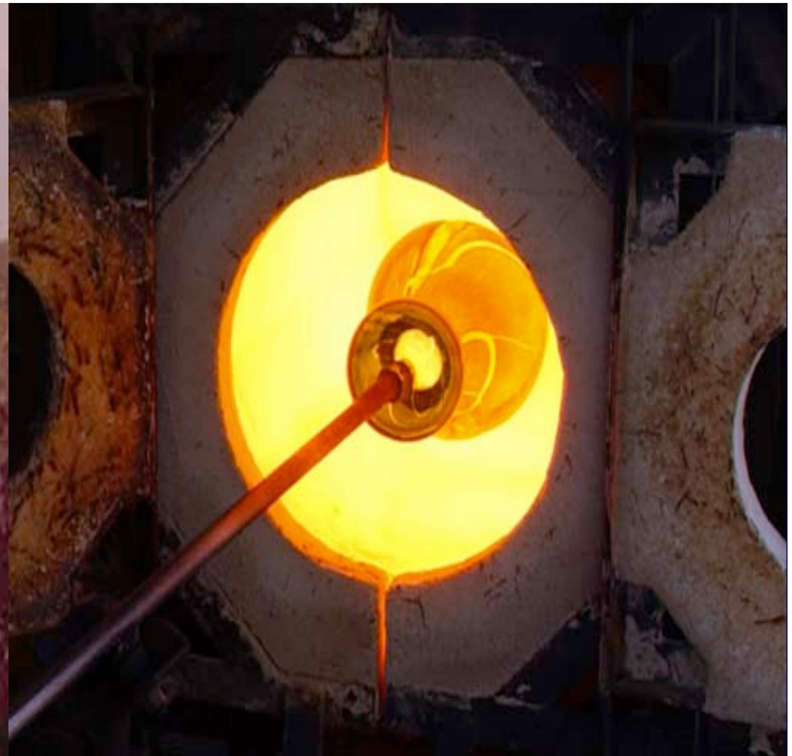
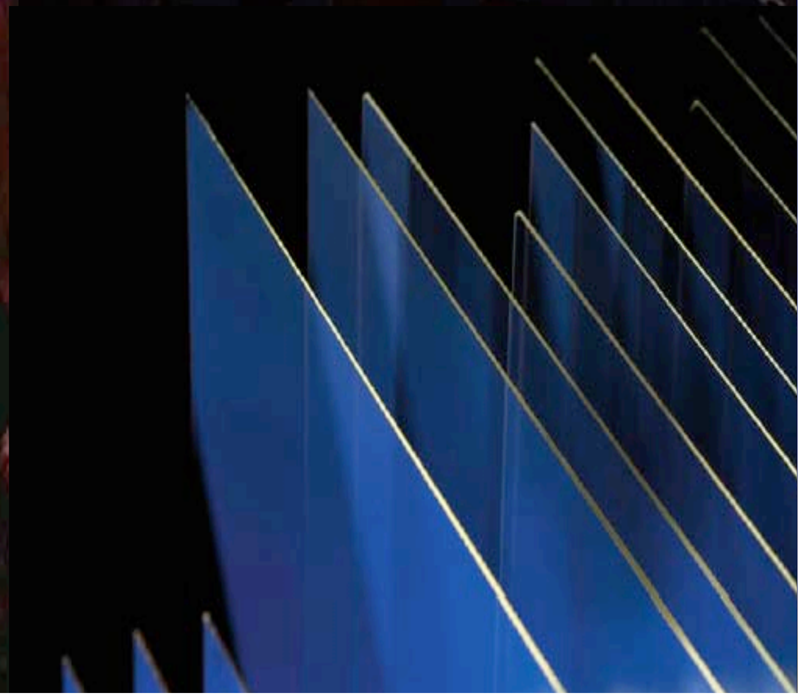
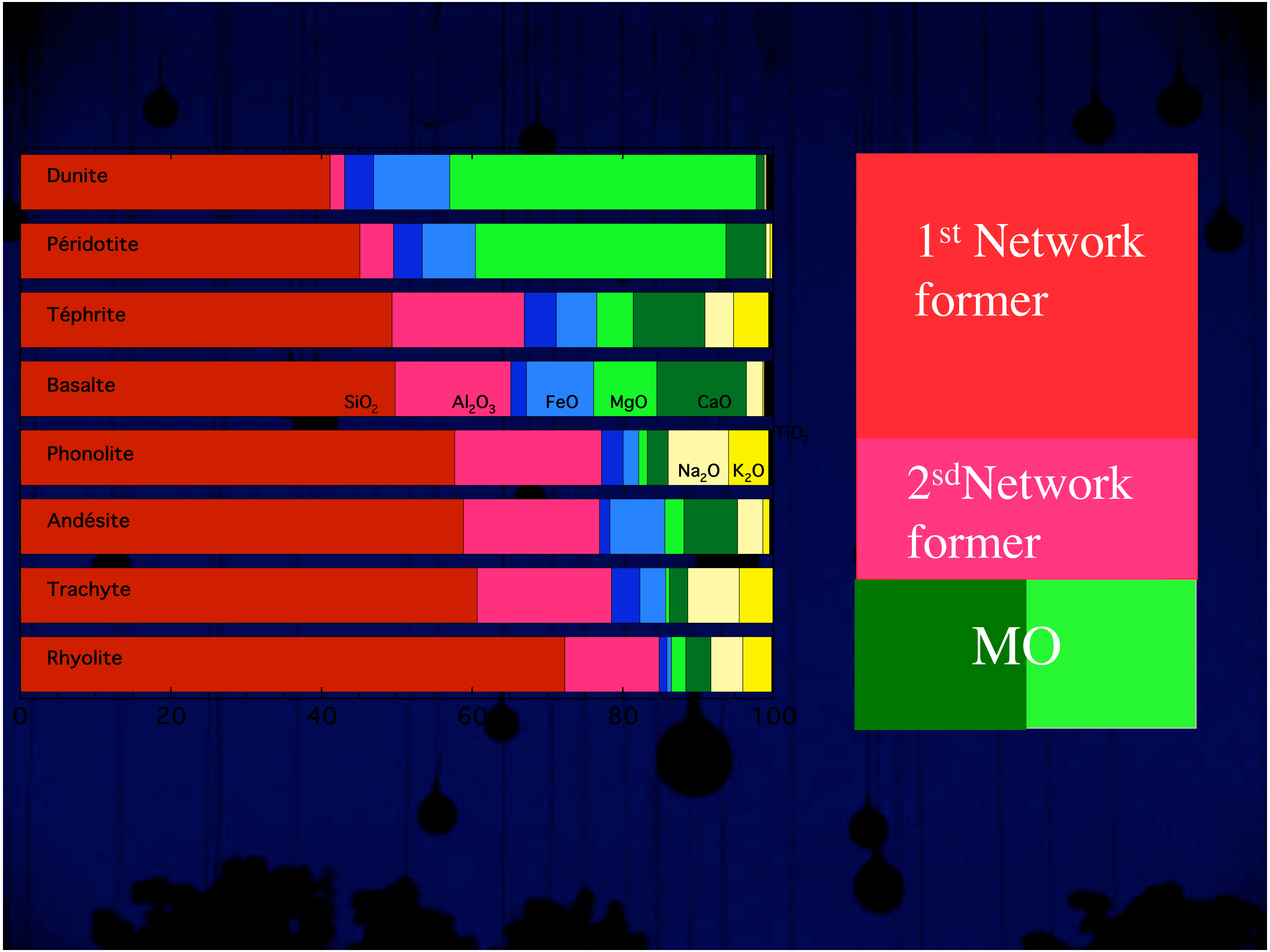
Structure and properties of glasses and melts in the $MgO-Al_2O_3-SiO_2$, $CaO-Al_2O_3-SiO_2$, $MgO-CaO-Al_2O_3-SiO_2$ systems

Daniel R. Neuville

Cormier L. [2], de Ligny D.[3], Flank A-M. [4], Henderson G.S. [5], Lagarde P.[4], Massiot D.[6], Millot F.[6], Montouillout V.[6], Rifflet J.C.[6], Richet P. [1], Roux J.[1]

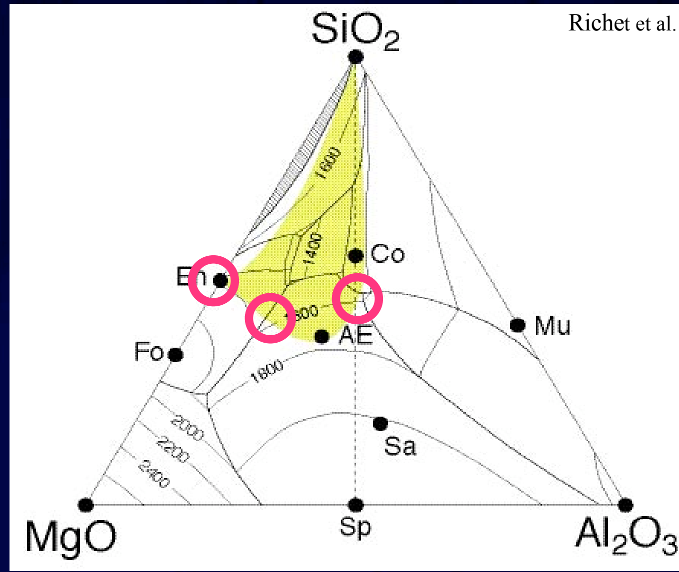
[1] Physique des Minéraux et des Magmas, IPGP-CNRS, 4 place Jussieu, 75252 Paris
[2]IMPMC, Universités PARIS 6 et 7, CNRS, 4 place Jussieu, 75252 Paris
[3]LPCML, Université Lyon 1, CNRS UMR 5620, 12 rue Ampère, 69622 Villeurbanne
[4] SOLEIL L'Orme des Merisiers, BP48, 91192 Gif s/Yvette, France.
[5]Dept of Geology, University of Toronto, 22 Russell St, Toronto, Canada
[6] CRMHT-CNRS, 1D av. Recherche Scientifique, 45071 Orléans cedex 2.



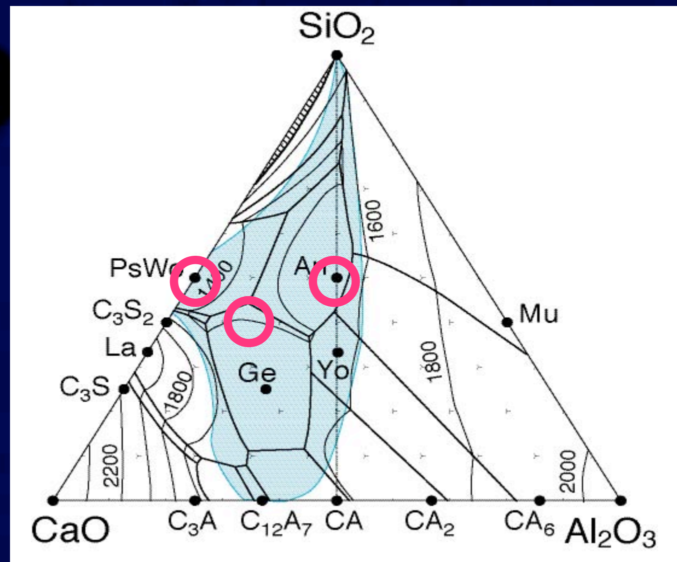
Dunite
Péridotite
Téphrite
Basalte
Phonolite
Andésite
Trachyte
Rhyolite
SiO2
Al2O3
FeO
MgO
CaO
TiO2
Na2O
K2O
0
20
40
60
80
100
1st Network former
2sdNetwork former
MO

1) MAS System

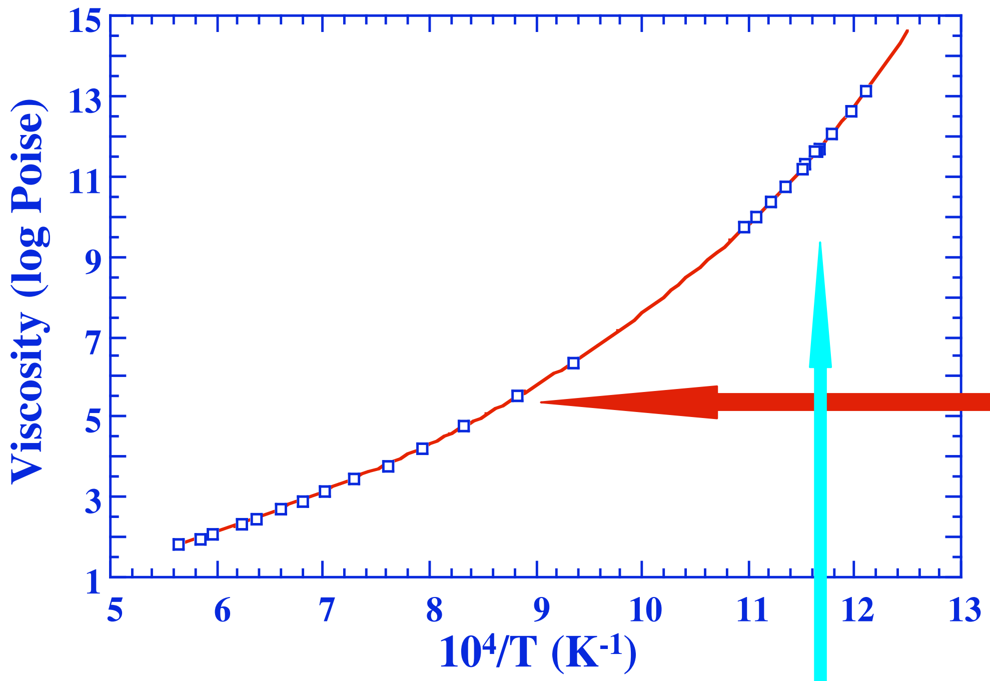


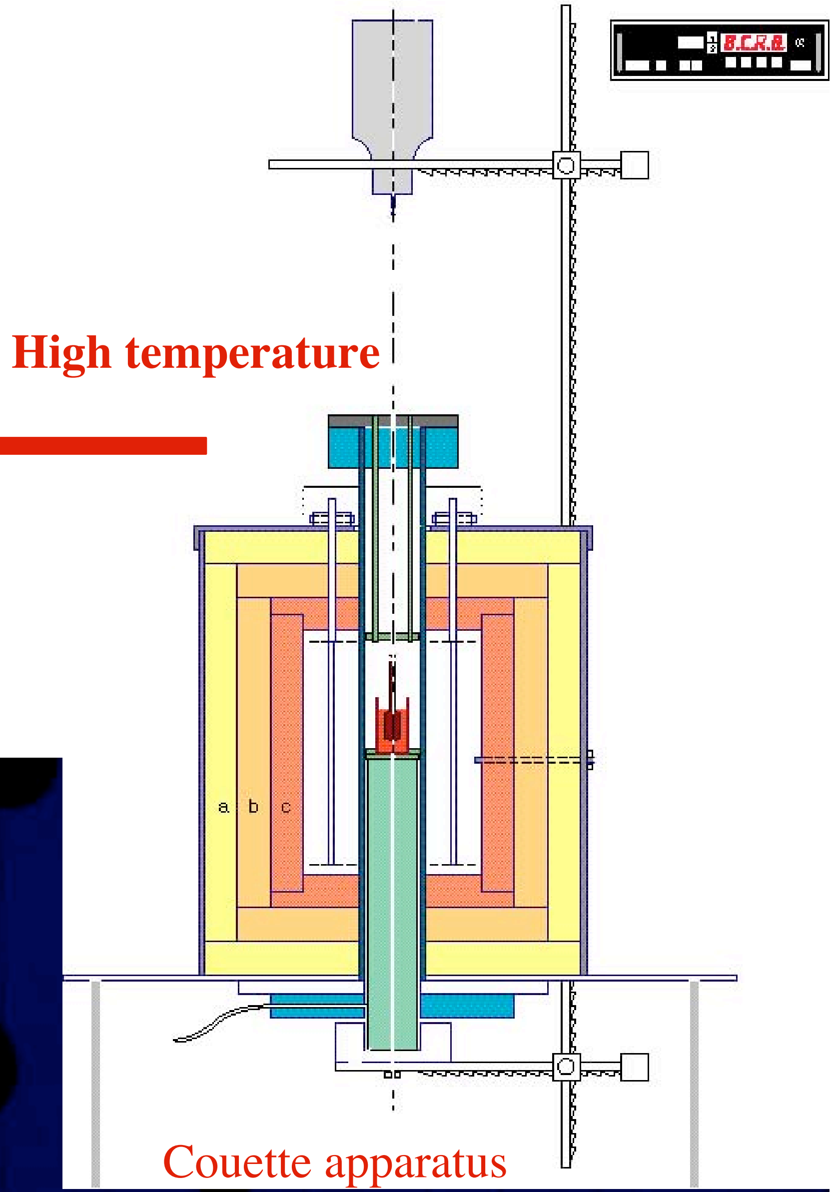
3) CMAS System

2) CAS System

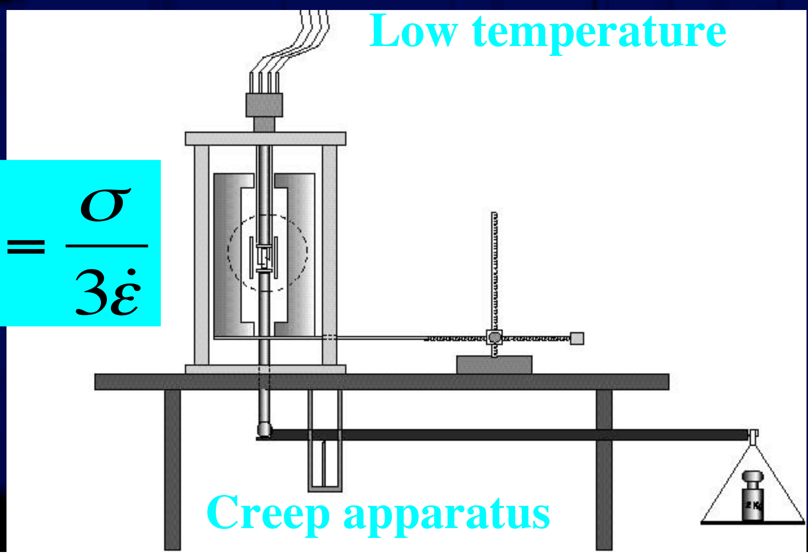


Viscosity measurements



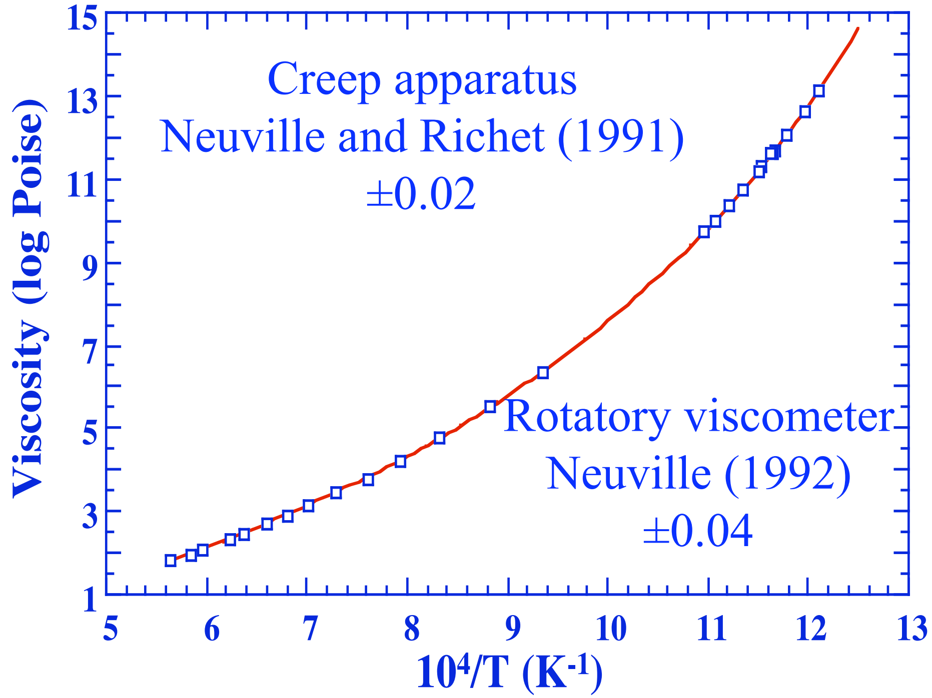


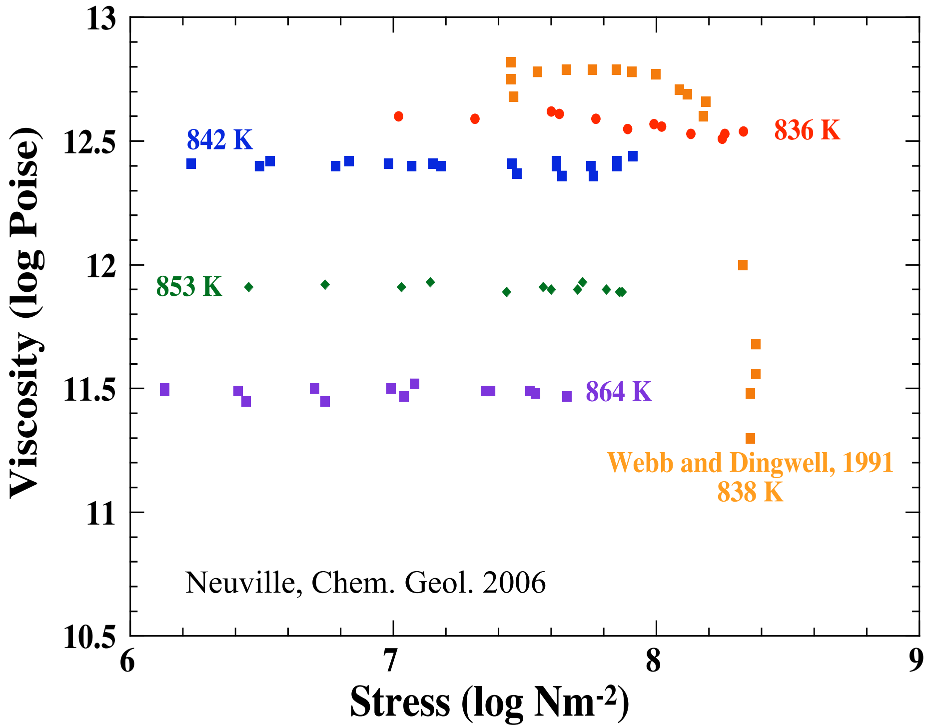
$$\eta = \frac{\sigma}{3\dot{\varepsilon}}$$



