



Basic data on glass structure and its influence on viscosity

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Big Questions ?

Erebus Volcano

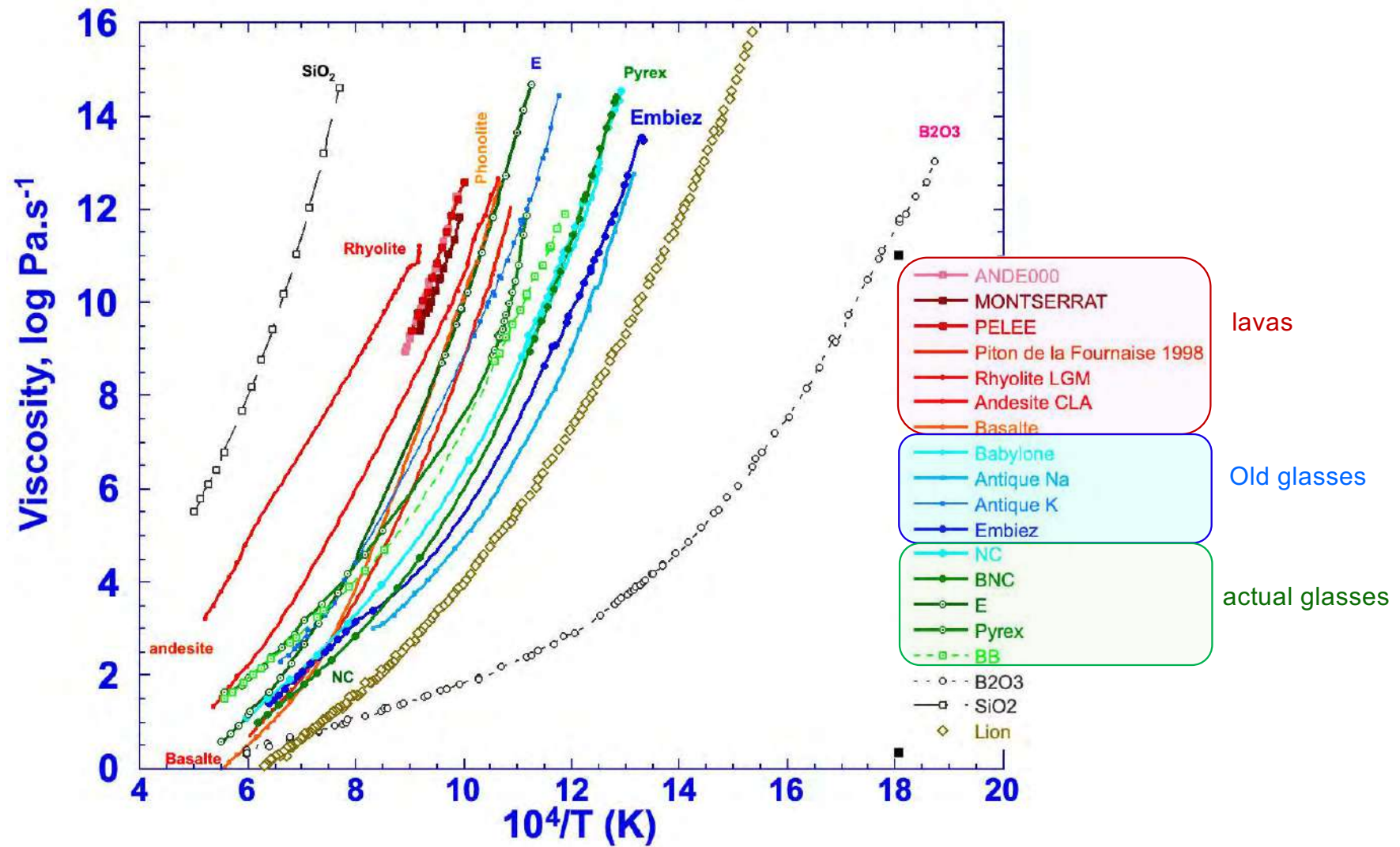


AGC Glass furnace



Raw materials
Fuel
Furnace atmosphere

Viscosities versus chemical compositions?



Possibility to use TVF equations and viscosity models

ELSEVIER

Journal of Volcanology and Geothermal Research 76 (1997) 319–327

Physics and Chemistry, Vol. 27, No. 4, 2001, pp. 360–370.
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Earth and Planetary Science Letters 271 (2008) 123–134

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Earth and Planetary Science Letters

journal homepage: www.elsevier.com/locate/epsl

Empirical method of calculating the viscosity of peraluminous silicate melts at high temperatures

Akio Goto^{a,*}, Hiroaki

[AMERICAN JOURNAL OF SCIENCE, VOL. 272, MAY, 1972, P. 438–475]

THE VISCOSITY OF MAGMATIC SILICATE LIQUIDS: A MODEL FOR CALCULATION

YAN BOTTINGA^{a,*} and DANIEL F. WEILL

Center for Volcanology, University of Oregon, Eugene, Oregon 97403

Augmented Adam-Gibbs model for glass melt viscosity and configuration entropy as functions of temperature and composition

Pavel Ferkel^{a,*}, Pavel Hrmáček^b, Albert A. Kruger^c

statistical modelling approach

Alexander Fluegel^d

Pacific Northwest National Laboratory, Richland, Washington

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Calculation of the Viscosity VI. The $R_2O-B_2O_3-SiO_2$ and Borosilicate

ZAO Termeks, ul Odoevskaya, Moscow, Russia

Structure Based Viscosity Model for Aluminosilicate Slag

Zhiming YAN^{1,2,3}, Ramana G. REDDY² and Xuewei LV^{1,3,4}

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2) Department of Metallurgical and Materials Engineering, The University of Alabama, Tuscaloosa, Alabama, 35487 USA.
3) Chongqing Key Laboratory of Vanadium-Titanium Metallurgy and New Materials, Chongqing University, Chongqing, 400044 China.
4) State Key Laboratory of Mechanical Transmissions, Chongqing University, Chongqing, 400044 China.

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2024, VOL. 12, NO. 4, 306–321
<https://doi.org/10.1080/21870764.2024.2407040>

THE CERAMIC SOCIETY OF JAPAN

THE KOREAN CERAMIC SOCIETY

Taylor & Francis Group

RESEARCH ARTICLE

OPEN ACCESS

Modeling viscosity of commercial glass melts: Adam–Gibbs equation and Gaussian process regression

Pavel Ferkel^{a,*}, Preeti Malviya^b, Pavel Hrmáček^c, Albert A. Kruger^d and Ashutosh Goel^e

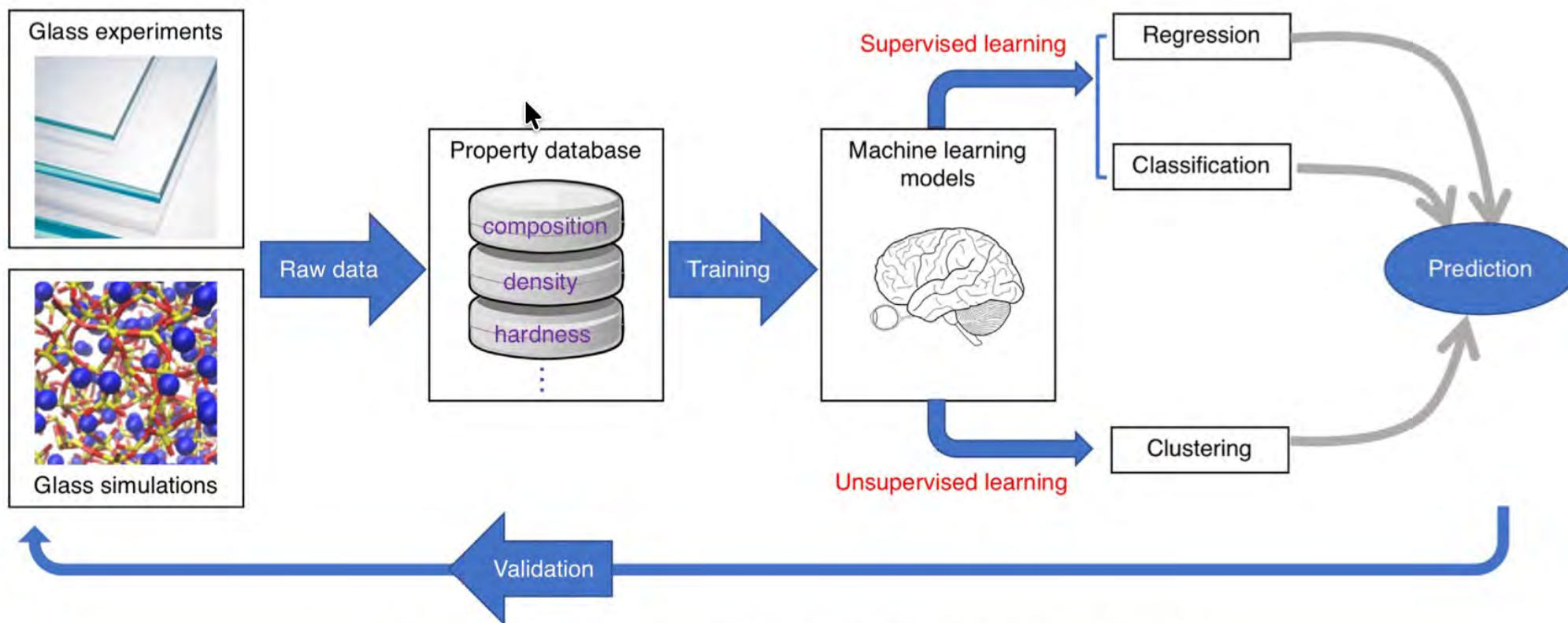


Fig. 1. Illustration of a typical application of machine learning to facilitate glass design.

Liu H., Fu Z., Yang K., Xu X., Bauchy M. (2019) Machine learning for glass science and engineering: A review. *Journal of Non-Crystalline Solids* X, 4, 100036

Big Questions ?

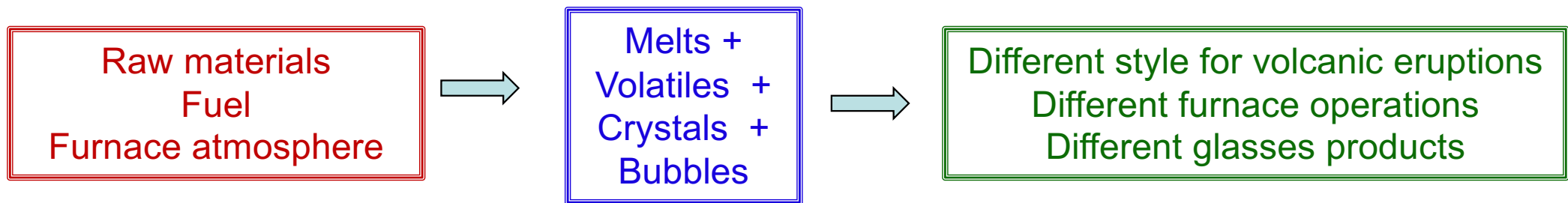
Erebus Volcano



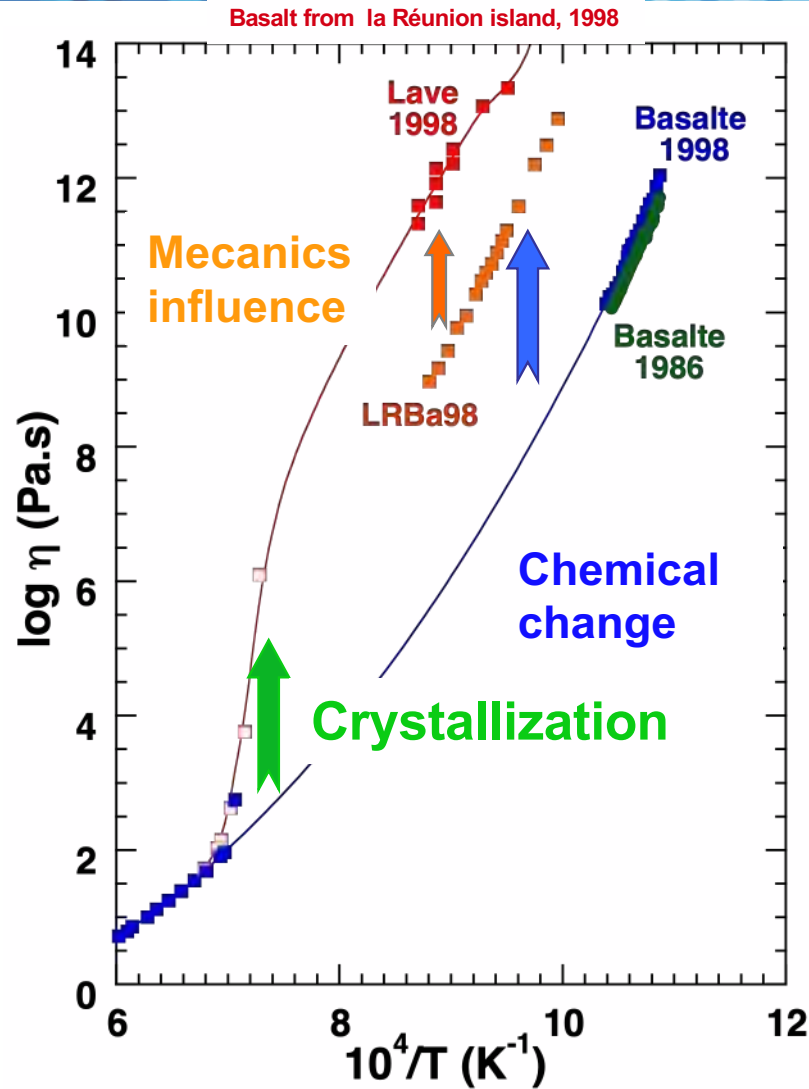
AGC Glass furnace



η



which parameters control the viscosity ?



- Chemical composition
- Temperature

Iron, aluminum, alkali,
earth-alkali

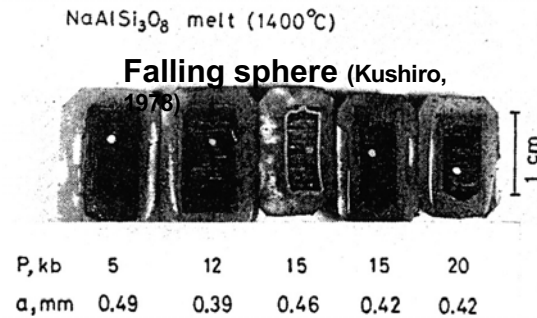
- Inclusions

Bubbles, crystals,
Volatils

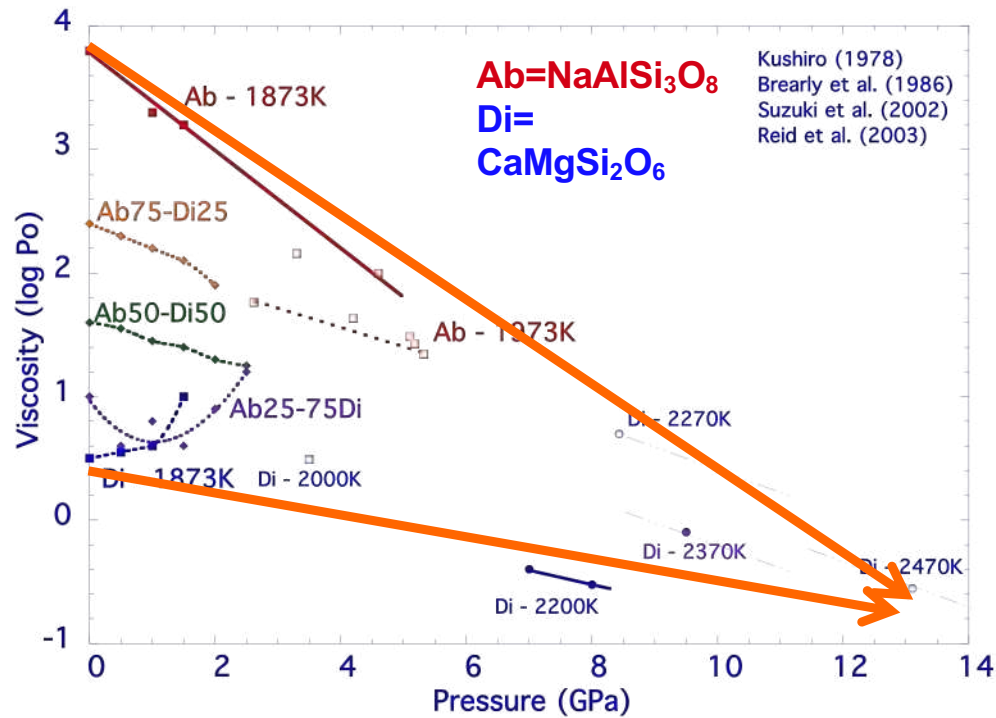
- Pressure

Villeneuve N, Neuville D.R. Boivin P., Bachelery P. and Richet P.
(2008) Magma crystallization and viscosity: A study of molten basalts
from the Piton de la Fournaise volcano (La Réunion island) Chemical
Geology, 256, 242-251.

Pressure effect

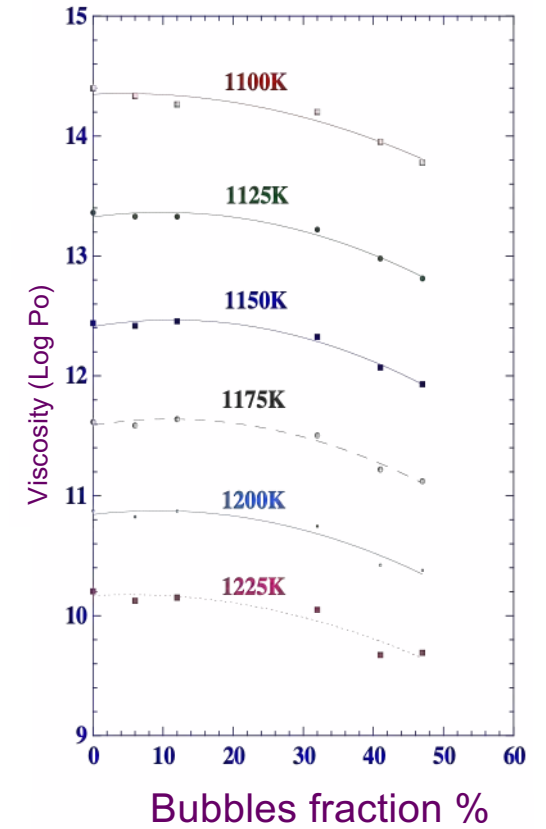
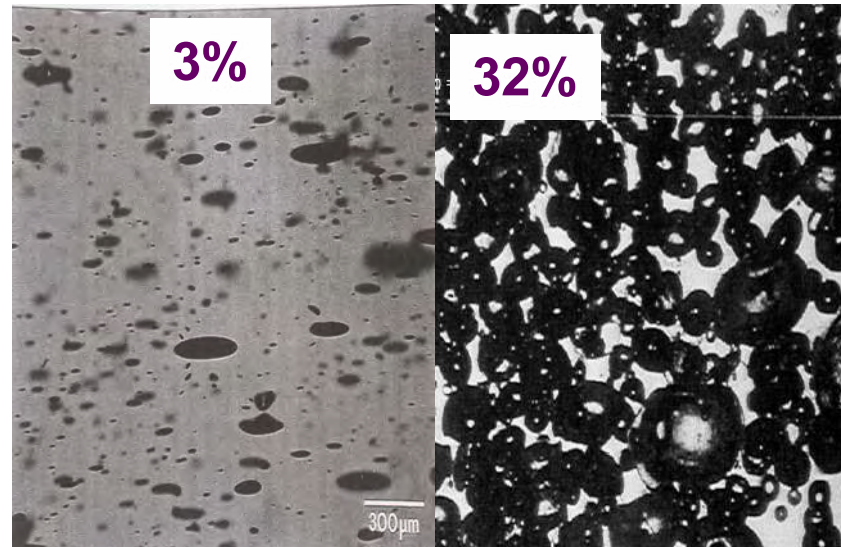
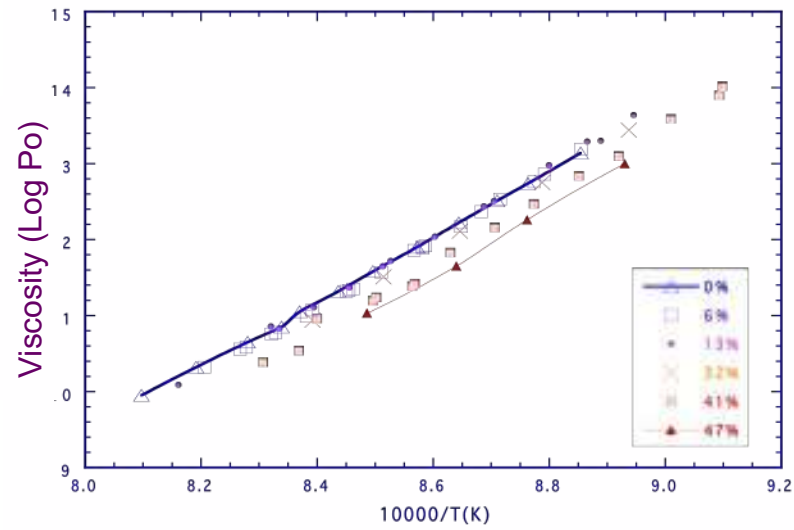


Falling-sphere method (Kushiro, 1978)
 And now, falling-sphere coupled with high resolution X-Ray CCD camera
 [Suzuki et al. (2002), Reid et al., (2003)]



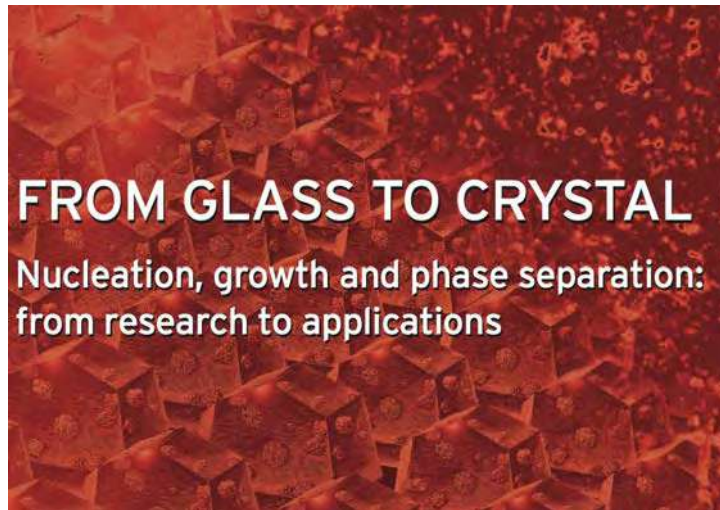
Pressure => Low effect on the viscosity for all chemical compositions

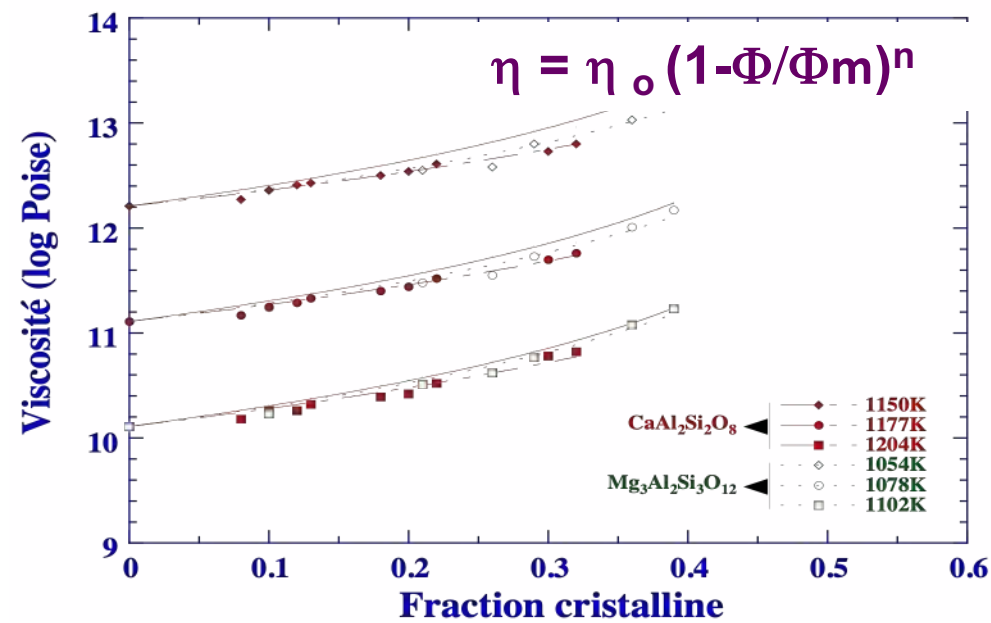
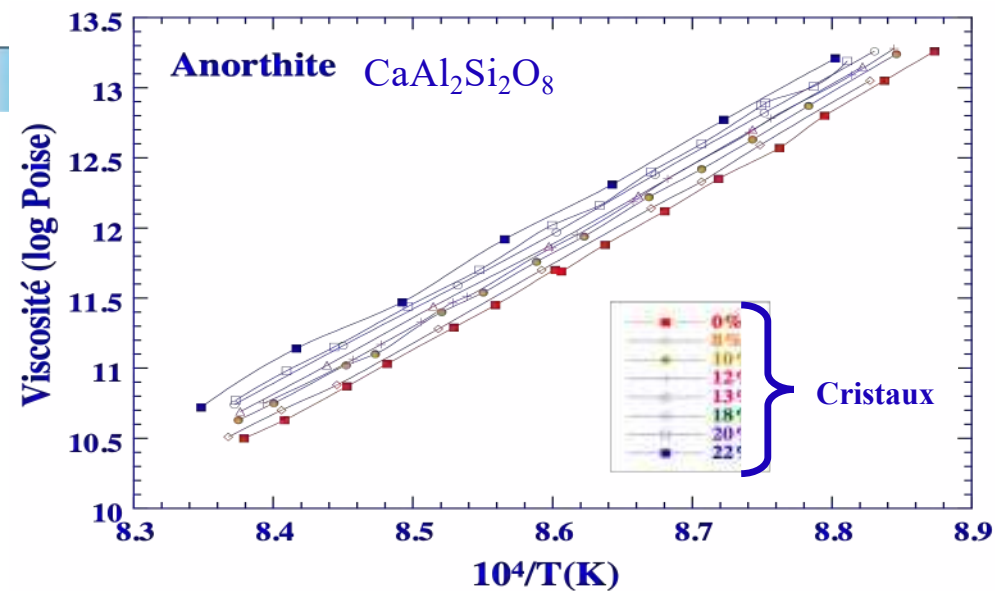
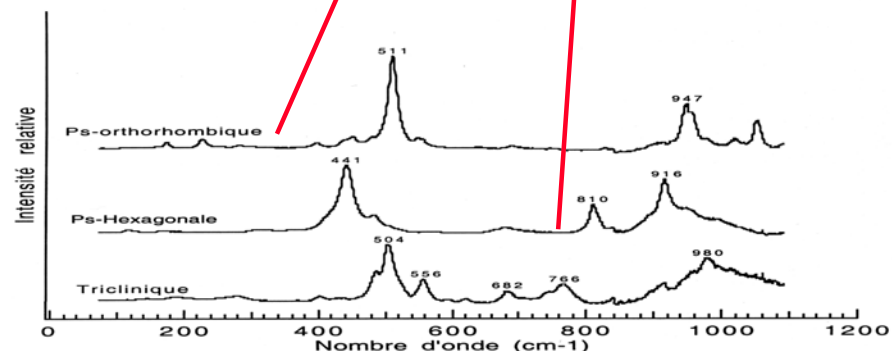
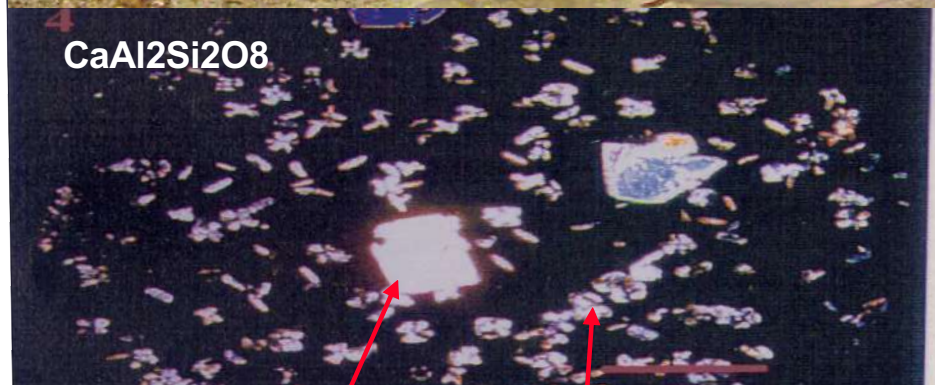
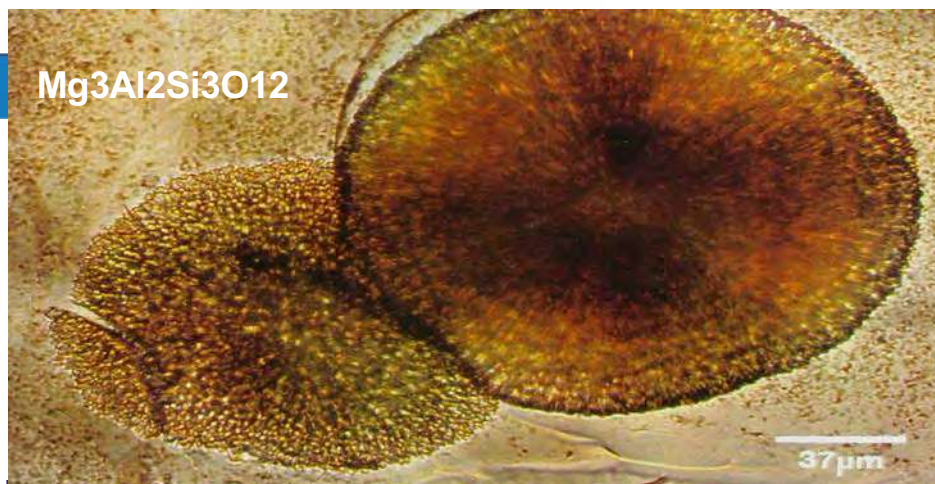
Bubble Effect



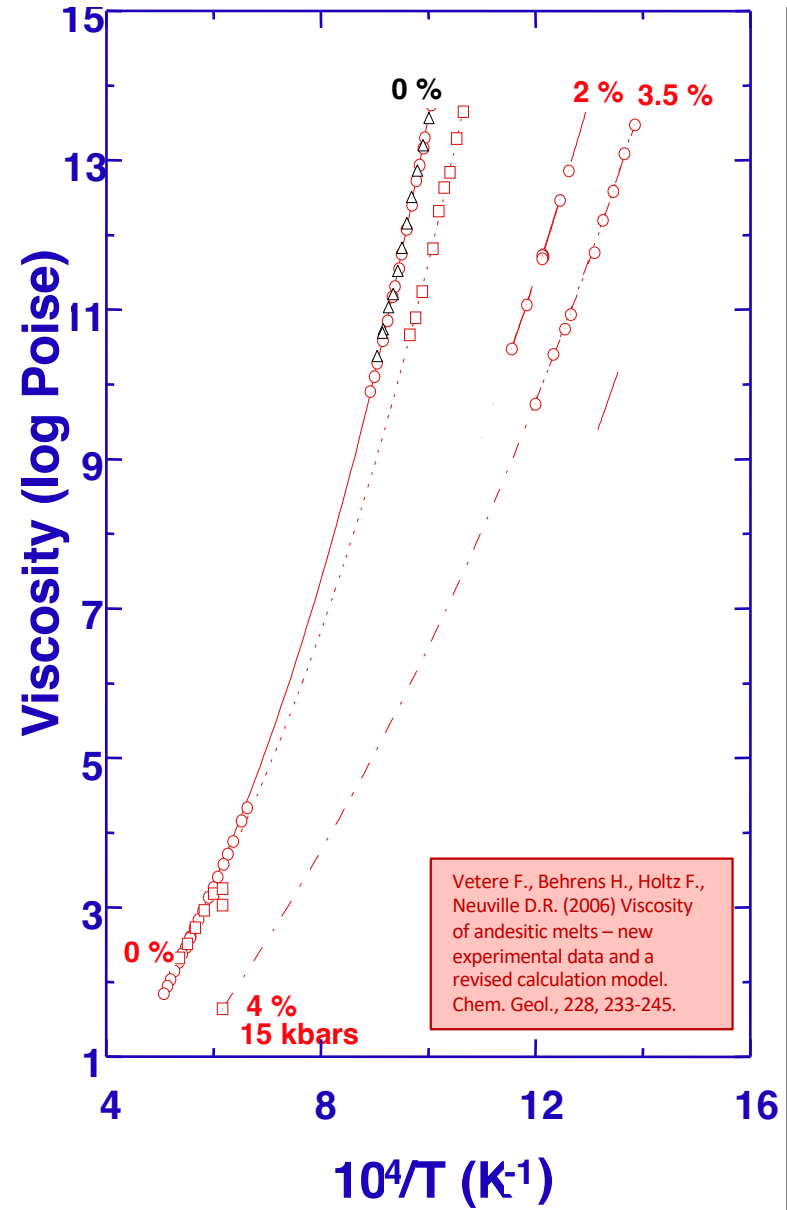
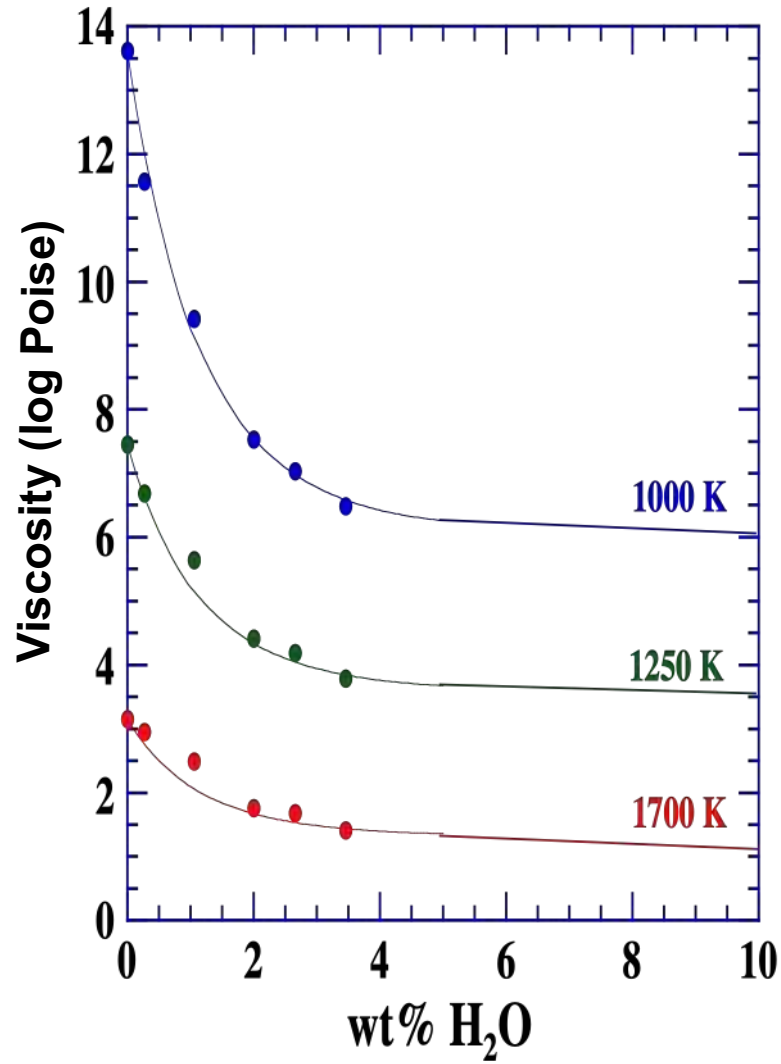
$$\eta = \eta_o (1 - \Phi/\Phi_m)^n$$

=> Small effect

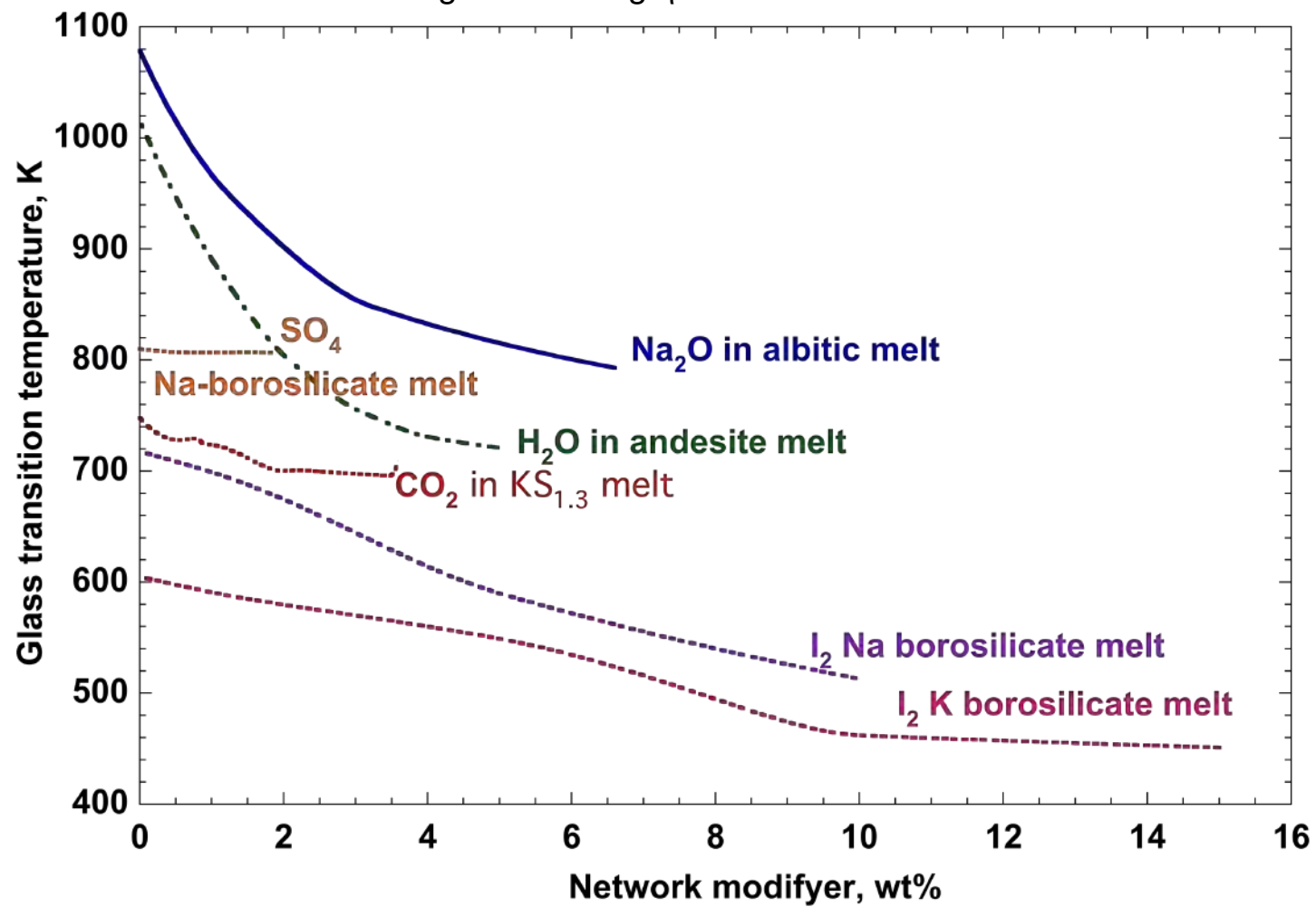




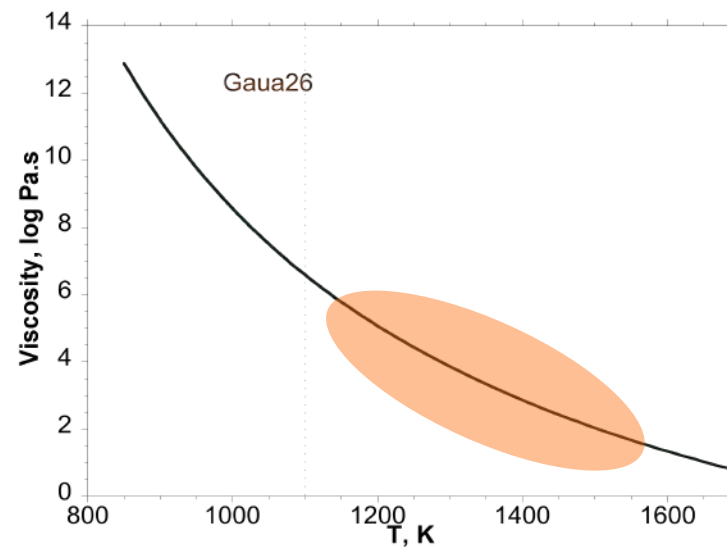
Volatiles Effect



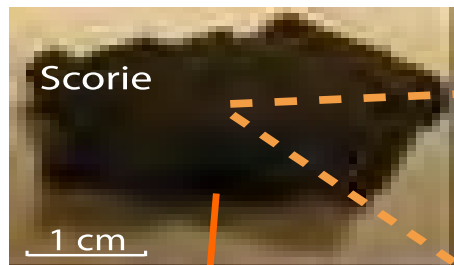
T_g measured by DSC with heating rate 10K/min
or T_g taken for log η = 12 Pa.s



Mont Garet, Vanuatu archipel, Métrich et al., 2016, JVGR

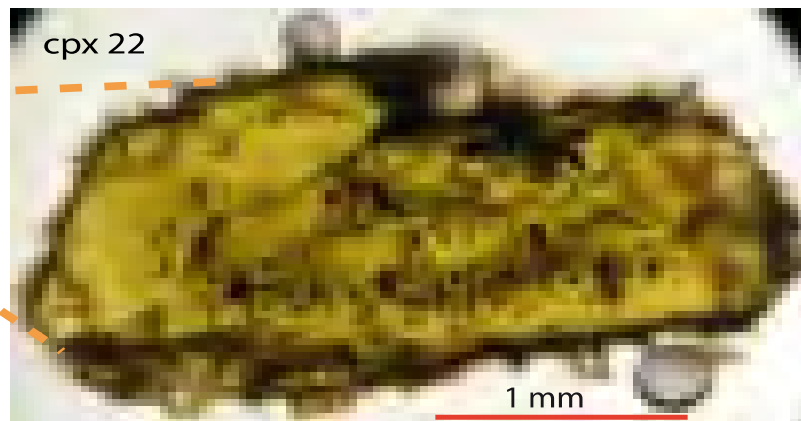


Métrich N., Bertagnini A., Garaebiti E., Vergnolle S., Bani Ph., Beaumais A., and Neuville D.R. (2016) Magma transfer and degassing budget during the 2009-2010 unrest at Mt Garet (Vanuatu arc). *Journal of Volcanology and Geothermal Research*. 322, 48-62.

