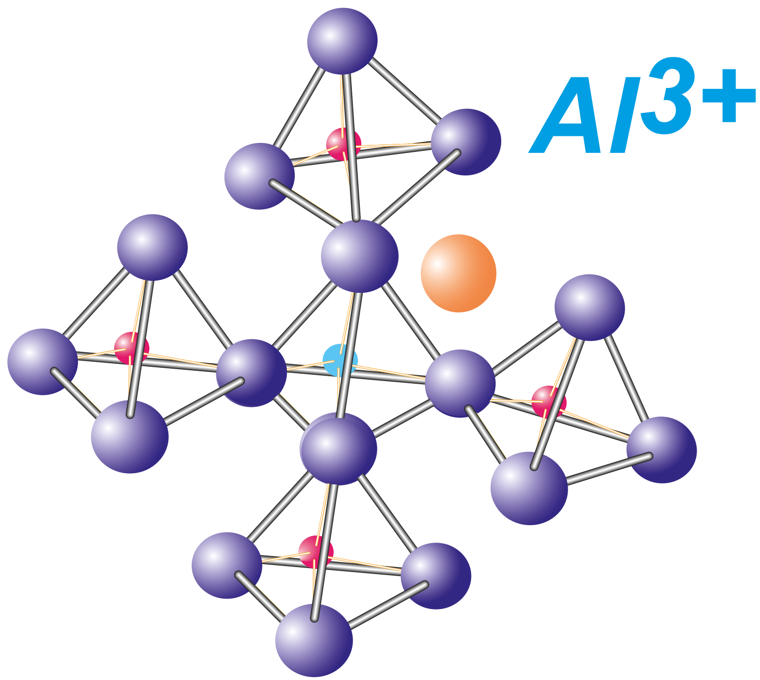
Zones rich with network formers

Relationships with conductivity, alteration etc

Al substitute to Si in tetrahedral position

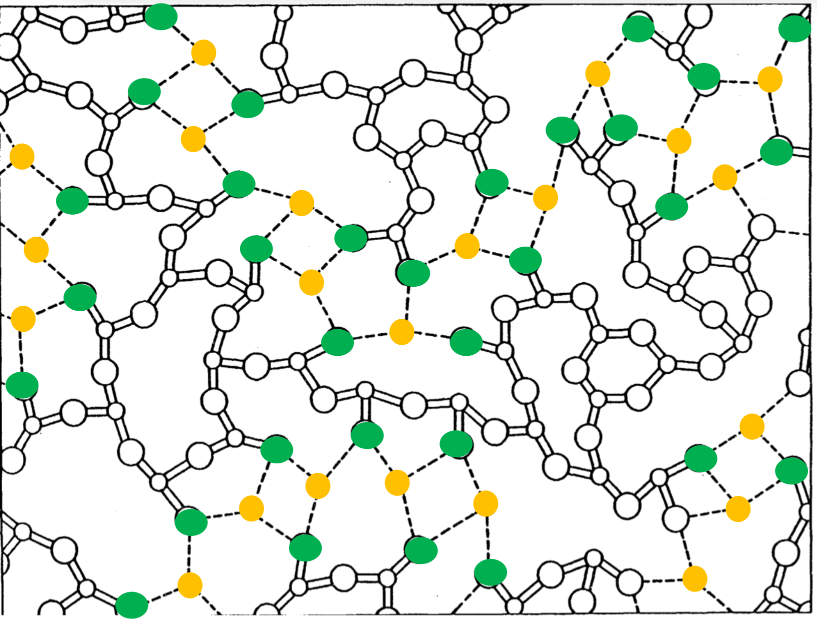
Al : (Ne)$3s^2 3p^1$: 3 valence electrons => ions Al^{3+}

$(AlO_4)^-$ charge electroneutrality ensures by the presence of alkali or alkaline earth

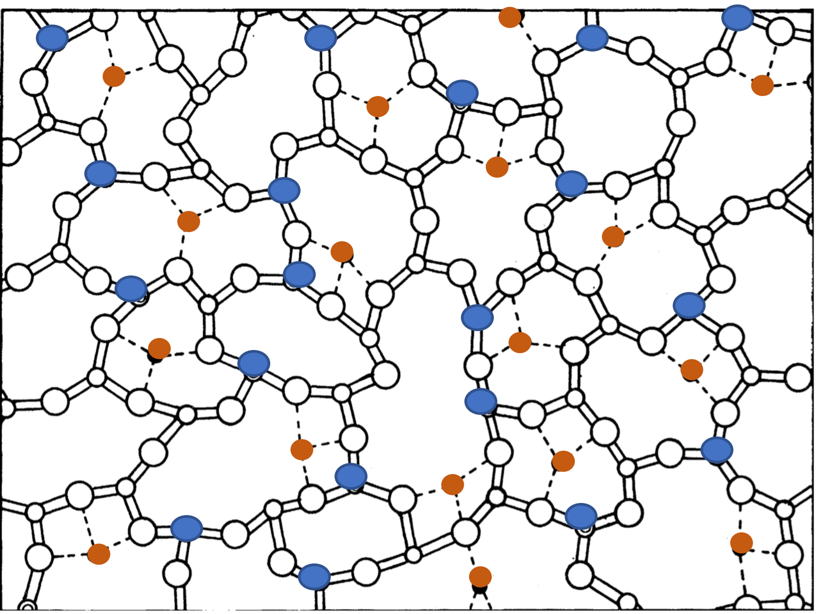


Similar for $(BO_4)^-$

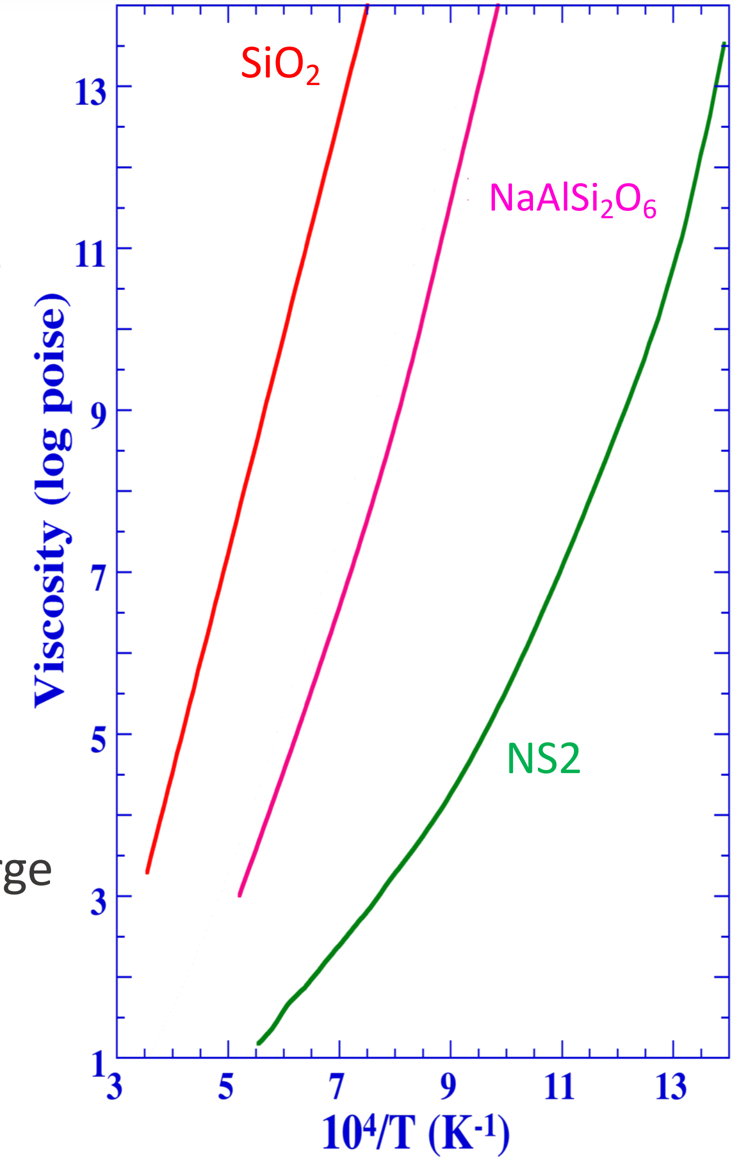
MRN - Modified random network versus CCRN Compensated Continuous Randon Network

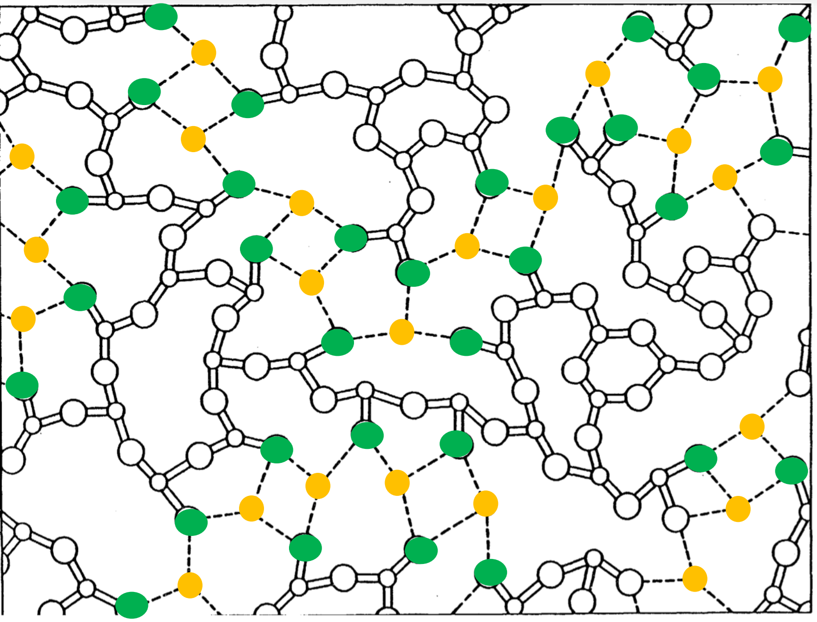


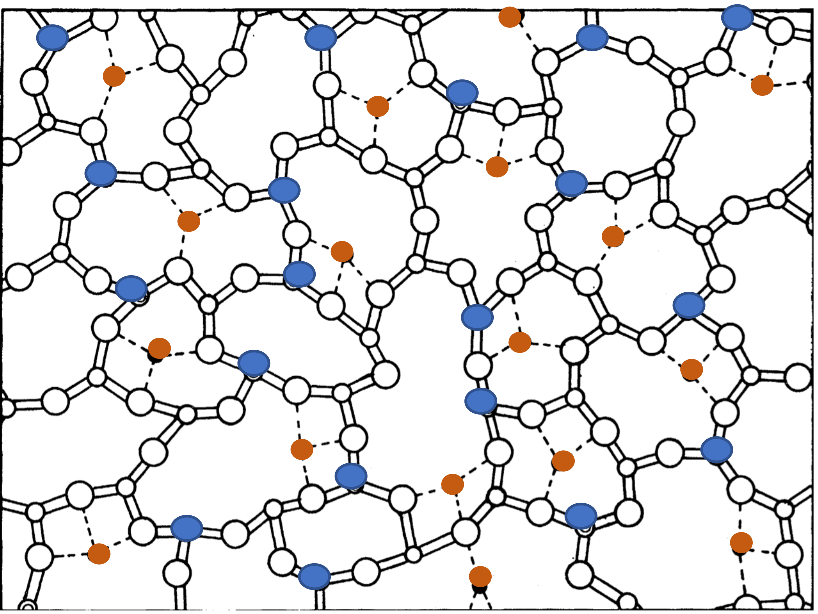
Cations connected to **NBO** associated to the negative charge of O^- **=> network modifier**