Viscosity measurements

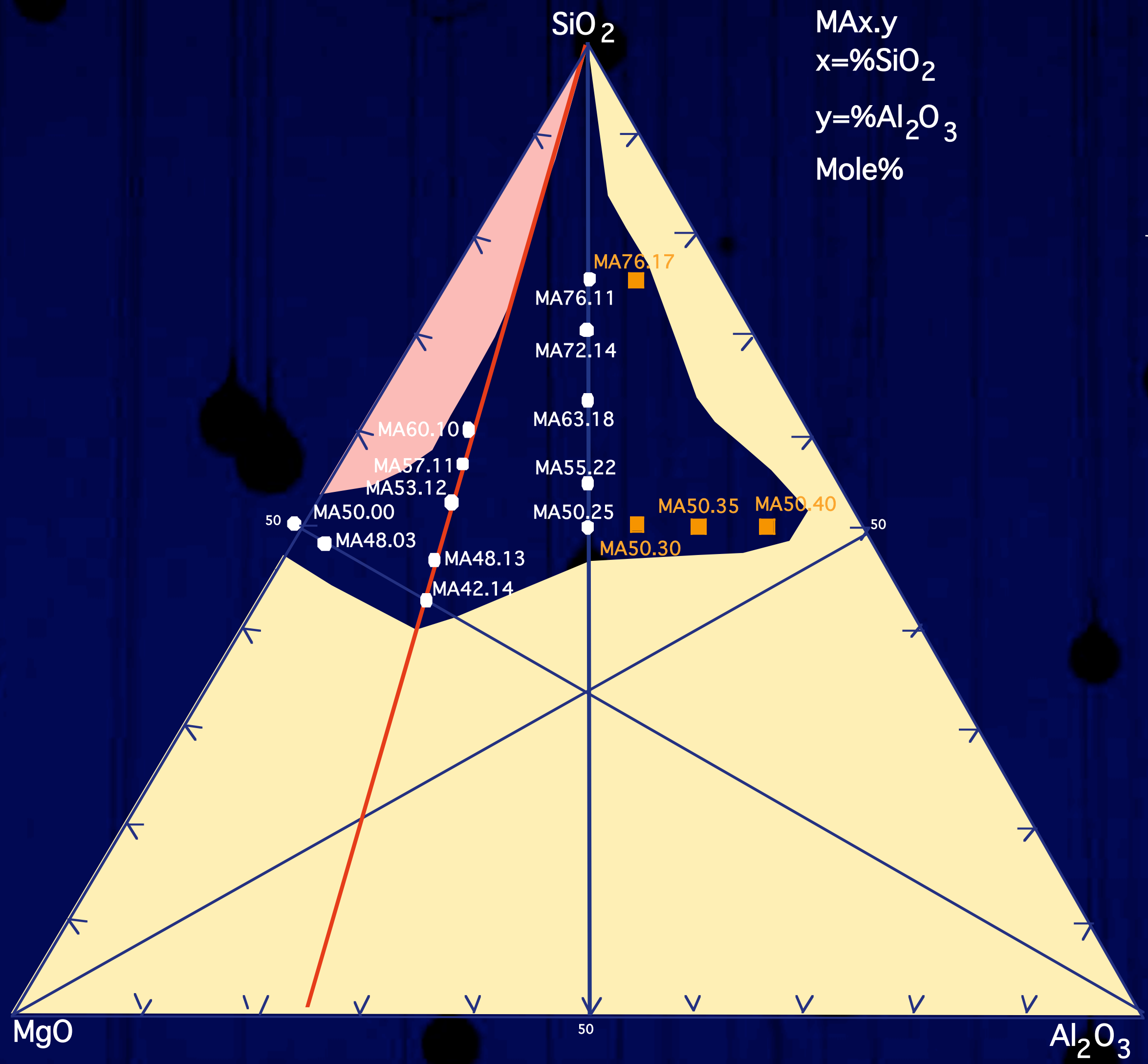
NBS710





$T_g \Rightarrow \eta = 10^{13}$ Poise

MAS

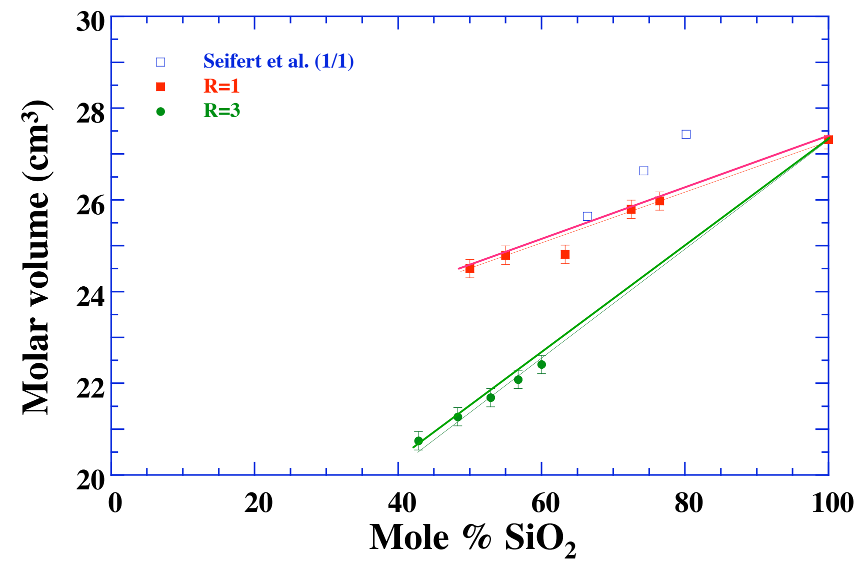


Normal quentch

Rapid quentch

MAS

$R=MgO/Al_2O_3$



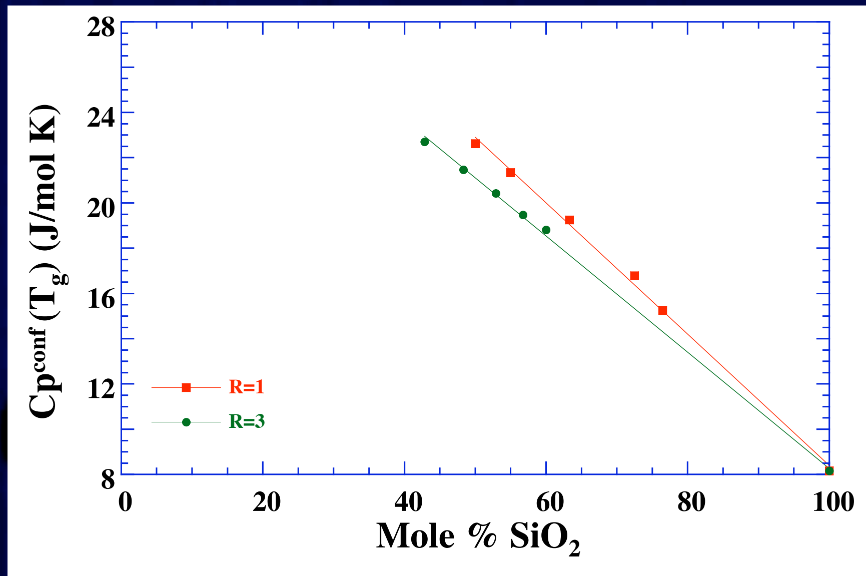
MV of glass increases linearly with SiO_2 and decreases with MgO

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

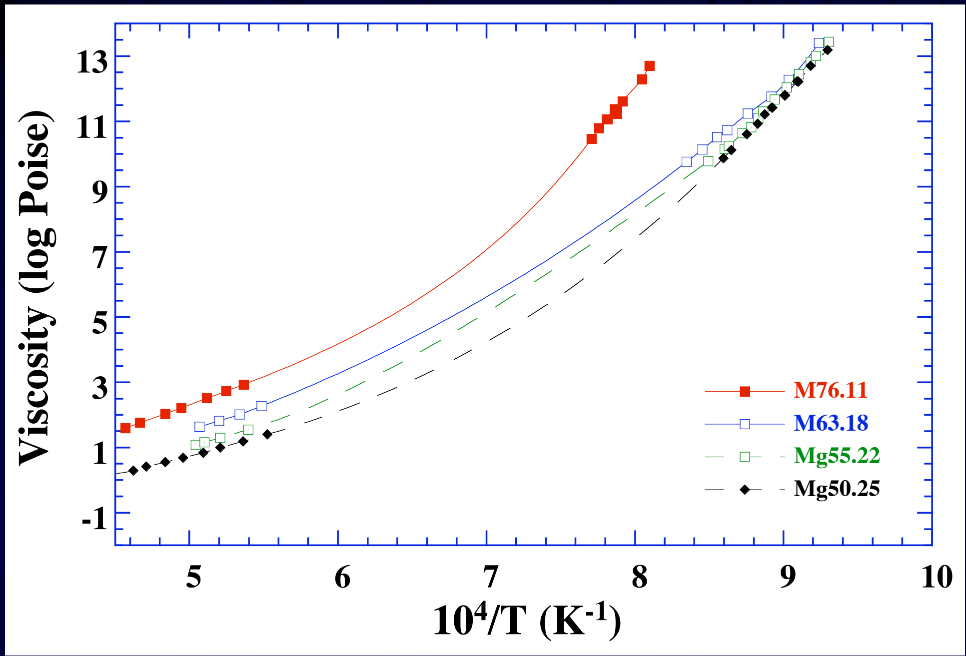
Tg => log η = 13 log Po

Configurational heat capacity increases with decreasing SiO_2 and increasing Al_2O_3 content.

After Richet (1987)
and Richet and Bottinga (1984)

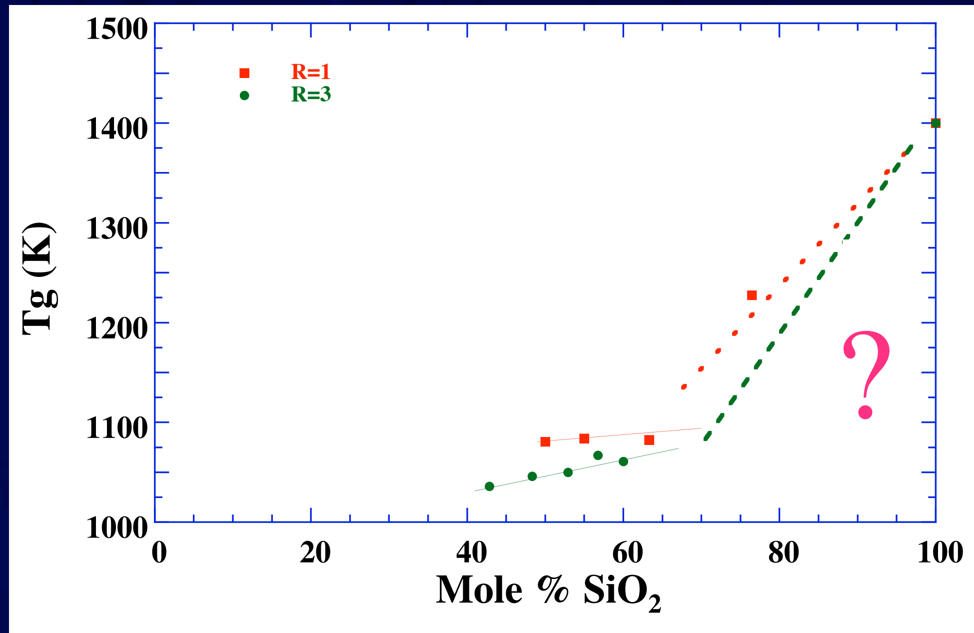


Viscosity MAS

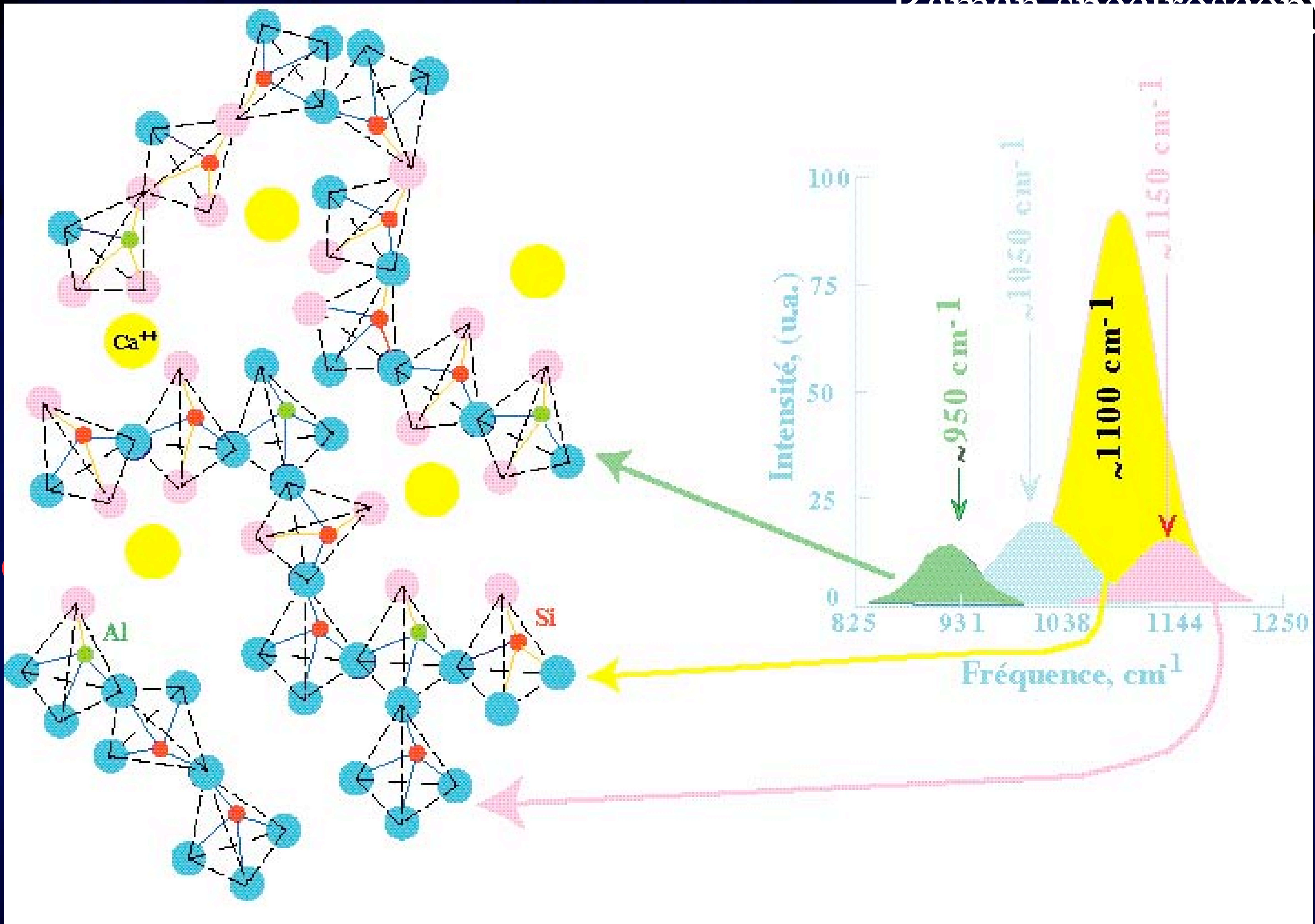


Viscosity increases strongly with SiO_2

Tg increases strongly with SiO_2 and very small variation between 50 and 70 mole % of SiO_2

