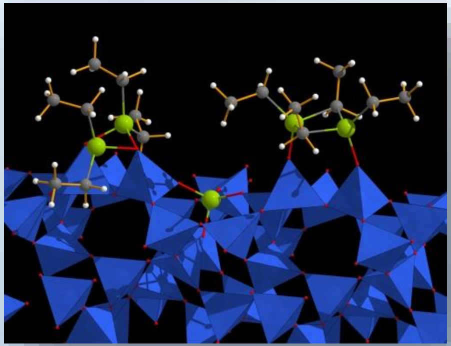
Very-High Temperature NMR of Oxide Glasses & Melts



© D. Neuville

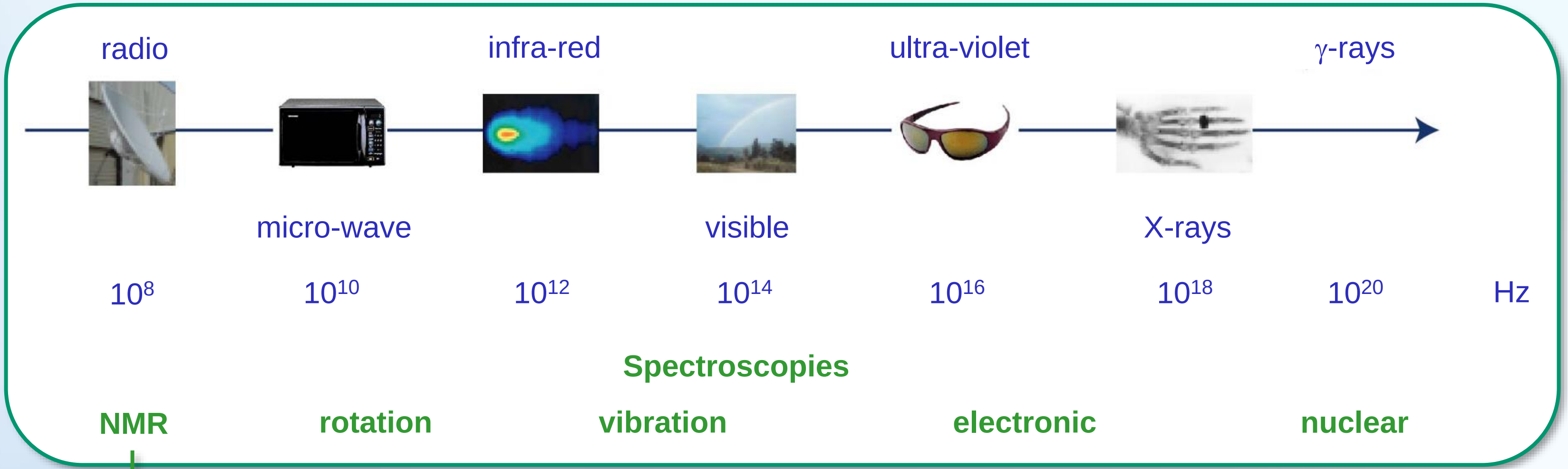
P. Florian, D. Massiot

CEMHTI-CNRS, Orléans, France

USTV ESRF School, Grenoble, November 2019

NMR & Motion…

Time Scales



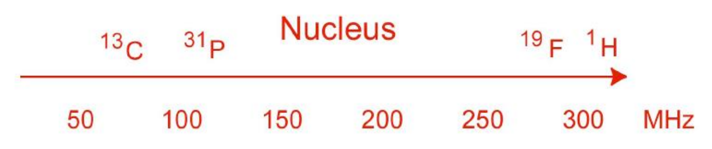
radio
infra-red
ultra-violet
γ-rays

micro-wave
visible
X-rays

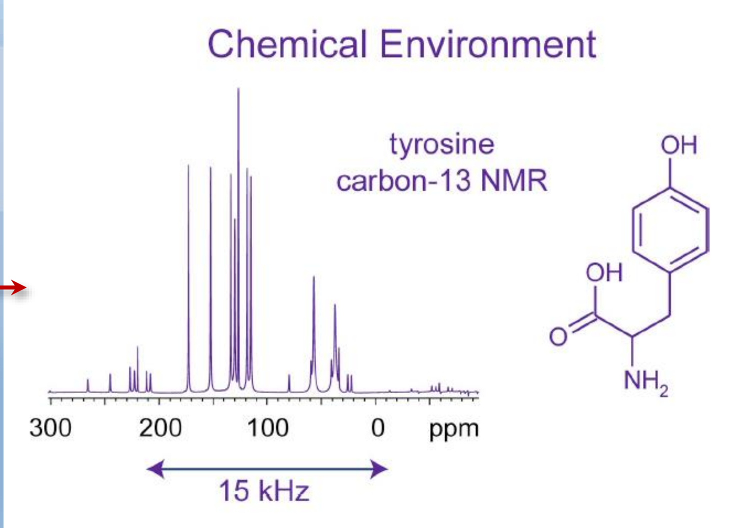
10^8 10^{10} 10^{12} 10^{14} 10^{16} 10^{18} 10^{20} Hz

Spectroscopies

NMR **rotation** **vibration** **electronic** **nuclear**



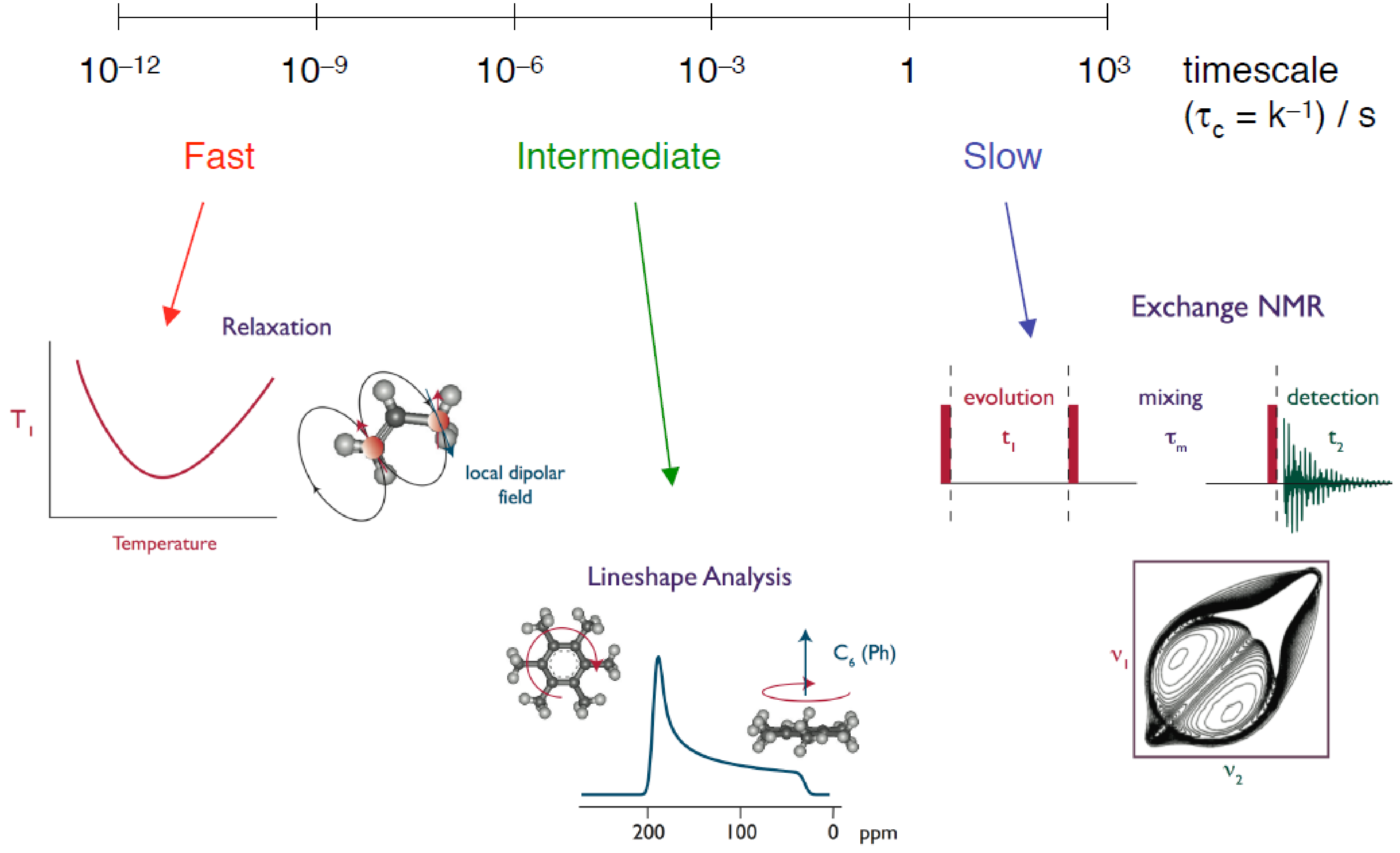
Nucleus



Chemical Environment

tyrosine
carbon-13 NMR

Timescales


10^{-12} 10^{-9} 10^{-6} 10^{-3} 1 10^{3} timescale ($\tau_c = k^{-1}$) / s

Fast

Intermediate

Slow

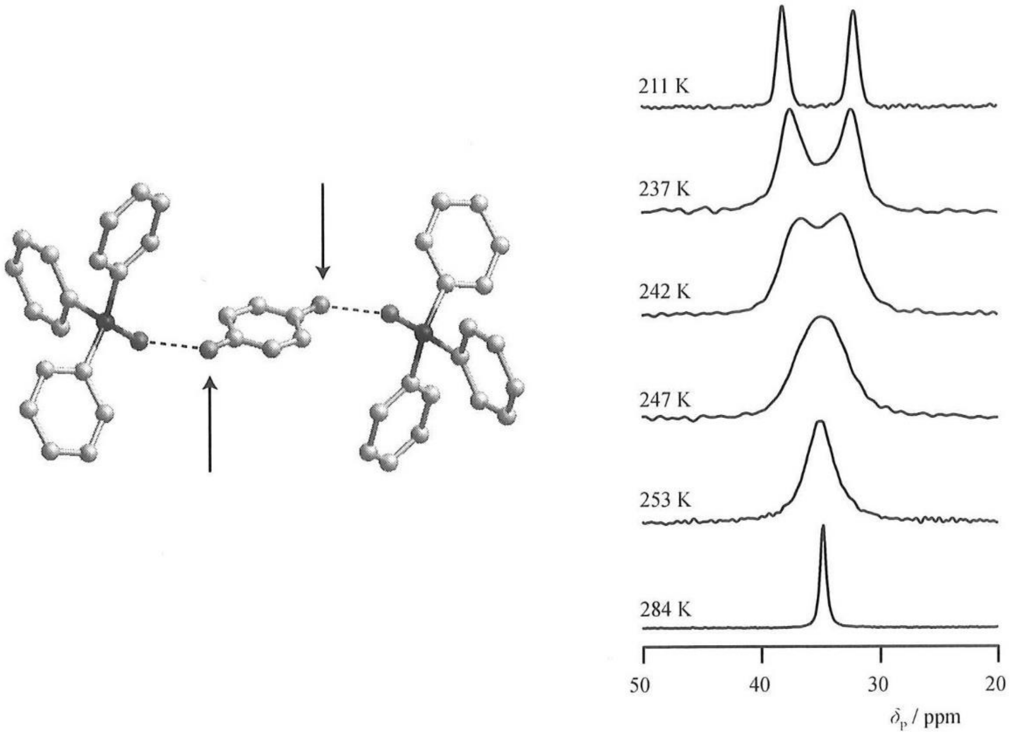
Relaxation

Lineshape Analysis

Exchange NMR

Effect of Dynamic « Disorder »

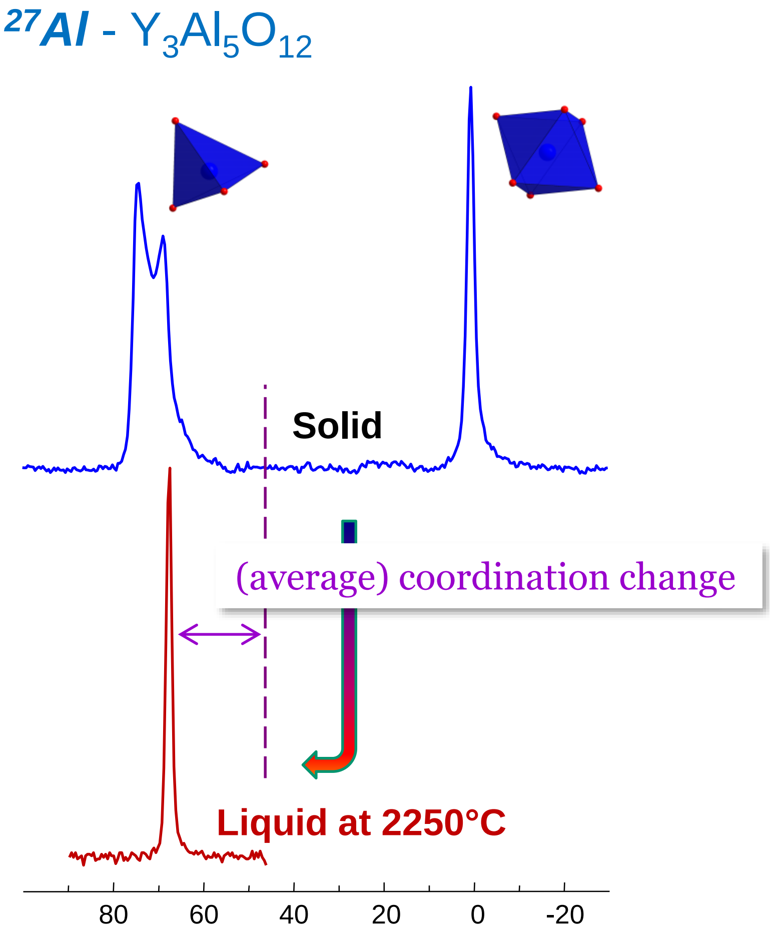
Effect of Mobility



^{31}P spectra of 3:2 adduct of phenol and triphenylphosphine oxide

NMR & Melts: What Can We Learn?

