

# La mécanique des Verres

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● 2 notions: Contraintes, Déformations

● Elasticité

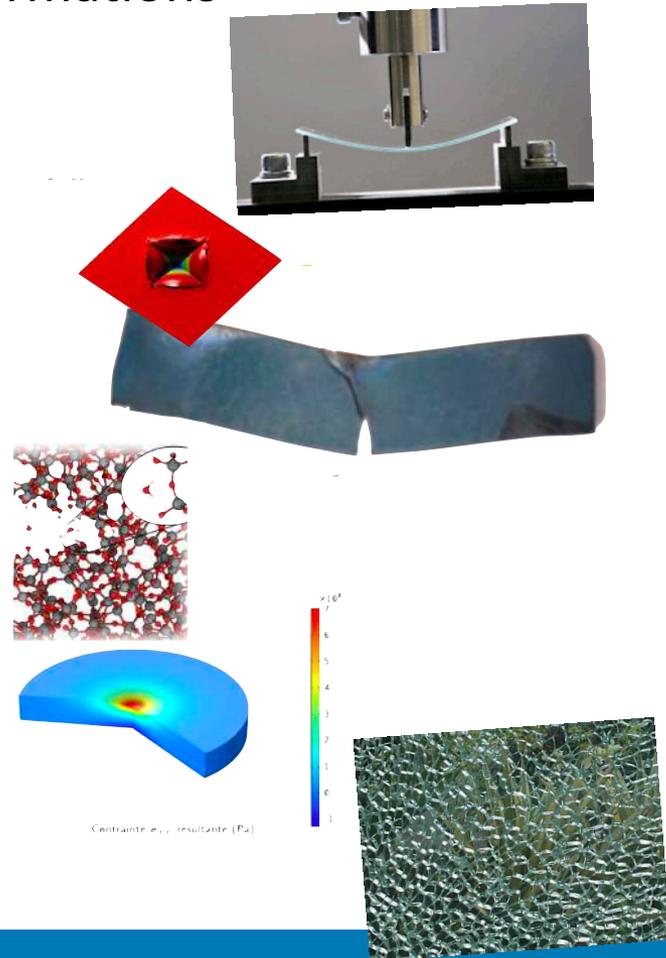
● Fragilité/Ductilité/Dureté

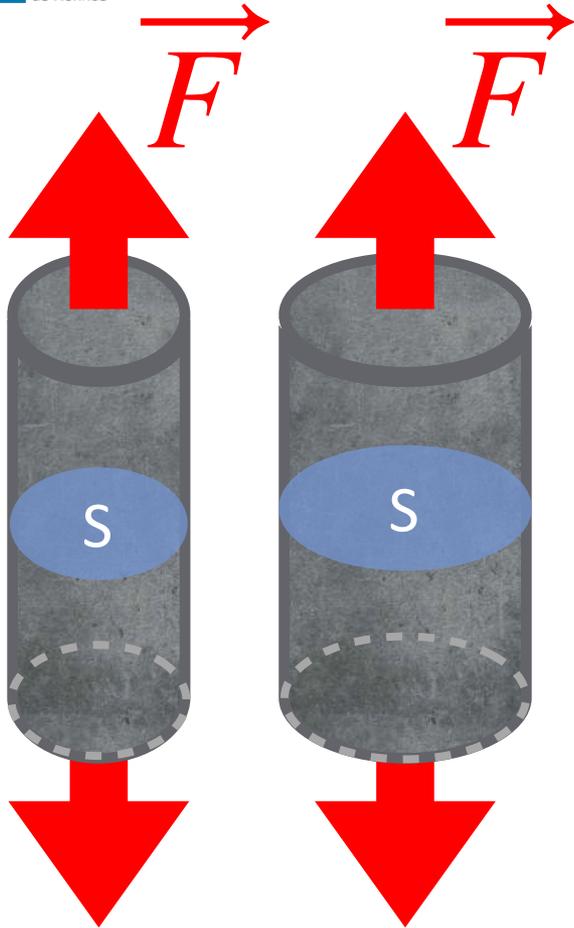
● Fissuration

● Fatigue statique

● Contraintes thermiques

● Trempes





Force à rupture, force pour un allongement  $\Delta L$ :