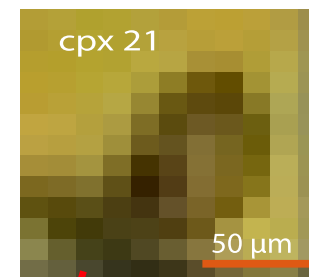


Clinopyroxene, Plagioclases,
Olivine,
FeTi oxide

- Analyze of residual melts
- Proportion of bubbles
- Proportion of crystals



Clinopyroxene,

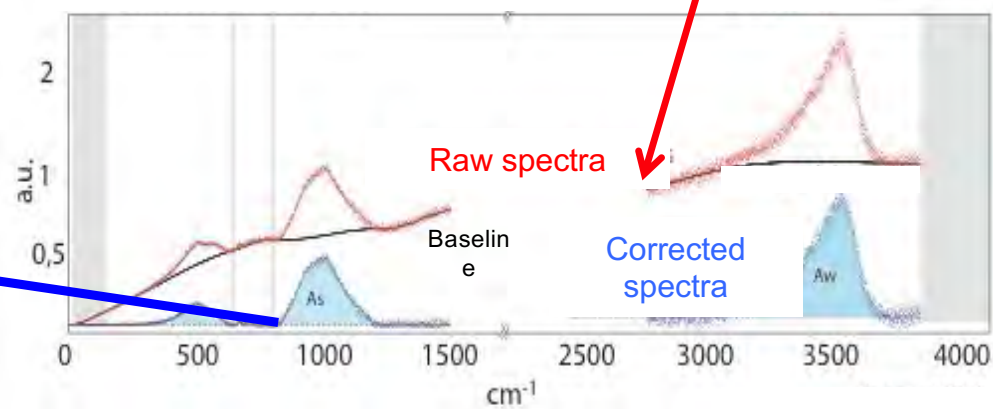


Fluid inclusion

**Raman
spectroscopy**

**Volatiles
quantification,
H₂O, CO₂...**

Losq et al., Amer Min, 2012
Amalberti et al., 2011, 2021



$$\text{Log}\eta_{\text{lava}} = \text{log}\eta_{\text{melt}} + X_{\text{volatile}} + Y_{\text{crystal}} + Z_{\text{bubble}}$$

$$\log\eta_{H_2O} = A + \frac{(B^{anh} + K_1 \times C_{H_2O} + K_2 \times C_{H_2O}^2)}{(T - (T_1^{anh} + K_3 \times C_{H_2O} + K_4 \times C_{H_2O}^2))}$$

Whittington et al., (2001)

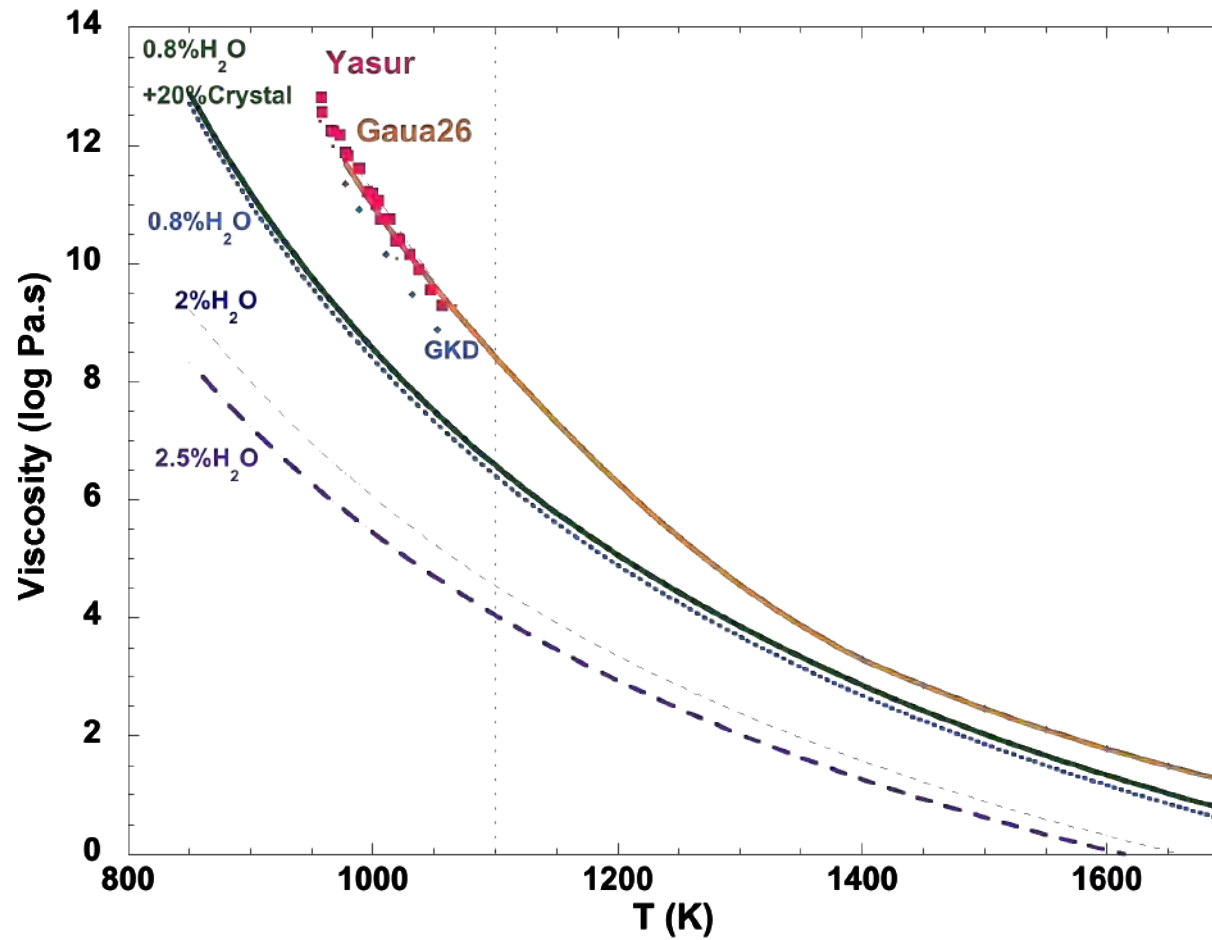
$$\eta = \eta_0 (1 - \Phi/\Phi_m)^{-n}$$

Roscoe, 1952

$$\eta_r(T) = \eta(\Phi, T) / \eta(0, T)$$

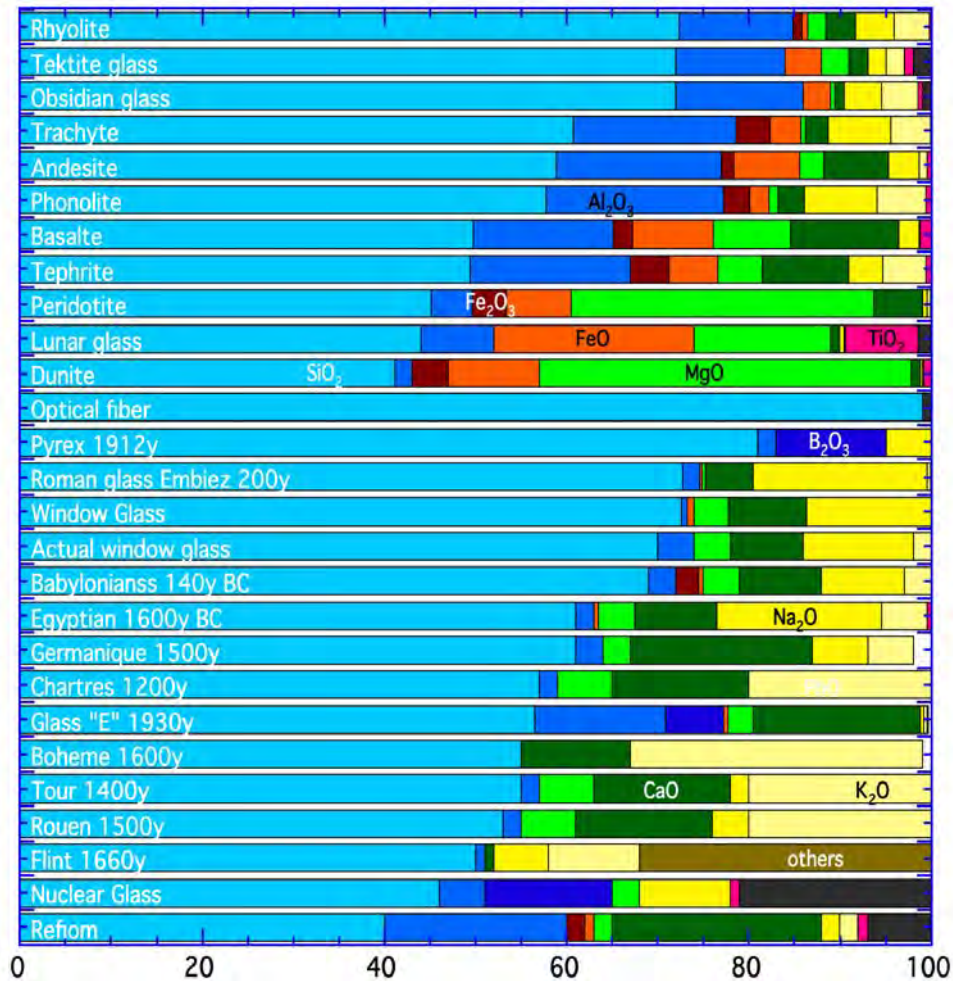
Lejeune et al., 1999

$$\text{Log}\eta_{\text{lava}} = \text{log}\eta_{\text{melt}} + X_{\text{volatile}} + Y_{\text{crystal}} + Z_{\text{bubble}}$$

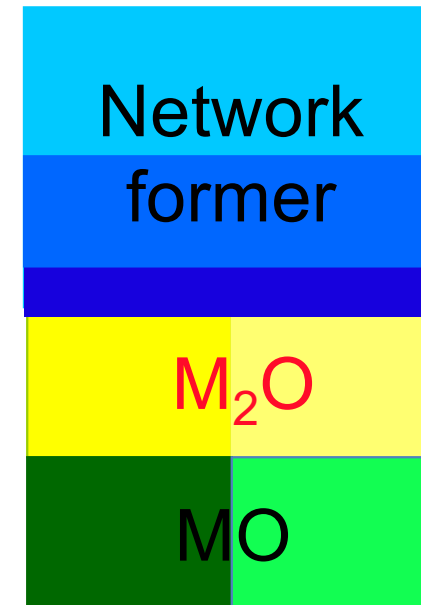


Métrich N., Bertagnini A., Garaebiti E., Vergnolle S., Bani Ph., Beaumais A., and Neuville D.R. (2016) Magma transfer and degassing budget during the 2009-2010 unrest at Mt Garet (Vanuatu arc). *Journal of Volcanology and Geothermal Research*. 322, 48-62.

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



$\Leftrightarrow$



Properties versus Structure ?

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

What is a network modifier or charge compensator ?

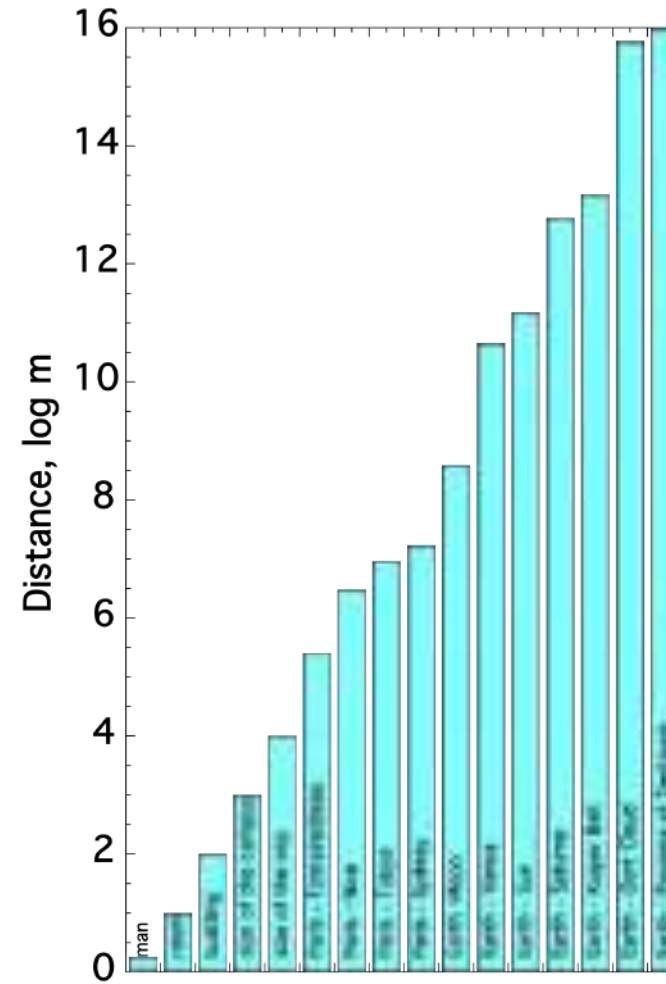
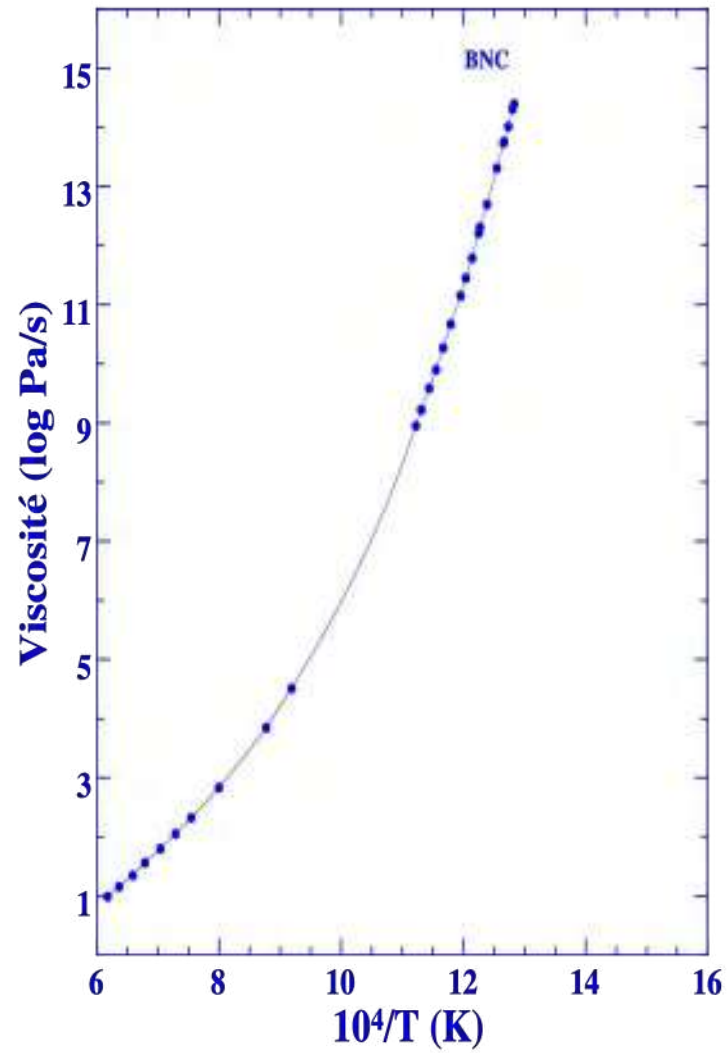
Why alkaline or earth-alkaline element changes role?

What happens in the case of transition elements?

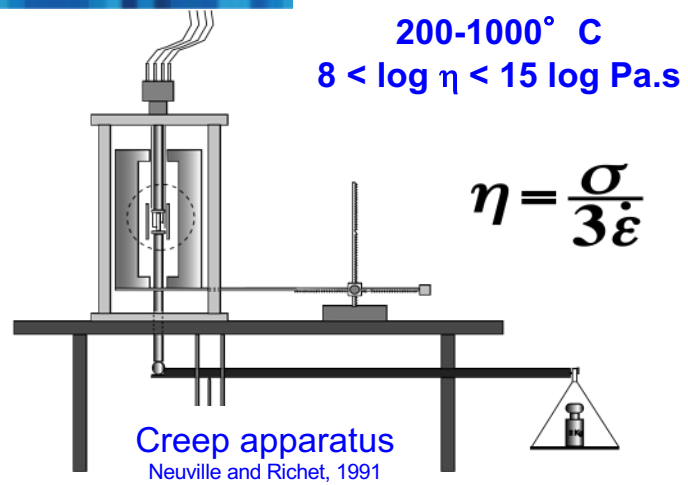
What happens during nucleation processes?

Redox talk tomorrow

A large number -> difficult to measure



Viscosity measurements



Cylinder
 $1 < d < 20 \text{ mm}$
 $4 < h < 15 \text{ mm}$

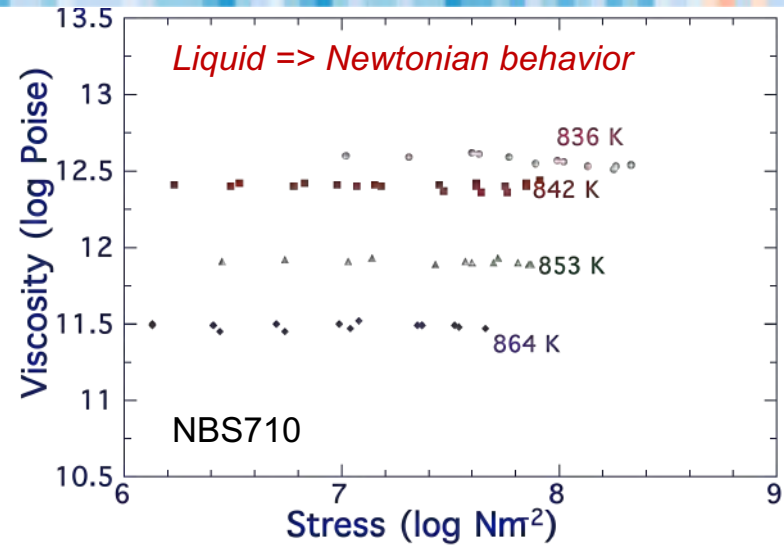
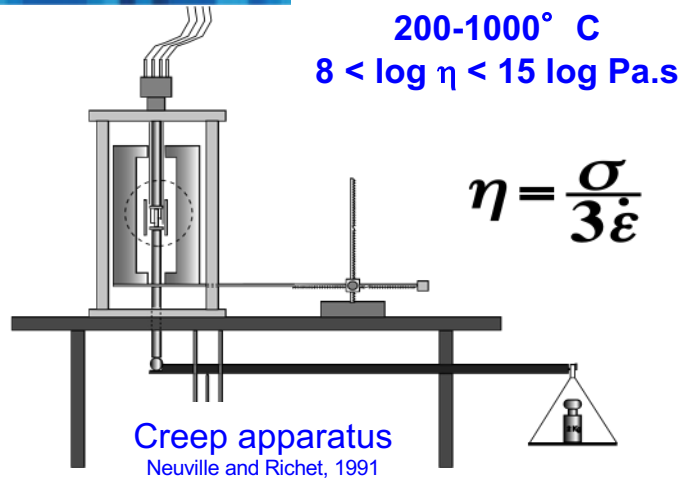
Or

Parallelograms
 $R = 3-4 \text{ mm}$

Temperature
 gradient
 $< 0,1^\circ \text{ C}$

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

Viscosity measurements

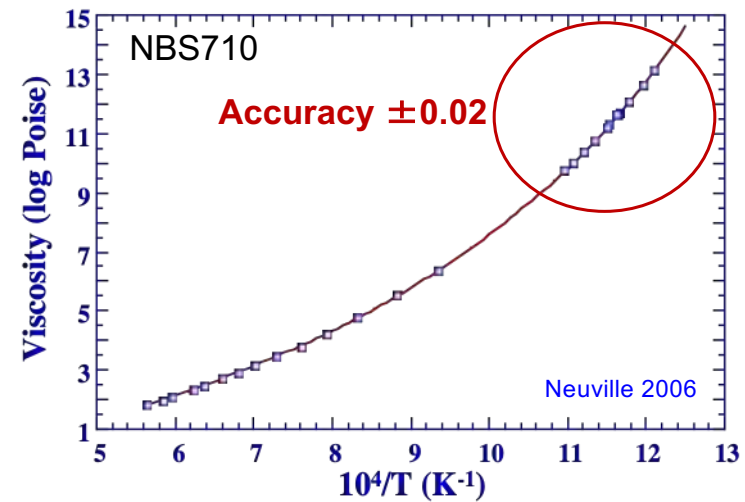


Cylinder
 $1 < d < 20 \text{ mm}$
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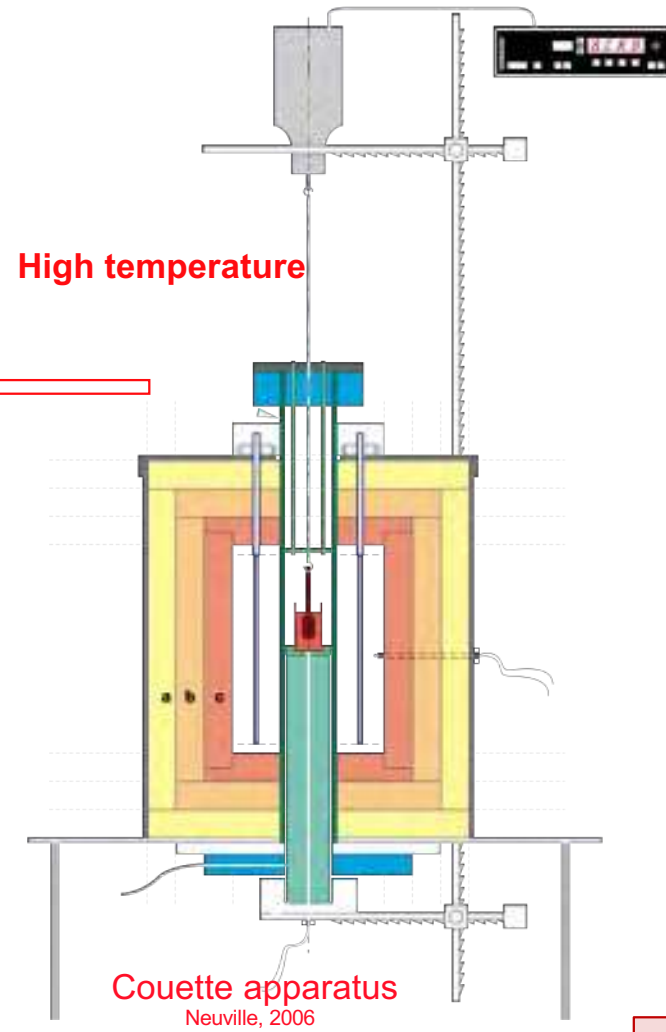
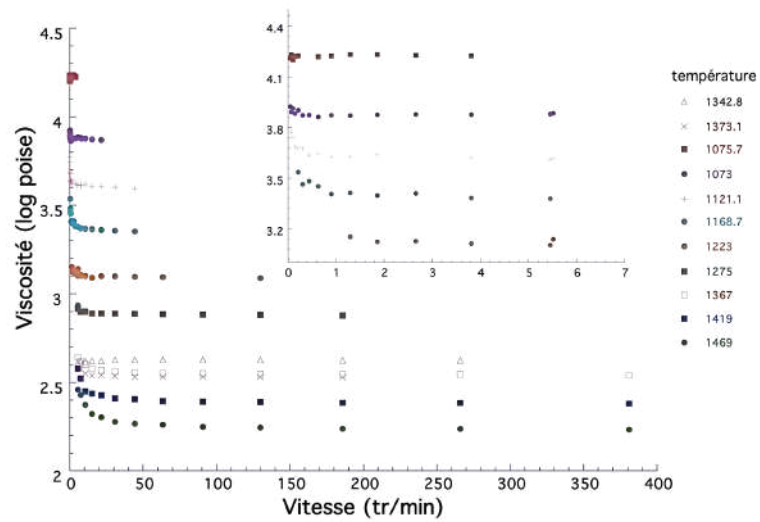
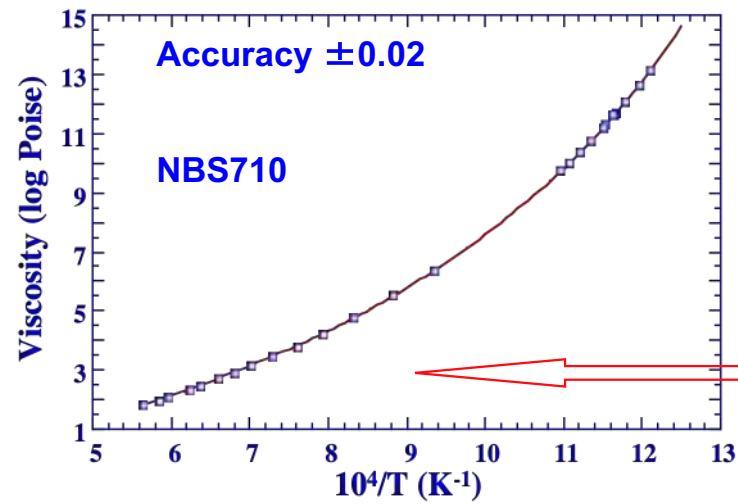
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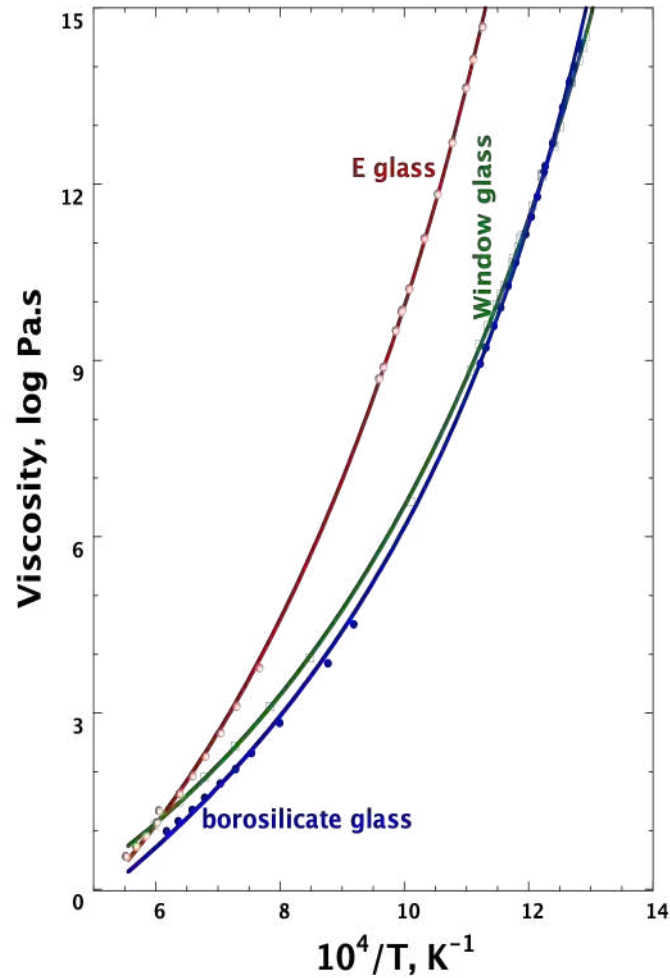


Viscosity measurements

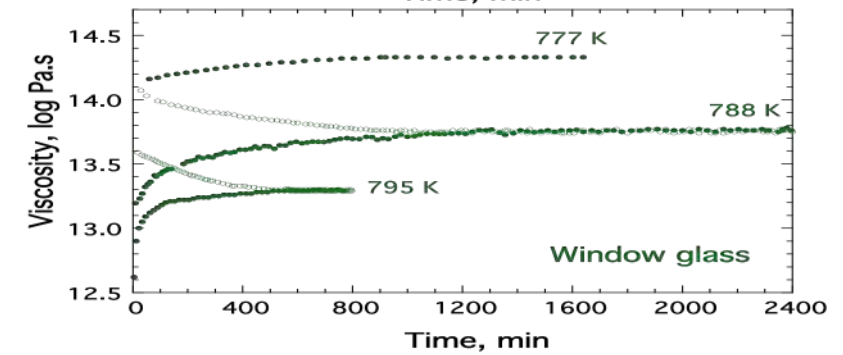
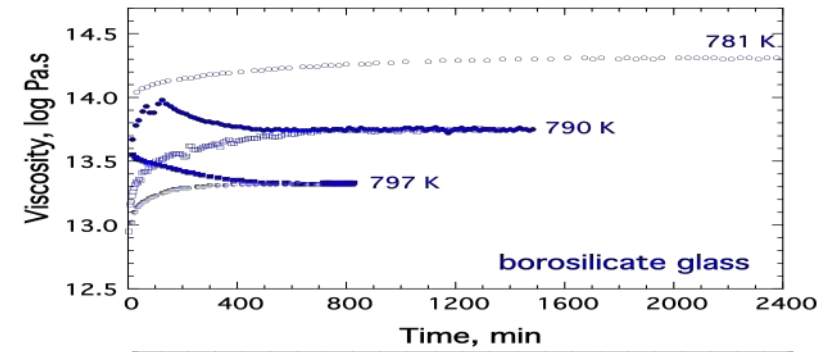
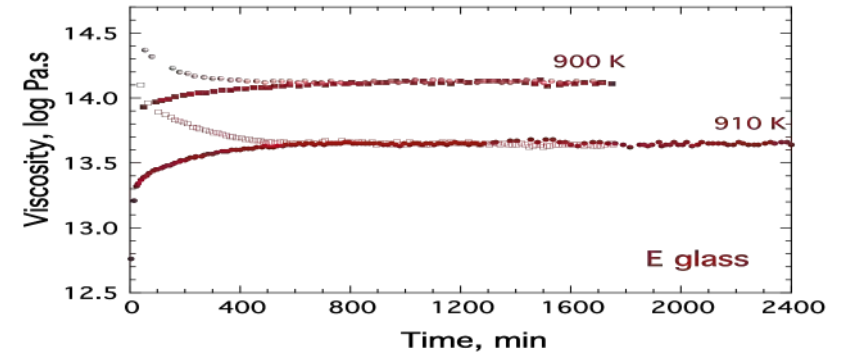


Neuville D.R. (2006) Viscosity, structure and mixing in (Ca, Na) silicate melts. *Chem. Geol.*, 229, 28-42.

Non-Newtonian behavior, relaxation problem?



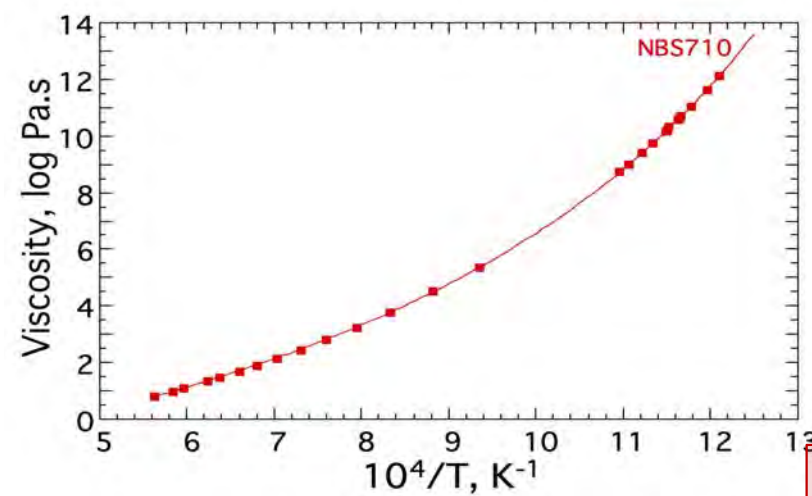
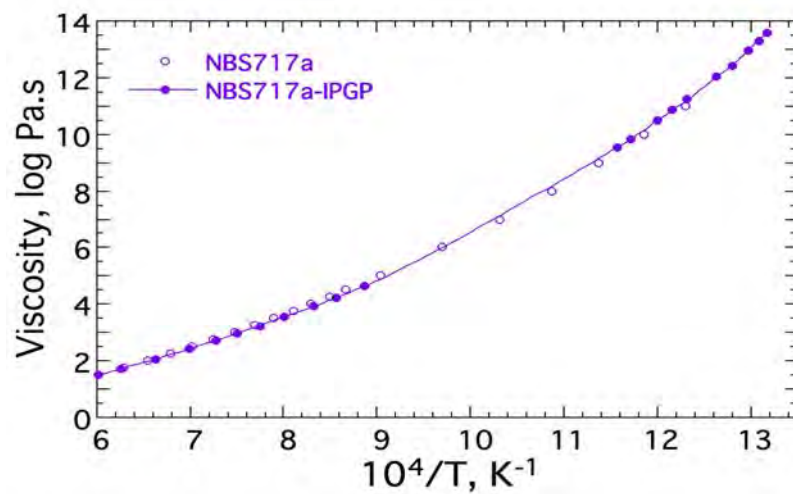
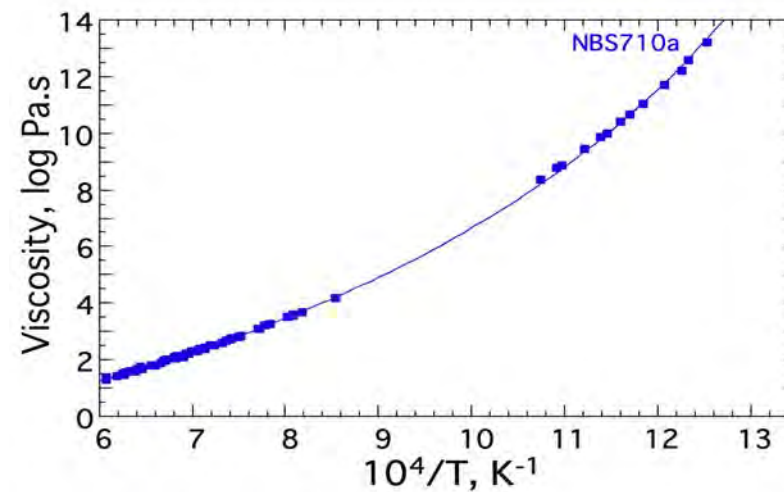
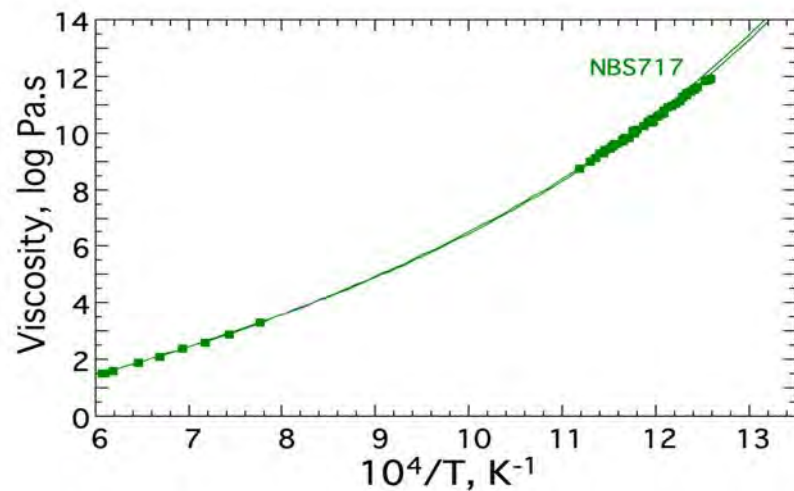
Sipp A., Neuville D.R. and Richet P. (1997) Viscosity and configurational entropy of borosilicate melts. J. Non-Crystal. Solids., 211, 281-293.



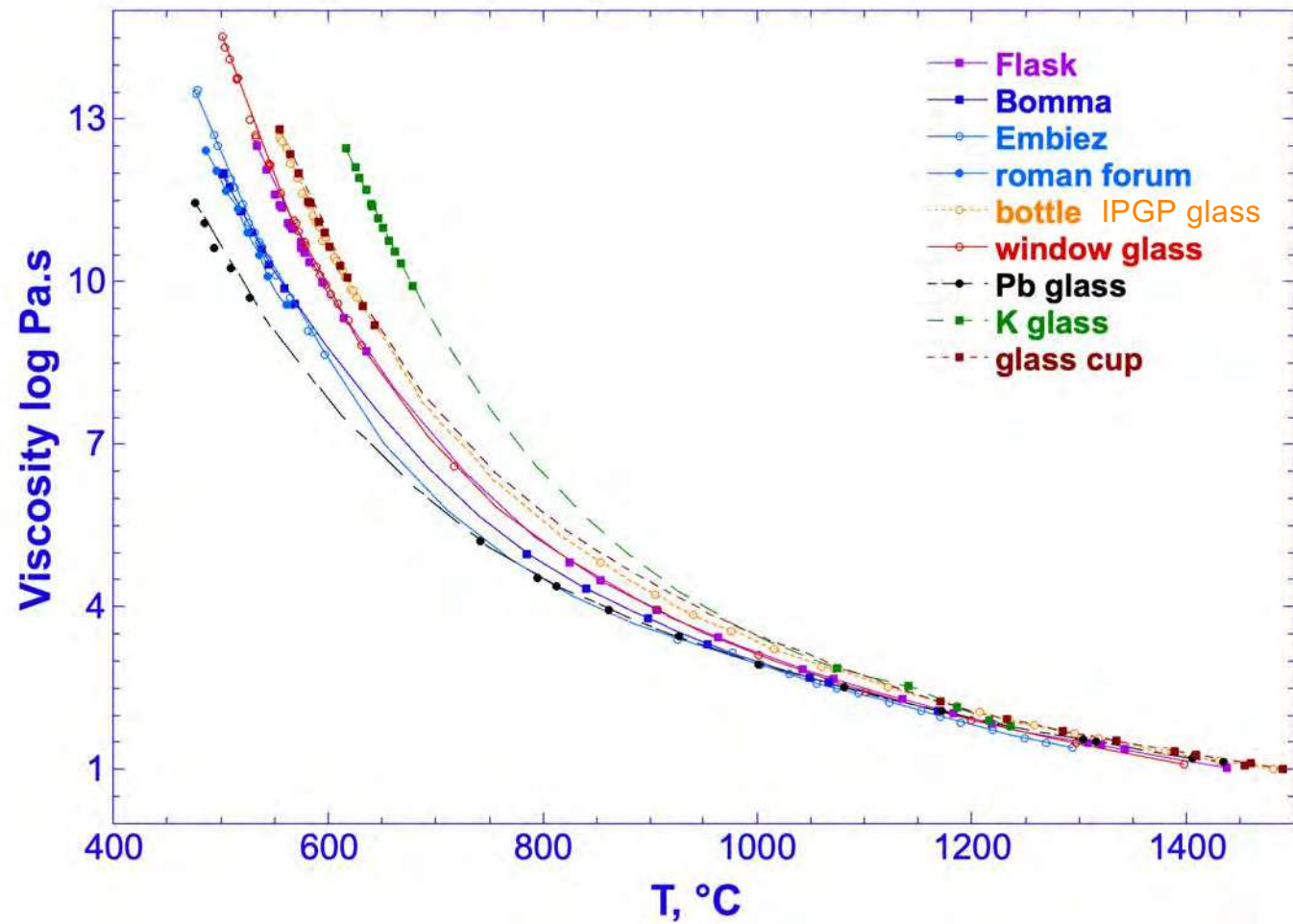
Viscosity measurements

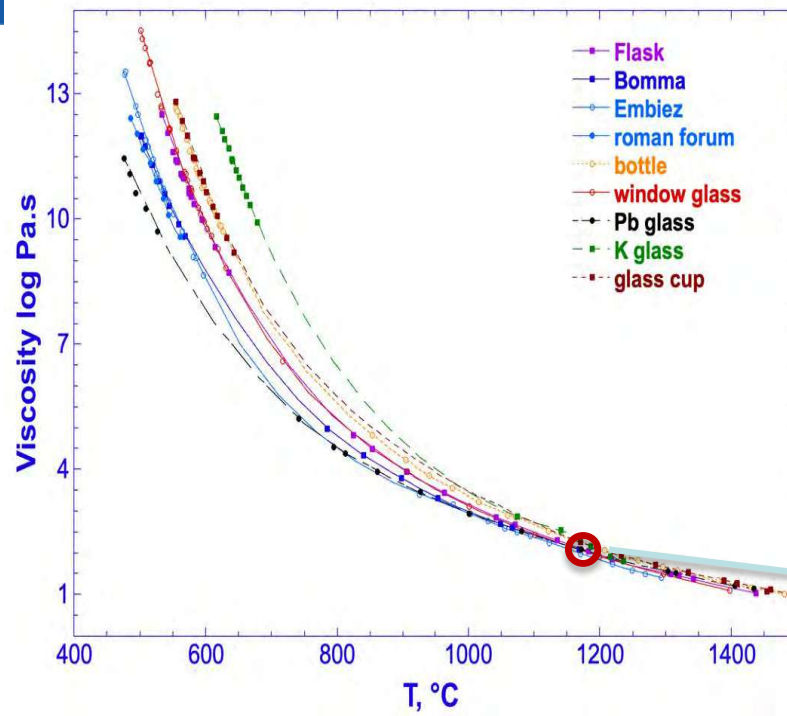
Viscosity measurements on the 4 NBS glasses : 710, 710a, 717 and the new 717a

Accuracy at low temperature **0,02** and at high temperature **0,03 log unit**.



