

# Composition-Structure-Mechanical properties relationships in glass : metallic, oxide, and non-oxide

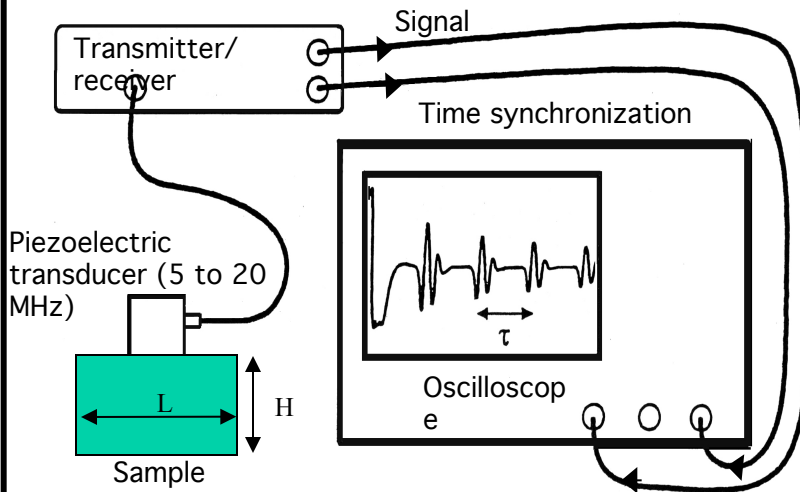


- **Interatomic bonding and atomic packing density:  
How it governs the elastic properties of glasses**
- **Shear viscosity**
- **What we know about indentation cracking, and fracture toughness**

- **Interatomic bonding and atomic packing density:  
How it governs the elastic properties of glasses**

# Measurement of elastic moduli by ultrasonic echography

## Measurements at ambient temperature

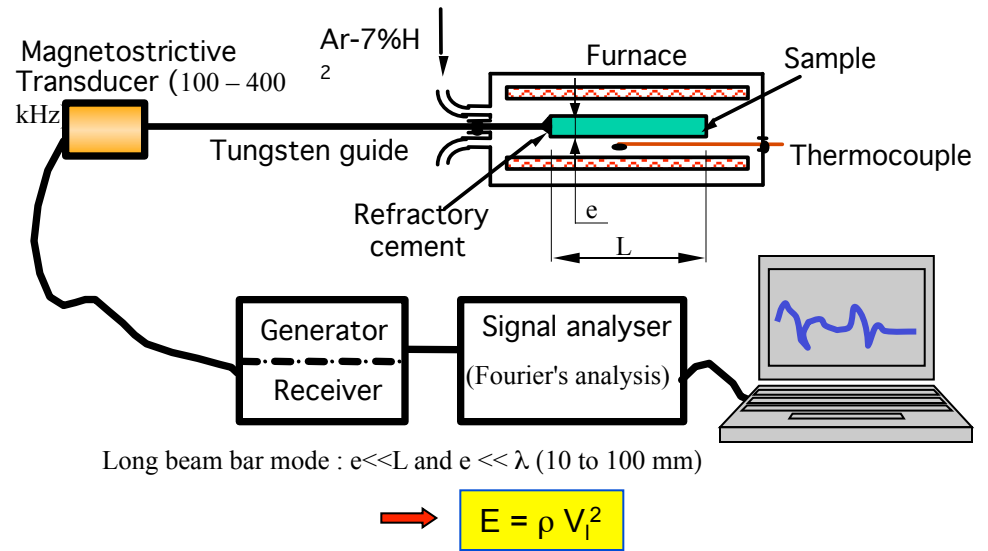


Elastic wave in semi-infinite medium :  $\lambda \ll L$  and  $\lambda \ll H$

$$\begin{aligned} E &= \rho (3V_l^2 - 4V_t^2) / ((V_l/V_t)^2 - 1) \\ G &= \rho V_t^2 \\ \nu &= E / (2G) - 1 \end{aligned}$$

Where:  $\rho$ : specific mass  
 $V_l$ : longitudinal wave velocity  
 $V_t$ : transverse wave velocity

## High temperature measurements



Long beam bar mode :  $e \ll L$  and  $e \ll \lambda$  (10 to 100 mm)

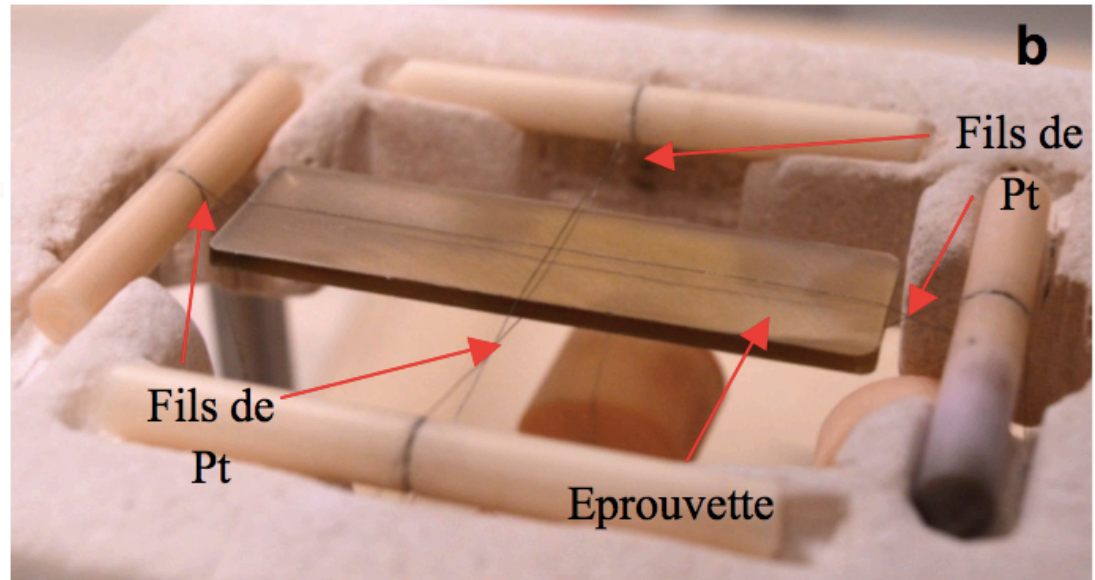
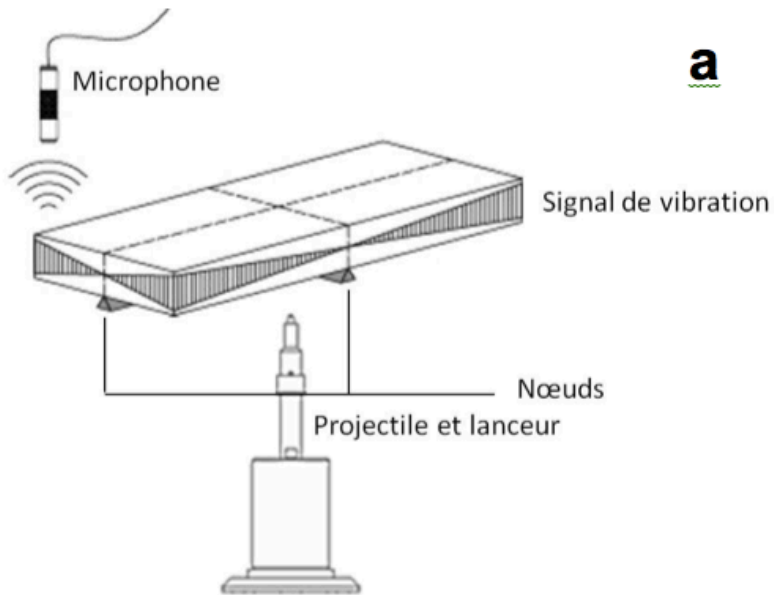
$$E = \rho V_l^2$$

## Small size specimens: Acoustic microscopy

When  $(L, H) < \lambda$ , regular piezoelectric transducers are unable to efficiently promote the propagation of shear waves through the specimen. Focused piezoelectric transducers can be used to propagate surface-type waves, also called Rayleigh waves, which velocity is given by:  $V_R = \zeta V_t$ , where  $\zeta$  is a function of Poisson's ratio, or of the  $V_l/V_t$  ratio.  $V_R$  and  $V_l$  are measured and  $V_t$  is optimised to satisfy the following equation:

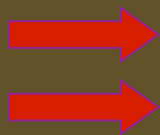
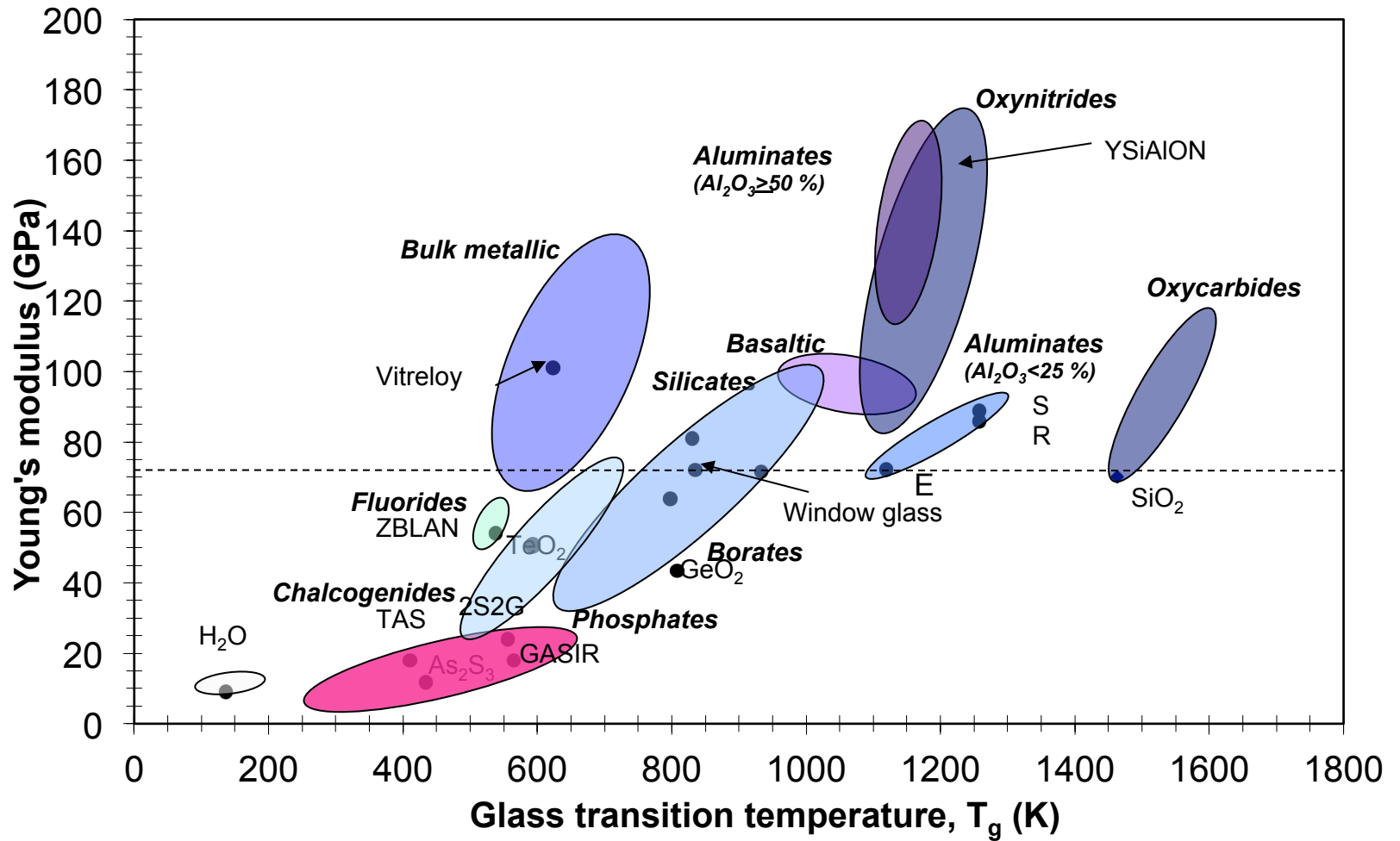
$$V_R = \frac{V_t (0.715 - (V_l/V_t)^2)}{0.750 - (V_l/V_t)^2}$$

# High Temperature Mechanical Resonance technique



*Schéma (a) et photographie (b) du dispositif RFDA en température.*

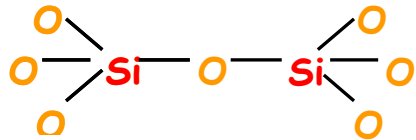
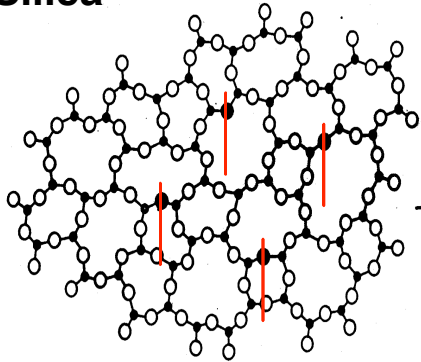




There is no direct correlation between  $E$  and  $T_g$   
 Elastic moduli are expressed in Pascals, i.e. in  $J/m^3$ , and are thus governed by the volume density of energy

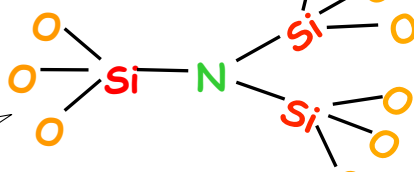
## 3D units and crosslinking

Silica

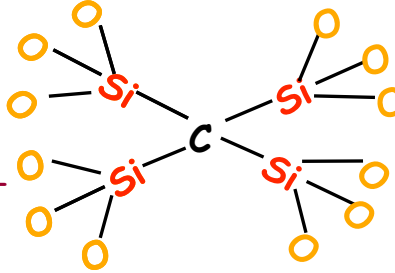


Substitution  
of  $3\text{O}^{2-}$  for  $2\text{N}^{3-}$

Silicon oxynitride



Substitution  
of  $2\text{O}^{2-}$  for  $1\text{C}^{4-}$



Silicon oxycarbide

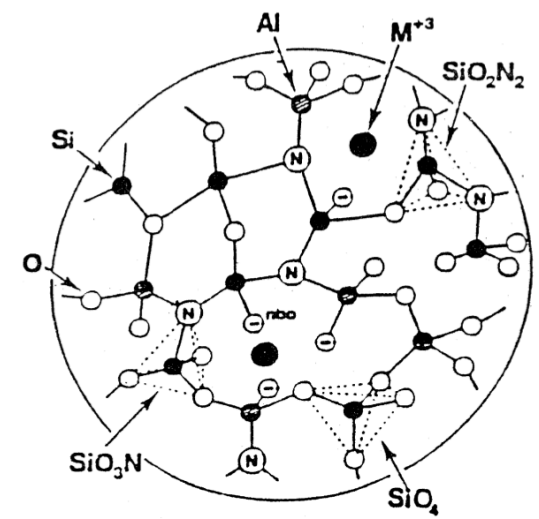
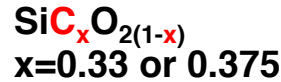


Fig. 7. Schematic representation of oxynitride glass structure (after [42]).

● **Playing on anions to increase the cross-linking degree of the glass network:**

*Increases the refractoriness ( $T_g > 750^\circ\text{C}$  for oxynitride and  $>1300^\circ\text{C}$  for oxycarbide glasses)*

*Increases the hardness*

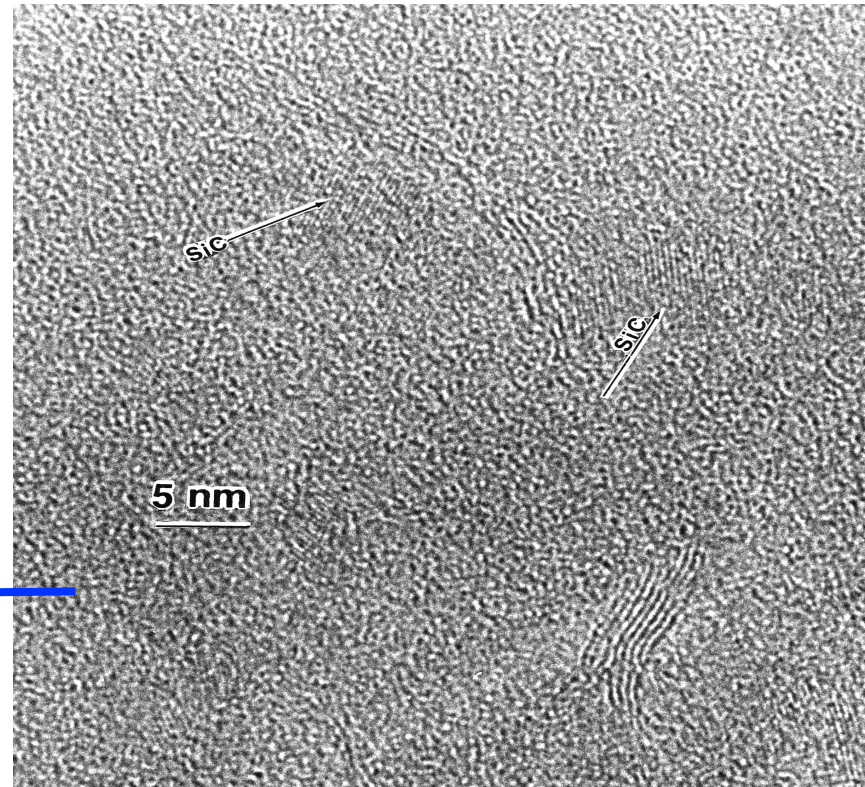
*Favours a normal indentation cracking behavior*

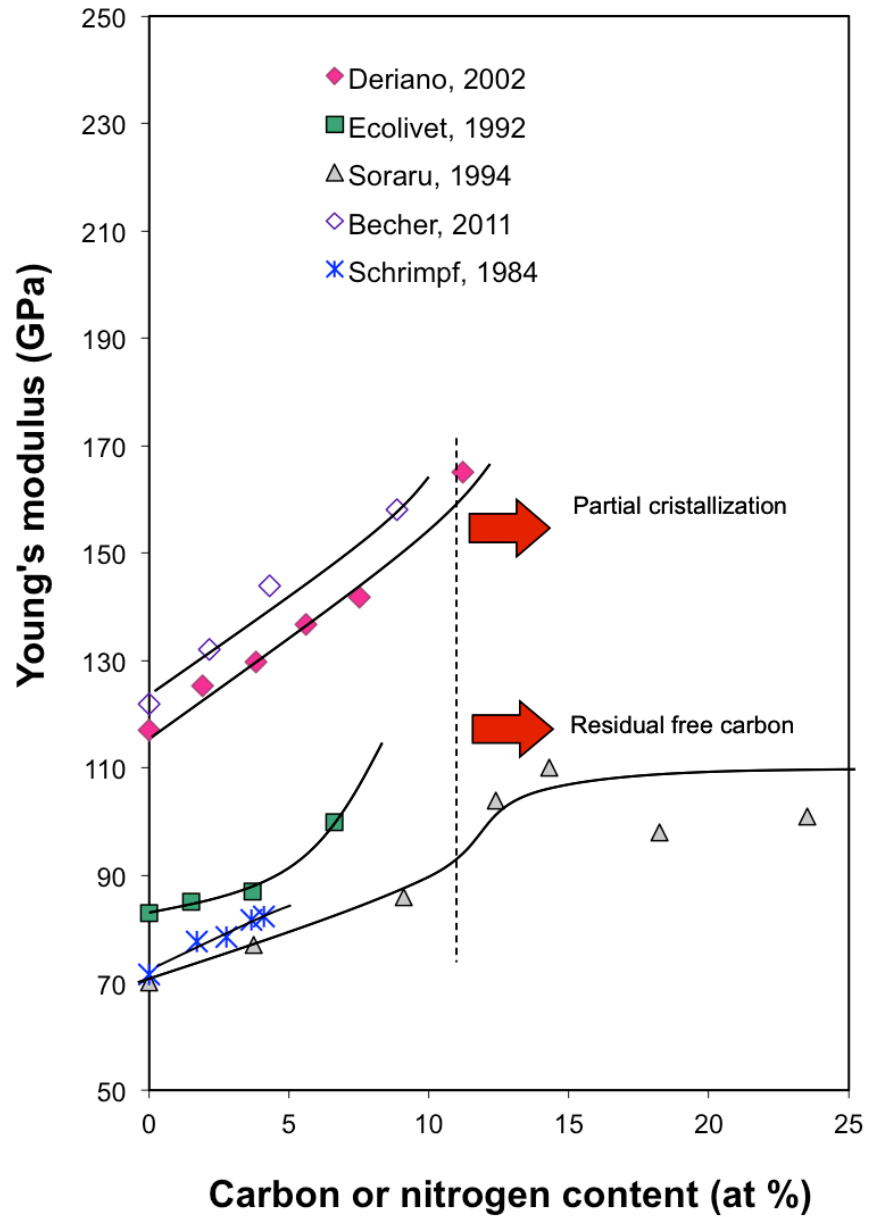
*Stiffens the glass*

### Crystallization

At  $T > 1200^\circ\text{C}$ , 2.4 to 2.6 nm large b-SiC crystals, which grow little during annealing

Crystallization proceeds through the increase of the number of nanocrystals







In an early study published in 1894 by Winkelmann and Schott,<sup>80</sup> a linear dependence was proposed between  $E$  and the glass composition. Interestingly, the obtained weighting coefficients revealed a stronger effect for  $\text{Na}_2\text{O}$  (98.1),  $\text{CaO}$  (98.1), or  $\text{K}_2\text{O}$  (69.7) than for the major glass former  $\text{SiO}_2$  (63.8), where the molar fraction of each oxide is weighted by the coefficients in the brackets (the resulting Young's modulus is expressed in GPa). Coefficients of 157 and 19.6 were attributed to glass formers such as  $\text{Al}_2\text{O}_3$  and  $\text{B}_2\text{O}_3$ , anticipating what we know today: Boron in  $\text{B}_2\text{O}_3$  forms relatively weakly bonded together  $\text{BO}_3$  triangles, whereas Al acts as a 3D glass former, mainly fourfold coordinated but allowing for a better atomic packing density than Si. These results already support the fact that it is necessary

$$E = \sum a_i f_i \quad \text{with } f_i: \text{fraction of the } i^{\text{th}} \text{ constituent}$$

<sup>1</sup> A. Winkelmann and O. Schott, "Ueber die elasticität und über die Zug- und Druckfestigkeit verschiedener neuer gläser in ihrer abhängigkeit von der chemischen zusammensetzung," *Ann. der Phys. (Leipzig)*, **51** 697-729 (1894).