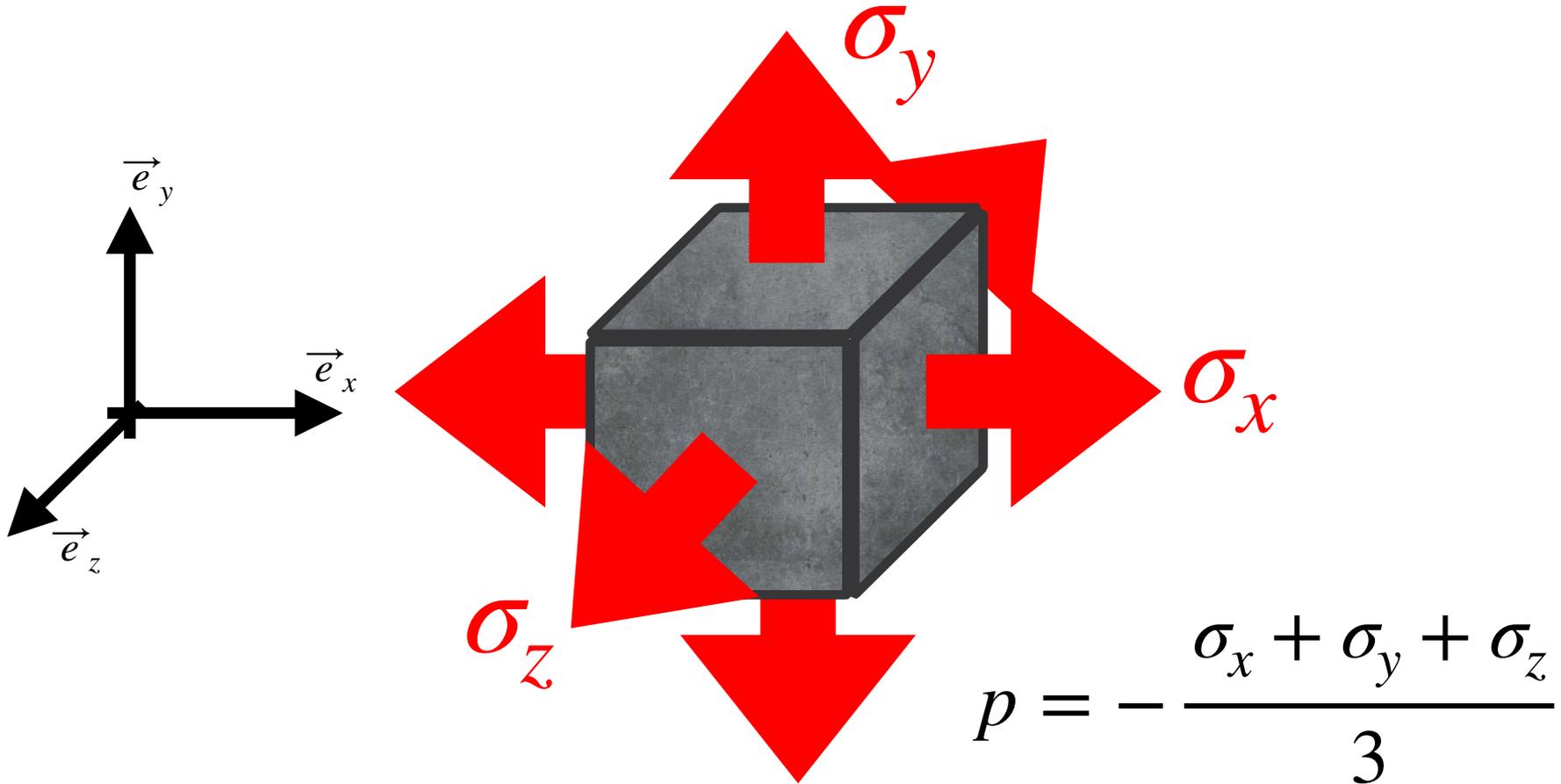
Ne dépend pas que du matériau...

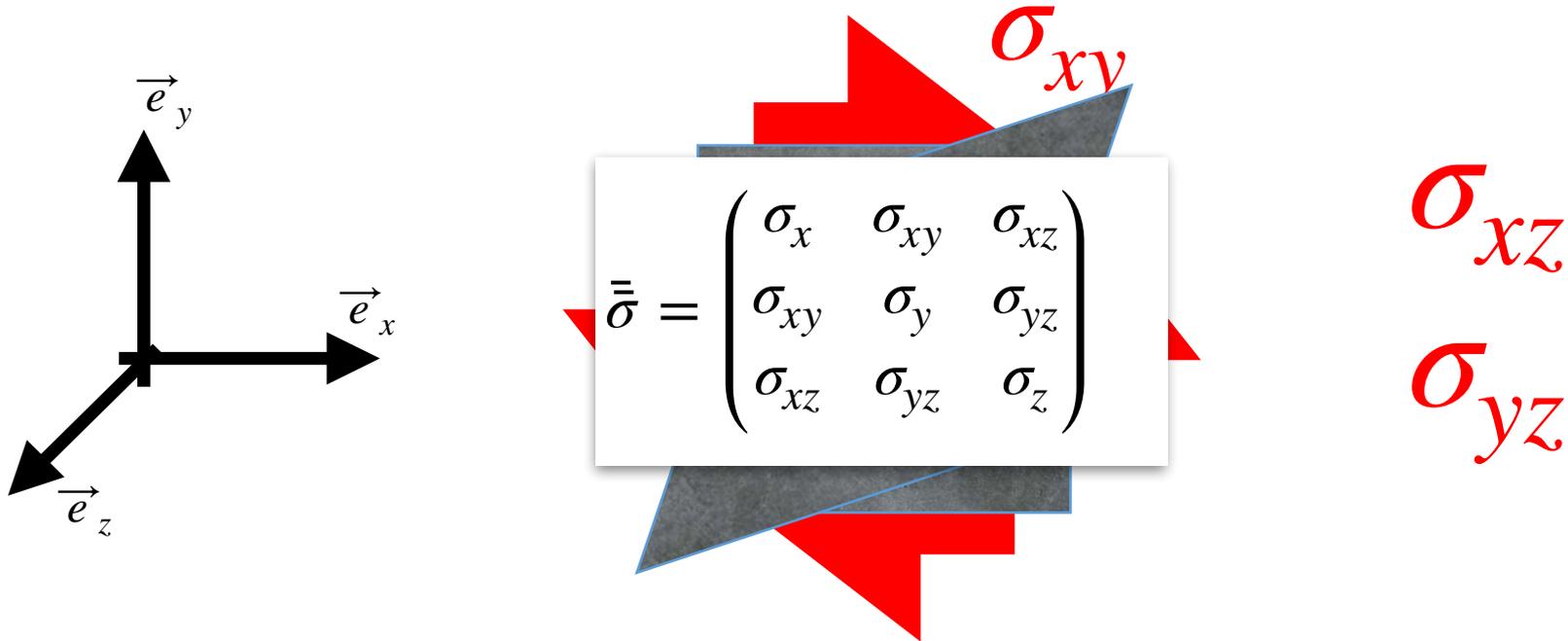
Mais aussi de la géométrie...