"Structure" of the Melt



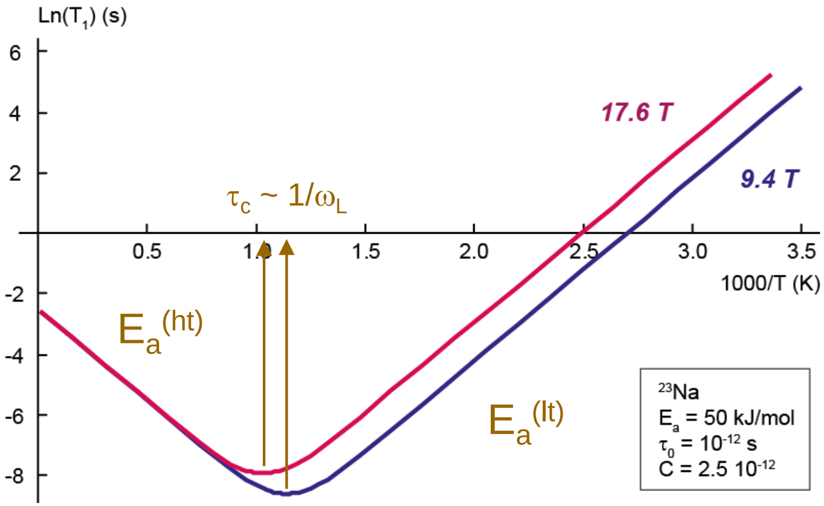
High-Temperature Dynamics

- ➡ "Brownian motion in a liquid or noncrystalline solid" (autocorrelation function α exp(-t/τ_c))
- ➡ Relaxation dominated by the fluctuation of the quadrupolar interaction

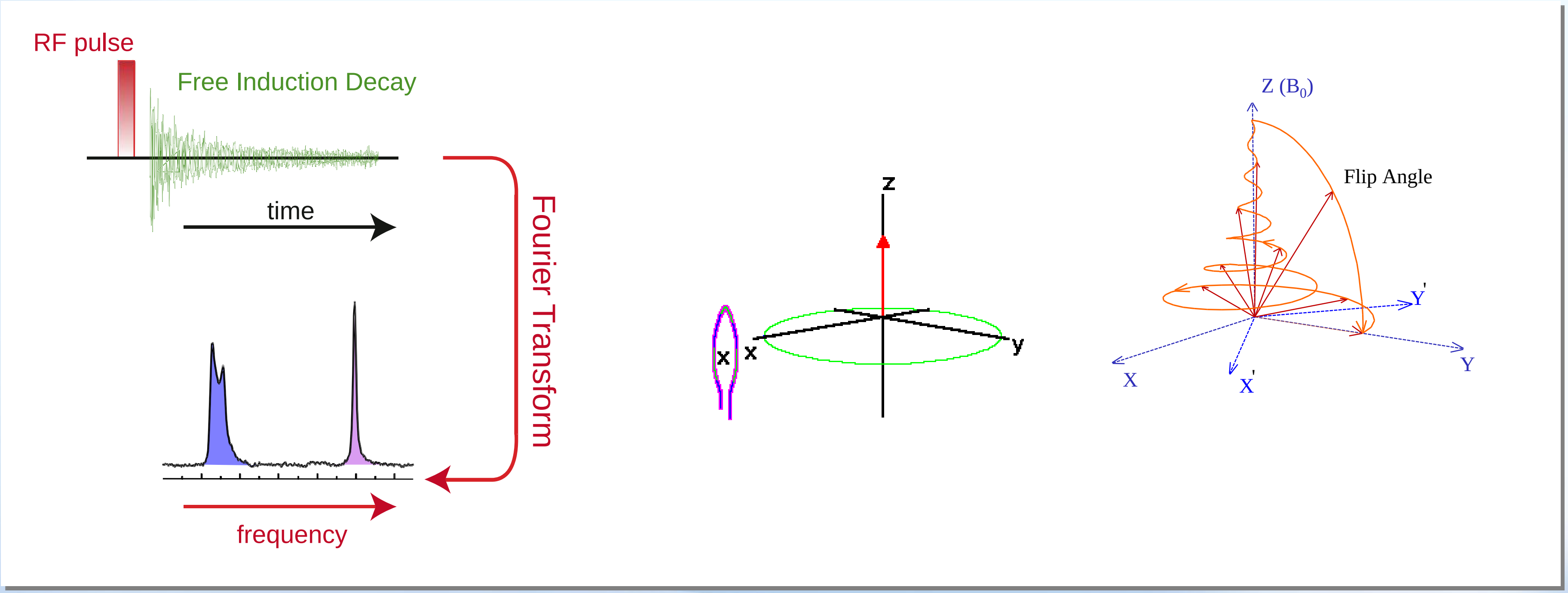
$$1/T_1 = C\left(\frac{\tau_c}{1+(\omega\tau_c)^2} + \frac{4\tau_c}{1+(2\omega\tau_c)^2}\right)$$

- ➡ Correlation time thermally activated

$$\tau_c = \tau_0 \exp\left(\frac{E_a}{kT}\right)$$



Relaxation



Two types of relaxation process:

- **Spin-lattice relaxation**. Involves exchange of energy with the lattice and requires transitions between Zeeman levels.
- **Spin-spin relaxation**. Involves loss of the x,y-components of the magnetization. Does not require energy to be exchanged with the surroundings and does not necessarily result in changes in the populations in the nuclear spin energy levels.

In Solids:

$$T_1 \neq T_2 \neq T_2^*$$

The Autocorrelation Function

→ Relaxation is caused by fluctuating local magnetic fields

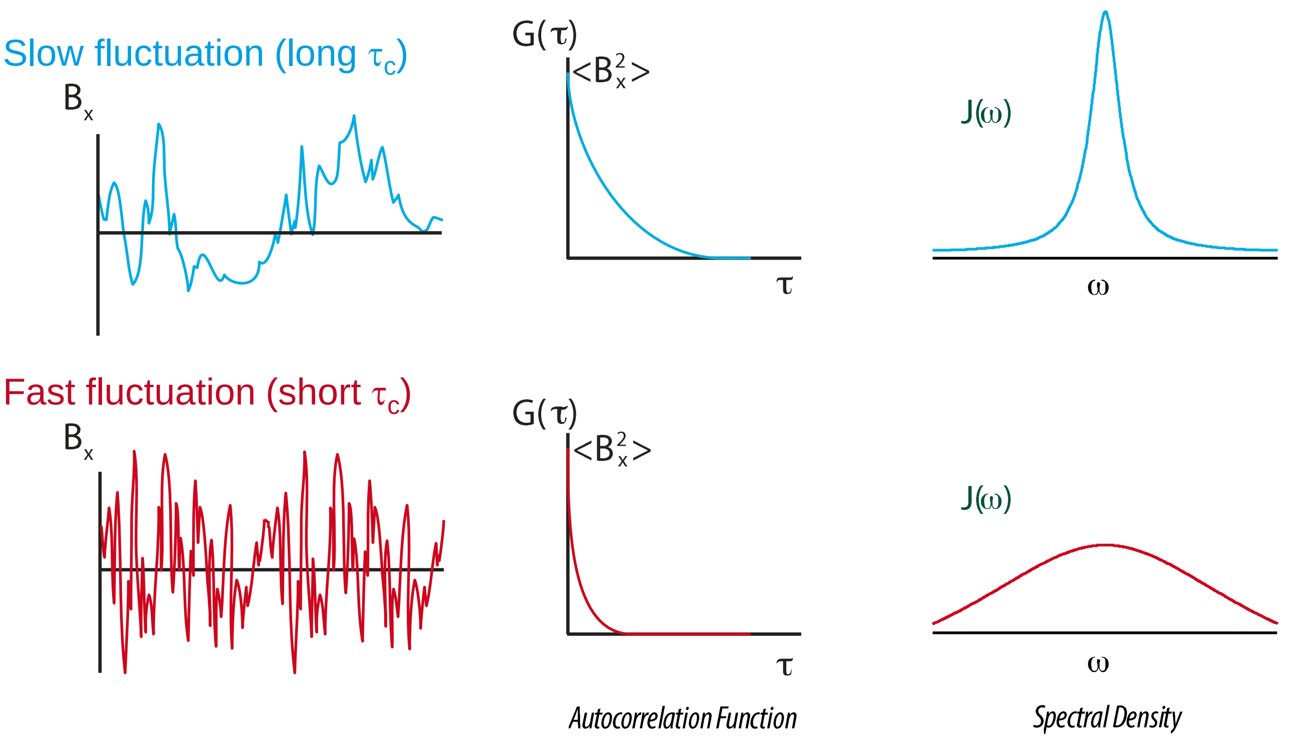
→ Fluctuations at the Larmor frequency cause spin-lattice relaxation

→ Local fields which are almost static are effective for the spin-spin relaxation.

The autocorrelation function of the local field descibes how rapidly the field fluctuate

$$G(\tau) = \langle B_x(t) B_x(t+\tau) \rangle \neq 0$$

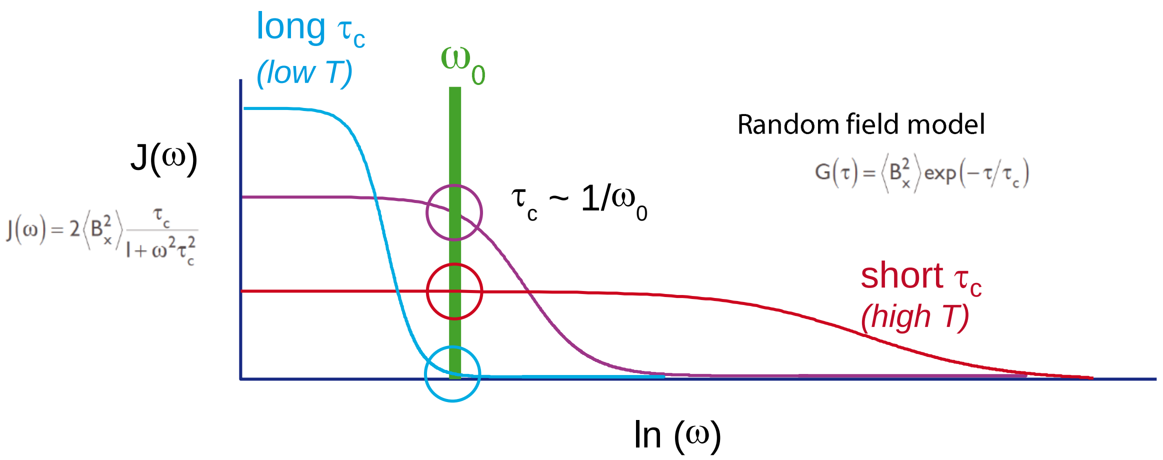
$$J(\omega) = 2\int_0^\infty G(\tau)\exp(-i\omega\tau)d\tau$$