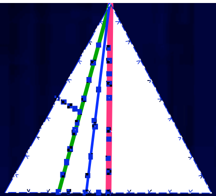


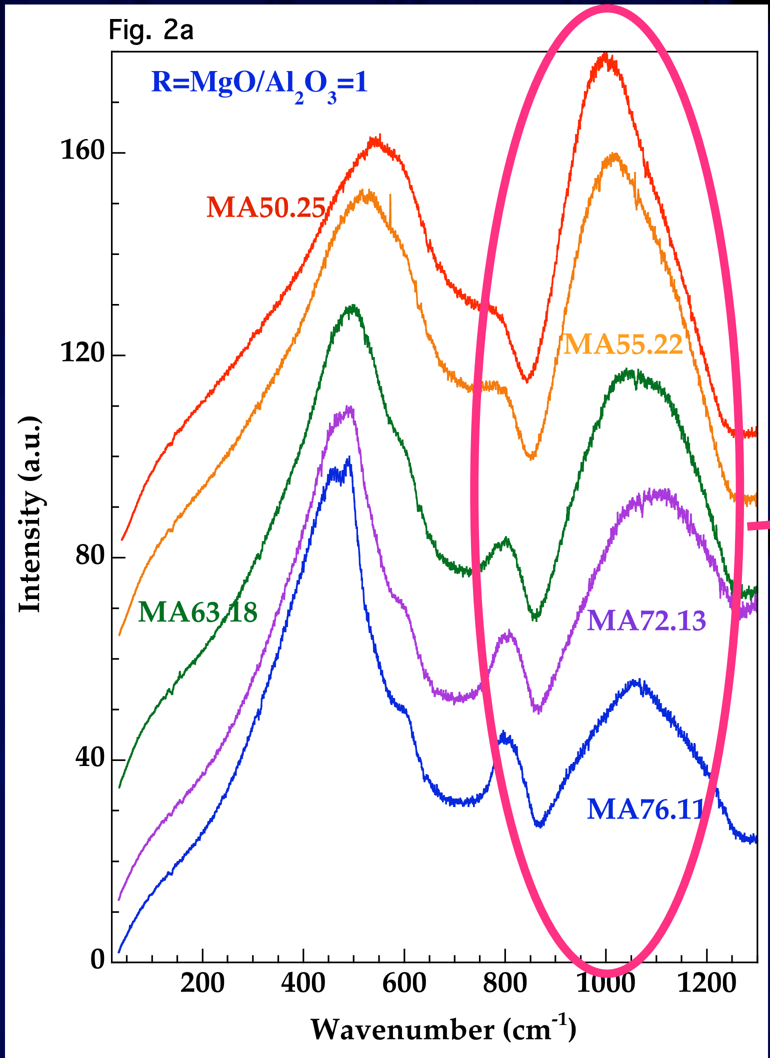
Raman spectroscopy

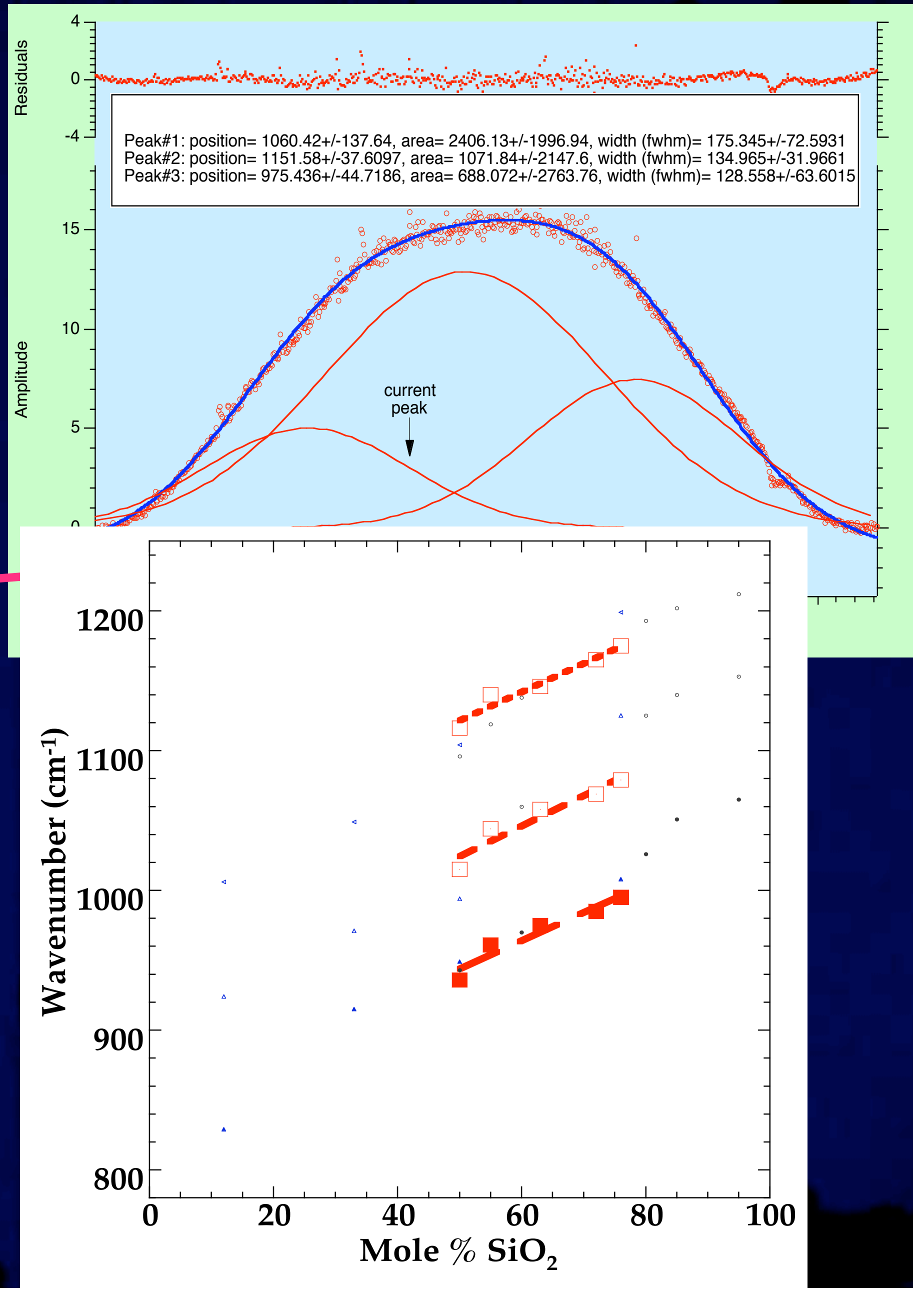


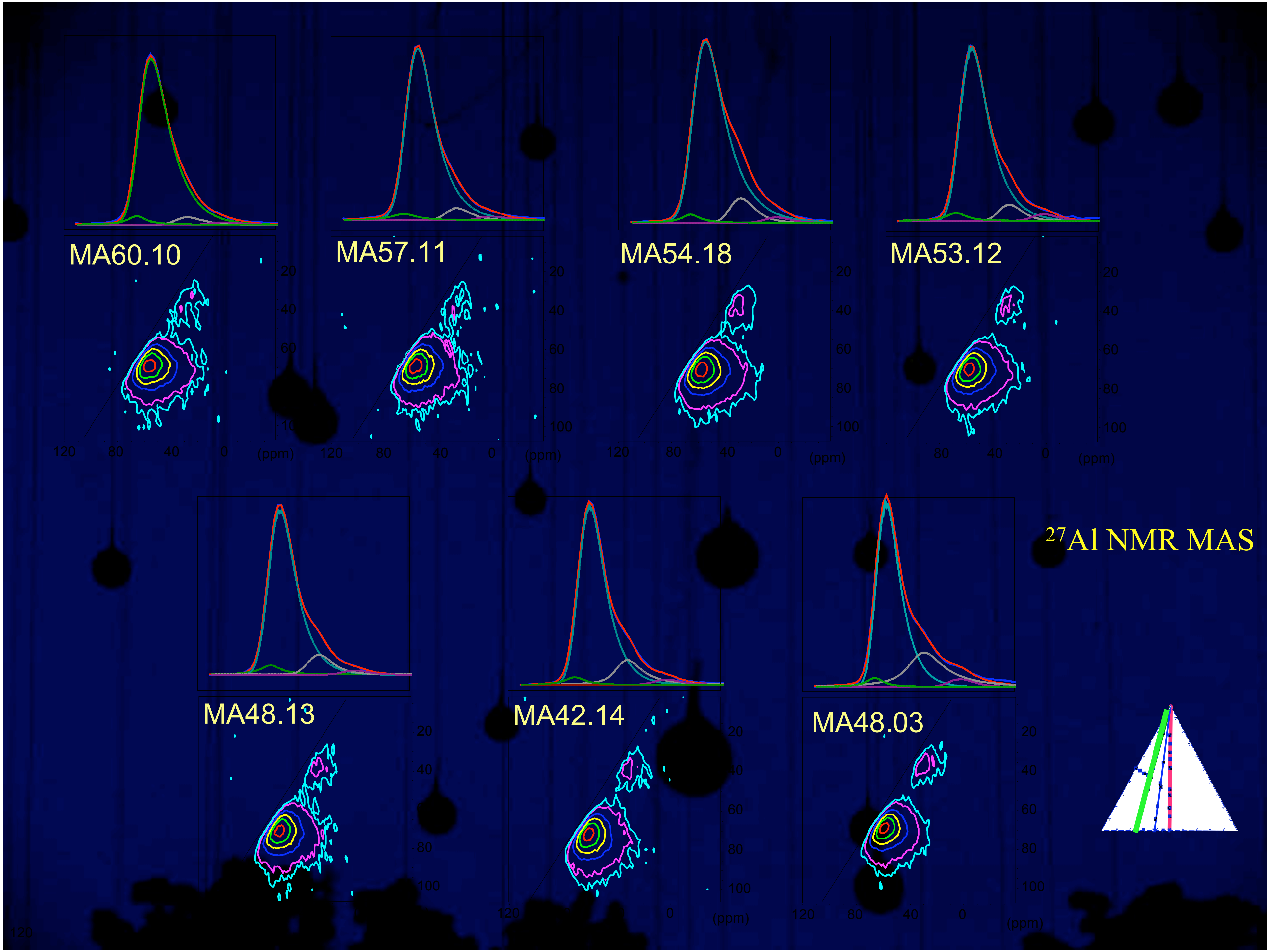
n: number of bridging oxygen

Raman spectroscopy MAS

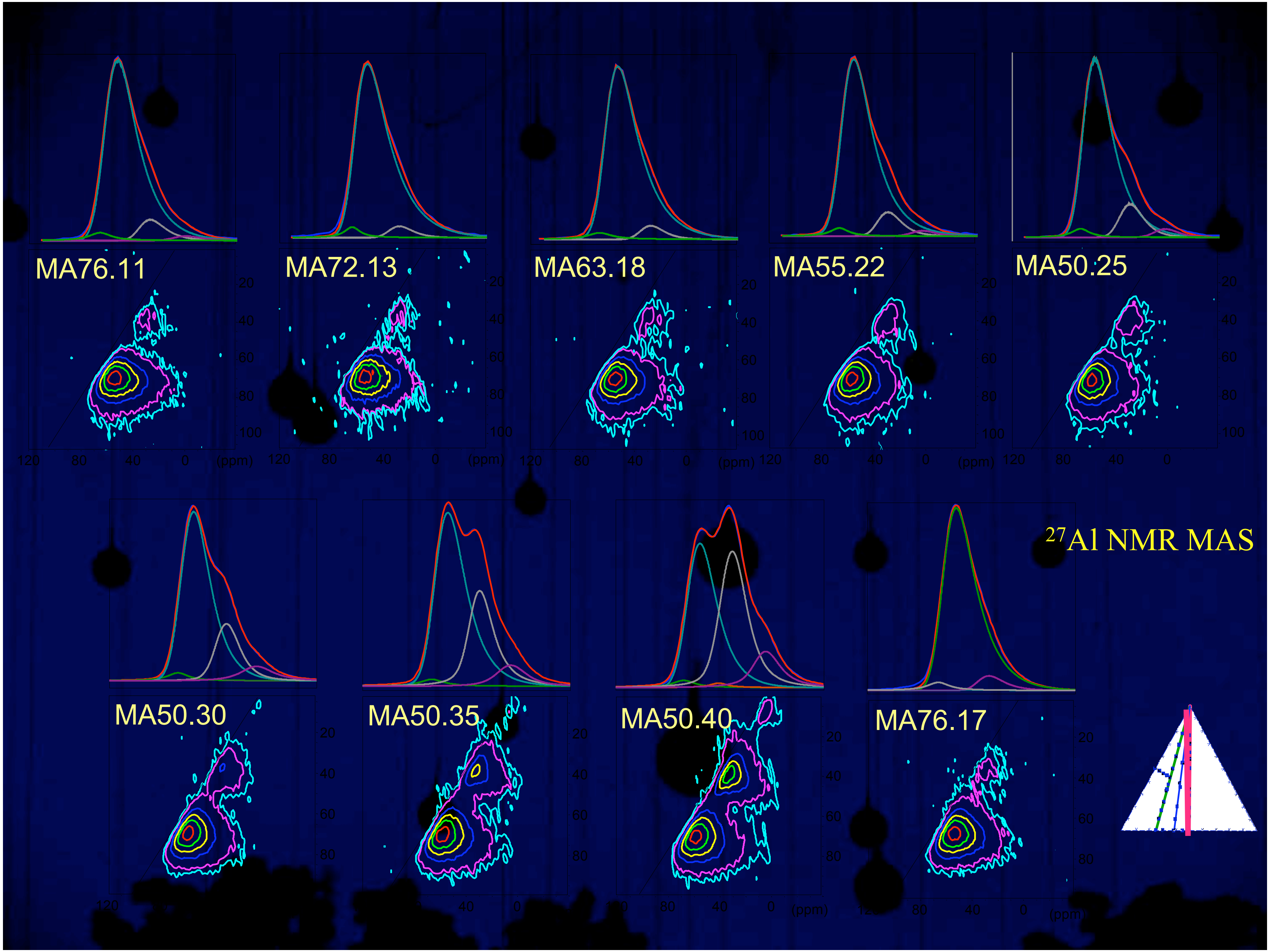








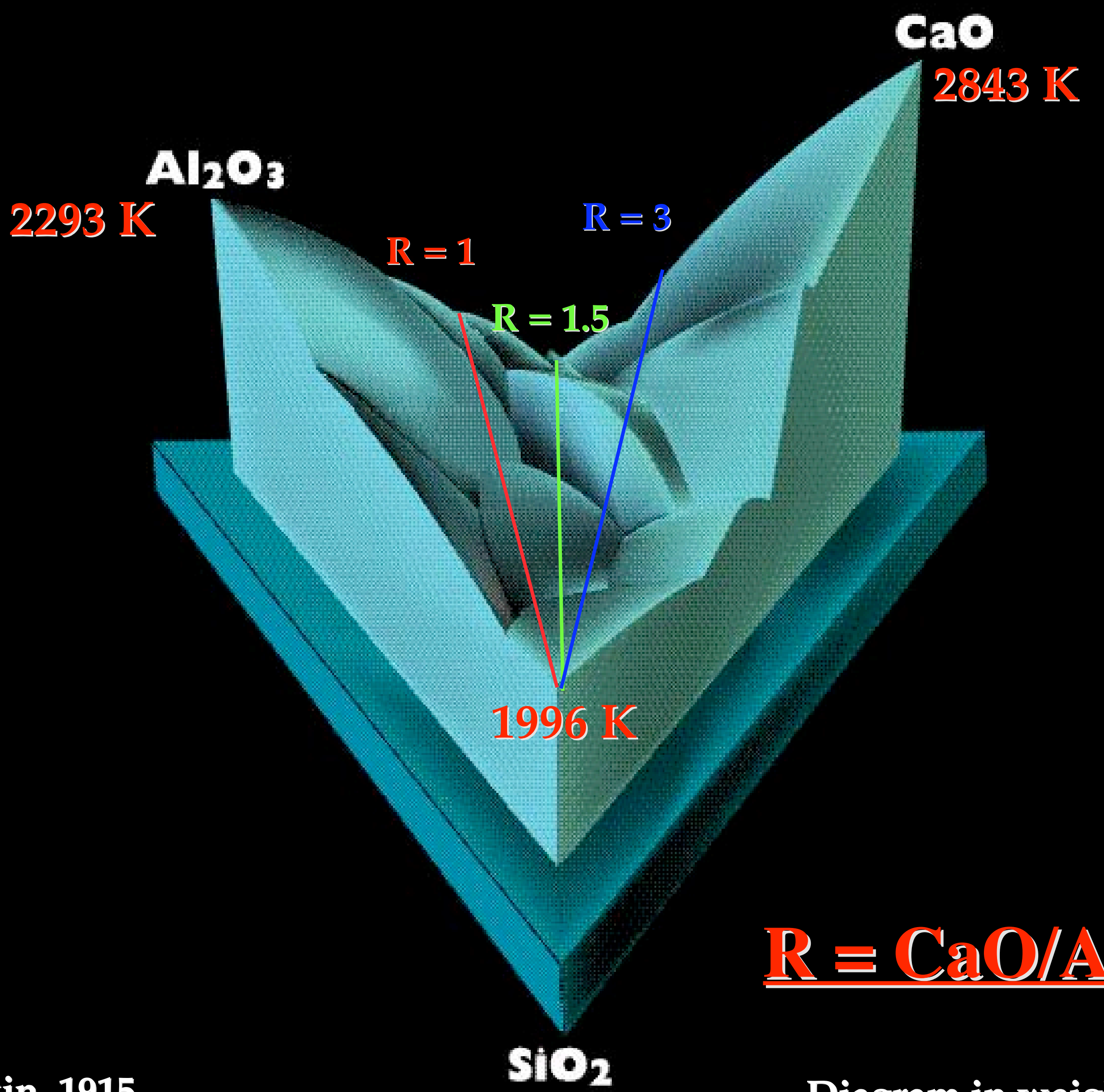
MA60.10
MA57.11
MA54.18
MA53.12
MA48.13
MA42.14
MA48.03
27Al NMR MAS
(ppm)


MA76.11
MA72.13
MA63.18
MA55.22
MA50.25
MA50.30
MA50.35
MA50.40
MA76.17
^{27}Al NMR MAS
(ppm)

MAS

Mg - Conclusions

- MV increases and C_p^{conf} decreases with SiO_2
- Viscosity and Tg increase with SiO_2 and Al_2O_3
- Viscosity and Raman spectroscopy for R=1 glasses => random substitution Si/Al, few structural changes
- NMR => ^{V}Al increases with Al_2O_3