Contrainte: 
$$\sigma = \frac{F}{S} \text{ Pa}$$

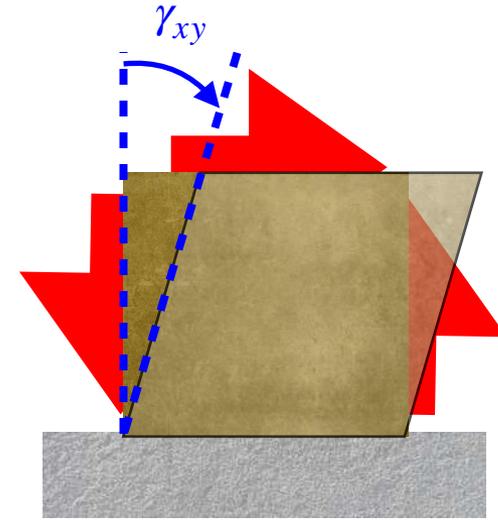
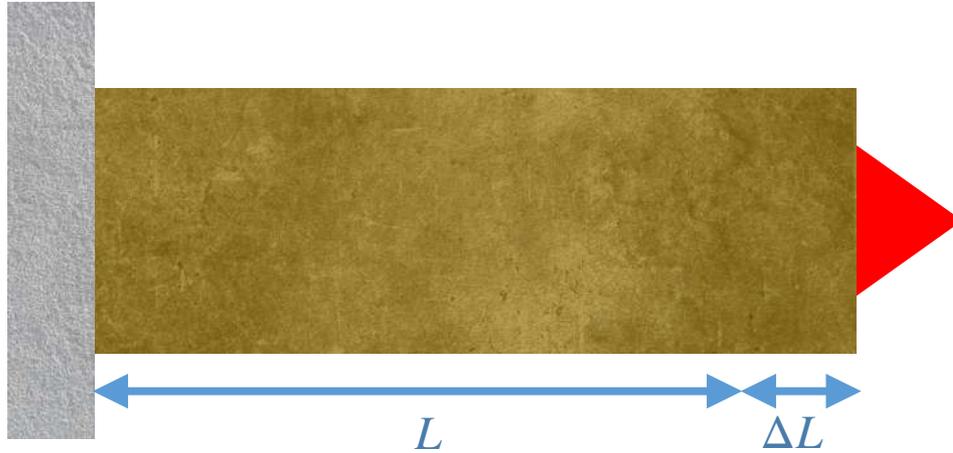
## Traction-Compression-Pression



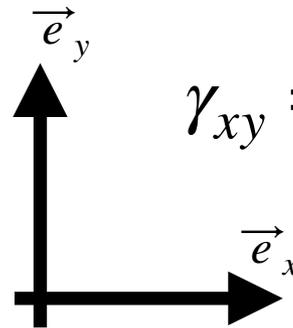


$\sigma = 3$  tractions/compressions + 3 cisaillements

$$\sigma = (\sigma_x + \sigma_y + \sigma_z) + (\sigma_{xy} + \sigma_{xz} + \sigma_{yz})$$