*"Elastic properties and short-to-medium range order in glasses", J. Am. Ceram. Soc., 90 [10] 3019-3039 (2007).*



# Poisson's ratio ( $\nu$ )

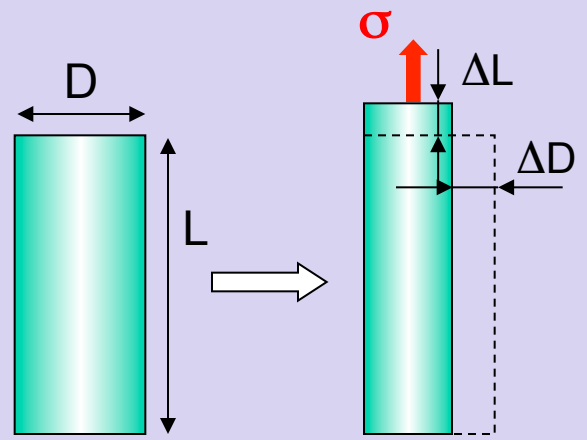


Siméon Denis POISSON

(1781-1840)

$$\Delta V/V = \text{Trace } \epsilon = (1-2\nu)\sigma/E$$

$$\nu = -\epsilon_t/\epsilon_l = -L/D \times \Delta D/\Delta L$$



$\nu < 110 >$  b.c.c. metals  
Metal foams (-0.8)

Polymer foams (-0.7)

Cork (0)

Cellular solids (0.1-0.4)

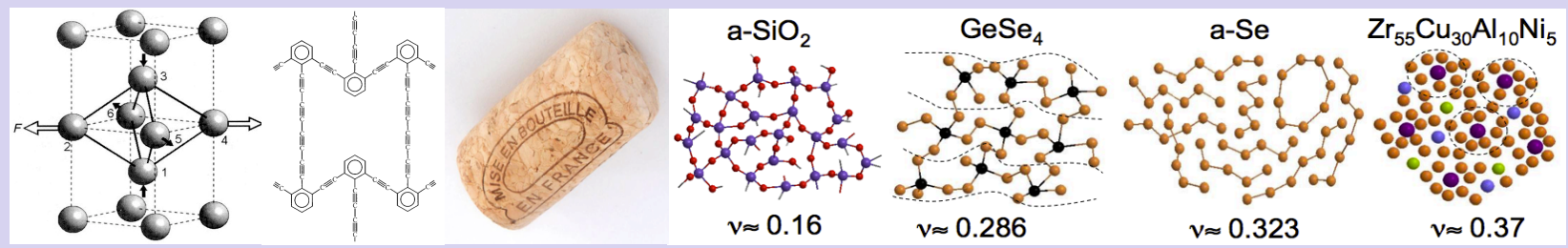
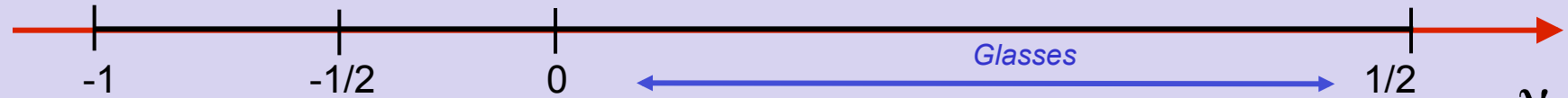
Central force model (Poisson) (0.25)

Steels (0.27)

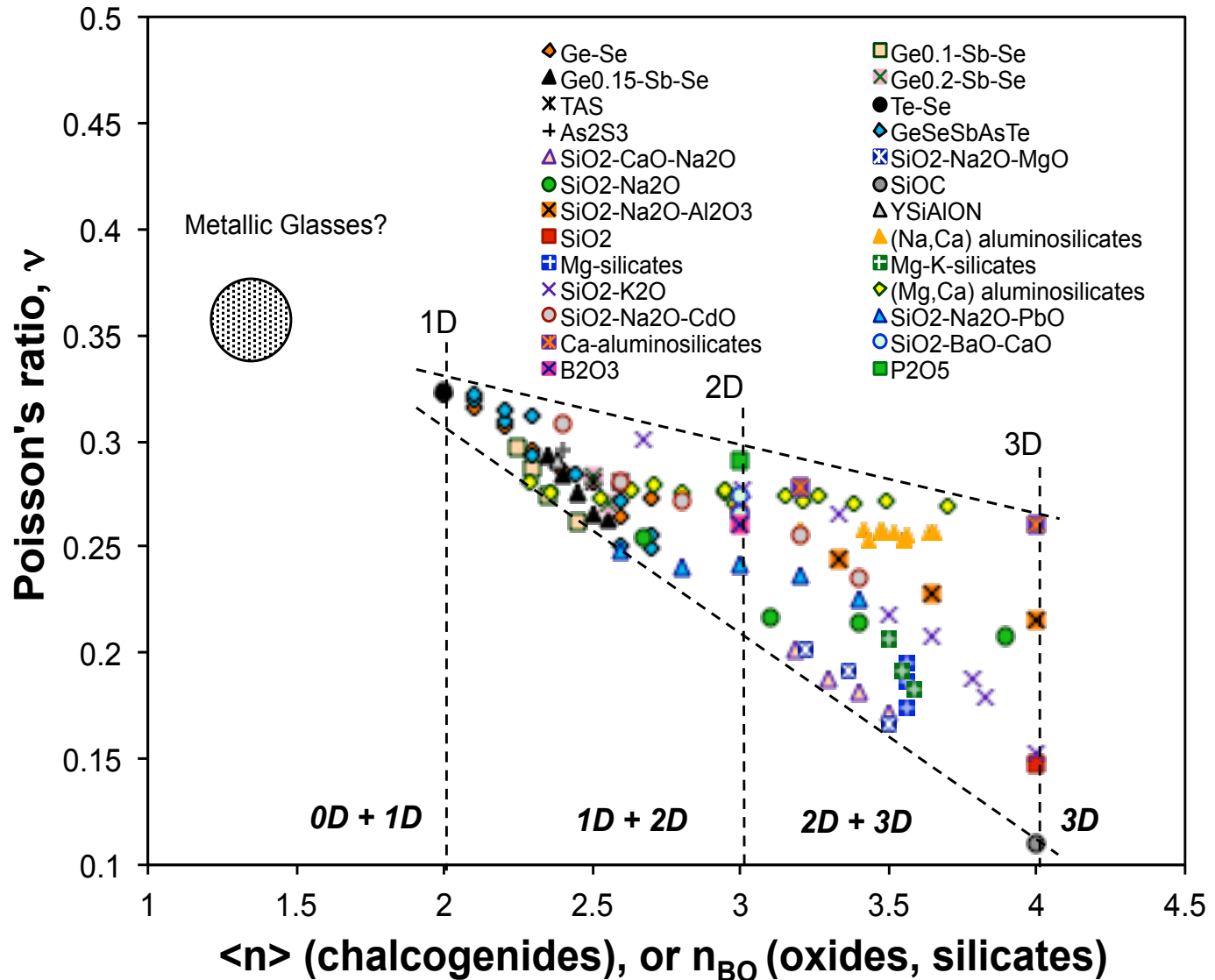
Aluminum (0.33)

Lead (0.45)

Rubber (0.5)



# Poisson's ratio and dimensionality



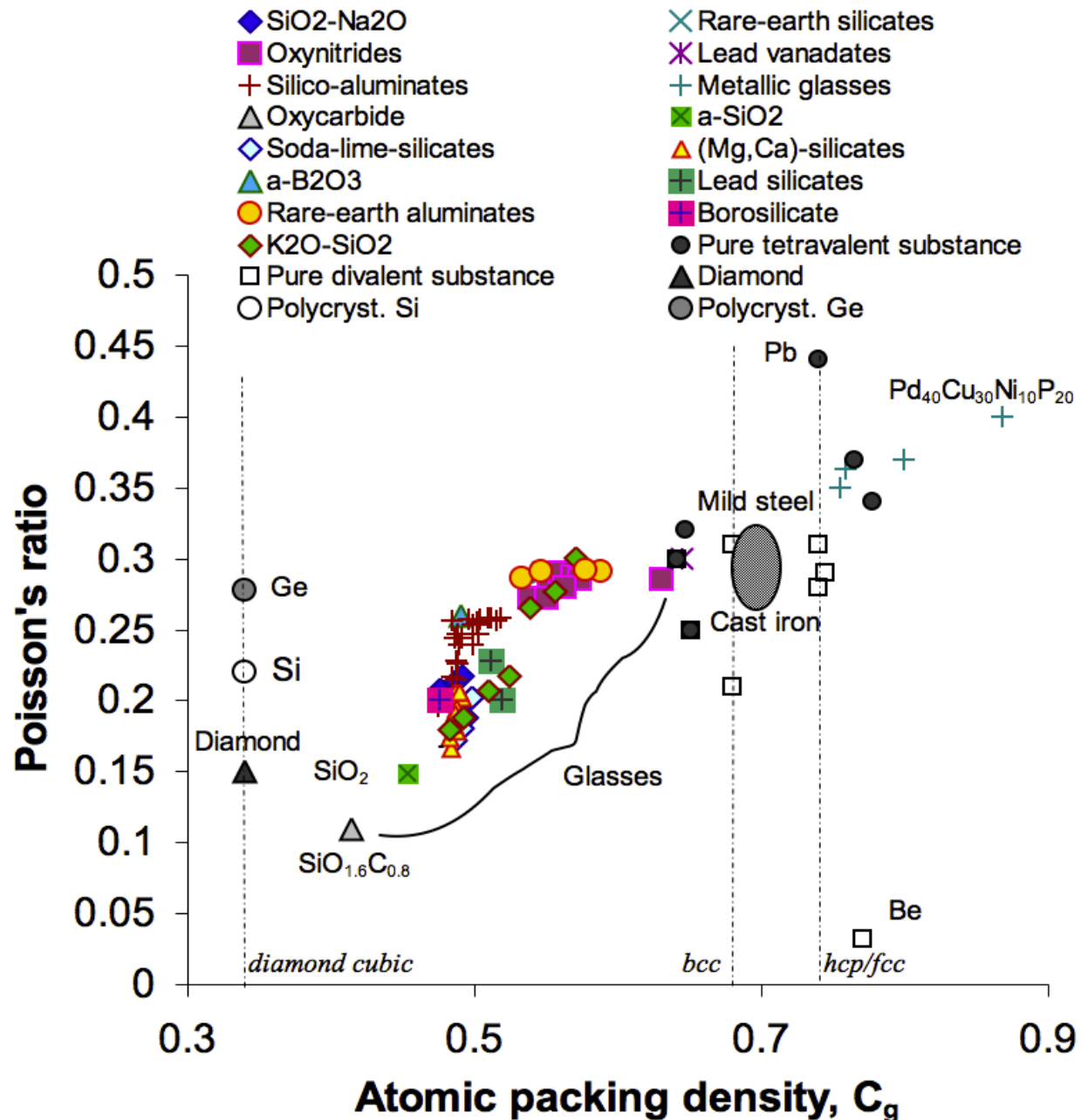
## General tendencies:

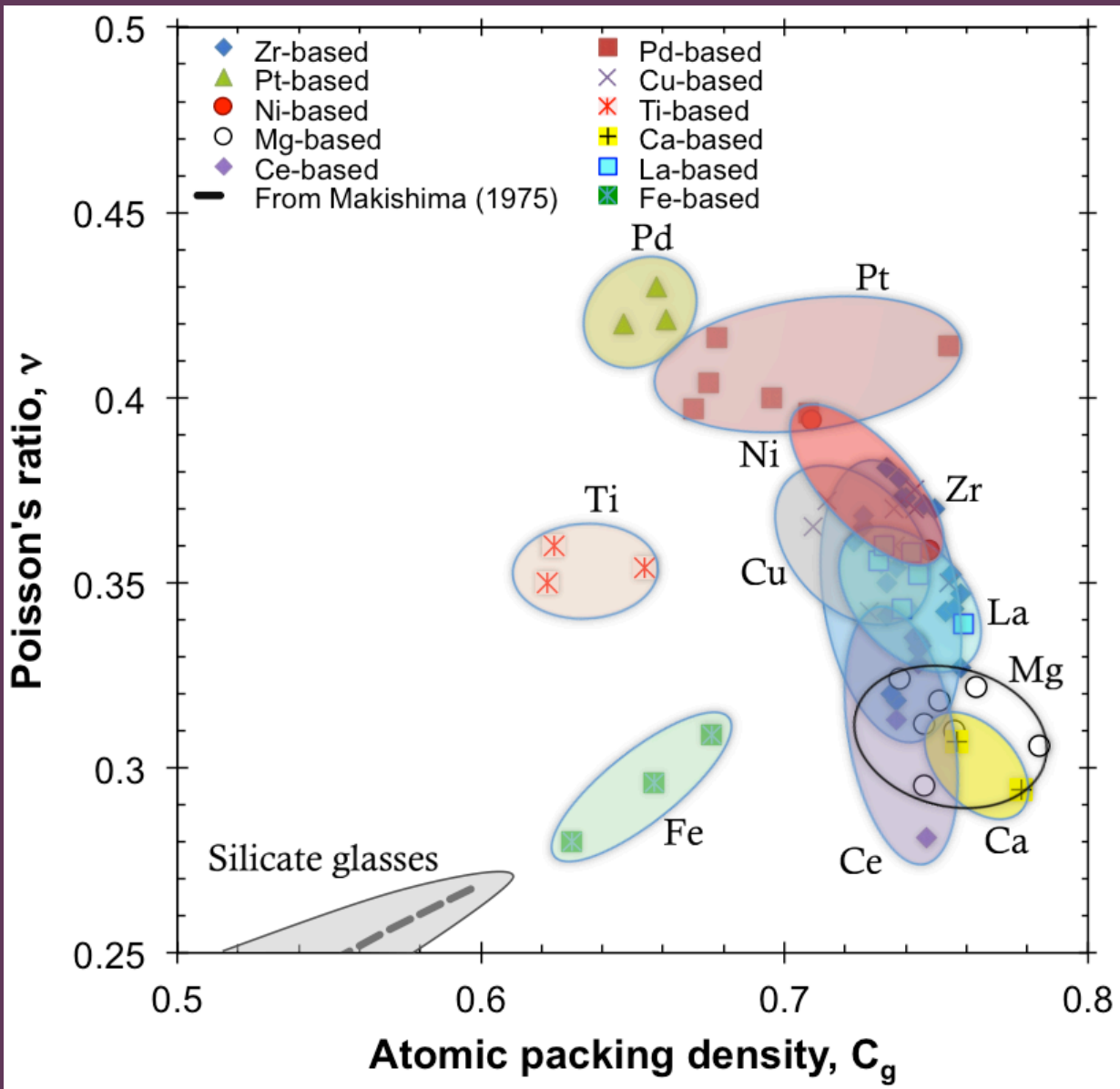
$$\nu_{cd} < \nu_{bcc} < \nu_{fcc,hcp}$$

For a given crystalline structure and valency, Poisson's ratio mostly increases with atomic number ( $Z$ ) (Lead ( $\nu_{Pb}=0.44$ ) and thallium ( $\nu_{Tl}=0.45$ ) with high  $Z$  have remarkably high Poisson's ratios)