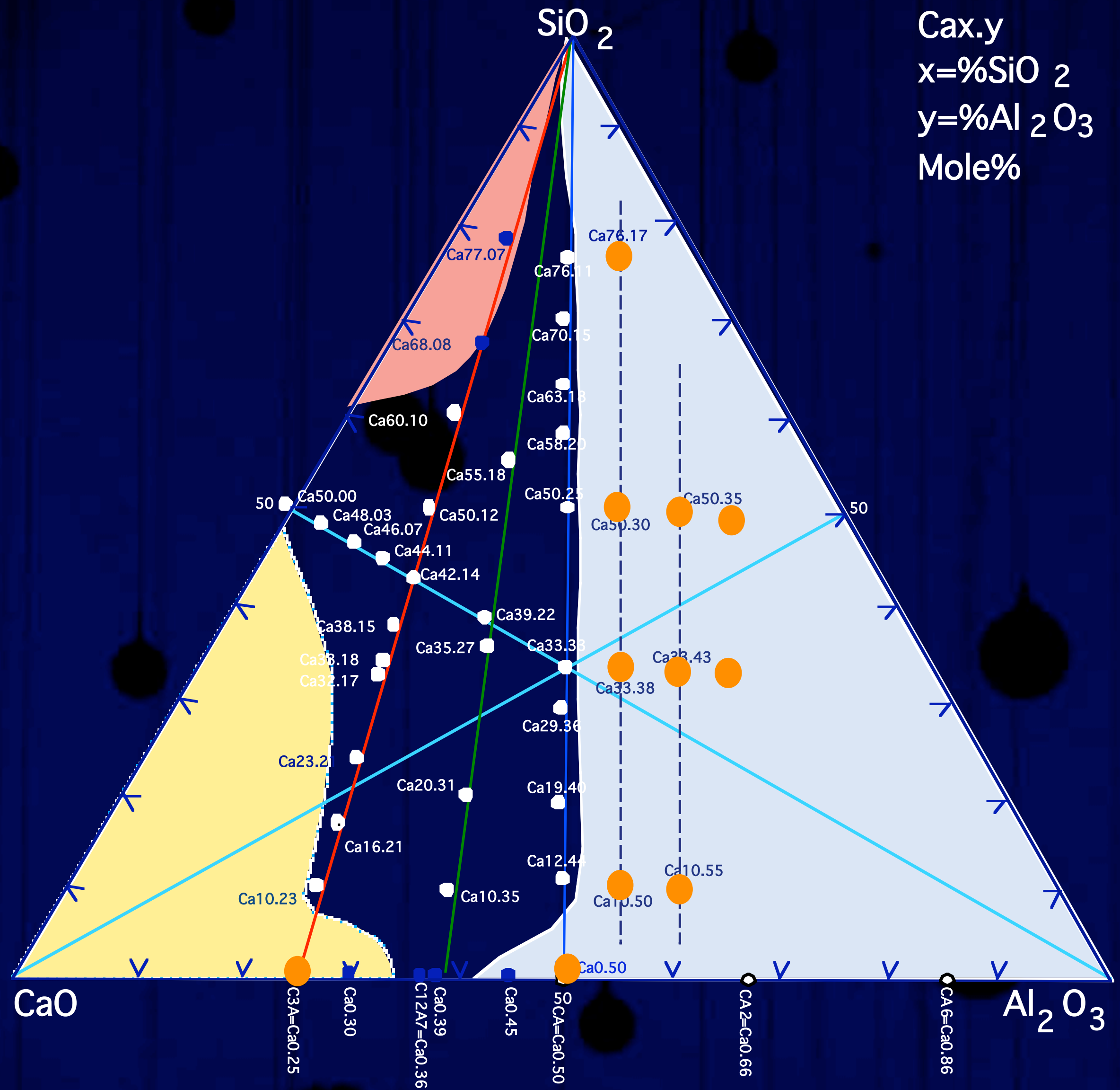


$R = CaO/Al_2O_3$

From Rankin, 1915

Diagram in weight %

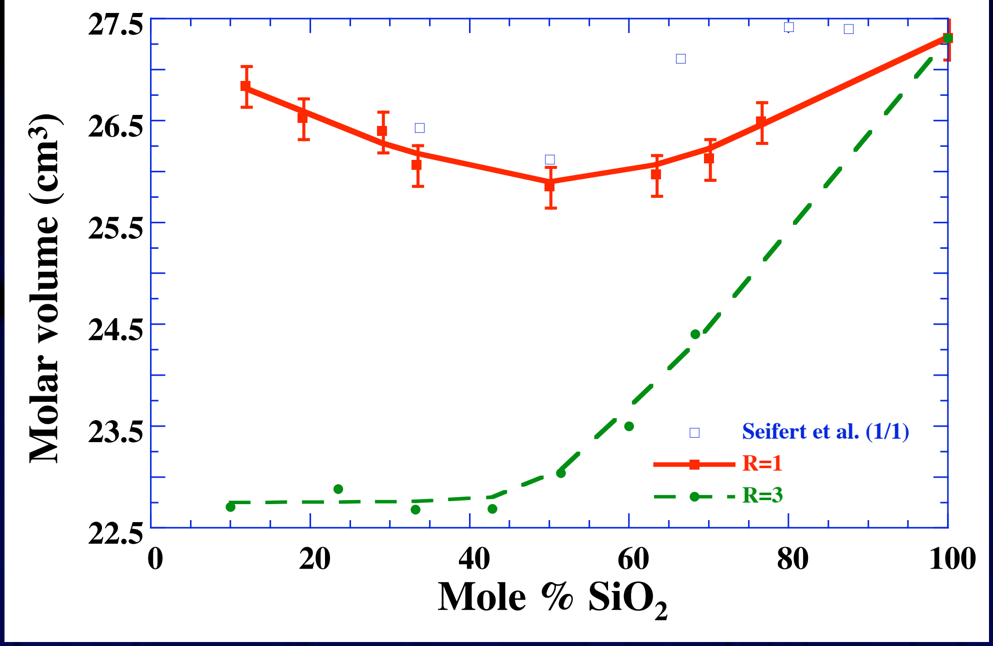
CAS



Normal quentch

Rapid quentch

CAS



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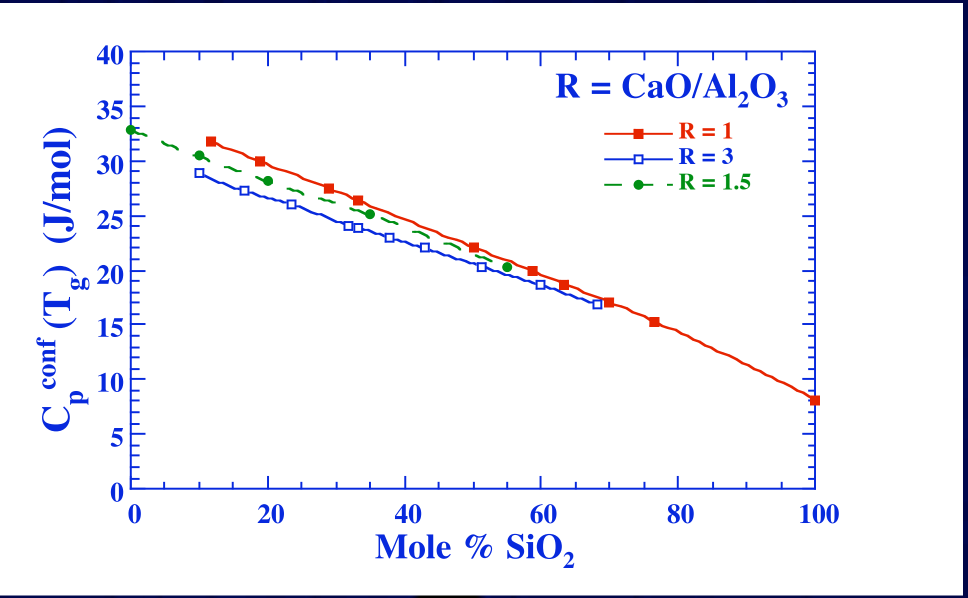
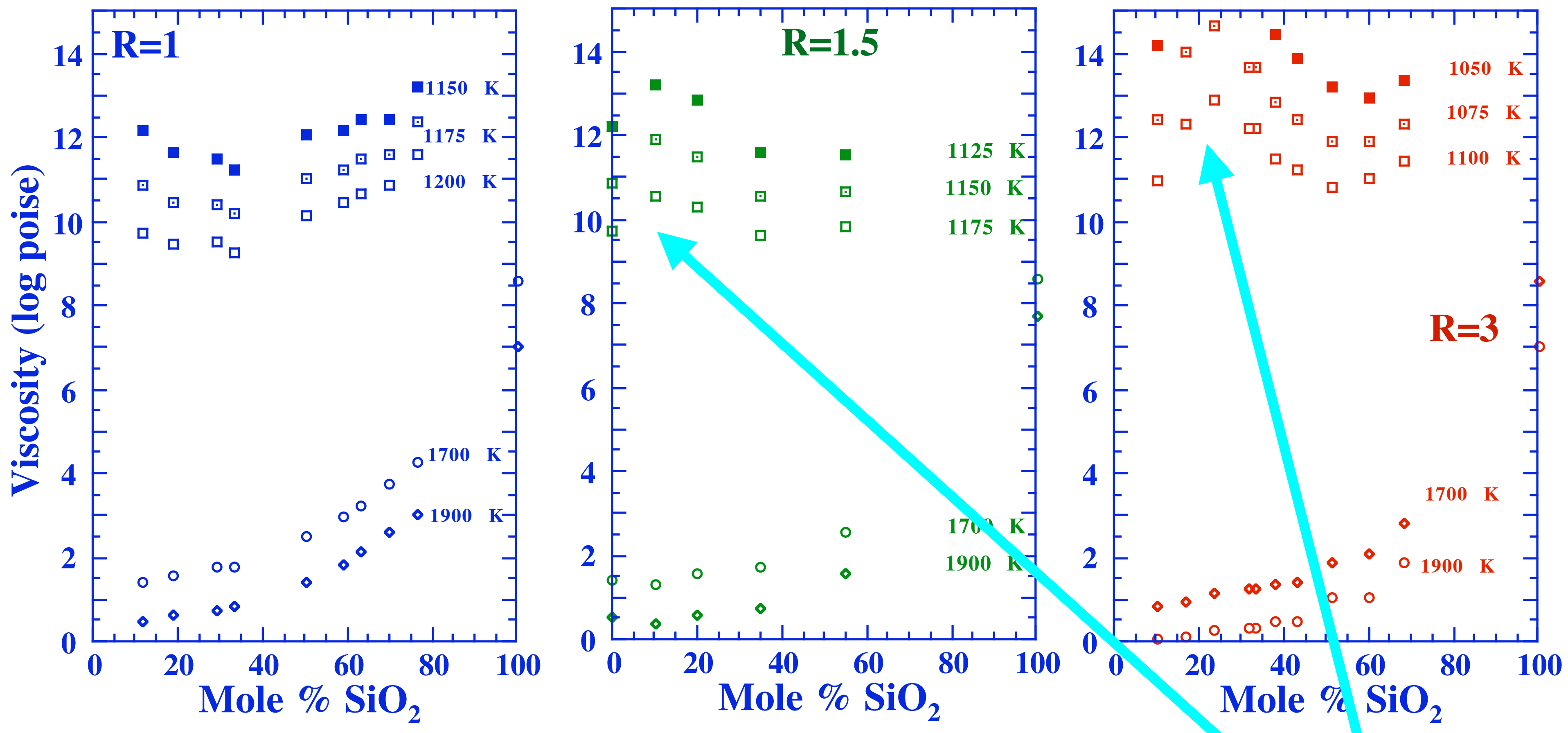
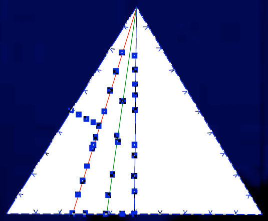


Viscosity as a function of SiO_2 for 3 joins $1<R=CaO/Al_2O_3<3$

CAS



Viscosity decreases with decreasing SiO_2 and increasing CaO



Decrease of viscosity from R=1 to R=3

Increase of viscosity at low SiO_2

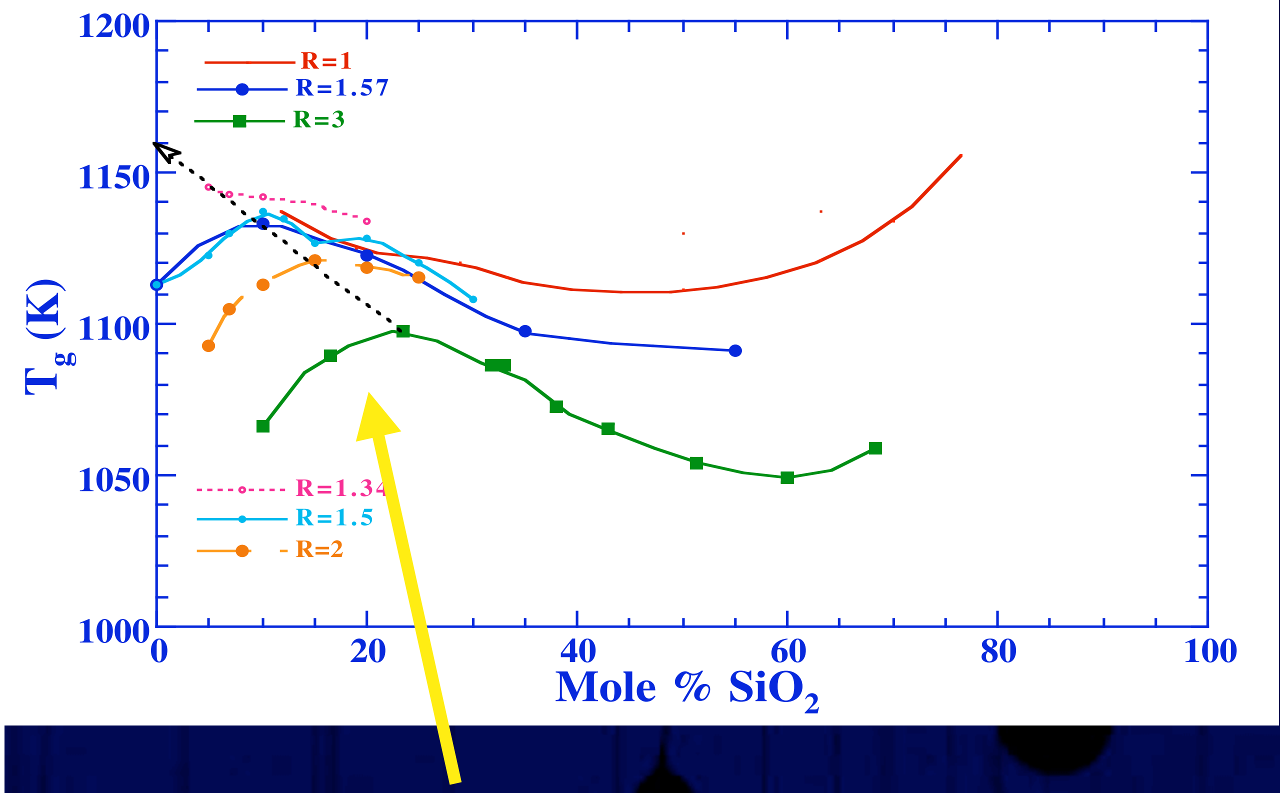
Neuville, 1992

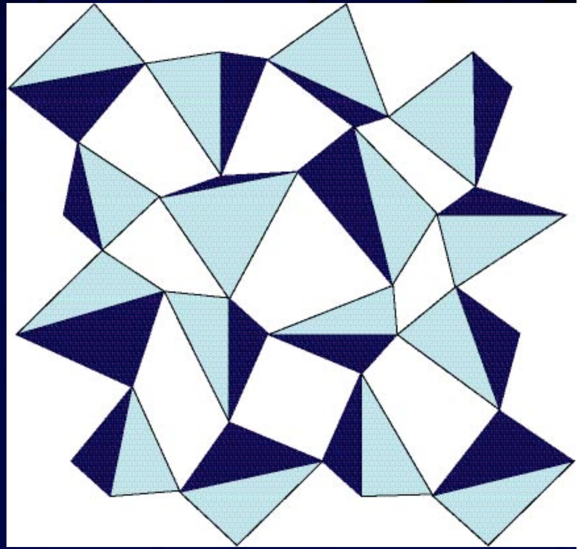
Glass transition temperature

CAS

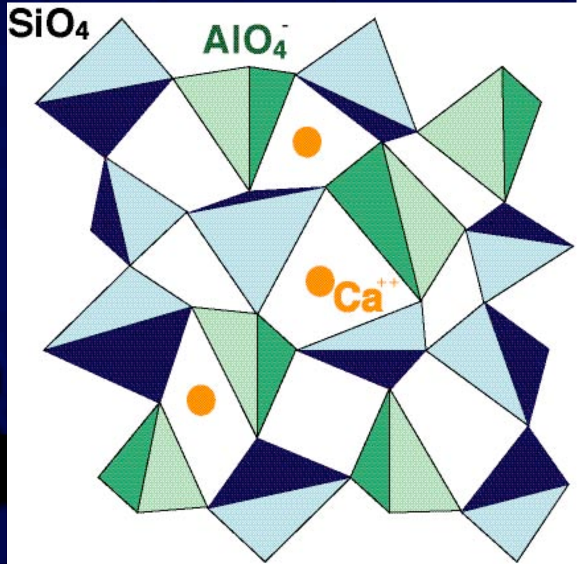
$T_g \Rightarrow \eta = 10^{13}$ poise

Tg = 1400 K
SiO_2 glass





T_g decrease with SiO_2



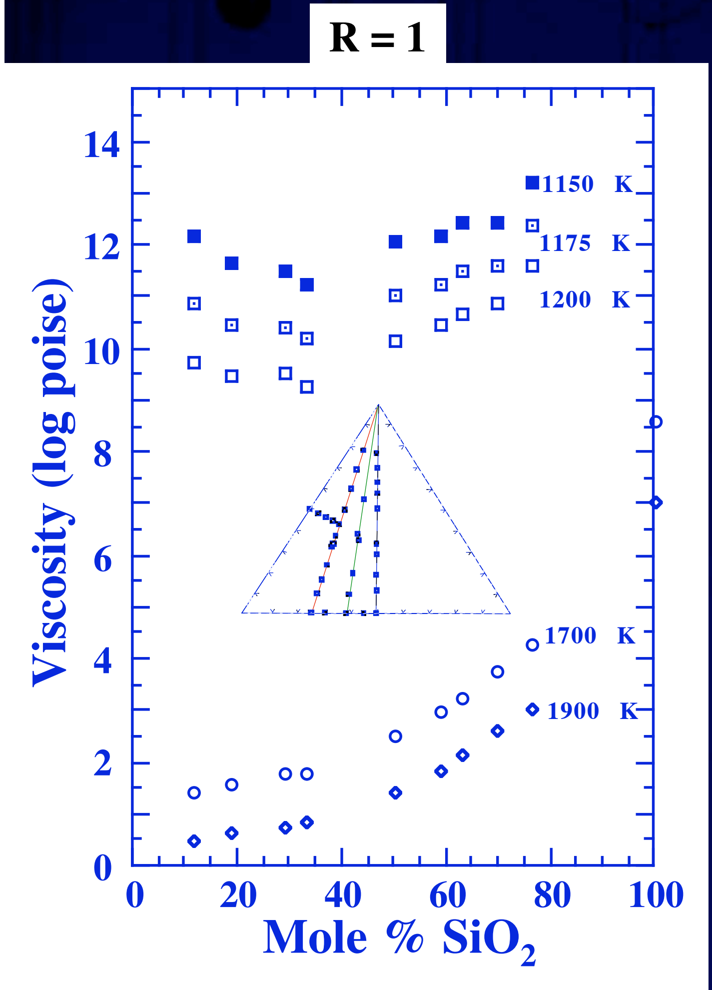
maximum in T_g at 10-20 mol% SiO_2

Neuville, 1992 Neuville et al. Chem. Geol., 2004, 213,153

Configuration Entropy

CAS

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



R = CaO/Al_2O_3

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

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

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

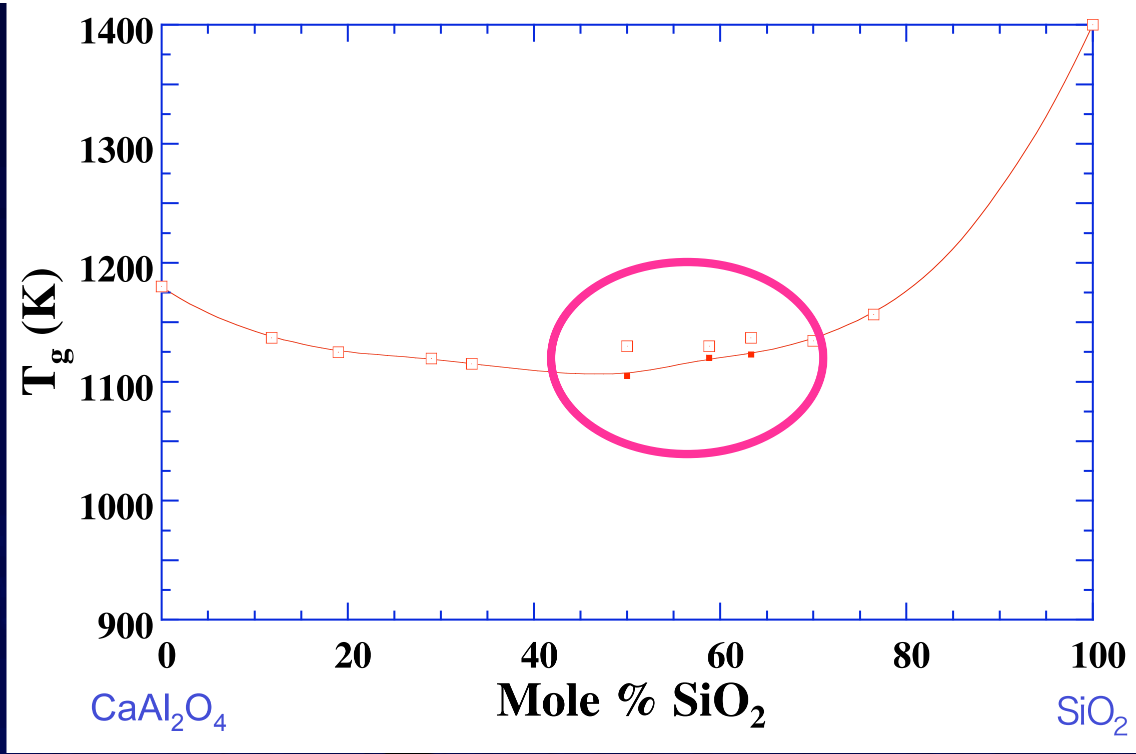
$$X_i = Al/(Al+Si)$$

Ideal mixing => random distribution

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

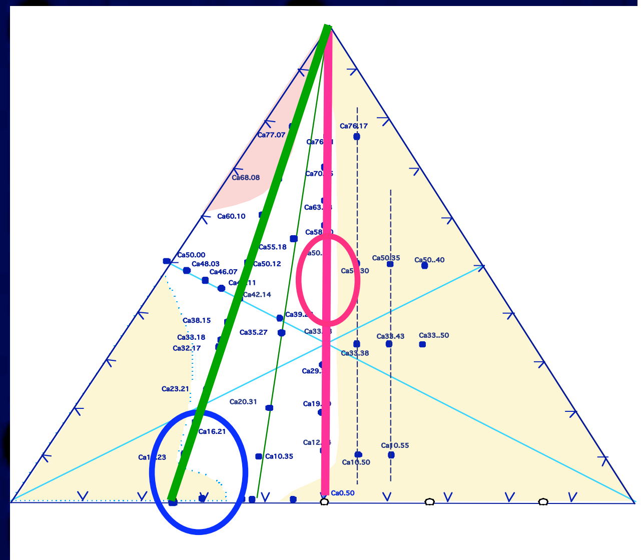
with $C_p^{conf} = C_p^{\,l} - C_{pg}(T_g)$