$$\epsilon_x = \frac{\Delta L}{L}$$



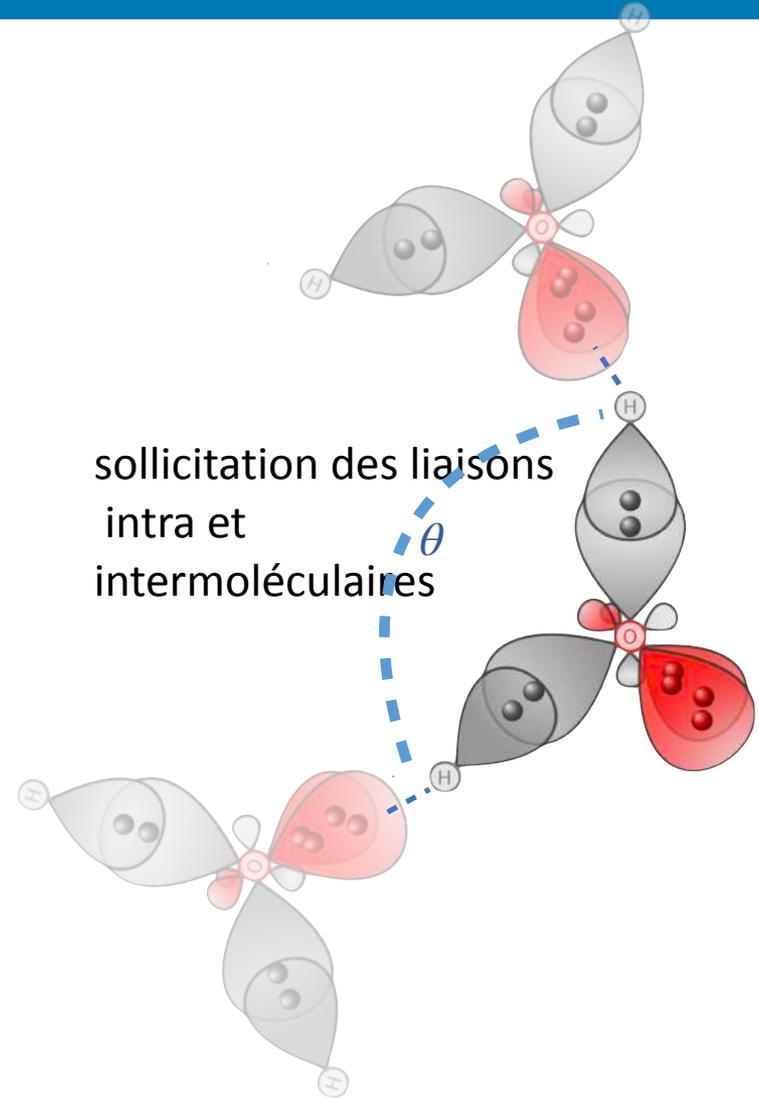
$\gamma_{xy} = \text{angle de glissement}$

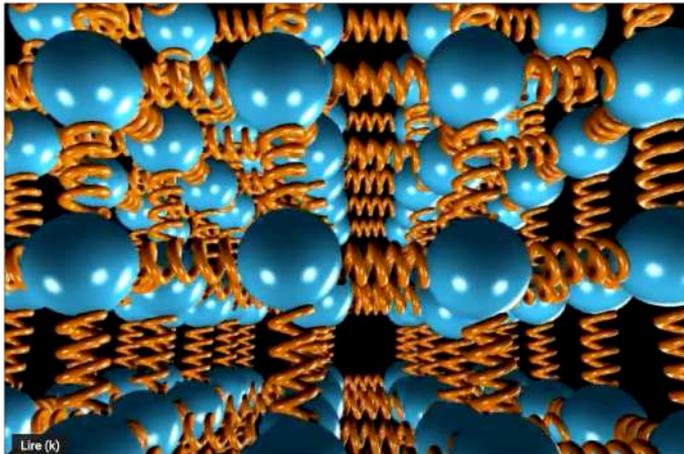
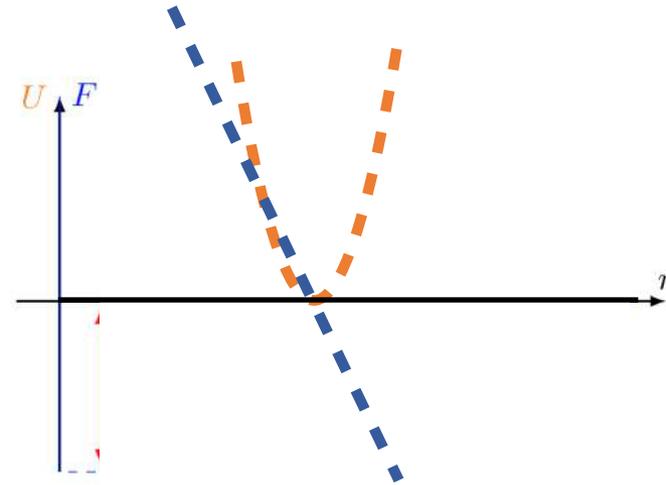
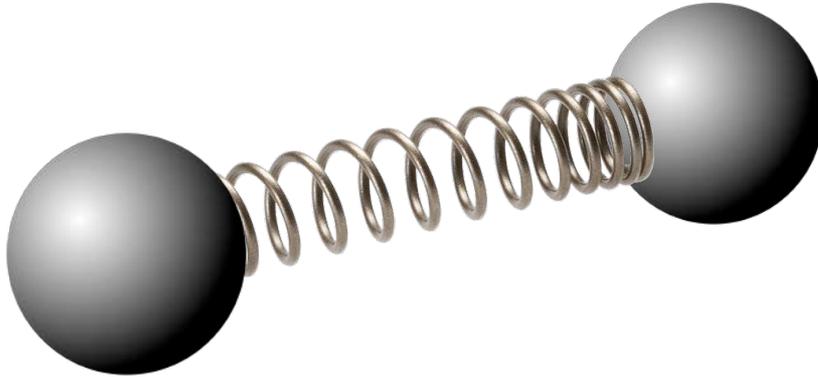
# Elasticité