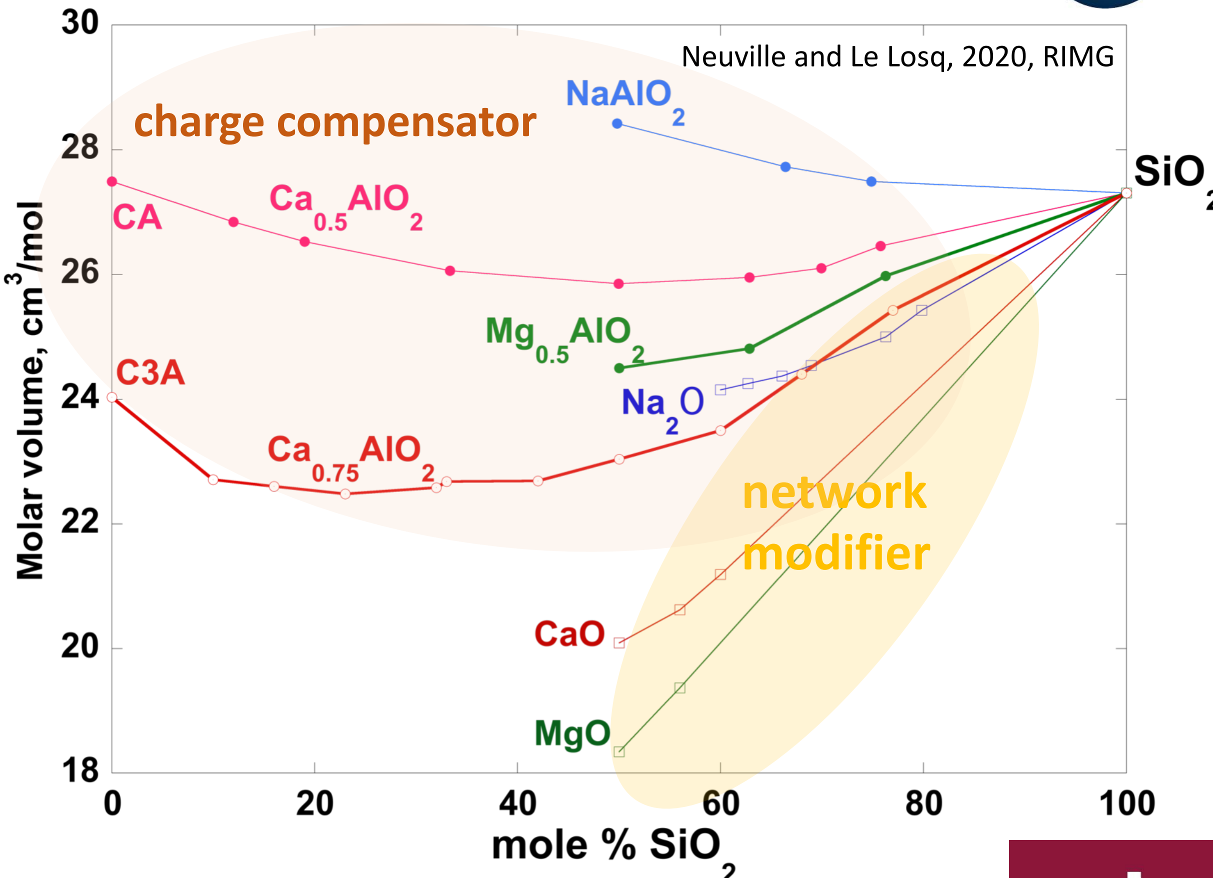


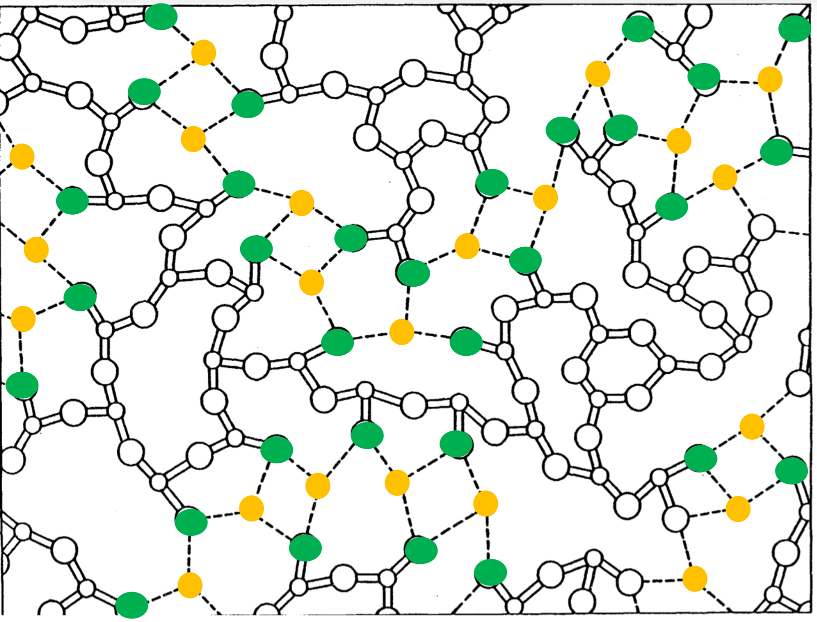
Cations connected to **BO** and acting as charge compensator near **$(AlO_4)^-$, $(BO_4)^-$** **=> charge compensator**

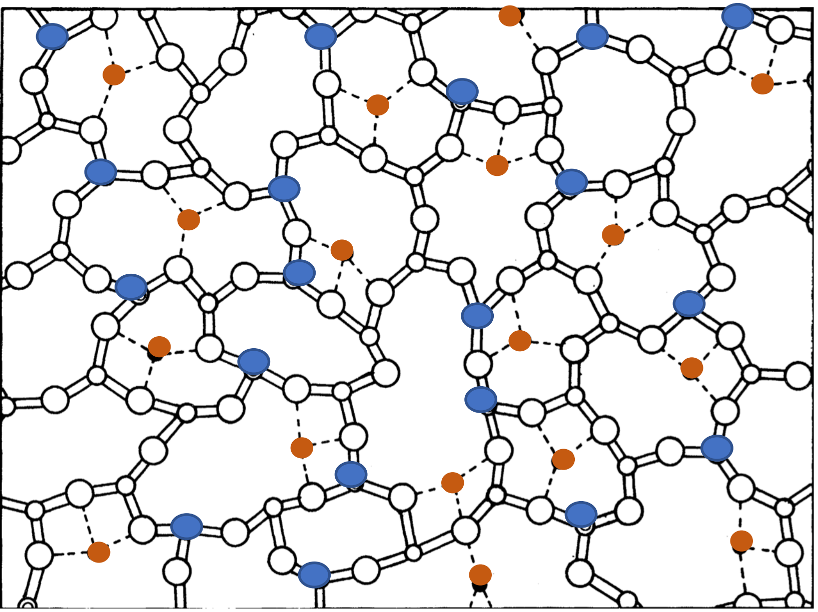


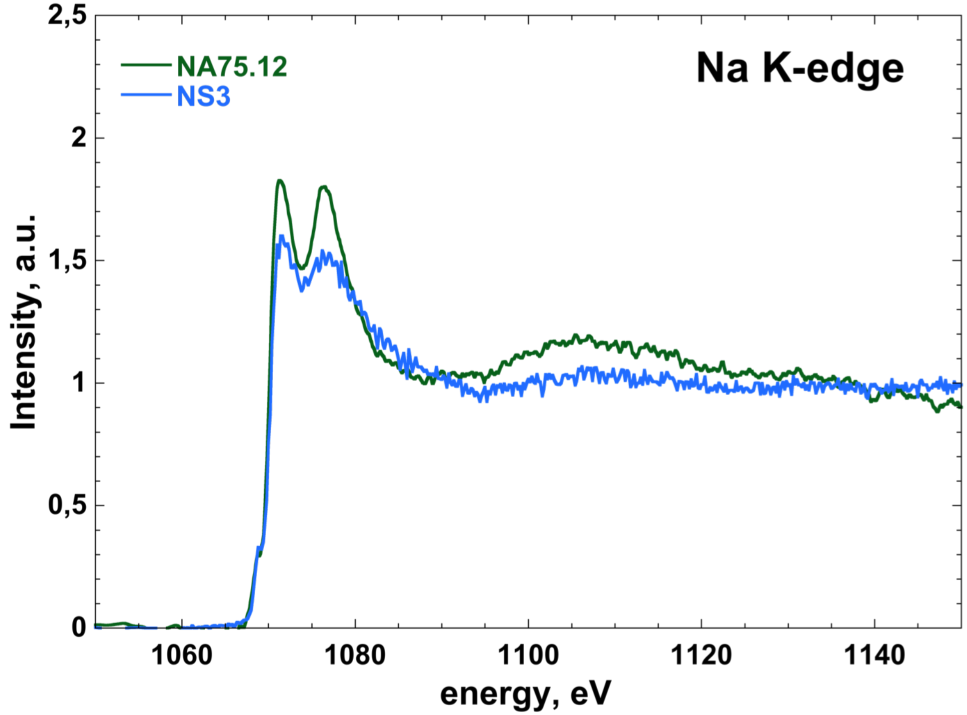





Neuville and Le Losq, 2020, RIMG
charge compensator
network modifier
NaAlO2
CA
Ca0.5AlO2
Mg0.5AlO2
Na2O
C3A
Ca0.75AlO2
CaO
MgO
SiO2
Molar volume, cm3/mol
mole % SiO2
30
28
26
24
22
20
18
0
20
40
60
80
100