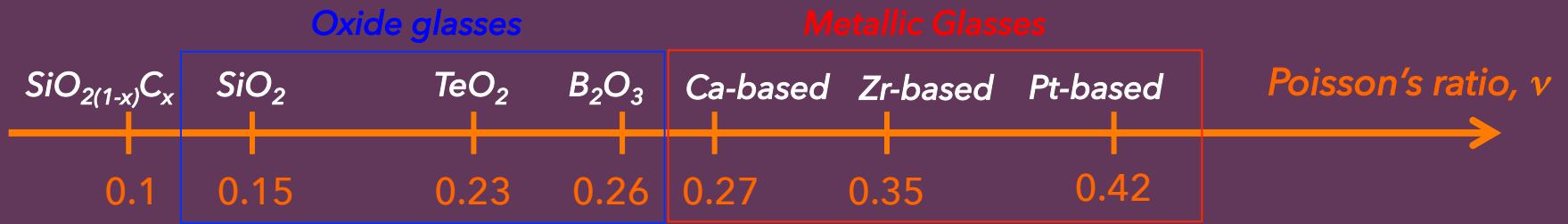
High melting points favor low Poisson's ratio (beryllium, combining a small  $Z$  and a melting point ( $T_m=1560$  K) much higher than those of the other elements in the same column, exhibits a remarkably small Poisson's ratio of 0.032)

$$C_g = \rho \sum f_i V_i / (\sum f_i M_i)$$







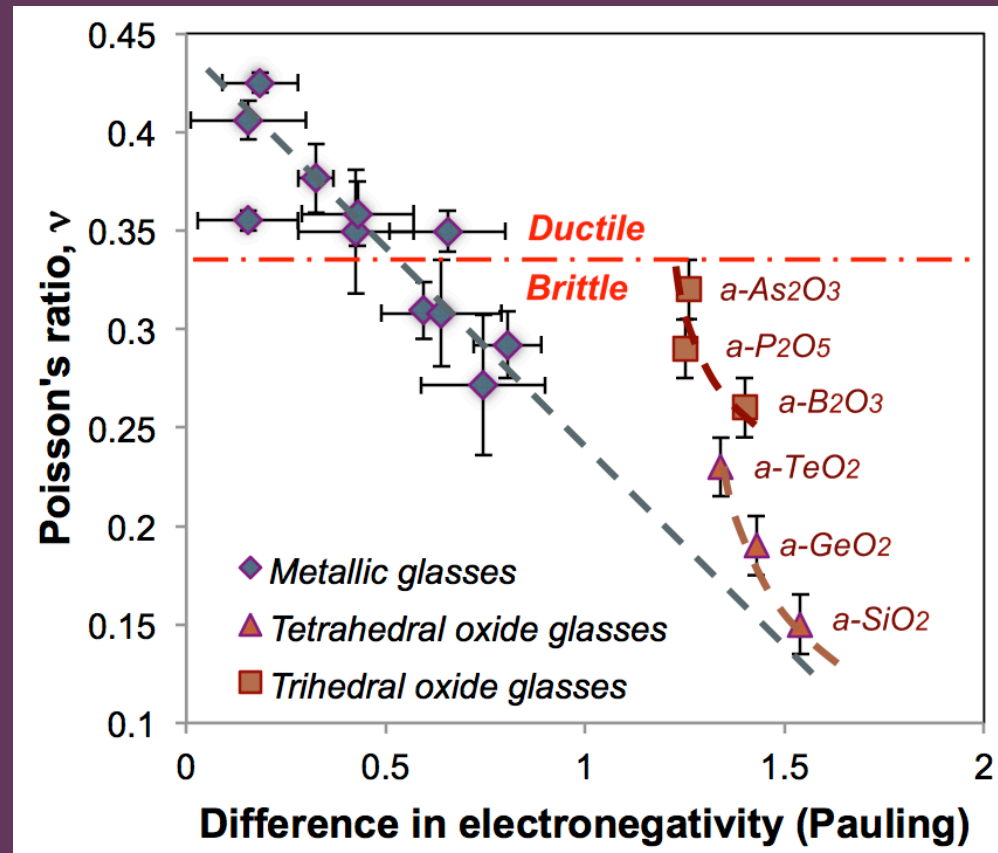


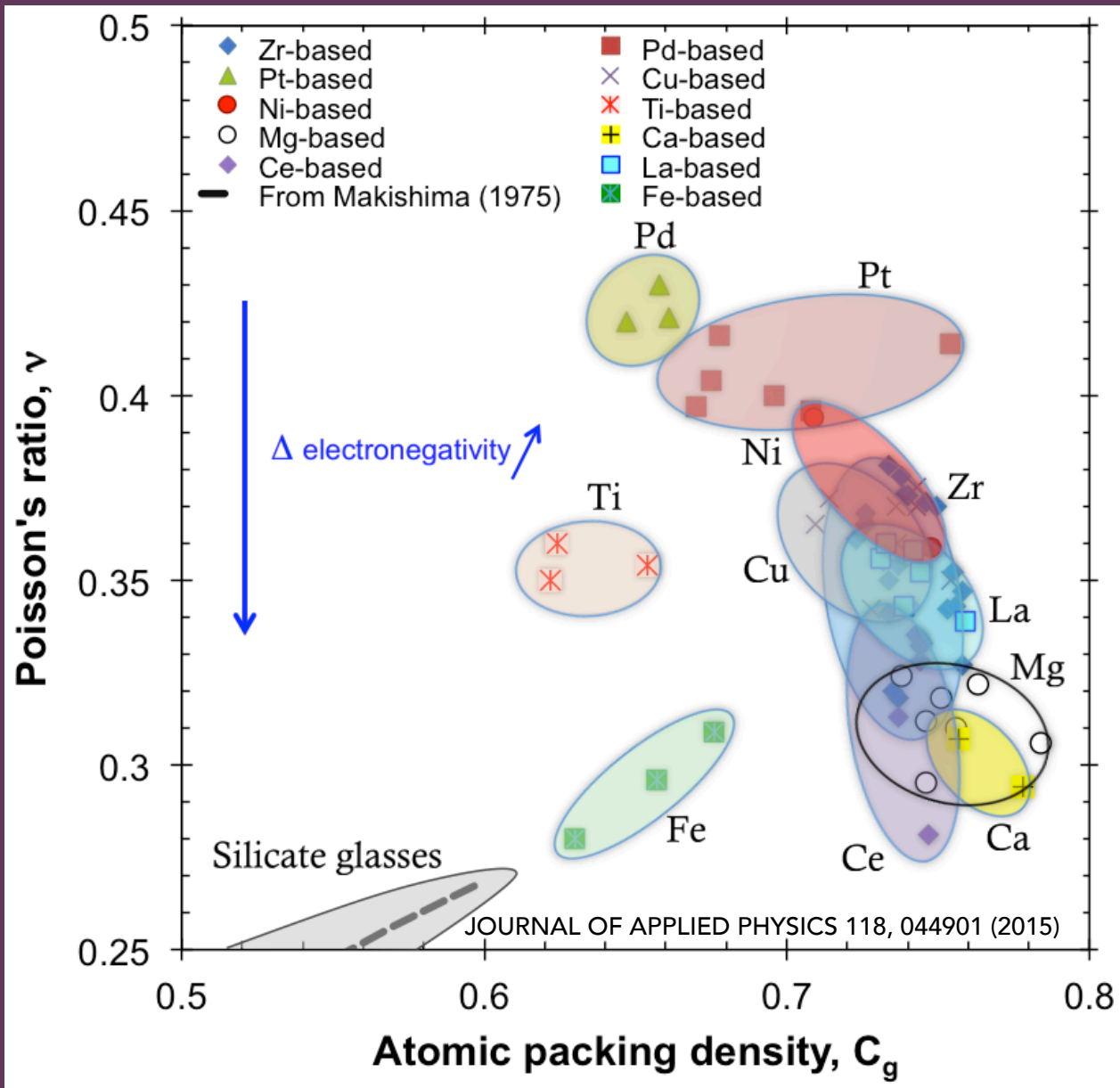
More directional bonding in the case of metal host elements such as Ce, Ca, or Mg due to localized f (for Ce) and sp (Ca, Mg) electrons

$\Delta e^-$  is taken as the electronegativity mismatch between the host and the two major secondary solute elements

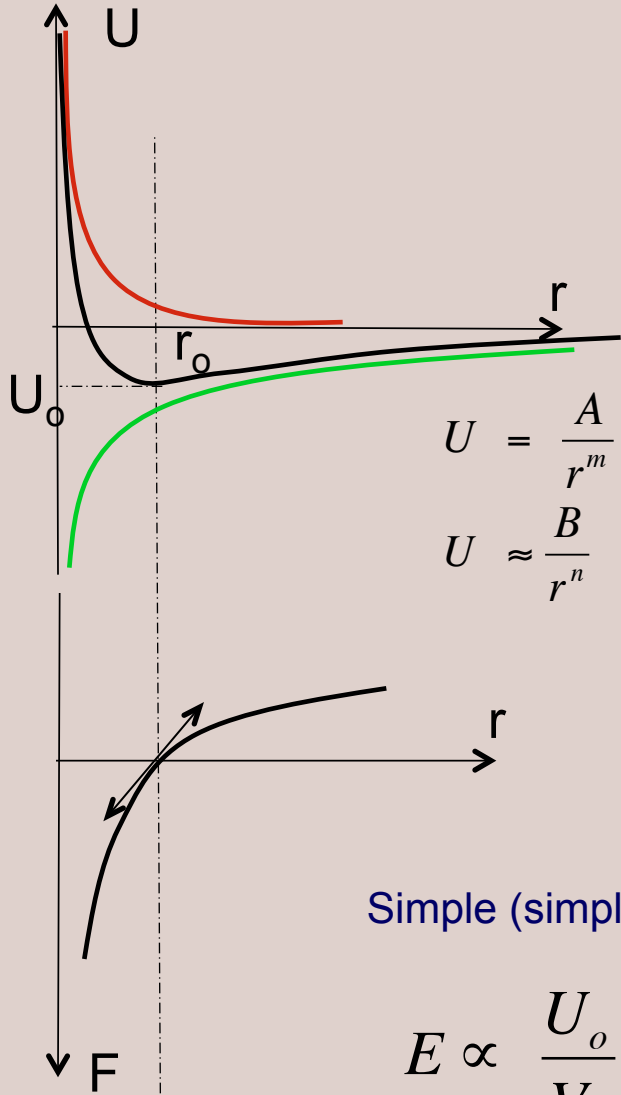
→  $\nu$  is correlated to  $\Delta e^-$

→ Ductility in MG for  $\nu > 0.32$  or for  $\Delta e^- < 0.5$





● Elasticity and atomic packing density:



$$E = \left. \frac{d\sigma}{d\varepsilon} \right|_{r_0}$$

$$\sigma = \frac{F}{r_o^2} \quad F = - \left. \frac{dU}{dr} \right|_{r_o}$$

$$\left. \begin{aligned} U &= \frac{A}{r^m} + \frac{B}{r^n} \\ U &\approx \frac{B}{r^n} \end{aligned} \right\}$$

$$\left\{ \begin{aligned} d\sigma &= - \left. \frac{1}{r_o^2} \frac{d^2U}{dr_o^2} \right|_{r_o} dr \\ d\varepsilon &= \frac{dr}{r_o} \end{aligned} \right. \rightarrow E = - \left. \frac{1}{r_o} \frac{d^2U}{dr_o^2} \right|_{r_o}$$

$$\left. \frac{d^2U}{dr^2} \right|_{r_o} \approx n(n+1) \frac{B}{r_o^{n+2}} \quad \left. \frac{d^2U}{dr^2} \right|_{r_o} \approx n(n+1) \frac{U_o}{r_o^2}$$

Simple (simplistic) case of a Mie / Grüneisen potential (1<sup>st</sup> Grüneisen rule):

$$E \propto \frac{U_o}{V_o}$$

Bulk modulus:

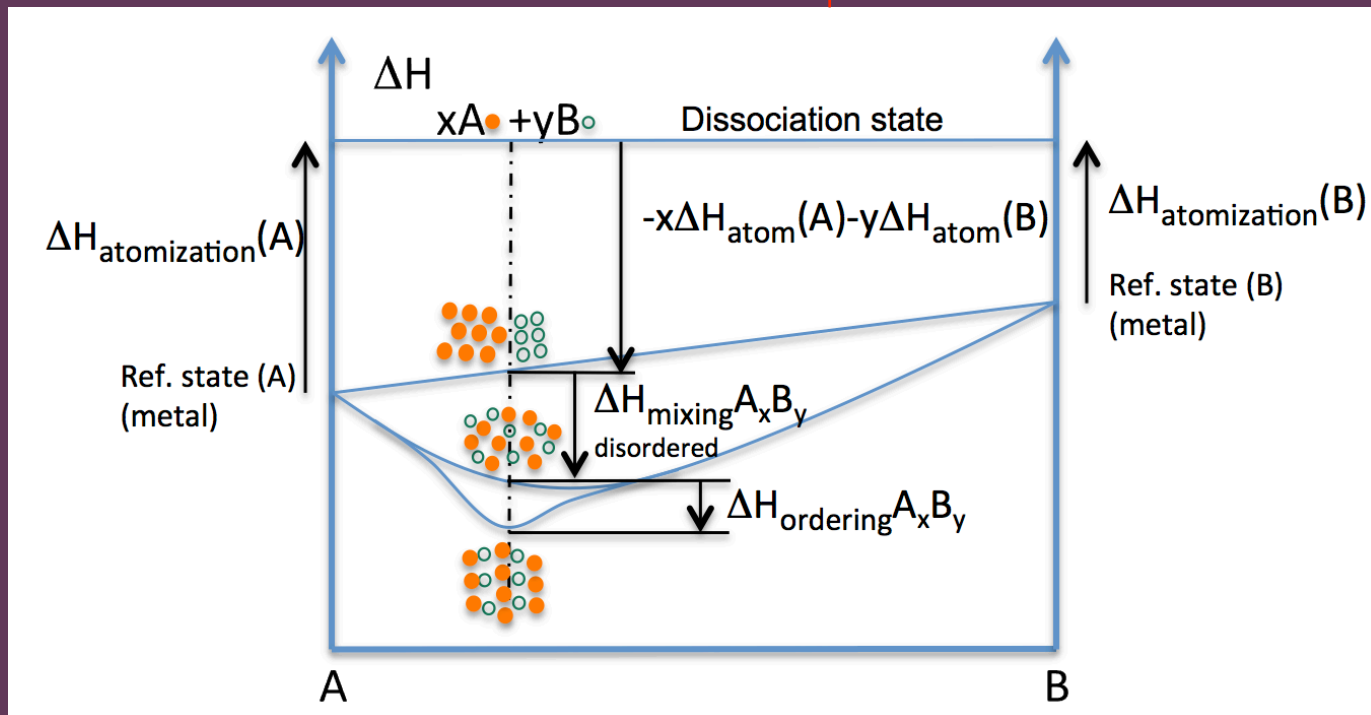
$$K = V_o \left. \frac{\partial^2 U}{\partial V^2} \right|_{V_o} = \frac{mn}{9V_o} U_o$$

$$U(r) = \frac{nU_o}{m-n} \left[ \left( \frac{r_o}{r} \right)^m - \frac{m}{n} \left( \frac{r_o}{r} \right)^n \right]$$

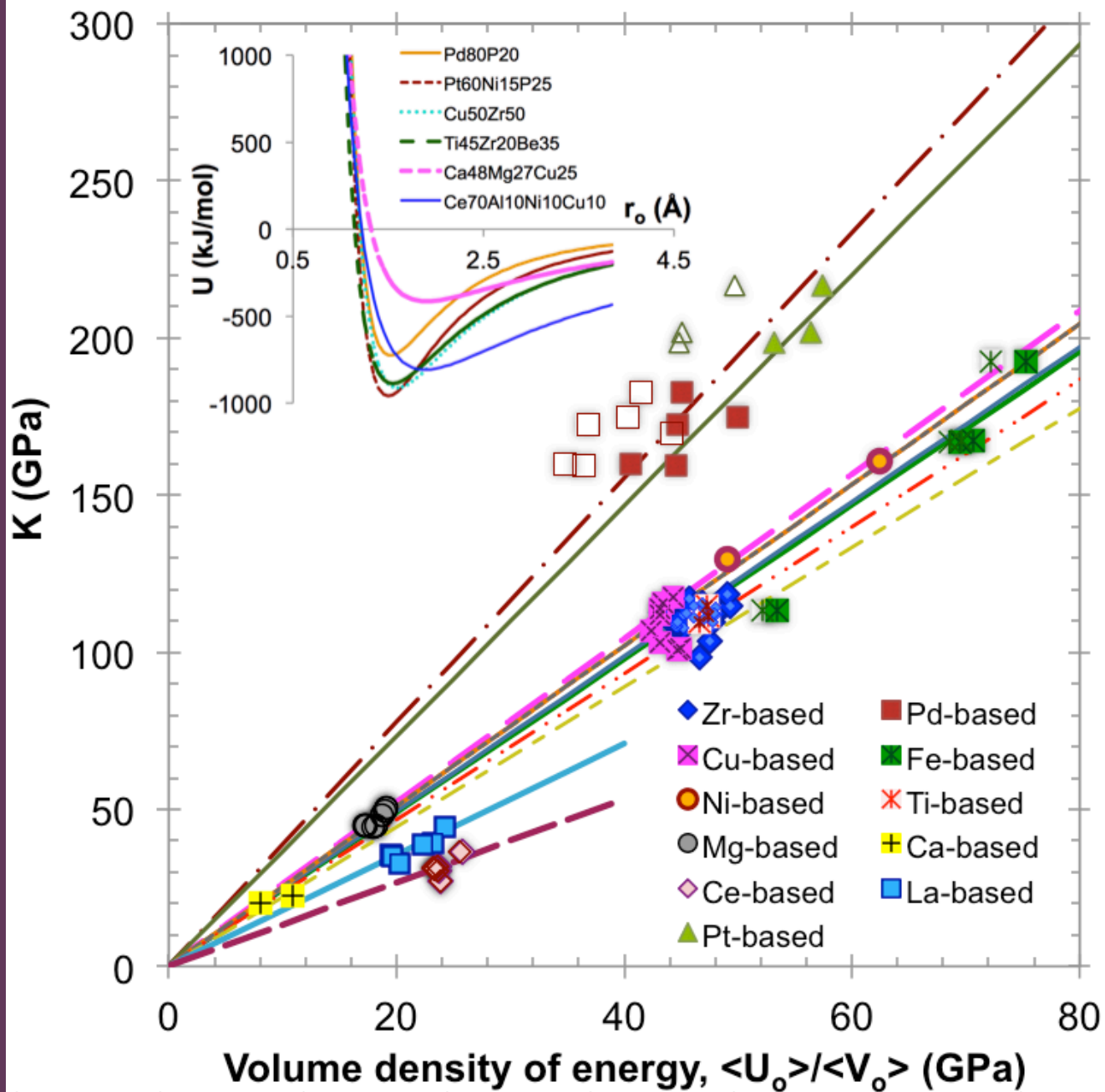
$$K = \frac{mnU_o}{9V_o}$$

$$\langle V_o \rangle = \sum_i f_i M_i / \rho$$

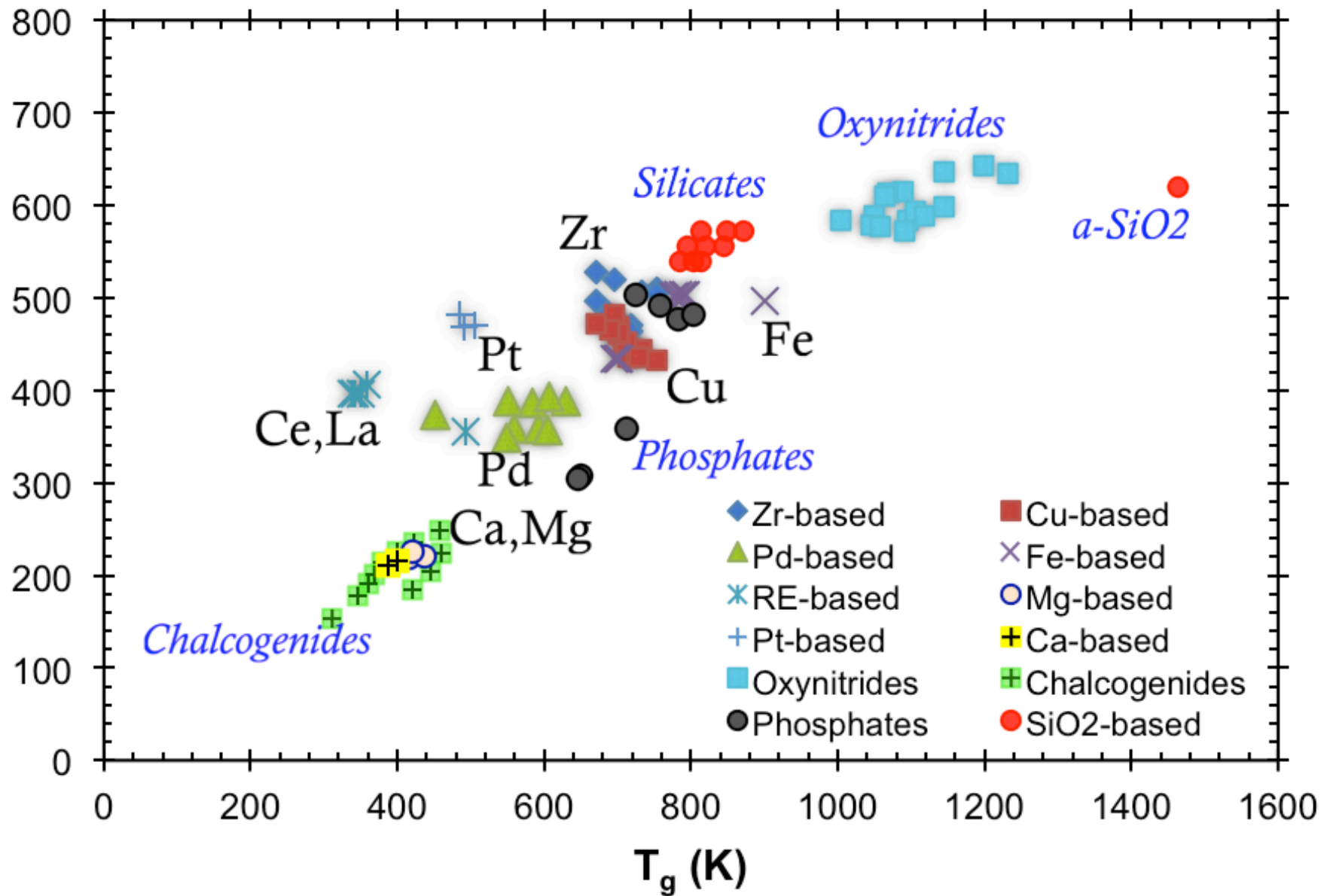
$$\langle U_o \rangle = x\Delta H_{at}(A,g) + y\Delta H_{at}(B,g) - \Delta H_{mixing}(A_xB_y)$$