Sollicitation macroscopique =

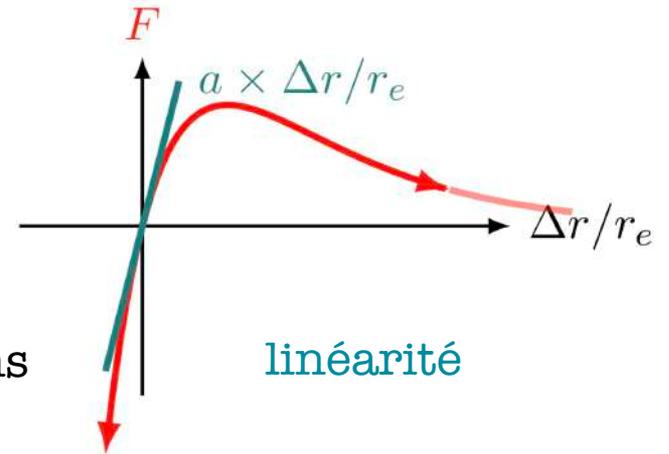
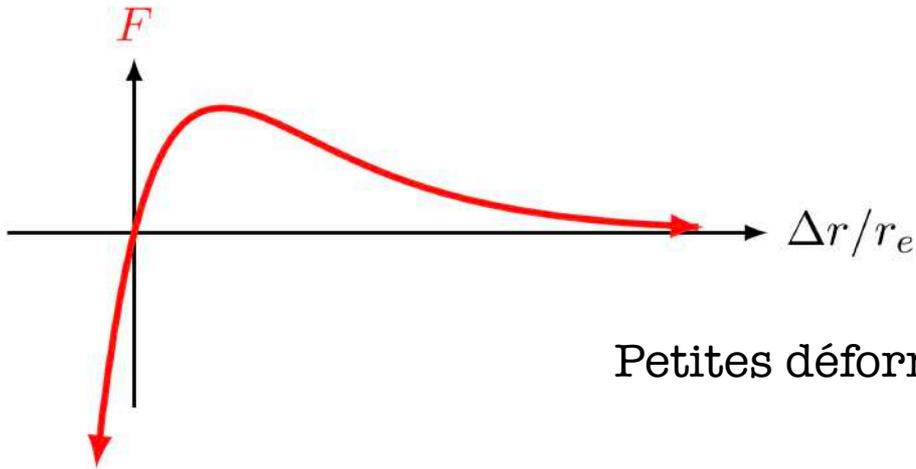
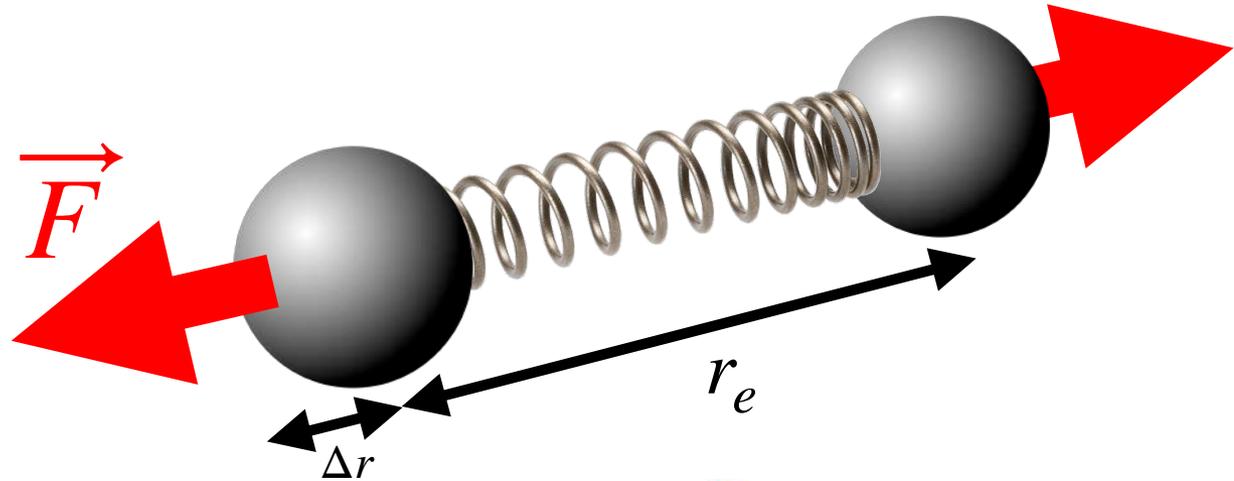
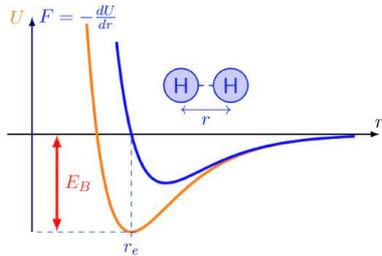