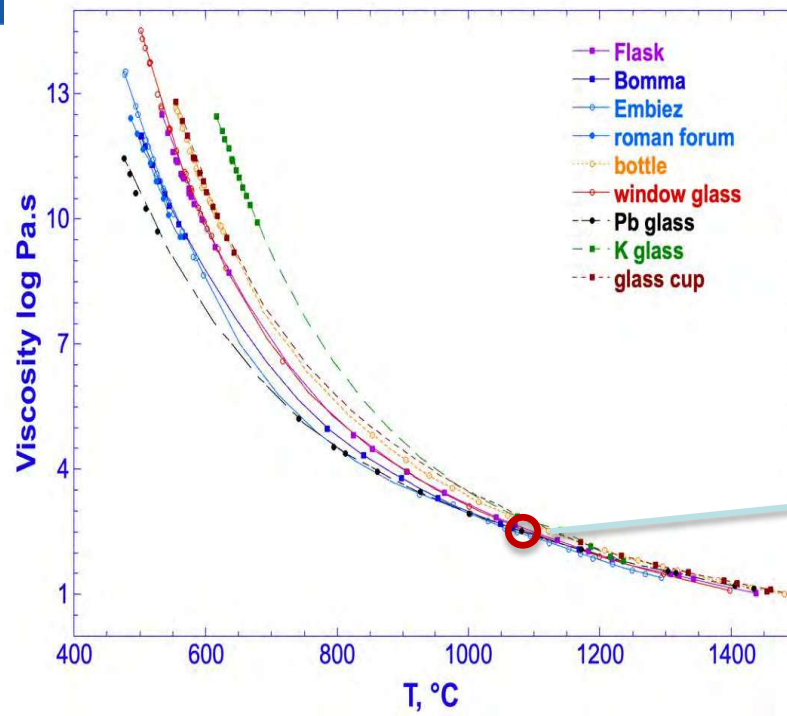
Viscosity measurements



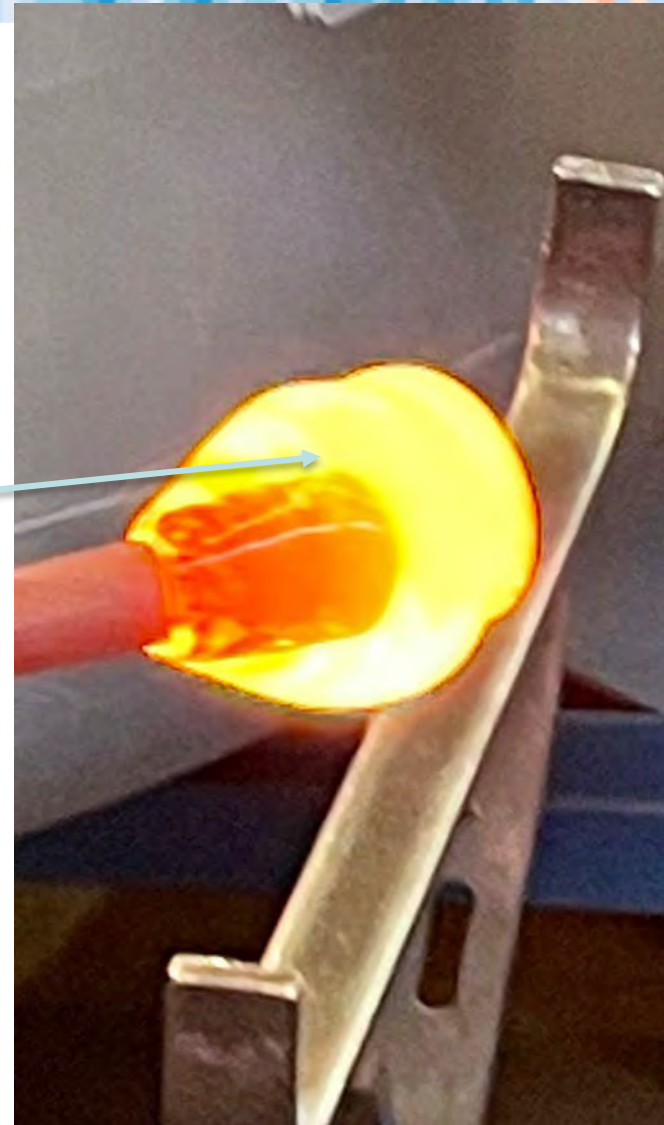


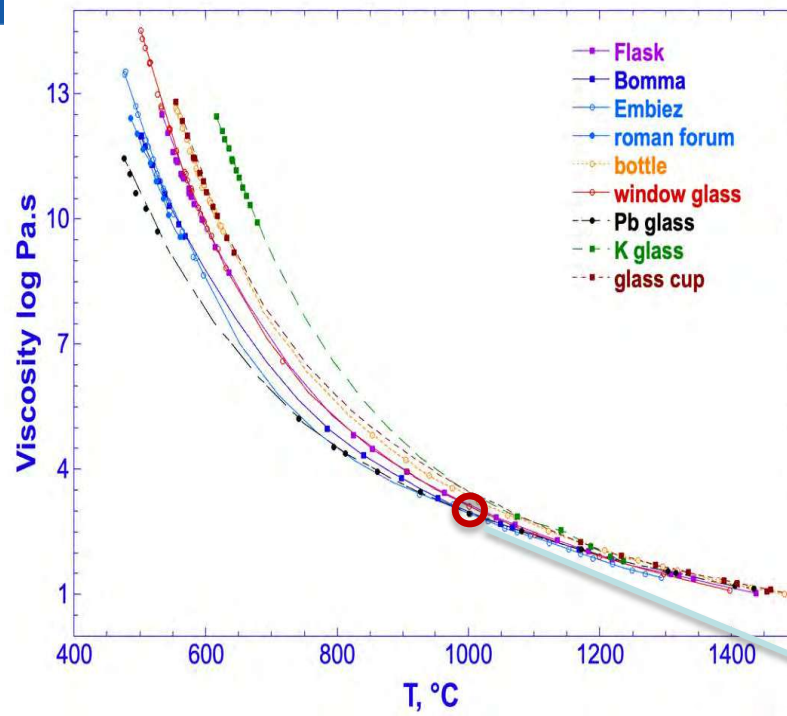
1150° C => ~2 log Pa.s





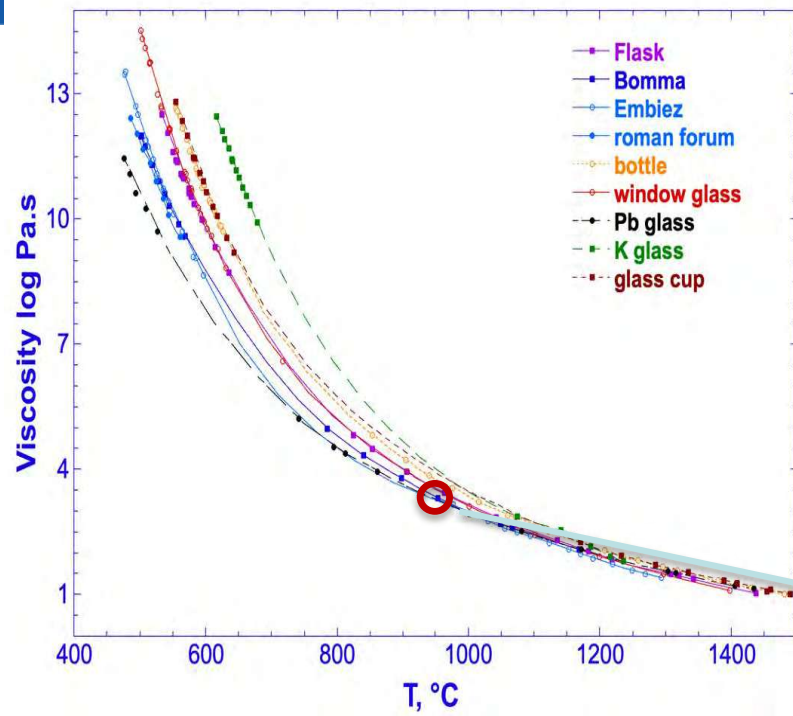
1060° C => ~2,6 log Pa.s





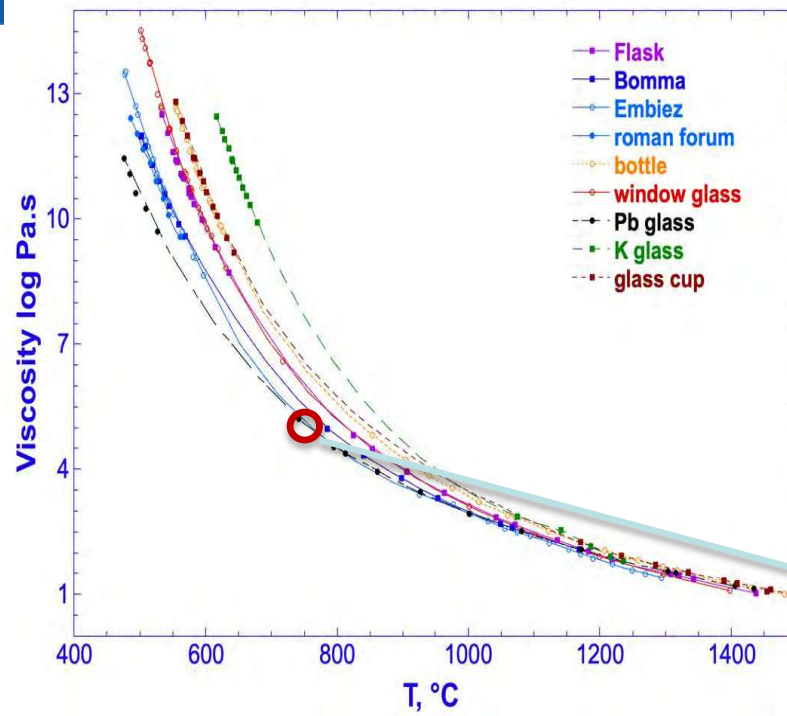
1060° C => ~3,2 log Pa.s





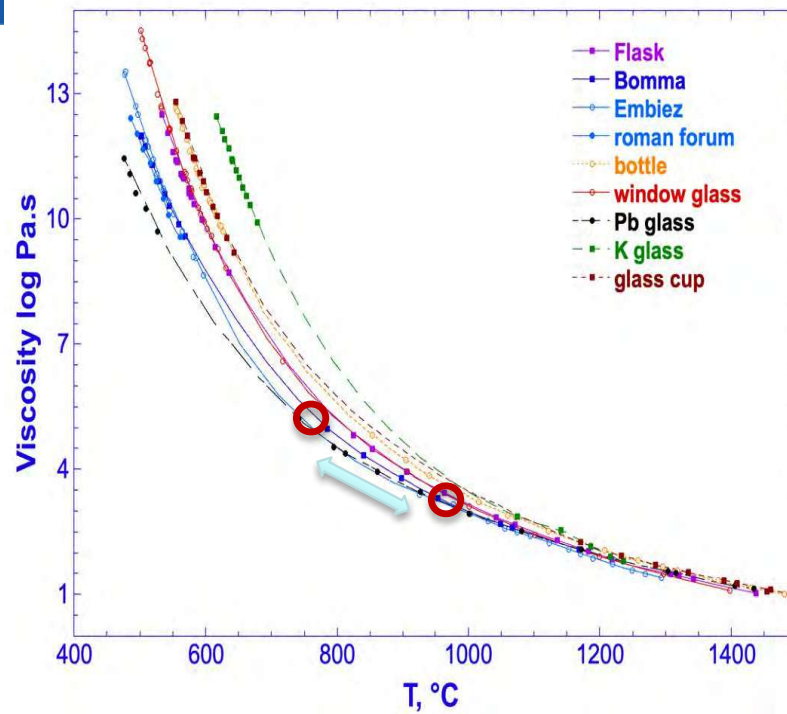
950° C => ~3,6 log Pa.s





720° C $\Rightarrow$ ~5,3 log Pa.s

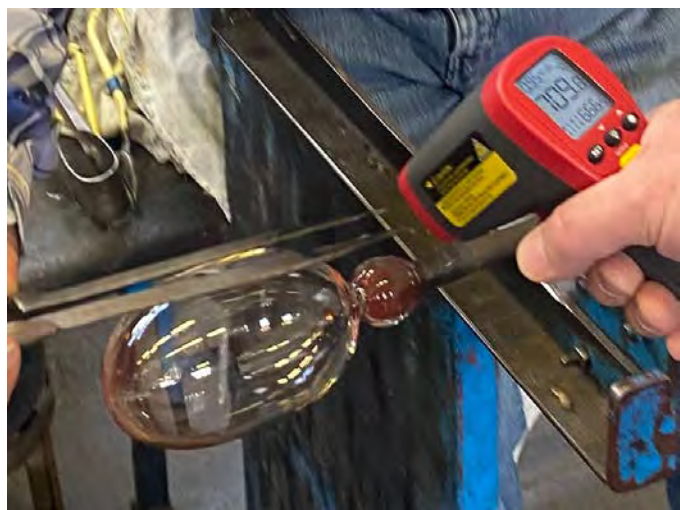




950° C => ~3,6 log Pa.s

720° C => ~5,3 log Pa.s



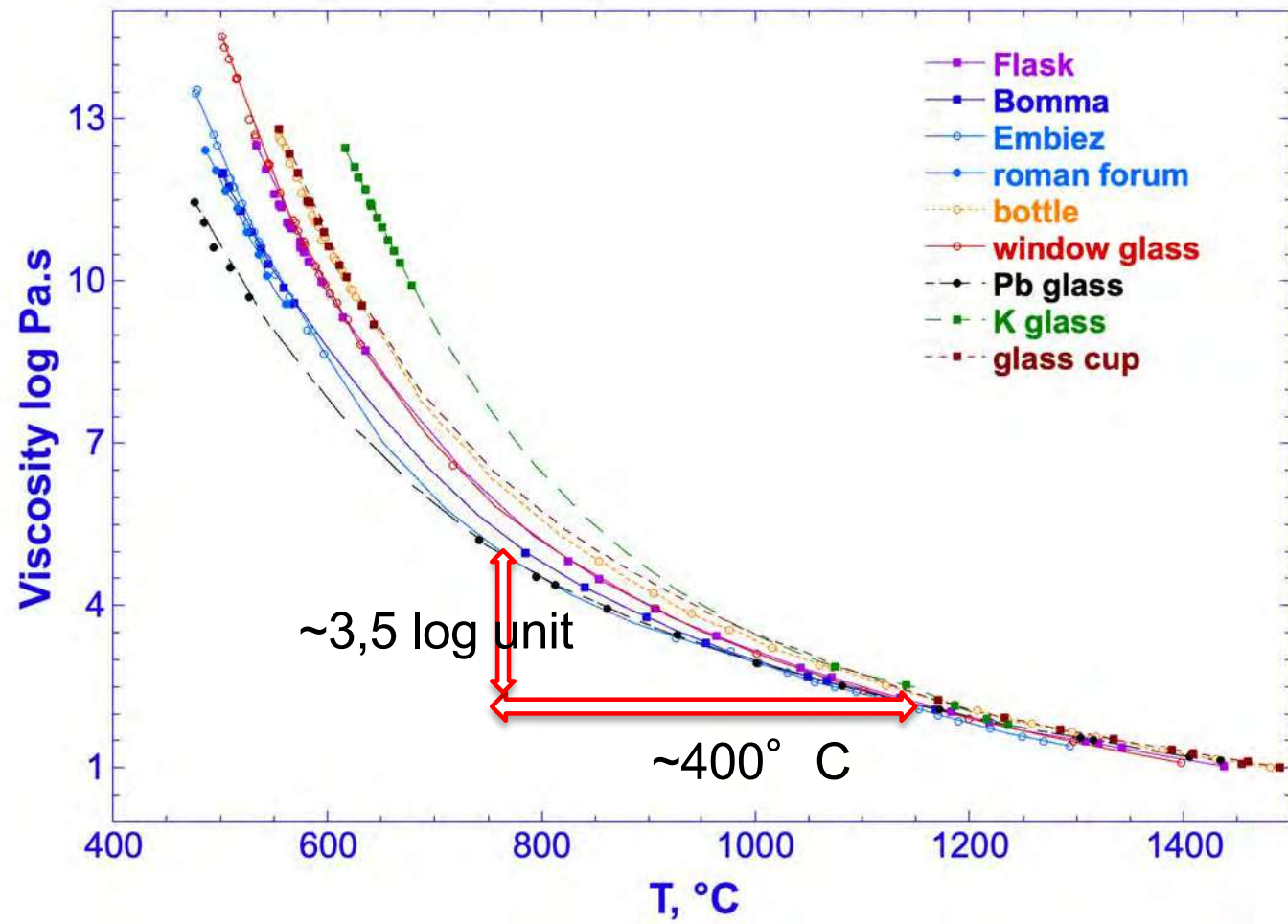


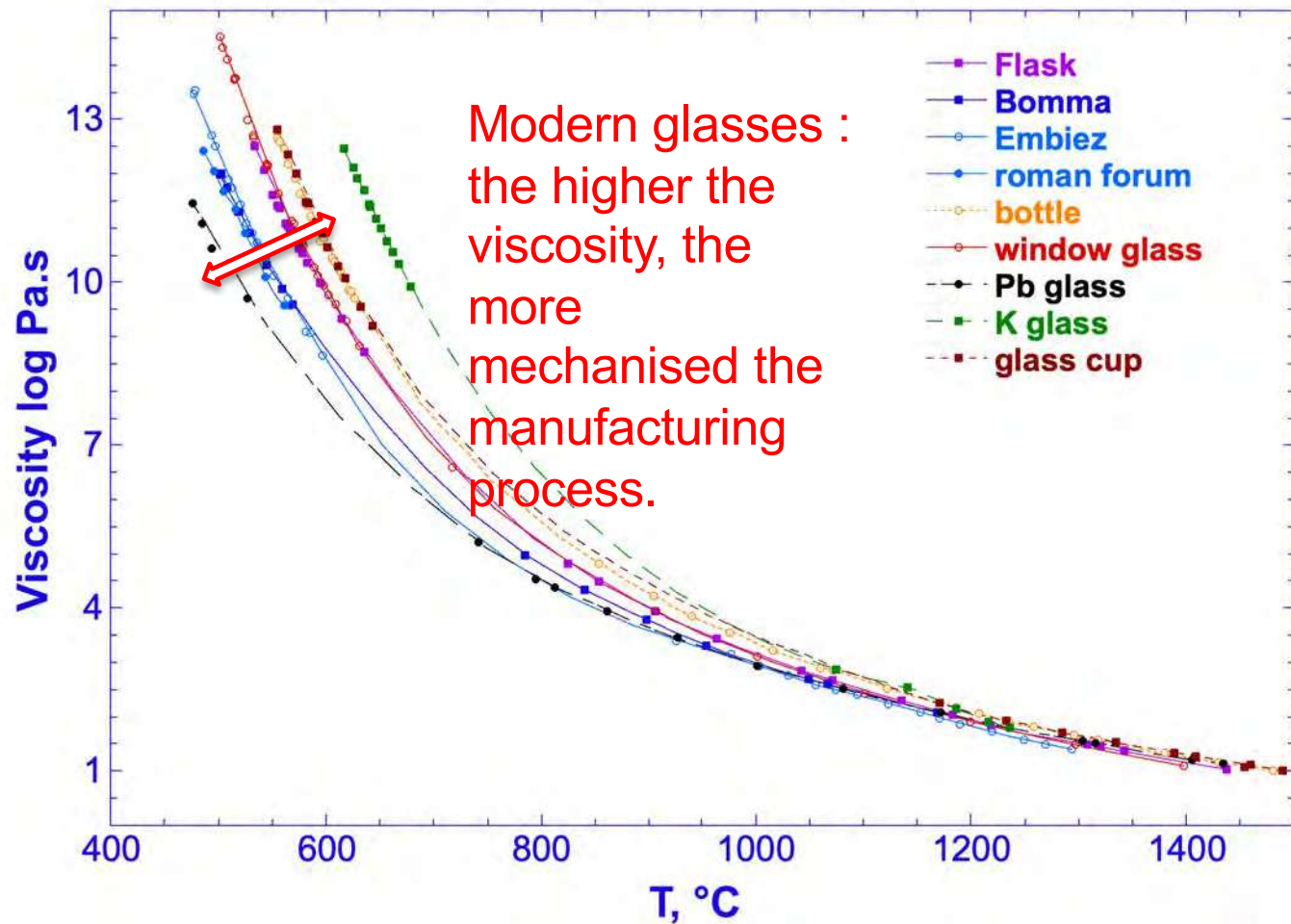


Claudine and Allain Guillot

Antoine Mexmain





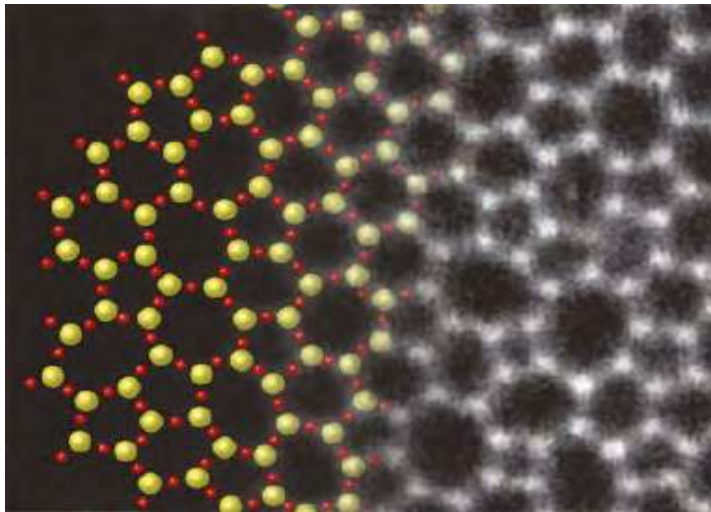




Back to the glasses and melts

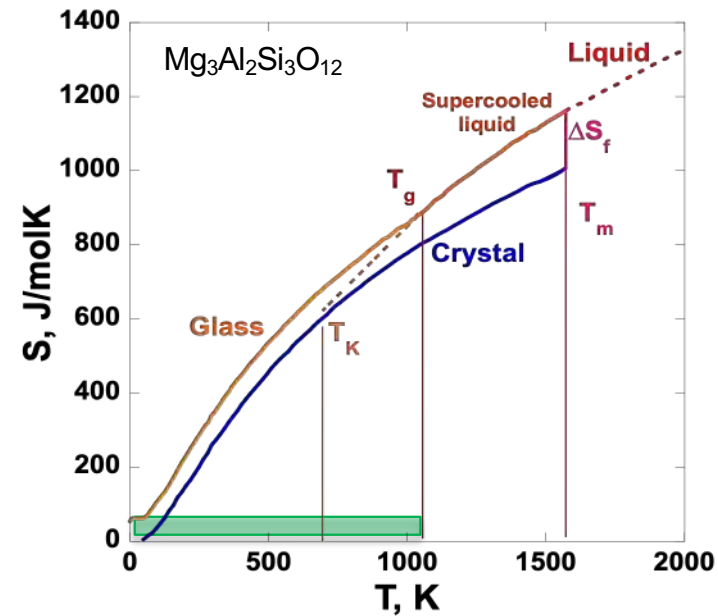
Glass is characterized by

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



Neuvill 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

Phase equilibria between melts and crystal

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

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

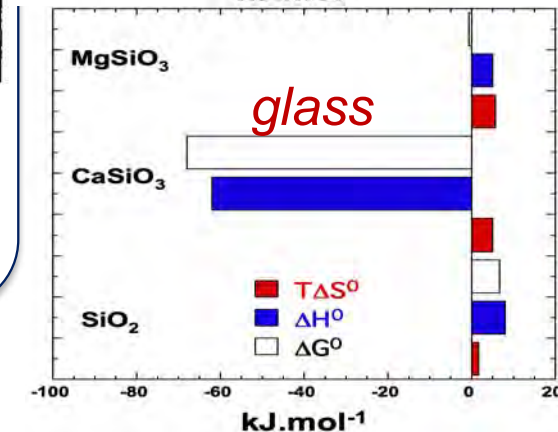
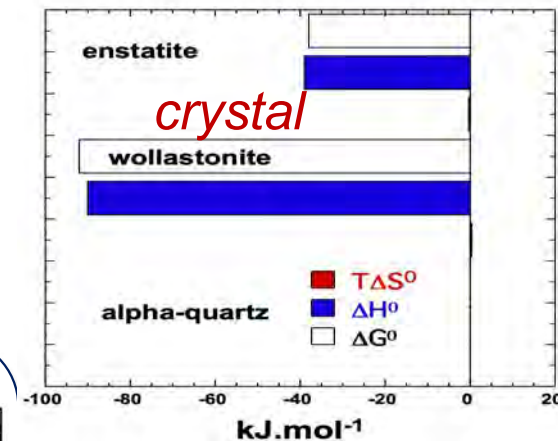
free enthalpy of formation with respect to oxides

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

$$\Delta G_f^0(T) = \Delta H_f^0(T) - T \Delta S_f^0(T)$$

$$S(0) = S^{\text{conf}}(T_g)$$

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 déchets nucléaires: Une nouvelle approche.
<https://www.researchgate.net/publication/343852518>

Phase equilibria between melts and crystal



Diopside
 $\text{CaMgSi}_2\text{O}_6$

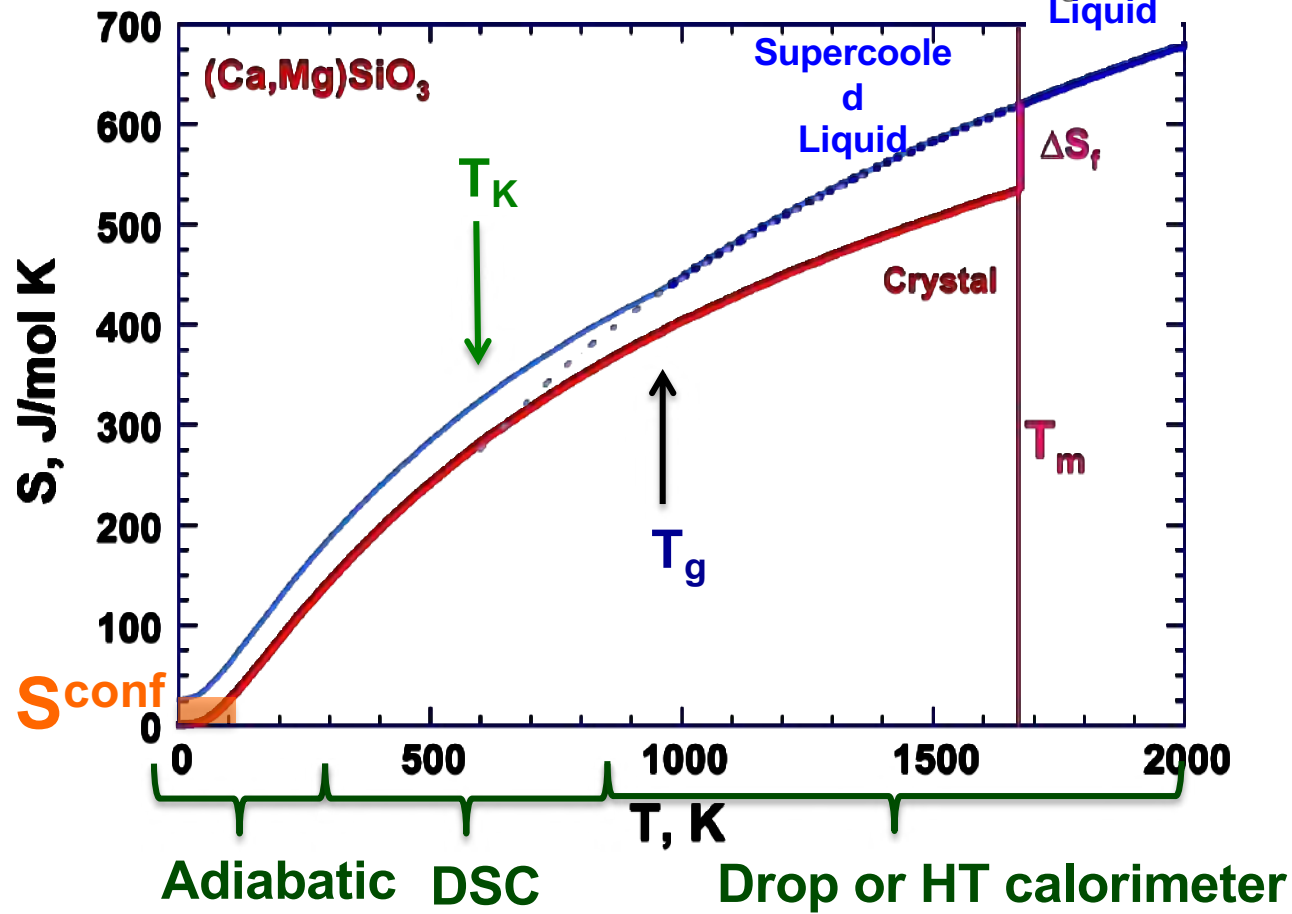


liquid

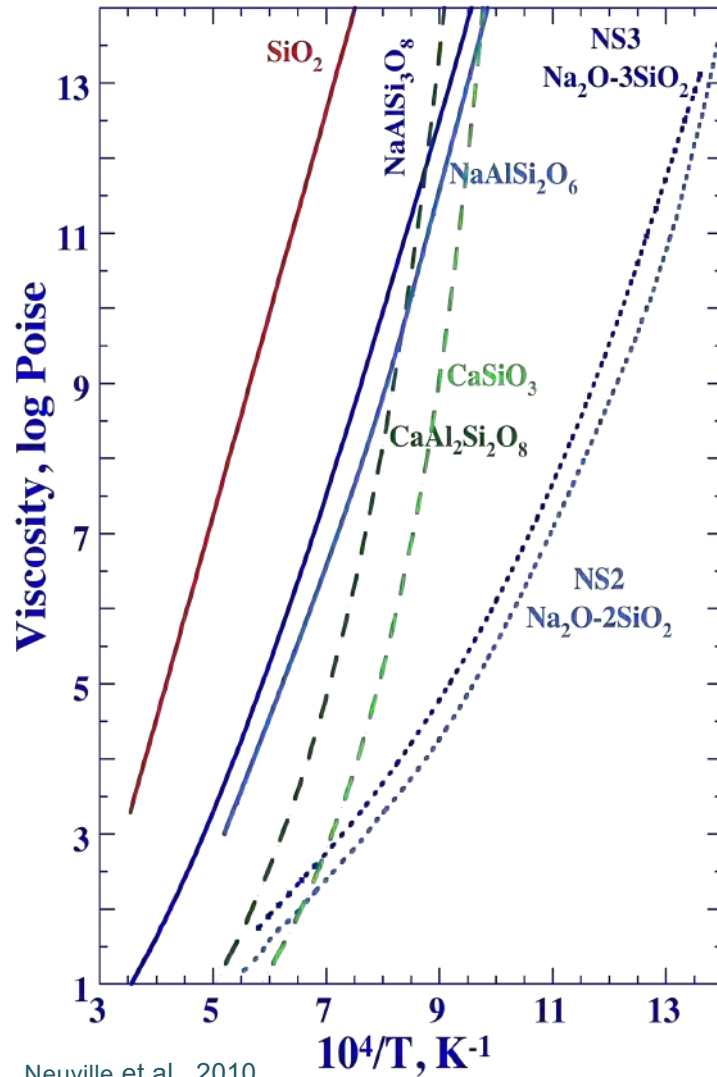


Glass

$$S^{conf}(T_g) = \int_0^{T_m} \frac{Cp^{Crystal}}{T} \cdot dT + \Delta S_f + \int_{T_m}^{T_g} \frac{Cp^{liquid}}{T} \cdot dT + \int_{T_g}^0 \frac{Cp^{glass}}{T} \cdot dT$$



How to fit viscosity ?



Arrhenius :

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

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

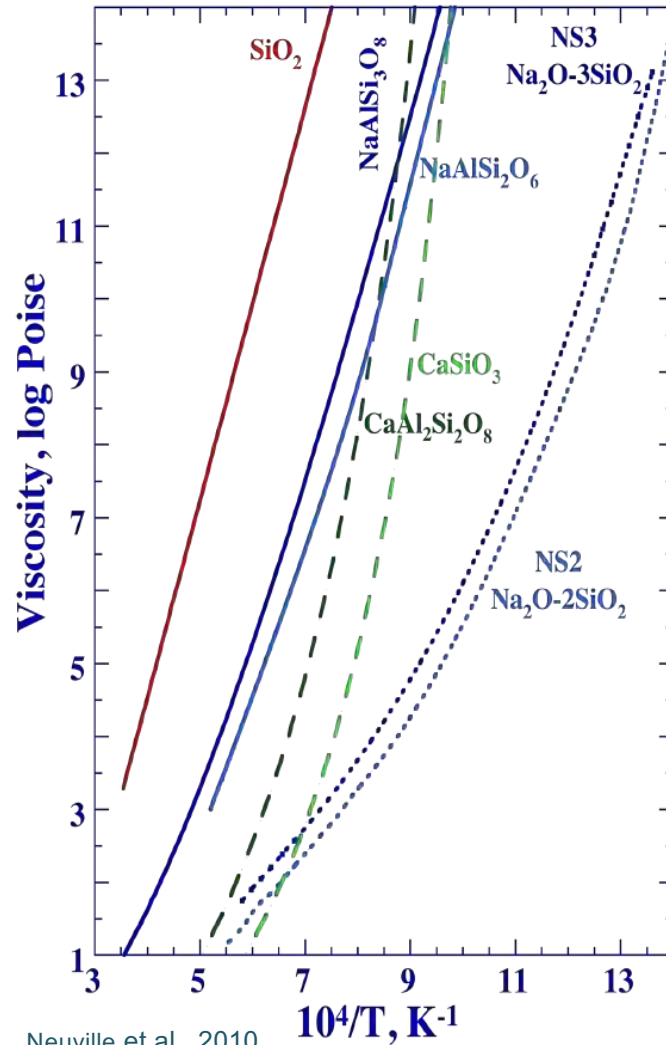
Yes but only for SiO_2 , GeO_2 , NaAlSiO_8 , KAlSiO_8 because activation energy change from 2000 kJ/mol at 1000 K up down 300 kJ/mol at 1800 K for NS3.

Need TVF equation

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

But just a fit

Viscosity equation ?



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

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....

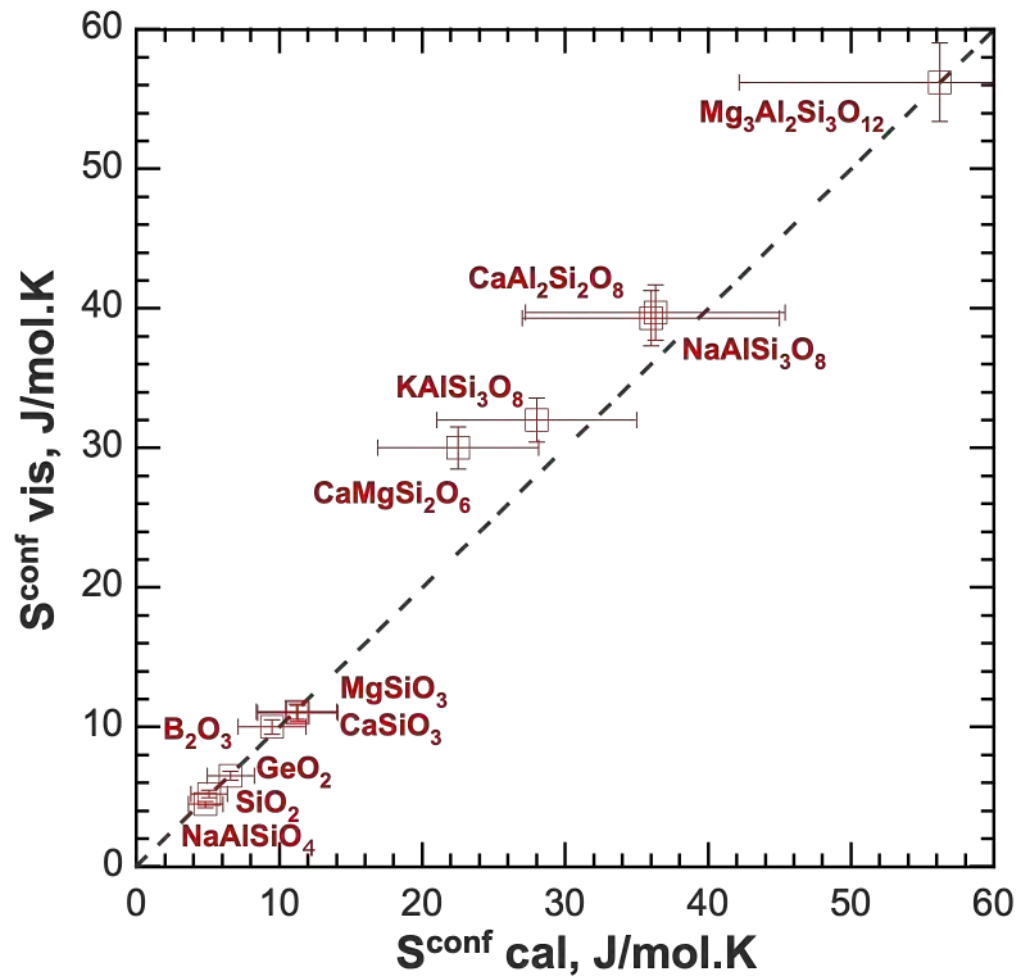
$$S^{\text{conf}}(T) = S^{\text{conf}}(T_g) + \int_{T_g}^T \frac{C_p^{\text{conf}}}{T} dt$$

$$C_p^{\text{conf}}(T) = C_{pg}(T_g) - C_{pl}(T)$$

Calorimetry measurements
=> Easy

Configurational entropy

Viscosimetry configurational entropy



Calorimetric 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

Any other equations?

The free-volume theory (Cohen and Grest, 1979)

$$\log \eta(T, x) = A_{FV}(x) + 2B_{FV}(x) / \left(T - T_{FV}(x) + \sqrt{\left((T - T_{FV}(x))^2 + C_{FV}(x)T \right)} \right)$$

The equation of Avramov and Milchev (1988)

$$\log \eta(T, x) = A_{AM}(x) + (12 - A_{AM}(x)) (T_g(x)/T)^{m(x)/(12 - A_{AM}(x))}$$

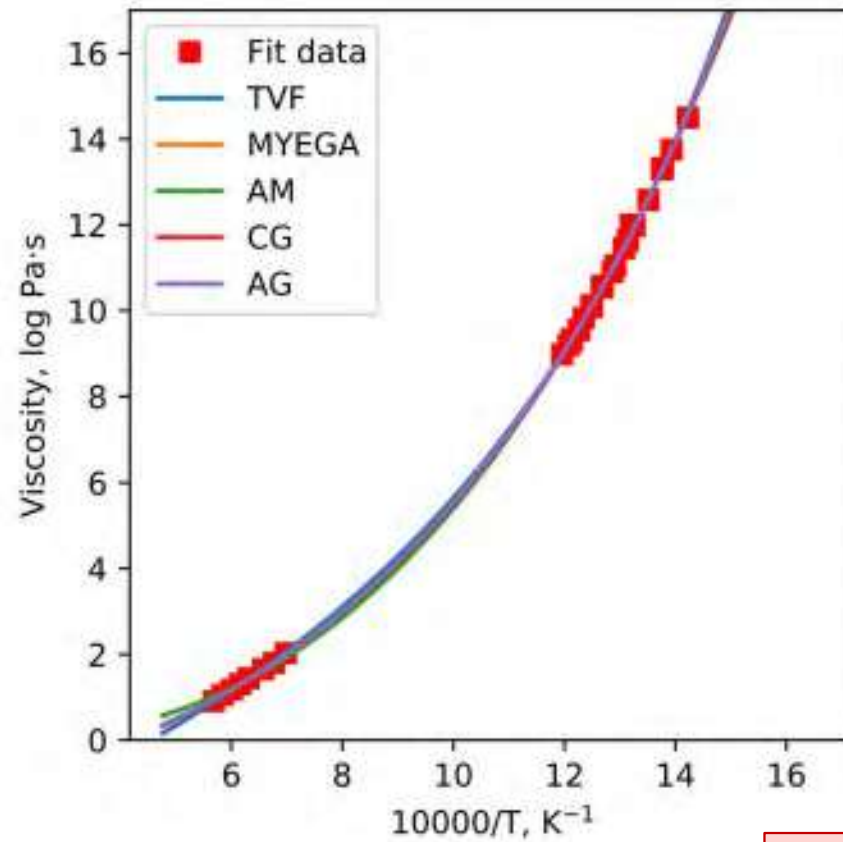
The MYEGA equation (Mauro et al., 2009)

$$\log \eta(T, x) = A_e(x) + (12 - A_e(x)) (T_g(x)/T) e^{(m(x)/(12 - A_e(x)) - 1) \left(\frac{T_g(x)}{T} - 1 \right)}$$

Any other equations?

NS4 : $\text{Na}_2\text{Si}_4\text{O}_9$

Measurement set: high and low temperature



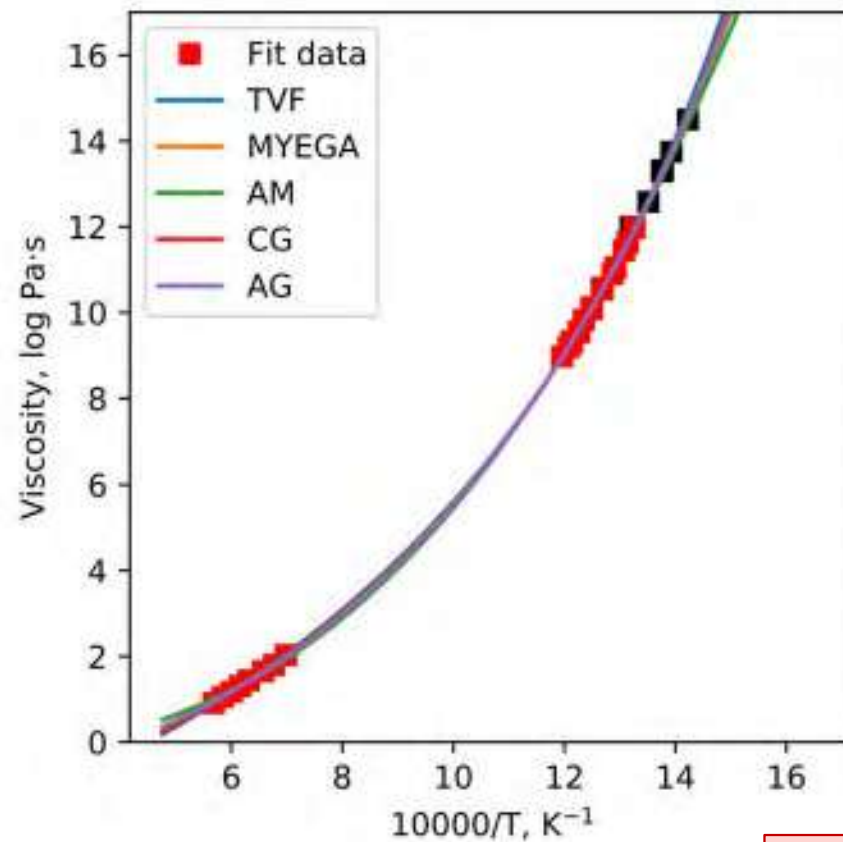
The set of equations yields good results and accurately reproduces the measurements

Neuvillle D.R. et Richet P. (1990) Viscosité et entropie des silicates fondus. Rivista del la Staz. Sper. Vetro, 6, 213-221.

Any other equations?