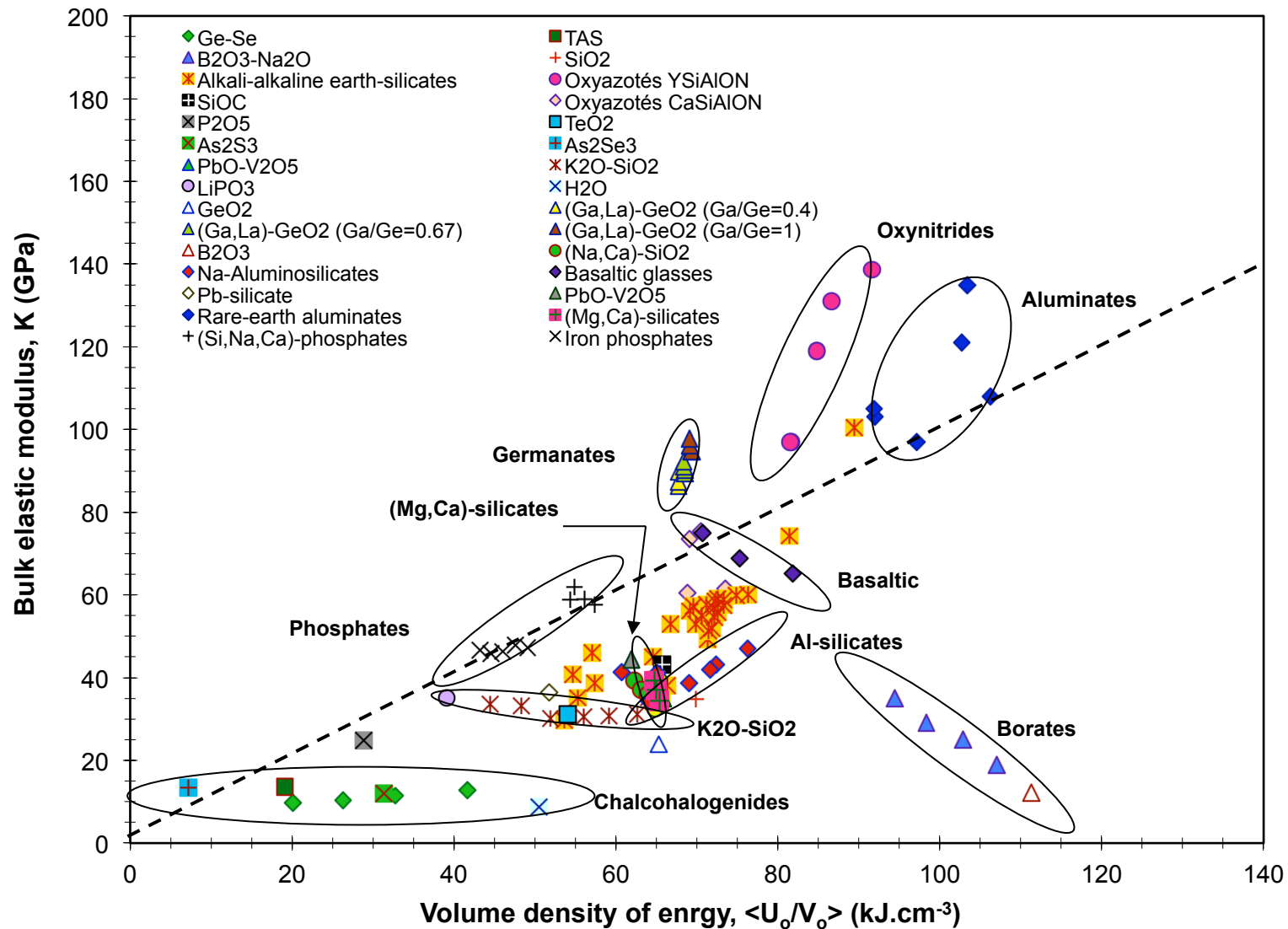






Dissociation energy (kJ/mol)



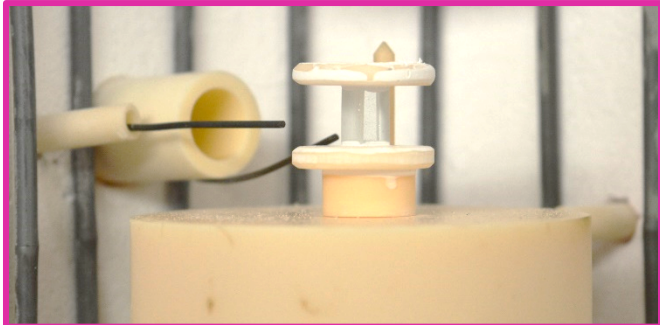
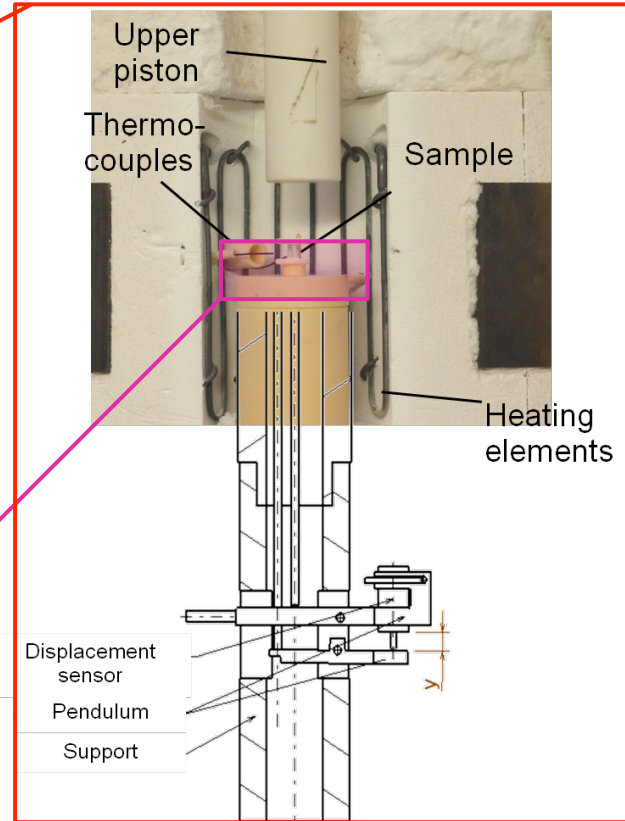
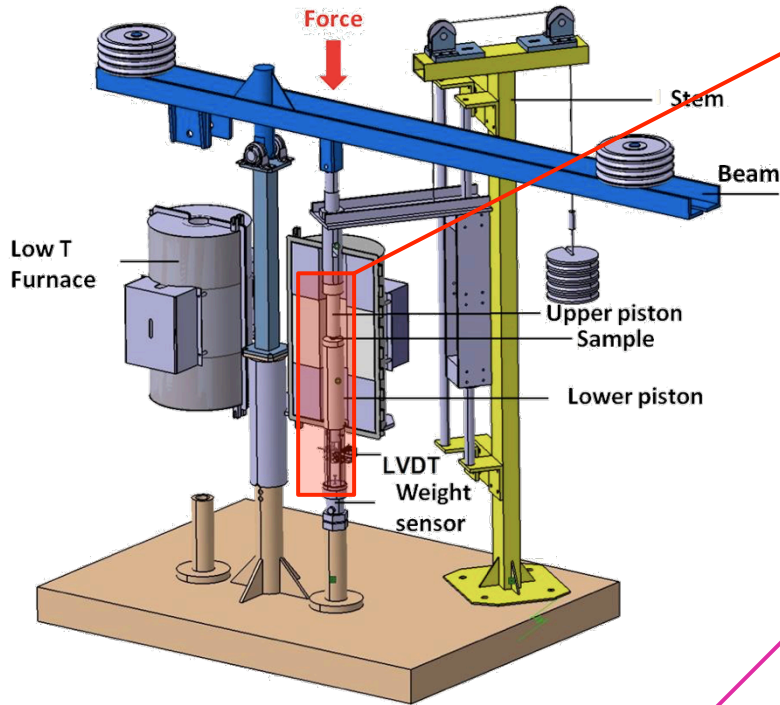


## Shear viscosity

*ii) Pourquoi les verres les plus rigides sont souvent très fragiles (au sens d'Angell)*

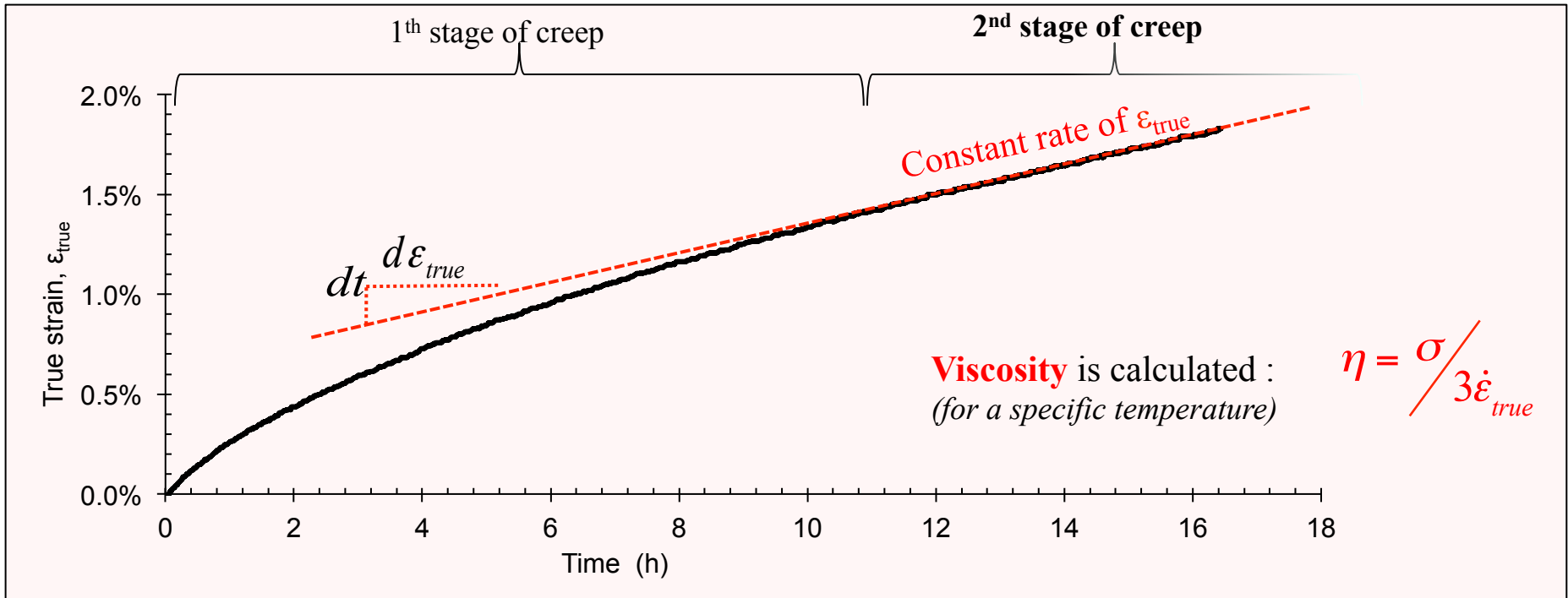
*iii) Est-ce que la viscosité linéaire existe vraiment?*

# Creep testing apparatus



- **Constant load apparatus**
- 2 thermocouples for **thermal** measurements
- Differential measurement of the **displacement**
- **Load cell** located at the bottom of the column

Example : Window Glass / 10 MPa / 0.98 T<sub>g</sub>

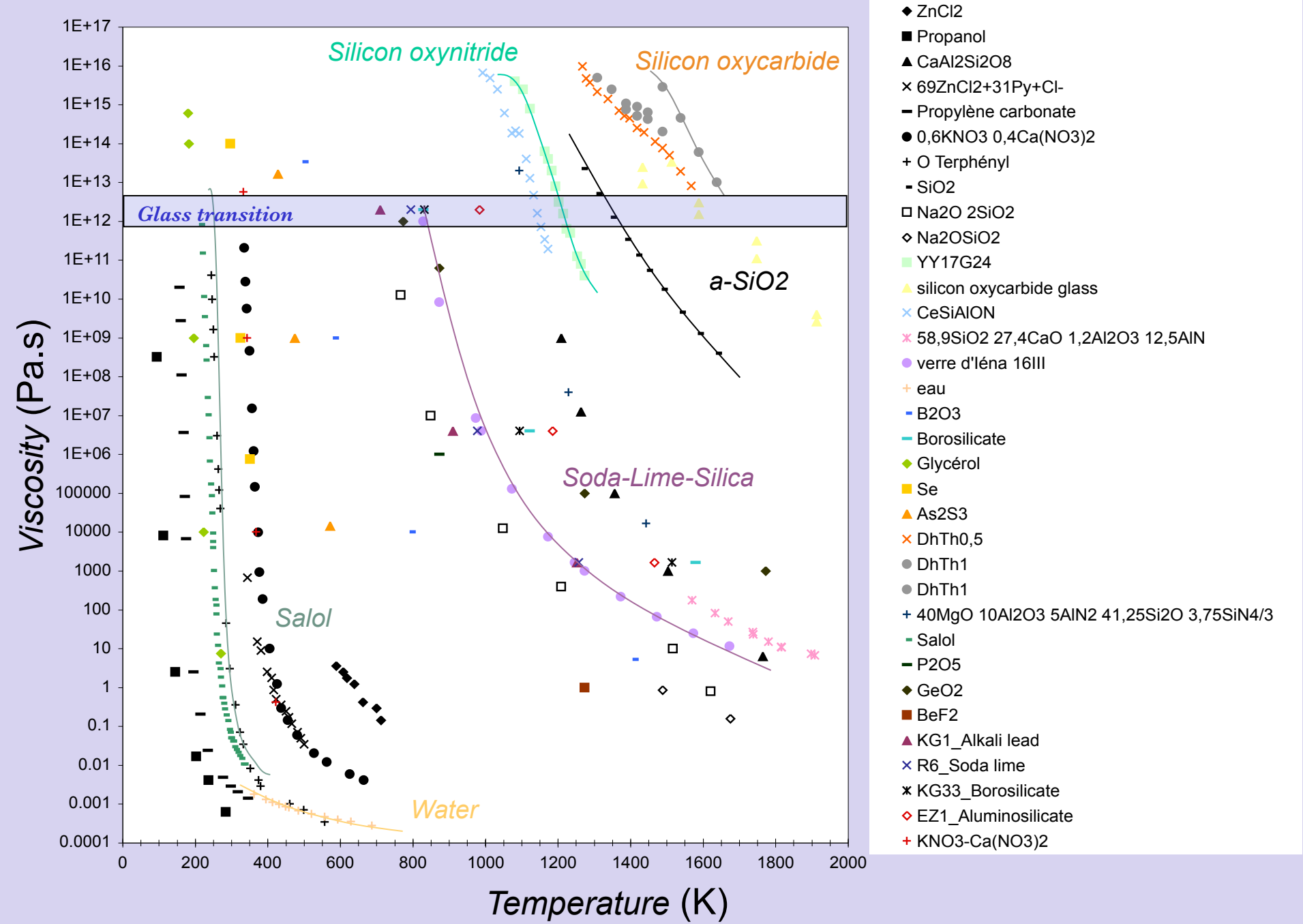


1 viscosity point = Constant temperature + waiting ( $\approx$  5 mins to.....6 days !)

$\eta \approx 10^8$  Pa.s

$\eta \approx 10^{14}$  Pa.s





**Boltzmann-Arrhenius** approach of thermally activated processes:

$$\tau = \tau_0 \exp[\Delta G_a / (RT)]$$

$\tau$ : the characteristic relaxation time

$\tau_0$ : a constant

T: temperature

R: perfect gas constant

$\Delta G_a$ : free activation enthalpy of the flow process

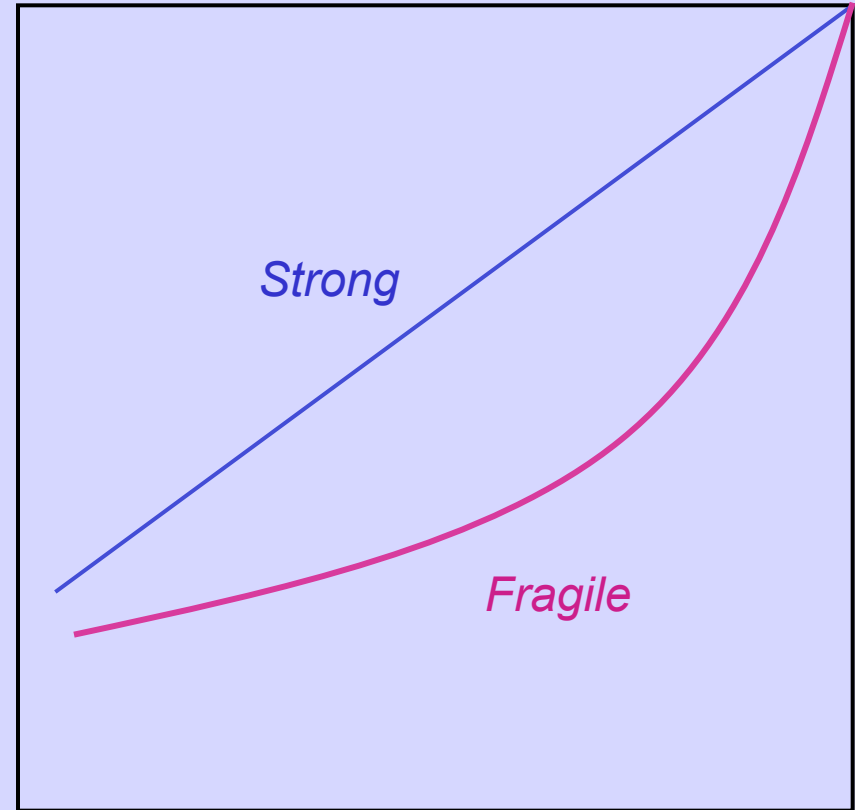
Assuming a simple Maxwell relaxation model

$$\eta = \mu \tau_0 \exp[\Delta G_a / (RT)] ,$$

where  $\mu$  is the shear elastic modulus.

$$\eta = \eta_0 \exp[\Delta G_a / (RT)]$$

Log  $\eta/\eta(T_g)$



$T_g/T$

*Observations: the heat for flow is temperature dependent, especially in the case of short glasses* → *VFT, WLF, AM, MYEGA... numerous empirical expressions*

*τροπή,τροπή...*

This is where entropy comes into play...