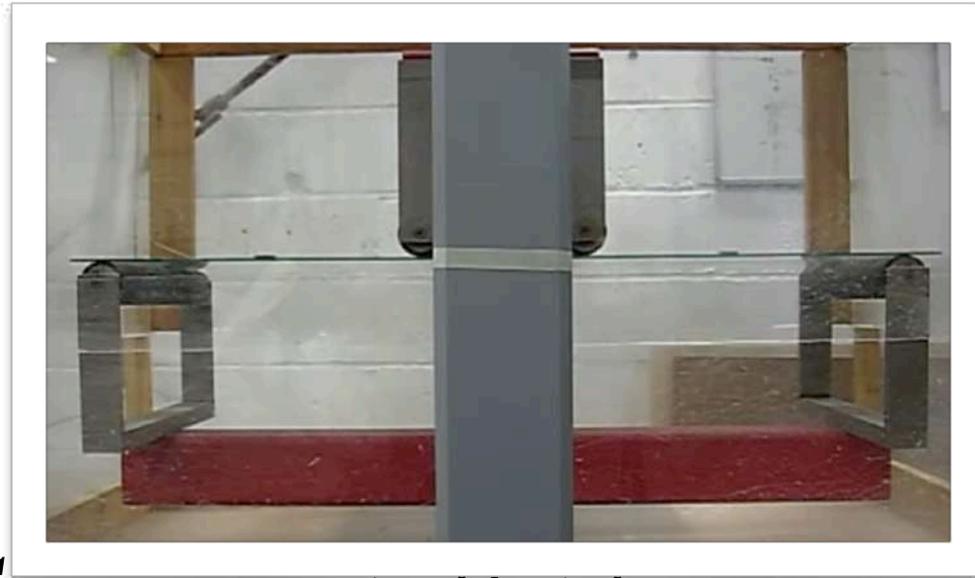
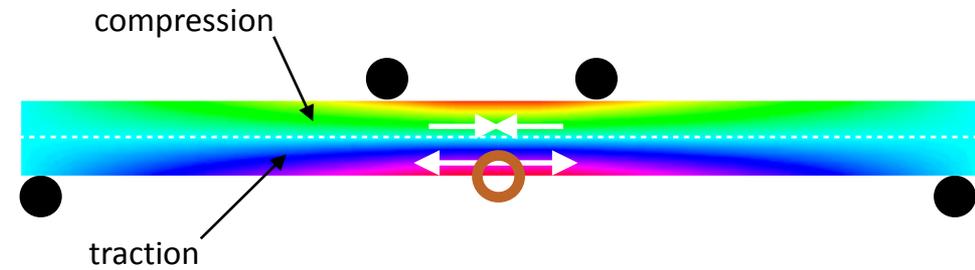
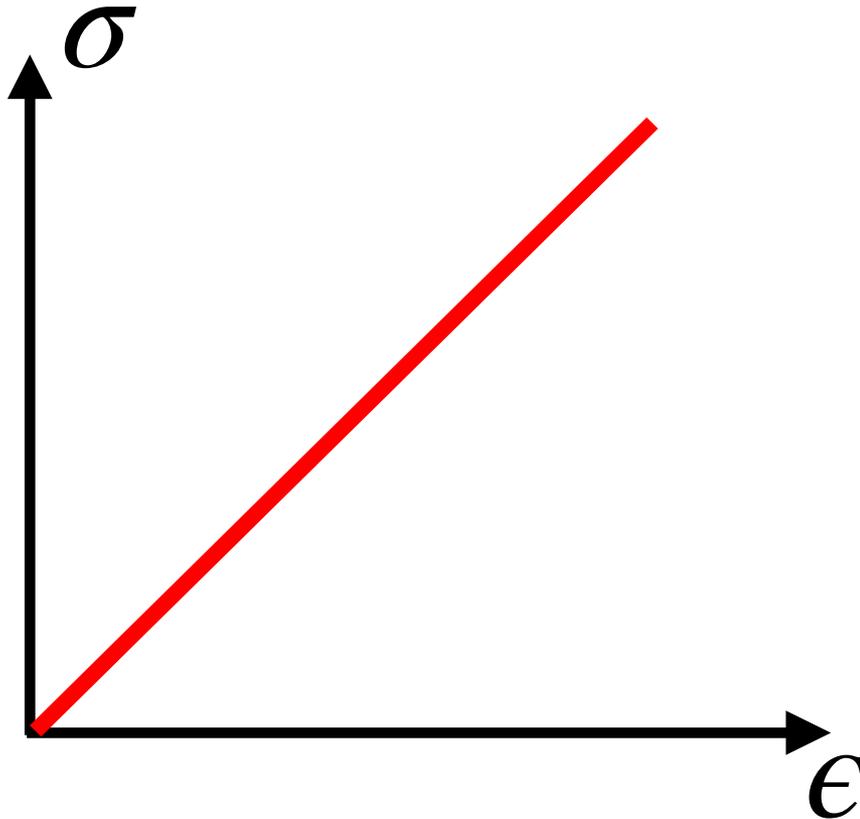