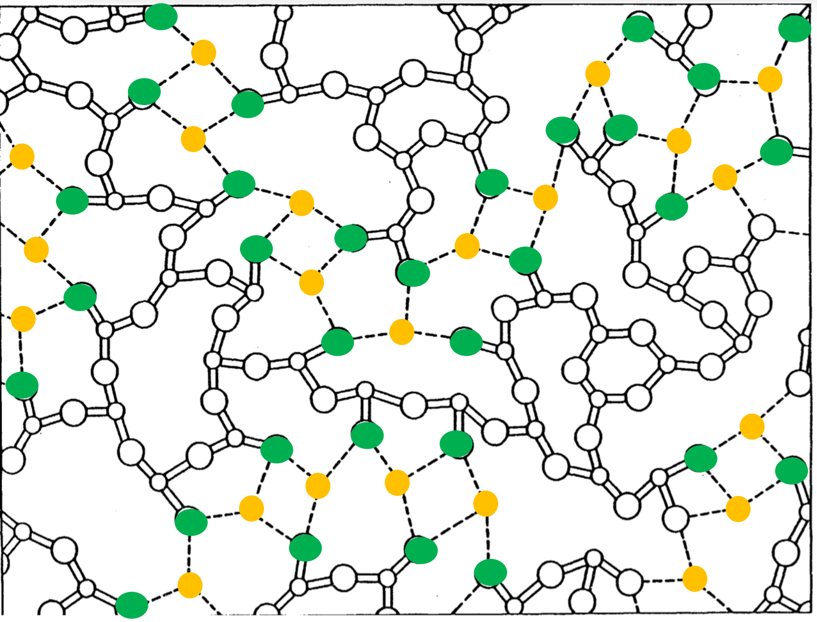


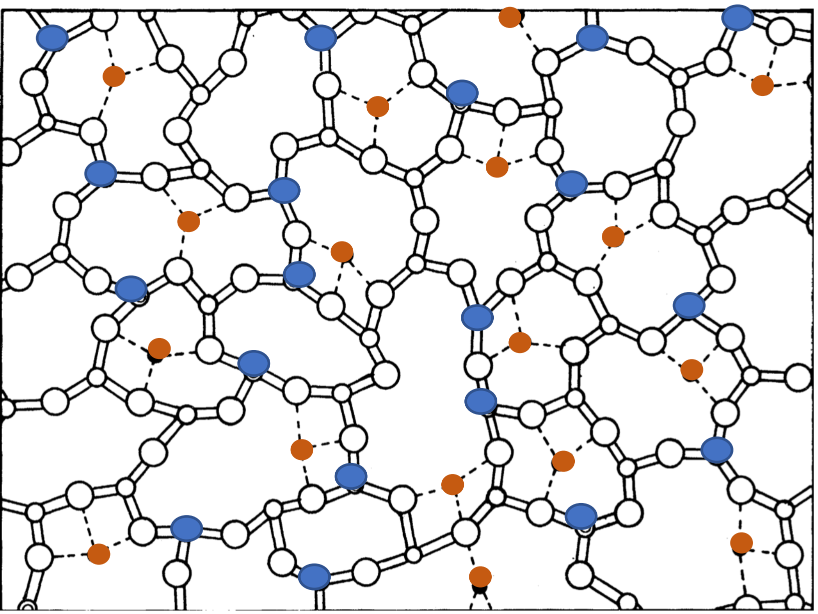


NS3 => [6]Na network modifyer

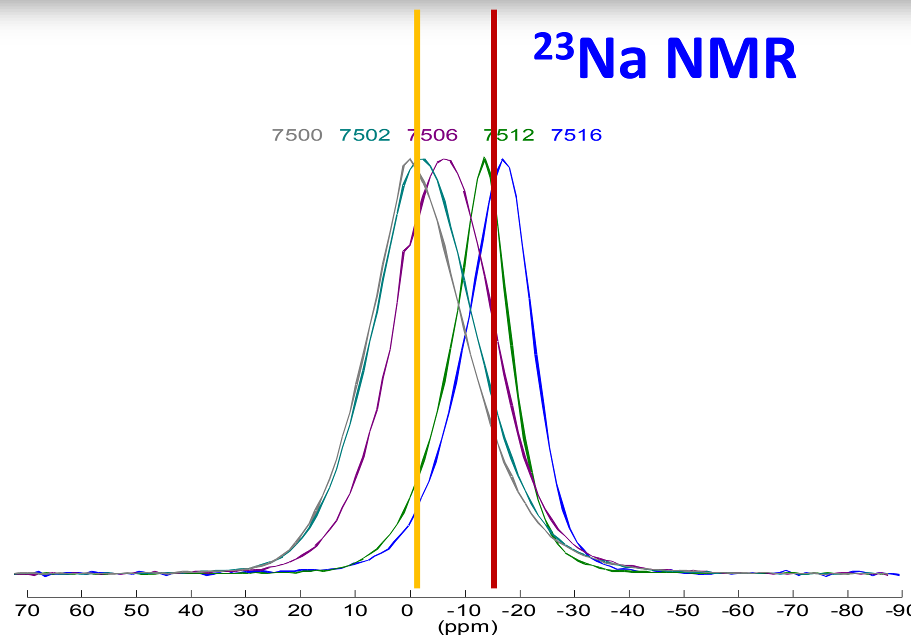
NA75.12 => [9]Na charge compensator

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.



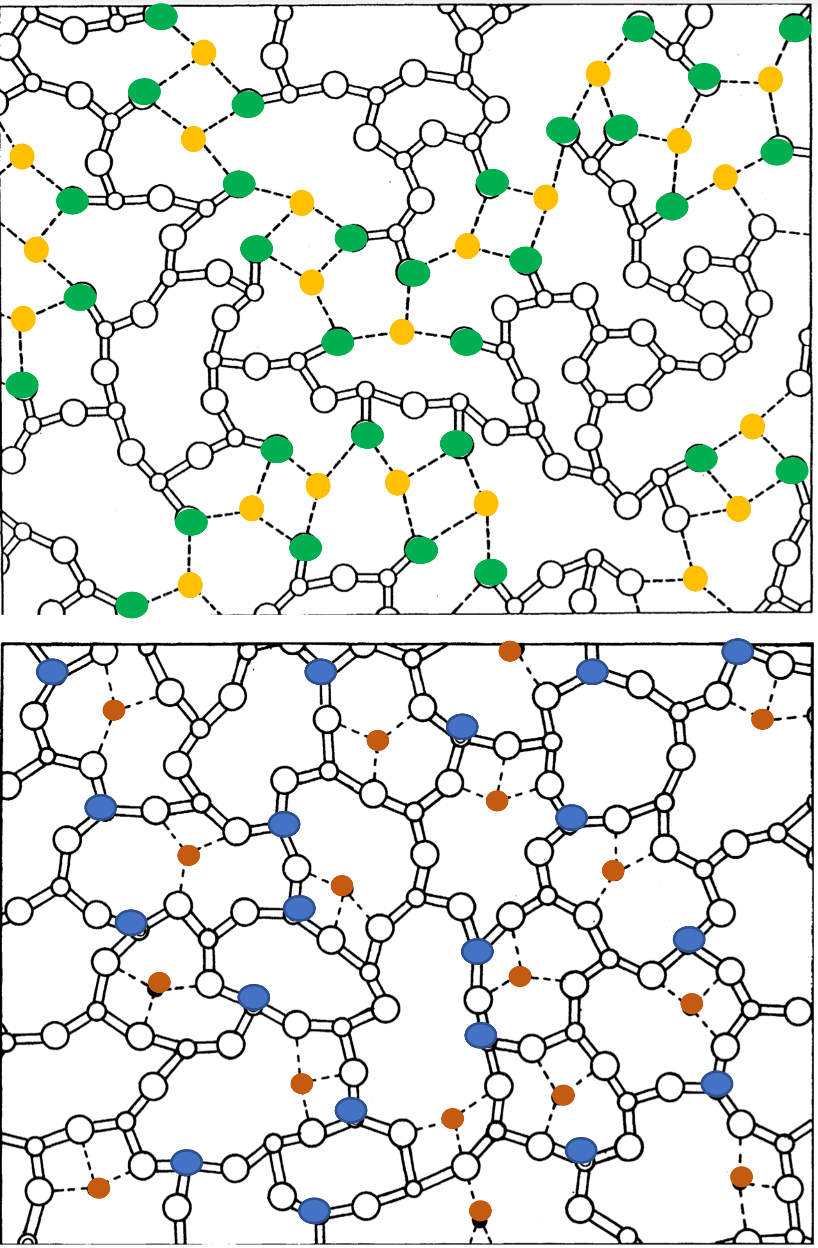


^{23}Na NMR



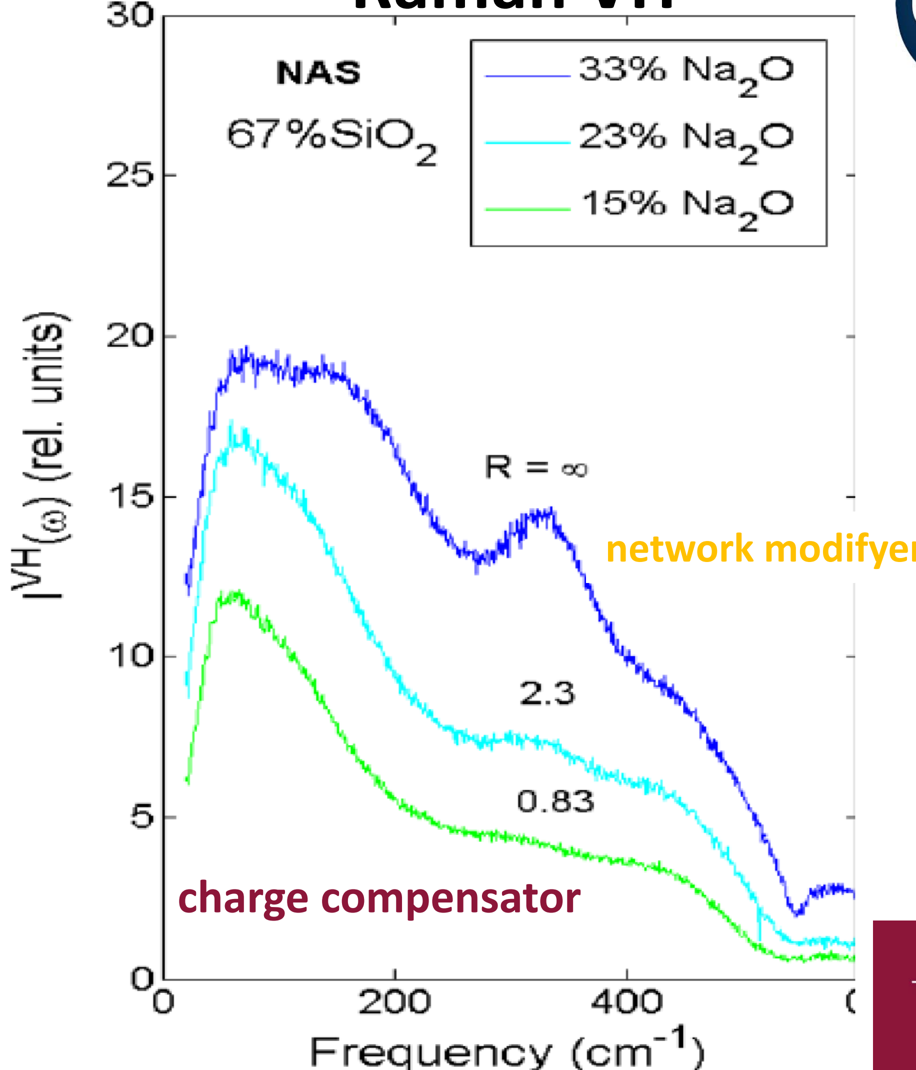
⇒ Chemical shift of ^{23}Na, from network modifyer to charge compensator