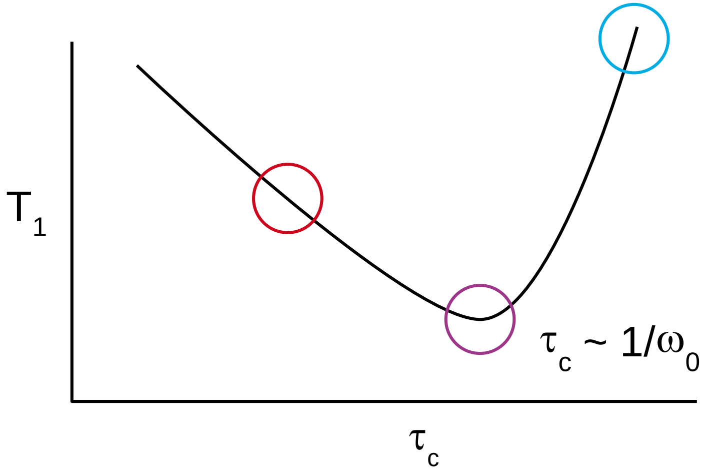


The Spectral Density

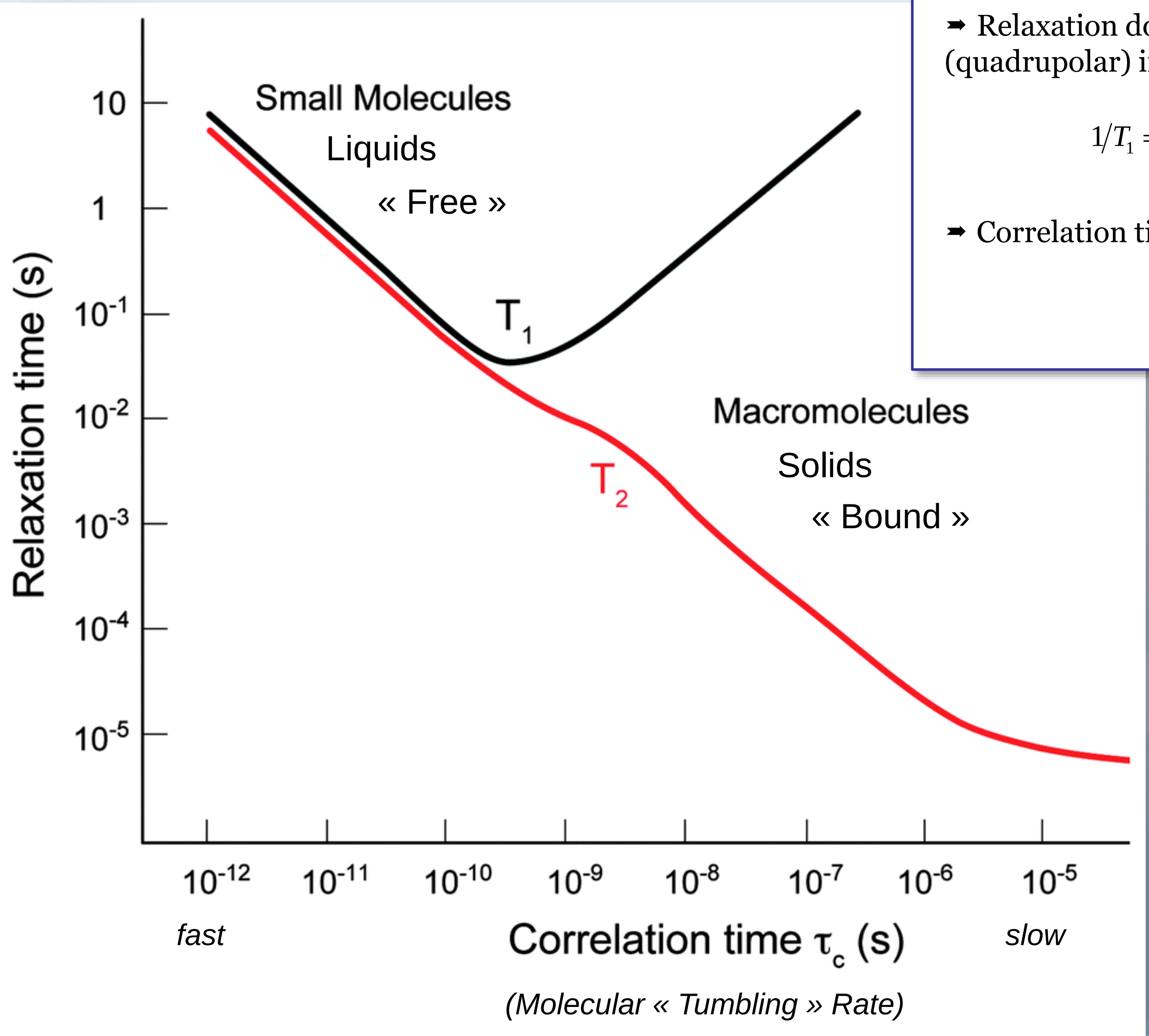
→ The highest the spectral density at a given frequency, the more efficient the relaxation

→ A T_1 minimum may appear as a function of temperature





T_1 and T_2 Relationships



- “Brownian motion in a liquid or noncrystalline solid” (autocorrelation function $\alpha \exp(-t/\tau_c)$)
- Relaxation dominated by the fluctuation of the (quadrupolar) interaction

$$1/T_1 = C\left(\frac{\tau_c}{1+(\omega\tau_c)^2} + \frac{4\tau_c}{1+(2\omega\tau_c)^2}\right)$$

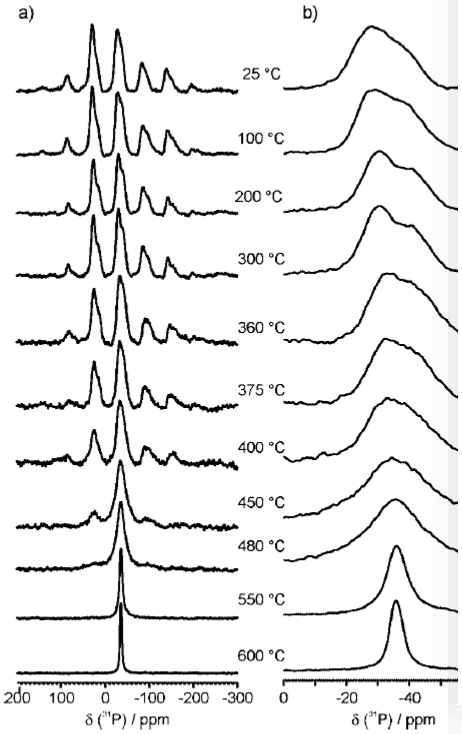
- Correlation time thermally activated

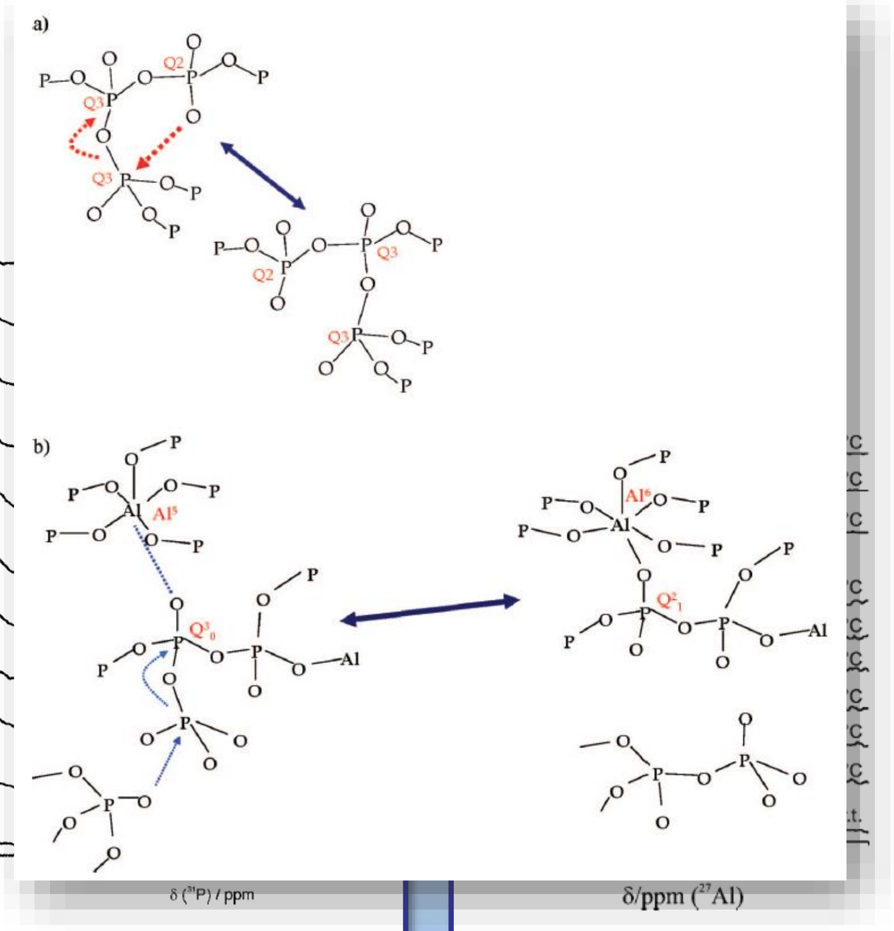
$$\tau_c = \tau_0 \exp\left(\frac{E_a}{kT}\right)$$