Youtube: Matter & Interactions

Elasticité = **réversibilité**

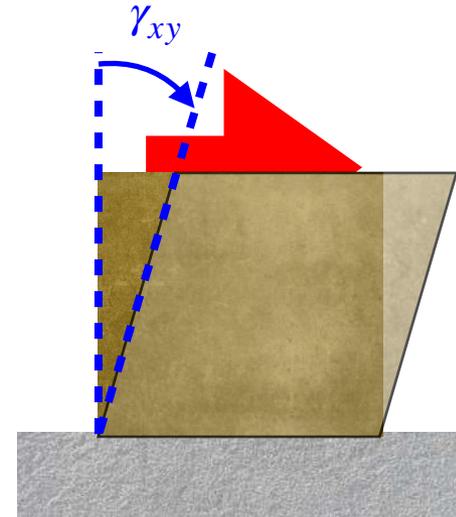
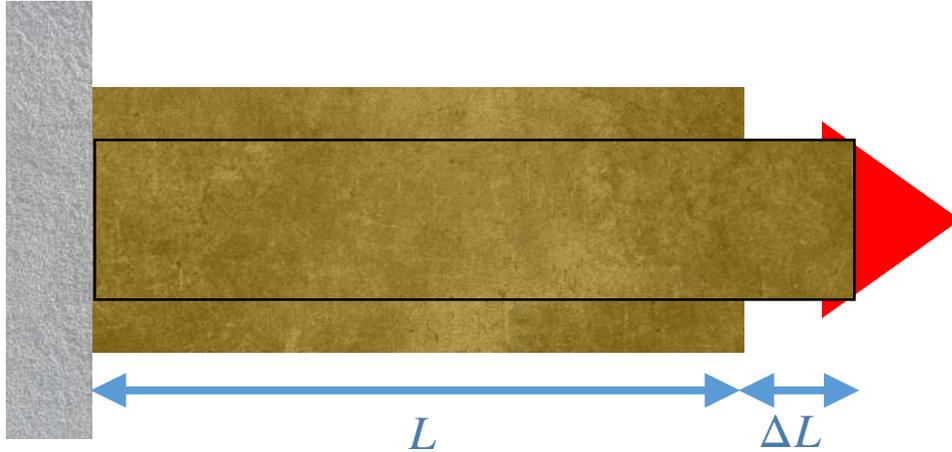
Quand j'étire une liaison  
et que je la relâche,  
elle revient à sa position d'origine





[www.trendglasstech.com](http://www.trendglasstech.com)

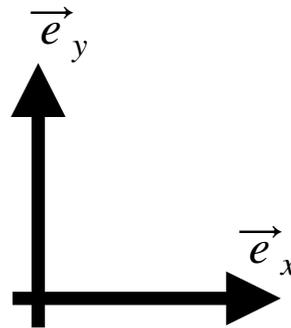
$$\sigma \propto \epsilon$$



$$\sigma_x = E \times \epsilon_x$$

$$\epsilon_y = -\nu \times \epsilon_x$$

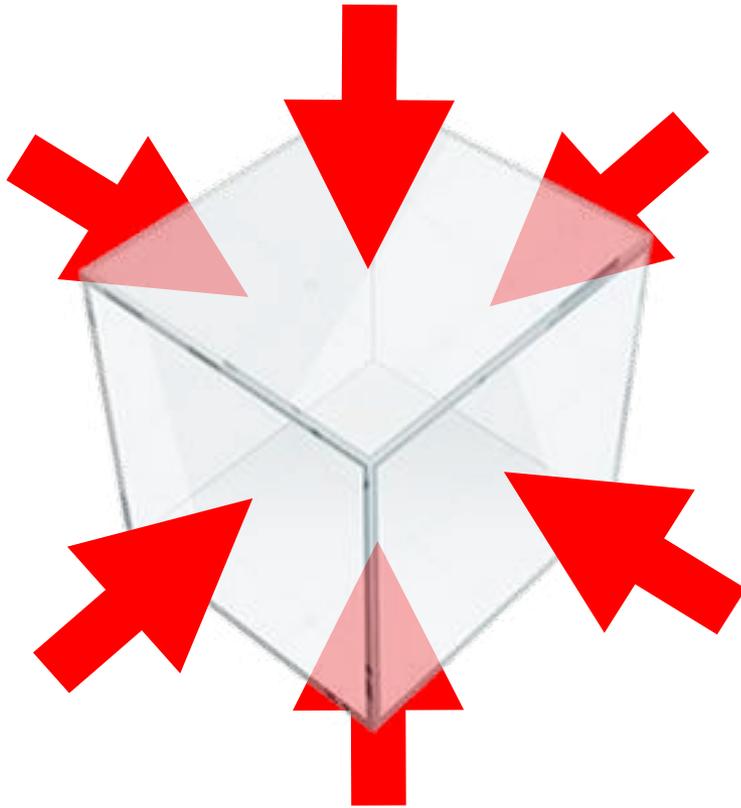
$E$ : Module de Young  
 $\nu$ : coeff. de Poisson