NS4 : $\text{Na}_2\text{Si}_4\text{O}_9$

Measurement set: high and low temperatures



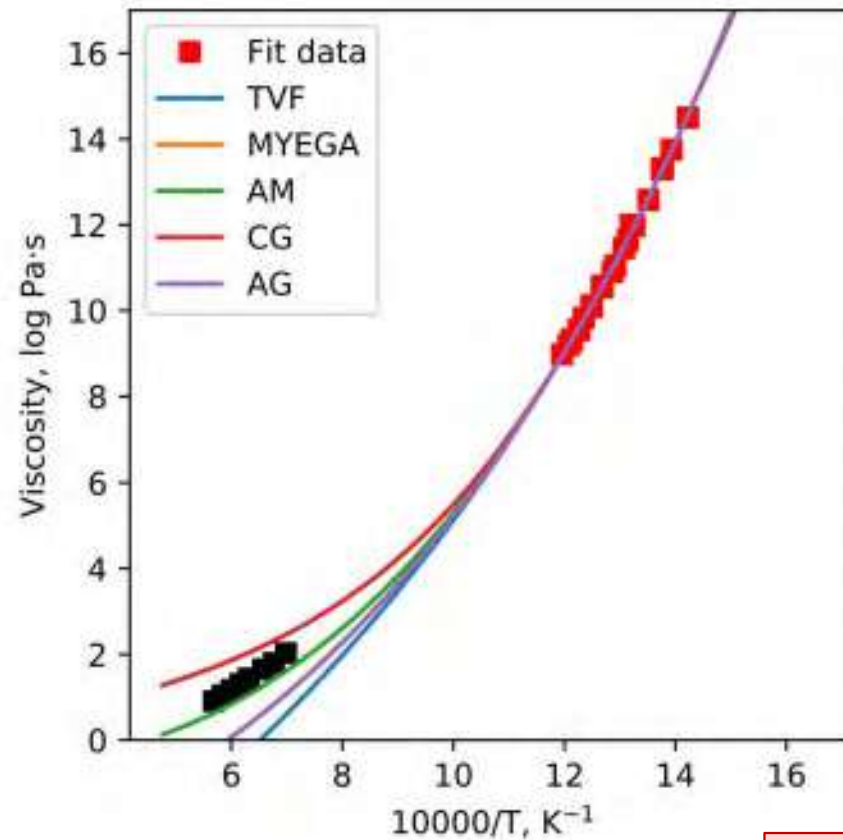
The set of equations yields good results and accurately reproduces the measurements

No measurements available for very high viscosities: extrapolation at low temperatures is difficult, except for AG

Neuvillle D.R. et Richet P. (1990) Viscosité et entropie des silicates fondus. Rivista del la Staz. Sper. Vetro, 6, 213-221.

Any other equations?

NS4 : $\text{Na}_2\text{Si}_4\text{O}_9$



Measurement set: high and low temperatures

The set of equations yields good results and accurately reproduces the measurements

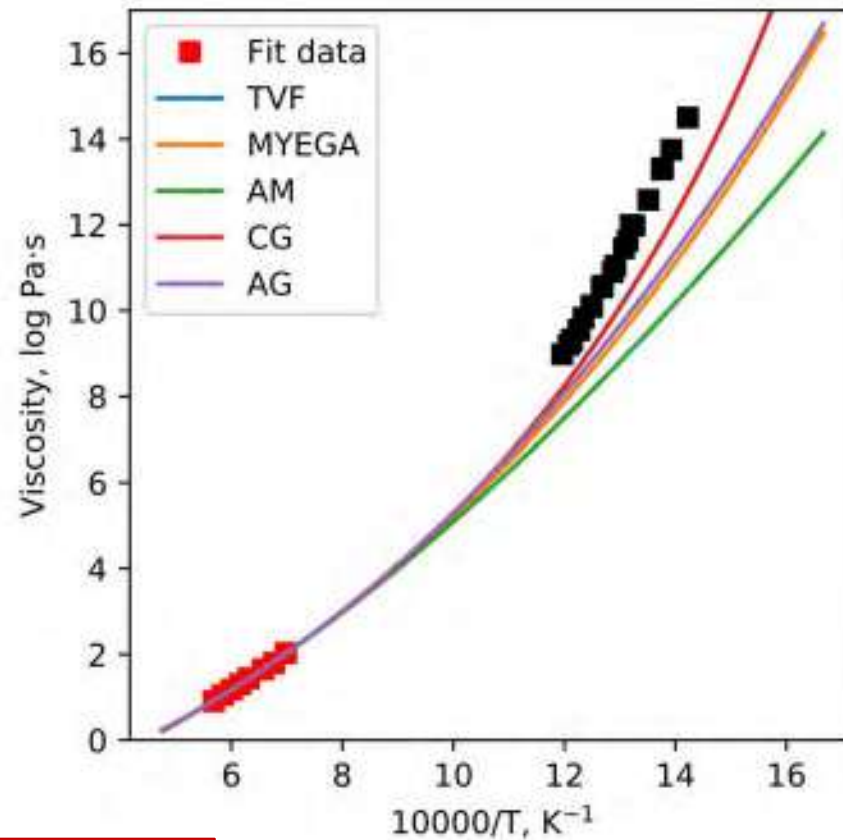
Measurements are lacking at very high viscosities: extrapolation at low temperatures is difficult except for AG

Measurements only at low temperatures: difficult except for AG and AM

Neuvillle D.R. et Richet P. (1990) Viscosité et entropie des silicates fondus. Rivista del la Staz. Sper. Vetro, 6, 213-221.

Any other equations?

NS4 : $\text{Na}_2\text{Si}_4\text{O}_9$



Measurement range: high and low temperatures

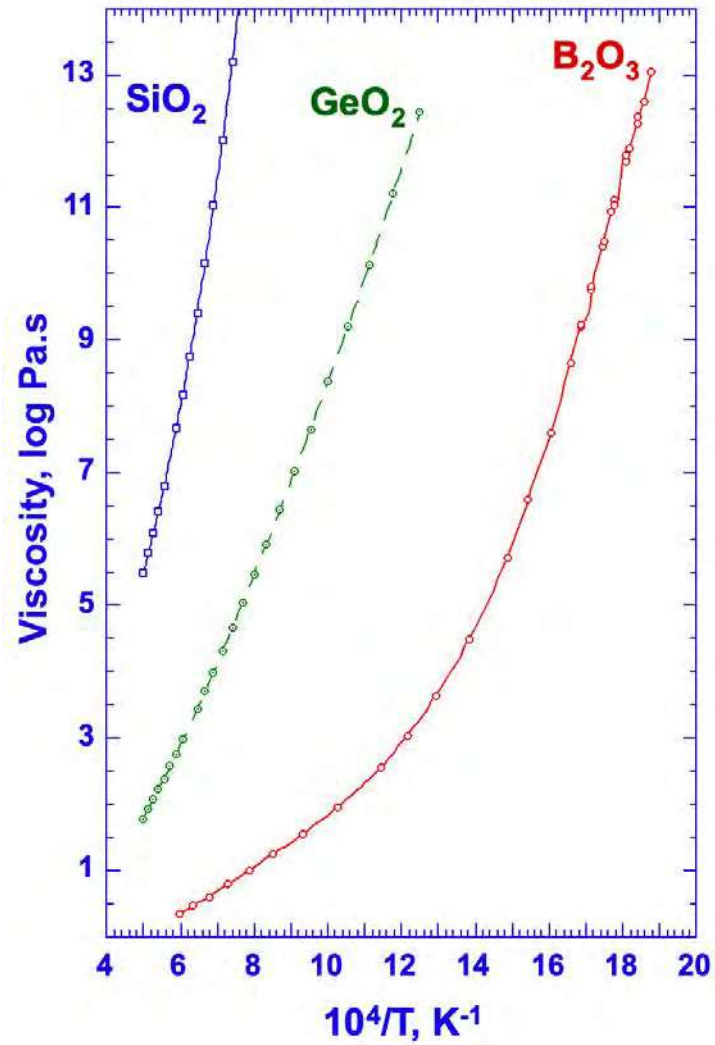
The set of equations yields good results and accurately reproduces the measurements

No measurements available for very high viscosities:
extrapolation at low temperatures: difficult except for AG

Measurements only at low temperatures: extrapolation difficult except for AG and AM

Measurements only at high temperatures: extrapolation very difficult except for CG and AG if Cp values are available

Network former

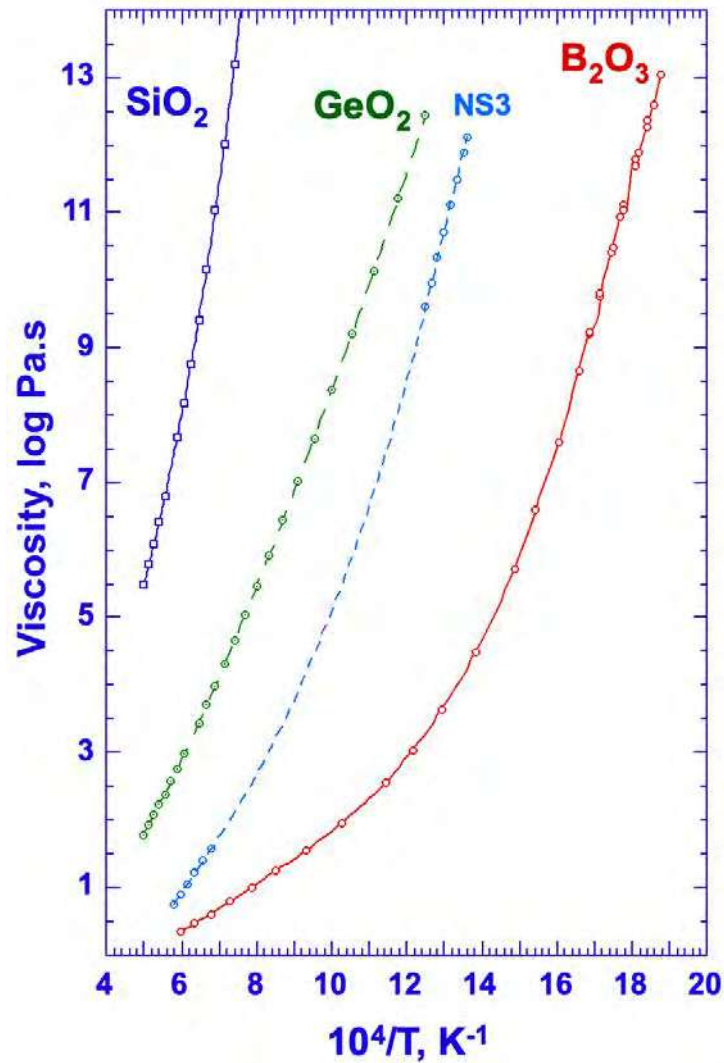


SiO_2 covalent bond
 SiO_4 tetrahedra

GeO_2 covalent bond
 GeO_4 tetrahedra

B_2O_3 covalent bond
 BO_3 triangle and BO_4 tetrahedra

Network former

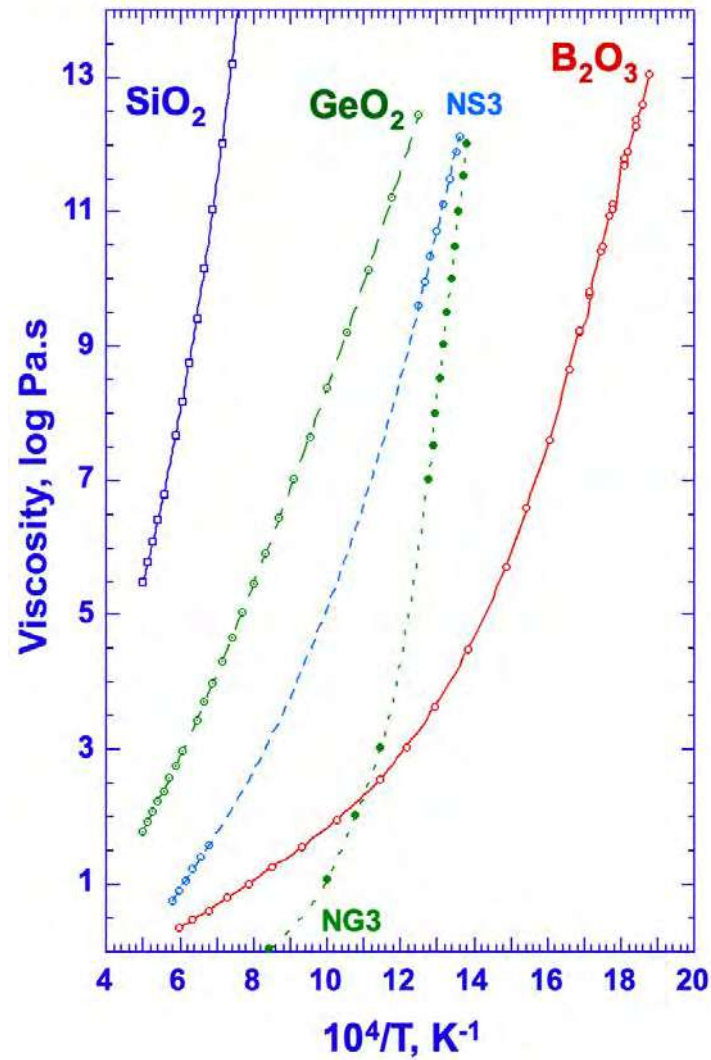


SiO_2 covalent bond
 SiO_4 tetrahedra
 Na_2O breaks the network
Viscosity decreases

GeO_2 covalent bond
 GeO_4 tetrahedra

B_2O_3 covalent bond
 BO_3 triangle and BO_4 tetrahedra

Network former

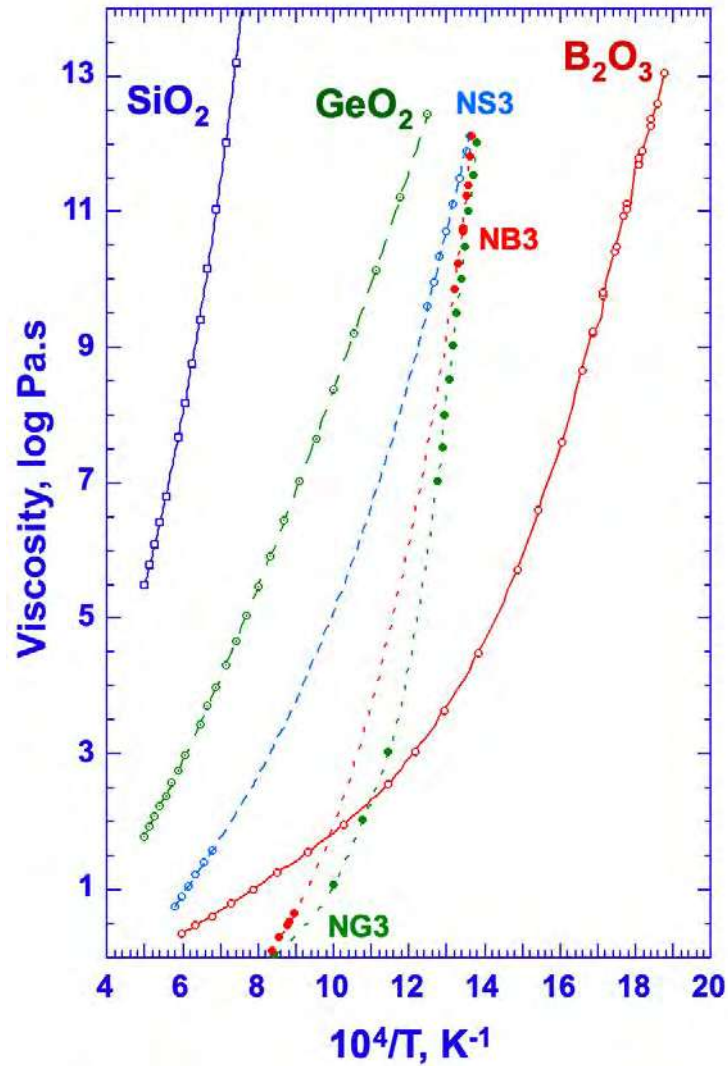


SiO₂ covalent bond
SiO₄ tetrahedra
Na₂O breaks the network
Viscosity decreases

GeO₂ covalent bond
GeO₄ tetrahedra
Na₂O breaks the network
Viscosity decreases

B₂O₃ covalent bond
BO₃ triangle and BO₄ tetrahedra

Network former

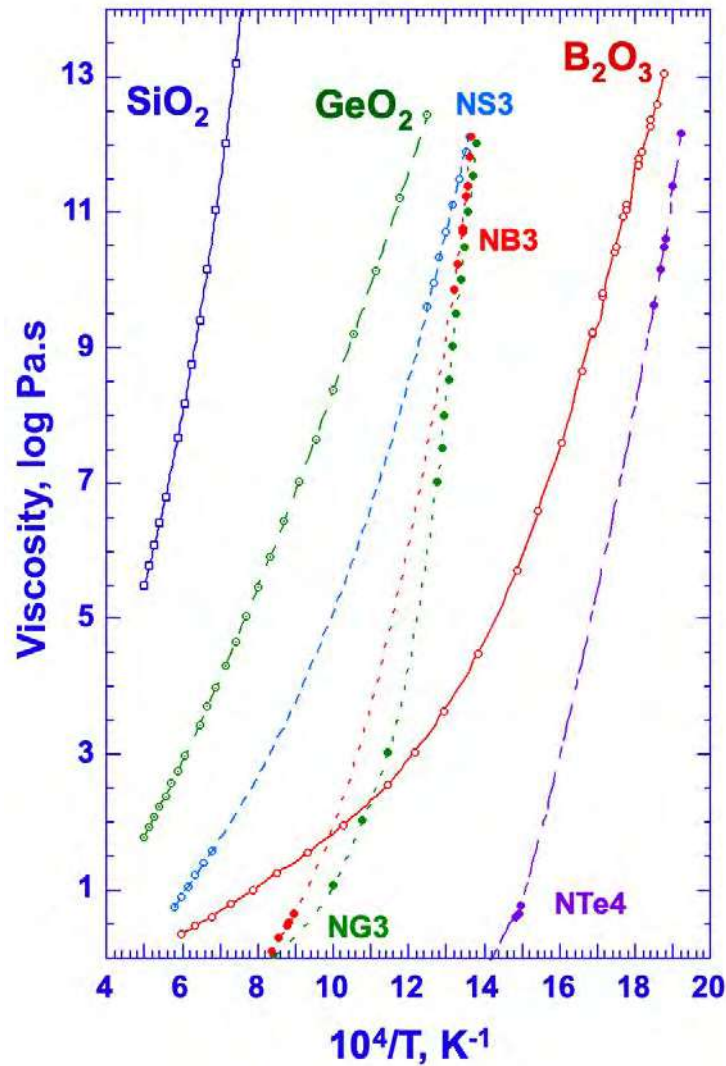


SiO₂ covalent bond
 SiO₄ tetrahedra
 Na₂O breaks the network
 Viscosity decreases

GeO₂ covalent bond
 GeO₄ tetrahedra
 Na₂O breaks the network
 Viscosity decreases

B₂O₃ covalent bond
 BO₃ triangle and BO₄ tetrahedra
 Na increases BO₄ content
 Viscosity increases

Network former



SiO₂ covalent bond
 SiO₄ tetrahedra
 Na₂O breaks the network
 Viscosity decreases

GeO₂ covalent bond
 GeO₄ tetrahedra
 Na₂O breaks the network
 Viscosity decreases

B₂O₃ covalent bond
 BO₃ triangle and BO₄ tetrahedra
 Na increases BO₄ content
 Viscosity increases

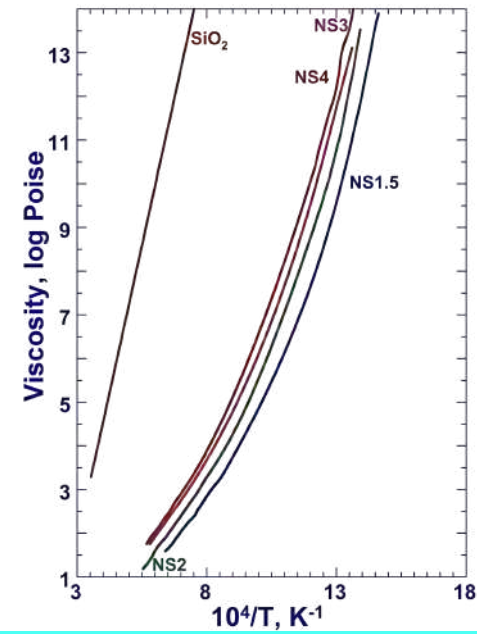
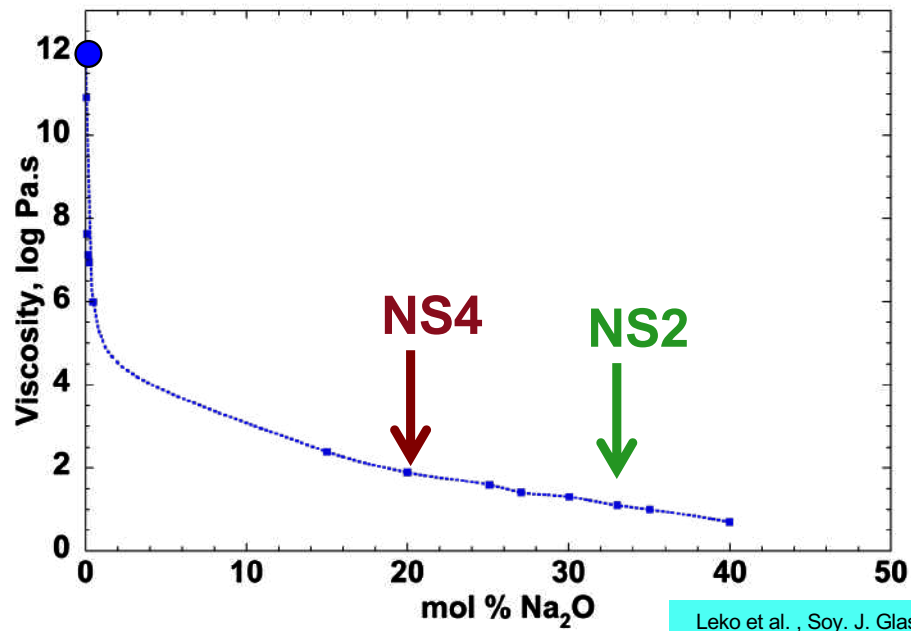
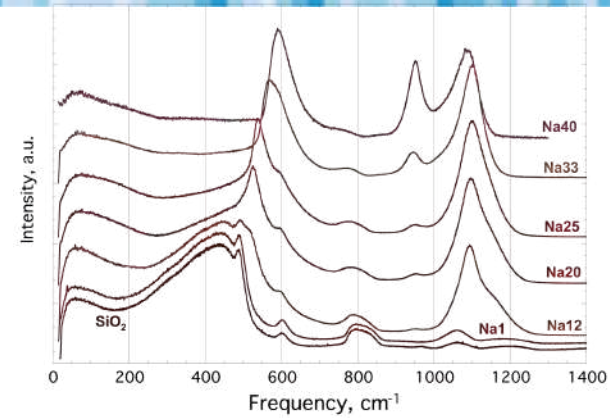
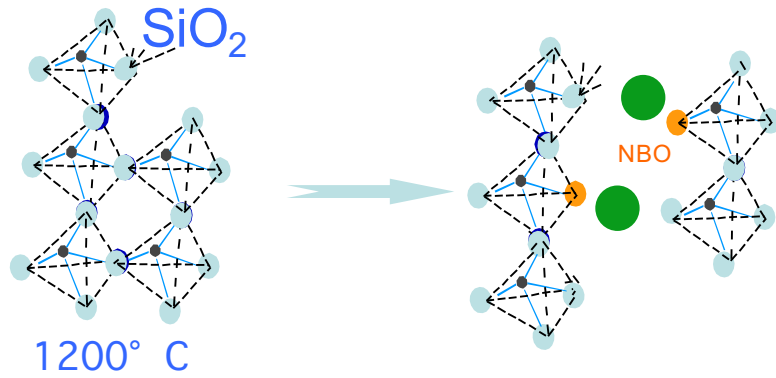
TeO₂ ionic bonding

SiO₂ : SiO₄ tetrahedra, 3D network, high connectivity
=> strong liquid
Alkali broke network, viscosity decreases, Tg.....

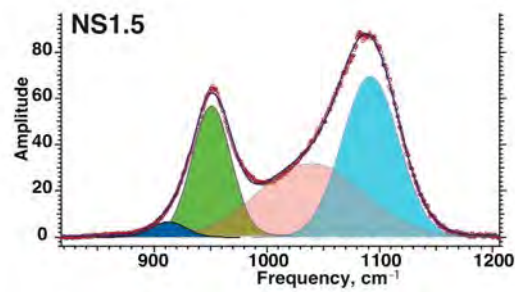
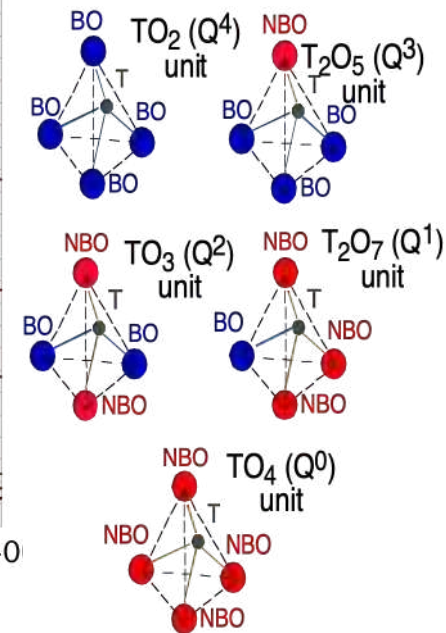
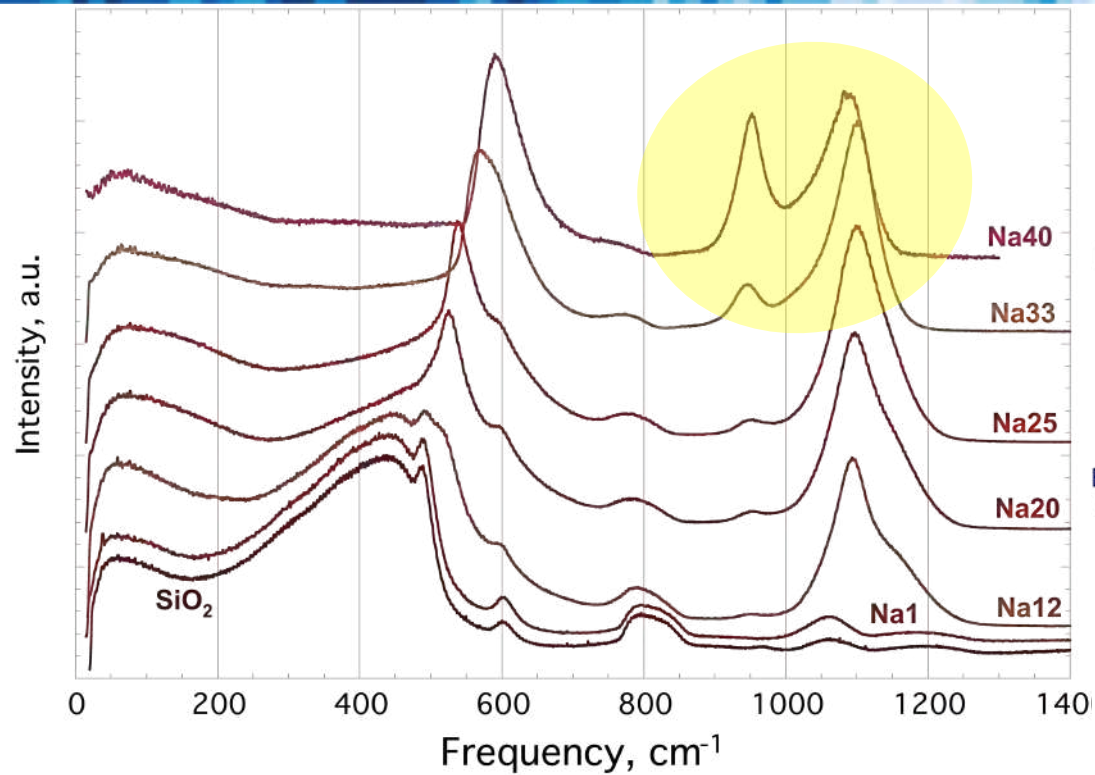
GeO₂ : GeO₄ tetrahedra, 3D network, high connectivity
=> strong liquid
Alkali broke network, viscosity decreases, Tg.....

B₂O₃ : BO₃ triangle, 2D network, low connectivity,
=> fragile liquid
With alkali : M₂O + BO₃ => BO₄ : 3D network

Structure versus properties of silicate melts



Raman spectra of $\text{SiO}_2\text{-Na}_2\text{O}$ glass



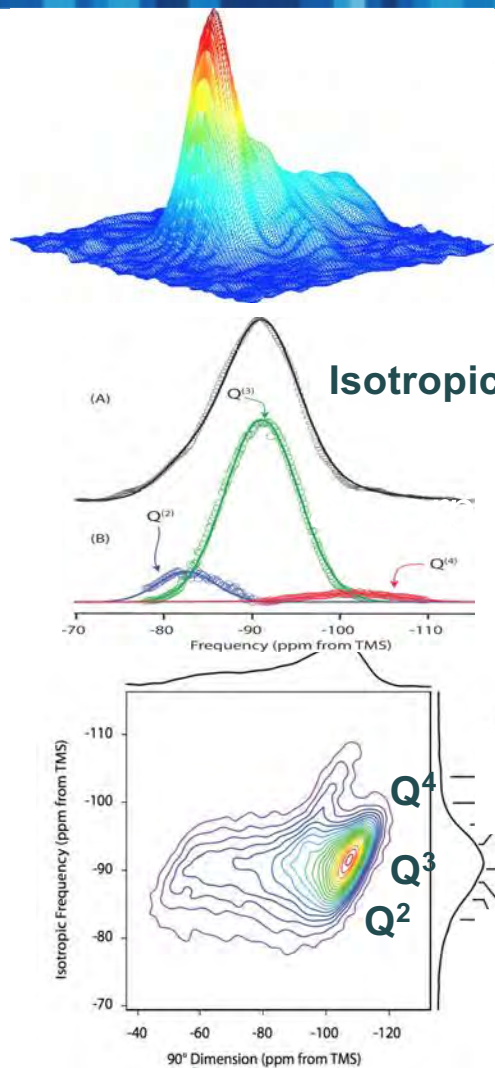
NMR

Q^n species

X-ray absorption

^{29}Si MAF Spectrum of $\text{K}_2\text{O}-2\text{SiO}_2$ glass

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



Isotropic MAS

Isotropic/anisotropic MAF

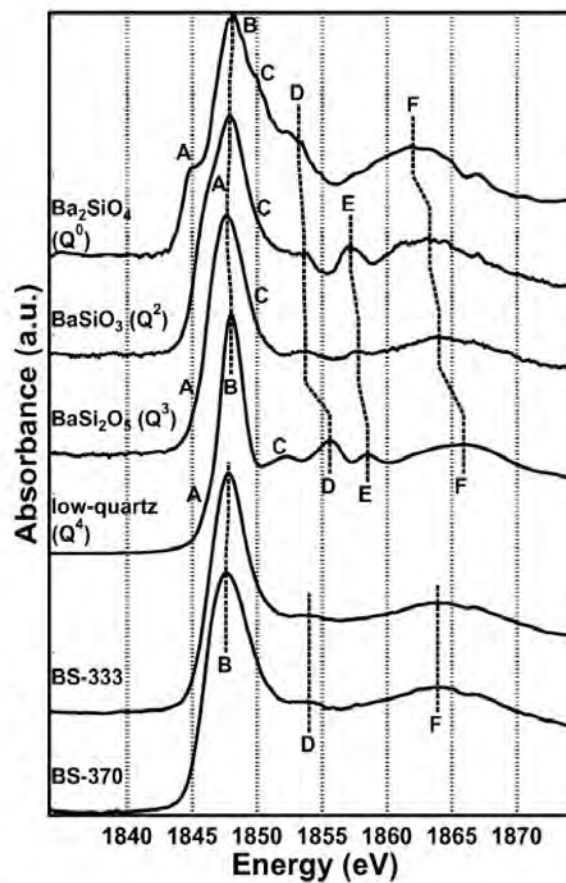
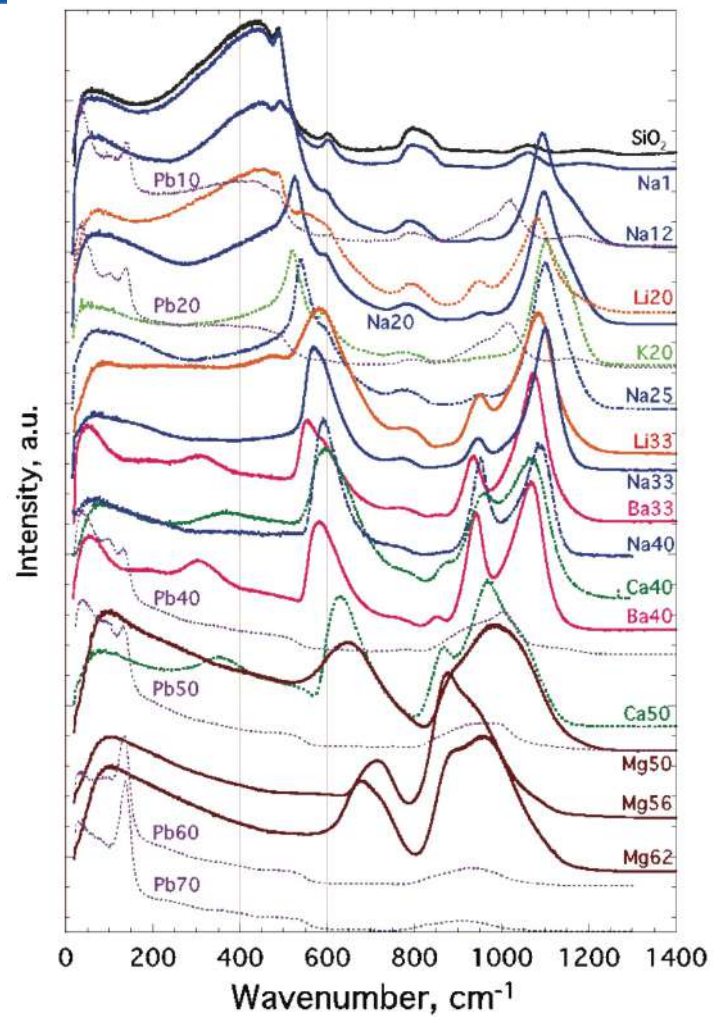


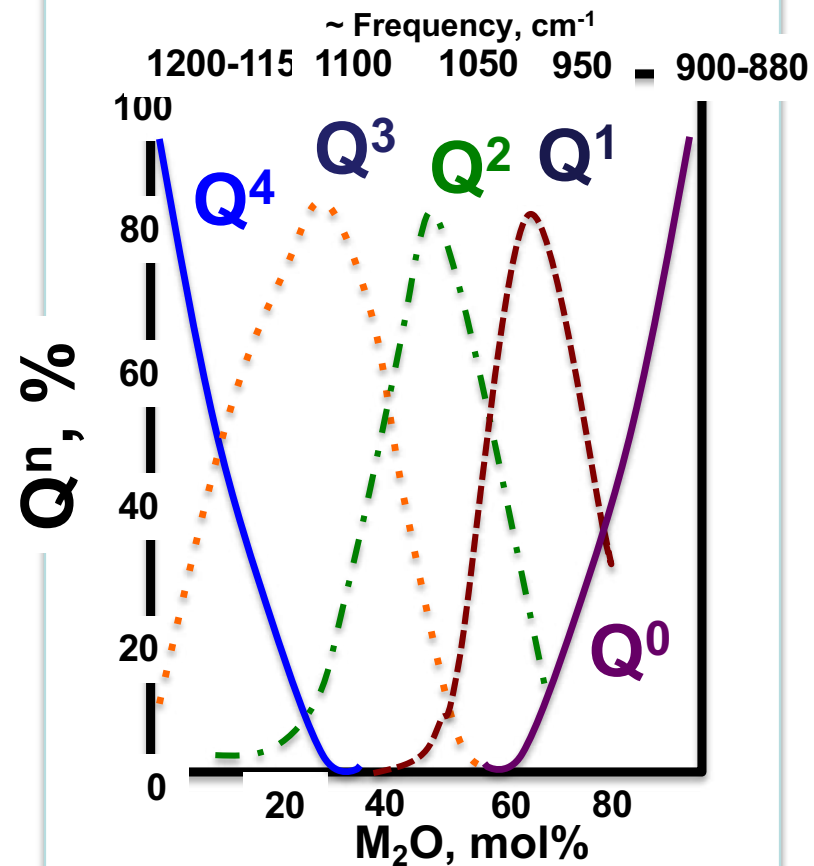
Fig. 1. Si K-XANES spectra of barium silicates, low quartz and the amorphous samples BS-333 and BS-370.

Si K-edge of $\text{BaO}-\text{SiO}_2$ glass
Bender et al., JNCS, 2002, 298, 99-108

Q^n species

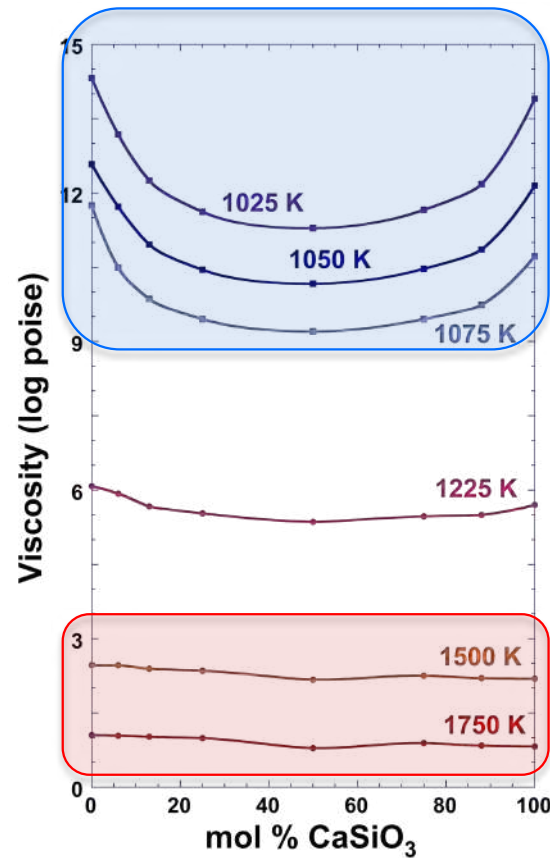
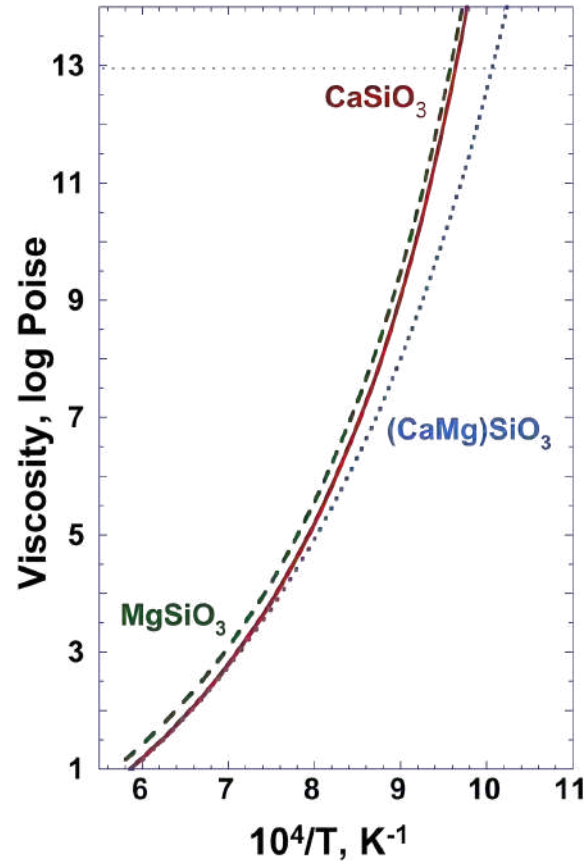


Drewitt J., Henet L., Neuville D.R., (2022) The structure of glasses from short distance order to long distance. In Neuville D.R., Henderson G.S, Dingwell D. B. (2022) "Geological melts" Review in Mineralogy and Geochemistry. DOI: 10.2138/rmg.2022.87.02



Neuville D.R., Henderson G.S and de Ligny D. (2014) [Advances in Raman Spectroscopy Applied to Earth and Material Sciences](#). In Henderson G.S, Neuville D.R., Down B. (2014) "Spectroscopic methods in Mineralogy and Material Sciences" Review in Mineralogy and Geochemistry, Vol 78, 509-541.

Ca/Mg mixing



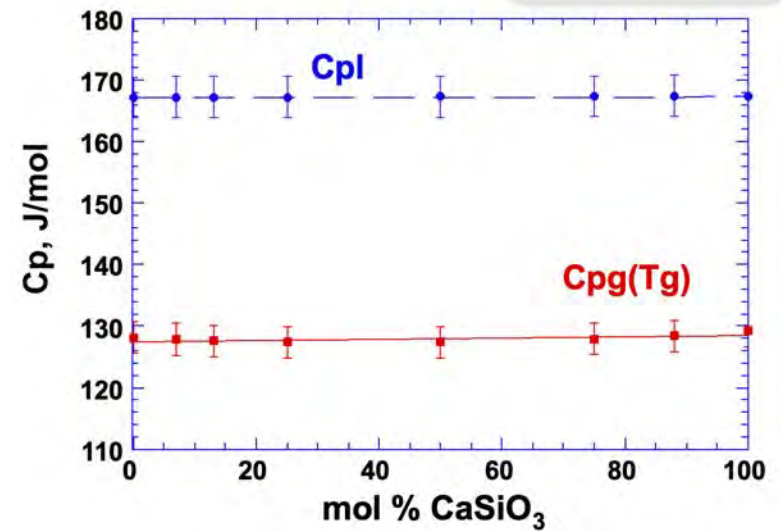
Neuville D.R. and Richet P. (1991) Viscosity and mixing in molten (Ca,Mg) pyroxenes and garnets. *Geochim. Cosmochim. Acta.*, 55, 1011-1021.