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



CAS

SiO_2
Tg=1400K

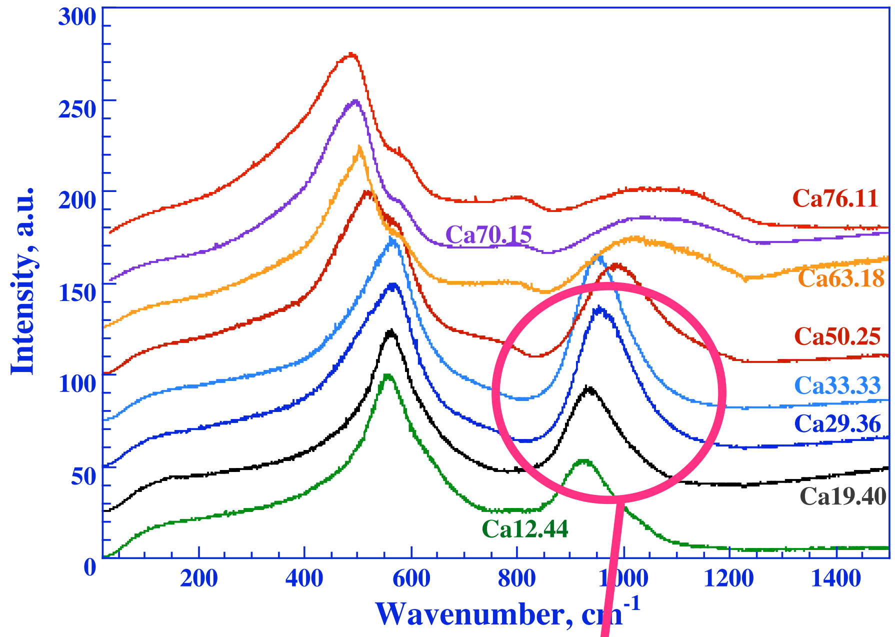


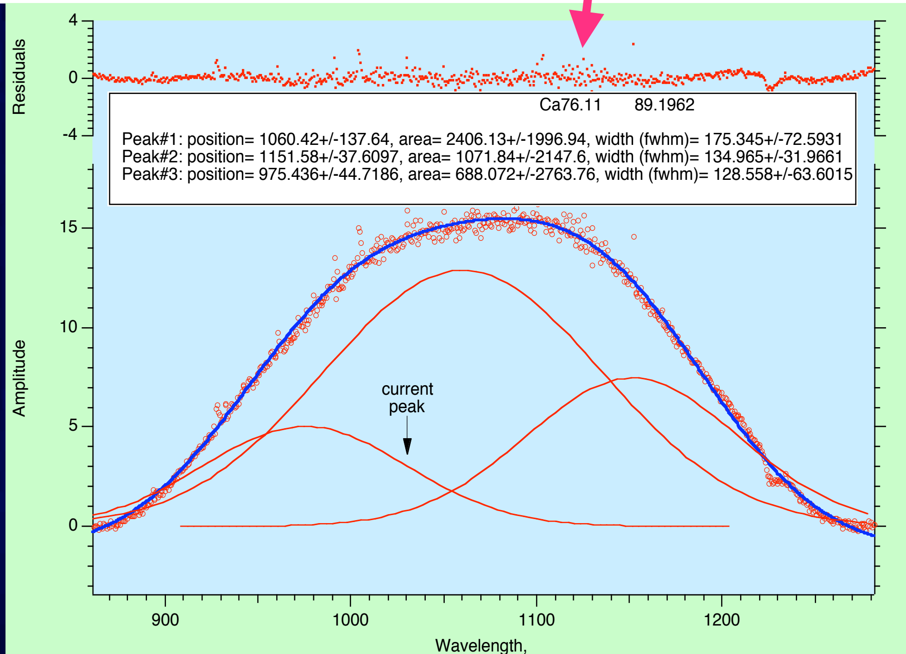
SiO_2 => Tetrahedra SiO_4
$CaAl_2O_4$ => Tetrahedra AlO_4
substitution of 1 Si by 1 Al and
Ca charge compensator

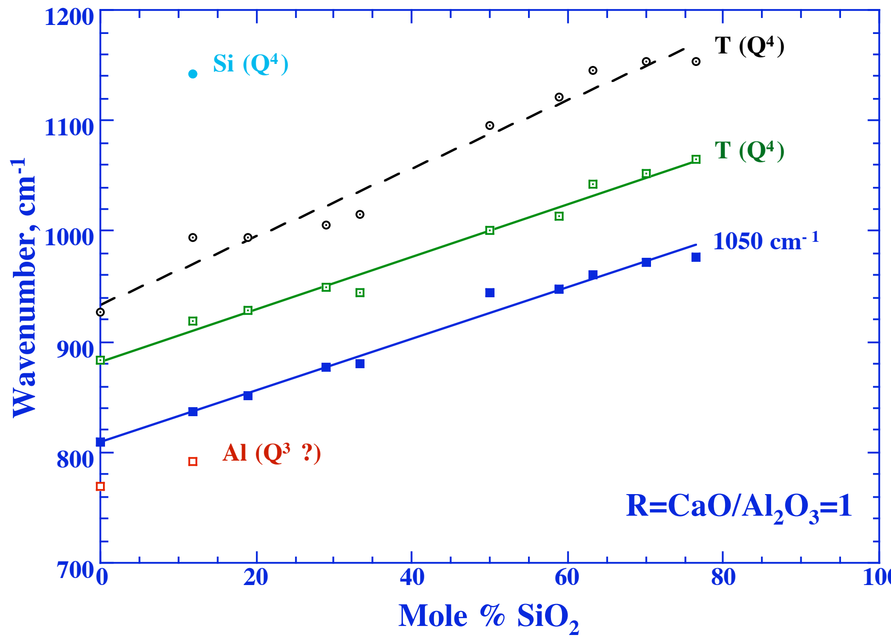
Anomaly ?

Decresase of wavenumbers with SiO_2

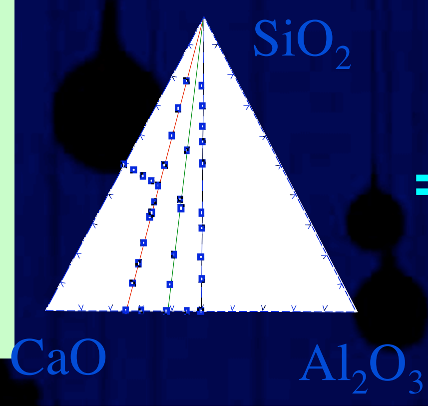
CAS







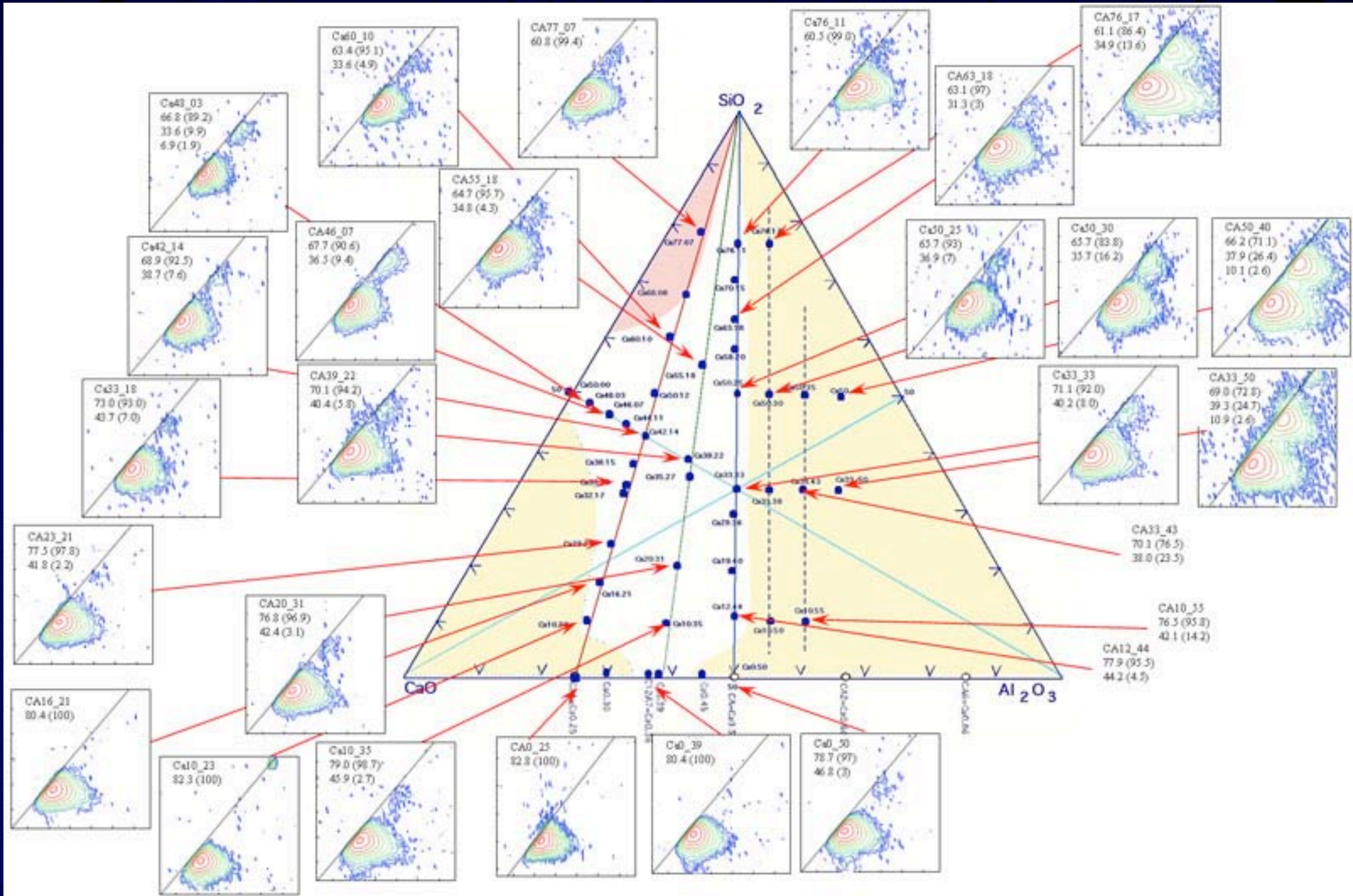
Neuville et al. GCA, 2004, 68, 5071



Al substitutes Si in Q^4

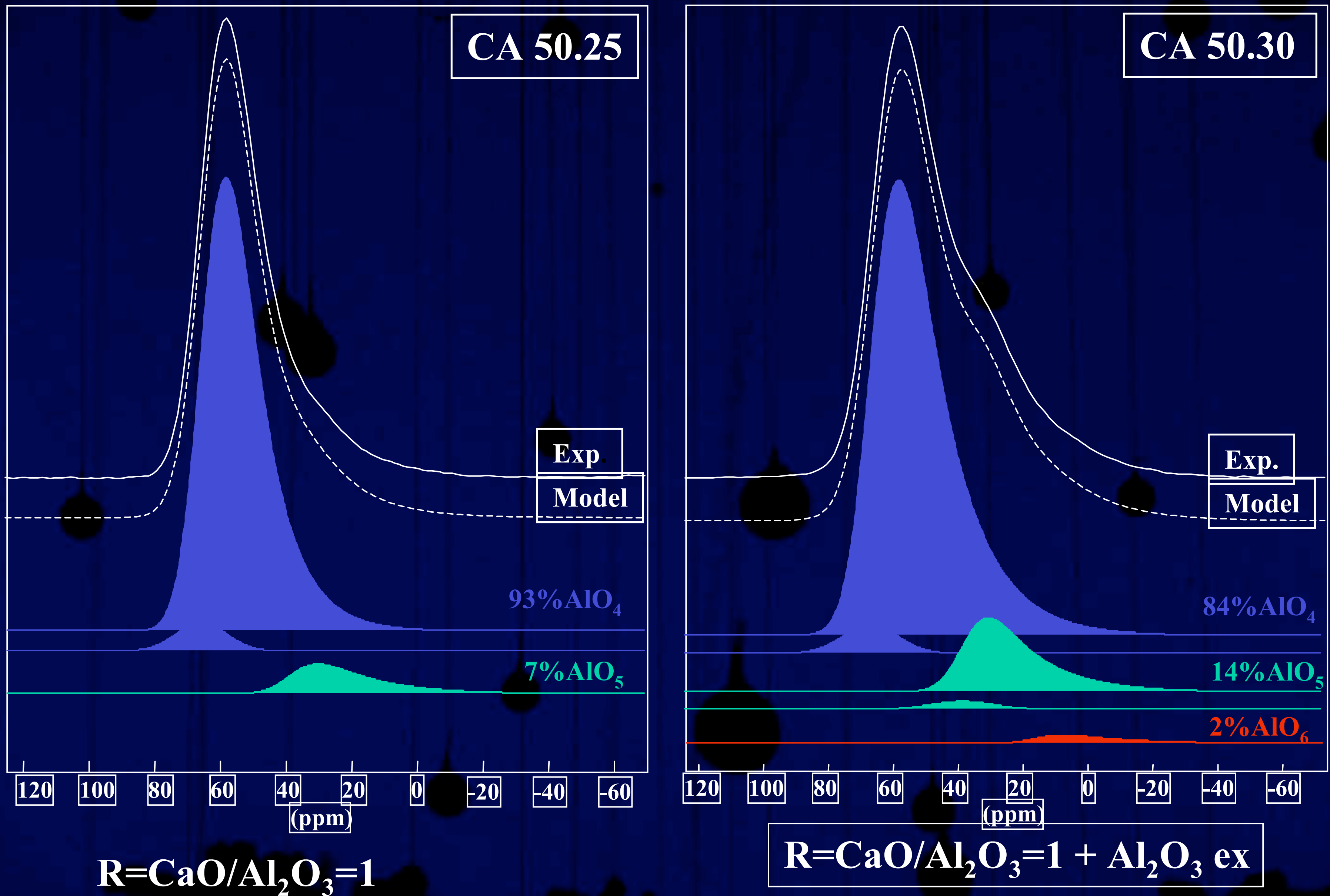
=> 890 cm^{-1} Al inQ^4

CAS



Neuville et al. GCA, 2004, 68, 5071, Neuville et al. Chem Geol., 2006, 229, 173

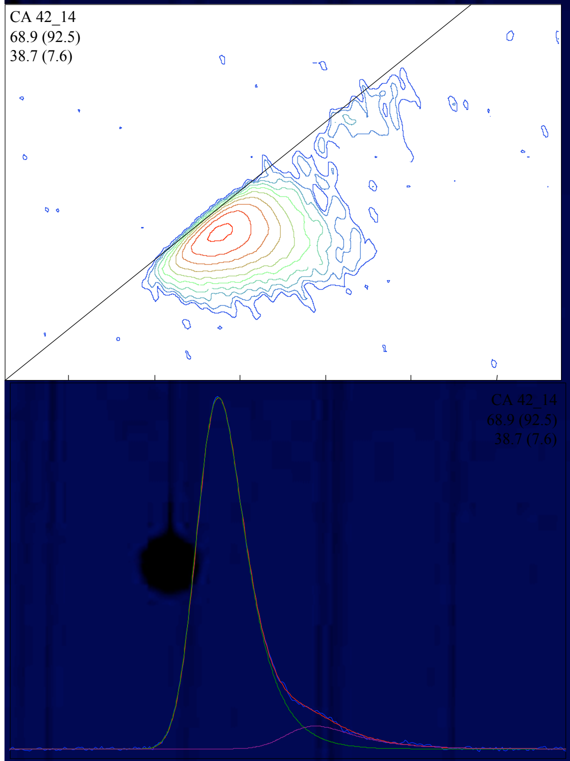
RMN 750MHz, CRMHT, Orléans, ^{27}Al 1D MAS