# ACTIVATION ENTROPY OF THE VISCOUS FLOW PROCESS

$$\eta = \eta_0 \exp[\Delta G_a / (RT)]$$



$$R \left. \frac{\partial \ln \eta}{\partial \frac{1}{T}} \right|_{\tau, stru} = \Delta G_a + \frac{1}{T} \left. \frac{\partial \Delta G_a}{\partial \frac{1}{T}} \right|_{\tau, stru}$$

$$- \left. \frac{\partial \Delta G_a}{\partial T} \right|_{\tau, stru} = \Delta S_a$$



$$R \left. \frac{\partial \ln \eta}{\partial \frac{1}{T}} \right|_{\tau, stru} = \Delta G_a + T \Delta S_a = \Delta H_a$$

$$\left. \frac{\partial \Delta G_b}{\partial T} \right|_{\tau, stru} = \frac{\Delta G_b}{\mu} \left. \frac{\partial \mu}{\partial T} \right|_{\tau, stru}$$

$$\Delta S_a = - \frac{\chi}{T} (\Delta G_a + \tau V_a) + \tau \frac{\partial V_a}{\partial T}$$

$$\Delta S_a^\mu$$

$$\Delta S_a^\tau$$

$$\chi = \frac{T}{\mu} \left. \frac{\partial \mu}{\partial T} \right|_{\tau, stru}$$

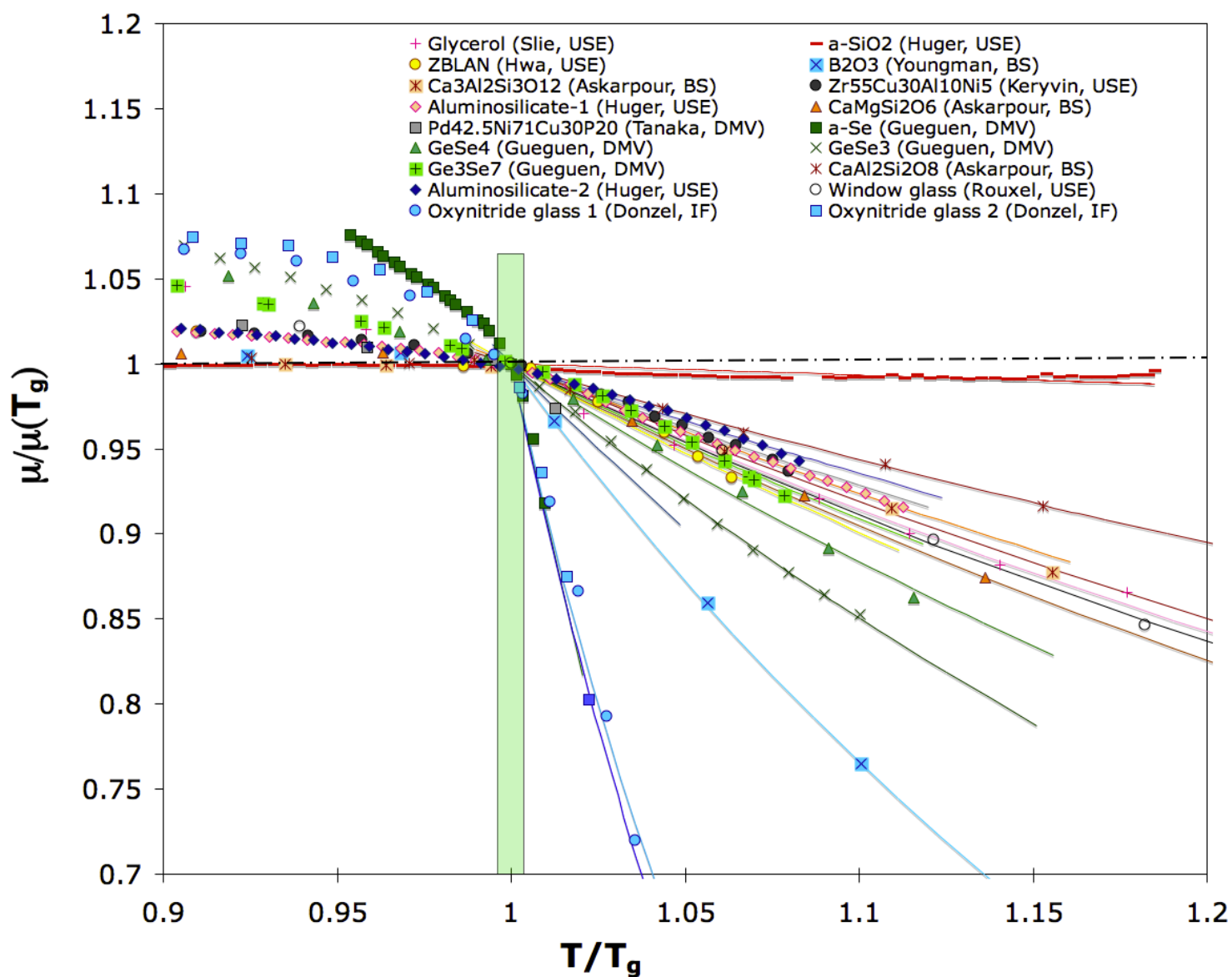


$$\Delta H_a = R \left. \frac{\partial \ln \eta}{\partial \frac{1}{T}} \right|_{\tau, stru}$$

$$\Delta S_a = - \frac{\chi}{(1-\chi)T} \Delta H_a$$

$$\Delta G_a = \frac{1}{(1-\chi)} \Delta H_a$$

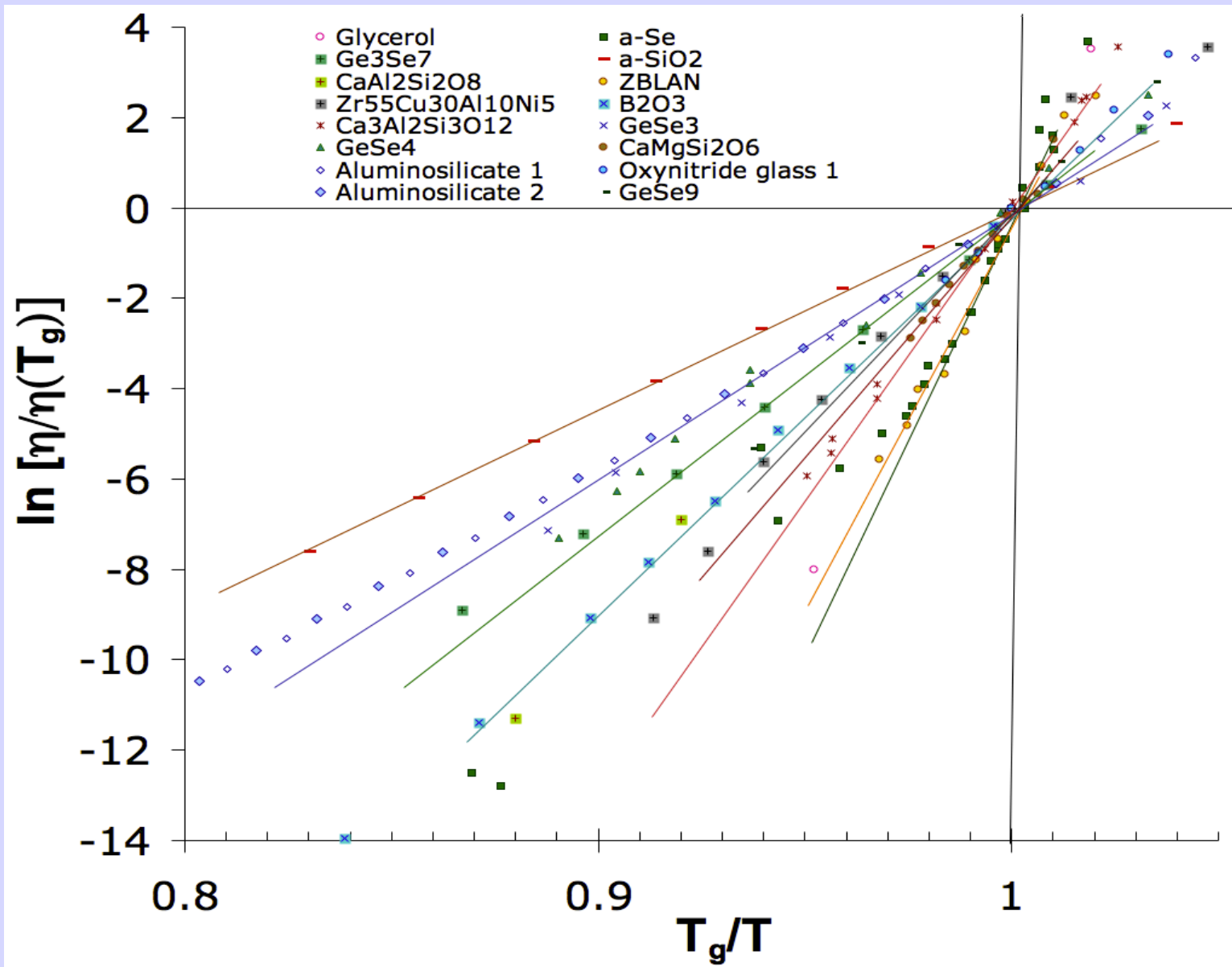
For  $\tau=10$  MPa and  $V_a=50$  cm<sup>3</sup>.mol<sup>-1</sup>,  $\tau V_a=500$  J.mol<sup>-1</sup>, to be compared with the order of activation energies, 100 to 1000 kJ.mol<sup>-1</sup>



For  $T > T_g$ ,  $\mu/\mu(T_g) = (T_g/T)^\alpha$

where  $\alpha$  ranges between 0.07 ( $a\text{-SiO}_2$ ) and 10 ( $a\text{-Se}$ )





$$\Delta H_a = R \left. \frac{\partial \ln \eta}{\partial (1/T)} \right|_{\sigma, stru}$$

Table 1

Physical properties of the glasses – Vickers hardness (Hv) values were measured with a 500 g load<sup>11</sup>; Young's and shear elastic moduli,  $E$  and  $G$ , were measured by means of ultrasonic echography<sup>15</sup> or calculated.<sup>15</sup>

Glass grade	Glass composition	N/e/o	Ca/e/o	$n_{BO}$	$\rho$ g cm <sup>-3</sup>	$T_g$ , °C determined by DTA $\pm 5$ °C	$T_g$ , °C from viscosity measurements	Hv, GPa	$E$ , GPa	$G$ , GPa	$\nu^a$
N 30 e/o	Ca <sub>11.88</sub> Si <sub>10</sub> O <sub>22.06</sub> N <sub>6.50</sub>	30.7	37.1	3.26	3.13	887	878 $\pm$ 5	7.73	–	–	–
N 36 e/o	Ca <sub>12.90</sub> Si <sub>10</sub> O <sub>20.93</sub> N <sub>7.98</sub>	36.4	39.2	3.22	3.02	912	896 $\pm$ 9	7.75	110	43.4	0.30
N 58 e/o	Ca <sub>11.04</sub> Si <sub>10</sub> O <sub>13.21</sub> N <sub>11.8</sub>	58	35.6	3.29	3.24	1010	995 $\pm$ 5	9.62	135	52.8	0.28

<sup>a</sup> Poisson's ratio ( $\nu$ ) is calculated by means of the classical relationship:  $\nu = E/(2G) - 1$ .

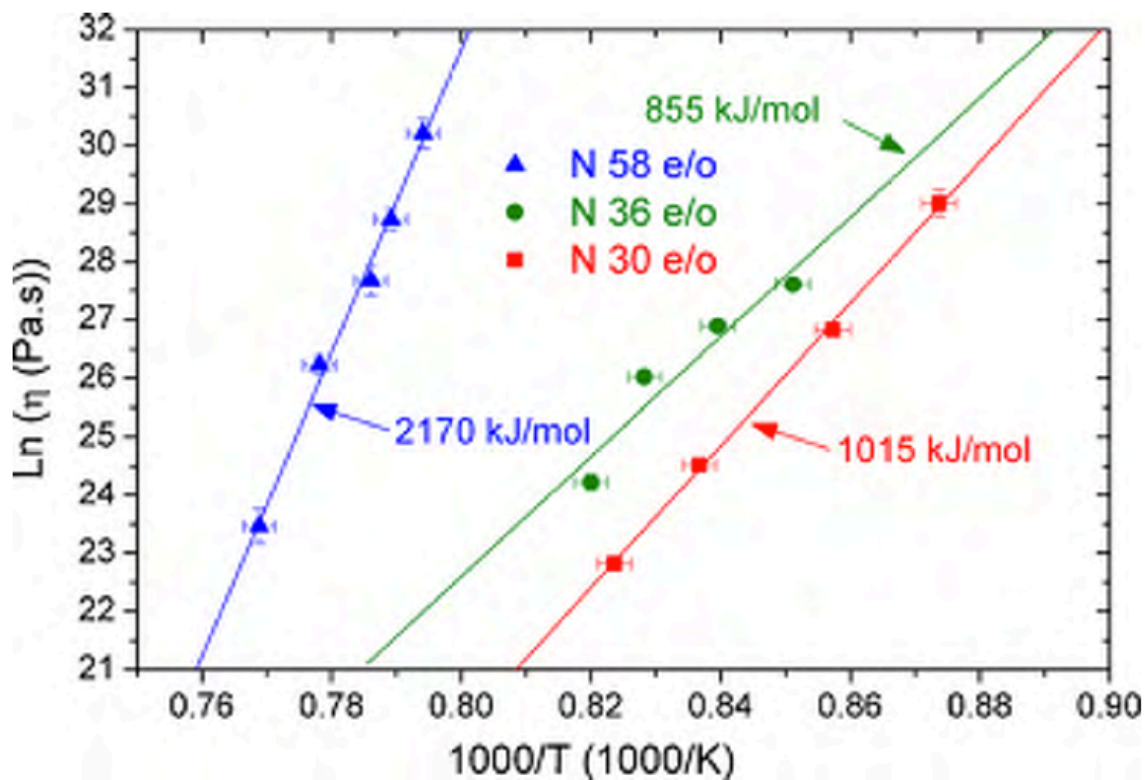
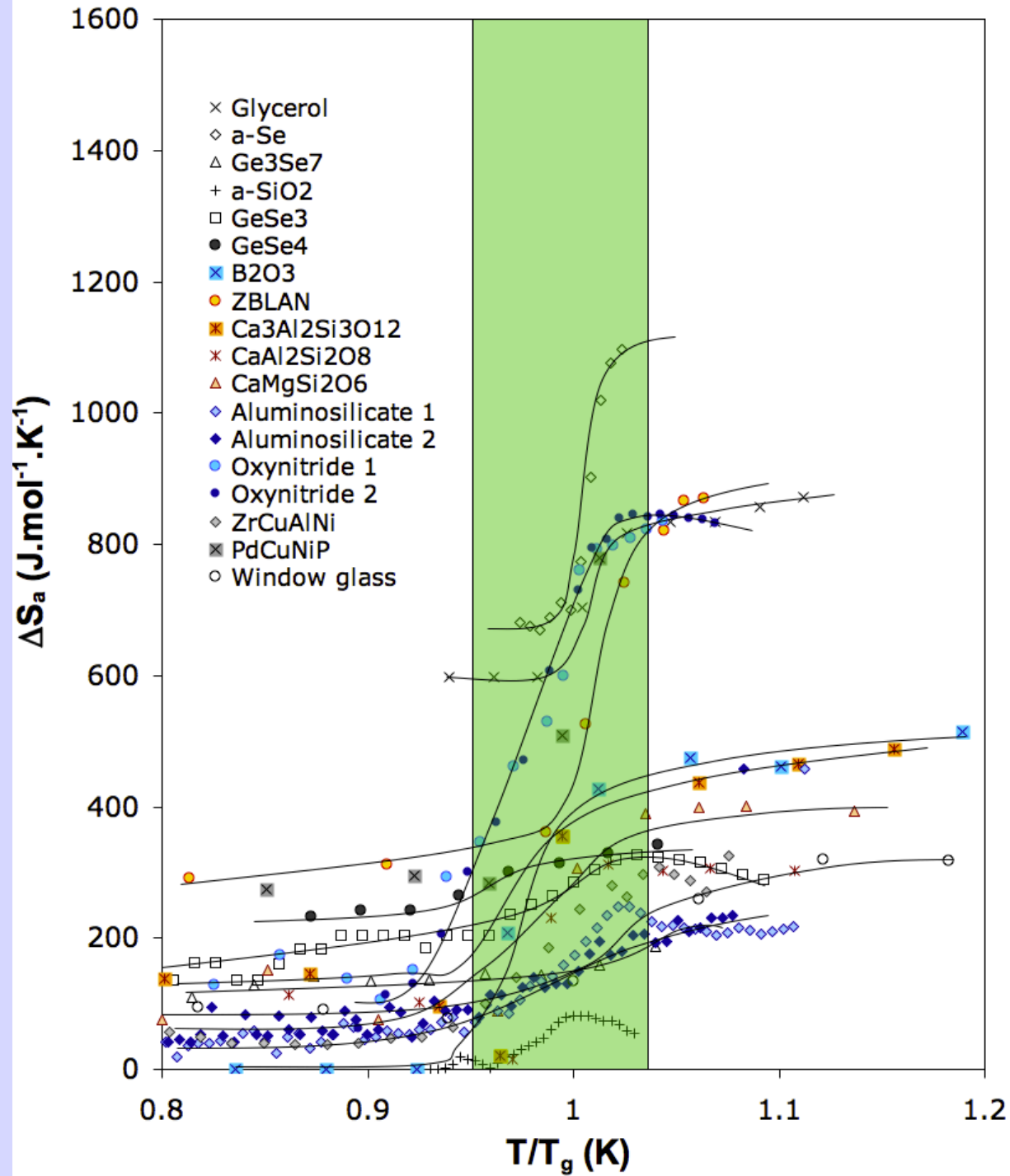
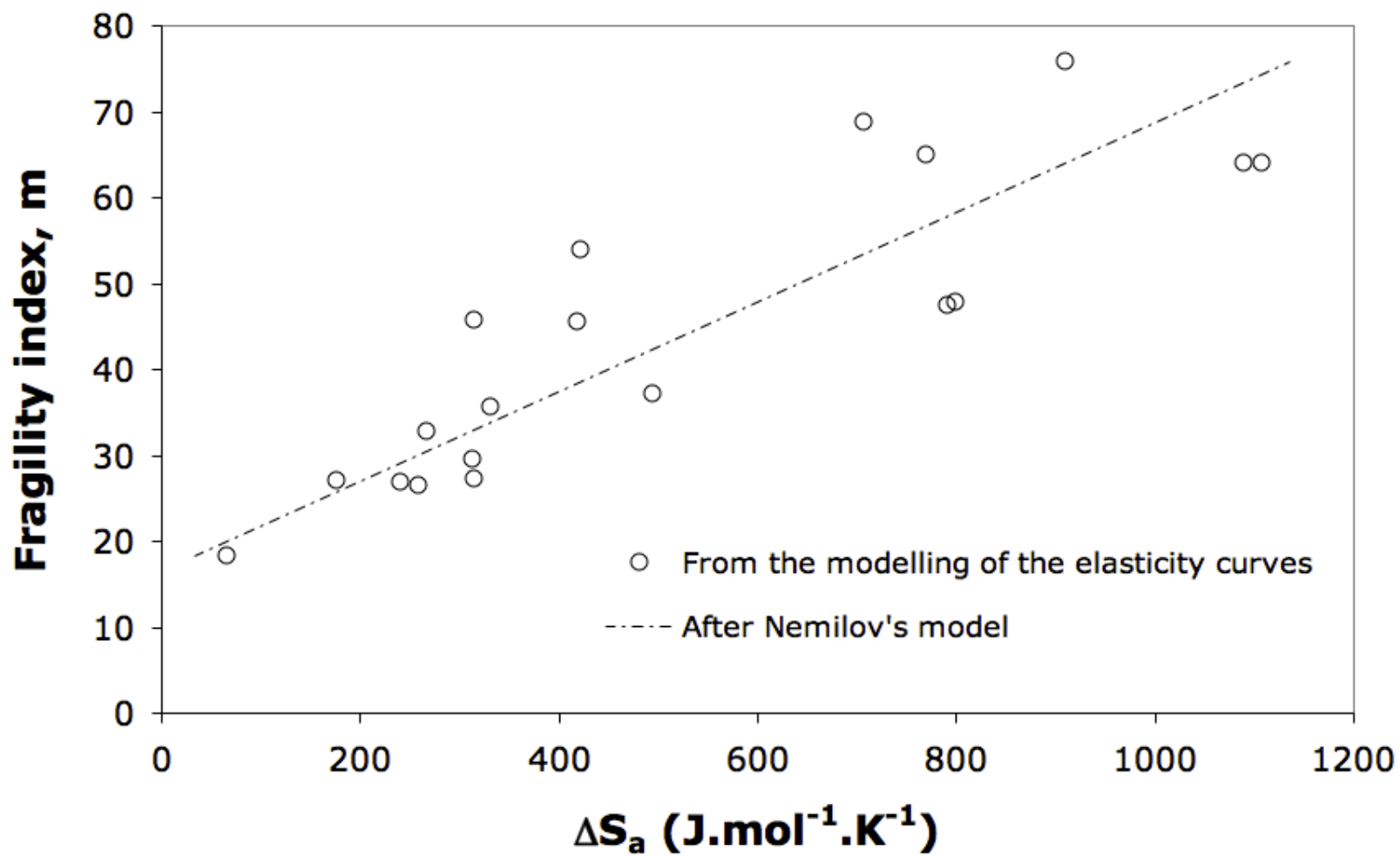


Fig. 2. Logarithm of the viscosity of Ca–Si–O–N glasses as a function of reciprocal temperature. The full lines correspond to the Arrhenius expression for viscosity.