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

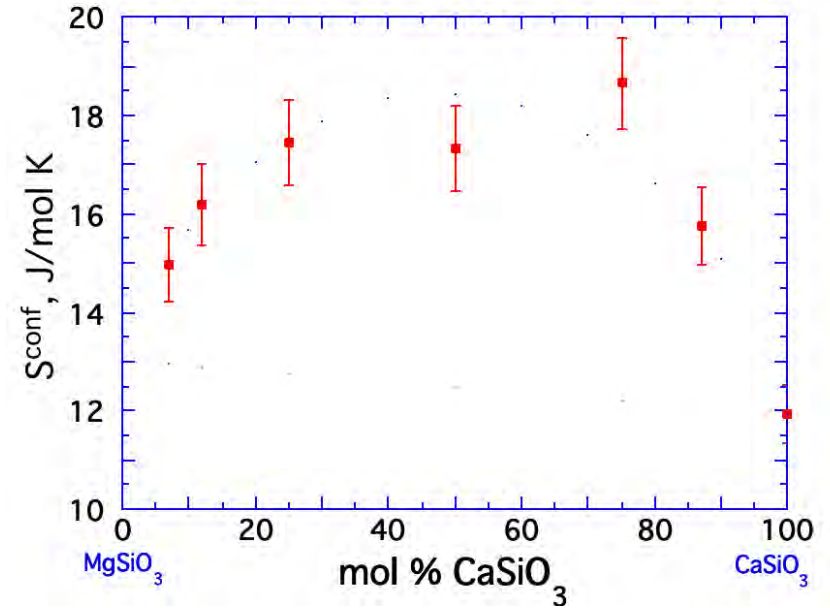
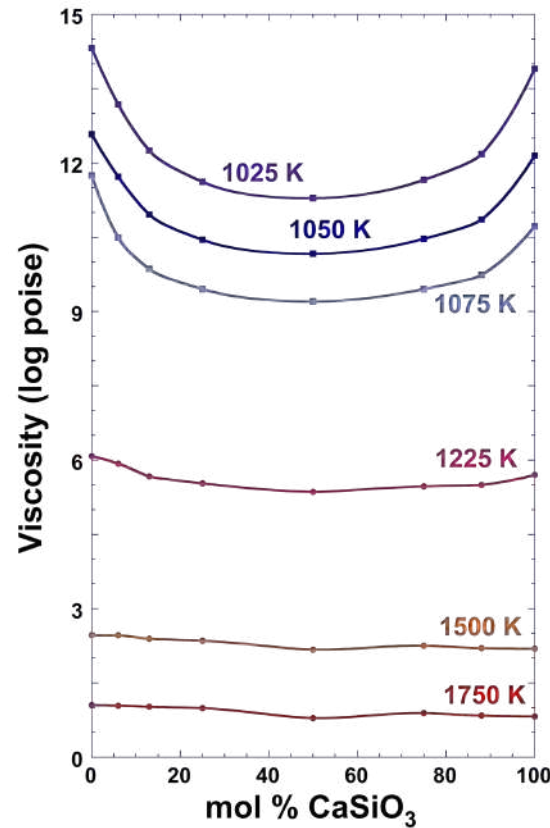
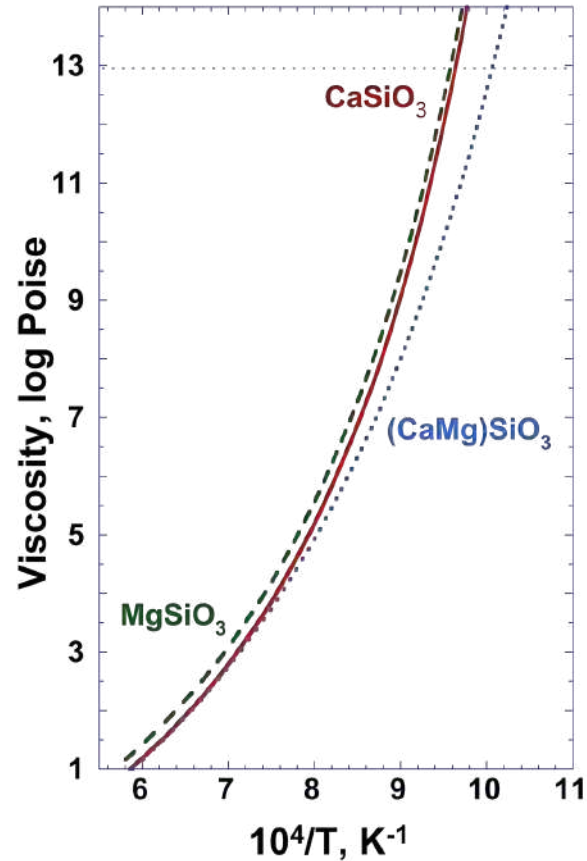
$$S^{conf}(T) = S^{conf}(T_g) + \int_{T_g}^T C_p^{conf} / T dt$$

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

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



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

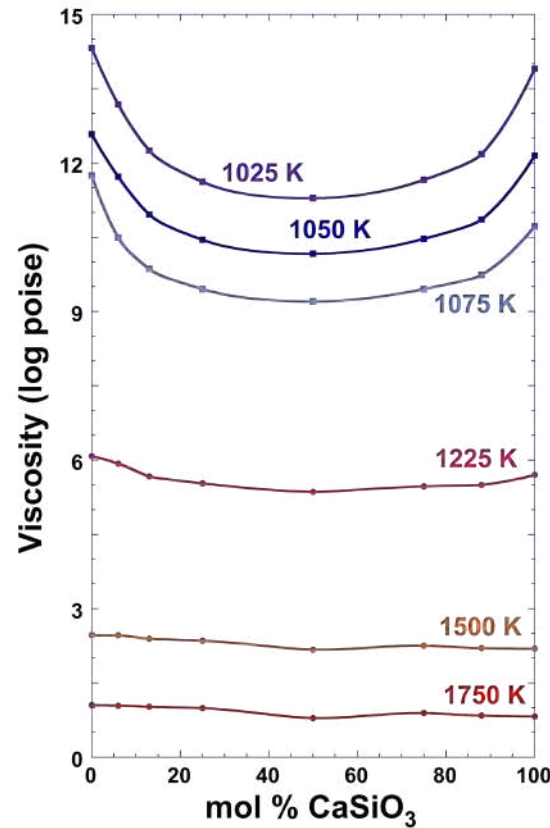
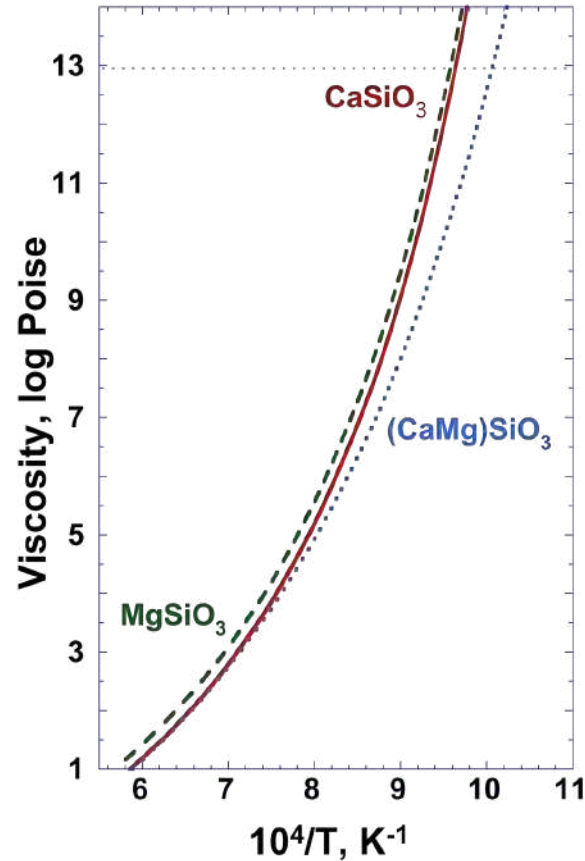


$$S^{\text{conf}}(T) = S^{\text{conf}}(T_g) + \int_{T_g}^T \frac{C_p^{\text{conf}}}{T} dt$$

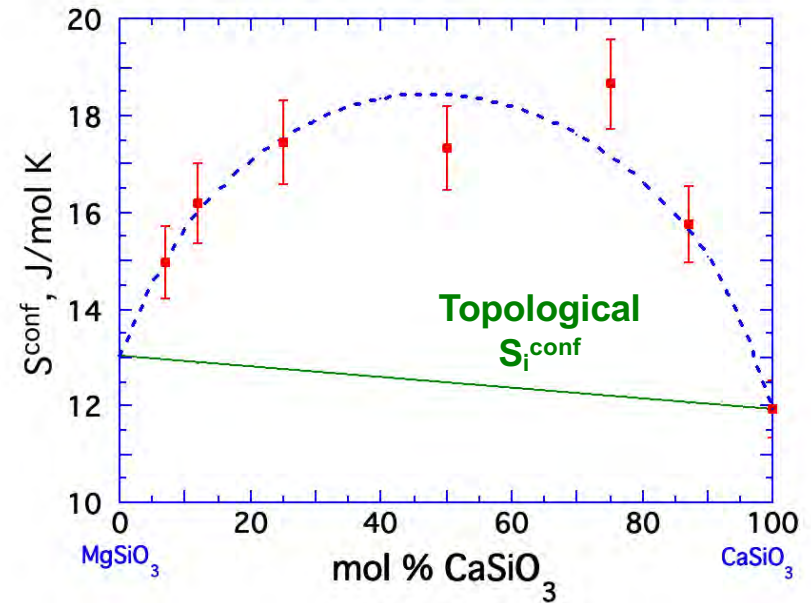
$$C_p^{\text{conf}} = C_{pl} - C_{pg}(T_g)$$

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

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



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



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

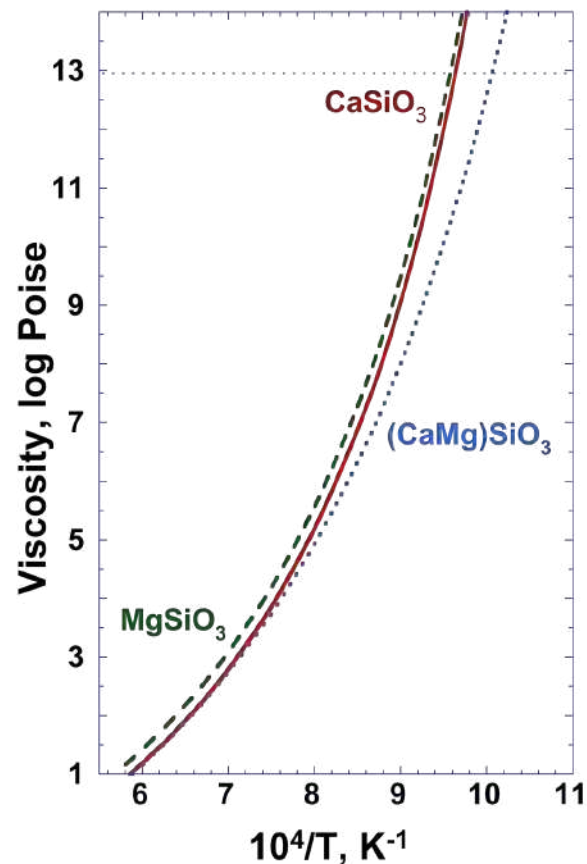
$C_p^{\text{conf}} = C_{pl} - C_{pg}(T_g)$

$$S^{\text{conf}}(T_g) = S^{\text{mix}} + \sum x_i S_i^{\text{conf}}(T_g)$$

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

Ideal mixing => random distribution

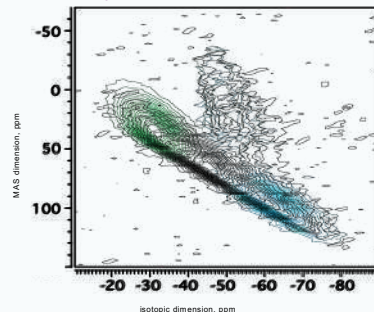
$$\log \eta = A_e + B_e/TS^{\text{conf}}(T)$$



O-NMR

Allwardt and Stebbins 2004

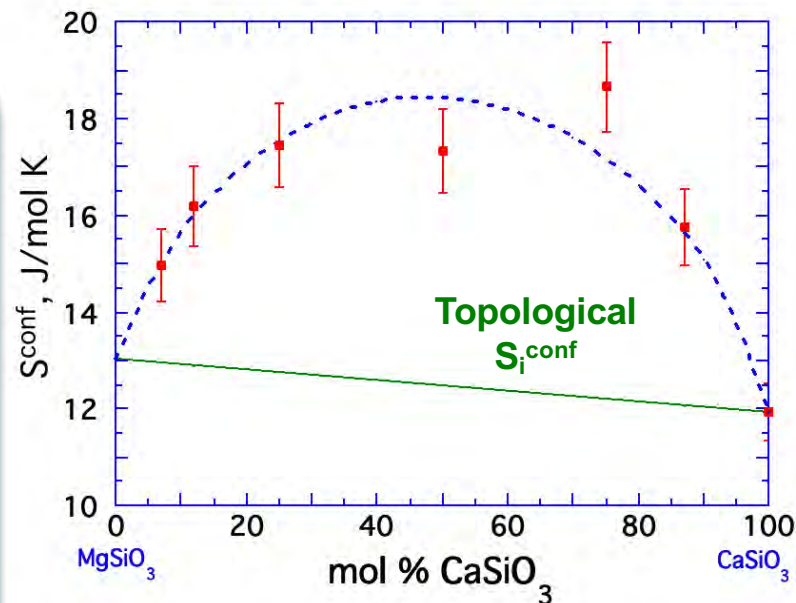
- “viewpoint” of the NBO
- ^{17}O chemical shifts depend strongly on which cations are nearby



- 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 ^{17}O MAS and 3QMAS NMR. American Mineralogist, 89, 777–784

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



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

$C_p^{\text{conf}} = C_{pl} - C_{pg}(T_g)$

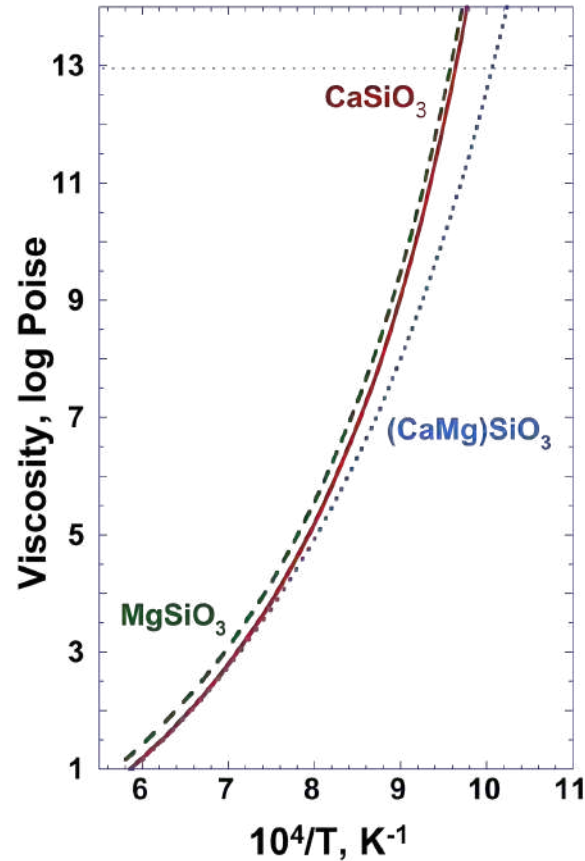
$$S^{\text{conf}}(T_g) = S^{\text{mix}} + \sum x_i S_i^{\text{conf}}(T_g)$$

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

Ideal mixing => random distribution

Ca/Mg mixing

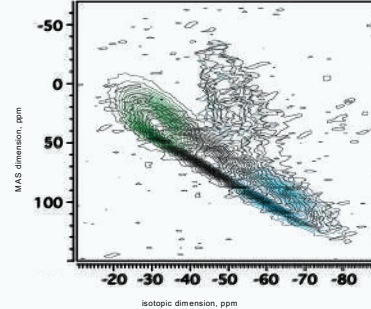
$$\log \eta = A_e + B_e / TS^{\text{conf}}(T)$$



O-NMR

Allwardt and Stebbins 2004

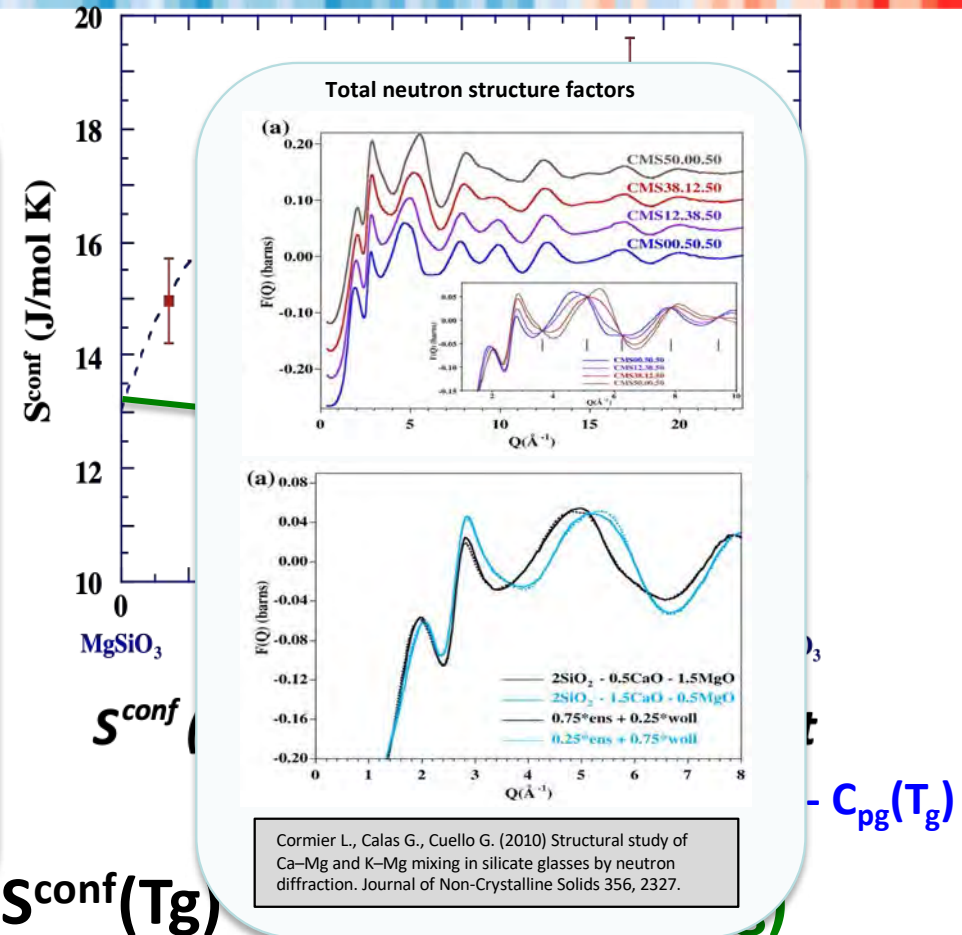
- “viewpoint” of the NBO
- ¹⁷O chemical shifts depend strongly on which cations are nearby



- detailed analyses of spectra support almost random distribution of Ca + Mg around NBO
- size difference of Ca²⁺ and Mg²⁺ 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

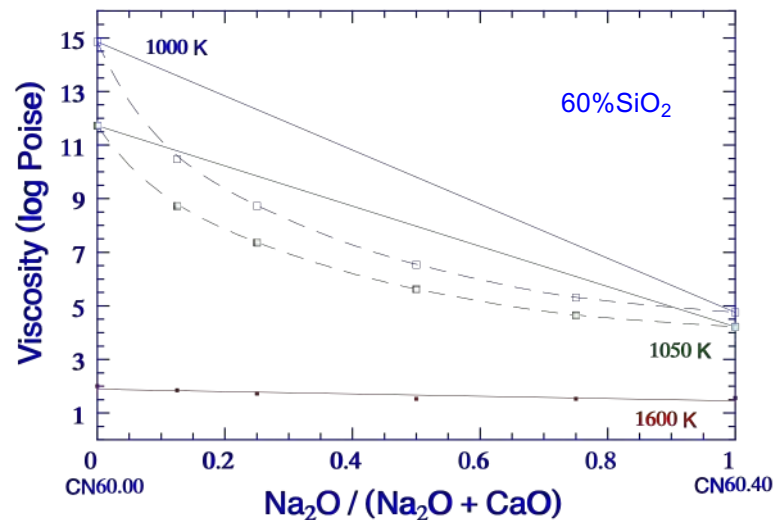
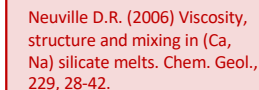
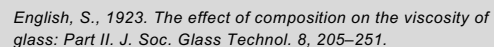
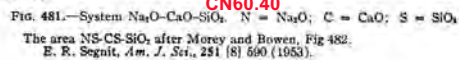
Neville D.R. and Richet P. (1991) Viscosity and mixing in molten (Ca,Mg) pyroxenes and garnets. Geochim. Cosmochim. Acta., 55, 1011-1021.



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

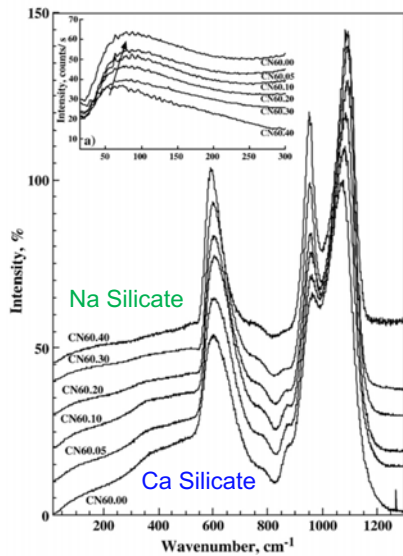
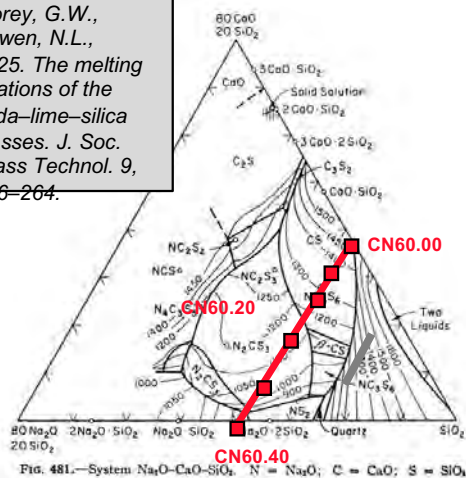
Ideal mixing => random distribution

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



Ca/Na mixing

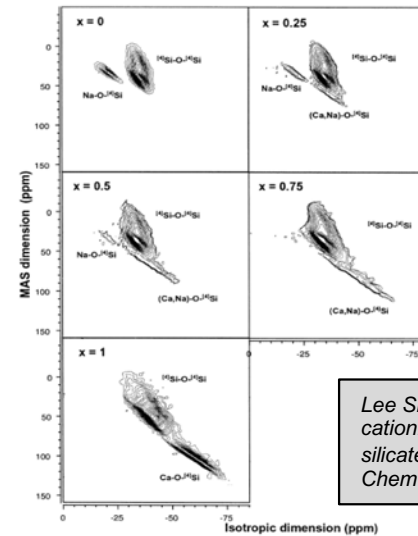
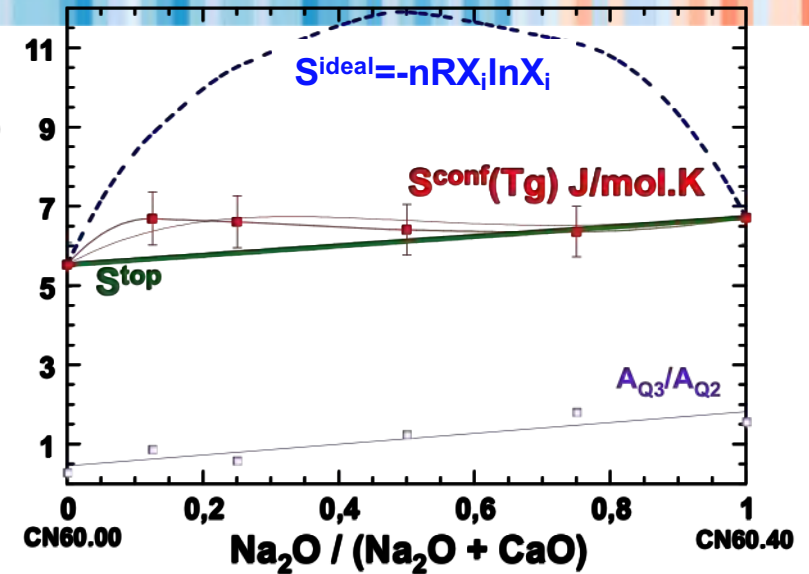
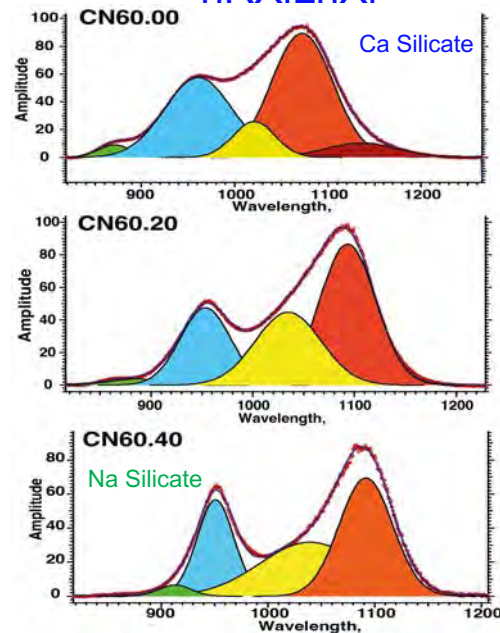
Morey, G.W.,
Bowen, N.L.,
1925. The melting
relations of the
soda-lime-silica
glasses. *J. Soc.
Glass Technol.* 9,
226-264.



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

$$S^{\text{conf}}(T_g) = S^{\text{mix}} + \sum x_i S_i^{\text{conf}}(T_g)$$

S^{ideal} : Random mixing =
Ideal mixing term : -
 $n R X_i \ln X_i$



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

Raman spectroscopy (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
cation mixing and ordering in Na-Ca
silicate glasses and melts. *J Phys
Chem B* 107:3141-3148

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

volume, ..

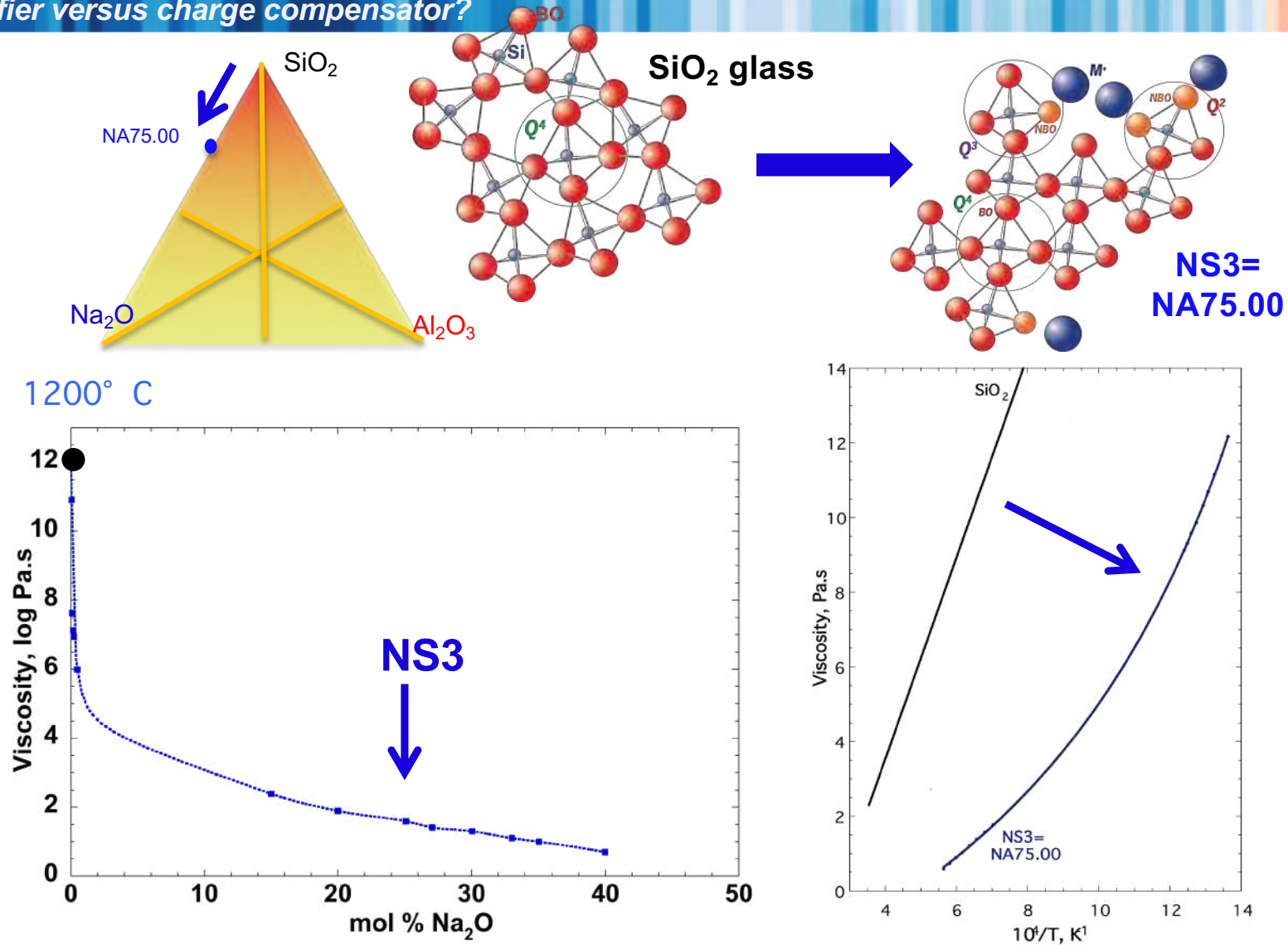
and

=> decrease viscosity, T_g , molar

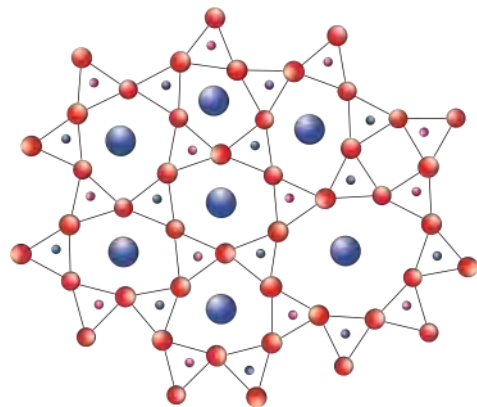
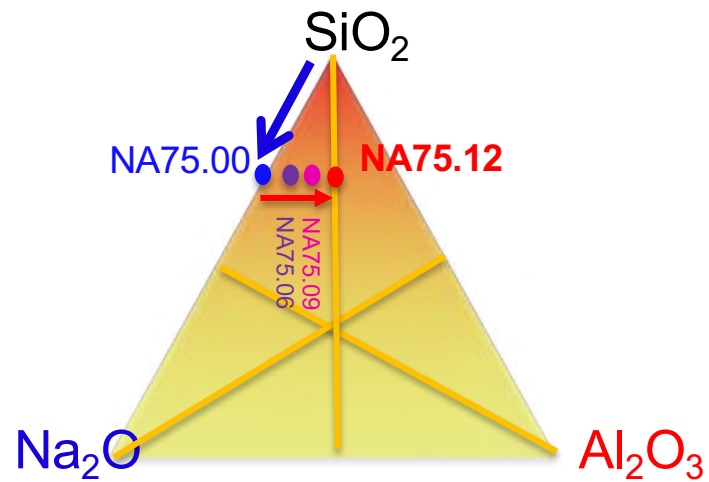
=> increase configurational entropy disorder....

How can be change in charge compensator ?

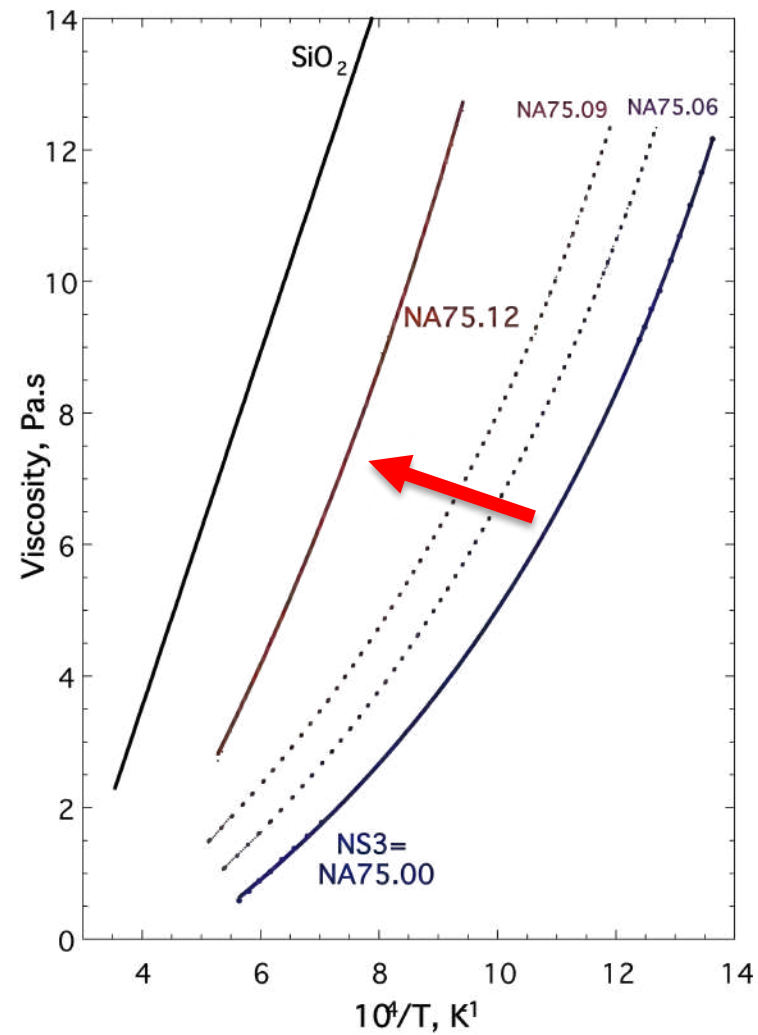
Network modifier versus charge compensator?



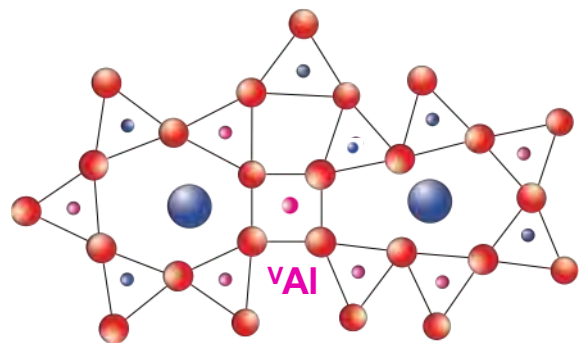
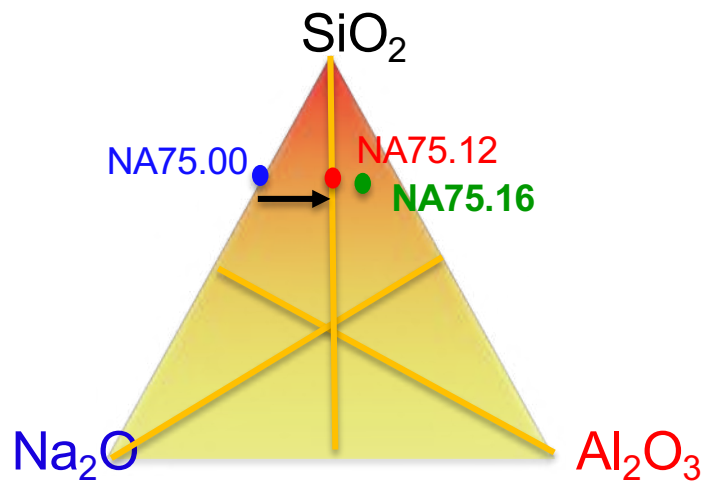
Network modifier versus charge compensator?



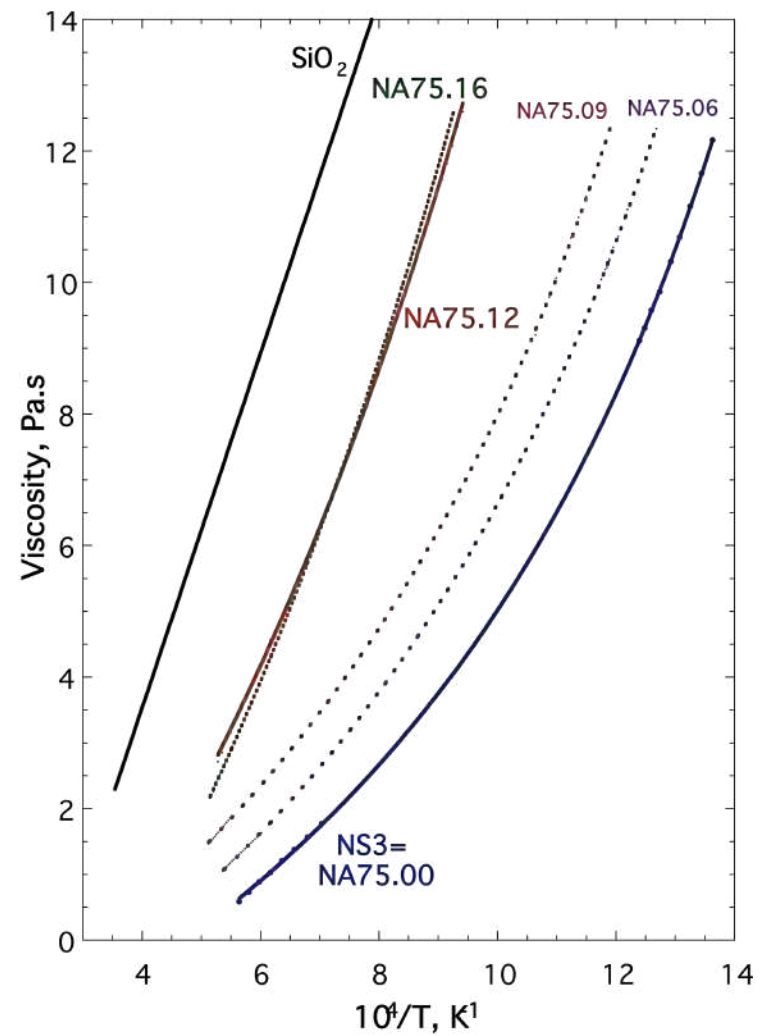
NA75.00 → NA75.12



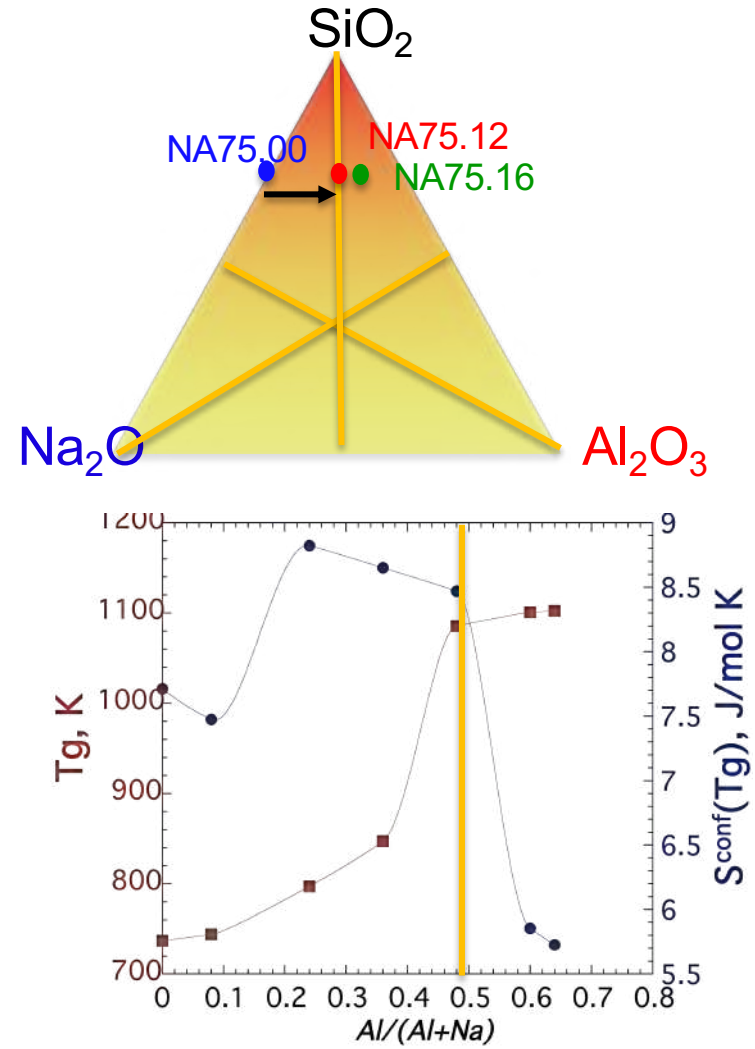
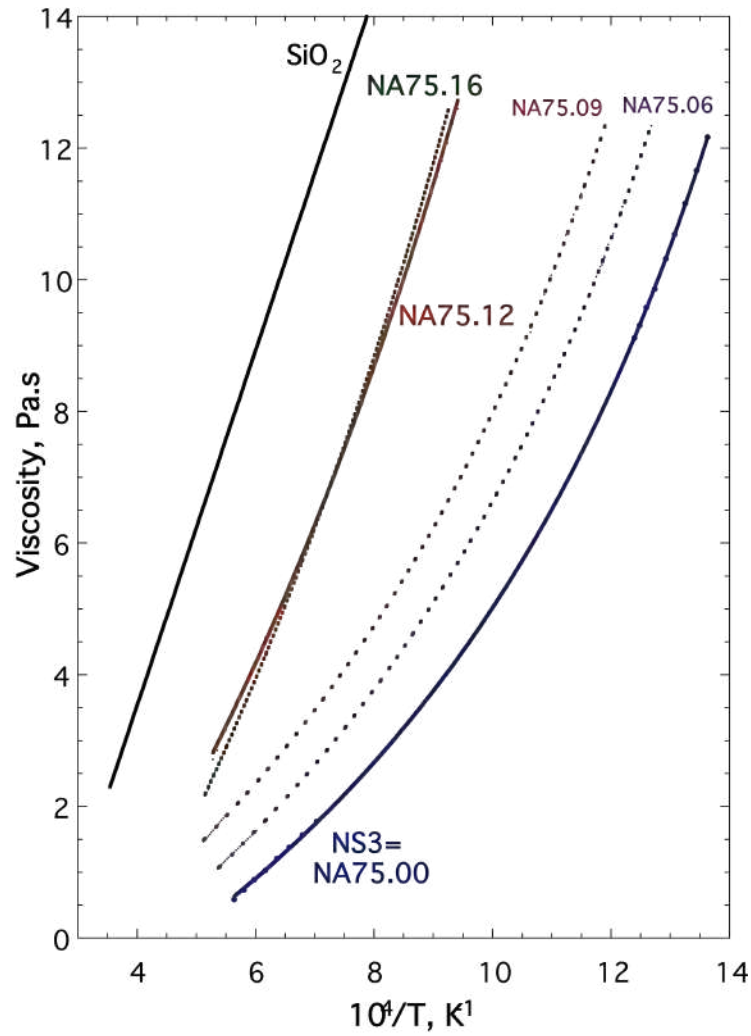
Network modifier versus charge compensator?