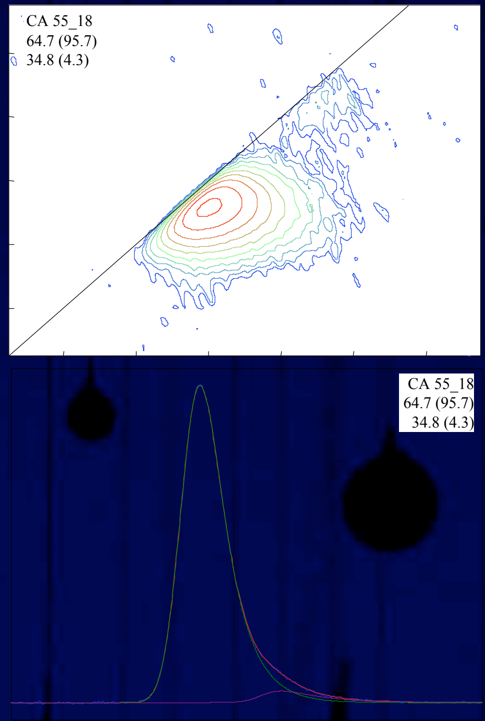
Neuville et al. GCA, 2004, 68, 5071

$R = CaO/Al_2O_3 = 3$

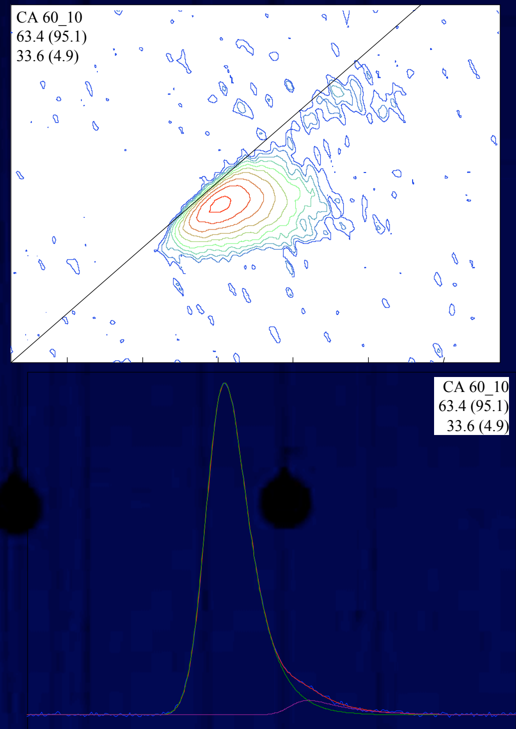
CA42.14

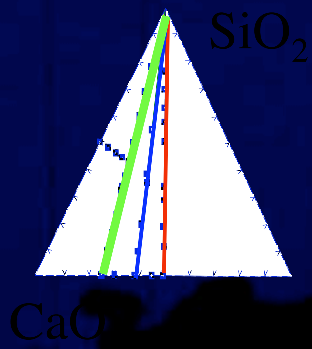


CA33.17



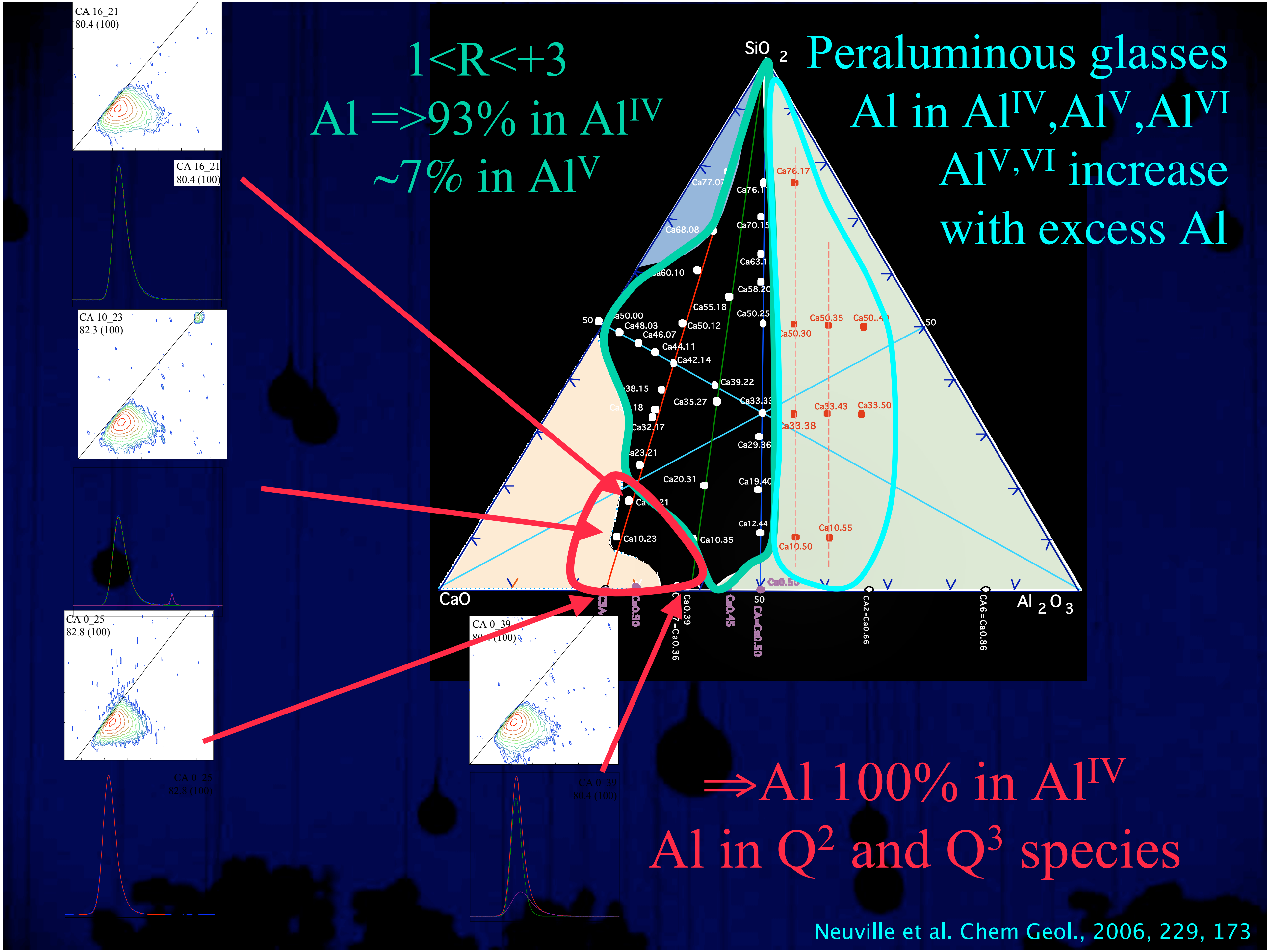
CA60.10





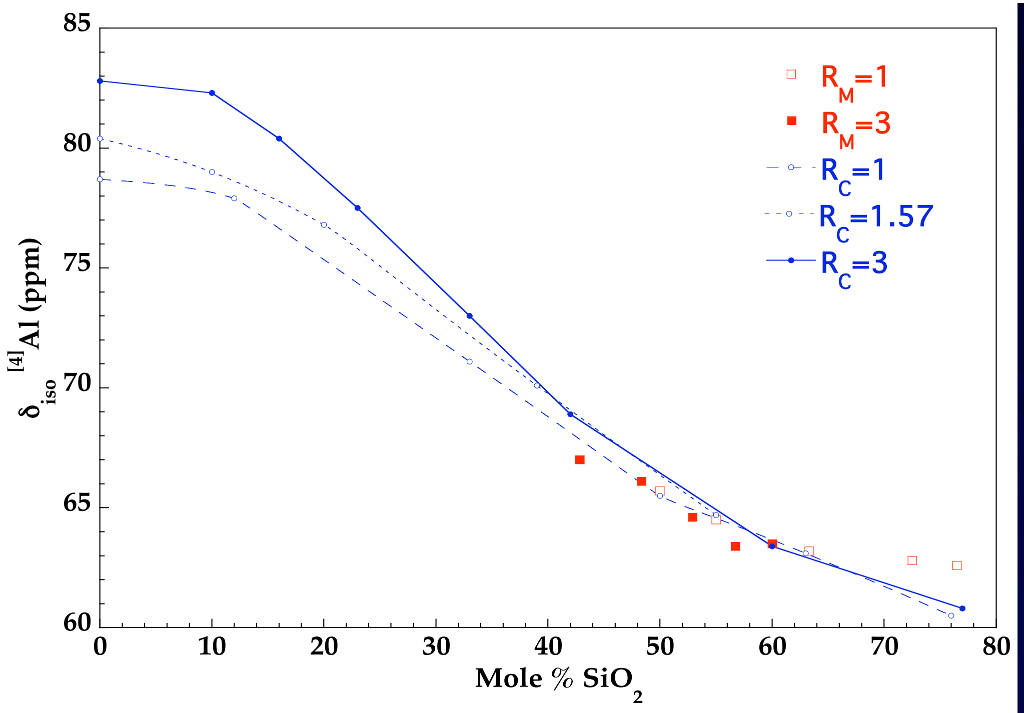
⇒1<R<3 92%Al^{IV} and 8%Al^{V} in glasses with classic (15°/s) and rapid quench (300°/s)

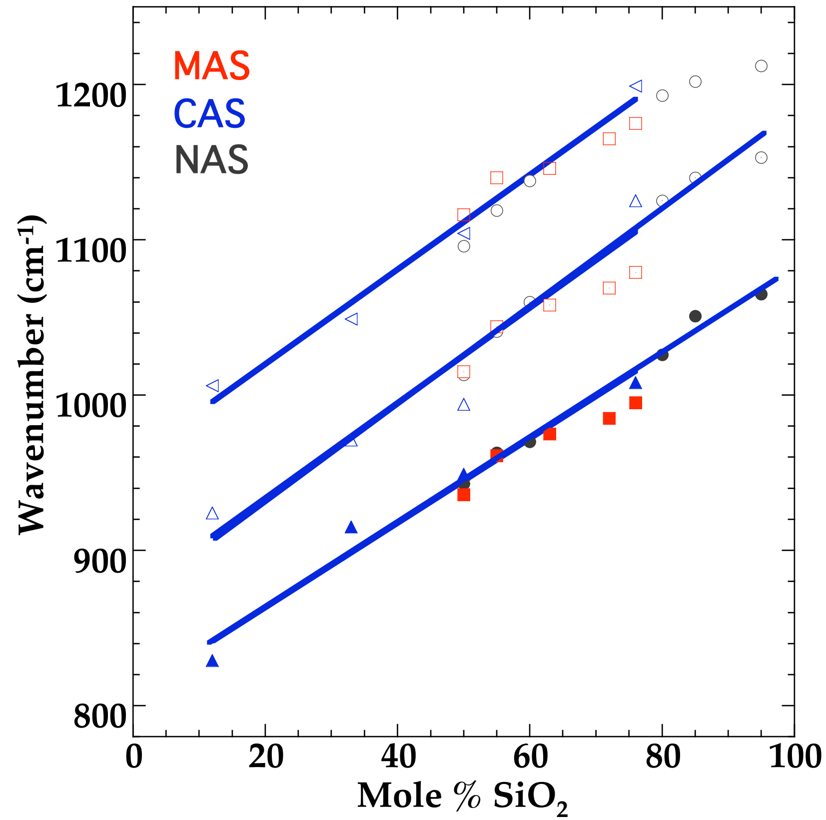
Neuville et al. JNCS, 2007



1<R<+3
Al =>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
⇒Al 100% in Al^IV
Al in Q^2 and Q^3 species
SiO2
CaO
Al2O3
CA 16_21
80.4 (100)
CA 10_23
82.3 (100)
CA 0_25
82.8 (100)
CA 0_39
Neuville et al. Chem Geol., 2006, 229, 173

δ_{iso} $^{[4]}Al$ independant of MO/Al_2O_3 and vary linearly with SiO_2

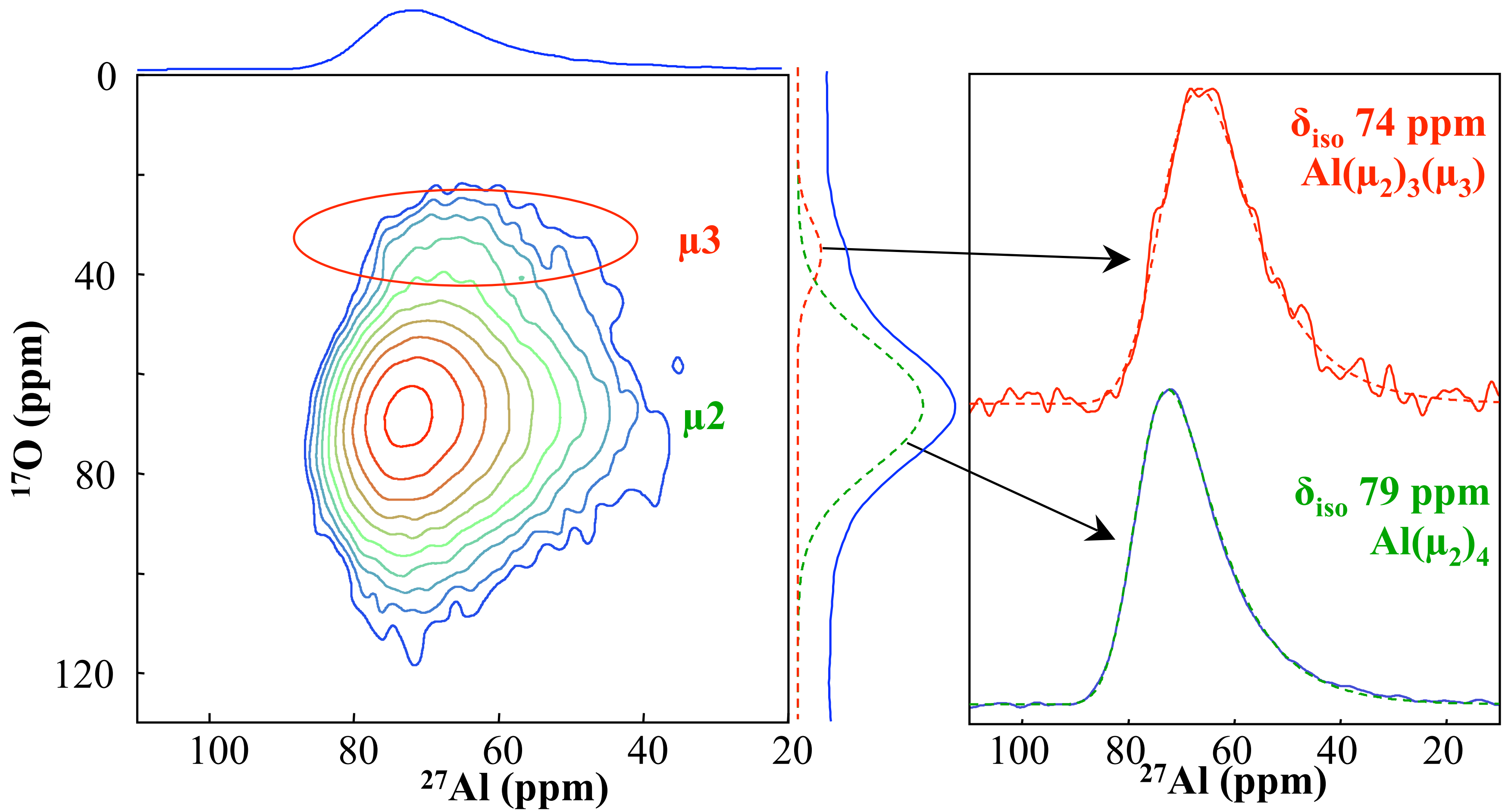




Neuville et al. Chem Geol., 2006, 229, 173

CaO Al_2O_3 - Glass

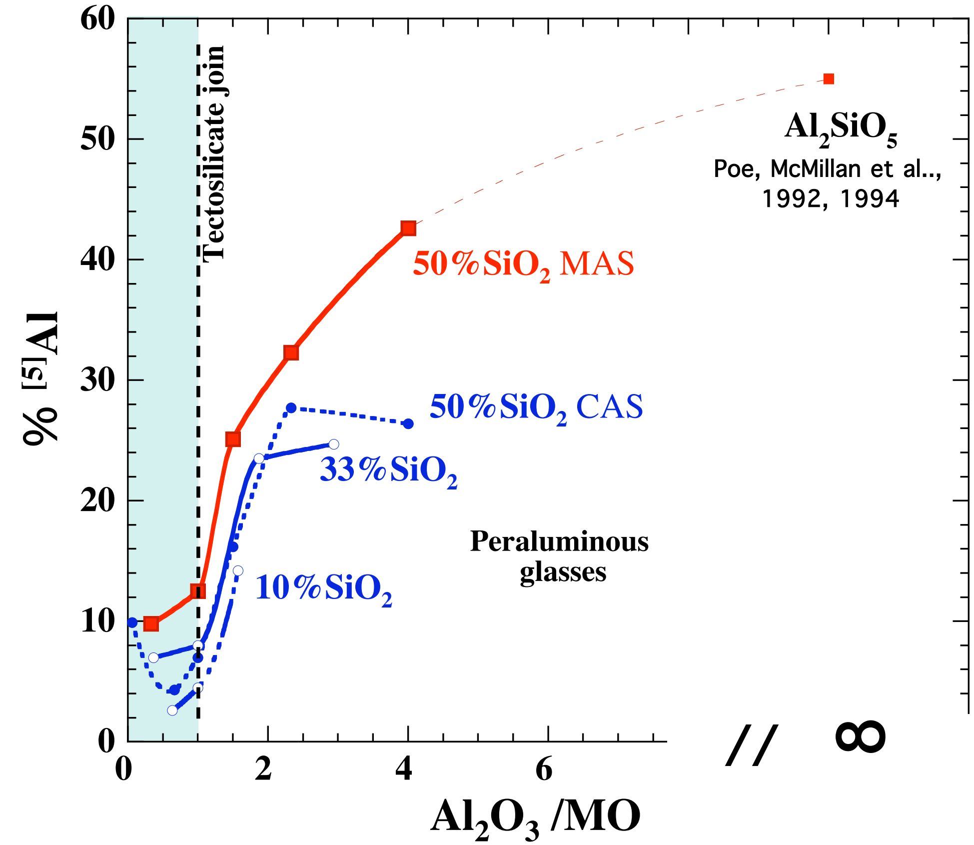
Hetero-nuclear correlation

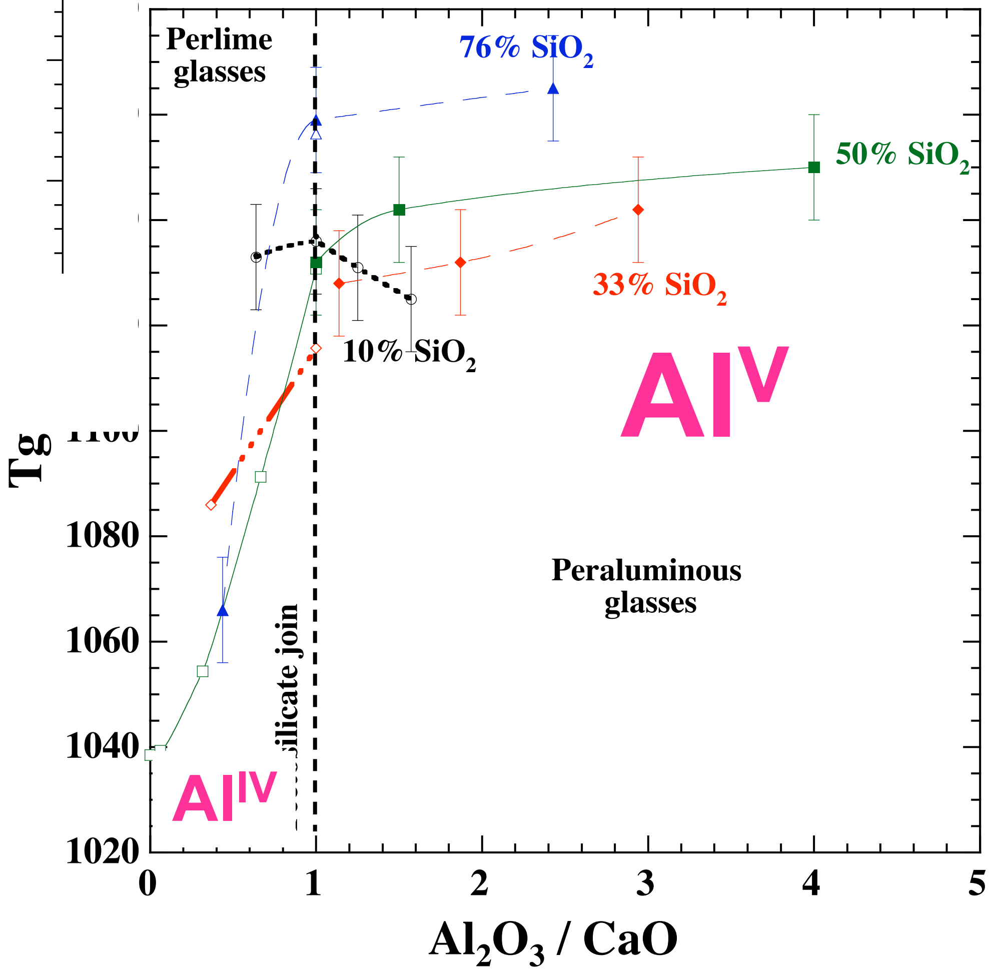


Consistent ^{17}O and ^{27}Al signature of $Al(\mu_2)_3(\mu_3)$ structural entities

D.Iuga, C.Morais, Z.Gan, D.R.Neuville, L.Cormier, D.Massiot *'NMR Heteronuclear Correlation between Quadrupolar Nuclei in Solids.'*
J. Am. Chem. Soc. **127** 11540-11541 (2005)

Al^V increases with Al_2O_3 content for $R=CaO/Al_2O_3<1$



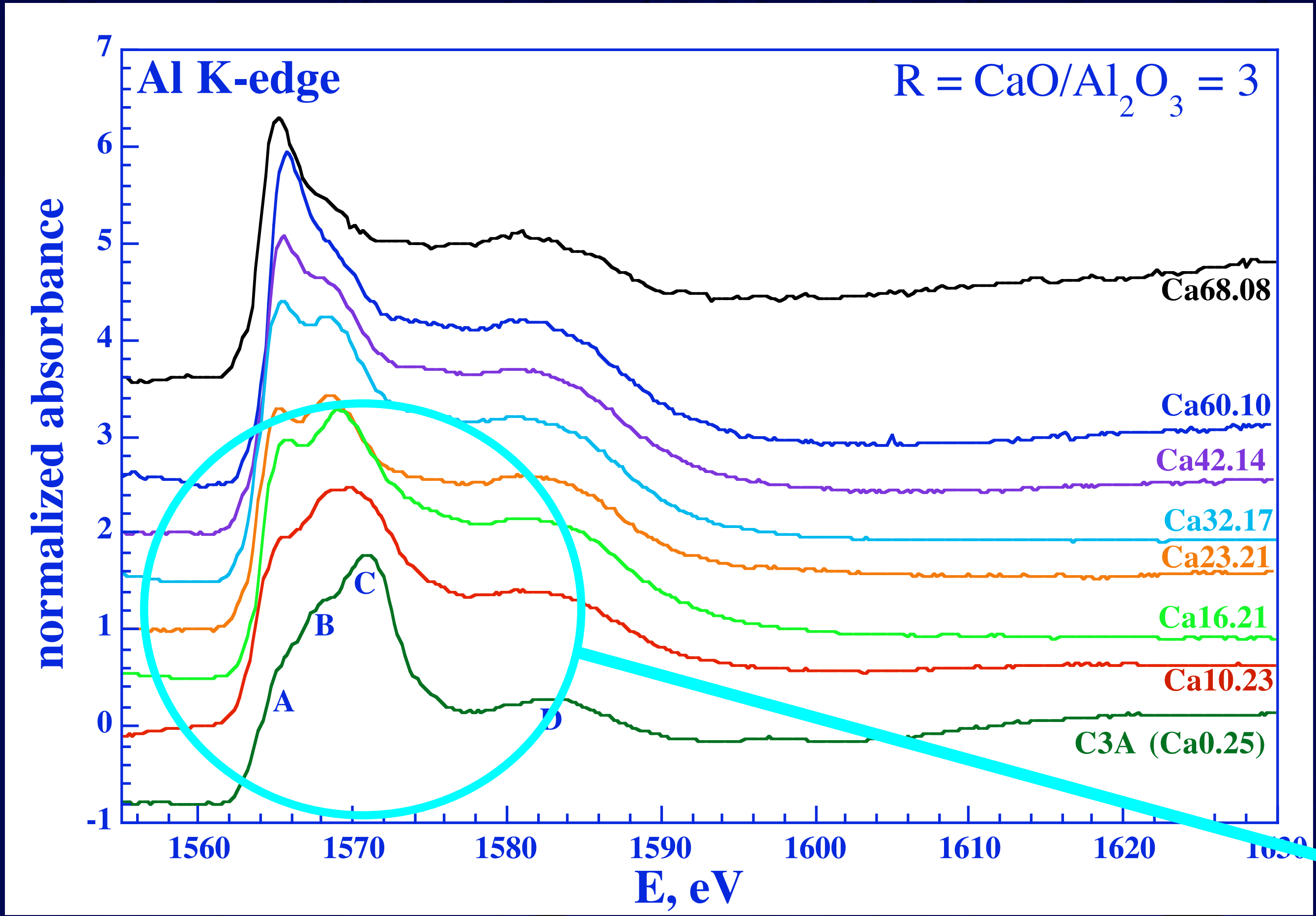


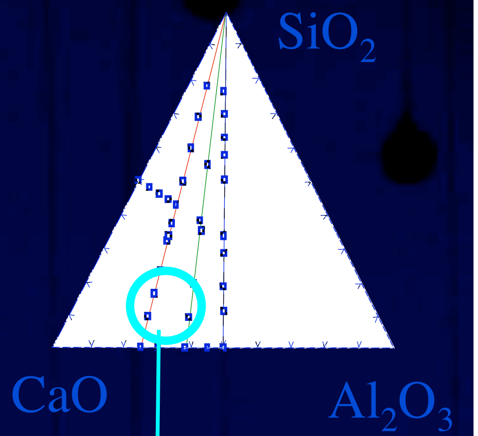
Al^V increases the viscosity
Al^V has a role of network former