NMR around T_g

Alumino-Phosphate Glasses

^{31}P MAS : $30K_2O \cdot xAl_2O_3 \cdot (70-x)P_2O_5$

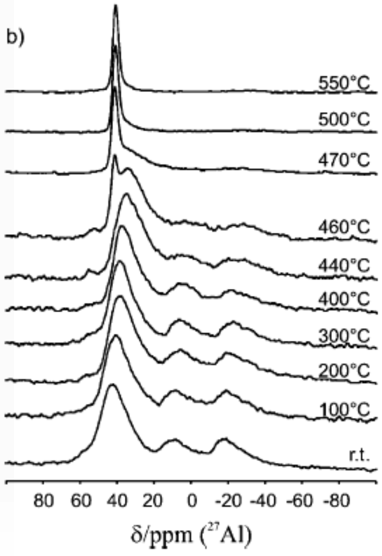




$\nu_R = 4.50kHz, B_0 = 4.7T$

Wegner S, J Phys Chem B **2009** *113* 416-425

^{27}Al MAS : $50K_2O \cdot xAl_2O_3 \cdot (50-x)P_2O_5$



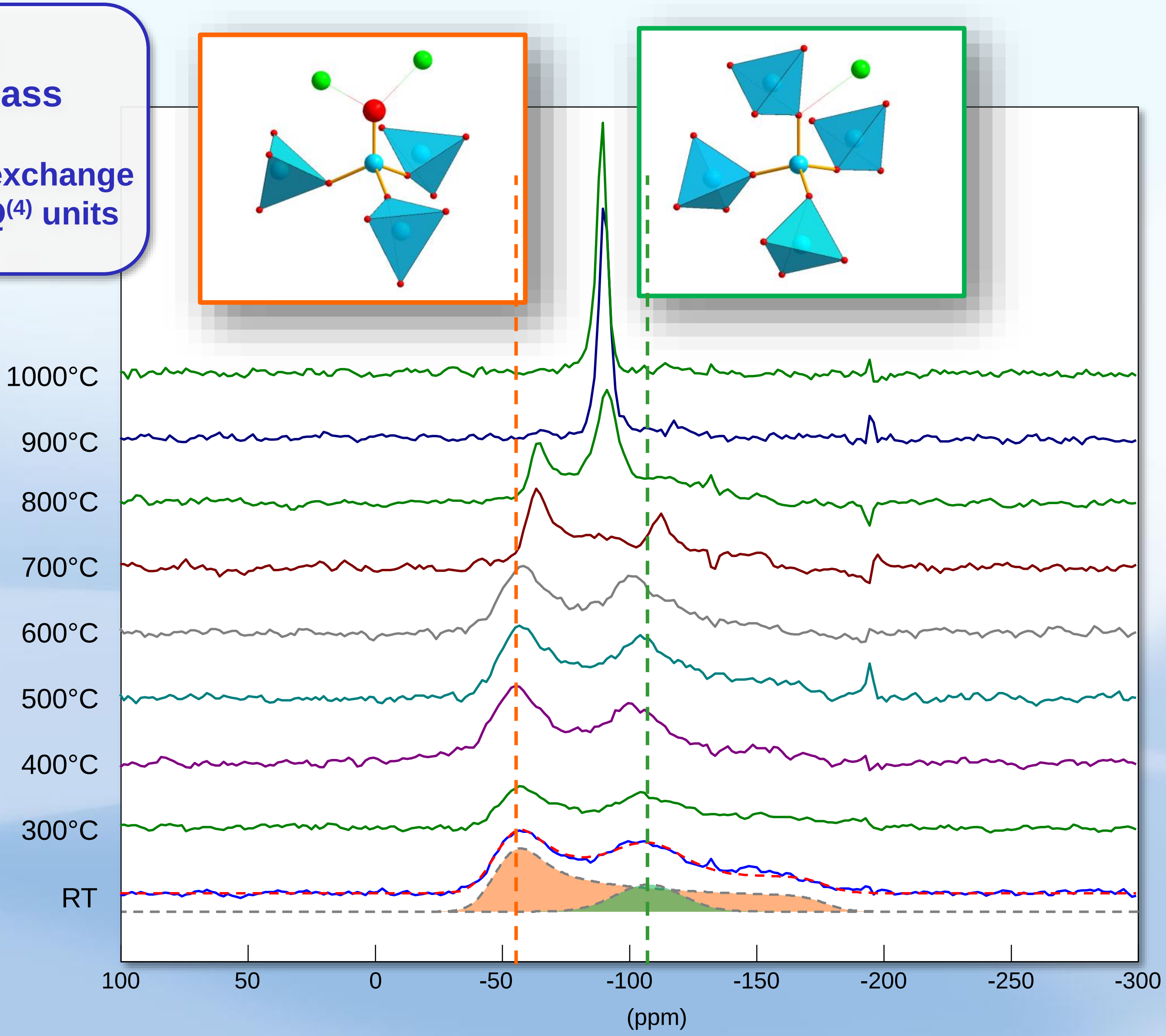
$\nu_R = 4.50kHz, B_0 = 7.0T$

van Wullen, J Phys Chem B **2007** *111* 7529-7534

The Silicate Glass Transition Dynamics

^{29}Si HT NMR
$5SiO_2 \cdot 2Na_2O$ glass

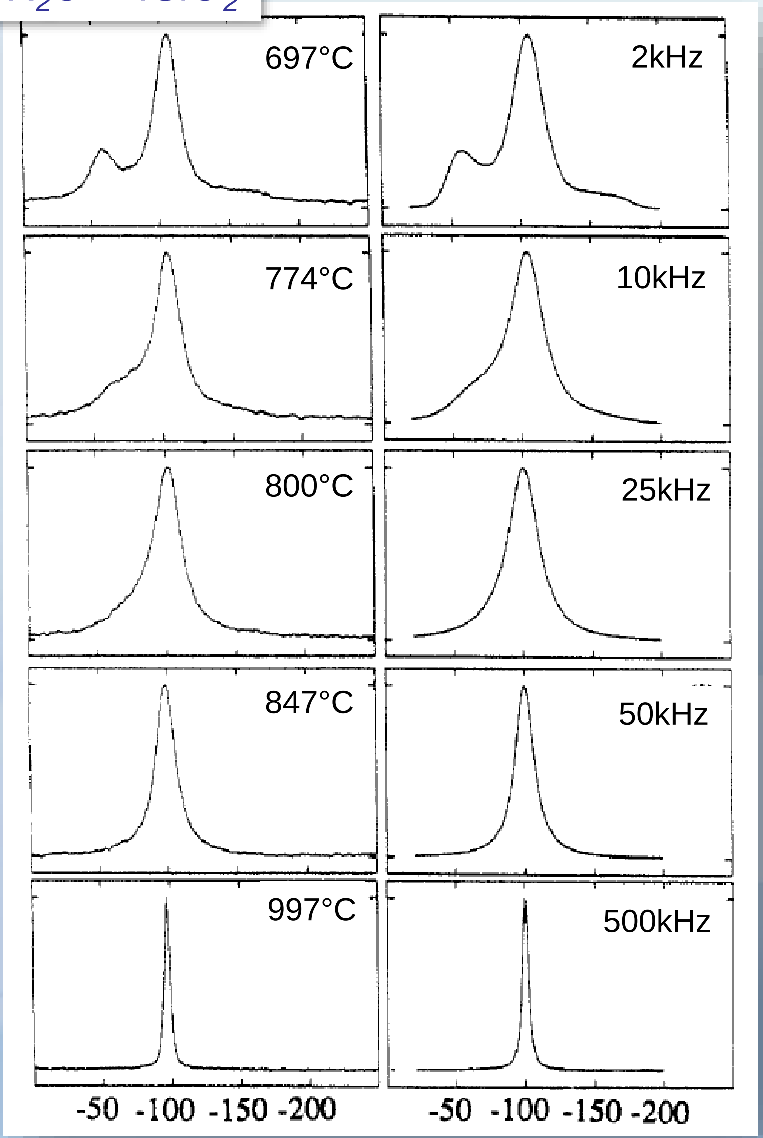
Progressive chemical exchange between the $Q^{(3)}$ and $Q^{(4)}$ units

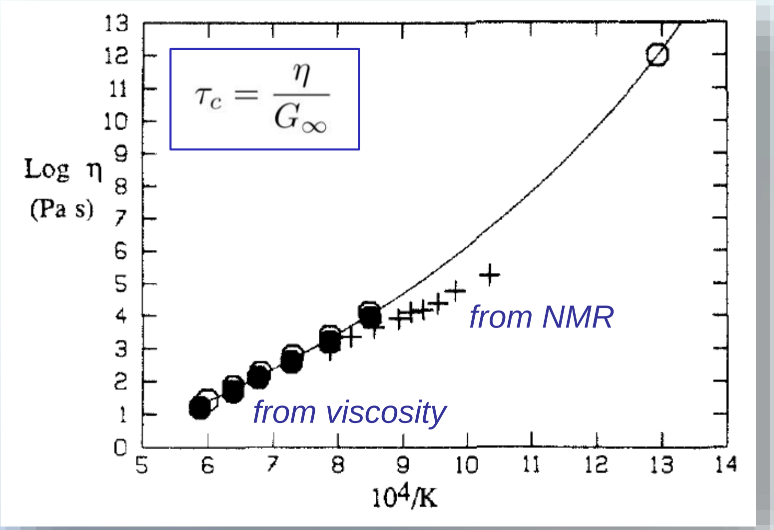


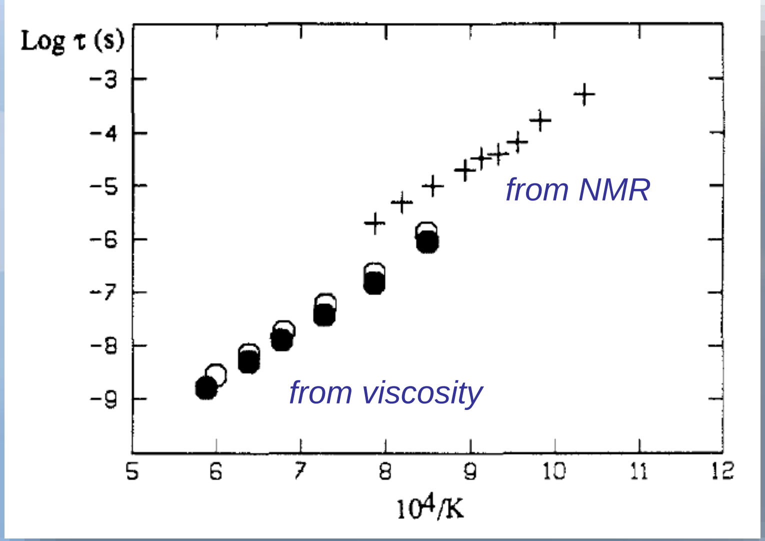
Charpentier, private comm. (2010)

The Silicate Glass Transition Dynamics

$K_2O \bullet 4SiO_2$





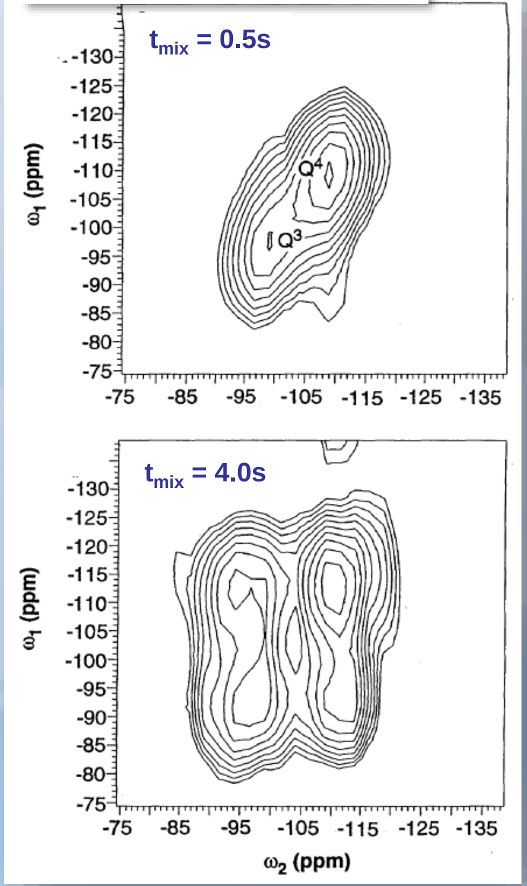


Farnan & Stebbins, J. Amer. Chem. Soc. **1990** *112* 32-38

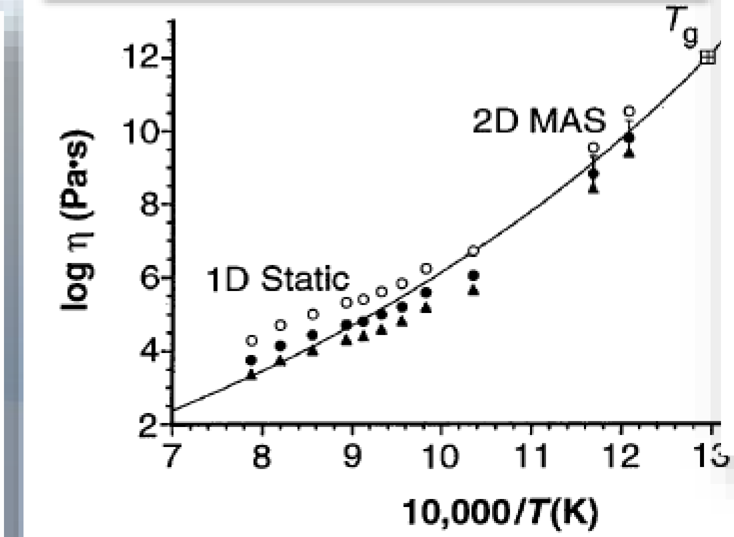
Probing Slow Motions in Silicates

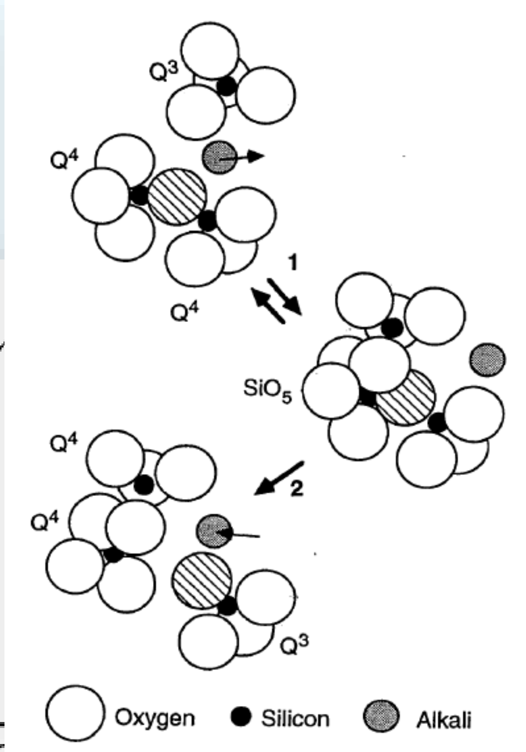
Georges, Am Miner 1995 80 878-884 [^{23}Na albite]
Stebbins, J. Phys Chem Miner 1989 16 763-766 [^{23}Na nepheline]
Farnan, Science 1994 265 1206-1209 [^{29}Si silicates]

$K_2{}^{29}Si_4O_9$ T=550°C
Exchange time ~ 3 ± 2 s



Timescales for microscopic vs macroscopic flow





Solid curve = bulk viscosity
Open circles = exchange times from NMR
Solid triangles = viscosity from NMR (Eyring)
Solid circles = from Stokes + Einstein-Smolukowski