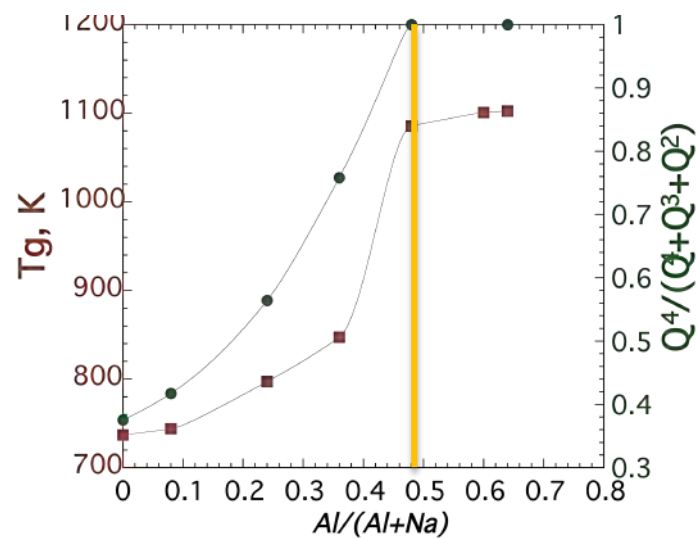
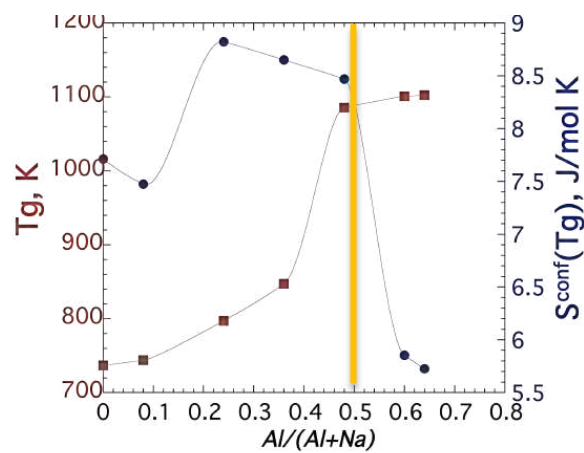
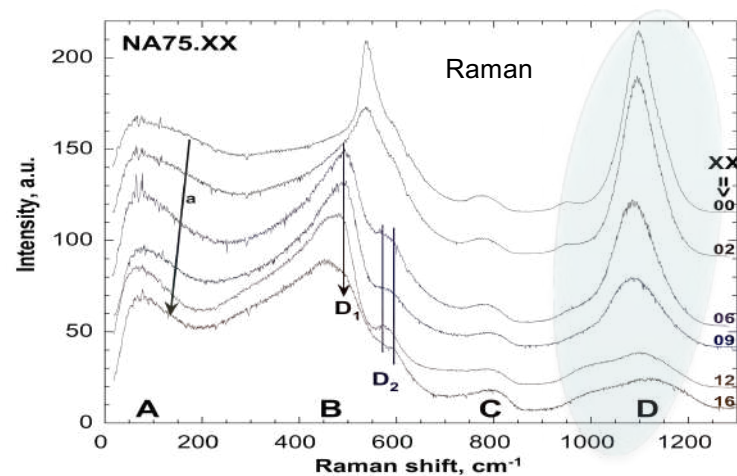
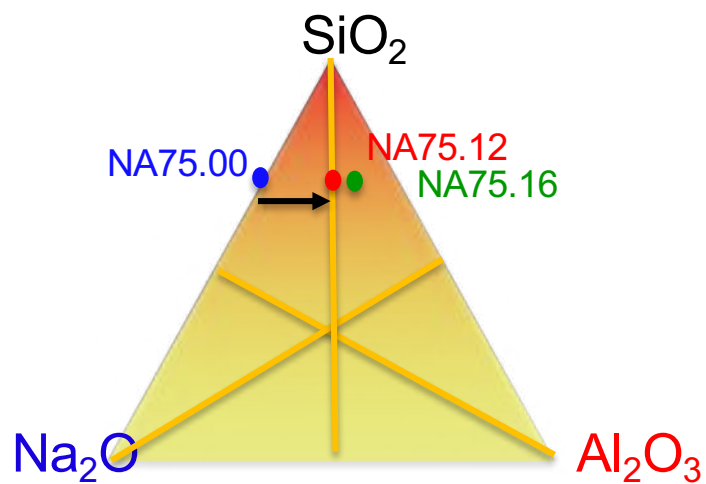
NA75.16
peraluminous composition



Network modifier versus charge compensator?

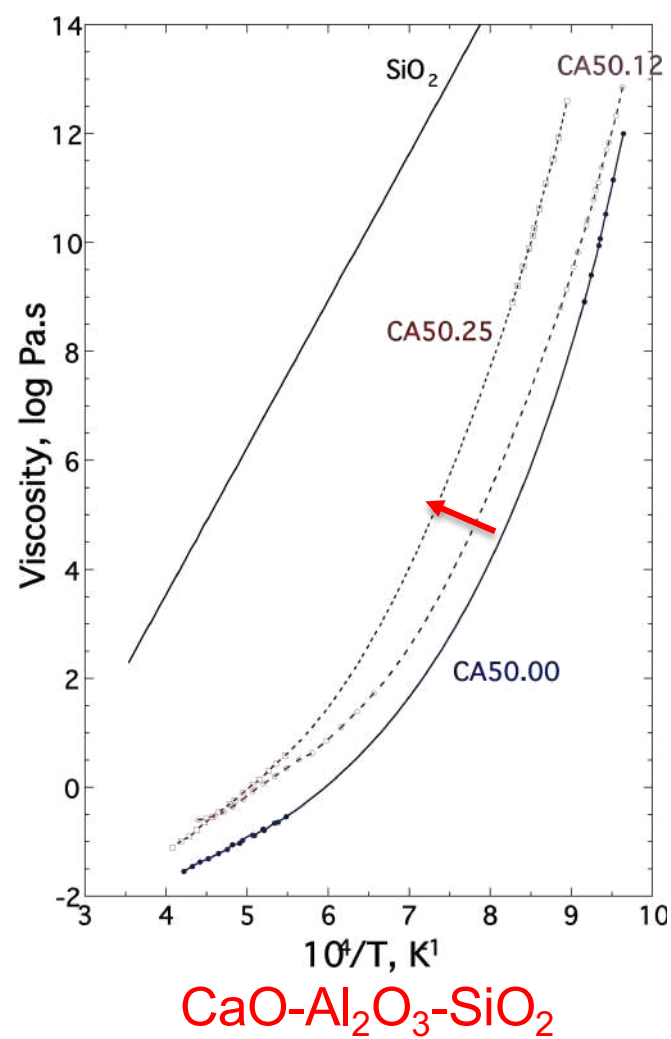
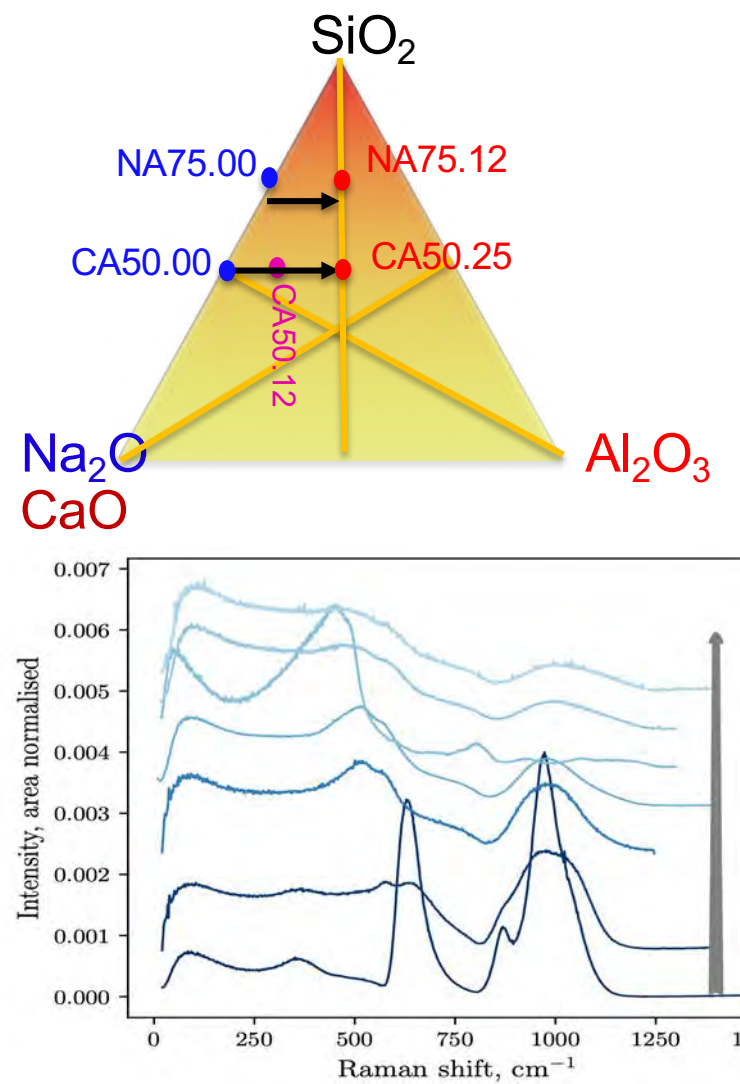


Network modifier versus charge compensator?

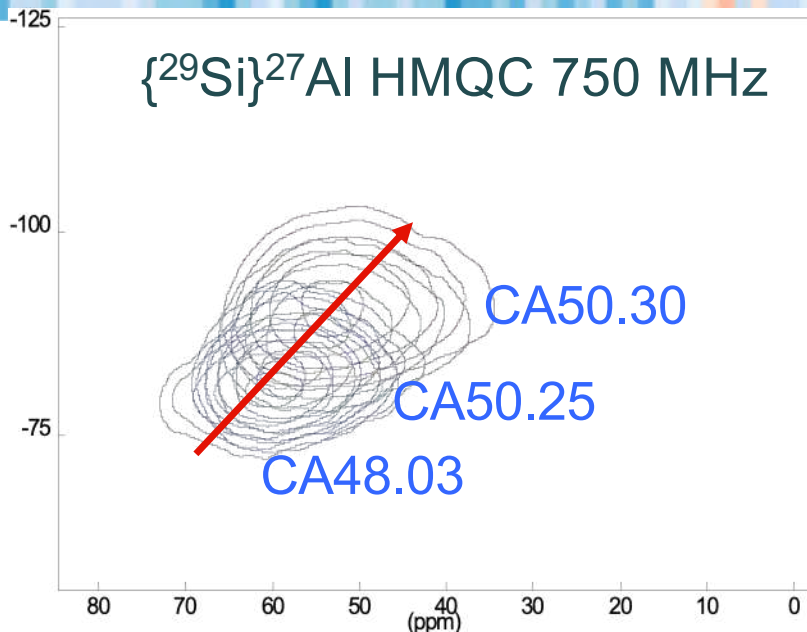
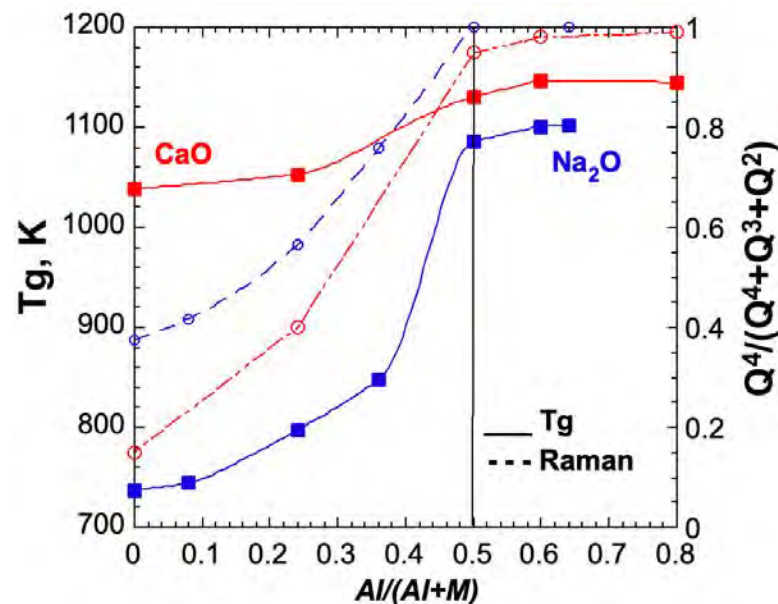
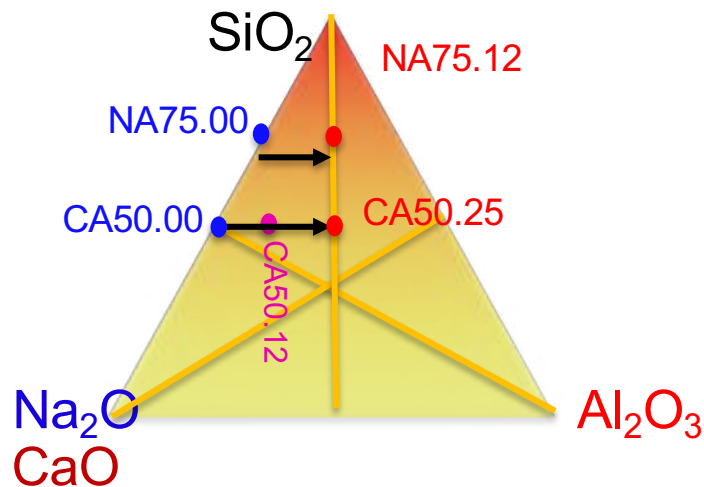


$\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$

Network modifier versus charge compensator?



Network modifier versus charge compensator?

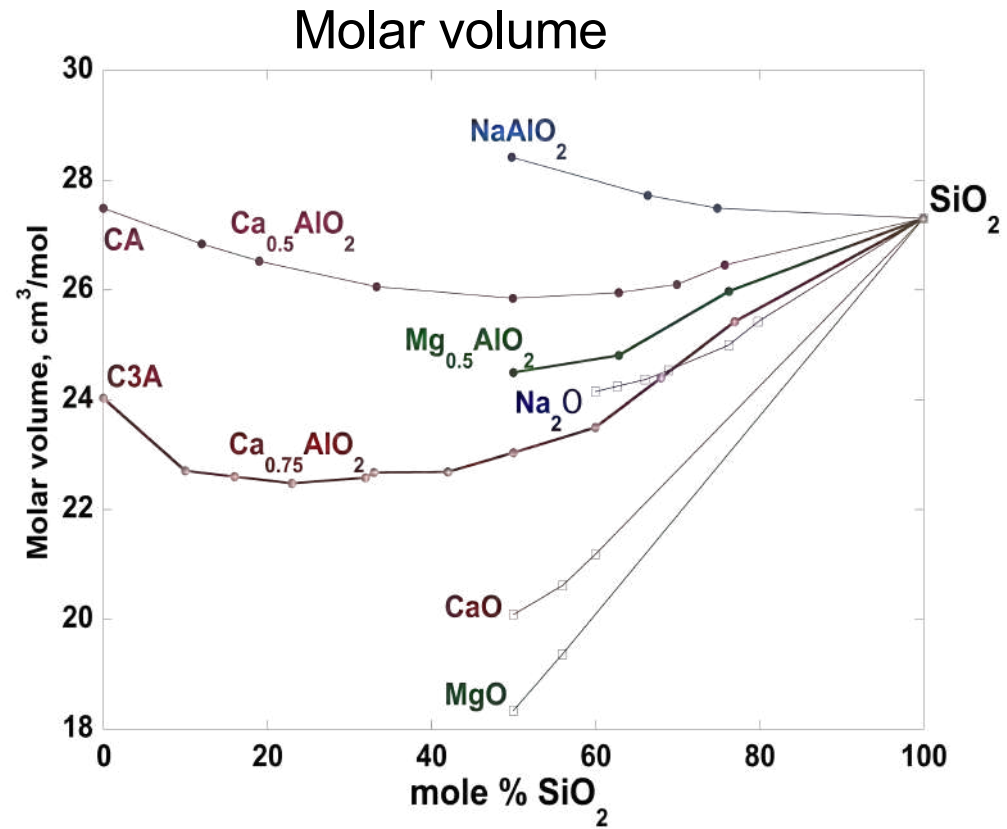
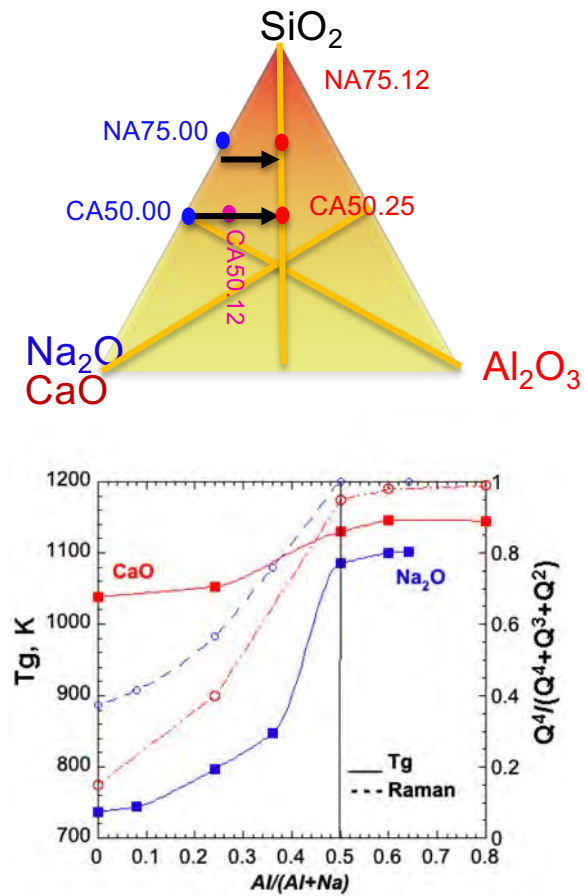


Good correlation between T_g and Q^n species

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 ($R=\text{MO}/\text{Al}_2\text{O}_3=1$).

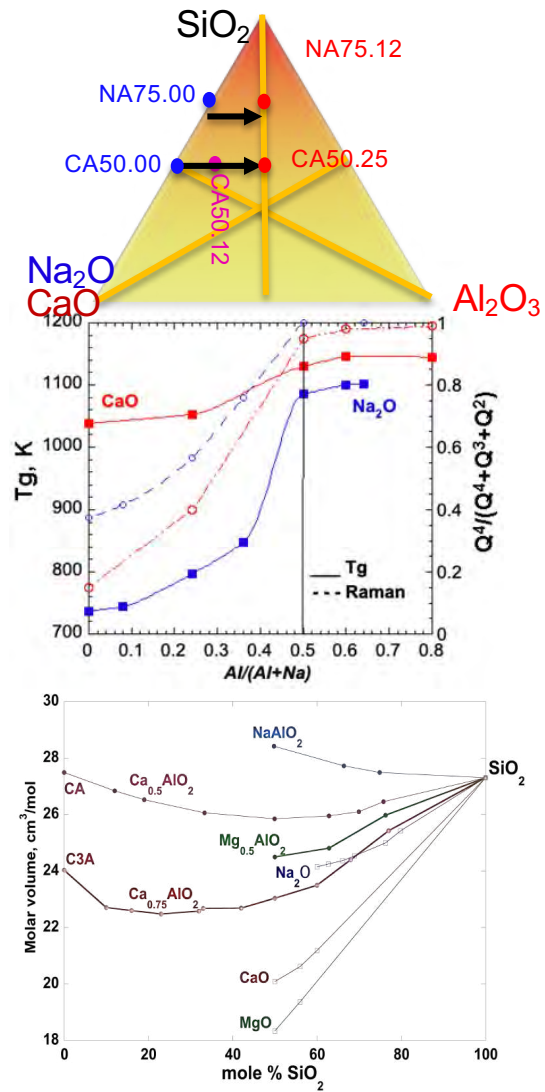
$^{[5]}\text{Al}$ and $^{[4]}\text{Al}$ are connected preferentially with Si in high Q species

Network modifier versus charge compensator?

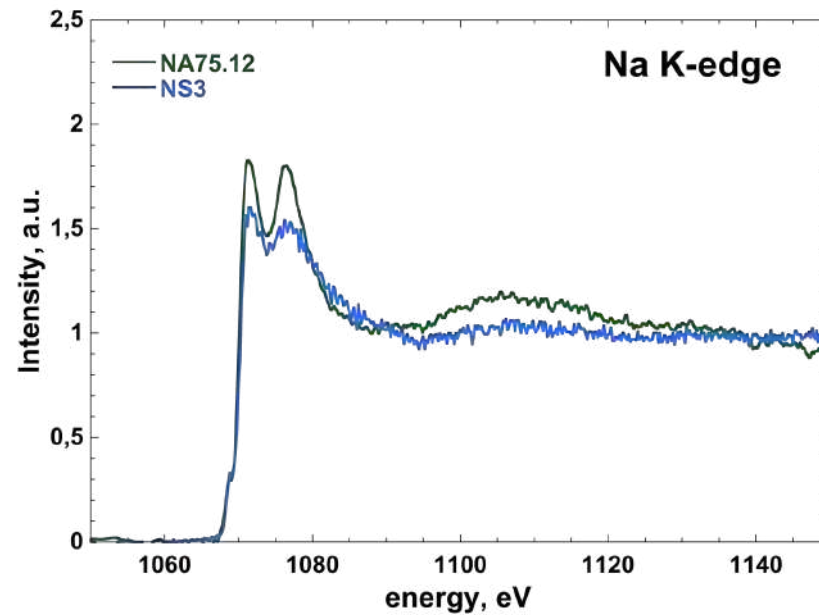


In Neuville D.R., Henderson G.S., Dingwell D. B. (2022) "Magmas, melts, liquids and glasses: Experimental insights " Review in Mineralogy and Geochemistry. DOI : 10.2138/rmg.2022.87.03

Network modifier versus charge compensator?



XANES

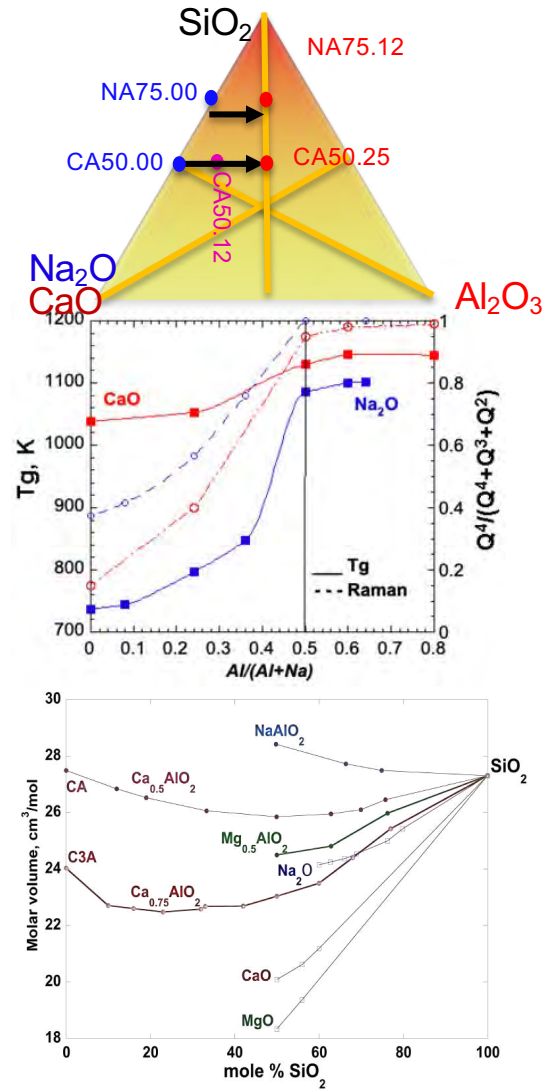


NS3 $\Rightarrow$ $[\text{Na}]^6$

NA75.12 $\Rightarrow$ $[\text{Na}]^9$

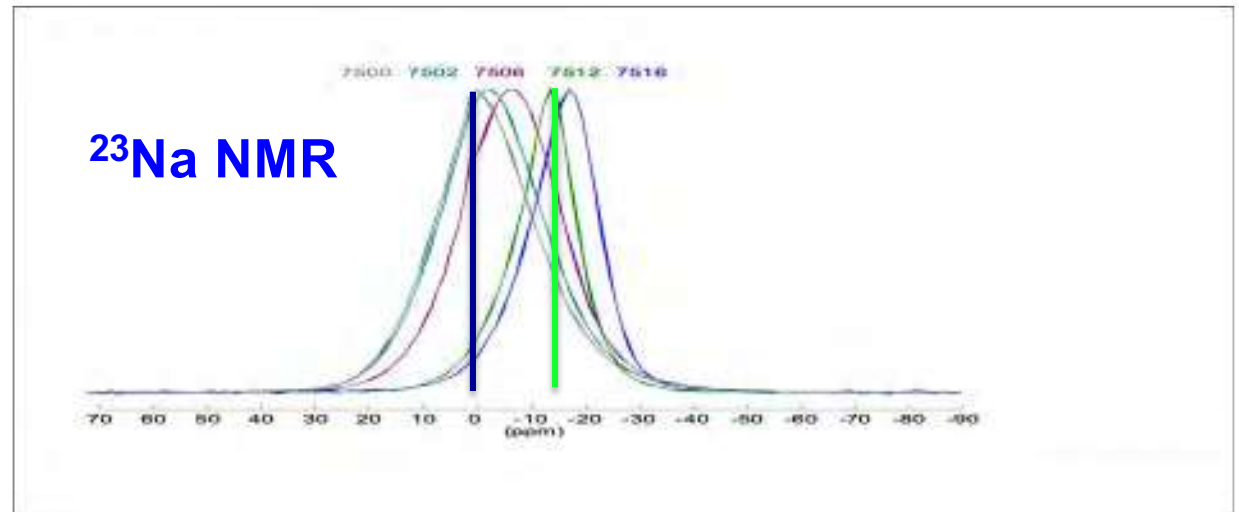
Neuvillle D.R., Cormier L. R., Flank A.M., Prado R.J. and Lagarde P. (2004) Na K-edge XANES spectra of minerals and glasses. Eur. J Mineral, 16, 809-816.

Network modifier versus charge compensator?



NMR

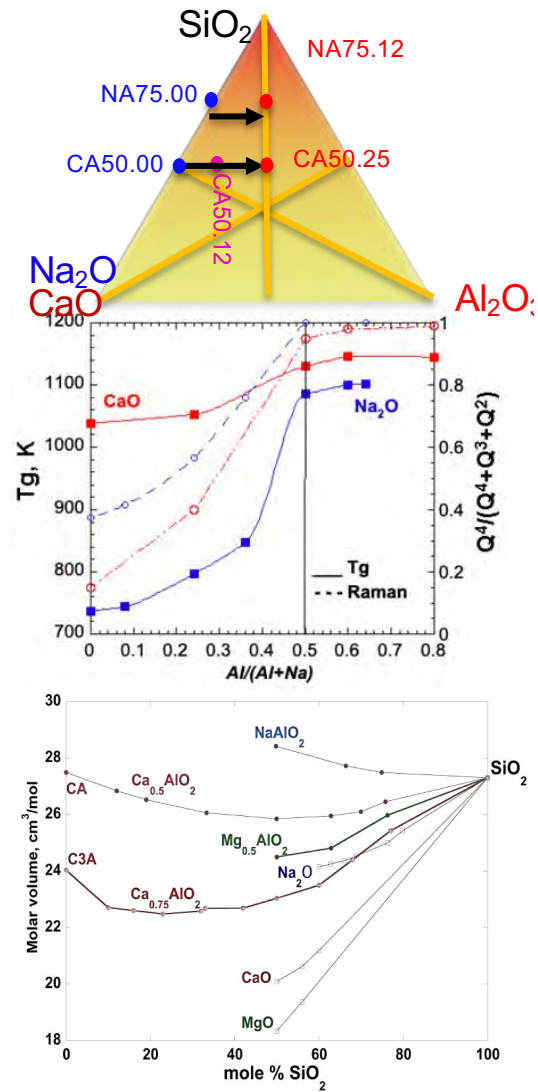
²³Na NMR



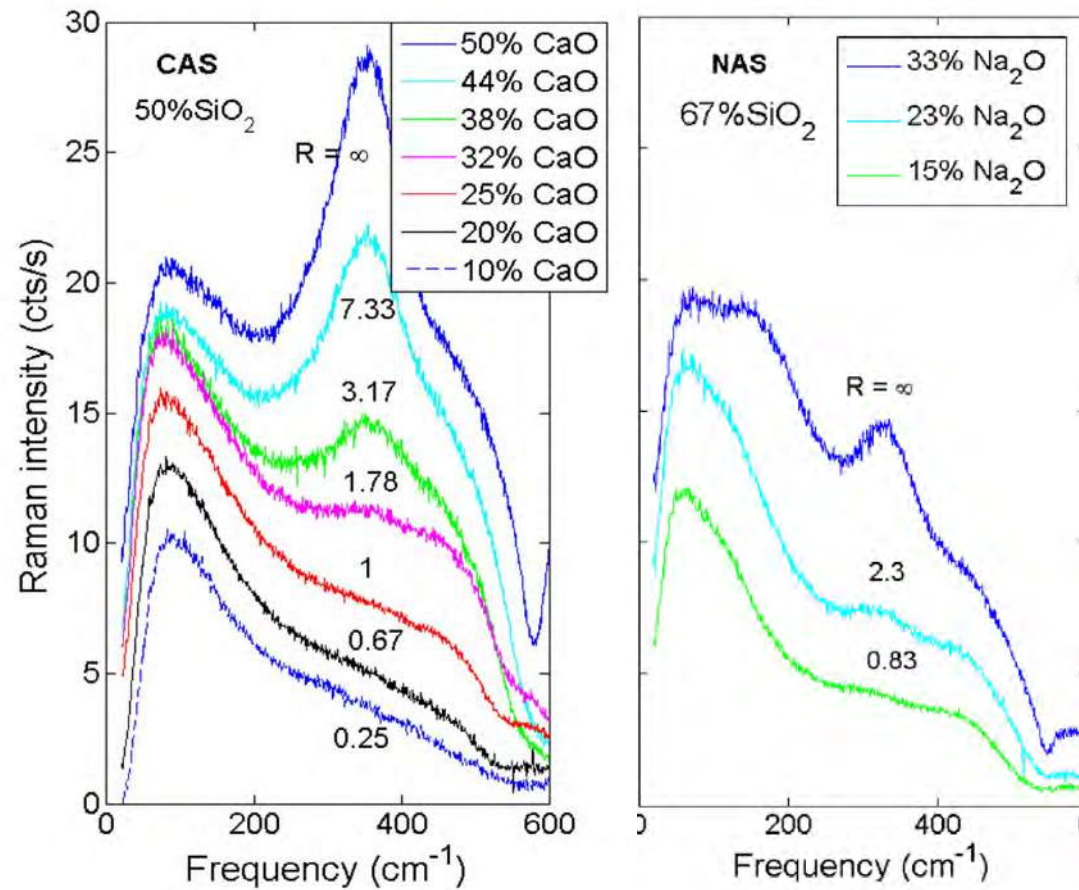
⇒ Chemical shift of ²³Na, from network modifier to charge compensator

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?

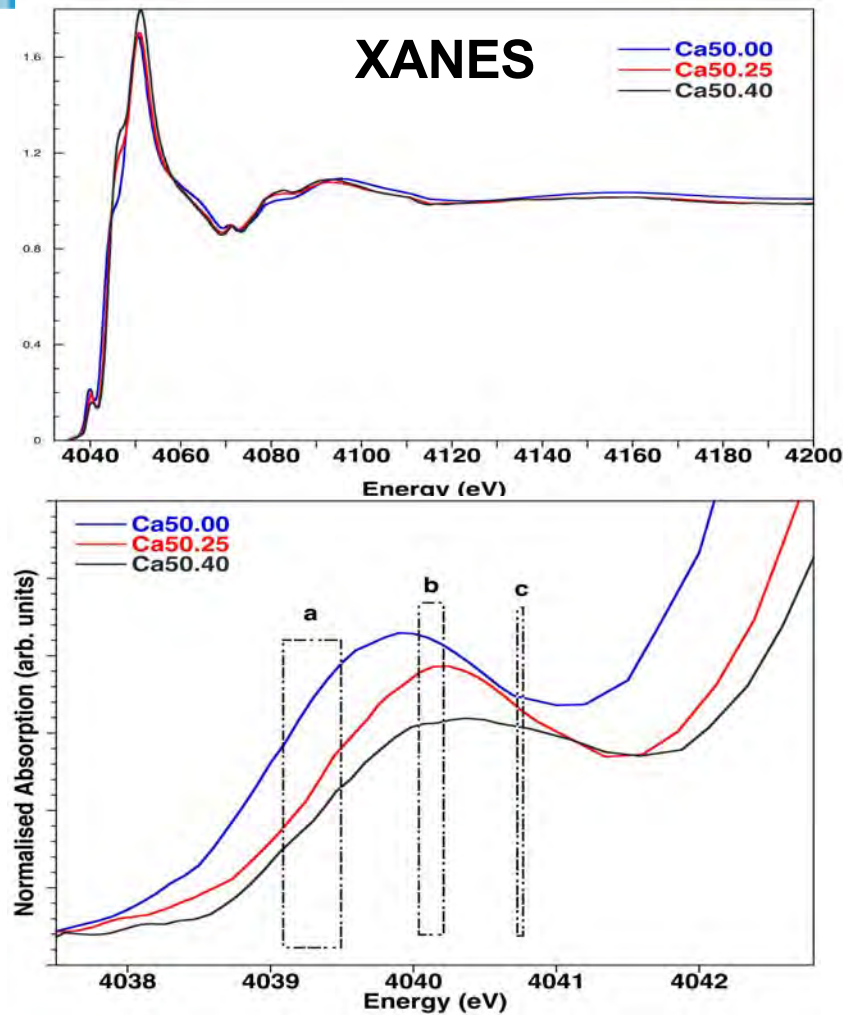
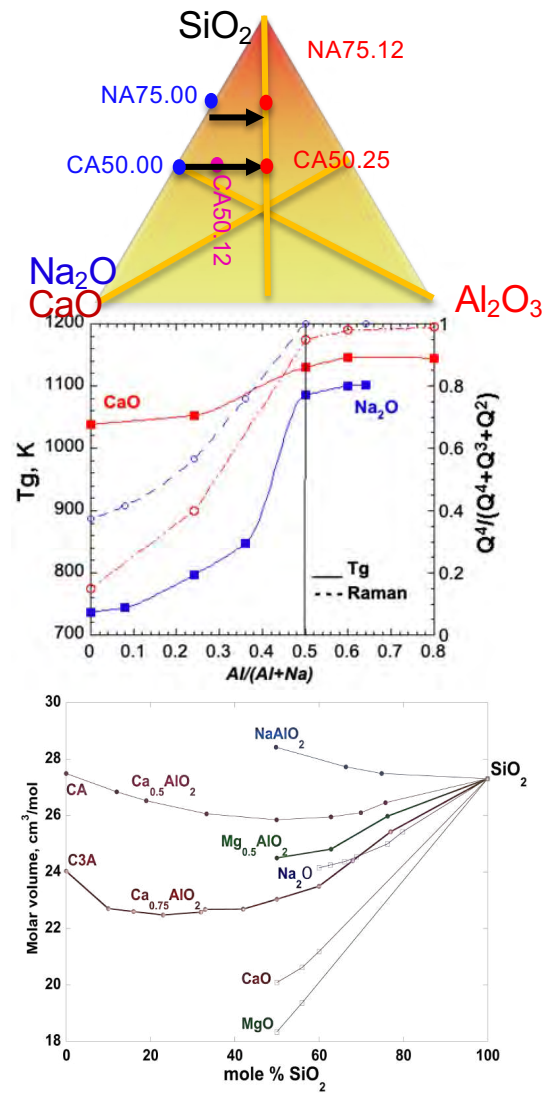


Raman VH



Hehlen B. and Neuville D.R. (2015) Raman response of network modifier cations in aluminosilicate 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.

THE
AMERICAN JOURNAL OF SCIENCE

[FOURTH SERIES.]

ART. I.—*The Ternary System $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$* ; by G. A. RANKIN. With Optical Study by FRED. E. WRIGHT.

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APPLICATION OF THE EQUILIBRIUM DIAGRAM TO PROBLEMS INVOLVING THE THREE OXIDES:

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To Certain Geological Inquiries.

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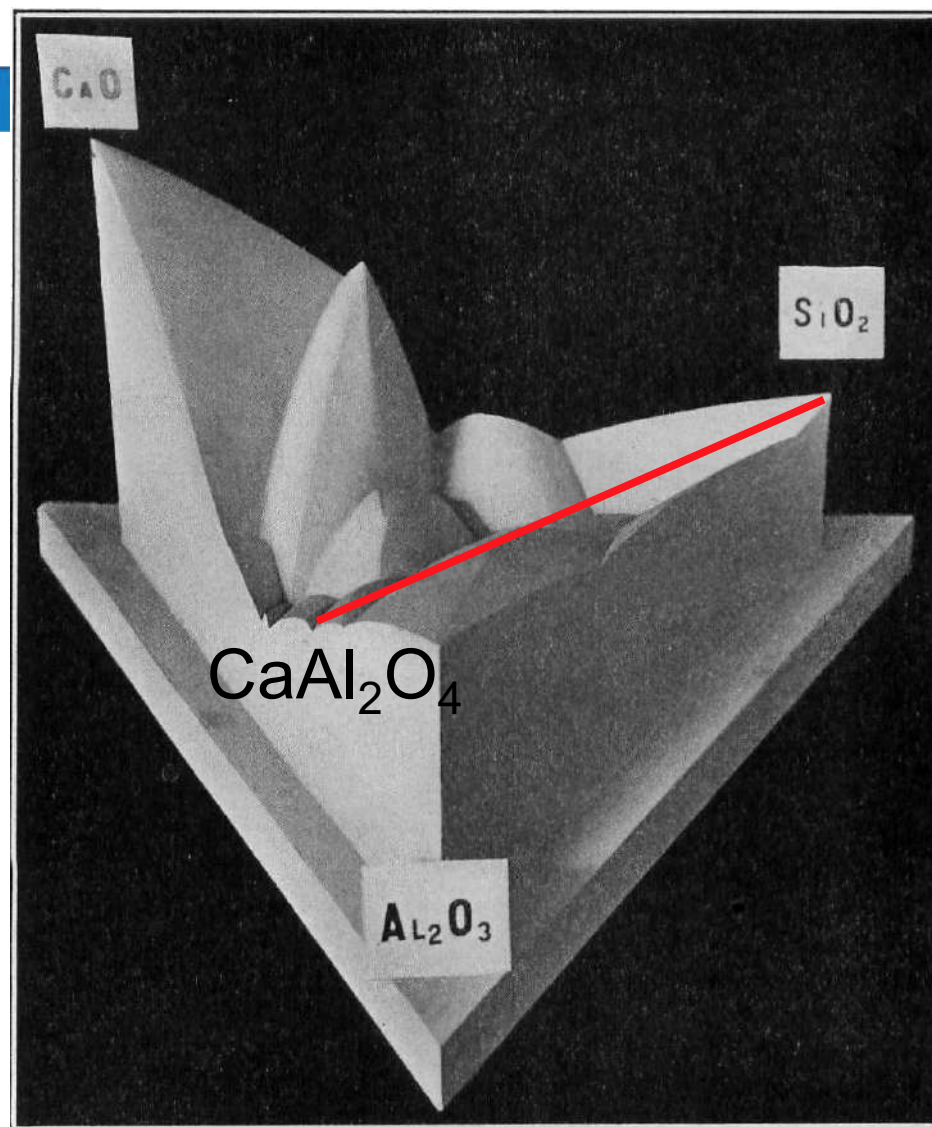
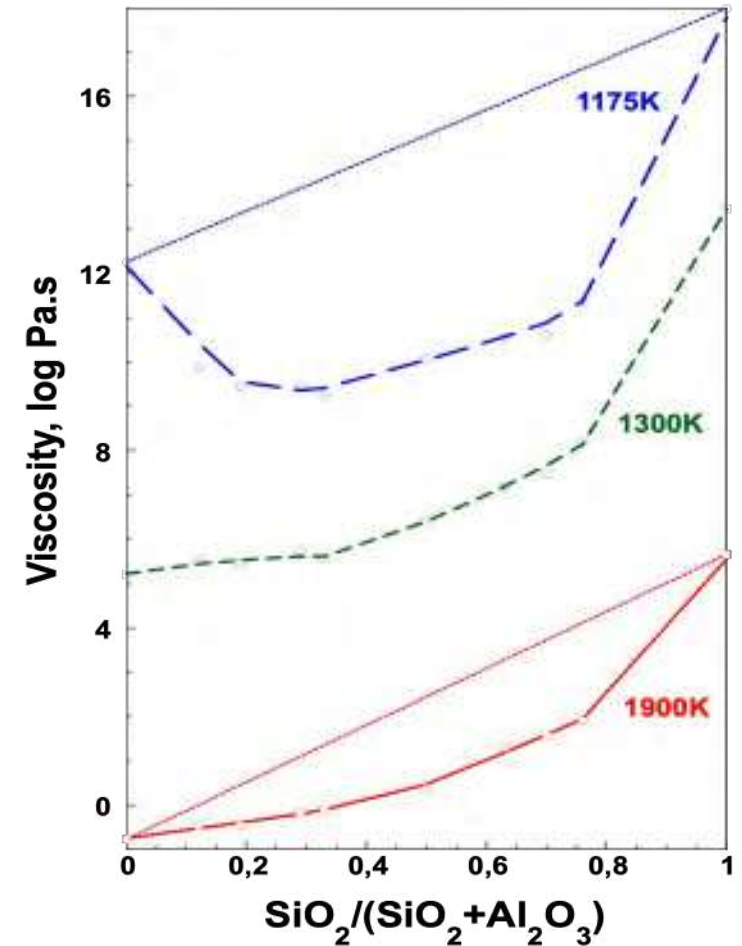
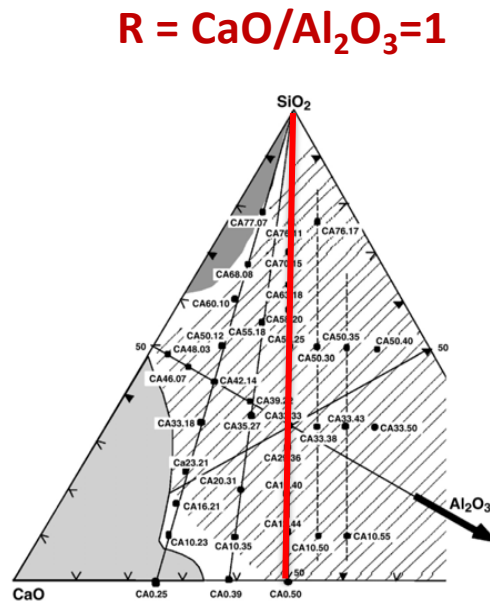
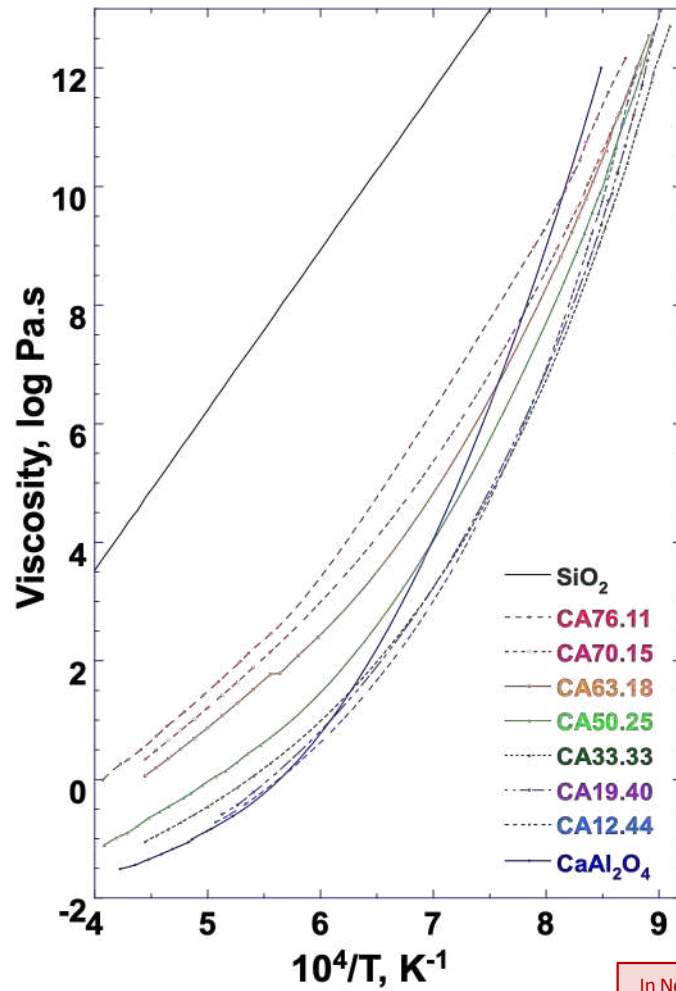


FIG. 10. Photograph of solid model showing relation of binary systems $\text{CaO}-\text{Al}_2\text{O}_3$ and $\text{Al}_2\text{O}_3-\text{SiO}_2$ to the ternary system.