Neuville et al. Chem Geol., 2006, 229, 173

CaO-Al_2O_3-SiO_2 glasses: Al K-edge

SA32 SUPERACO- LURE



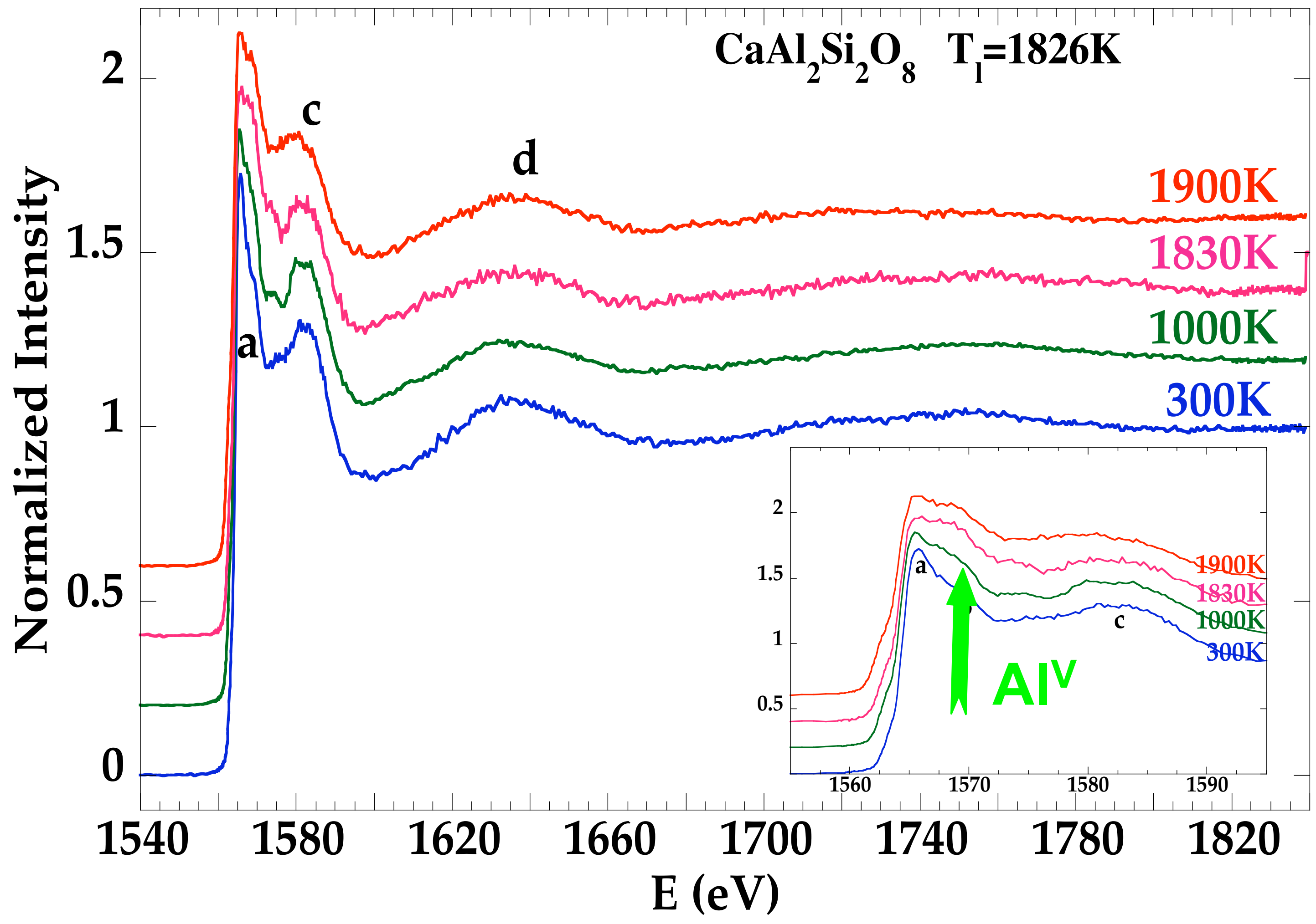


Al in 4-fold coordination

Al in Q^2 species

Neuville et al. Chem. Geol., 2004, 213,153

Al K-edge



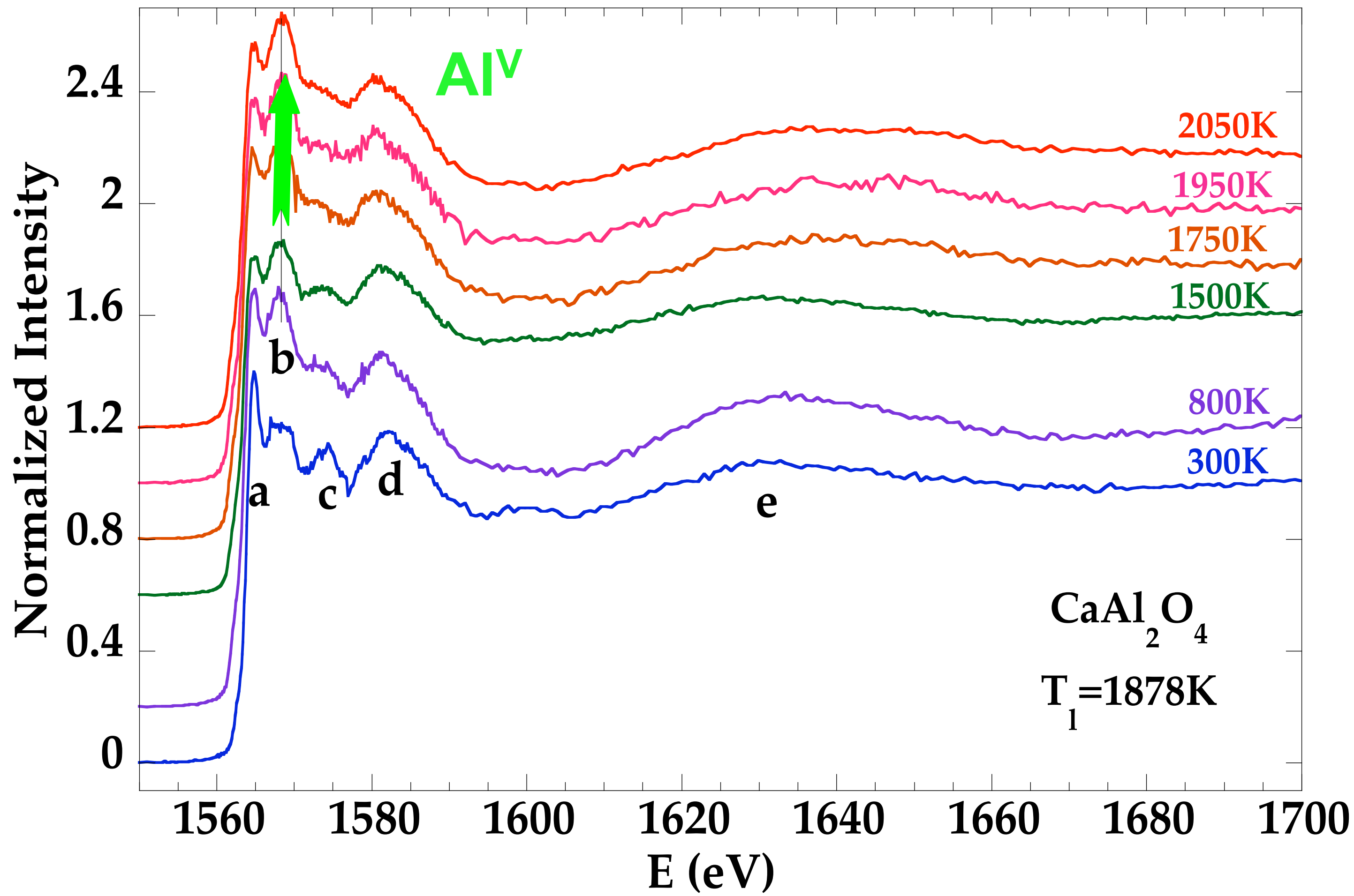
Anorthite
$CaAl_2Si_2O_8$

Crystal and melt 1000K => Al in 4 fold coordination

with increasing temperature few Al in 5 fold coordination appear according with NMR (Coté, 1993) and Raman spectroscopy (Daniel et al, 1995)

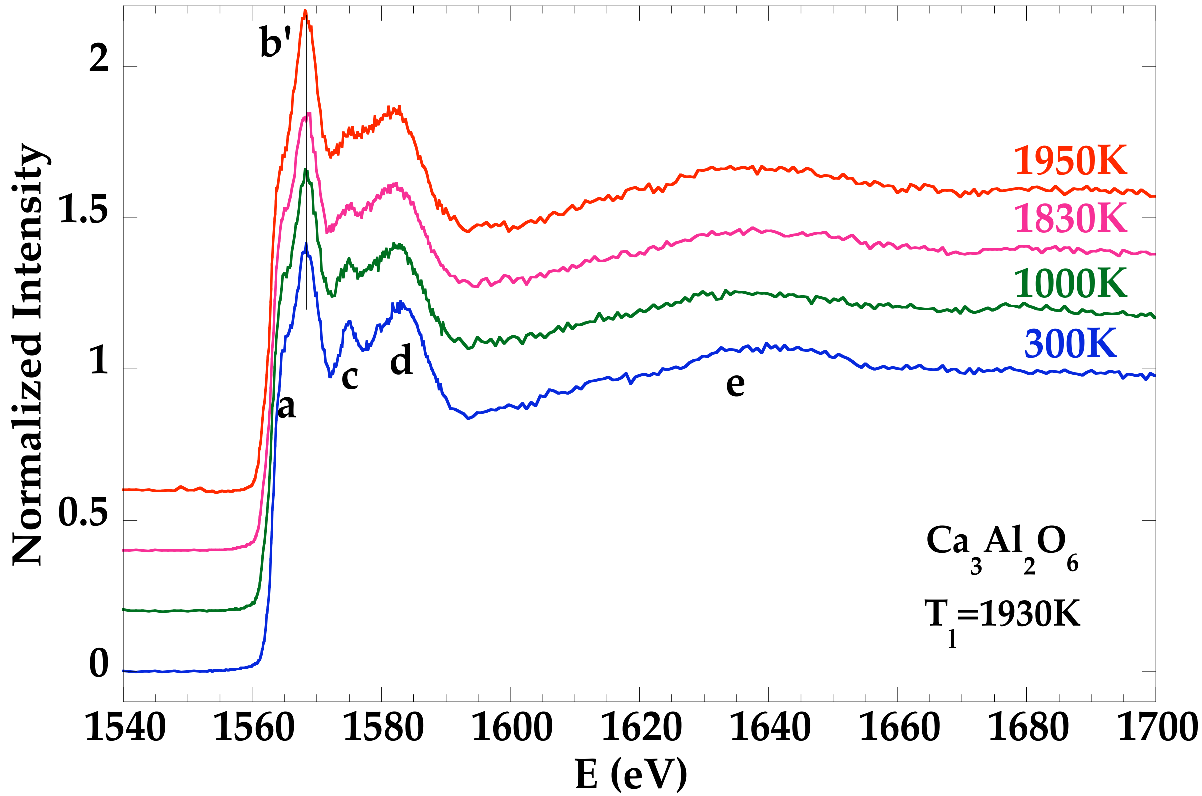
Al K-edge

CA = $CaAl_2O_4$



Crystal and melt => Al in 4 fold coordination

with increasing temperature few Al in 5 fold coordination appear according with NMR (Couture et al, 1990)

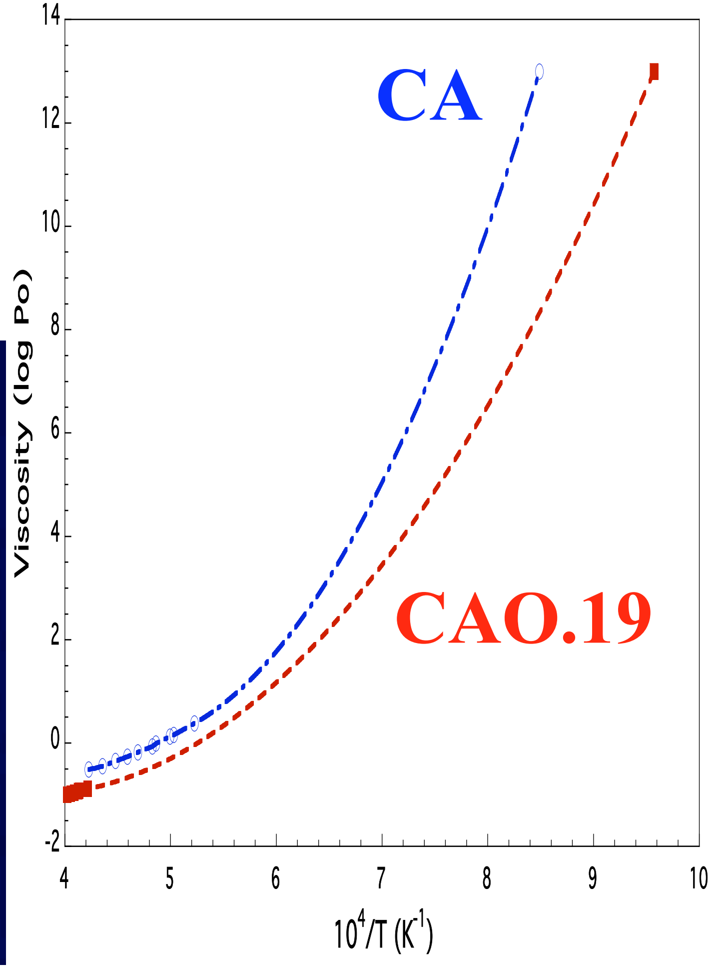


Al K-edge

C3A = $Ca_3Al_2O_6$

Crystal => Al in 4 fold coordination with 2 Bridging Oxygen, Q^2 species
with increasing temperature no changes are observed

Viscosity decrease with CaO, and Al evolves from Q^4 to Q^2 with CaO

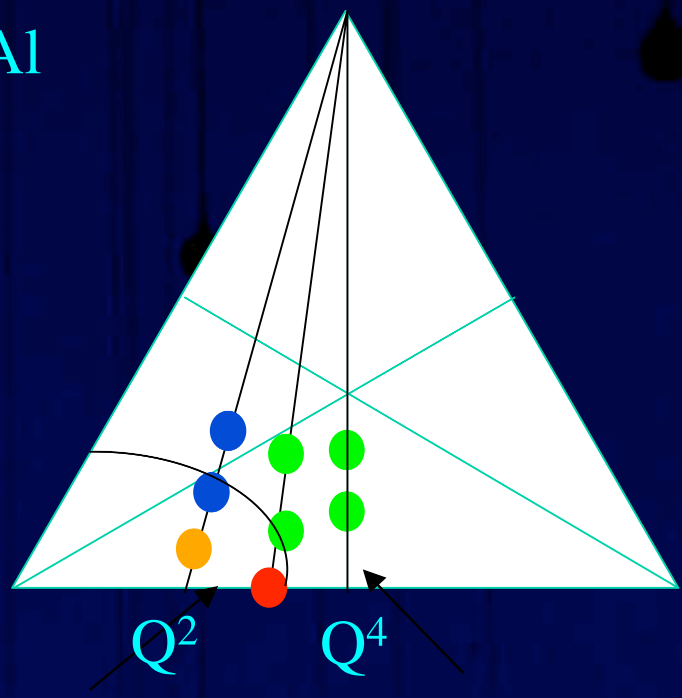


Neuville et al., 2007, Amer Mineral.

Ca-Conclusions

Explanations for the increase of Tg at low SiO_2 content

- Glasses R=1 : Q^4
  few structural change - substitution Si/Al
  ⇒ polymerization not change
  ⇒ no Tg maximun
  ⇒ $^{[5]}$Al explain the Tg deviation

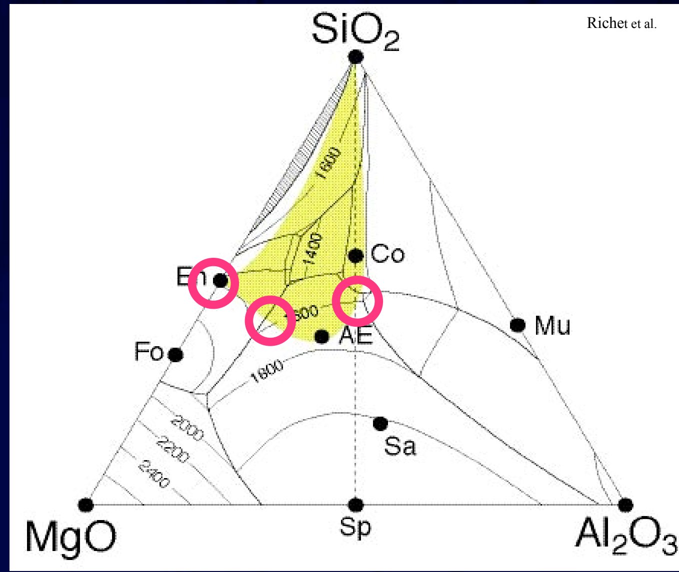


- High content in CaO : Al in Q^2 low Tg

- With increase of SiO_2 or Al_2O_3 : Q^4
  Al enters preferentialy in Q^4 species
  ⇒ the connectivity of the network is increases => higher viscosity
  ⇒ high Tg

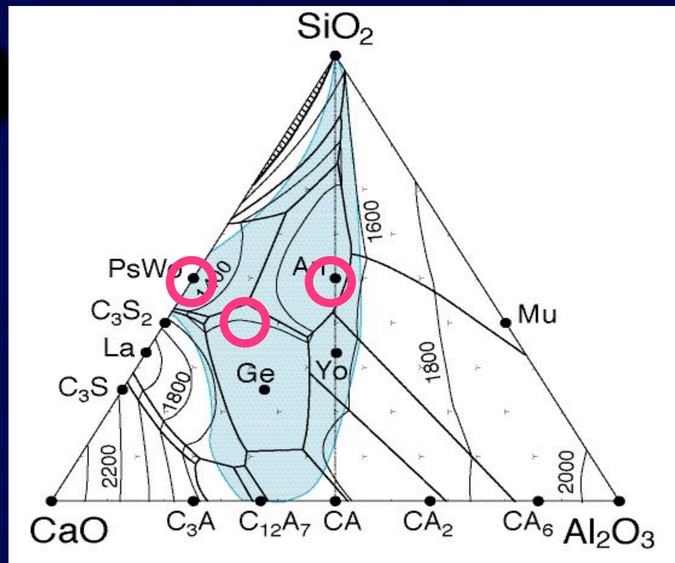
- Not need O tricluster to explain viscosity variation