$$\boldsymbol{\tau}_s = \eta_s / G_\infty$$

$$\eta = 2k_B T \boldsymbol{\tau} / d^3$$

$$D = k_B T \boldsymbol{\tau} / 3\pi a d^2$$

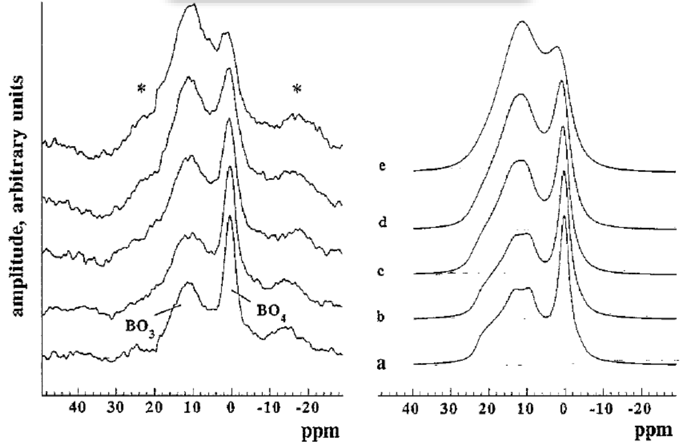
$$D = d^2 / 2\tau$$

Farnan and Stebbins, Science **1994** *265* 1206-1209

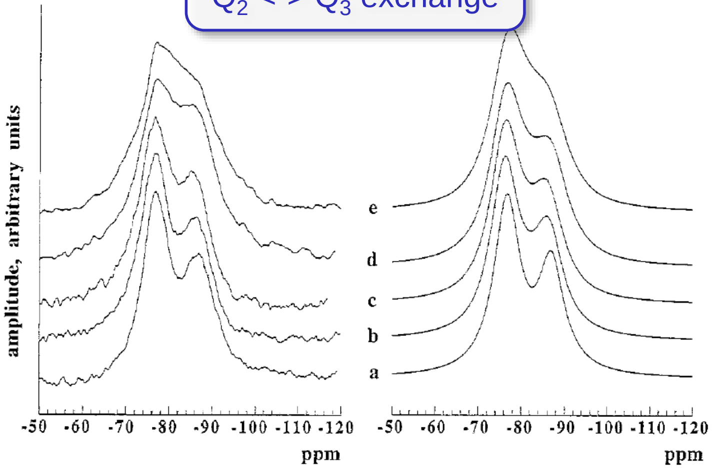
The Boro-Silicate Decoupling Case

44.5 Na_2O • 11 B_2O_3 • 44.5 SiO_2

^{11}B MAS NMR:
BO_3 <-> BO_4 exchange

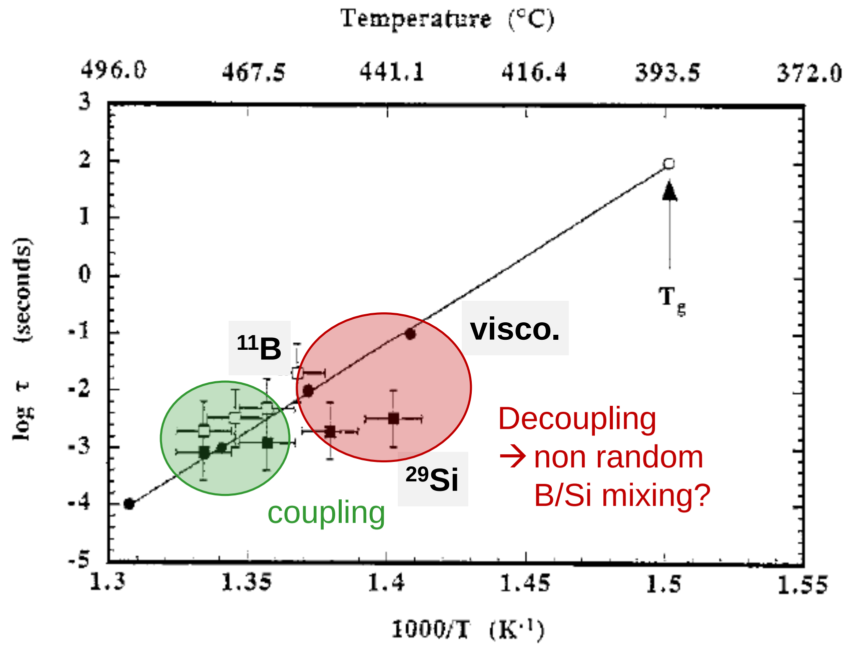


^{29}Si MAS NMR:
Q_2 <-> Q_3 exchange



Line Widths as Transverse Relaxation Time

- ☞ At high T: coupling between B-O and Si-O bond breaking, with oxygen ions moving into and out of the coordination polyhedra of B and Si with similar average rate.
- ☞ At low T: most Si-O bond breaking and site exchange is taking place at frequencies up to 50 times faster than the timescale of viscosity.



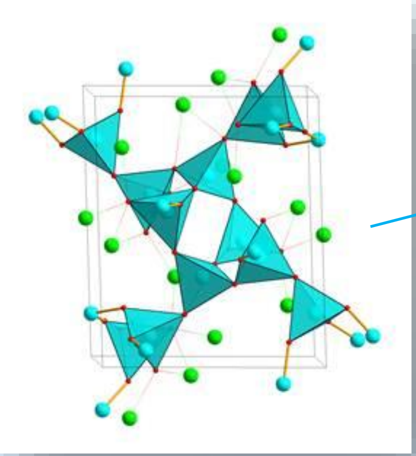
Decoupling
→ non random
B/Si mixing?

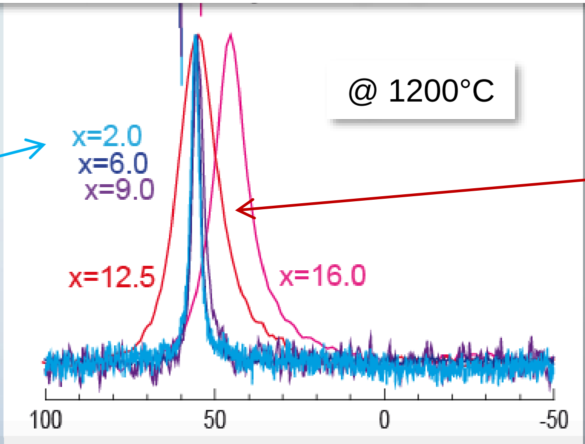
Inverse of species exchange rate data derived from ^{11}B and ^{29}Si data compared with shear relaxation times calculated from viscosity (Maxwell relation).

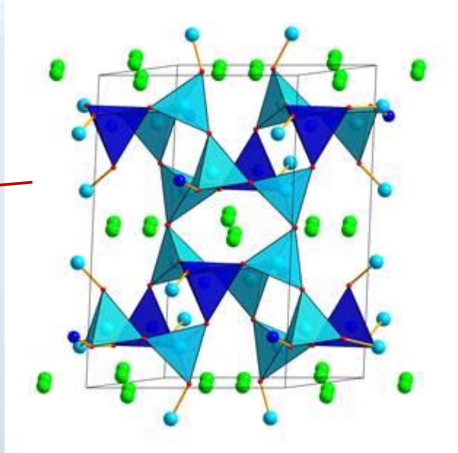
Stebbins et al., J. Non Cryst. Solids **1998** *224* 80-85

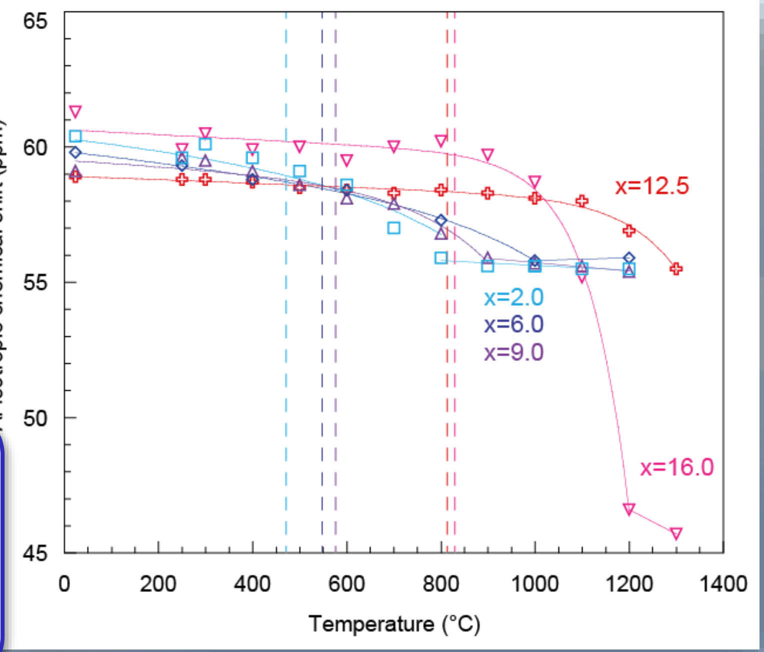
$Na_2Si_3O_7$–$NaAlSi_3O_8$: ^{27}Al NMR

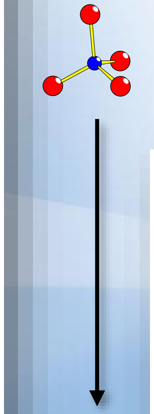
(25-x) Na_2O • x Al_2O_3 • 75 SiO_2

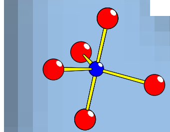


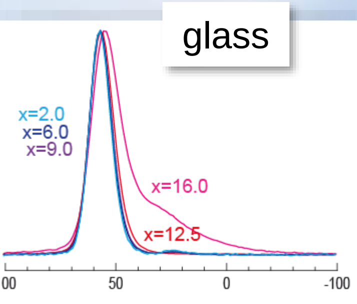










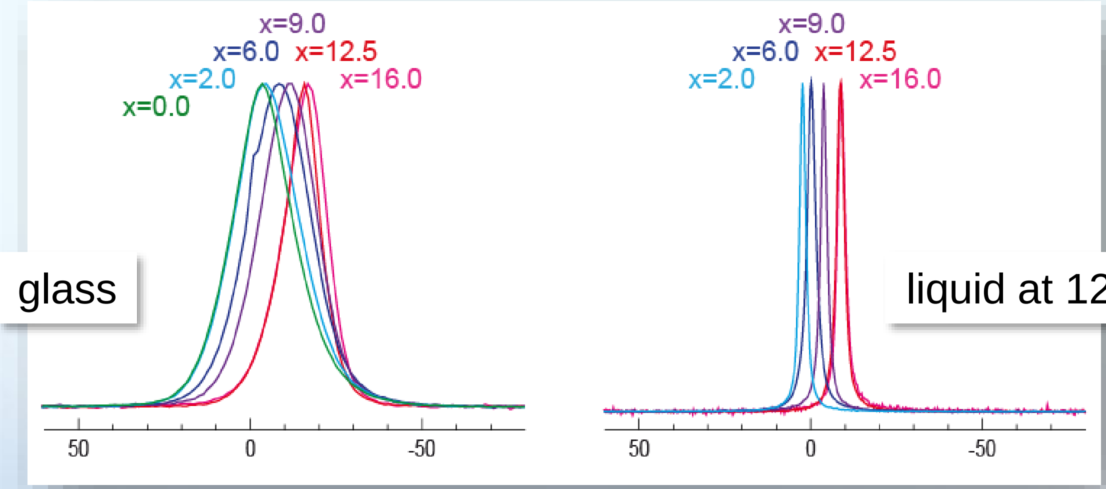


^{27}Al HT NMR
Na_2O • Al_2O_3 • SiO_2 glasses

Chemical exchange between AlO_5 and AlO_4 units

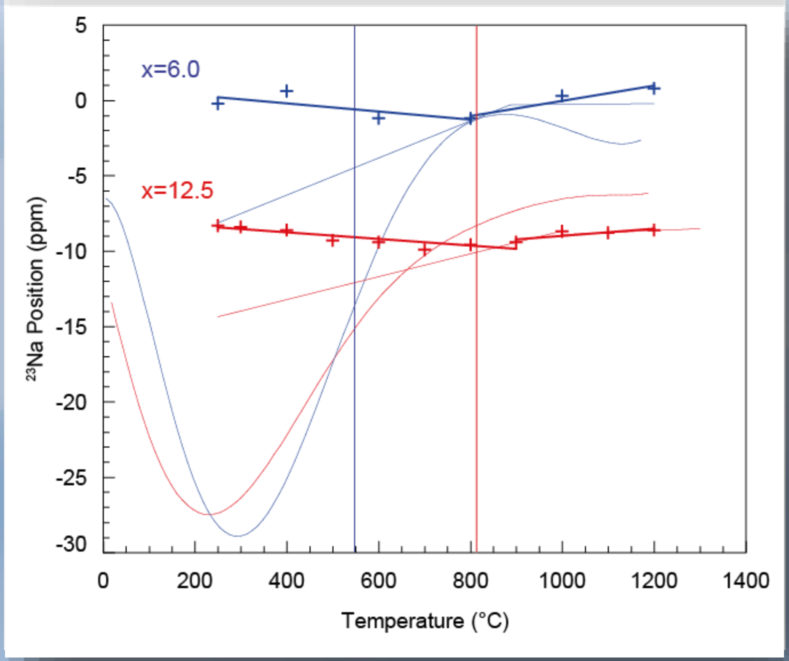
LeLosq et al., Geochim. Cosmochim. Acta **2014** *126* 495-514

^{23}Na Position vs Temperature



glass

liquid at 1200°C



Increase of
Average d(NaO)