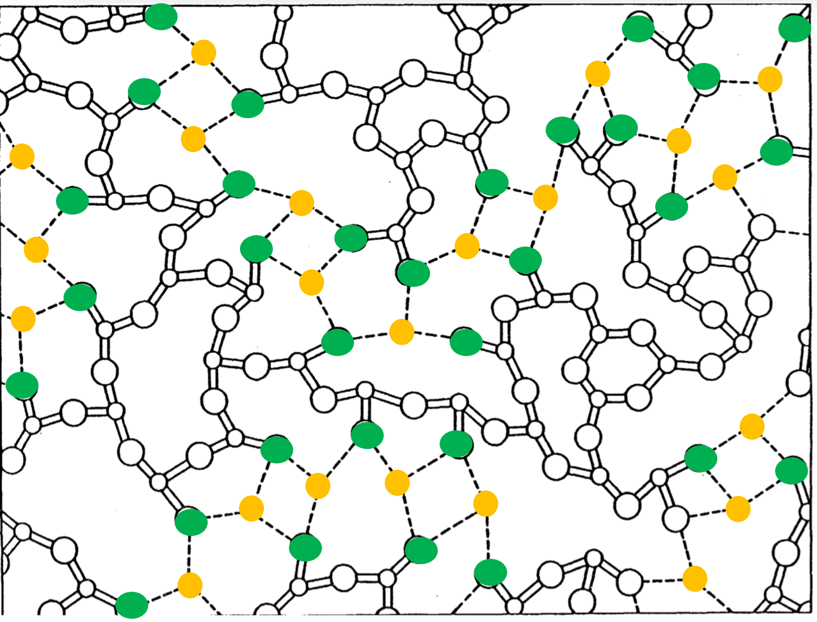
Le Losq Ch., Neuville D.R., Florian P., G.S. Henderson and Massiot D. (2014) Role of Al3+ on rheology and nano-structural changes of sodium silicate and aluminosilicate glasses and melts. Geochimica Cosmochimica Acta, 126, 495-517.

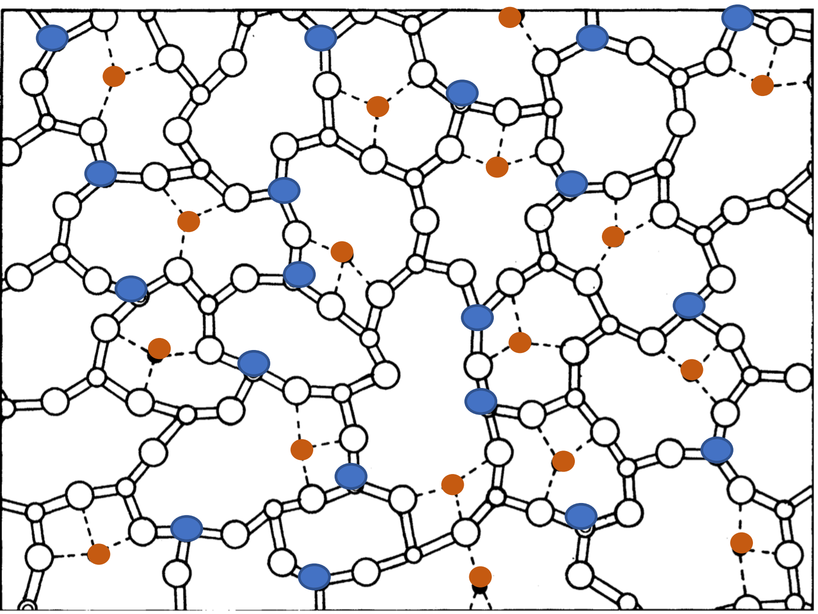


Hehlen B. and Neuville D.R. (2015) Raman response of network modifier cations in alumino-silicate glasses. The Journal of Physical Chemistry B. 119, 4093–4098.

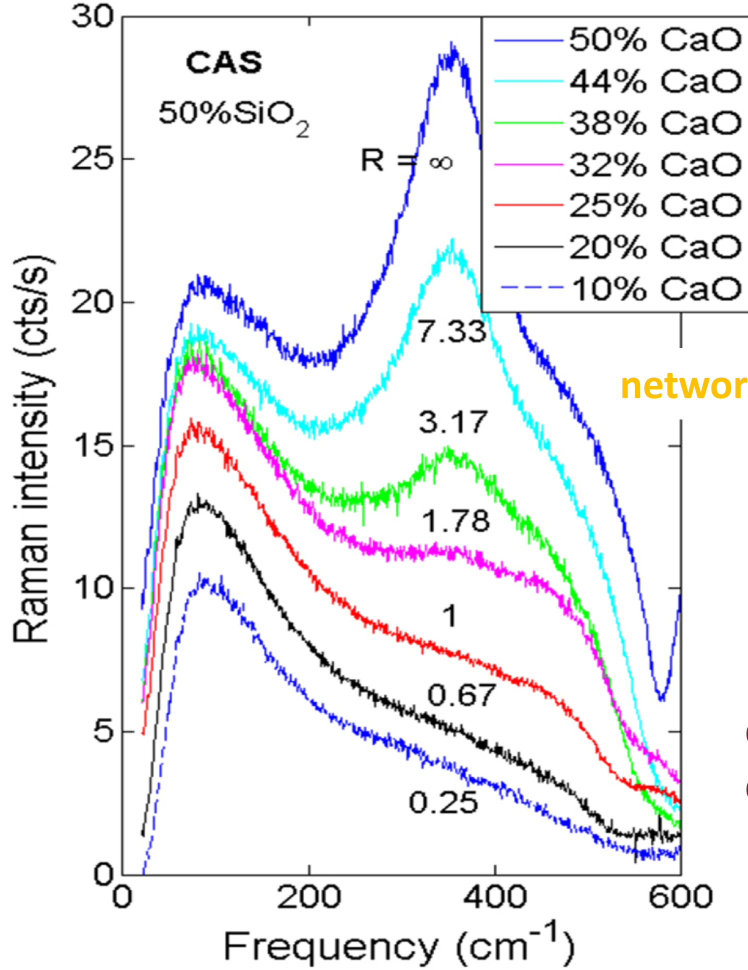
Raman VH







Raman VH

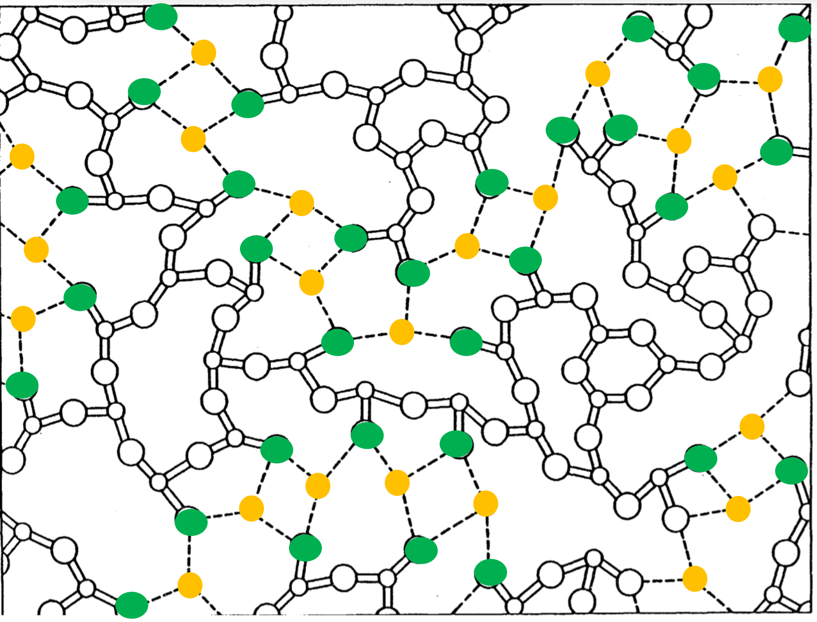


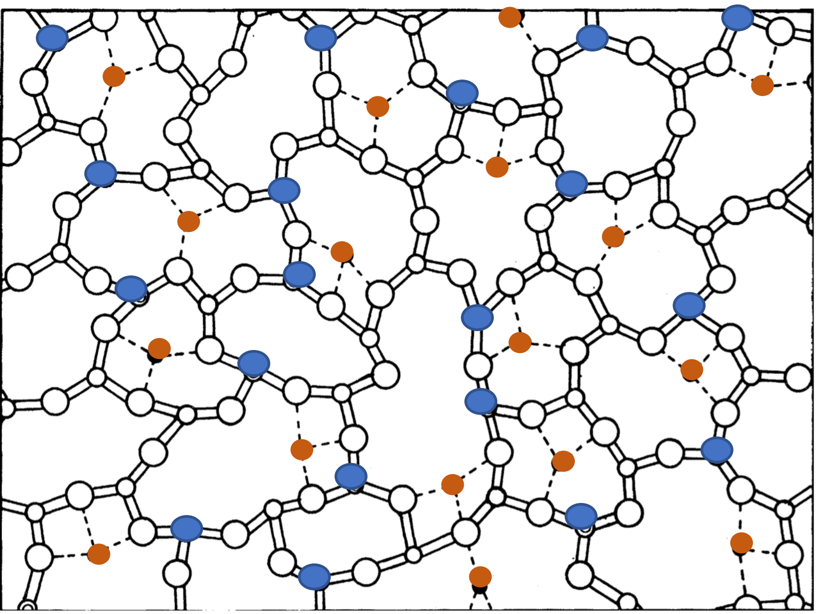
network modifyer

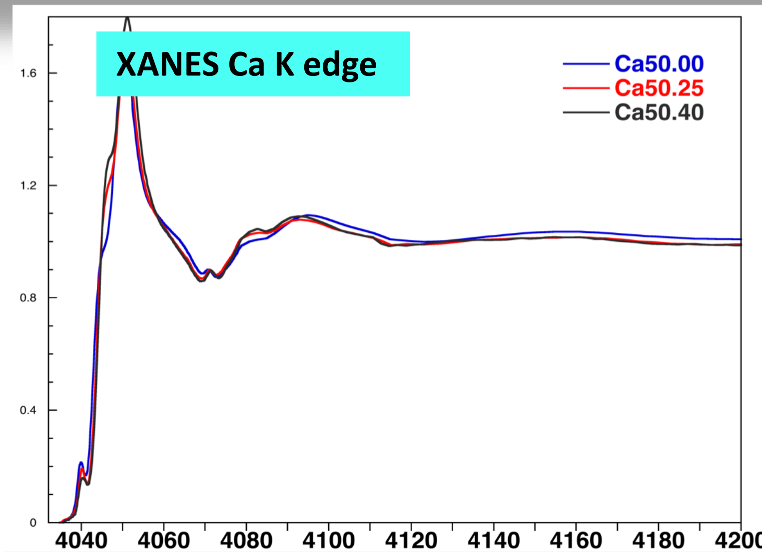
charge compensator

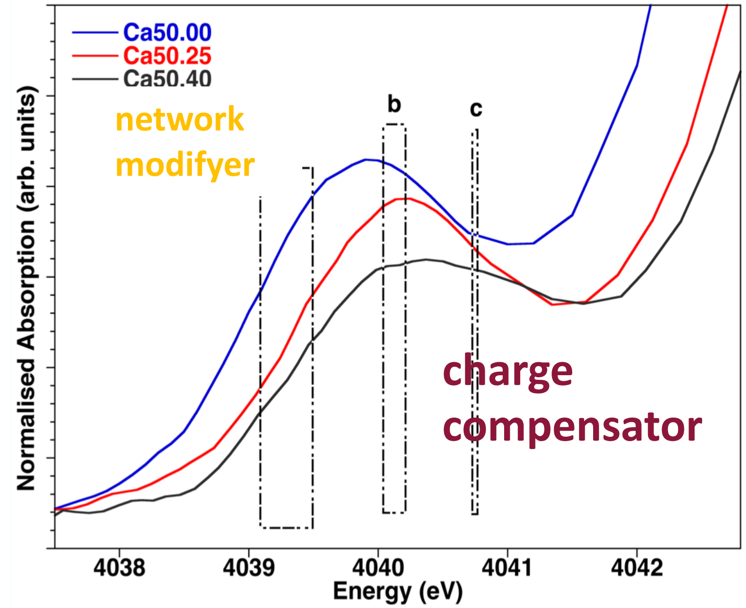
Hehlen B. and Neuville D.R. (2015) Raman response of network modifier cations in alumino-silicate glasses. The Journal of Physical Chemistry B. 119, 4093–4098.