Yes, we believe there is some confinement or some segregation of nitrogen in the network





$$\left\{ \begin{aligned} \frac{\partial \Delta G_a}{\partial T} \Big|_{\sigma, stru} &= \frac{\Delta G_a}{\mu} \frac{\partial \mu}{\partial T} \Big|_{\sigma, stru} \\ \mu / \mu(T_g) &= (T_g / T)^\alpha \end{aligned} \right.$$



$$\Delta G_a = \Delta G_a(T_g) (T_g / T)^\alpha$$



$$\eta = \eta_o \exp \left[ \frac{\Delta G_a(T_g) (T_g / T)^\alpha}{RT} \right]$$

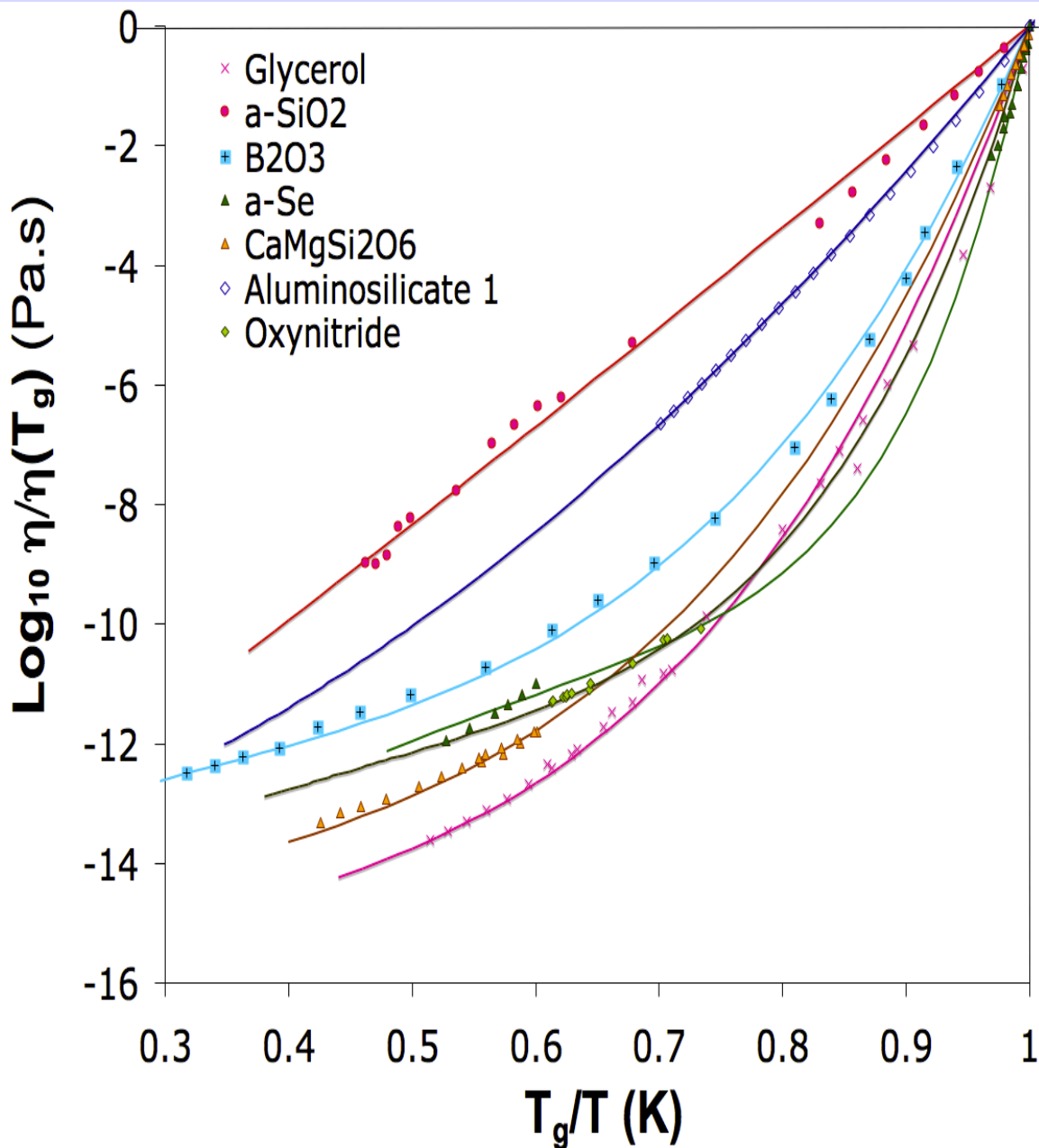
with

$$\left\{ \begin{aligned} \Delta G_a(T_g) &= \frac{\Delta H_a(T_g)}{\left( 1 - \frac{T_g}{\mu(T_g)} \frac{\partial \mu}{\partial T} \Big|_{T_g} \right)} \\ \eta_o &= \mu(T) \eta(T_g) / \mu(T_g) \end{aligned} \right.$$

*Equivalent to Avramov-Milchev equation*

with:  $\mu(T) = \mu_\infty \exp(E_u / T)$

*Equivalent to MYEGA equation*

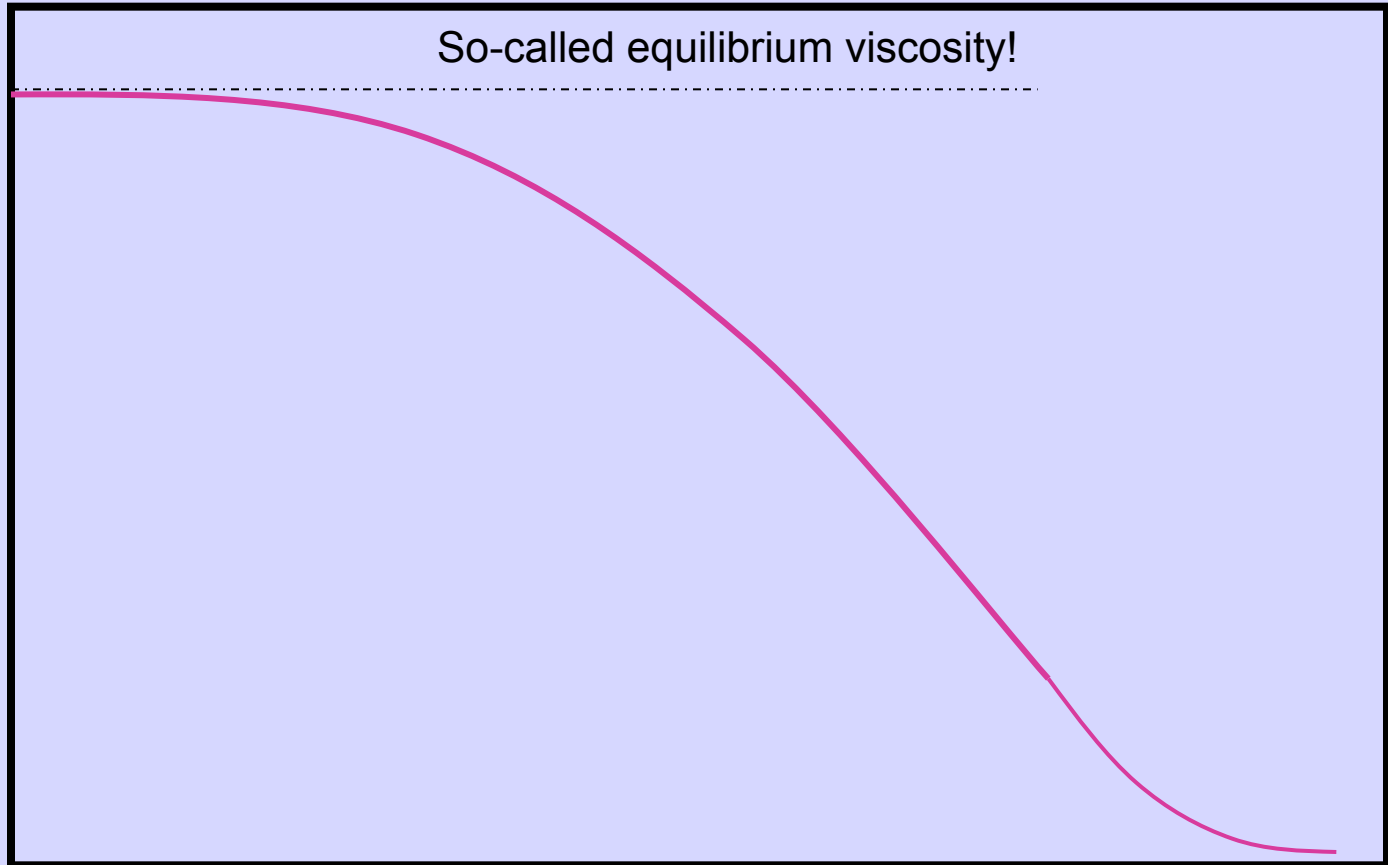




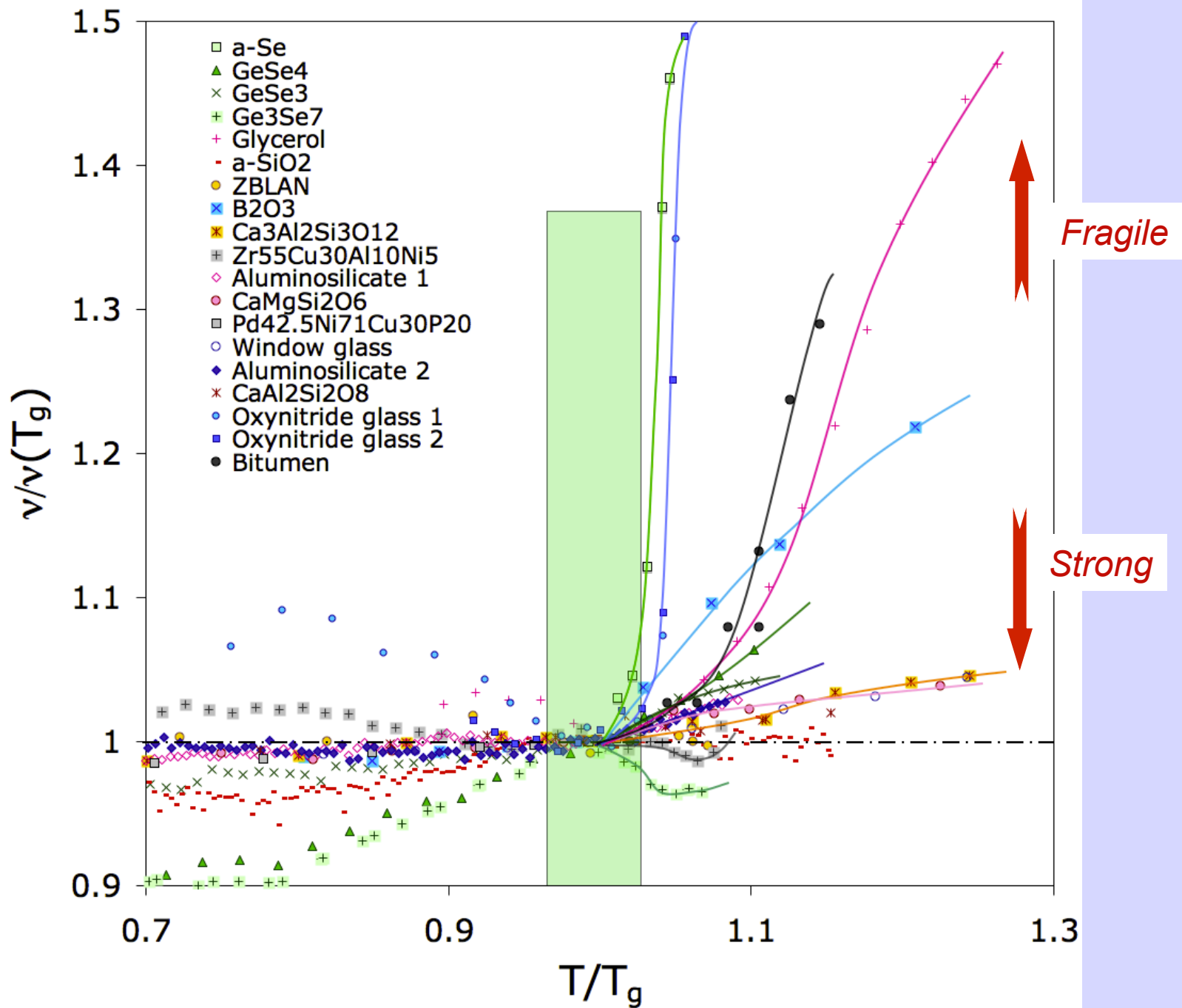
- 
- iii) Est-ce que la viscosité linéaire existe vraiment?

## *Stress or strain-rate dependence*

Log  $\eta$

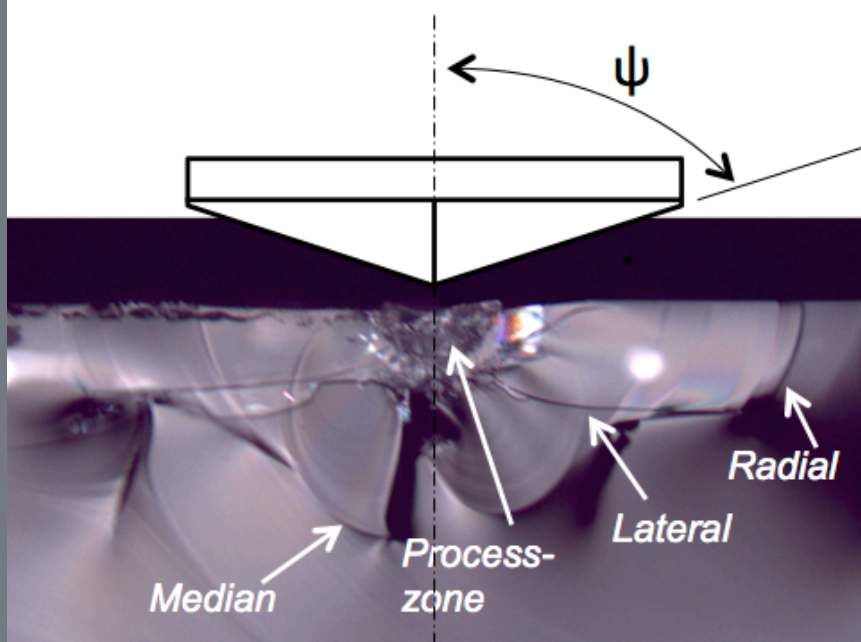


Log stress

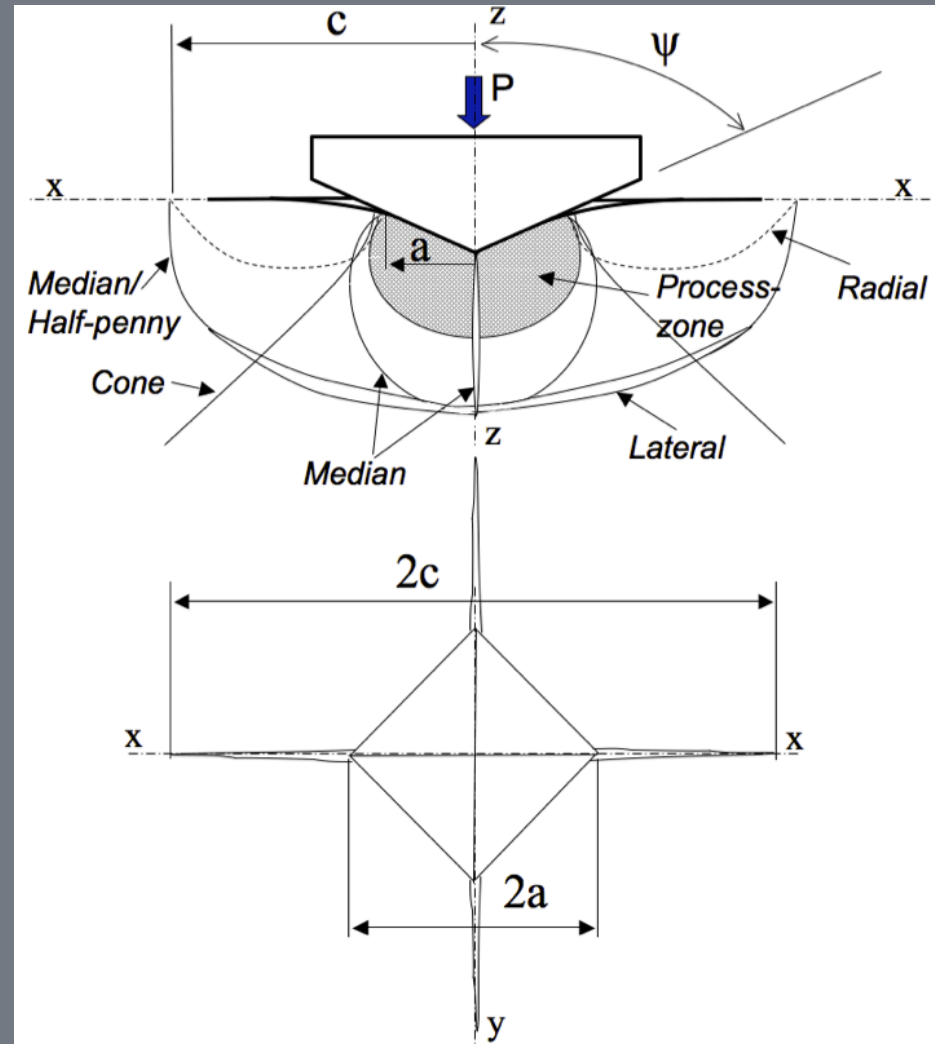
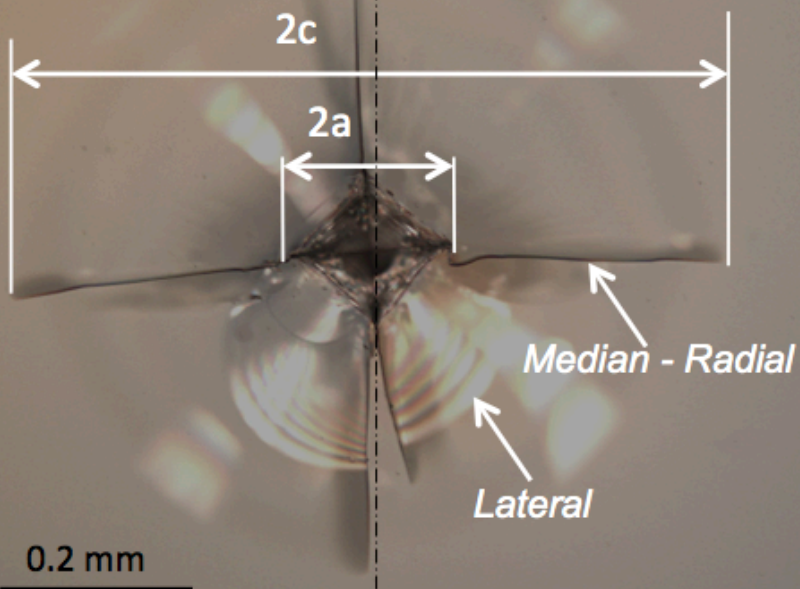