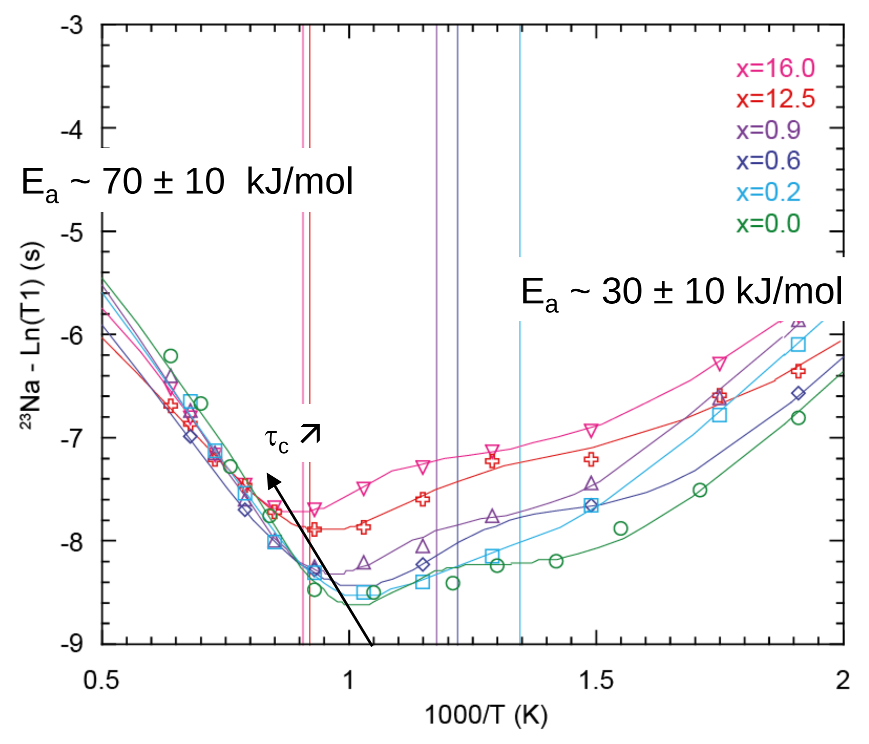
LeLosq et al., private communication

George et al., SSNMR 1997 10 9-17

^{23}Na & ^{27}Al Relaxation Times

(25-x) Na_2O • x Al_2O_3 • 75 SiO_2

Na



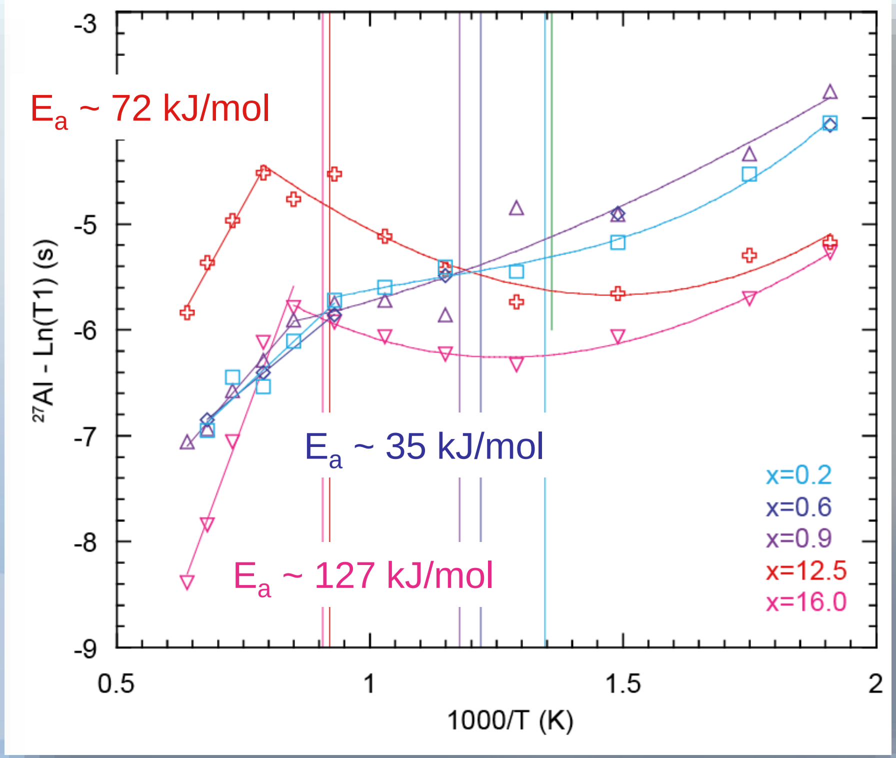
liquid

$E_a(^{24}Na)$ = 57 ± 12kJ/mol

« solid »

Jump diffusion

Al



liquid

Effects of polymerisation

« solid »

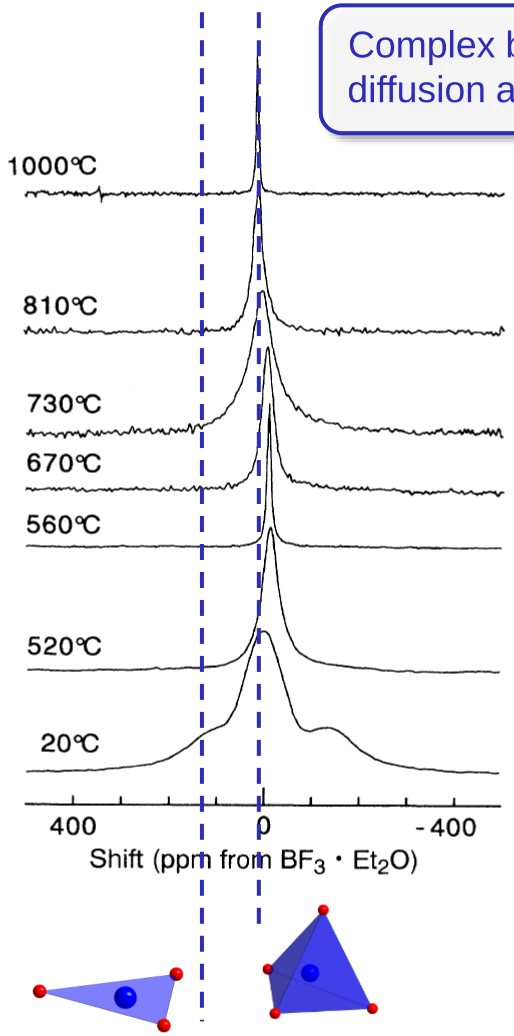
Na diffusion

LeLosq et al., private communication

NMR in the Molten State

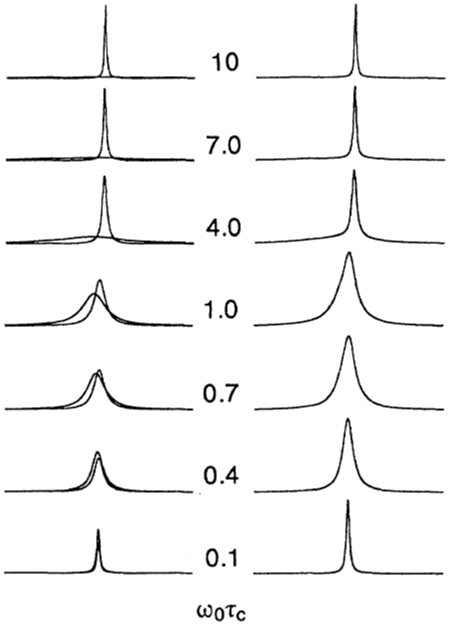
The Borate Liquids Dynamics

$0.33\ Na_2O \cdot 0.67\ B_2O_3$



Complex behavior mixing rotational diffusion and NMR dynamics effects

Line Widths as Transverse Relaxation Time



Isotropic rotational diffusion

$$\langle S_x\rangle + i\langle S_y\rangle = \langle S_z\rangle^T i\exp[-i\omega_0(t-t_0)]$$

$$\times[\tfrac{3}{5}\exp(-b_1 t)+\tfrac{2}{5}\exp(-b_2 t)]$$

$$b_1 = C(J_0+J_1+iQ_1)$$

$$b_2 = C(J_1+J_2-iQ_1+iQ_2)$$

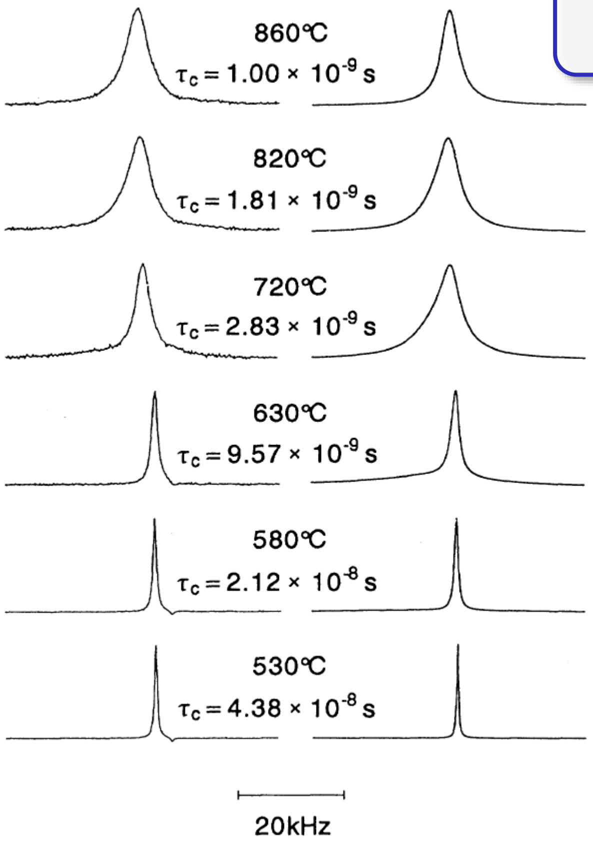
Hyperfine second-order dynamic quadrupolar shift

$$Q_n = n\omega_0\tau_c^2(1+n^2\omega_0^2\tau_c^2)^{-1}$$

Inagaki et al., Phys. Rev. B **1993** *47* 674-680

The Borate Liquid Dynamics

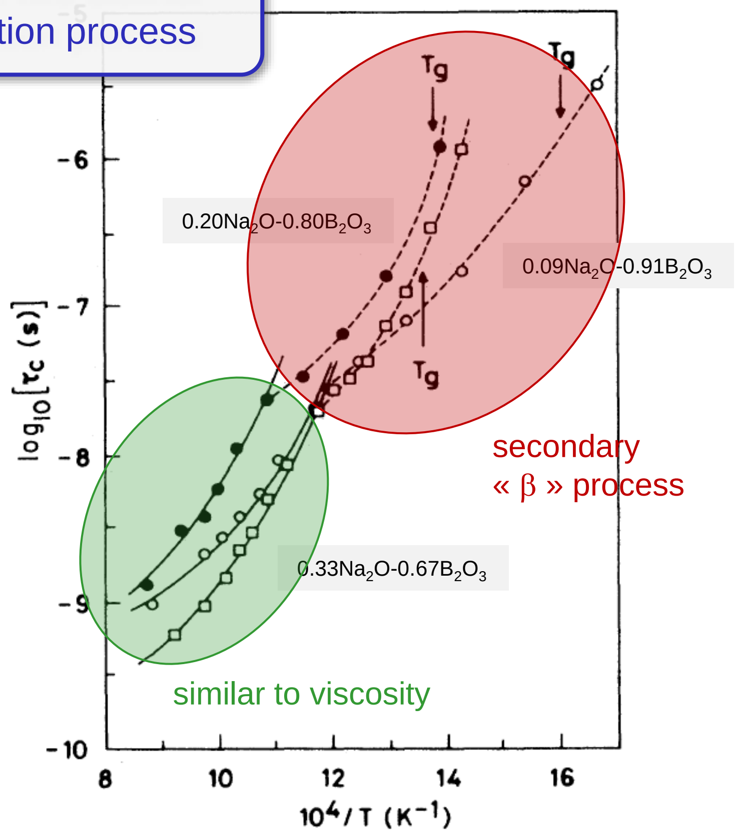
$0.09\ Na_2O \bullet 0.91\ B_2O_3$



Experimental (left) ^{11}B line shapes and calculated (right) using the parameters of the longitudinal relaxation data

Line Widths as Transverse Relaxation Time

Crossover between two distinct orientational relaxation process



secondary « β » process

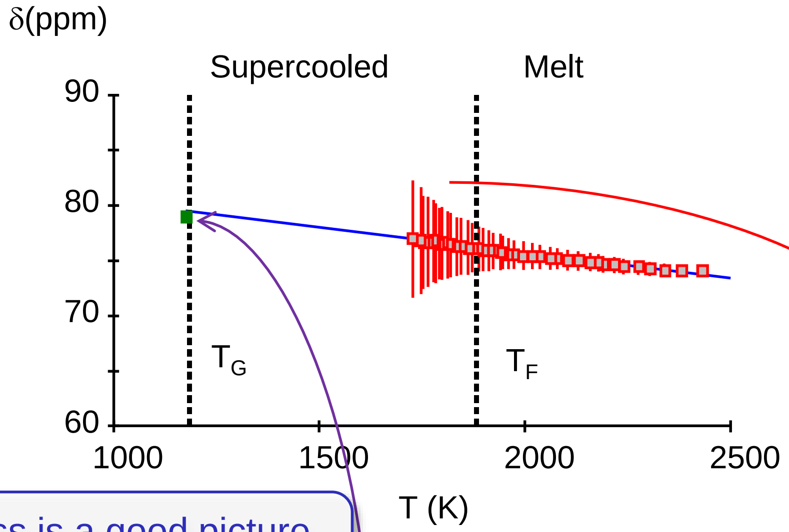
similar to viscosity

^{11}B NMR correlation times obtained from longitudinal data. The solid lines are Vogel-Tamman-Fulcher fits for the α orientational-relaxation processes (viscosity). The dashed line represents β processes (restricted BO_3 rotations).