1) MAS System

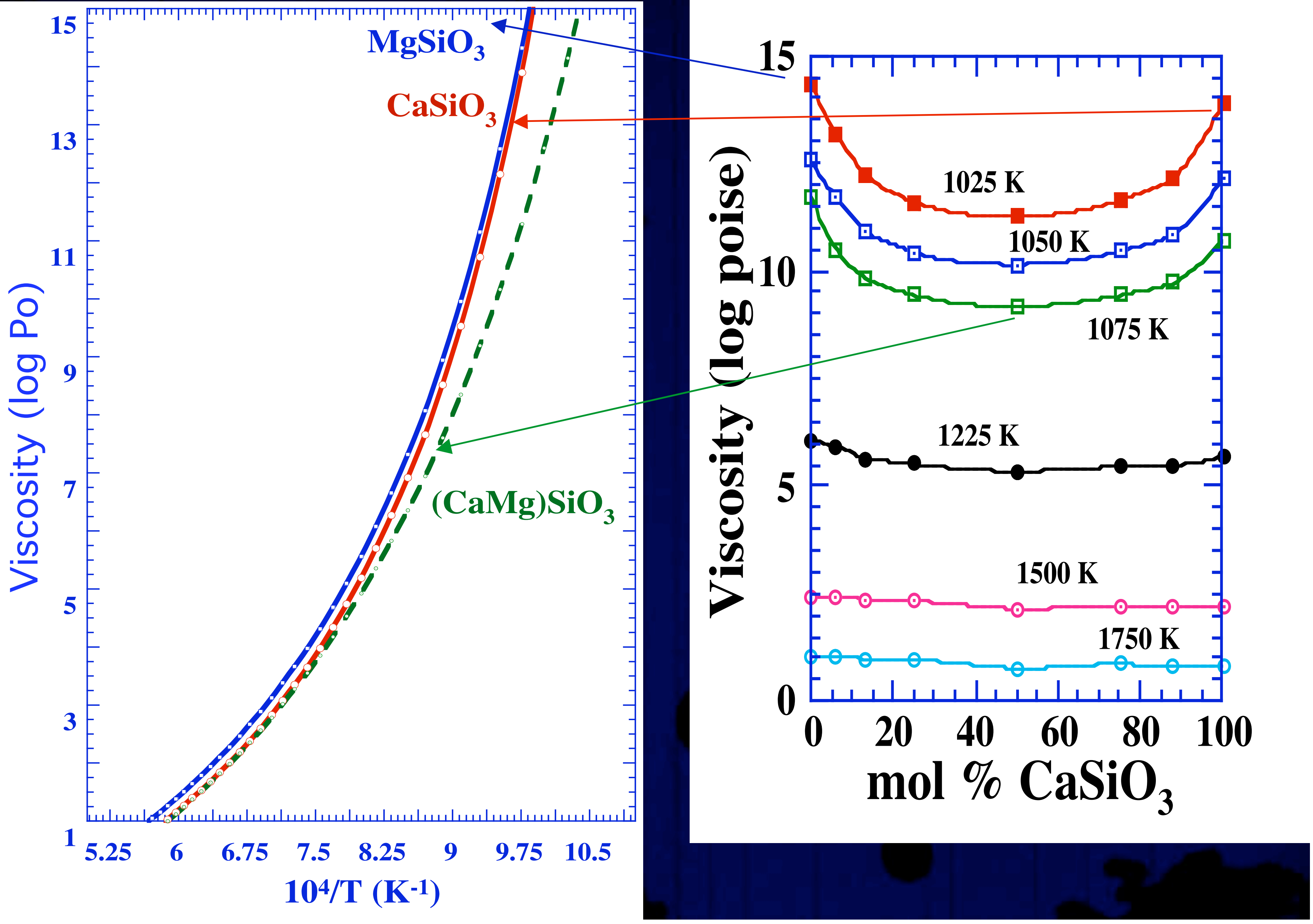


3) CMAS System

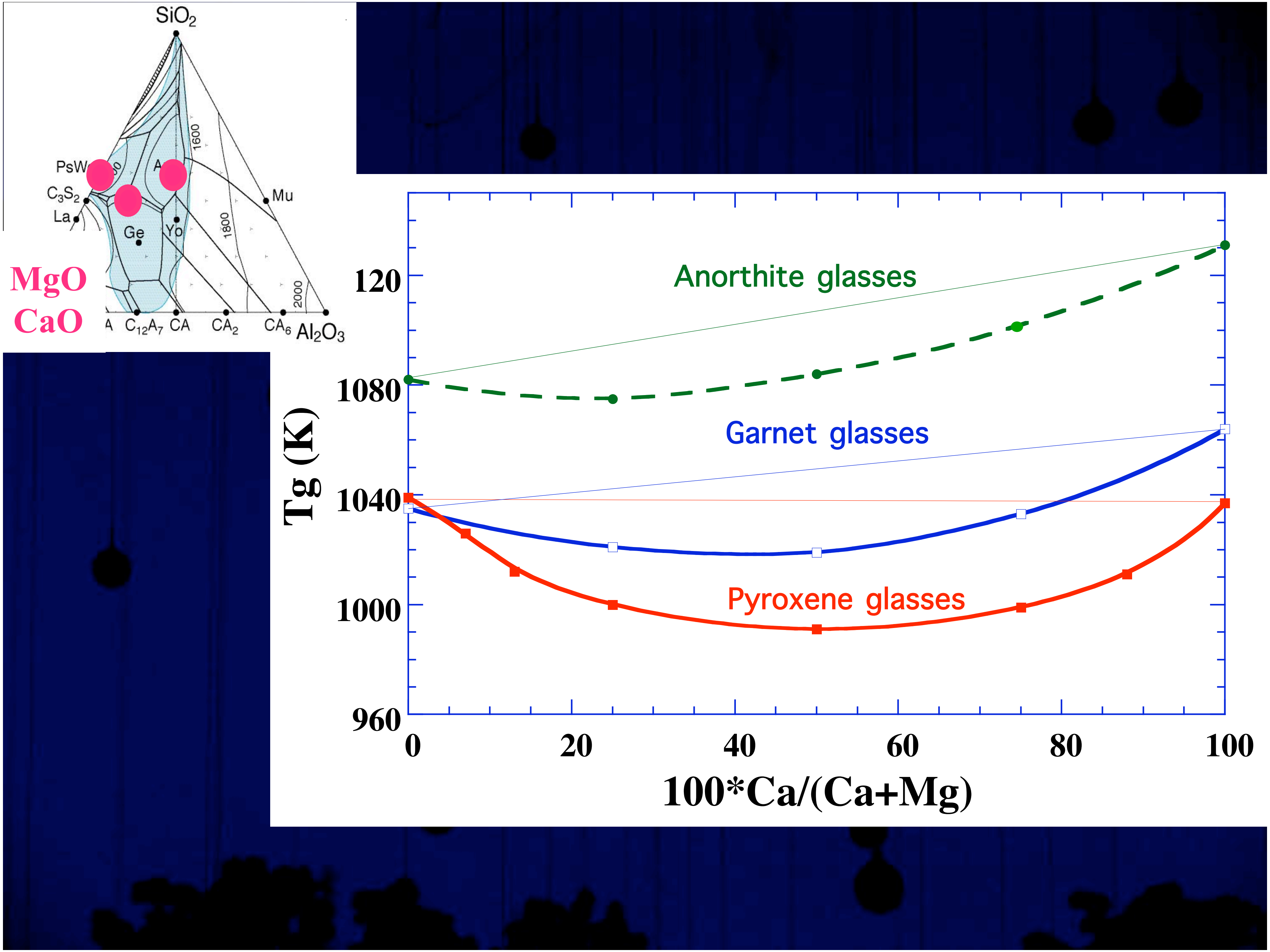
2) CAS System

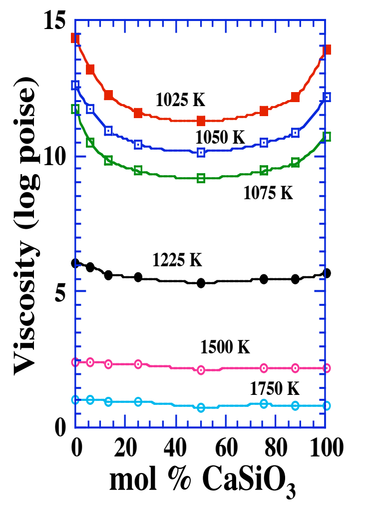


Mixing Ca/Mg



MgSiO3
CaSiO3
(CaMg)SiO3
Viscosity (log Po)
15
13
11
9
7
5
3
1
5.25
6
6.75
7.5
8.25
9
9.75
10.5
10⁴/T (K⁻¹)
Viscosity (log poise)
15
10
5
0
1025 K
1050 K
1075 K
1225 K
1500 K
1750 K
0
20
40
60
80
100
mol % CaSiO3


SiO2
PsW
C3S2
La
Ge
Yo
A
Mu
1600
1800
2000
C12A7
CA
CA2
CA6
Al2O3
MgO
CaO
Anorthite glasses
Garnet glasses
Pyroxene glasses
Tg (K)
960
1000
1040
1080
120
0
20
40
60
80
100
100*Ca/(Ca+Mg)



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

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

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

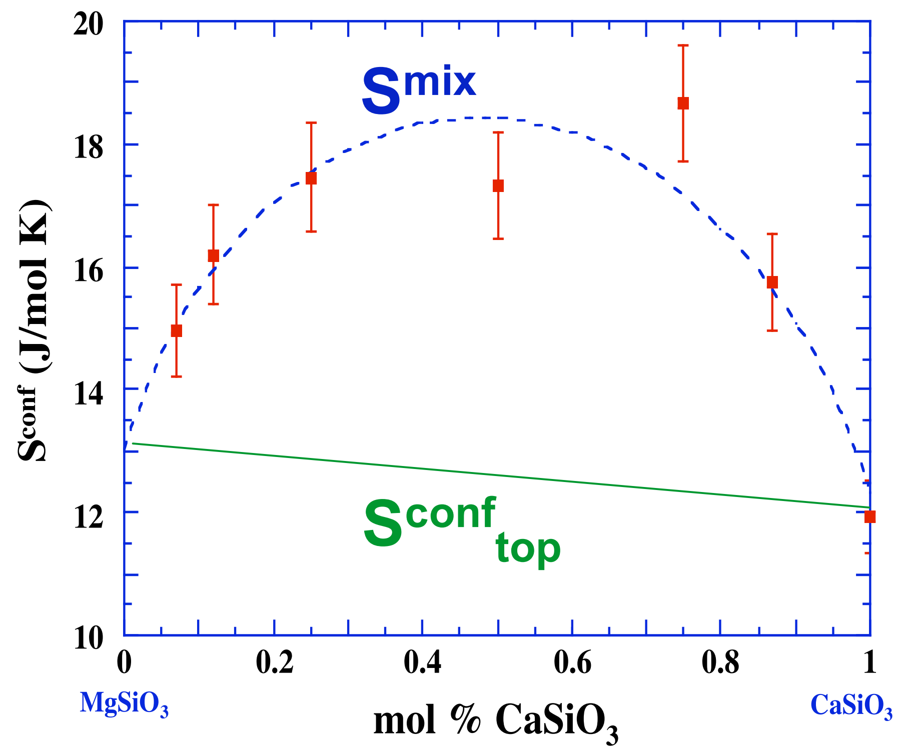
$S^{mix} = -\, nR\, X_i \ln X_i$

$X_i = Ca/(Ca+Mg)$

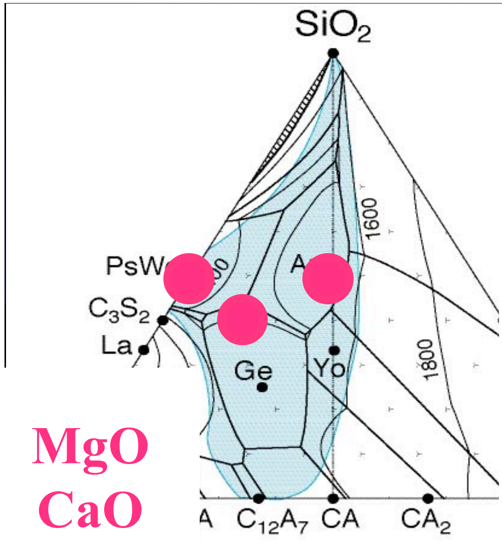
Ideal mixing => random distribution

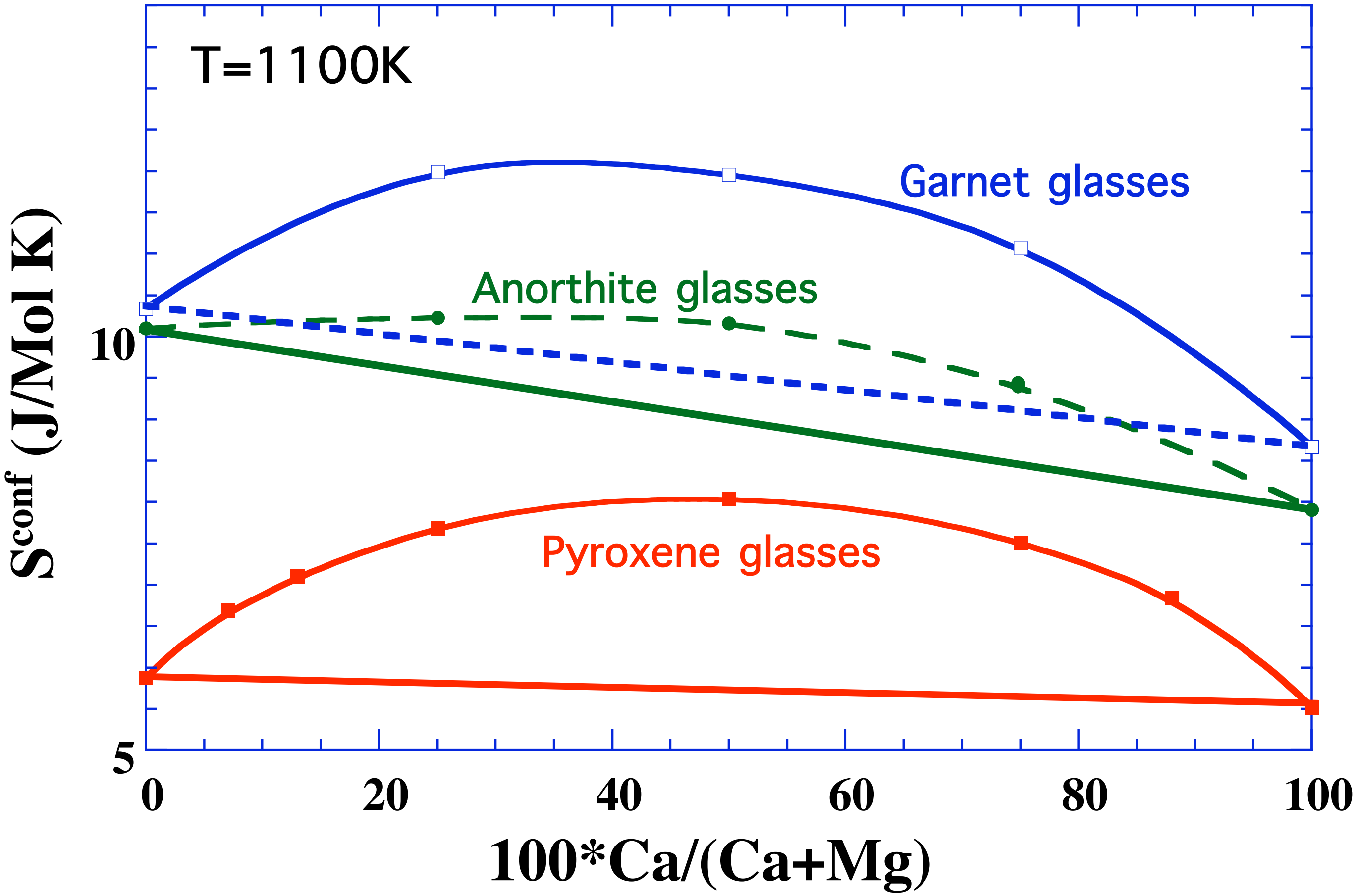
$$S^{conf}(T) = S^{conf}(T_g) + \int_{T_g}^{T} C_p{}^{conf}/T \, dT \,.$$

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

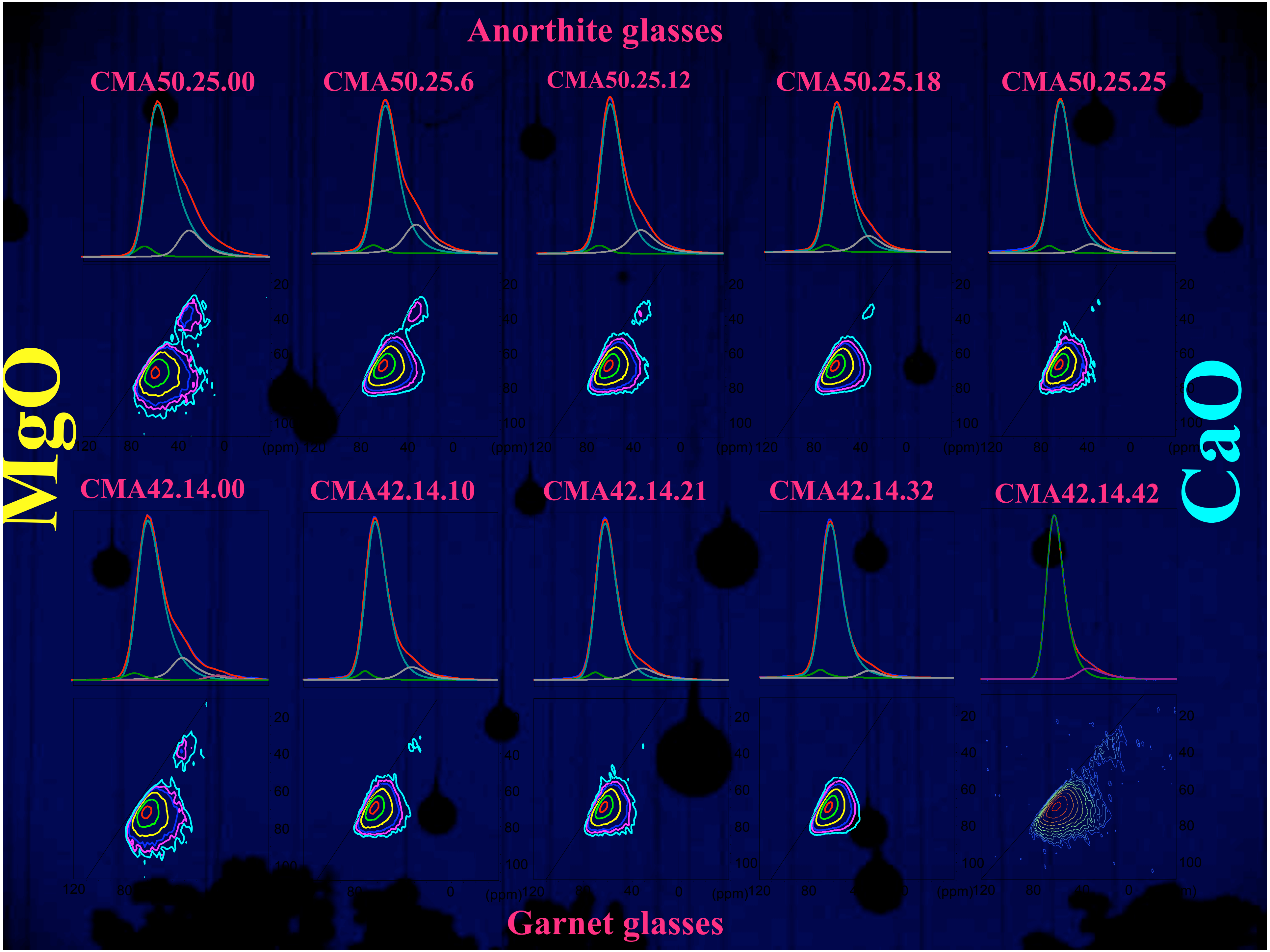


Neuville and Richet, GCA, 1991





1unit formula



Anorthite glasses
CMA50.25.00
CMA50.25.6
CMA50.25.12
CMA50.25.18
CMA50.25.25
CMA42.14.00
CMA42.14.10
CMA42.14.21
CMA42.14.32
CMA42.14.42
MgO
CaO
Garnet glasses
(ppm)

Ca/Mg-Conclusions

- No significant changes in Raman spectroscopy

- viscosity measurements show a minimum at Tg which can be explain by an ideal mixing term in the configurational entropy

- the proportion of $^{[5]}Al$ increases with Al_2O_3

Conclusions

- R=1 : substitution of Si by Al in Q^4 species see by Raman, NMR are in good agreement with viscosity and configurational entropy

- per-MO glasses: low amount of $^{[5]}Al$ and for the CAS system, Al in Q^2 species for low SiO_2 content.

- peraluminous glasses: $^{[5]}Al$ increases with Al_2O_3

- Tg increases with $^{[5]}Al$ => $^{[5]}Al$ can be a network former

- Ca/Mg mixing => $^{[5]}Al$ increases with Mg and viscosity can be predict using an ideal mixing term

- No tricluster oxygen to explain properties variation in MAS, CAS, CMAS and probably also in NAS