Atomic structure in oxide glass, Greaves and Ngai, 1995

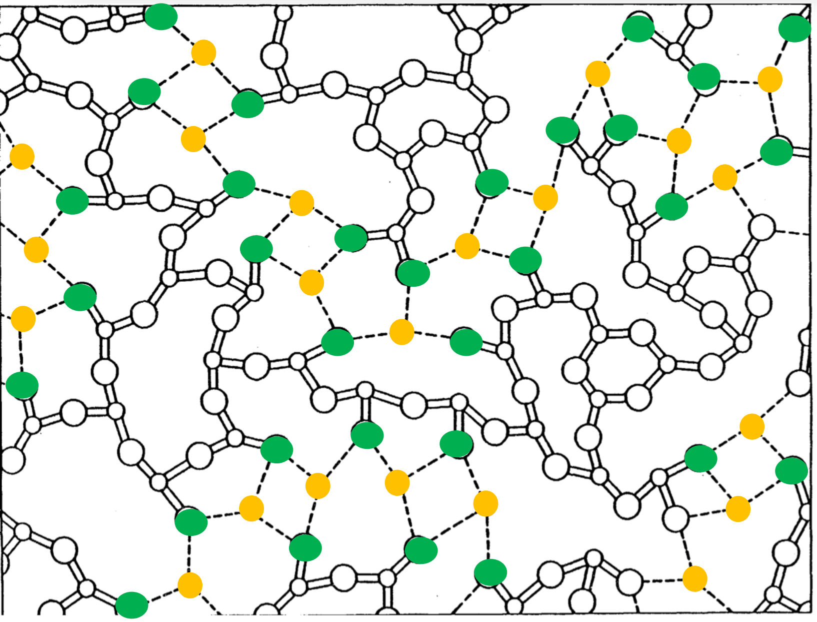


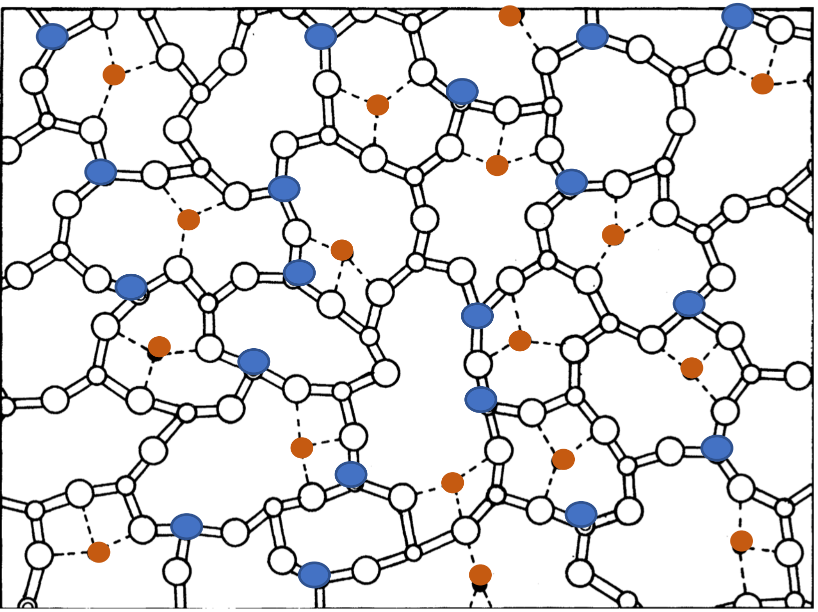


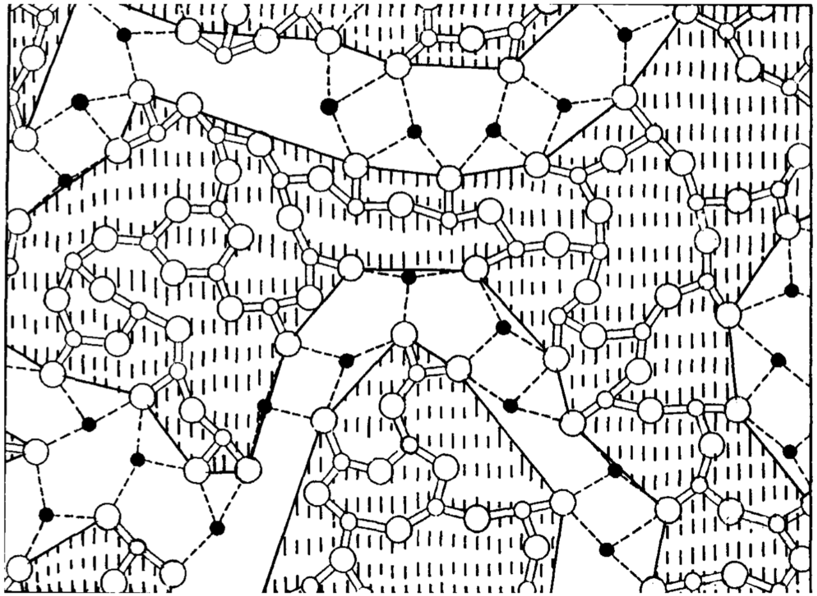




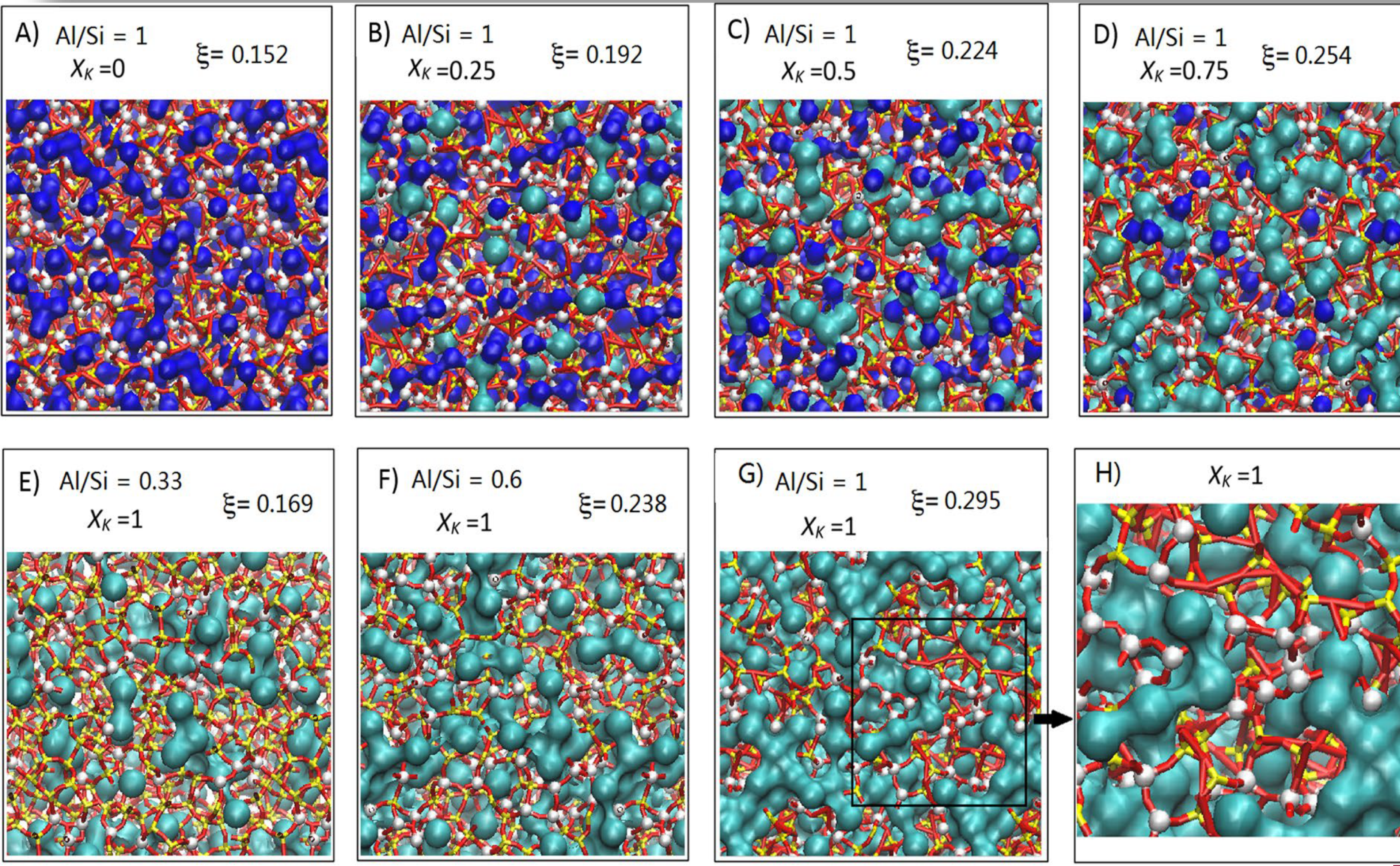
Cicconi M.R., de Ligny D., Gallo T. M., Neuville D.R. (2016) Ca Neighbors from XANES spectroscopy: a tool to investigate structure, redox and nucleation processes in silicate glasses, melts and crystals. American Mineralogist, 101, 1232-1236.