CaO-Al₂O₃-SiO₂ system

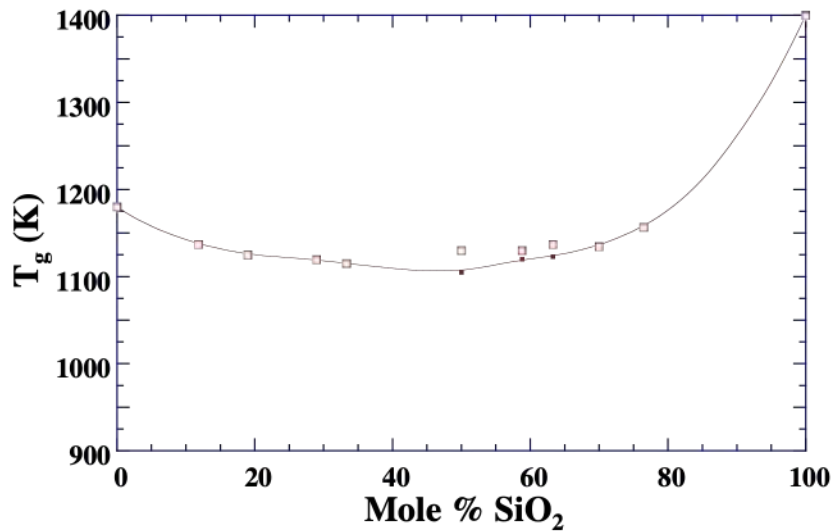


In Neuville D.R., Henderson G.S, Dingwell D. B. (2022) "Magmas, melts, liquids and glasses: Experimental insights " Review in Mineralogy and Geochemistry. DOI : 10.2138/rmg.2022.87.03

CaO-Al₂O₃-SiO₂ system

Configuration Entropy Theory

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



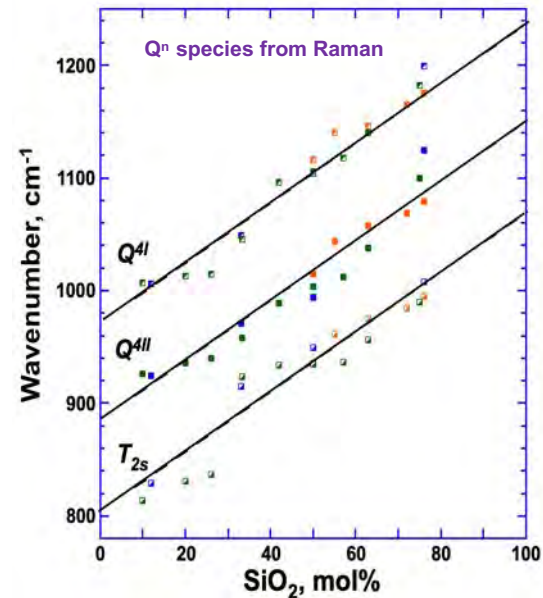
$$S^{mix} = -nR X_i \ln X_i$$

$$X_i = \text{Al}/(\text{Al}+\text{Si})$$

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

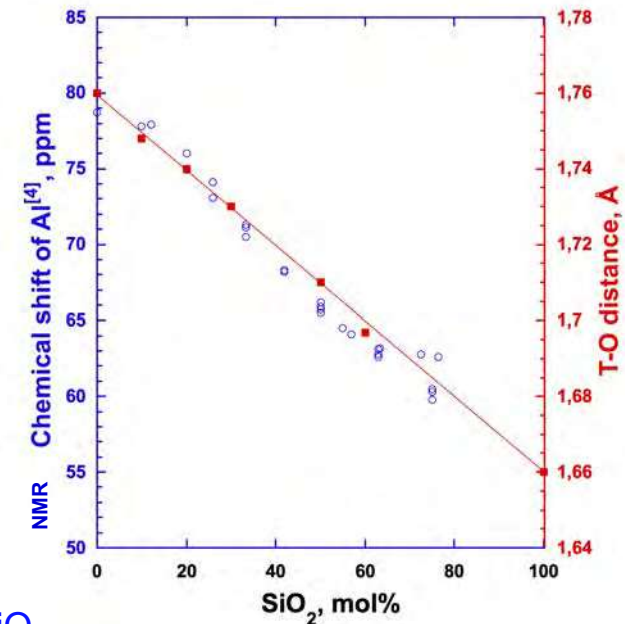
Substitution of Si by Al in Q⁴ species along the join R=1



SiO₂ => Tetrahedra SiO₄

CaAl₂O₄ => Tetrahedra AlO₄

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

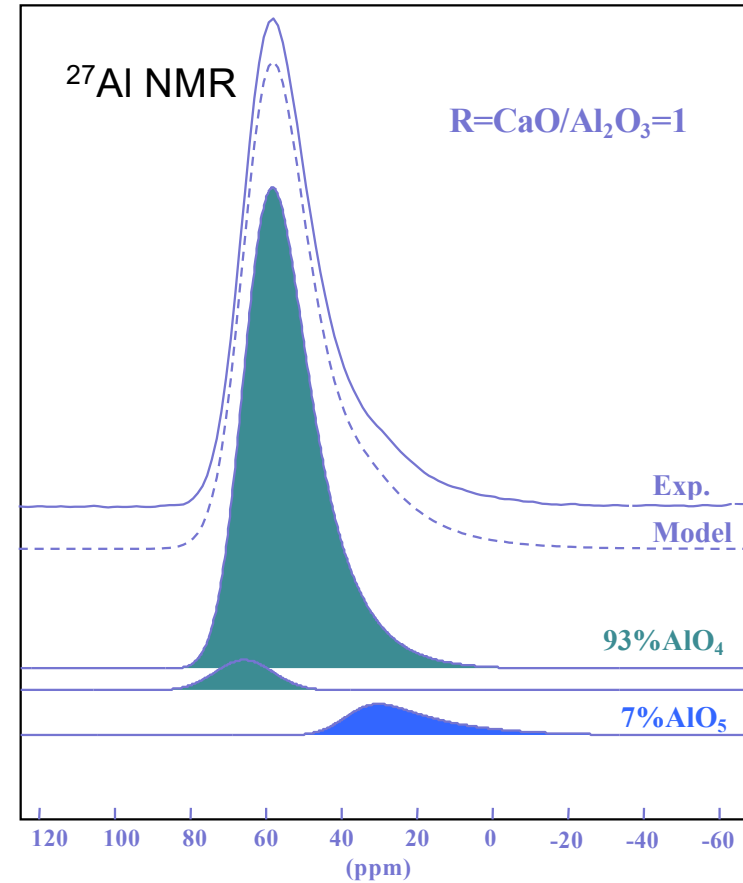
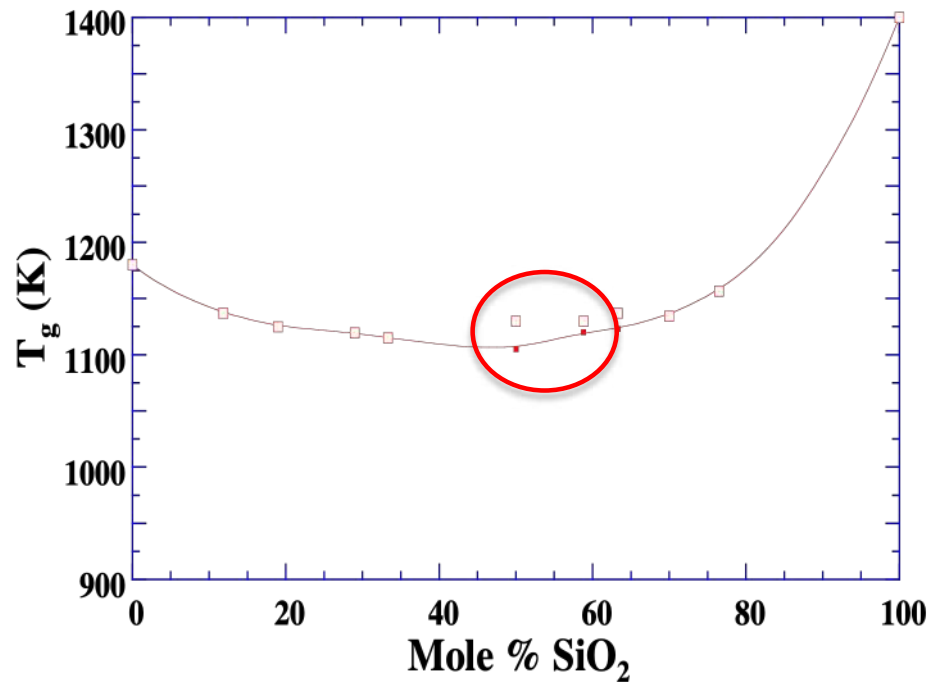


Drewitt J., Hennet L., Neuville D.R., (2022) The structure of glasses from short distance order to long distance. In Neuville D.R., Henderson G.S, Dingwell D. B. (2022) "Magmas, melts, liquids and glasses: Experimental insights " Review in Mineralogy and Geochemistry. DOI : 10.2138/rmg.2022.87.02

CaO-Al₂O₃-SiO₂ system

Configuration Entropy Theory

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



Laurent
Cormier
Paris

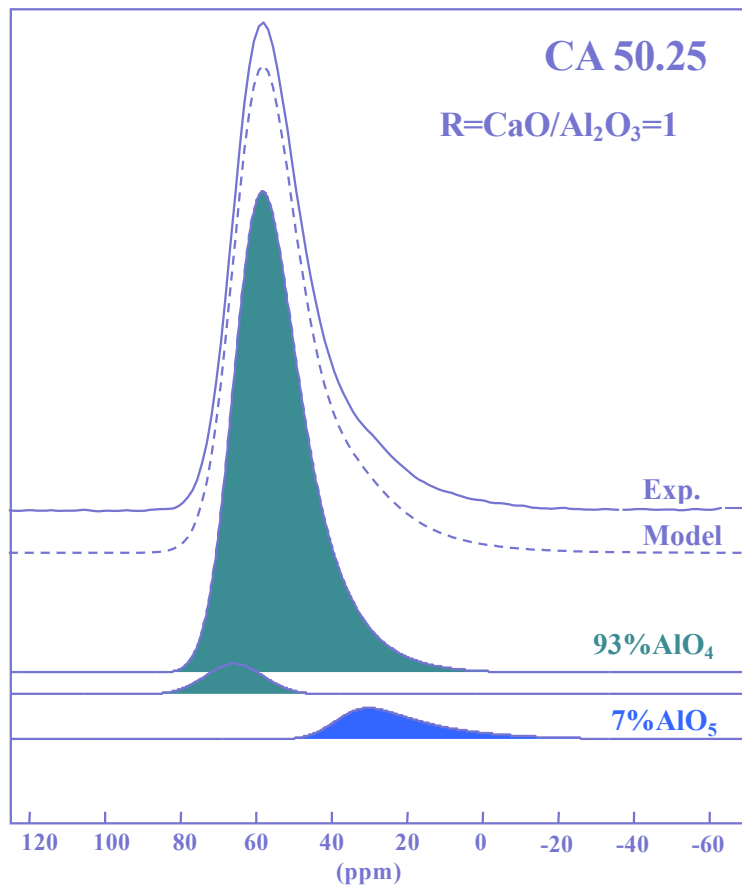


Dominique Massiot
Orléans

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

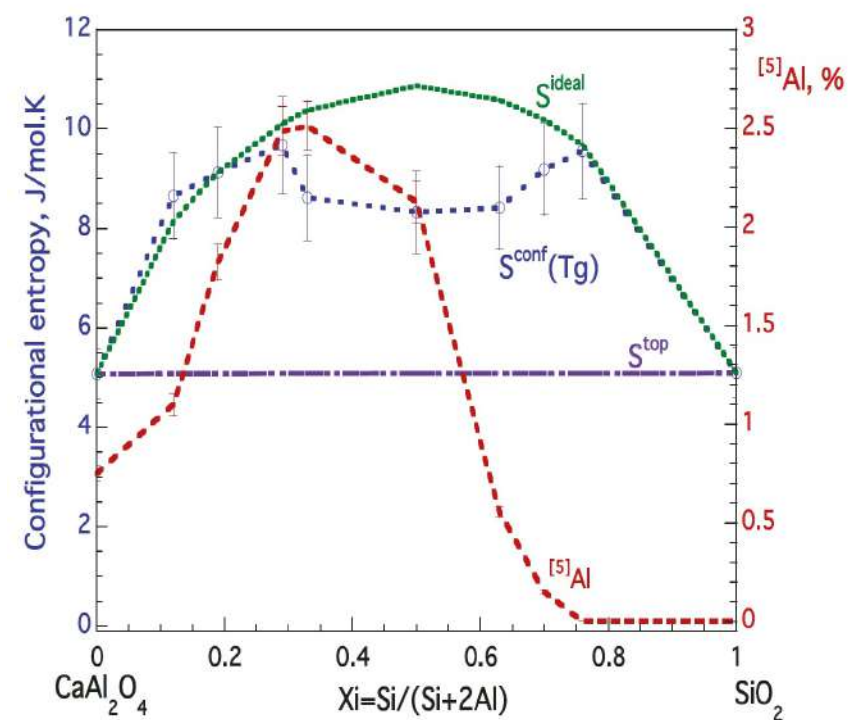
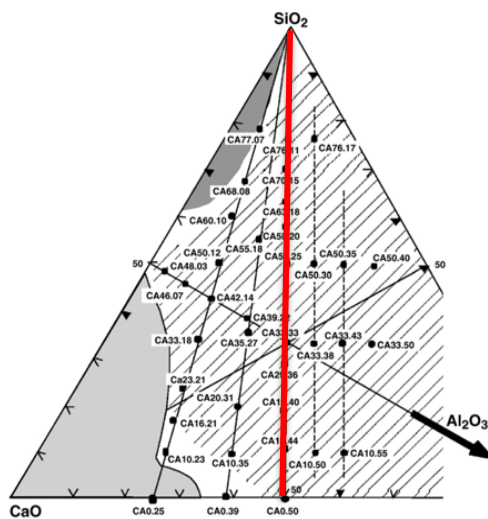
CaO-Al₂O₃-SiO₂ system

RMN 750MHz, CRMHT, Orléans, ²⁷Al 1D MAS



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

R = CaO/Al₂O₃=1



In Neuvillle 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

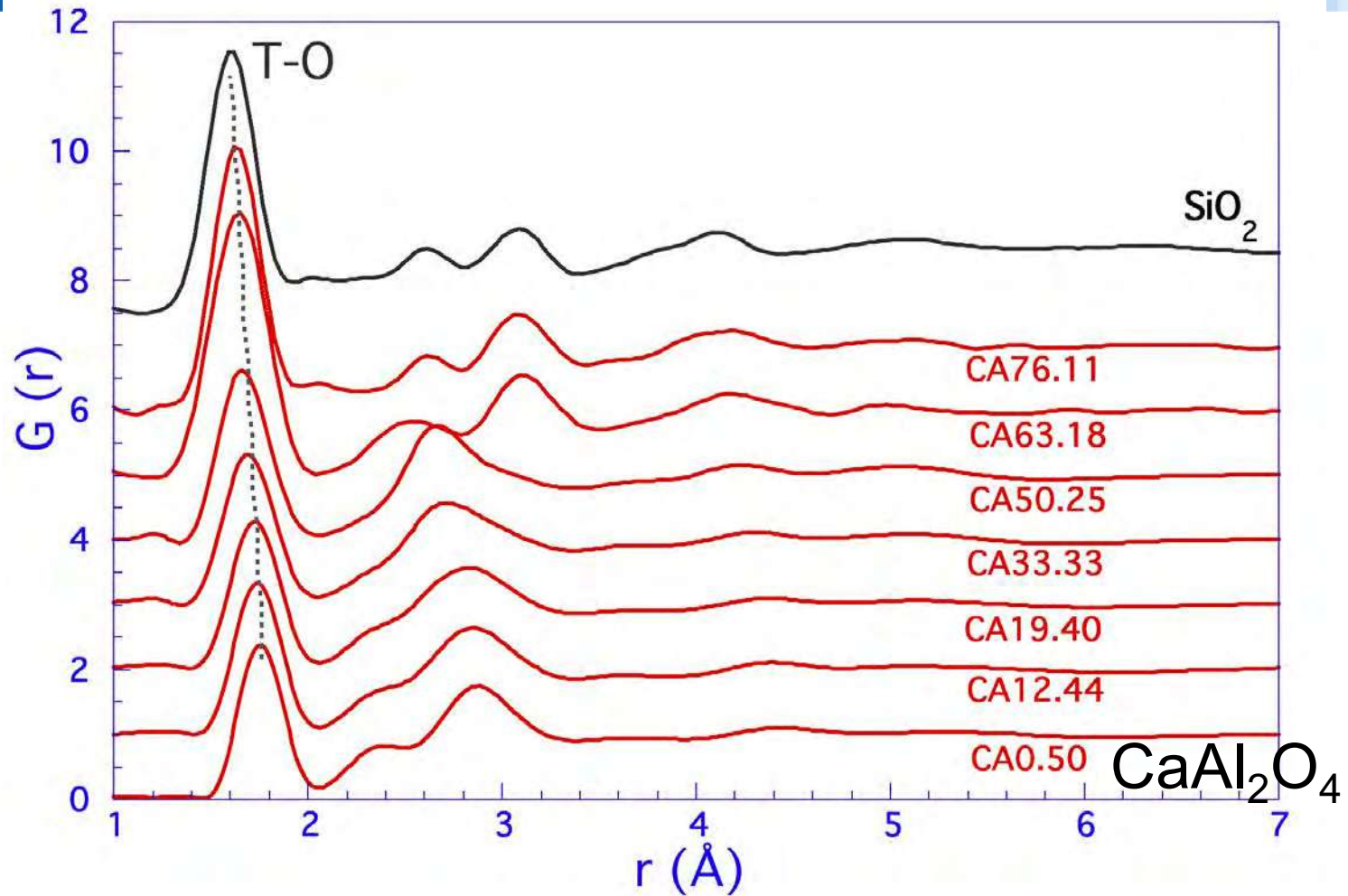
X-ray diffraction



Laurent Cormier
Paris

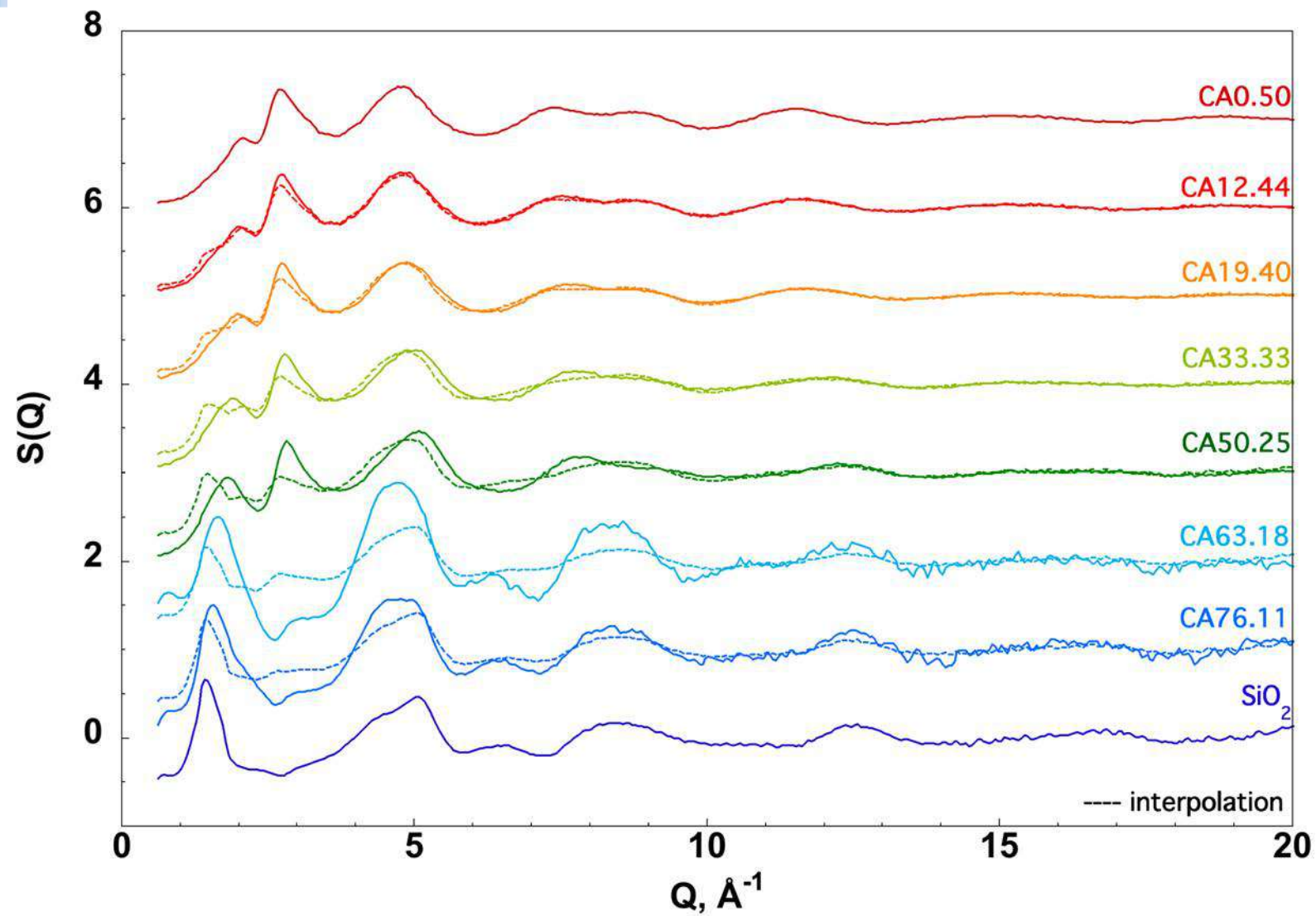


Louis Hennet
Orléans



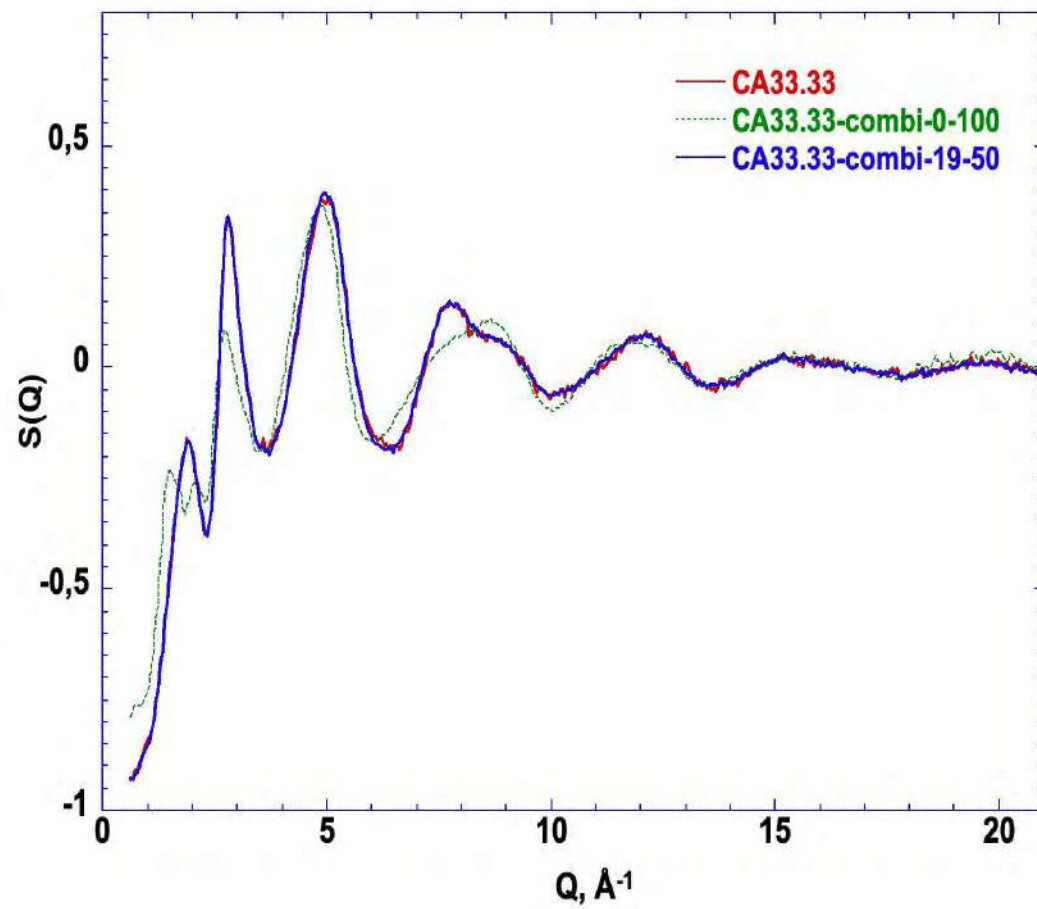
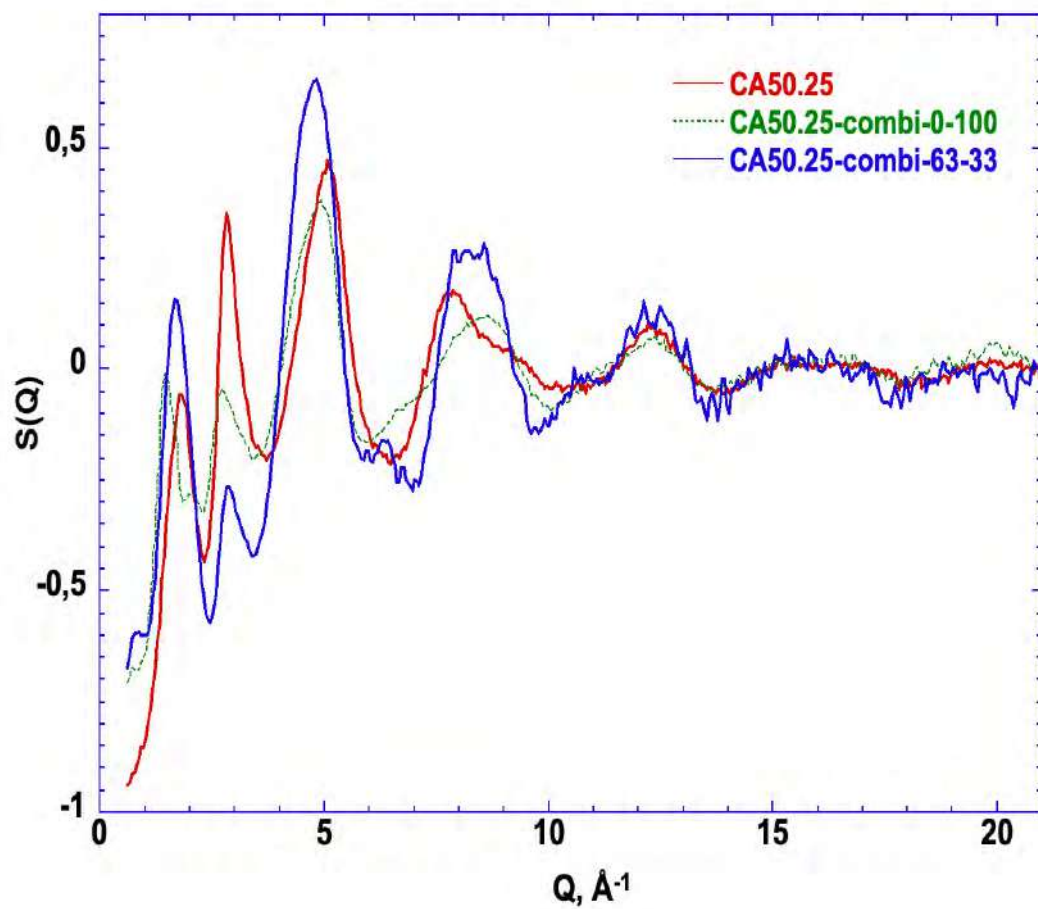
In Neuville D.R., Henderson G.S., Dingwell D. B. (2022) "Magmas, melts, liquids and glasses: Experimental insights"
" Review in Mineralogy and Geochemistry. DOI : 10.2138/rmg.2022.87.03

Total X-ray structure factors



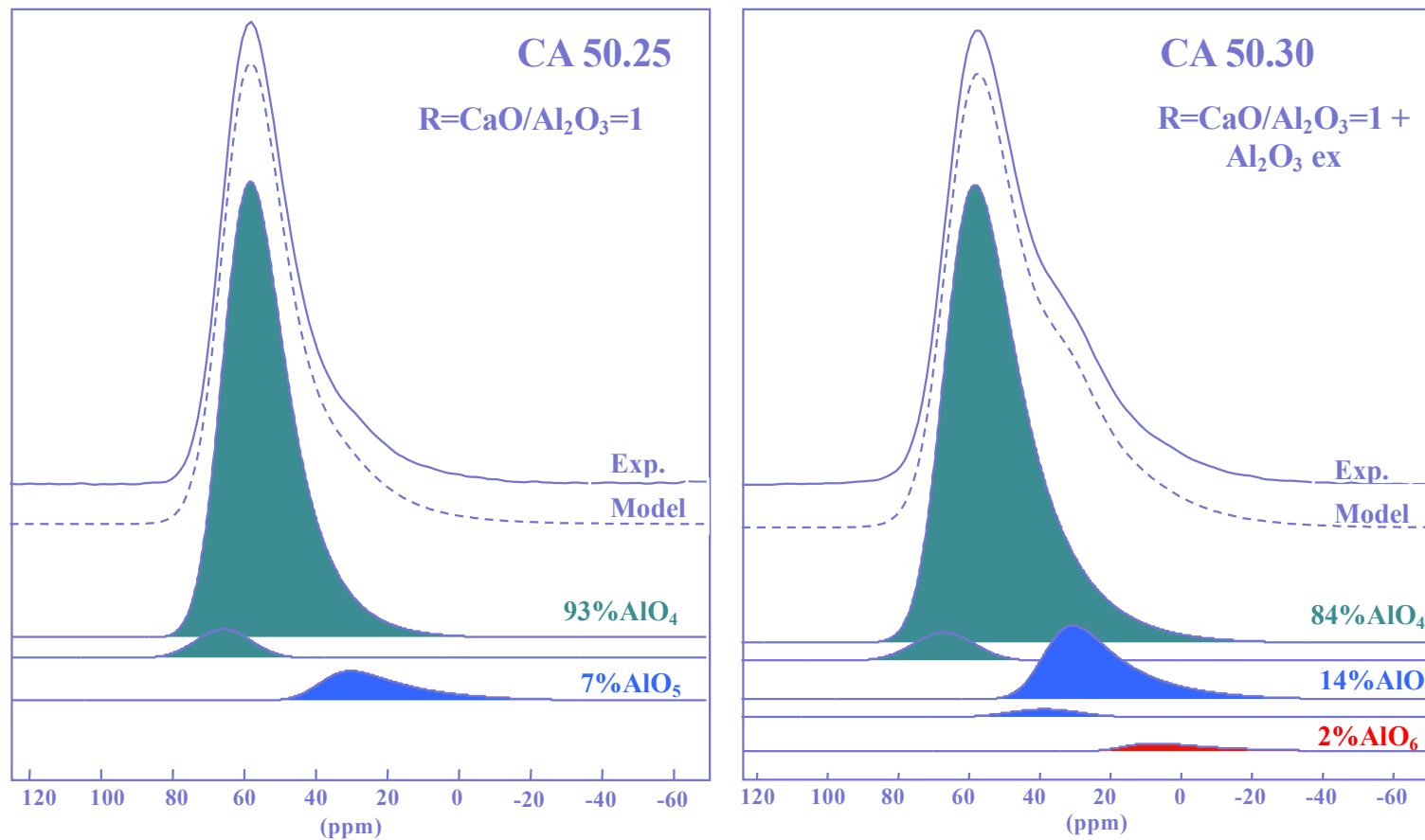
- - interpolation
— measures

Total X-ray structure factors



$\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ system

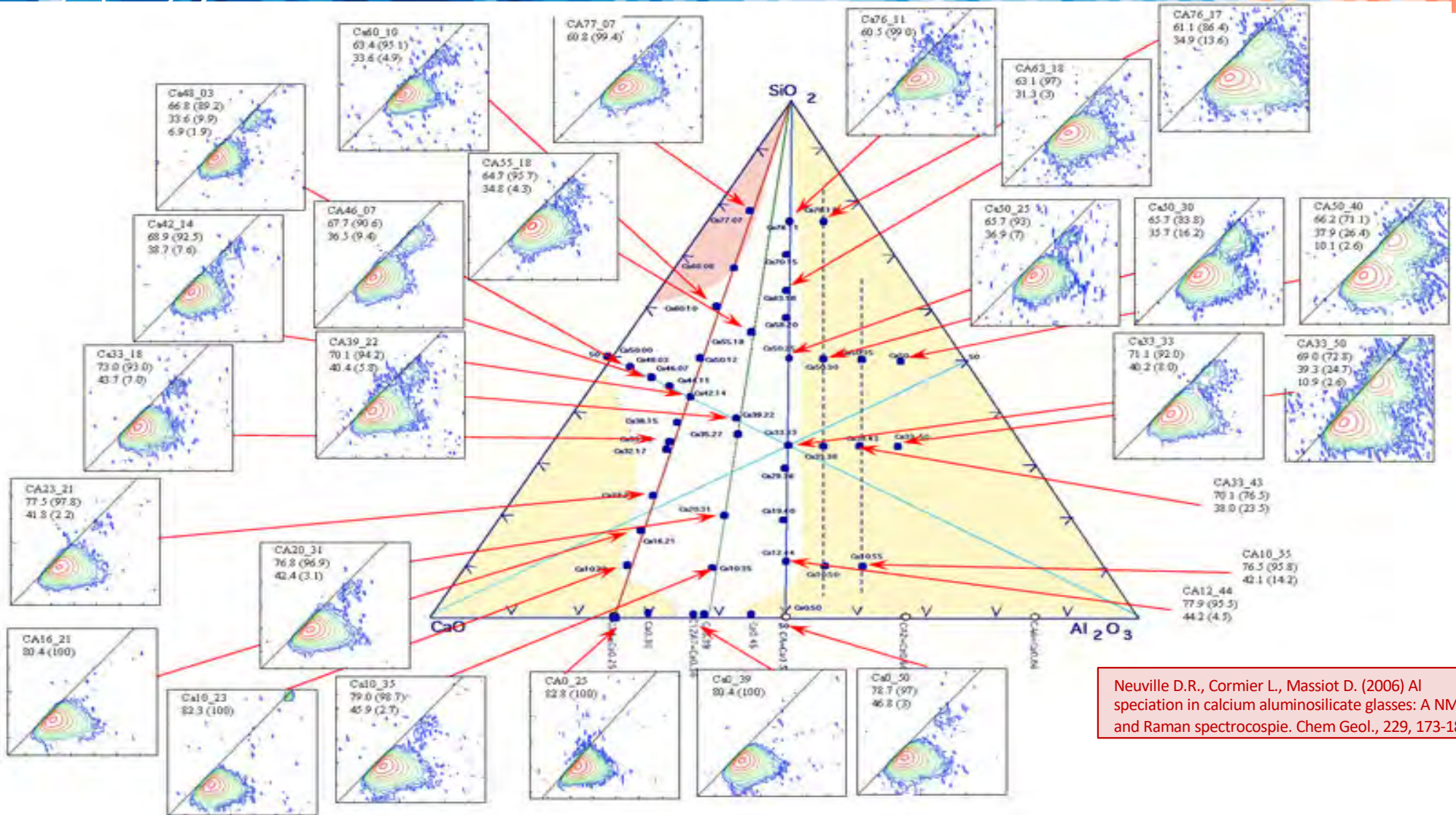
^{27}Al NMR



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

CaO-Al₂O₃-SiO₂ system



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

CaO-Al₂O₃-SiO₂ system

CA 16_21
80.4 (100)

CA 10_23
82.3 (100)

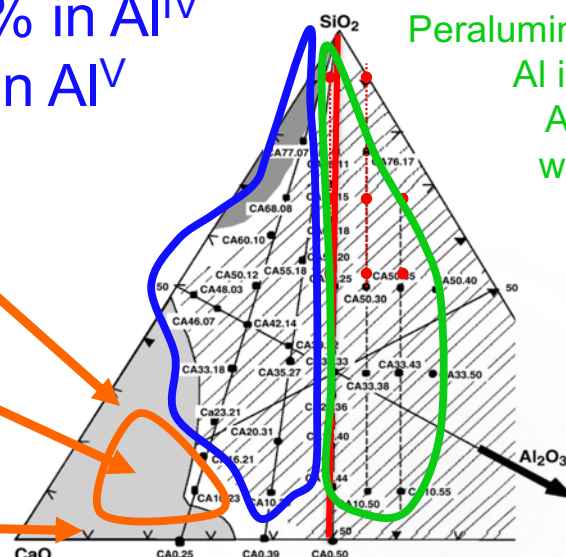
CA 0_25
82.8 (100)

CA 16_21
80.4 (100)

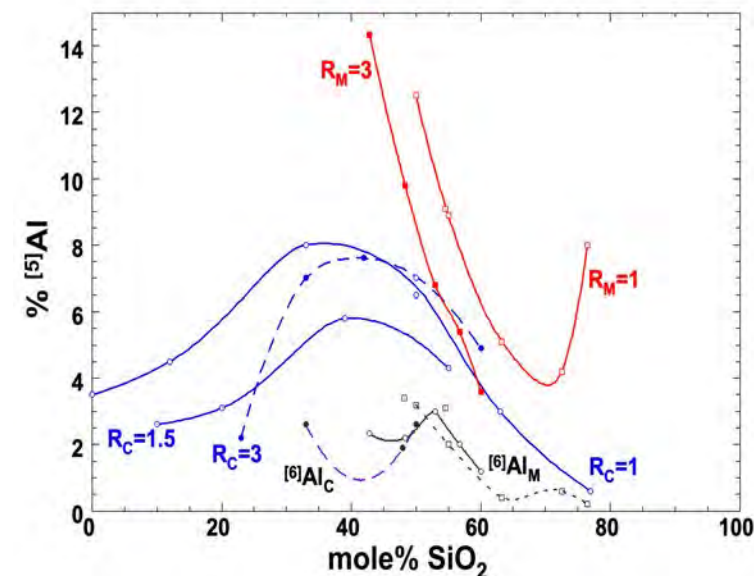
CA 0_25
82.8 (100)

$1 < R < +3$ $R = \text{CaO}/\text{Al}_2\text{O}_3 = 1$
Al $\Rightarrow$ 93% in Al^{IV}
~7% in Al^V

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

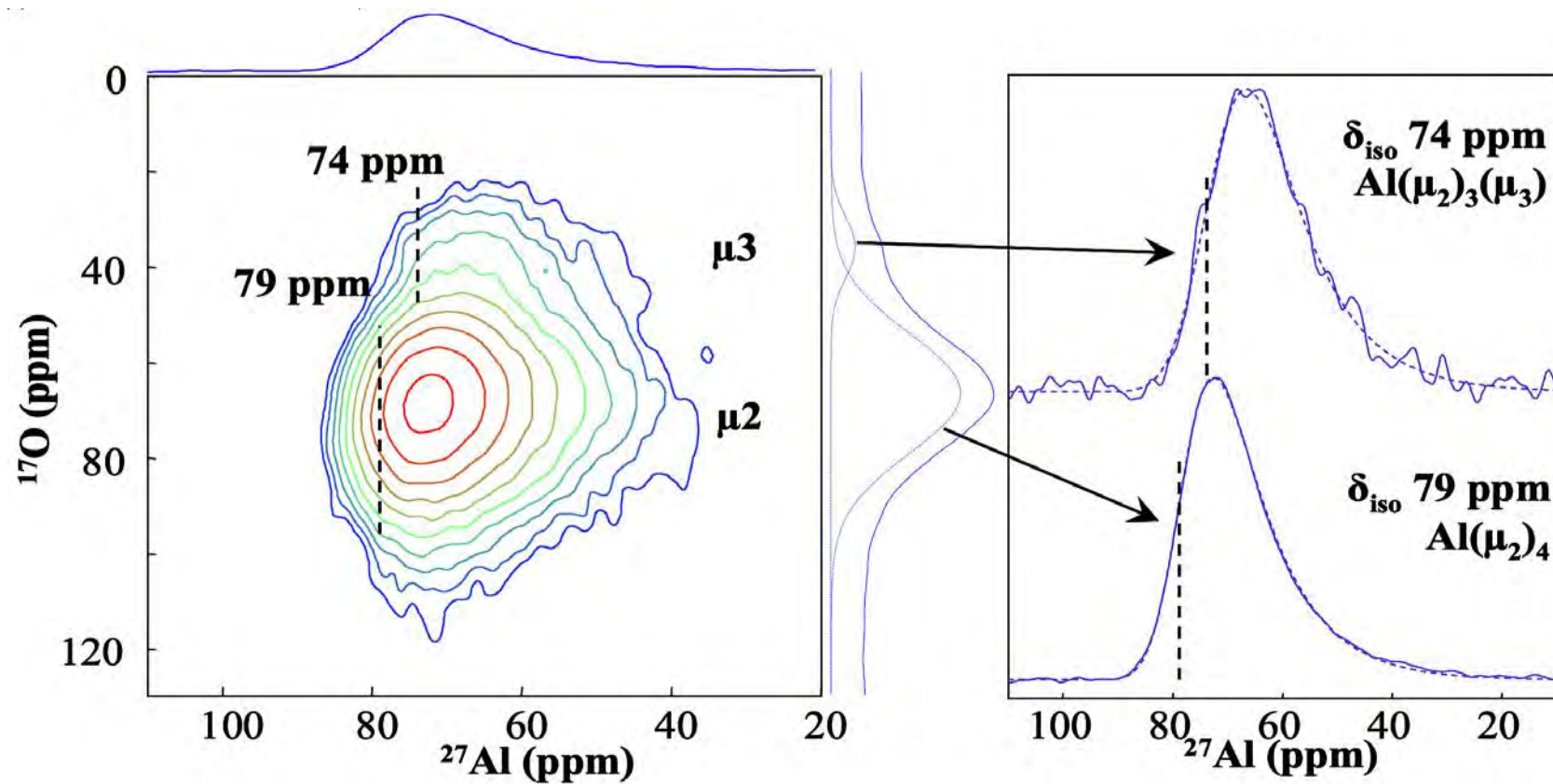


$\Rightarrow$ Al 100% in Al^{IV}
Al in Q² and Q³ species



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

CaO-Al₂O₃-SiO₂ system and tricluster oxygen

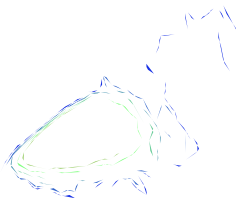
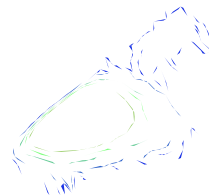
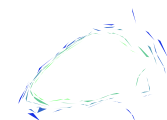


Iuga D., Morais C., Gan Z., Neuville D.R., Cormier L., Massiot D. (2005) ²⁷Al/¹⁷O NMR correlation in crystalline and vitreous materials. J. Amer. Chem. Soc., 127, 11540-11542.