**What we know about hardness, indentation cracking,  
and fracture toughness**

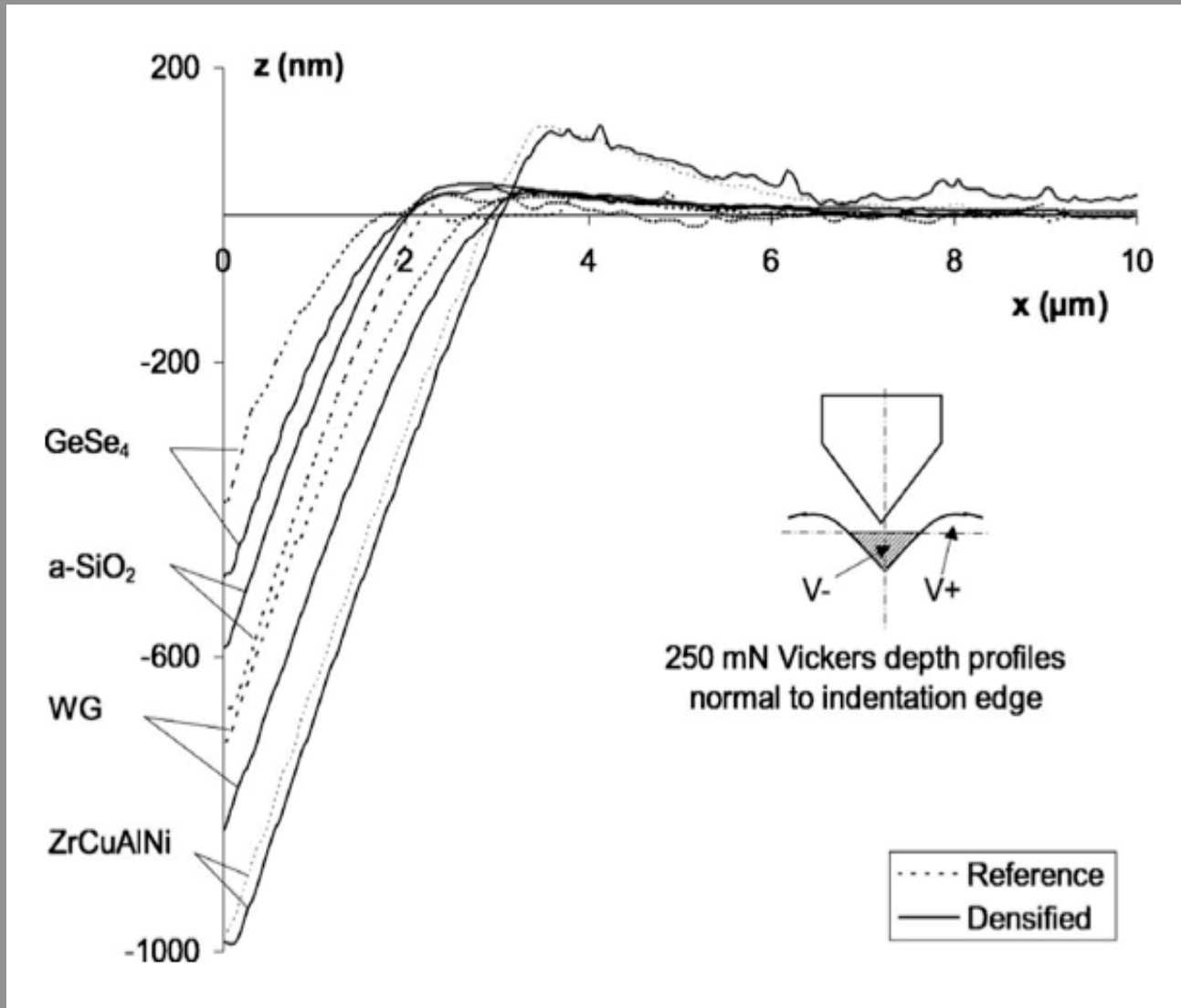


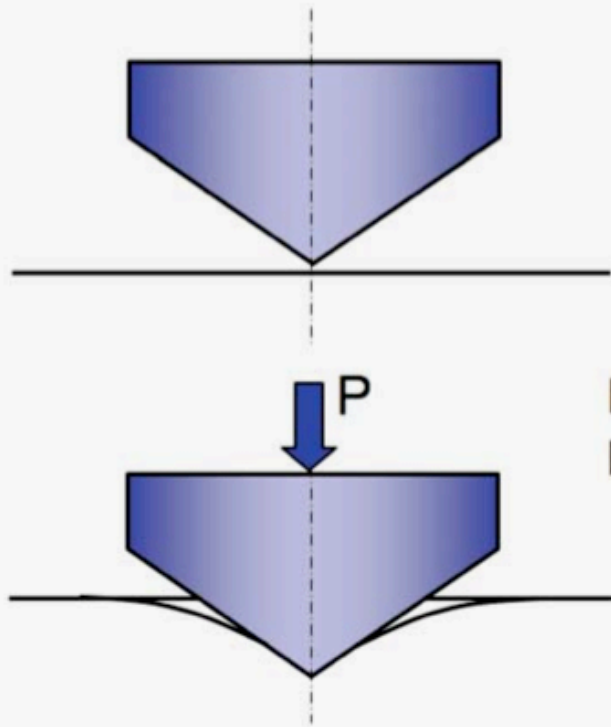
Soda-Lime-Silicate  
Vickers – 10 kgs





# Isochoric shear flow contribution (pile-up)



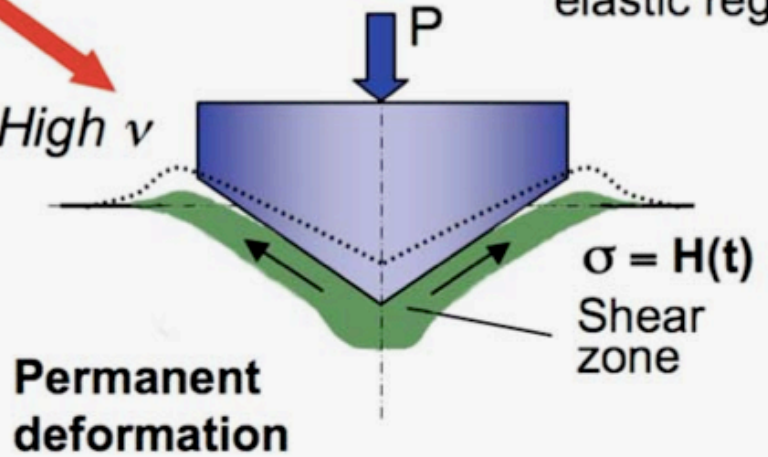
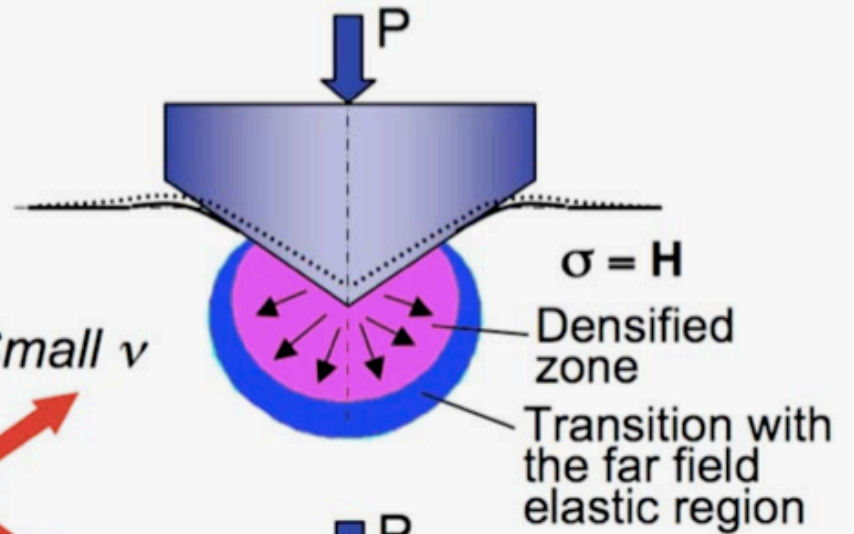


Instantaneous elasticity  
 $\sigma = H_{el} \gg H$

Relaxation  
 process

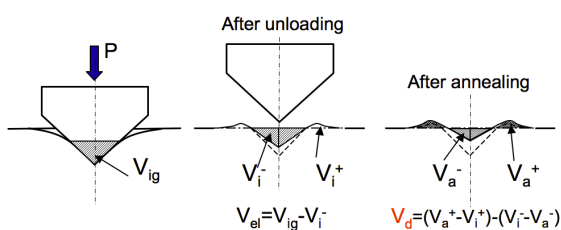
*Small  $\nu$*

*High  $\nu$*



Permanent  
 deformation

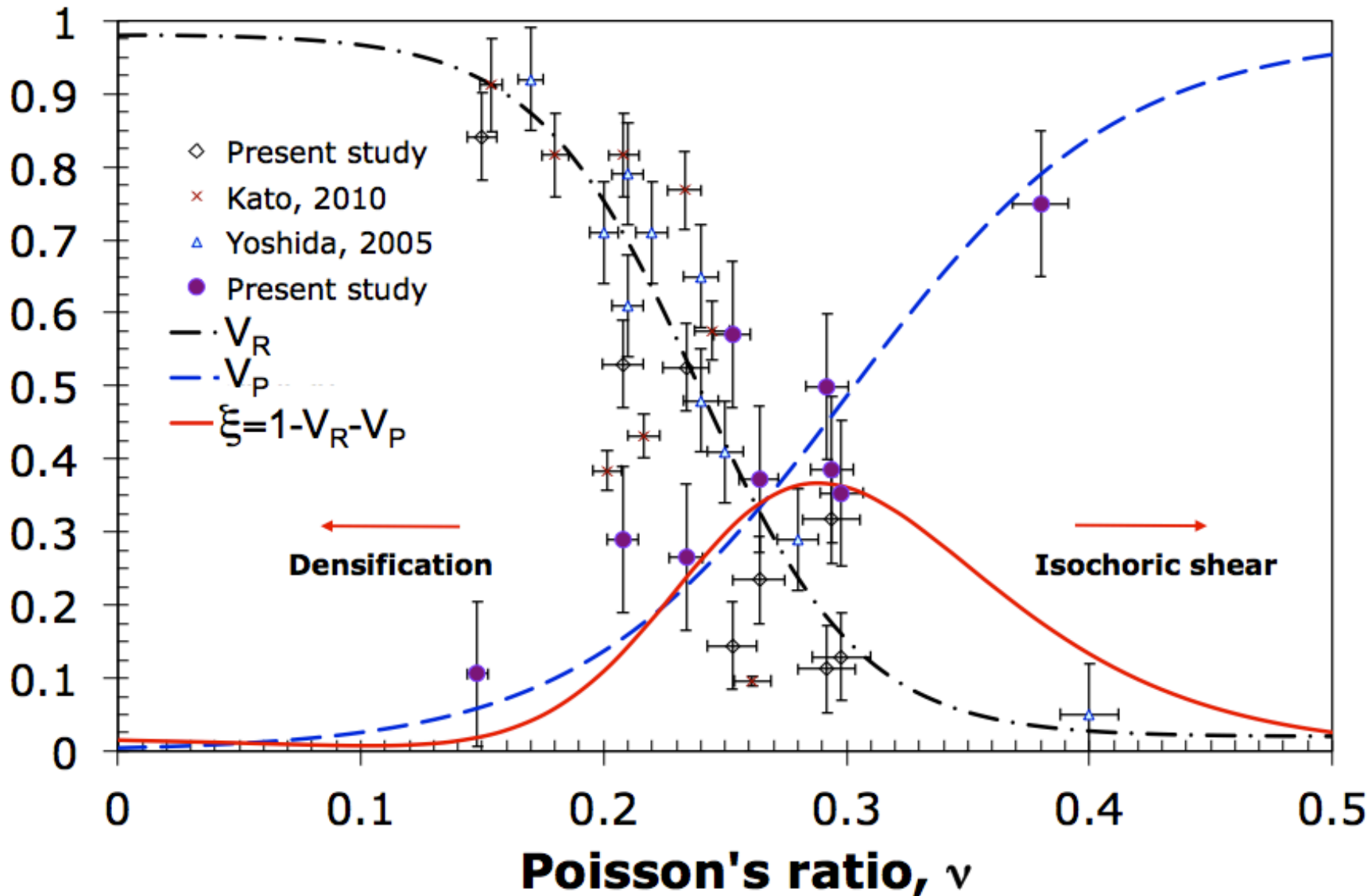
$$V_R = V_d / V_i^-$$



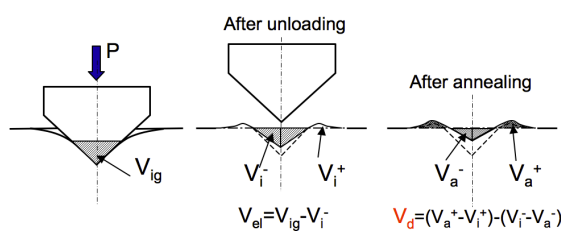
$$V_P = [V_i^+ - (V_a^+ - V_i^+)] / V_i^-$$

$$V_P = (2V_i^+ - V_a^+) / V_i^-$$

Recovery and pile-up  
volumes ( $V_R$  and  $V_P$ )

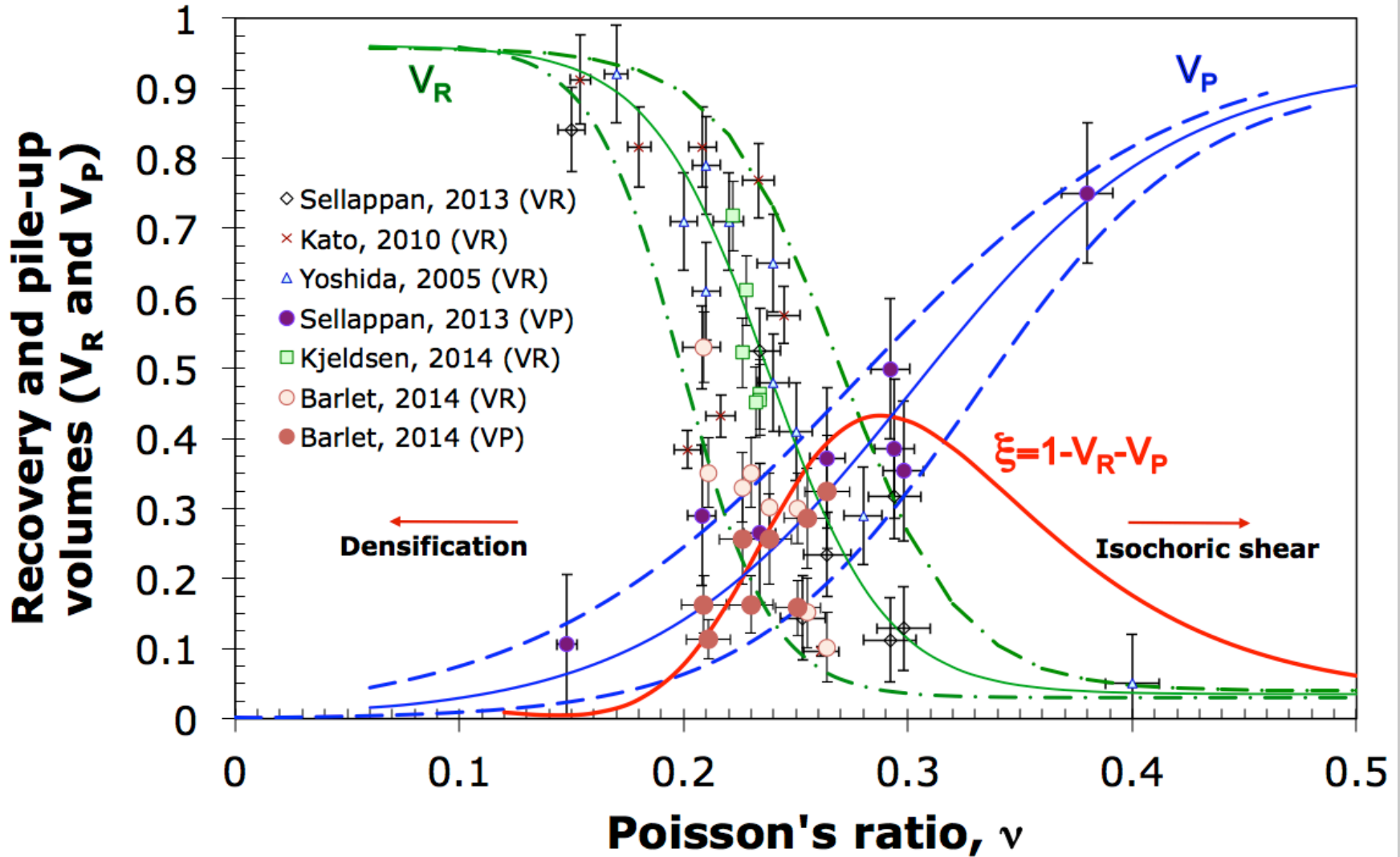


$$V_R = V_d / V_i^-$$



$$V_P = [V_i^+ - (V_a^+ - V_i^+)] / V_i^-$$

$$V_P = (2V_i^+ - V_a^+) / V_i^-$$



$$\sigma_{rr} = \frac{P}{2\pi r^2} [1 - 2\nu - 2(2 - \nu)\cos\theta] + \frac{4B}{r^3} [(5 - \nu)\cos^2\theta - 2 + \nu] \quad (1)$$

$$\sigma_{\theta\theta} = \frac{P}{2\pi r^2} \frac{(1 - 2\nu)\cos^2\theta}{1 + \cos\theta} - \frac{2B}{r^3} (1 - 2\nu)\cos^2\theta \quad (2)$$

$$\sigma_{\phi\phi} = \frac{(1 - 2\nu)P}{2\pi r^2} \left[ \cos\theta - \frac{1}{1 + \cos\theta} \right] + \frac{2B}{r^3} (1 - 2\nu)(2 - 3\cos^2\theta) \quad (3)$$

$$\sigma_{r\theta} = \frac{P}{2\pi r^2} \frac{(1 - 2\nu)\sin\theta\cos\theta}{1 + \cos\theta} + \frac{4B}{r^3} (1 + \nu)\sin\theta\cos\theta \quad (4)$$

$$\sigma_{r\phi} = \sigma_{\theta\phi} = 0 \quad (5)$$

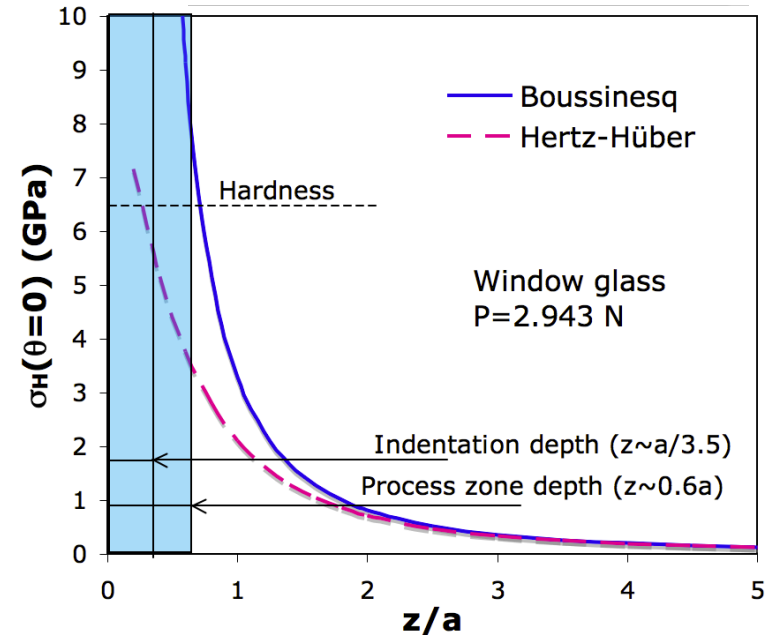
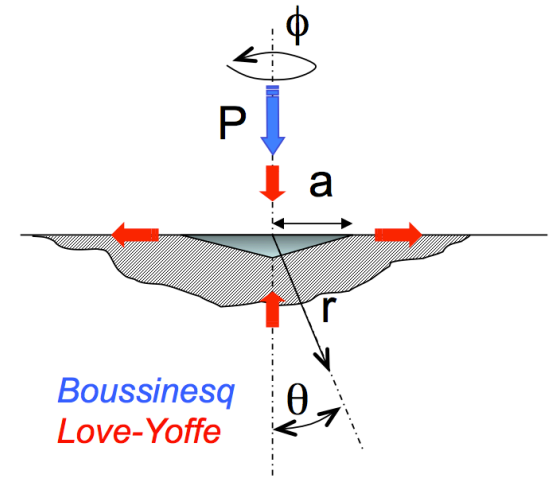
P : indentation load and