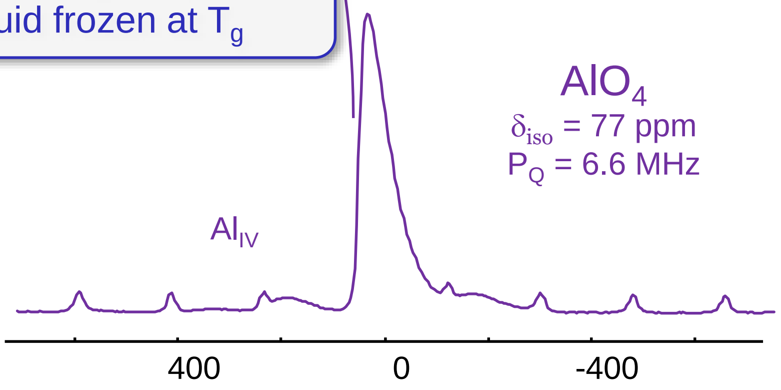
Inagaki et al., Phys. Rev. B **1993** *47* 674-680

From Liquid to Glass: $CaAl_2O_4$

Structure



Glass is a good picture of liquid frozen at T_g



Dynamics

Extreme narrowing

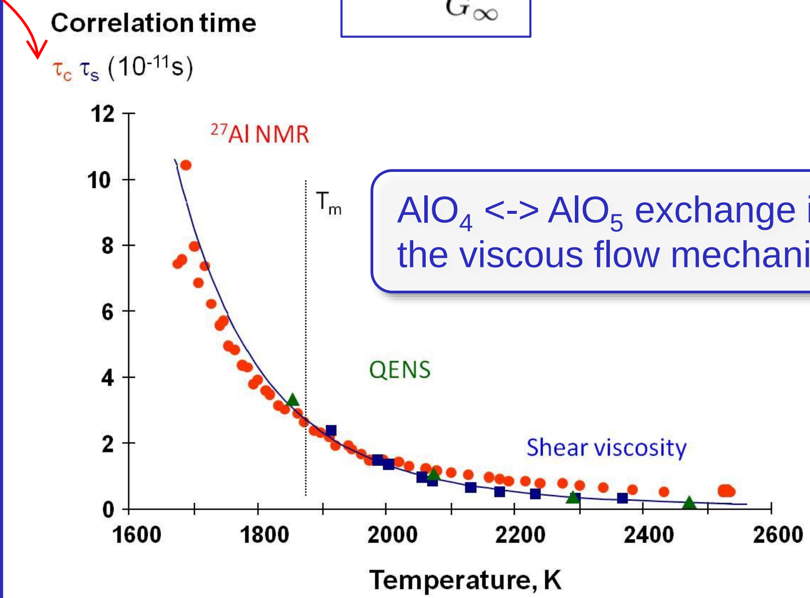
$$T_1 = \frac{1}{\pi \Delta\nu_{1/2}}$$

Quadrupolar Relaxation

$$\frac{1}{T_1} = \frac{3}{10}\pi^2 \frac{2I+3}{I^2(2I-1)} \overline{C}_{Q\eta}^2 \tau_c^2$$

Shear Viscosity

$$\tau_c = \frac{\eta}{G_\infty}$$



AlO_4 <-> AlO_5 exchange is the viscous flow mechanism

Massiot et al., J. Phys. Chem. **1995** *99* 16455-16459

Kozally et al., Phys. Status Solidi C **2011** *8* 3155-3158
Neuville et al., Rev. Miner. Geochem. **2014** *78* 779-800

Adding Silica: Effects on Dynamics

NMR

$$T_1 = \frac{1}{\pi\Delta\nu_{1/2}}$$

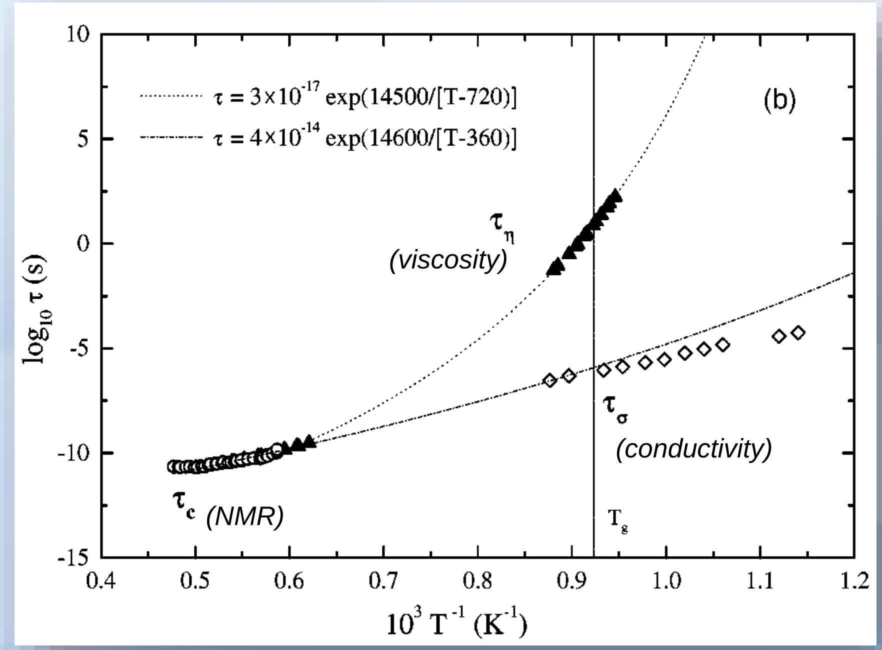
$$\frac{1}{T_1} = \frac{3}{10}\pi^2\frac{2I+3}{I^2(2I-1)}\overline{C}^2_{Q\eta}\tau_c^2$$

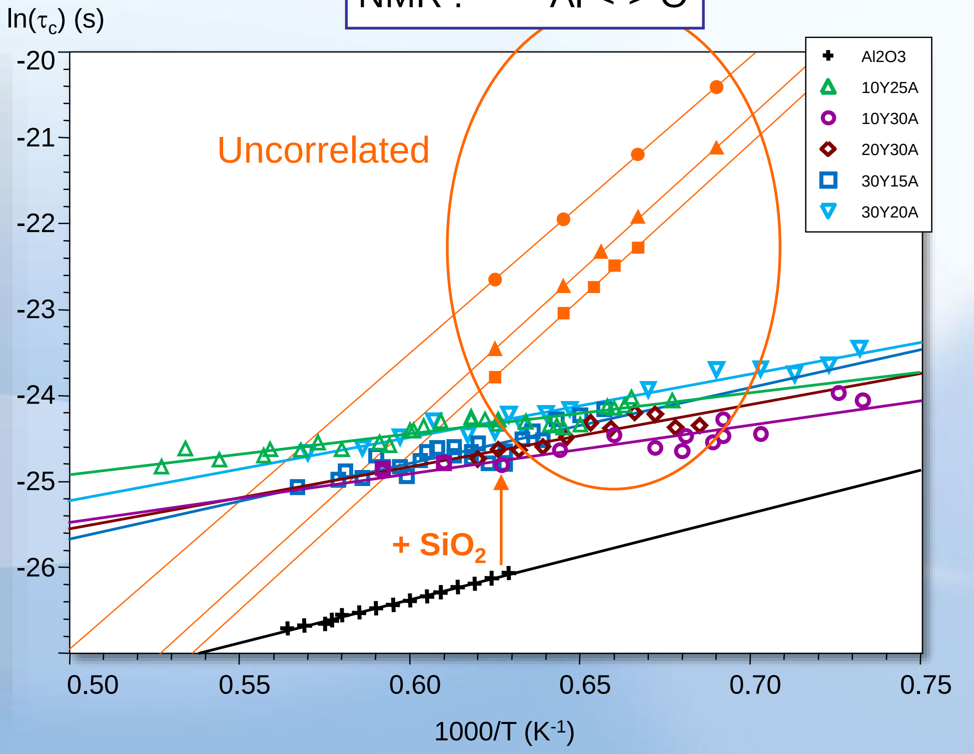
Viscosity

$$\tau_c = \frac{\eta}{G_\infty}$$

Saito *et al.*, *J. Am. Ceram. Soc.*, 2003, **86**, 711-716

Viscosity : Si- / -O
NMR : Al <-> O





CA3627, CA4412

Al_2O_3-SiO_2-Y_2O_3 (SiO_2 > 50mol%)

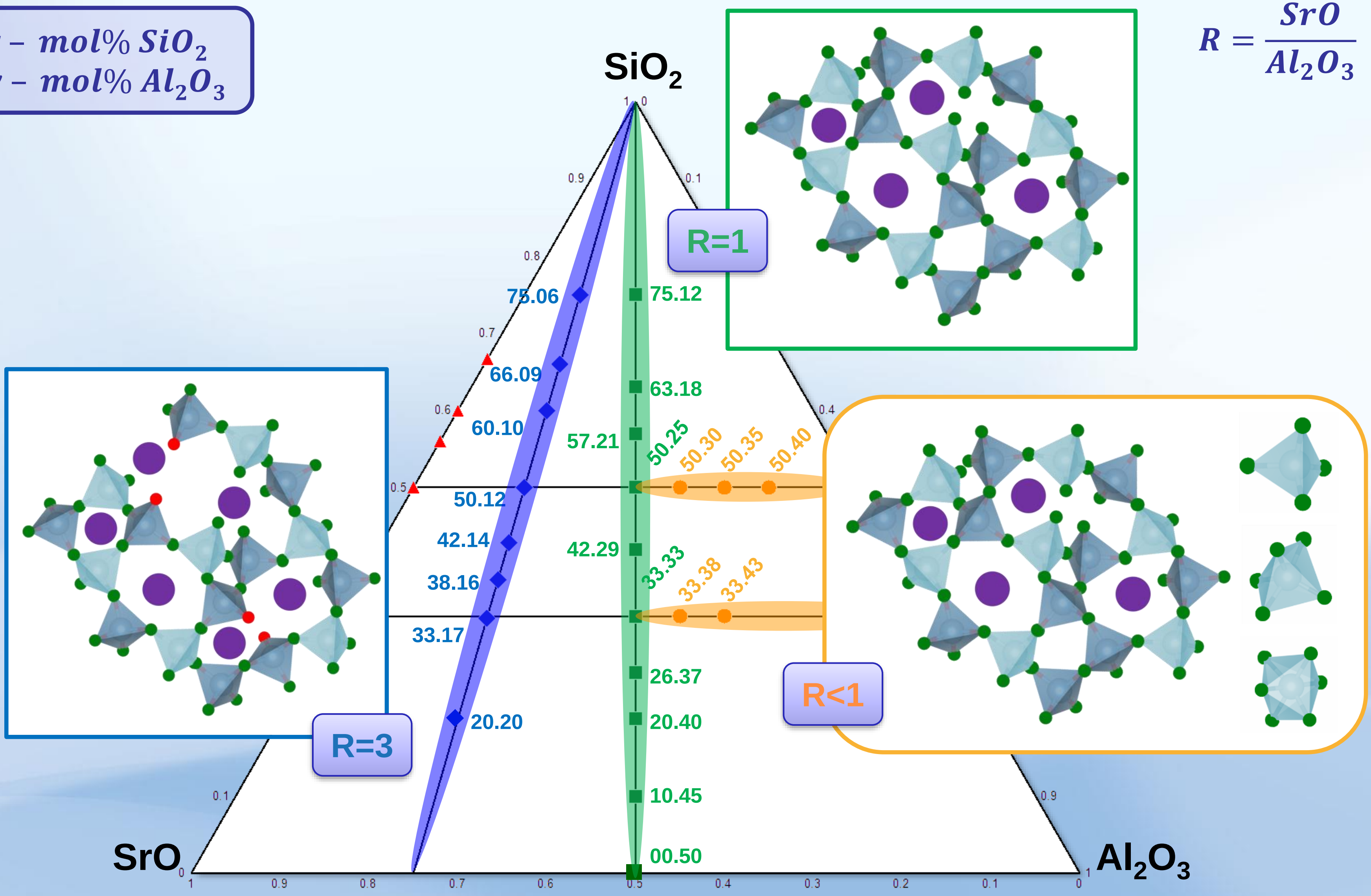
Gruener et al., Phys. Rev. B ***64****(2) (2001)*