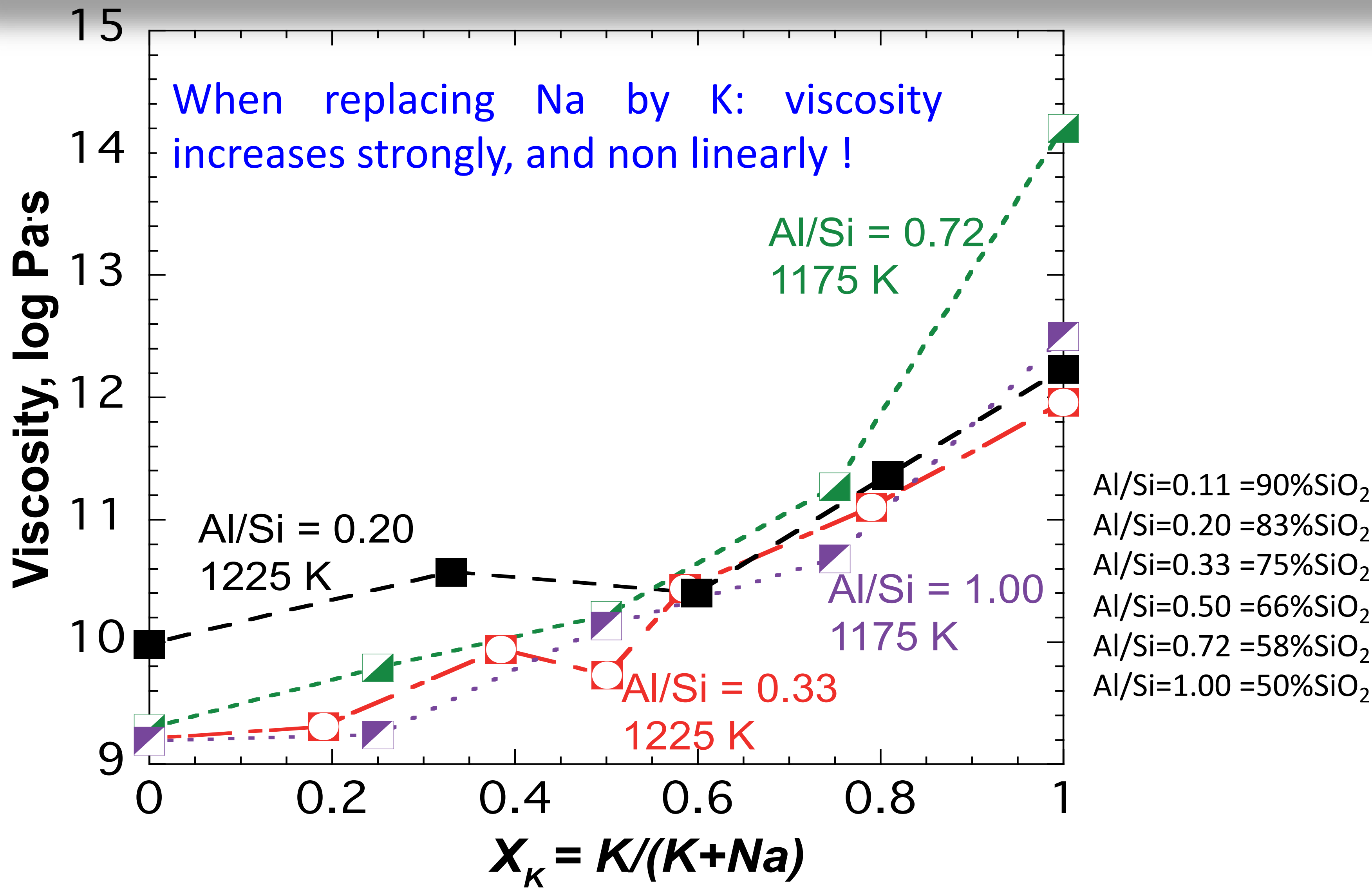




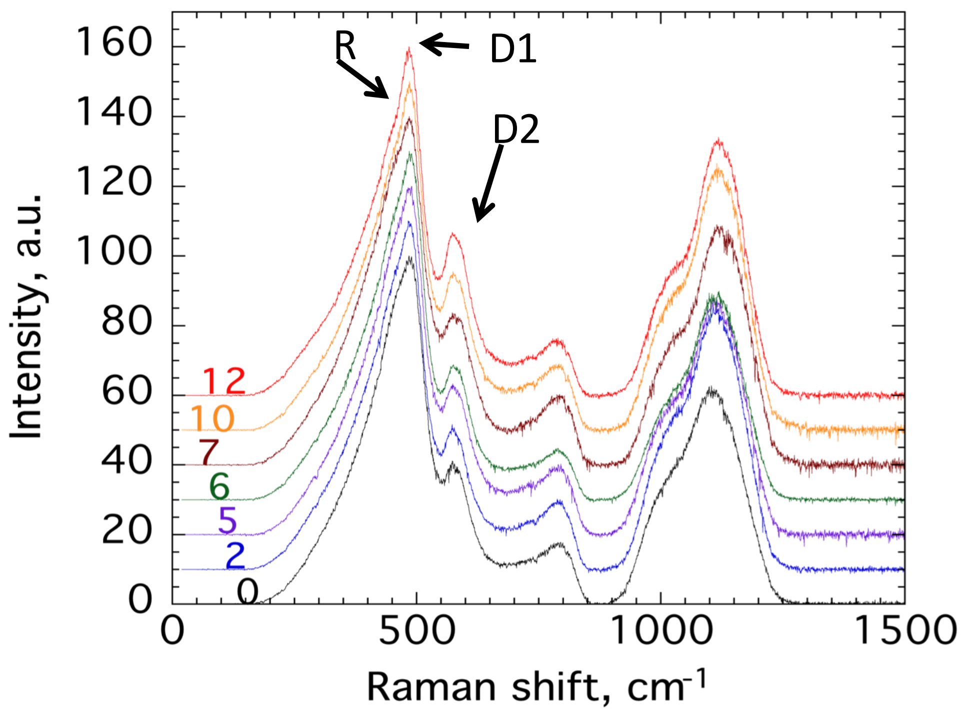
Strong Relationships between structure, and properties conductivity, viscosity, alteration etc….

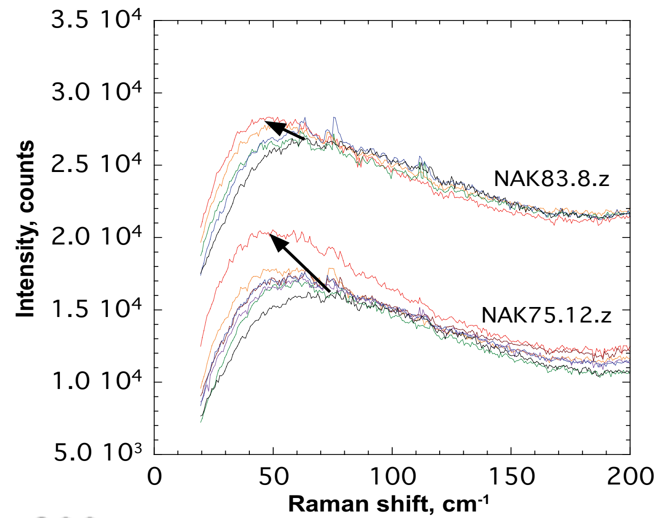


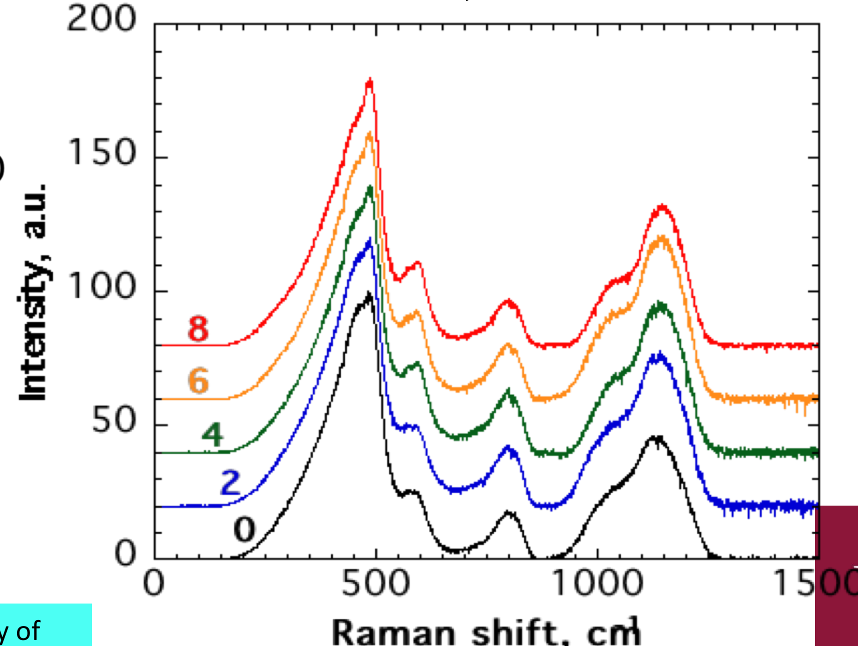
Le Losq C, Neuville D.R., Florian P., Massiot D., Zhou Z., Chen W., Greaves N. (2017) Percolation channels: a universal idea to describe the atomic structure of glasses and melts. Scientific Reports, 7, Article number: 16490, doi:10.1038/s41598-017-16741-3