CA42.14

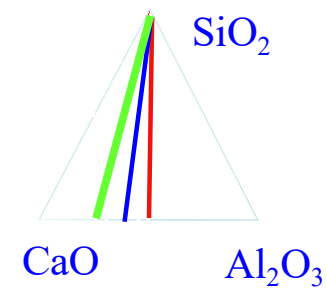
CA33.17

CA60.10

CA 42_14
68.9 (92.5)
38.7 (7.6)CA 55_18
64.7 (95.7)
34.8 (4.3)CA 60_10
63.4 (95.1)
33.6 (4.9)CA 42_14
68.9 (92.5)
38.7 (7.6)CA 55_18
64.7 (95.7)
34.8 (4.3)CA 60_10
63.4 (95.1)
33.6 (4.9)

$\Rightarrow 1 < R < 3$ 92%Al^{IV} and 8%Al^V in glasses
with classic (15° /s) and rapid quench (300° /s)

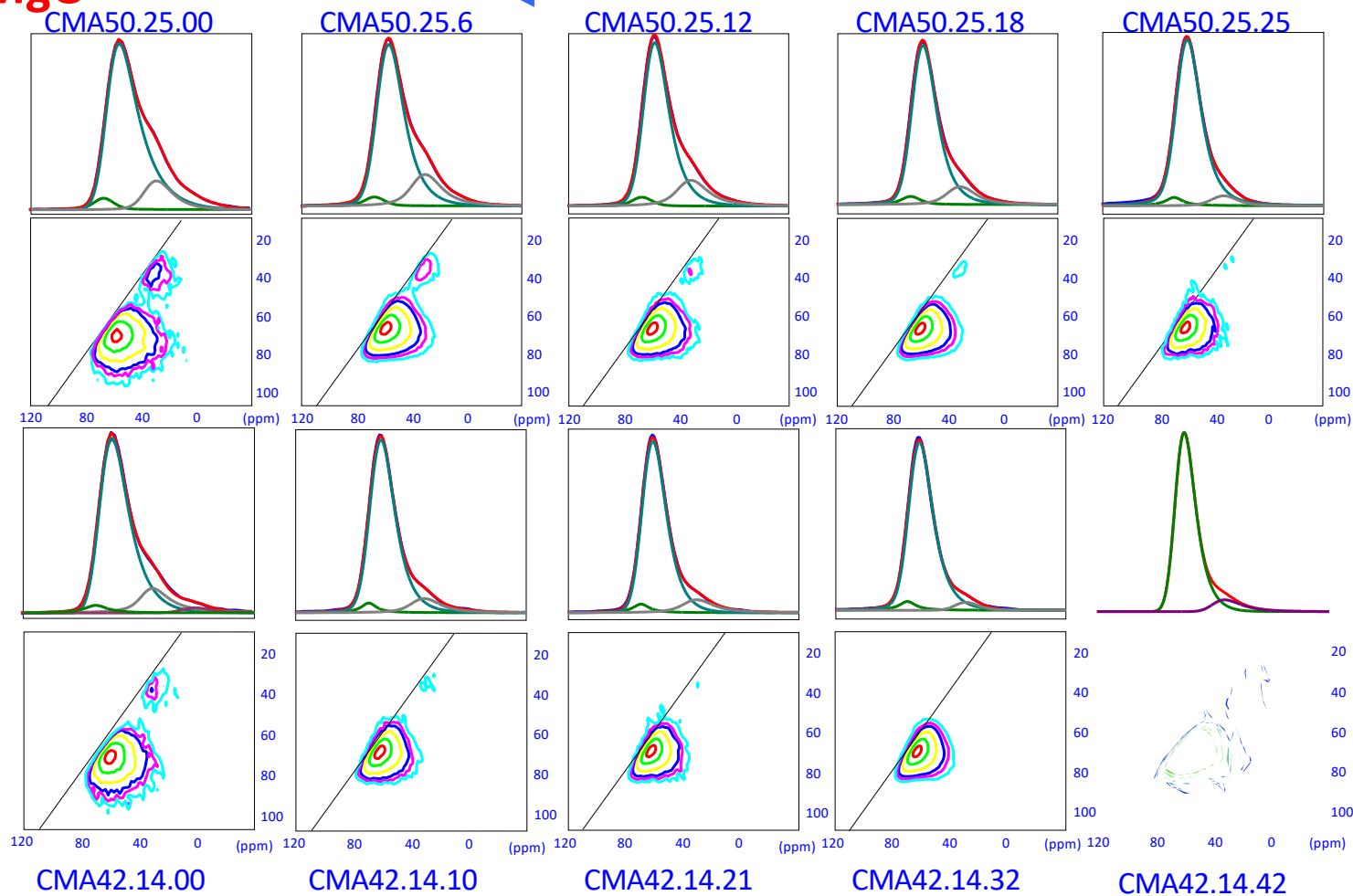
Neuville D.R., Cormier L., Montouillout V., Massiot D. (2007) Local environment of Al in aluminosilicate glasses: a NMR point of view. J. Non Crystal Solid, 353, 180-185



MgO-CaO-Al₂O₃-SiO₂ system

MgO

CaO

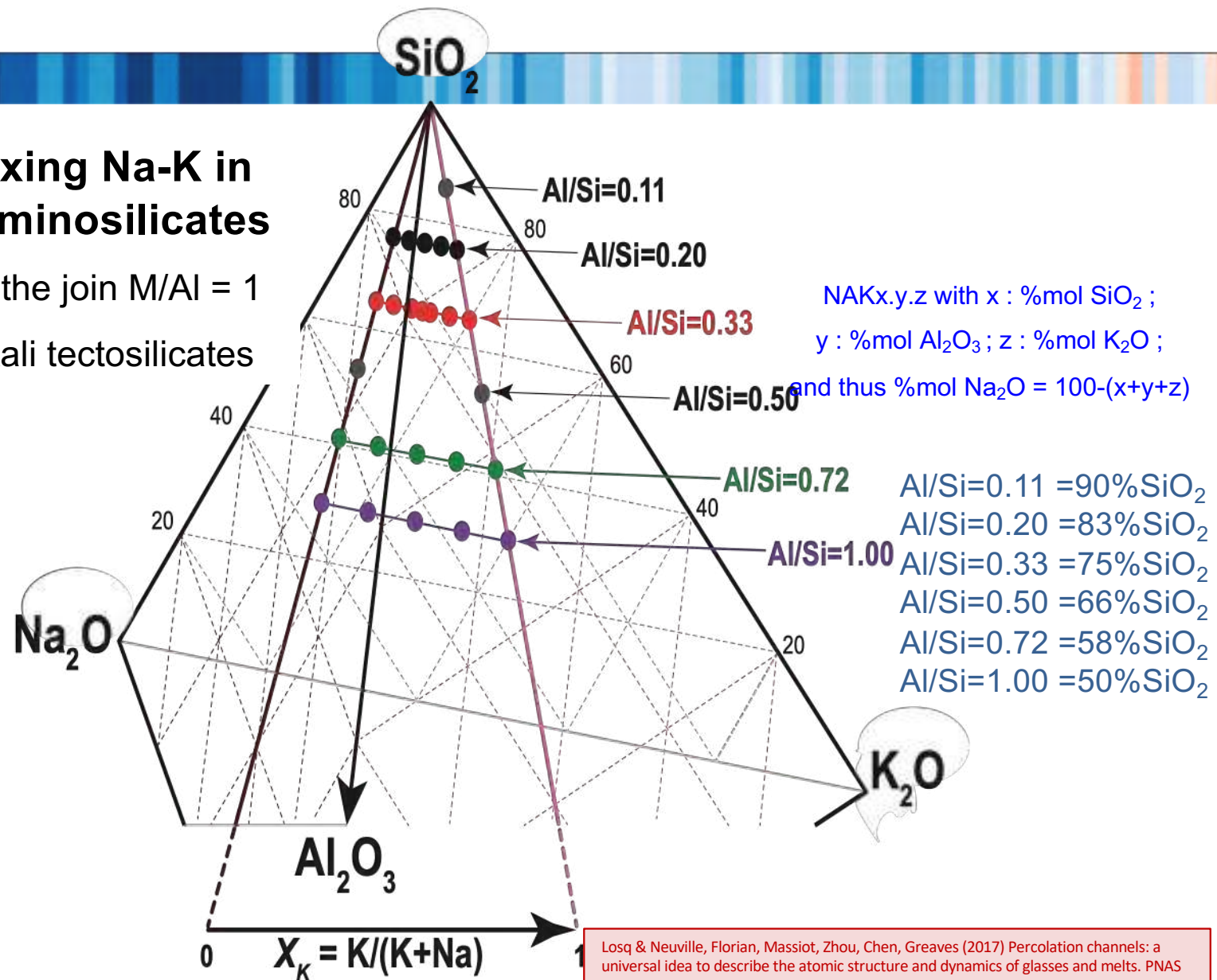


Neuvill D.R., Cormier L., Montouillout V., Florian P., Millot F., Rifflet J.C. and Massiot D. (2008) Structure of Mg- and Mg/Ca aluminosilicate glasses: 27Al NMR and Raman spectroscopy investigations. American Mineralogist 83, 1721-1731.

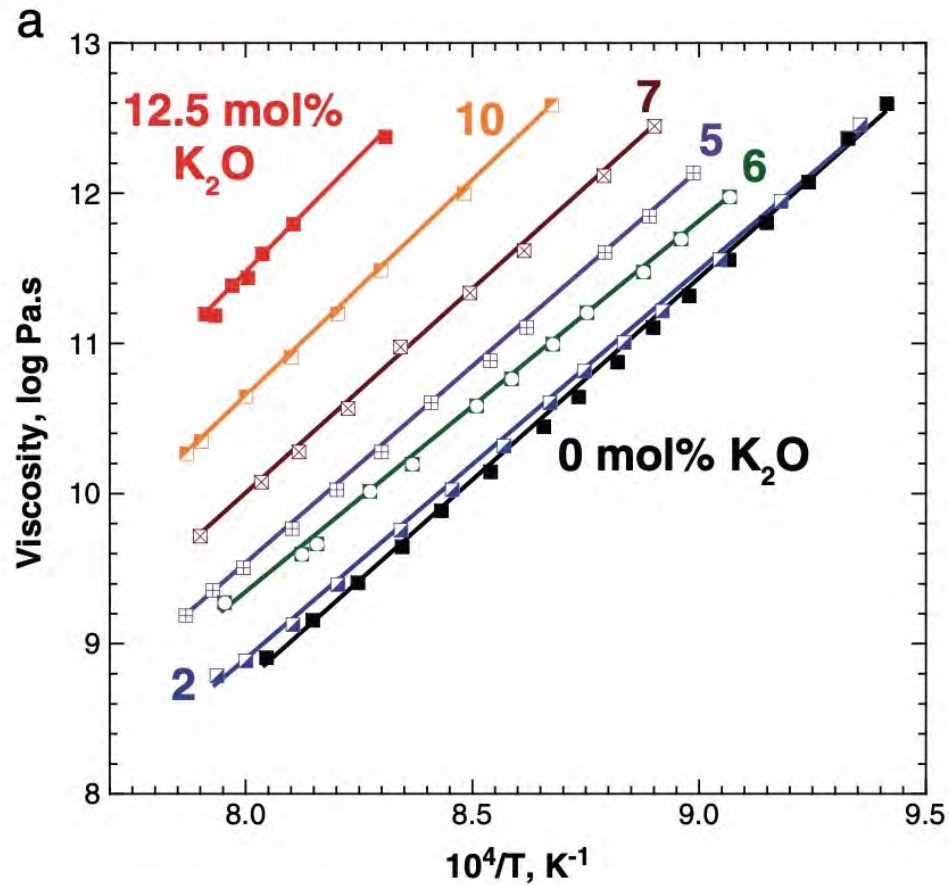
Mixing Na-K in aluminosilicates

On the join $M/Al = 1$

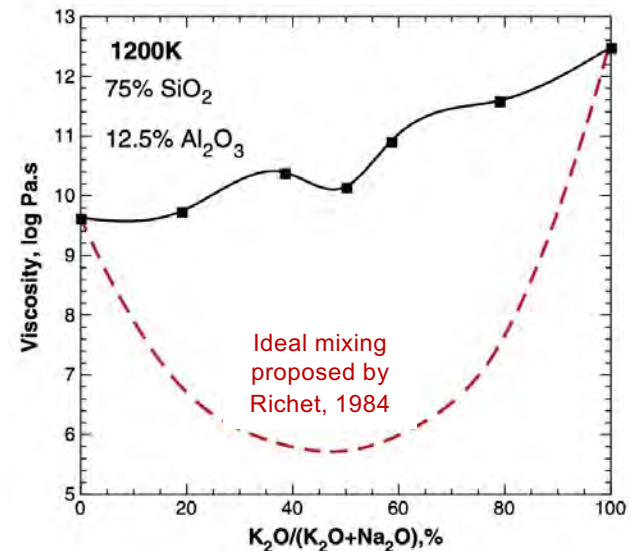
Alkali tectosilicates



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

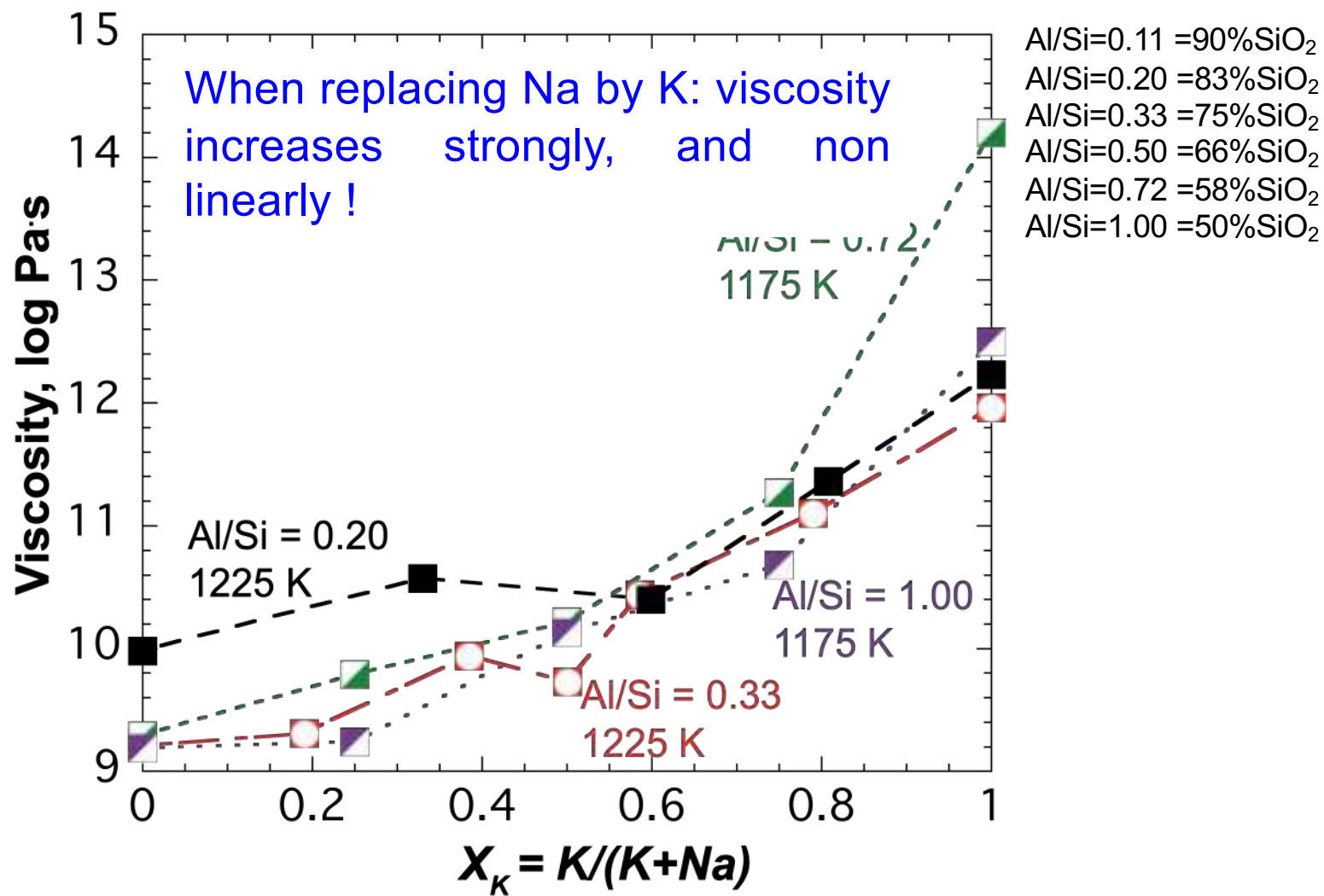


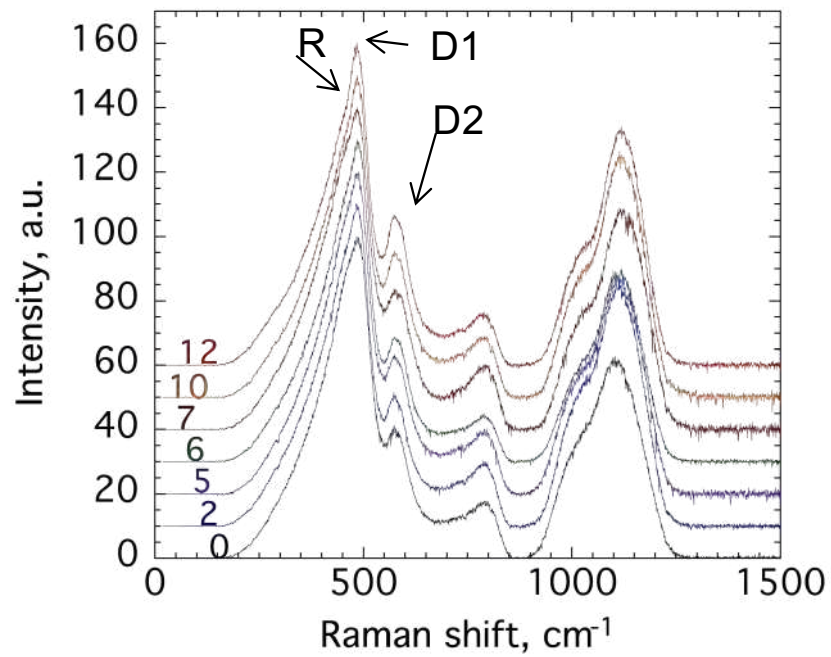
When replacing Na by K:
viscosity increases strongly...



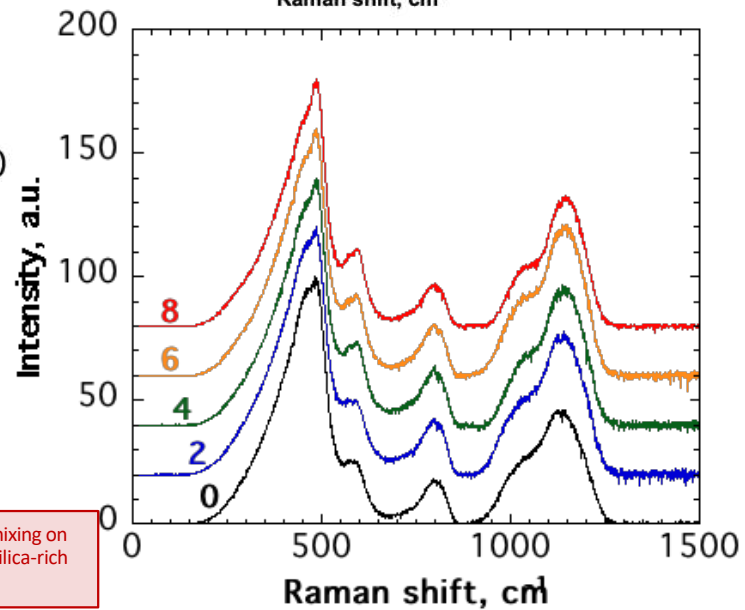
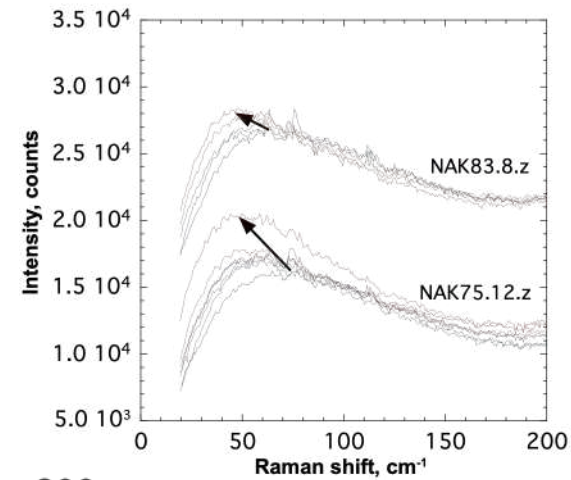
Na and K do not mix
randomly
⇒ Viscosity,
thermodynamics
⇒ Structure

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.

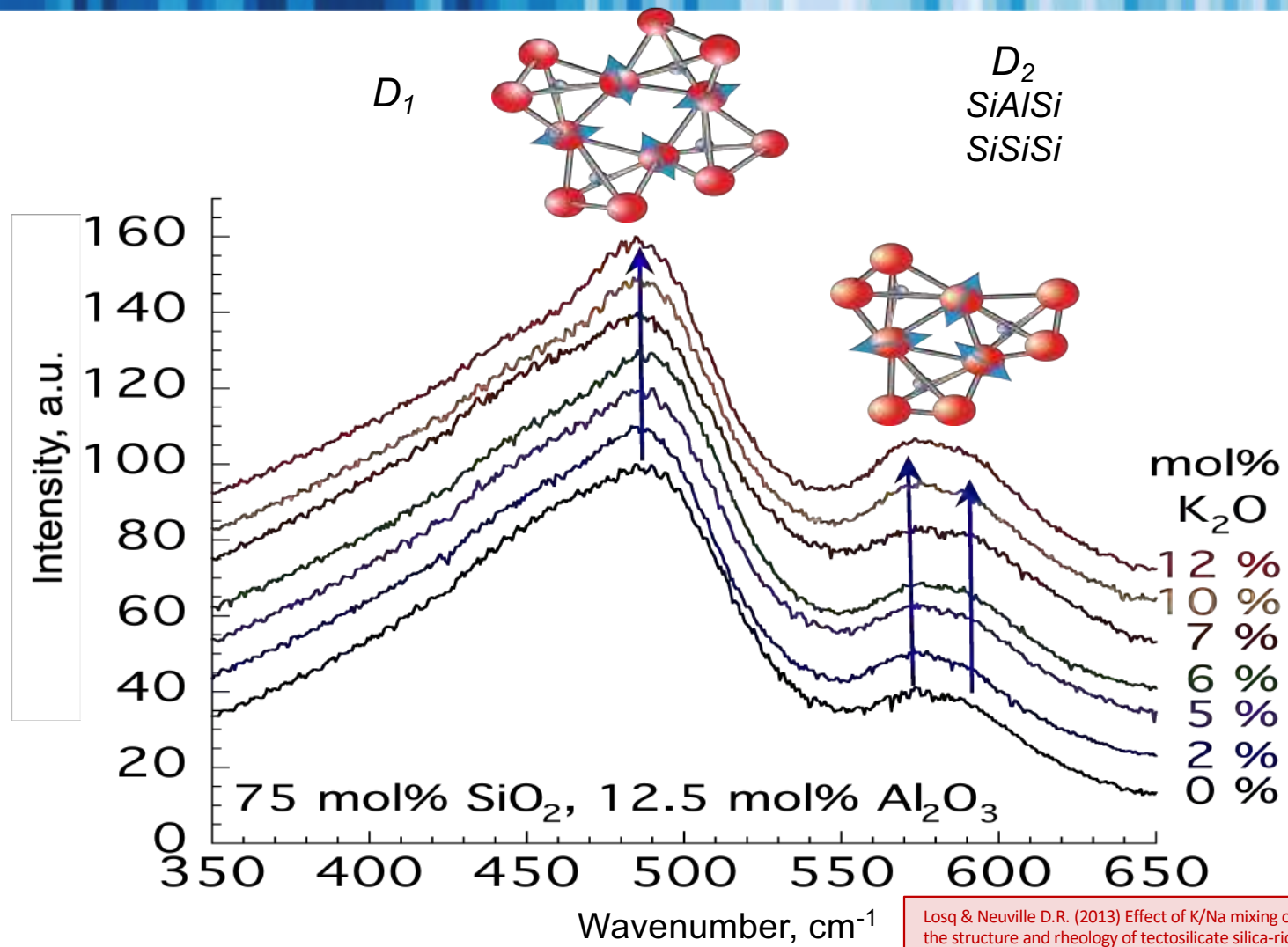




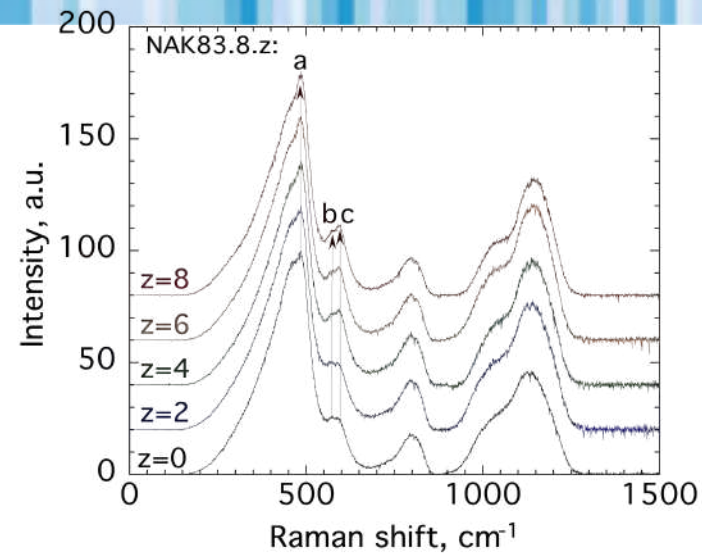
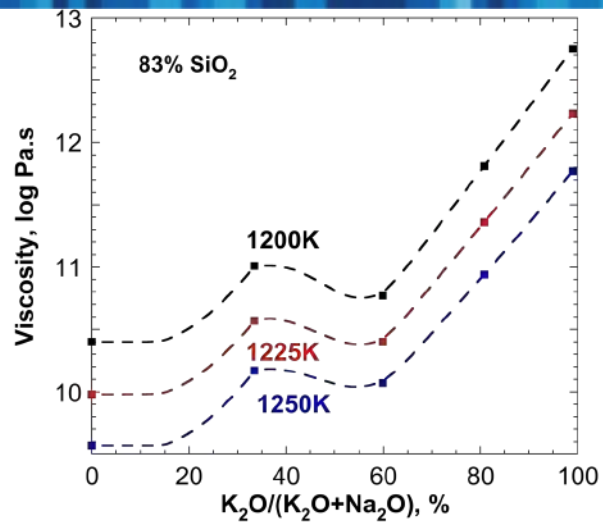
- Boson peak increase in I and decreases in frequency with K like close than SiO₂
- D1 and D2 increase with K
- New D2 band



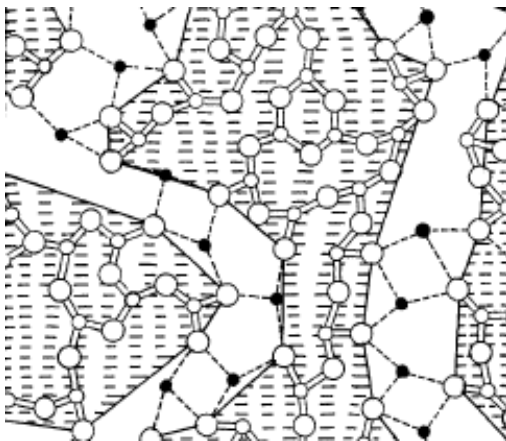
Losq & Neuville D.R. (2013) Effect of K/Na mixing on the structure and rheology of tectosilicate silica-rich melts. *Chemical Geology*, 346, 57-71.



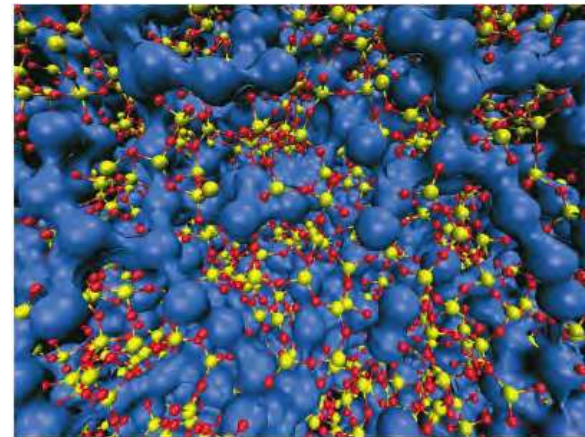
Losq & Neuville D.R. (2013) Effect of K/Na mixing on the structure and rheology of tectosilicate silica-rich melts. Chemical Geology, 346, 57-71.



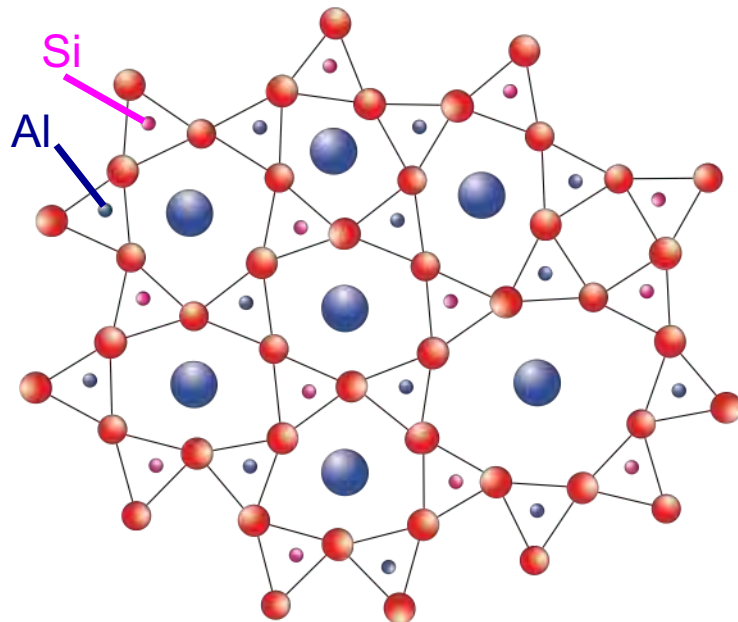
Greaves, 1985: MRN



Meyer et al., 2004

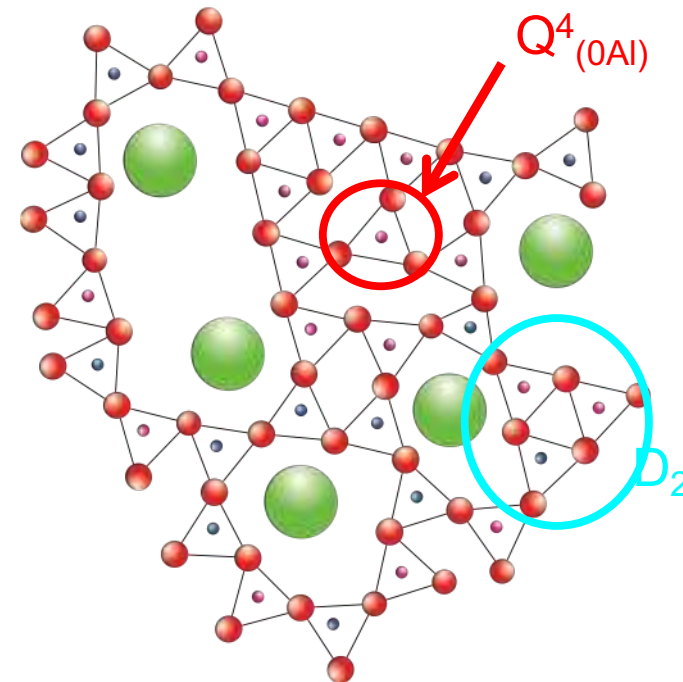


Na tectosilicates



Compensated Continuous
Random Network
From Greaves and Ngai, 1995

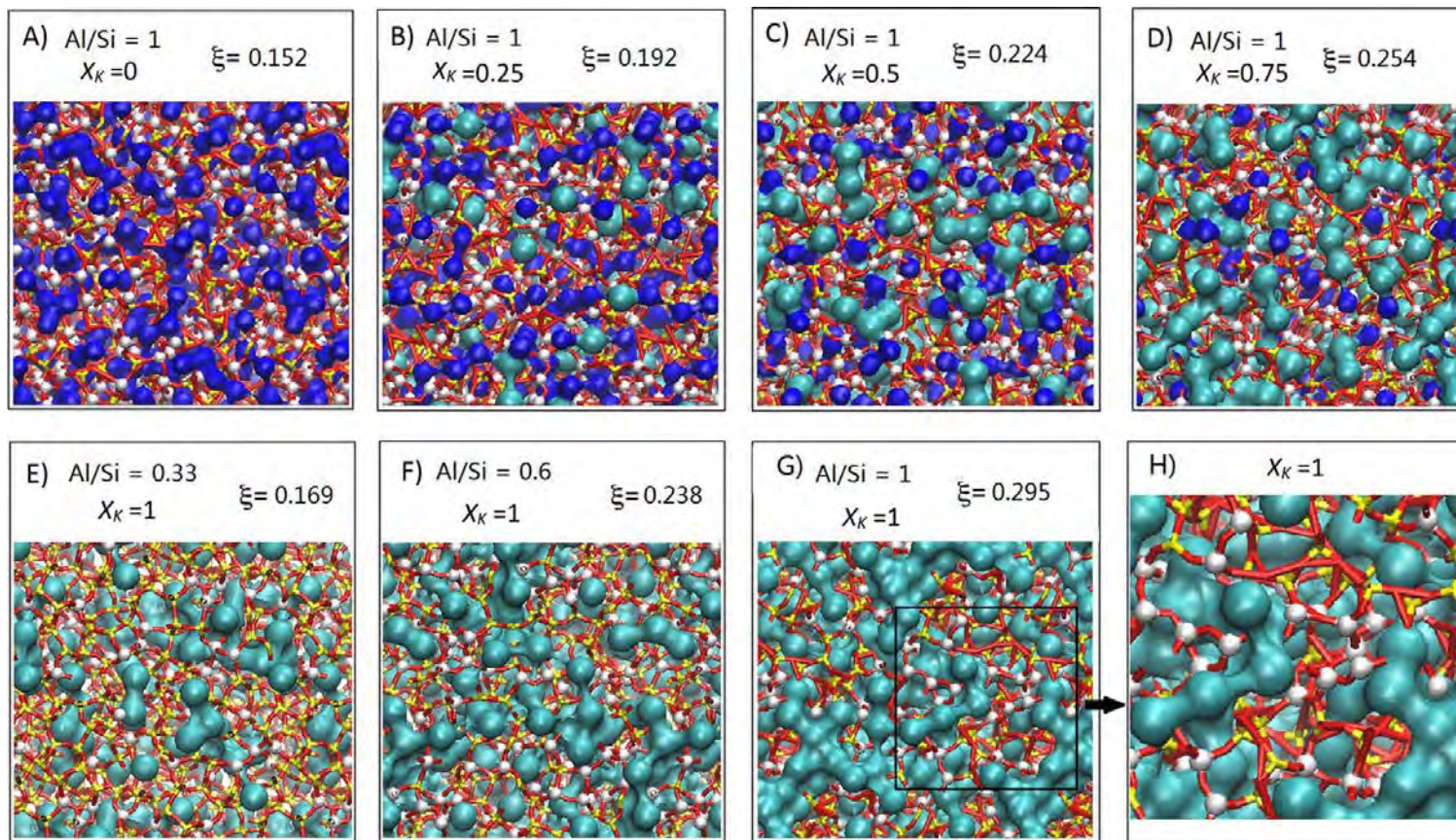
K tectosilicates



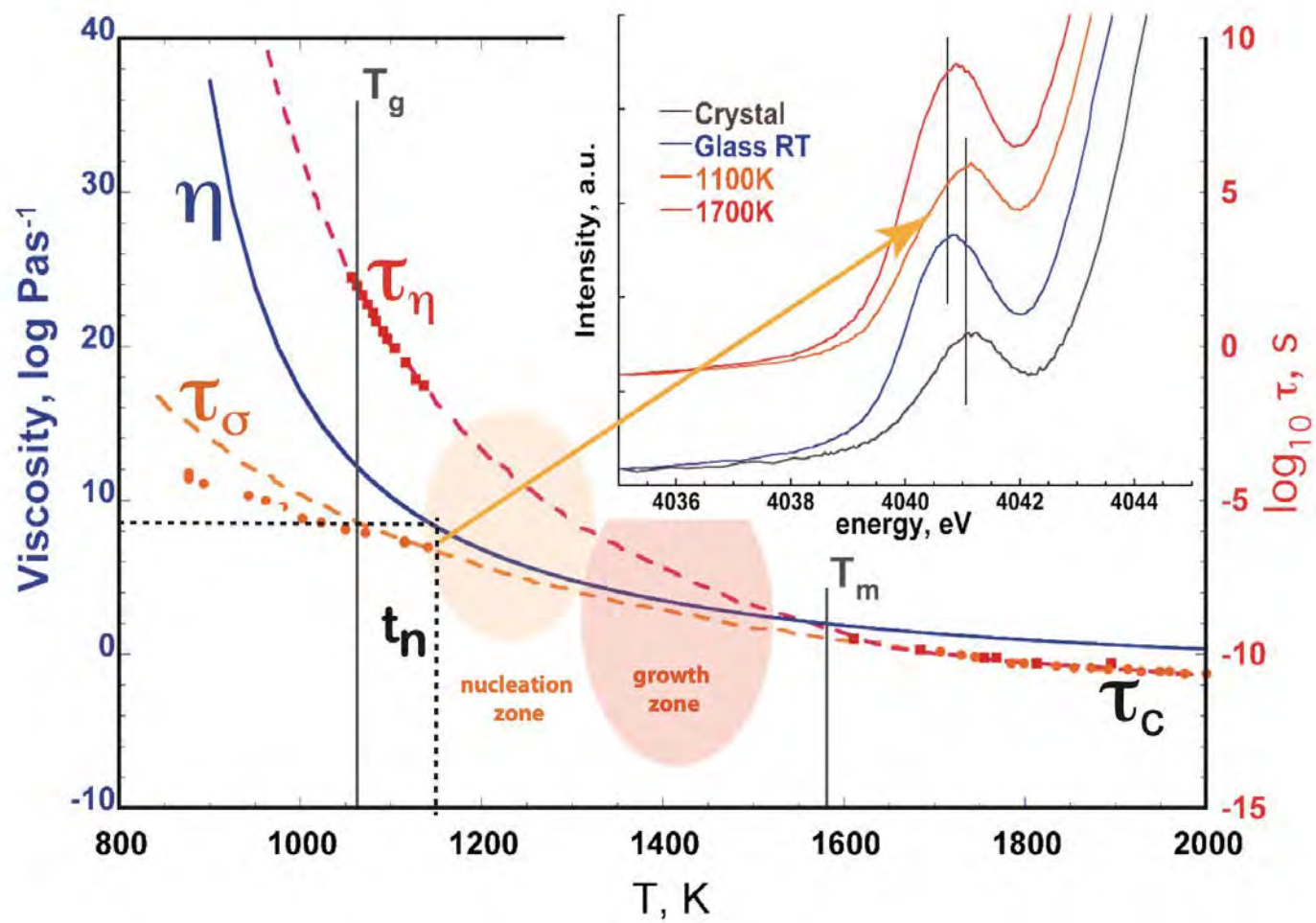
We propose a new version:
Compensated Modified
Random Network

Na and K are in different structural positions
⇒ Two different networks
⇒ 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



SiO_2 , GeO_2 => strong network former

B_2O_3 (BO_3 , BO_4), 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} => generally 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⁺/Ca²⁺ and Na⁺/Sr²⁺ or Na⁺/M²⁺ 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.*
- *[⁵Al is probably a good network former or reticulator*