Florian et al., J. Phys. Chem. B. ***111*** *9747 (2007)*

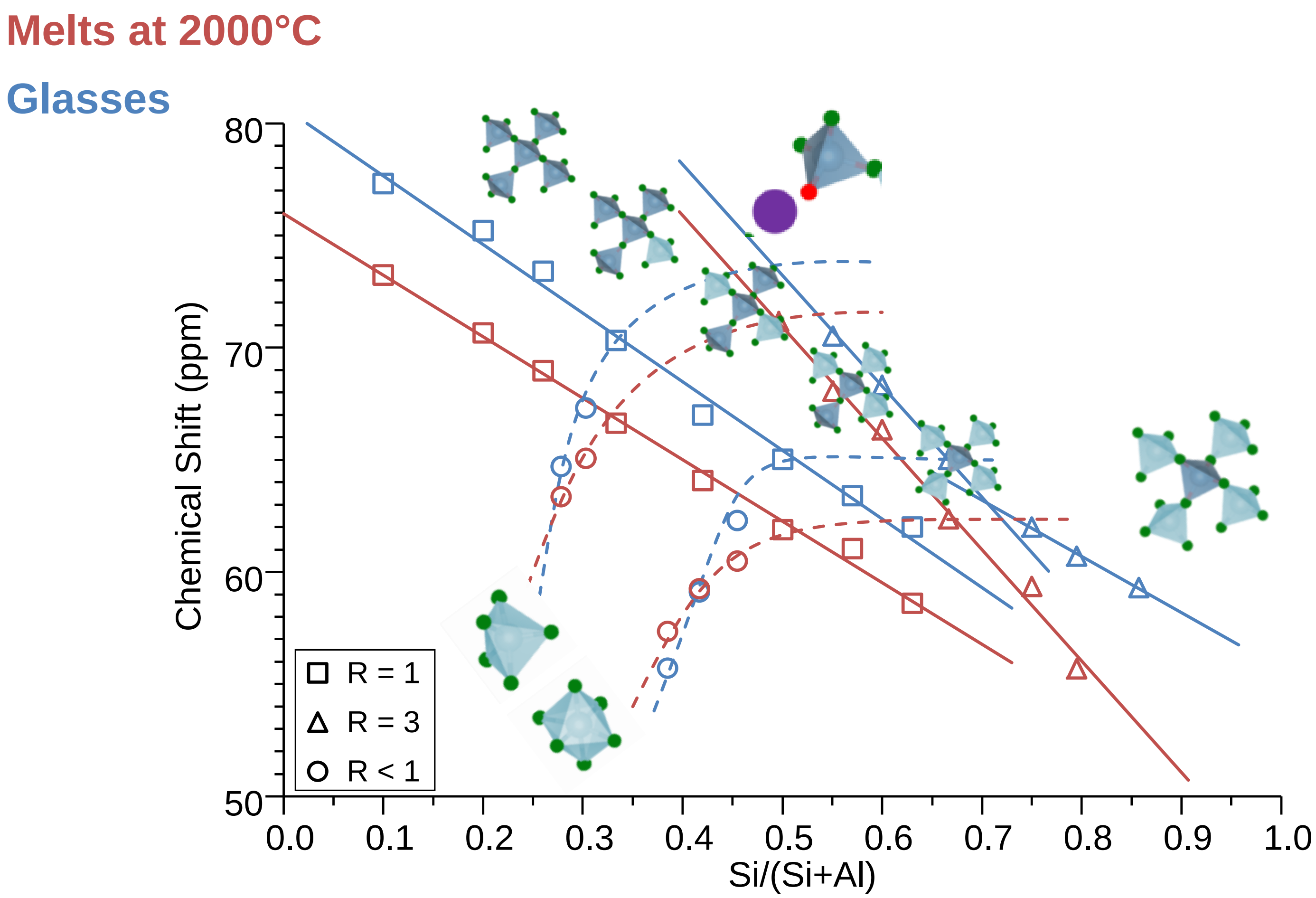
Alkaline-Earth AluminoSilicates

xx – mol% SiO_2
yy – mol% Al_2O_3

$$R = \frac{SrO}{Al_2O_3}$$



Structure of the $SrO\text{-}Al_2O_3\text{-}SiO_2$ Melts



Novikov et al (2017),
Chem. Geol. ***461*** *115*
Charpentier et al. (2018),
J. Phys. Chem. B 122 9567-9583
Florian et al. (2018),
Phys Chem. Chem. Phys., ***20*** *27865-27877*

- R = 1: distribution of Si/Al is random in the melt
- R = 3: presence of NBOs on Al in the melt, not always in the glass
- R < 1: complex behavior with competing mechanisms

Dynamics of Viscous Flow

NMR

$$\pi\Delta\nu_{1/2} = 1/T_1 = \frac{3}{10}\pi^2\frac{2I+3}{I^2(2I-1)}\overline{C}^2_{Q\eta}\tau_c$$

random walk theory
of activated diffusion

$$\boxed{D=\gamma\langle\lambda^2\rangle\nu}\exp(-\Delta G/k_BT)$$

jump distance

vibration frequency (~Debye)

enthalpie of defects formation

NMR ⇔ Al-O vibrations: $\boxed{\nu = 1/\tau_c^{NMR}}$

- *Correlation with oxygen diffusion if oxygen jump is on the same timescale as thermal vibrations*
- *At Tg/T ~ 2, coupling occur only in the most fragile liquids (i.e. low SiO_2)*
- *Coupling occur at high T in all liquids*

Viscosity

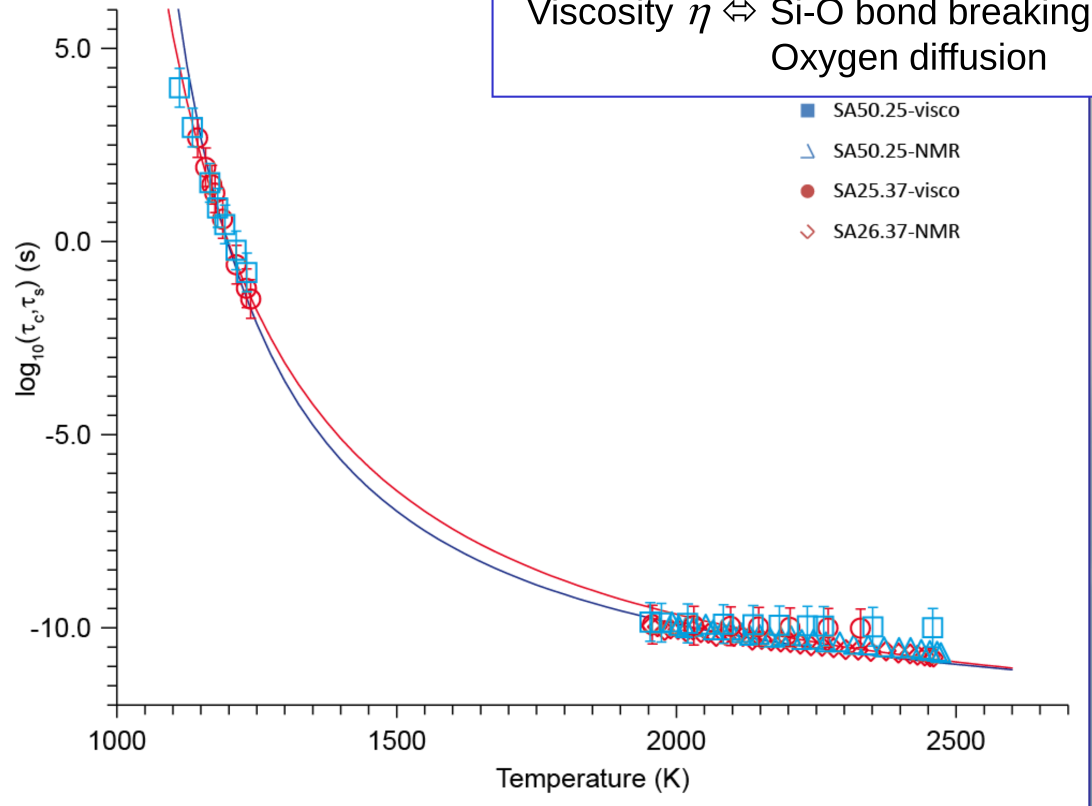
$$\tau_c = \eta/G_\infty$$

Dingwell & Webb
Euro. J. Miner. ***2*** *427 (1990)*

Eyring: oxygen self-diffusion

$$D = k_BT/\eta\lambda$$

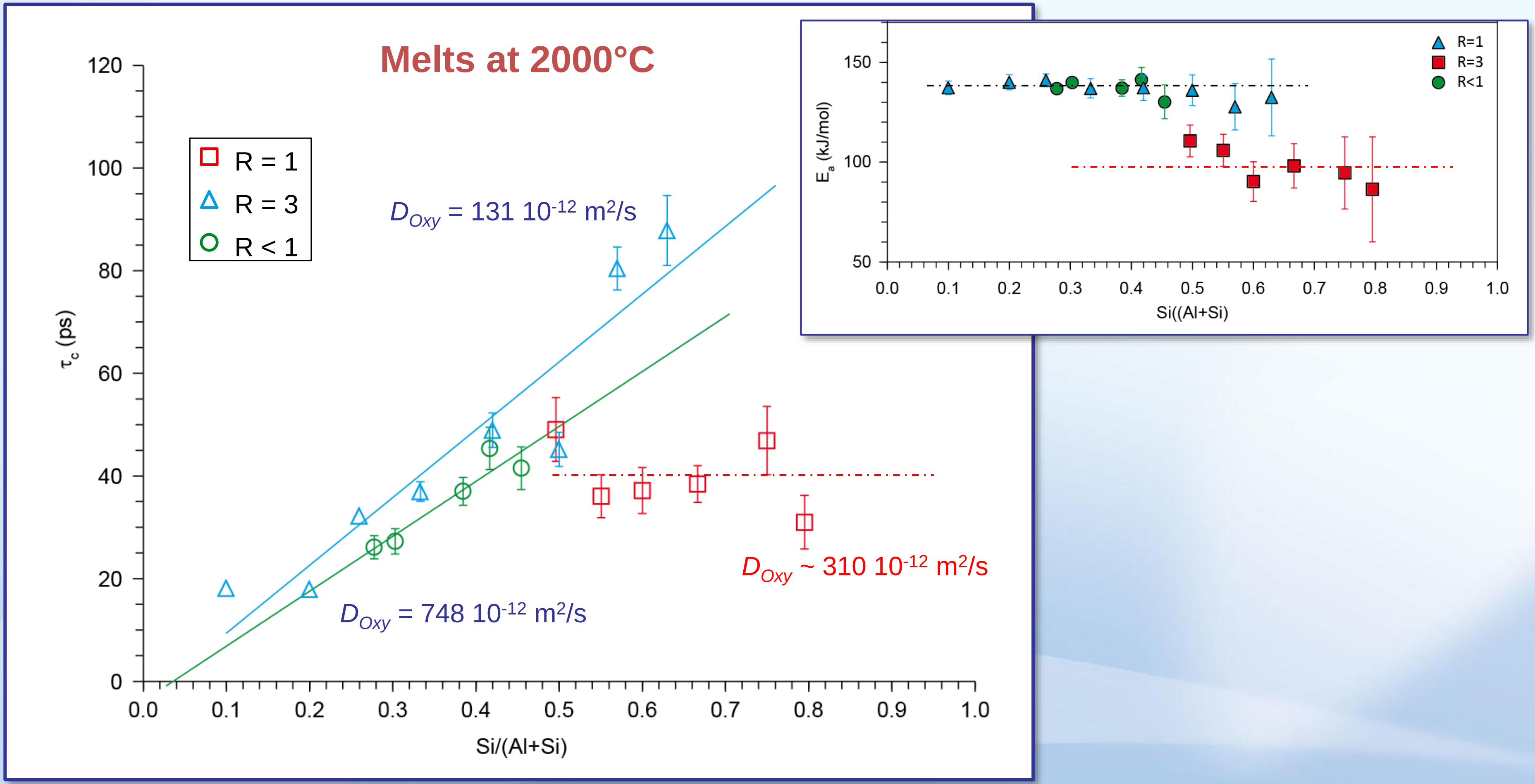
Viscosity η ⇔ Si-O bond breaking
Oxygen diffusion



Wert, Phys. Rev. ***79*** *601 (1950)*
Zener, J. Appl. Phys. ***22*** *372 (1951)*
Perkins & Begeal, J. Chem. Phys. ***54*** *1683 (1971)*

Urbain et al., Geochim. Cosmochim. Acta ***46*** *1061 (1982)*
Novikov et al., Chem. Geol. ***461*** *115 (2017)*

Dynamics of the $SrO-Al_2O_3-SiO_2$ Melts



Increase content of SiO_2 increases correlation time (⇔ $D_O \downarrow$ *and* $\eta \uparrow$)

The presence of NBO

- stabilizes correlation time → oxygen diffusion ~ $310\ 10^{-12}\ m^2/s$
- reduces the activation energy → oxygen diffusion made easier

Florian et al. (2018),
Phys Chem. Chem. Phys., ***20*** *27865-27877*

Class is Over…

Do Science & Have Fun!

Aknowledgements

CEMH *rance*
Domin
Cather
Patricl *USA*
Domin
Bruno
Laurer
Anne-
Vincer
Aydar
Yannic
Philipp

TRÈS GRANDES INFRASTRUCTURES DE RECHERCHE
Résonance Magnétique Nucléaire, Très Hauts Champs
FR3050 CNRS

Réunion d'Utilisateurs

15 Oct — 7ème Réunion des Utilisateurs organisée par ICSN Gif/Yvette
Gif-sur-Yvette

Evènements

18 Mai — Formation Atelier Pratique en RMN
Grenoble

Remerciements : « Financial support from the TGIR-RMN-THC Fr3050 CNRS for conducting the research is gratefully acknowledged.»

Le TGE décentralisé RMN Très Hauts Champs, est un réseau constitué d'équipes de recherche reconnues au niveau international en RMN, exploitant des spectromètres RMN Hauts Champs.

Le Réseau est une structure ouverte à une communauté nationale et internationale d'utilisateurs. Il a pour but de répondre au mieux aux attentes scientifiques des communautés d'utilisateurs et aux experts de la spectroscopie RMN.
Les laboratoires d'accueil proposent l'accès à leurs installations à hauts champs magnétiques, accompagné d'une expertise scientifique des possibilités offertes par les méthodes les plus récentes pour les développements de nouvelles directions de recherche.