Le Losq C, 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

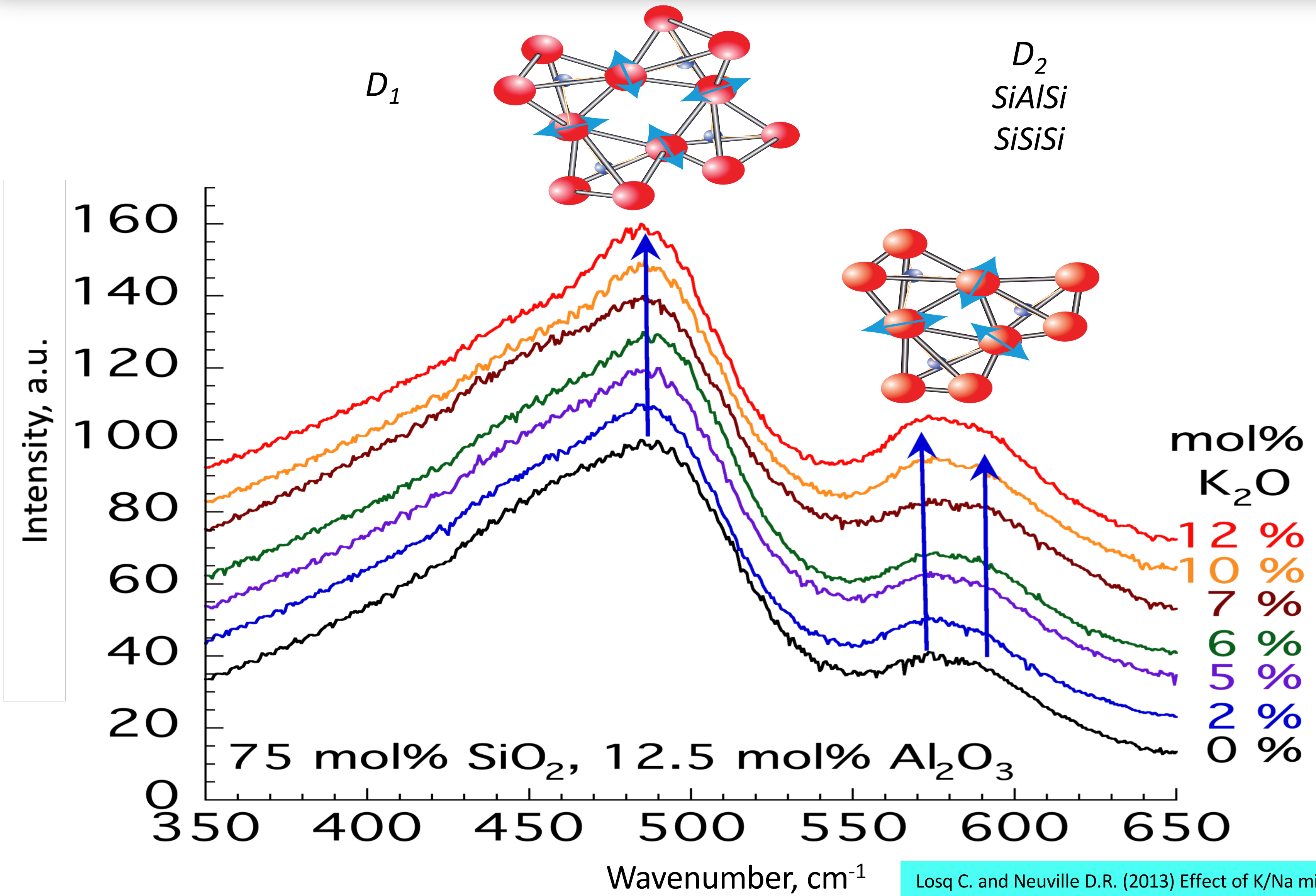






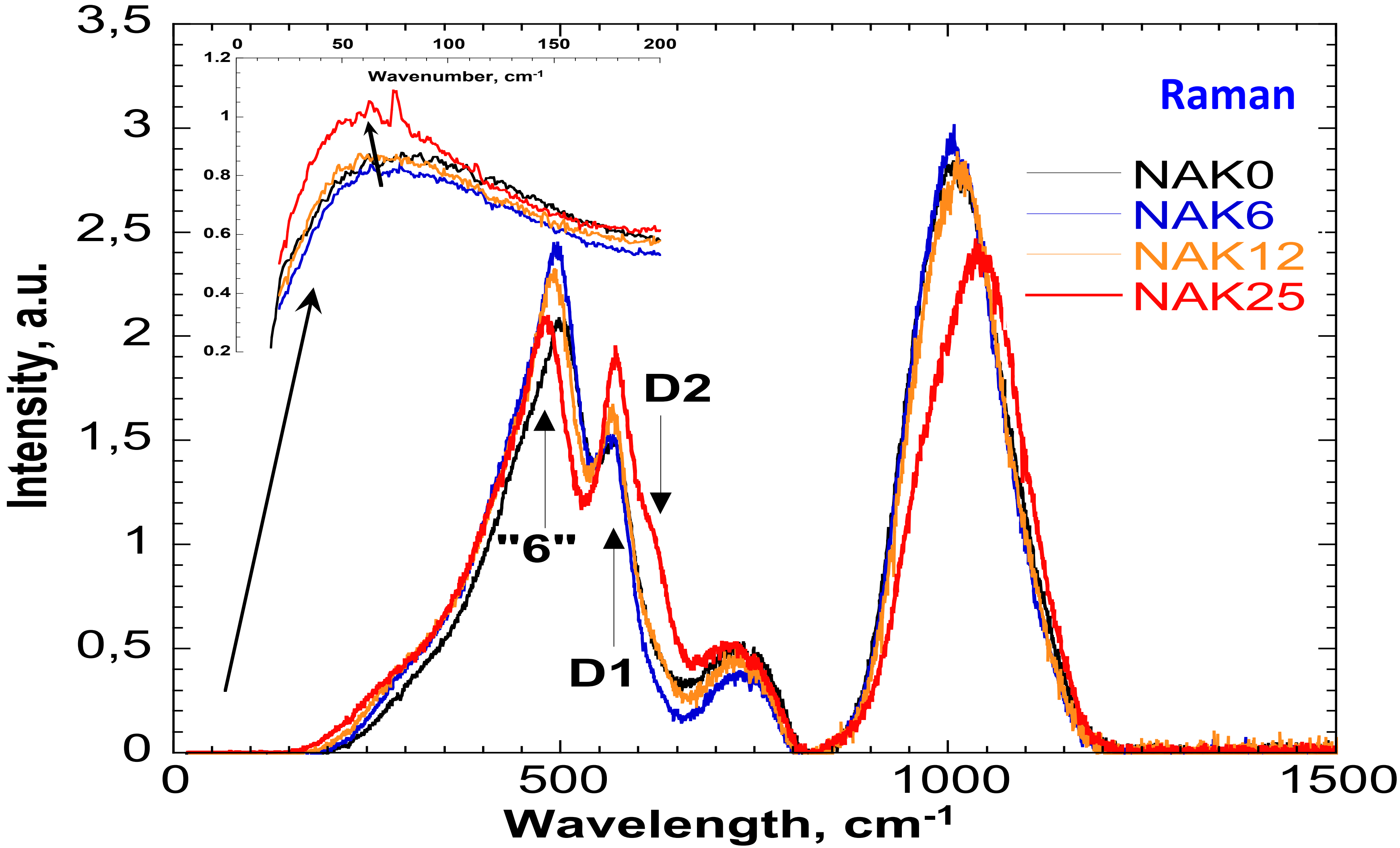
- Boson peak increase in I and decreases in frequency with K like close than SiO2
- D1 and D2 increase with K
- New D2 band

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.



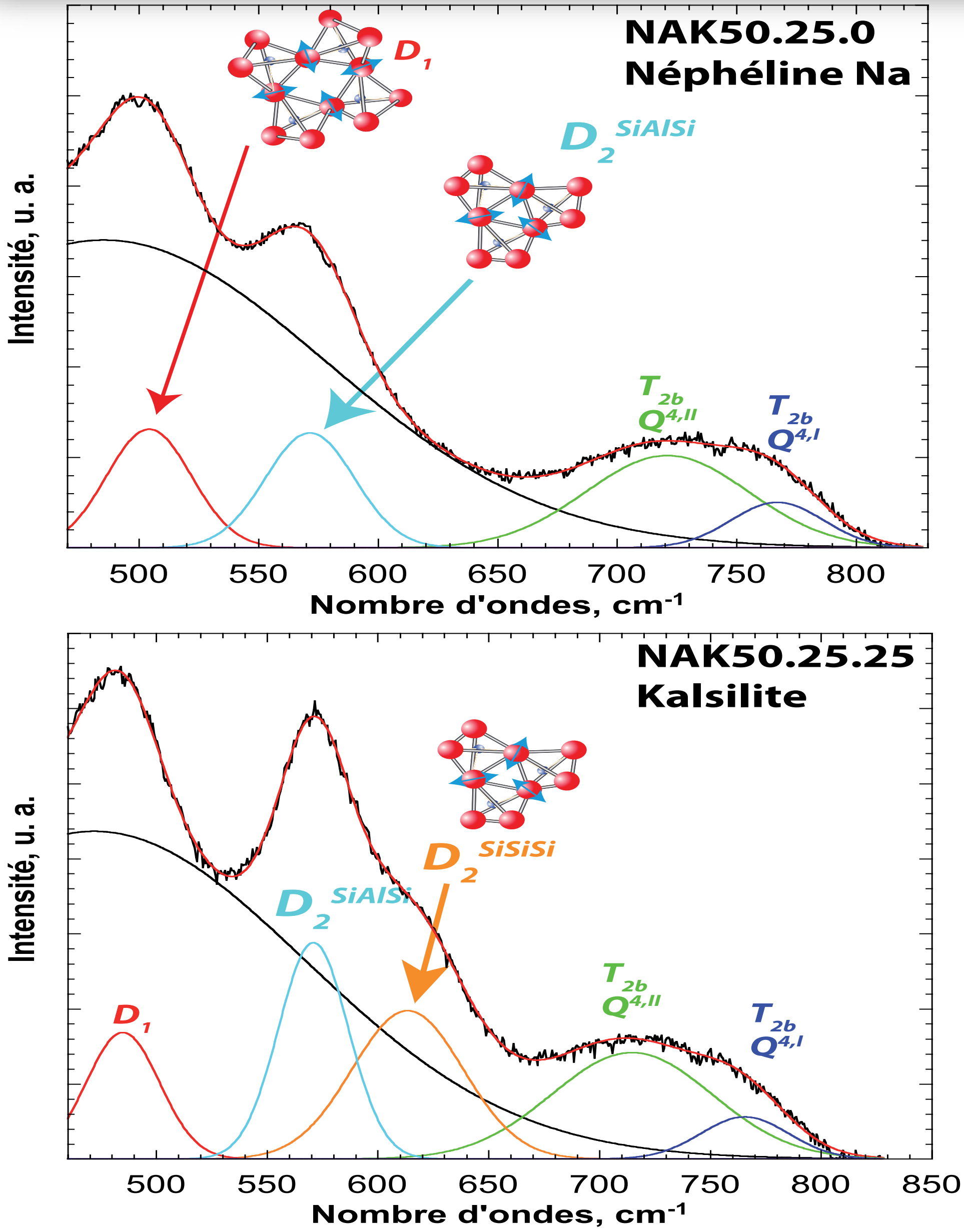
Losq C. and Neuville D.R. (2013) Effect of K/Na mixing on the structure and rheology of tectosilicate silica-rich melts. Chemical Geology, 346, 57-71.