— : Boussinesq's field

— : blister field,

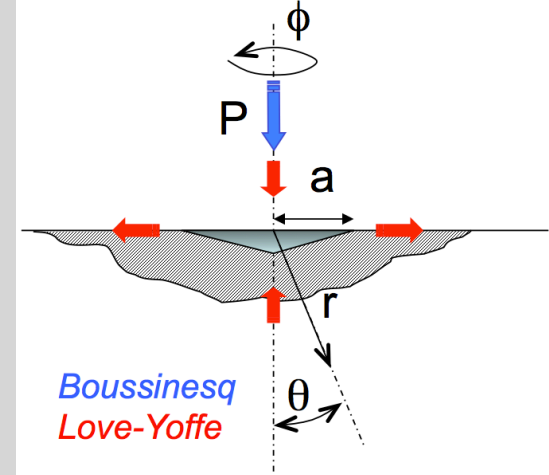
$$B = \frac{3E}{4\pi(1 + \nu)(1 - 2\nu)} (1 - V_R - V_P)V_i^- \quad (6)$$

$$\left( V_i^- = \frac{2a^3}{3\tan\psi} \right) \quad (7)$$



Paramount importance of Poisson's ratio  $\nu$

For silicate glasses,  $E/H$  is typically between 10-15



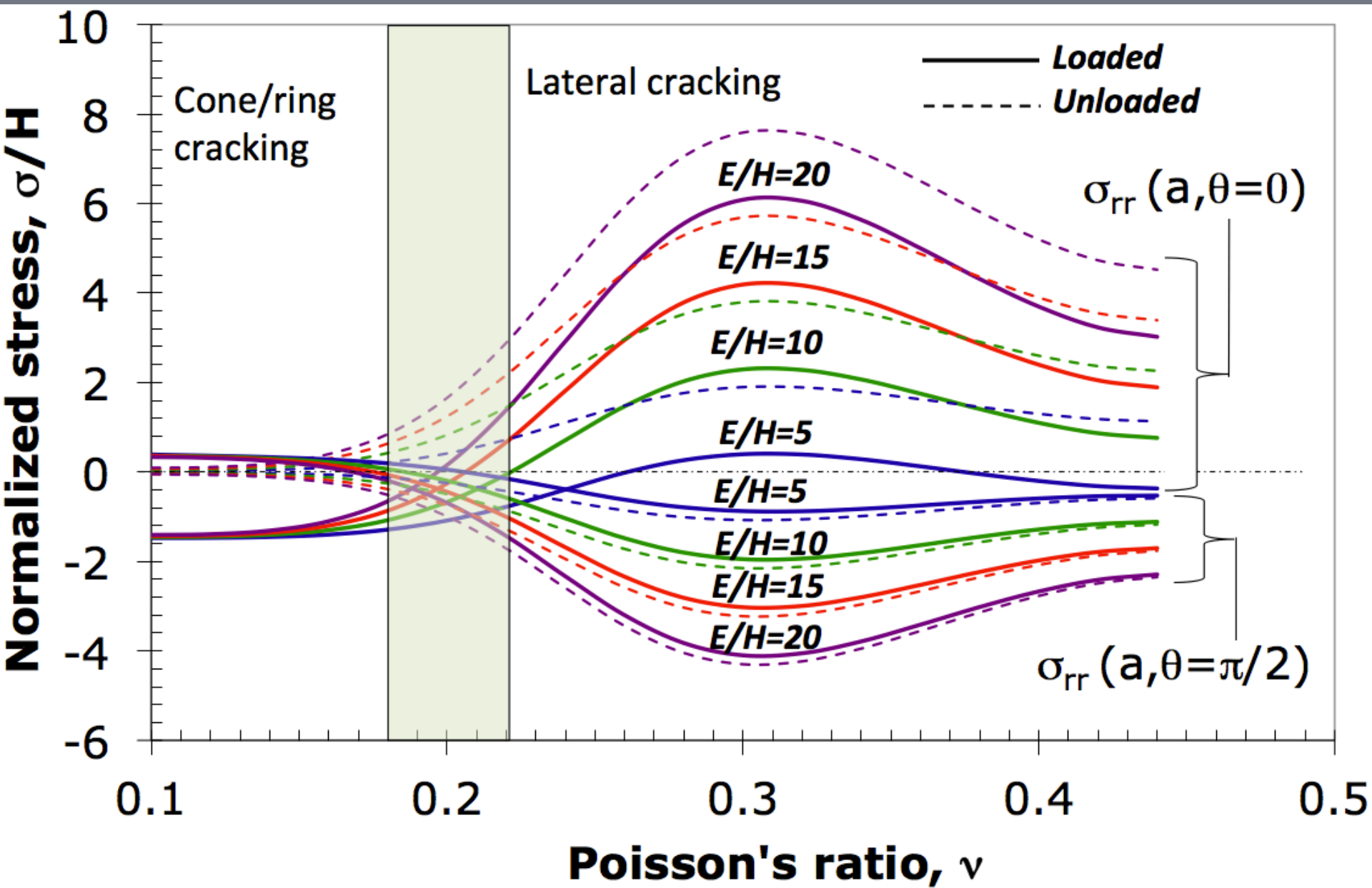
**Ring cracks :** 
$$\sigma_{rr}(r = a, \theta = \pi / 2) / H = \frac{1 - 2\nu}{2} + \frac{2(\nu - 2)(1 - V_R - V_P)}{\pi(1 + \nu)(1 - 2\nu) \tan \psi} (E / H)$$

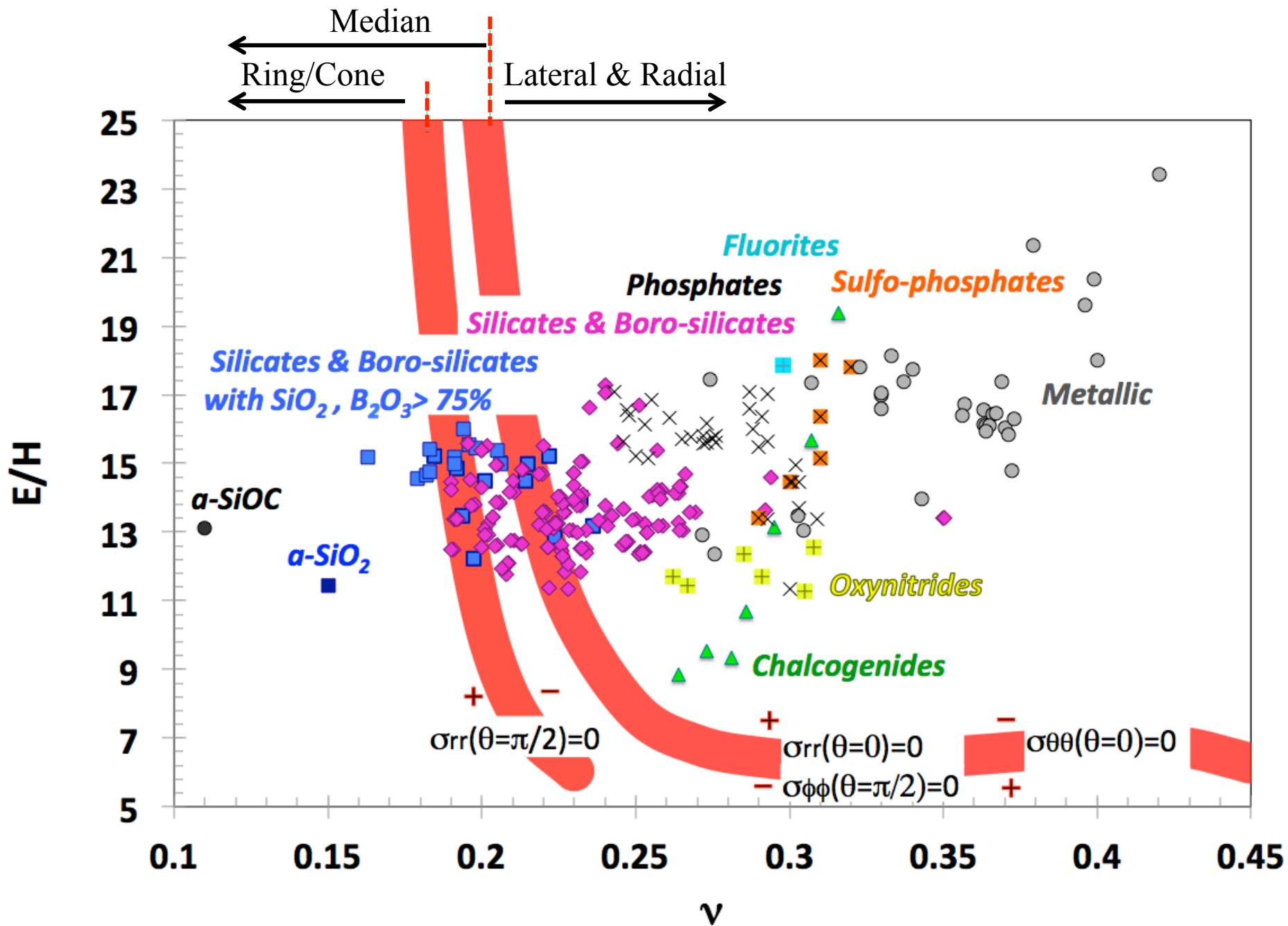
**Radial cracks :** 
$$\sigma_{\phi\phi}(r = a, \theta = \pi / 2) / H = \frac{2\nu - 1}{2} + \frac{2(1 - V_R - V_P)}{\pi(1 + \nu) \tan \psi} (E / H)$$

**Median cracks :** 
$$\sigma_{\theta\theta}(r = a, \theta = 0) / H = \frac{1 - 2\nu}{4} - \frac{(1 - V_R - V_P)}{\pi(1 + \nu) \tan \psi} (E / H)$$

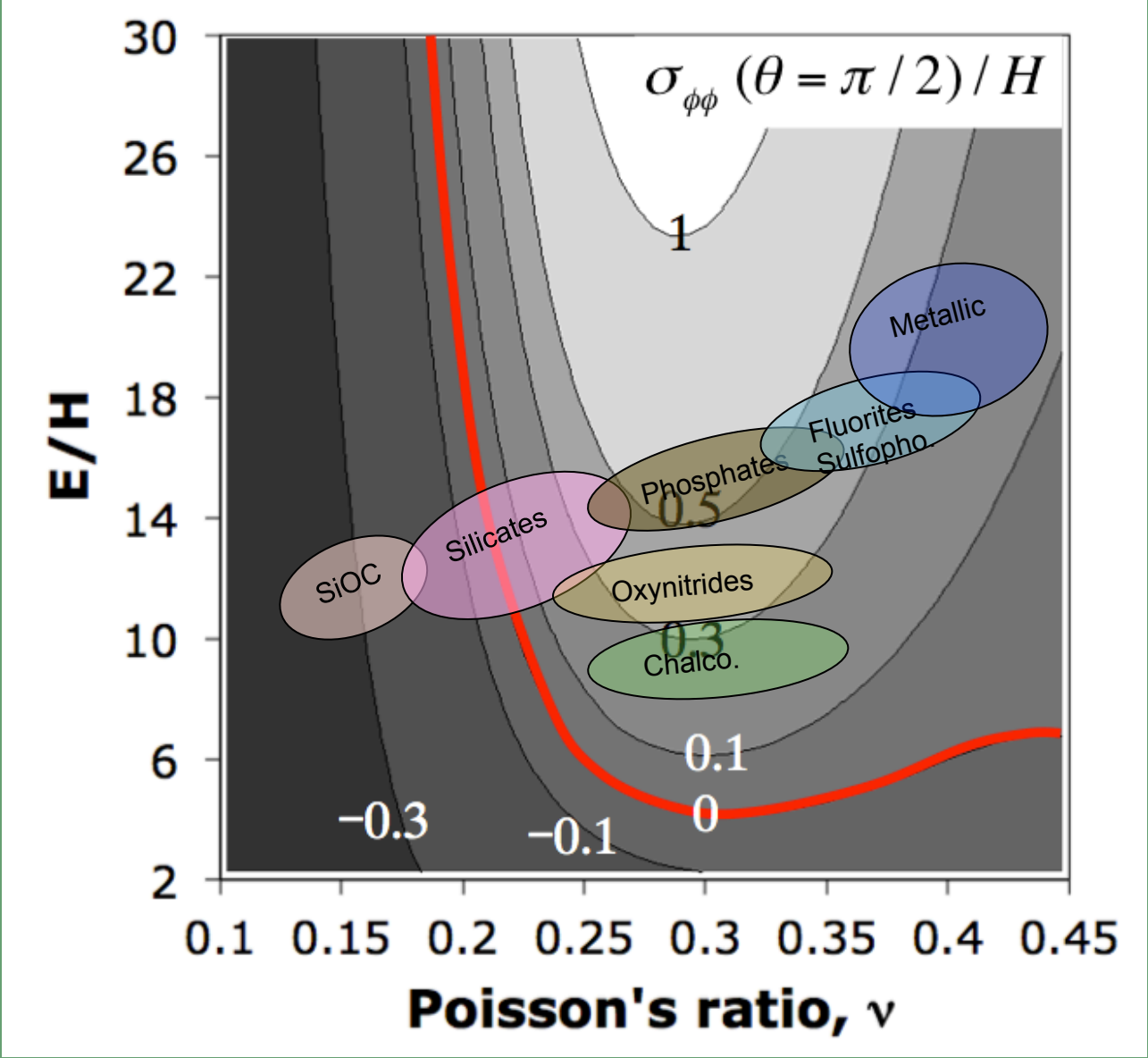
**Sub-surface lateral cracks :** 
$$\sigma_{rr}(r = a, \theta = 0) / H = -\frac{3}{2} + \frac{6(1 - V_R - V_P)}{\pi(1 + \nu)(1 - 2\nu) \tan \psi} (E / H)$$

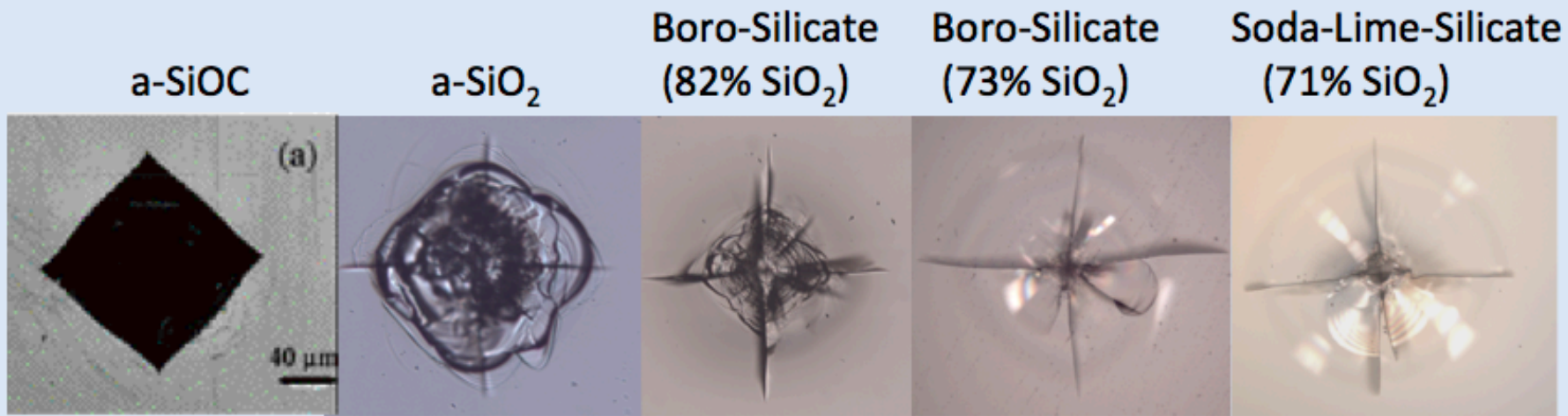






# Radial cracking





*0.11*

*0.15*

*0.195*

*0.208*

*0.234*

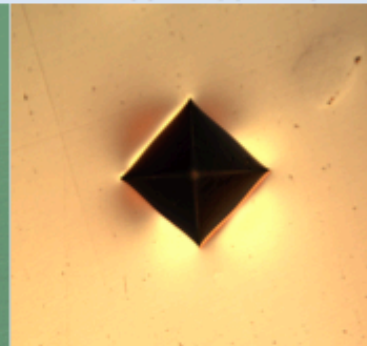
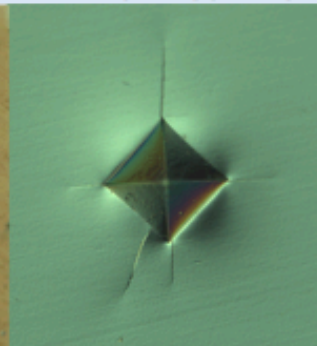
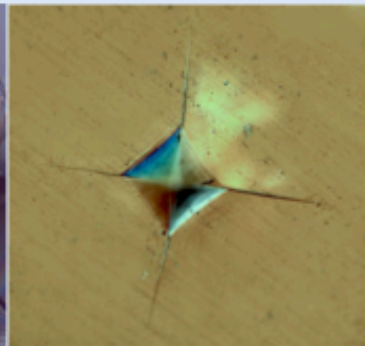
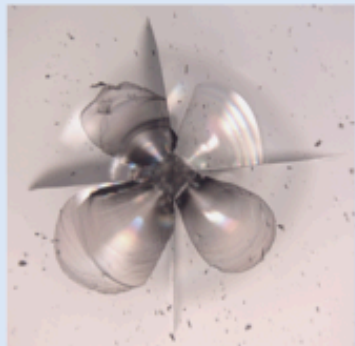
Boro-Lime-Silicate  
(37.5% SiO<sub>2</sub>)

Fluorite

Oxynitride Silicate

Zr<sub>40</sub>Cu<sub>50</sub>Al<sub>10</sub>

Zr<sub>60</sub>Cu<sub>30</sub>Al<sub>10</sub>



*0.292*

*0.298*

*0.308*

*0.35*

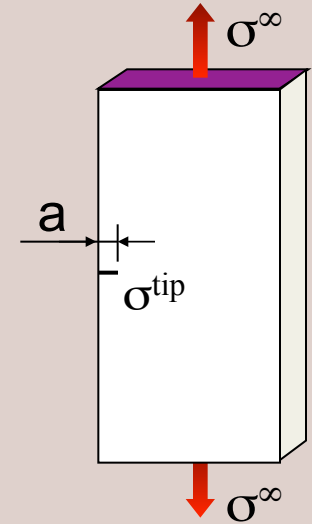
*0.373*

*v*

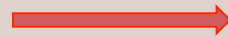
$$K_I \propto \sigma^\infty \sqrt{a} \propto \sigma^{tip} \sqrt{\rho}$$

At fracture:

$$K_{Ic} \propto \sigma_c \sqrt{\rho} \propto \sigma_r \sqrt{a}$$



$$G_{Ic} = \frac{K_{Ic}^2}{E^*}$$



$$K_{Ic} = \sqrt{\frac{2\gamma E}{1-\nu^2}}$$

$$\gamma = \frac{1}{2} \left( \frac{\rho}{M_0} \right)^{2/3} \mathcal{N}^{-1/3} \sum_i x_i n_i U_{oi}$$

$$\gamma = \frac{1}{2} \left( \sum_i 4/3\pi x_i r_i^3 \right)^{-2/3} \mathcal{N}^{-1/3} C_g^{2/3} \langle U_o \rangle$$

« As she has the beauty of glass, she has its brittleness » (Polyeucte, Corneille)

● **Toughness and practical strength:**

$$K_I = \sigma Y \sqrt{c} \quad \text{with}$$

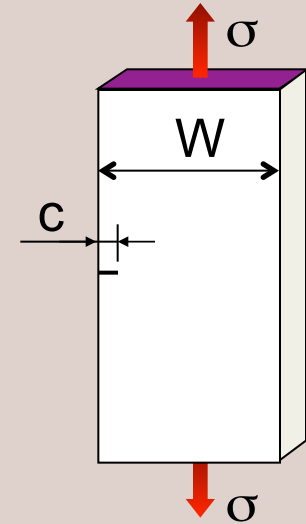
$$K_I = 1.12 \sigma \sqrt{(\pi c)}$$

$K_I$ : Stress intensity factor in mode I (opening)

$\sigma$ : Applied stress

$c$ : Flaw size

$Y$ : Shape factor



**At the onset of fracture:  $K_I = K_{Ic}$  et  $\sigma = \sigma_r$**

With  $\sigma_r = 200$  MPa and  $K_{Ic} = 0.7$  MPa $\sqrt{m}$ ,  $c = 2$   $\mu\text{m}$ !



The flaw size is a fact of the problem