At lower SiO_2 concentration…

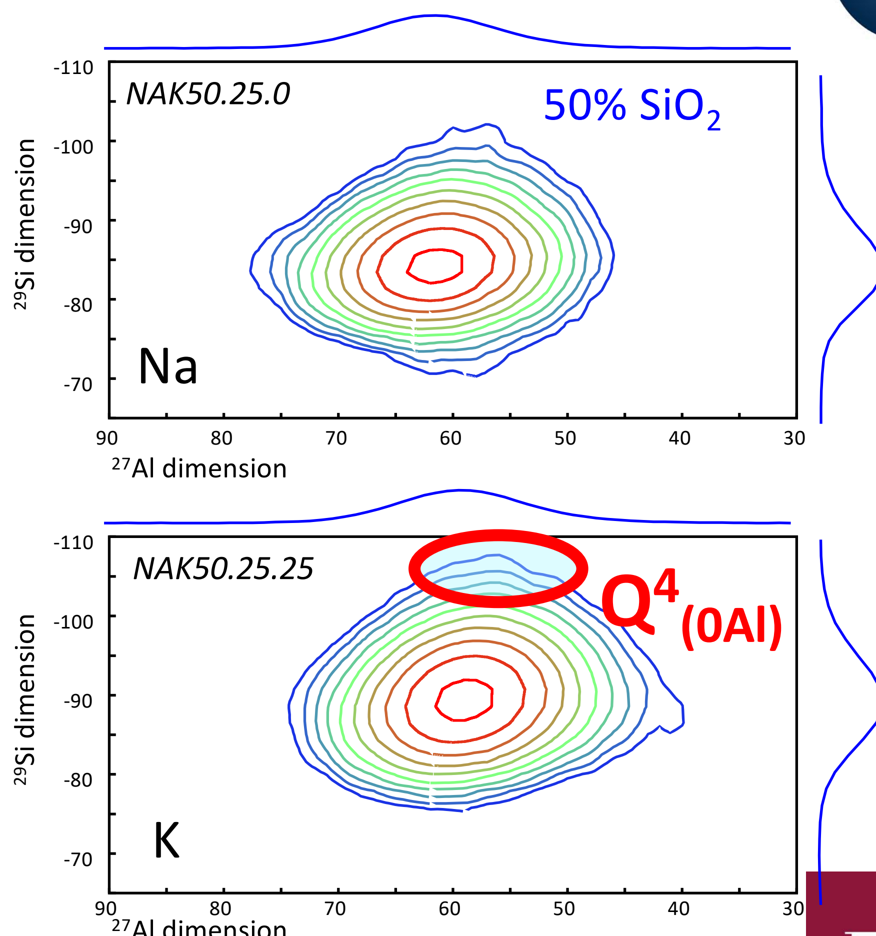


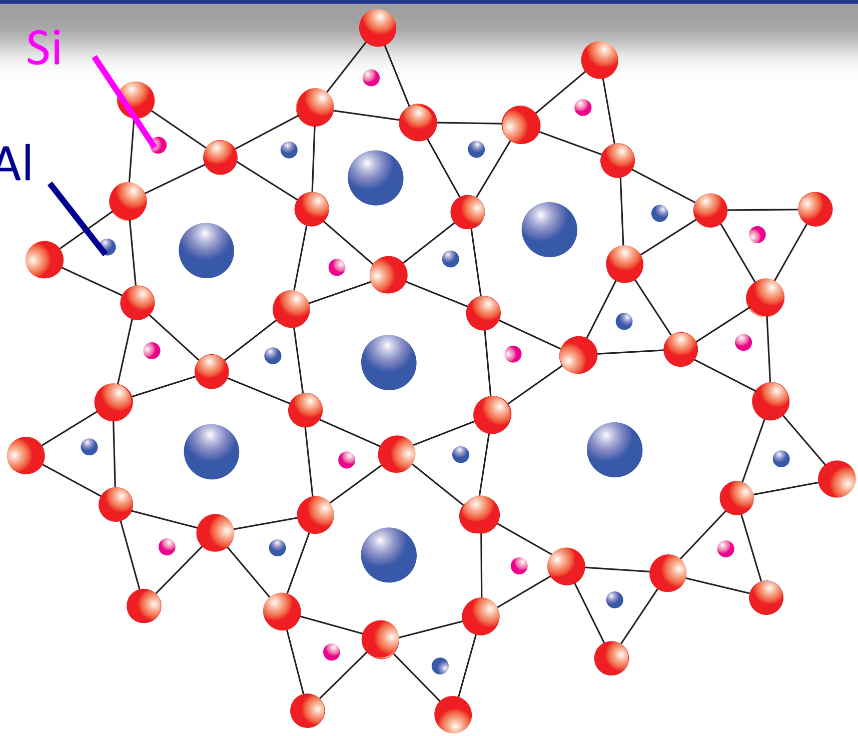
Le Losq C, Neuville D.R., Florian P., Massiot D., Zhou Z., Chen W., Greaves N. (2017) Percolation channels: a universal idea to describe the atomic structure of glasses and melts. Scientific Reports, 7, Article number: 16490, doi:10.1038/s41598-017-16741-3

Glassy nepheline-kalsilite
$NaAlSiO_4$-$KAlSiO_4$

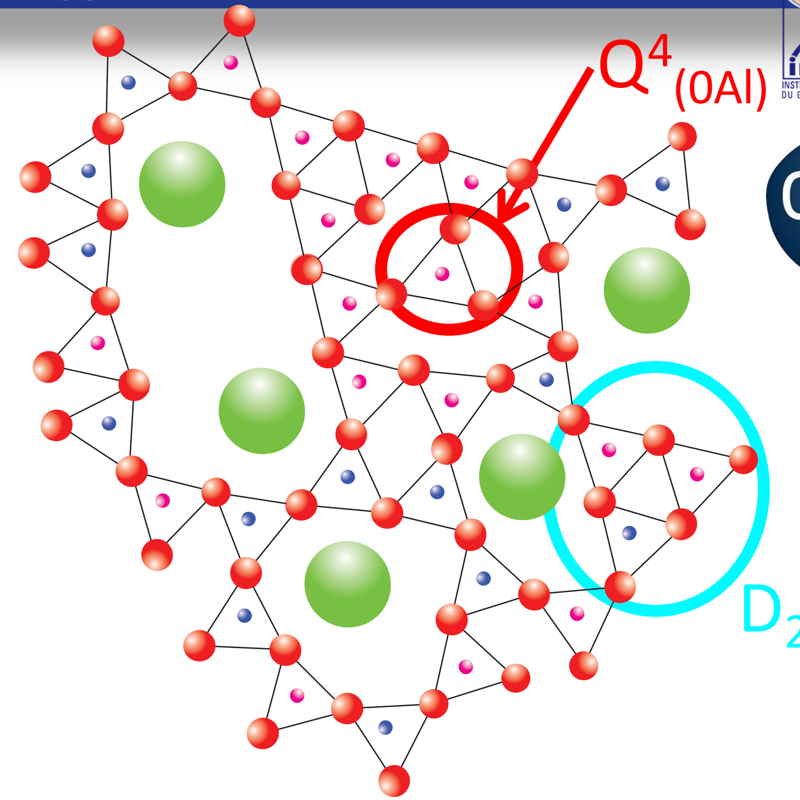


{29Si}27Al HMQC dipolar SR421 MAS 10kHz

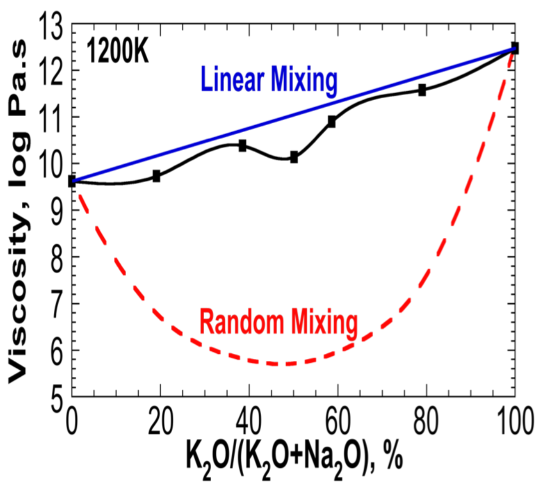




Na tectosilicates



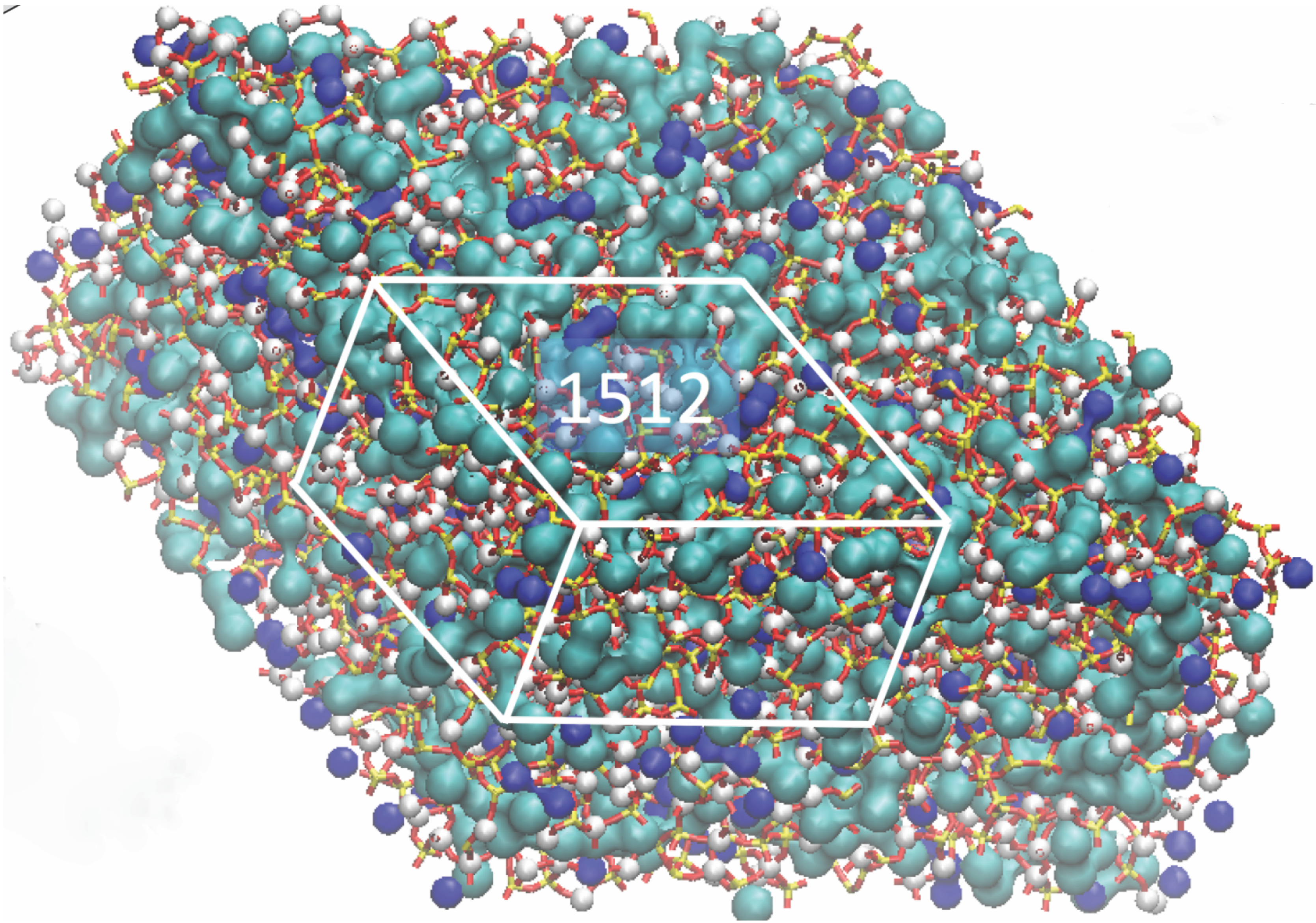
K tectosilicates



Na and K are in different structural positions

⇒ Two different networks

⇒ Non random mixing


1512

WELCOME ESRF & ILL Directors of Research				
General Introduction - D. NEUVILLE	X-ray Emission Spectroscopy - P. GLATZEL	Raman Spectroscopy - B. HEHLEN	Static NMR - P. FLORIAN	Ab initio simulation - M. GONZALEZ
Coffee break	Coffee break	Coffee break	Coffee break	Coffee break
X-ray & neutron scattering - G. VAUGHAN & G. CUELLO	X-ray Imaging - M. COTTE	IR Spectroscopy - D. de SOUSSA M.	Dynamic NMR - D. MASSIOT	Access to instruments - F. d'ACAPITO & E. MITCHELL
				Round Table and Conclusions
Lunch	Lunch	Lunch	Lunch	Lunch
X-ray Spectroscopy - Y. JOLY	X-ray Photoemission Spectroscopy - D. FOIX	Practicals	XPCS - B. RUTA	
Coffee break	Coffee break		Coffee break	
Practicals	Practicals	Coffee break	Practicals	
		Visits to beamline		