$$\sigma_{xy} = \mu \times \gamma_{xy}$$

$\mu$ : Module de cisaillement

$$\mu = \frac{E}{2(1 + \nu)}$$

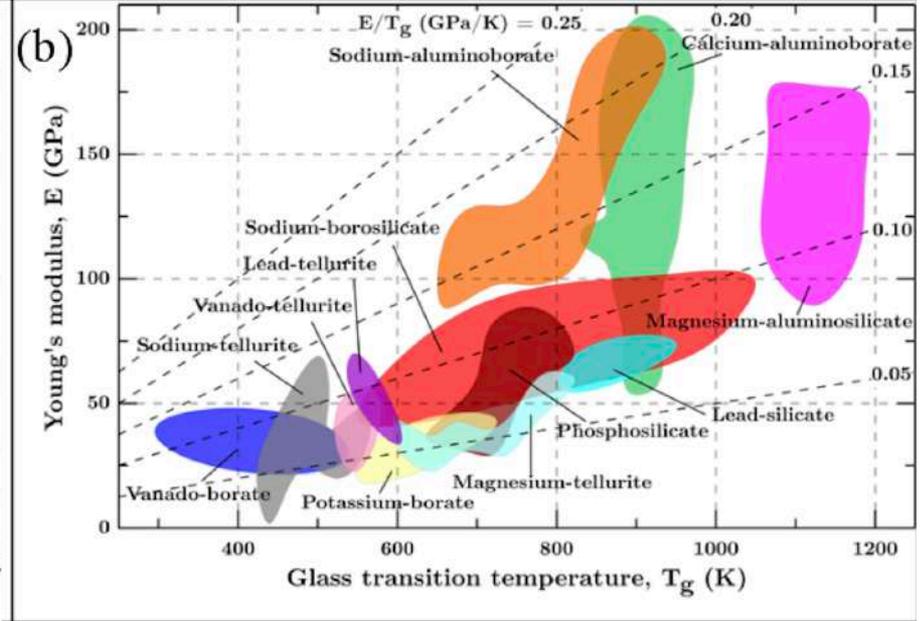
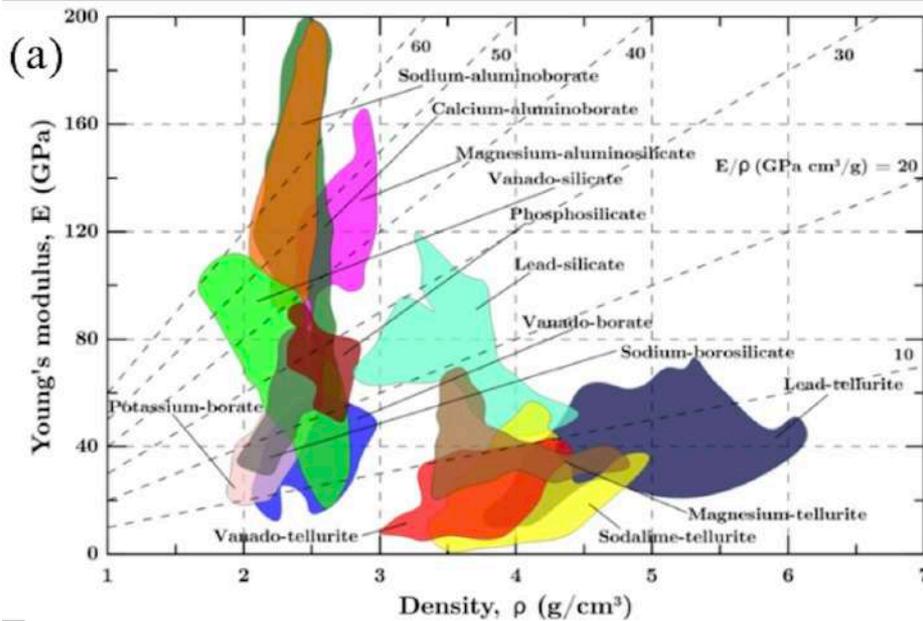


$$p = - \frac{\sigma_x + \sigma_y + \sigma_z}{3}$$

$$p = - k \times \frac{\Delta V}{V}$$

$k$  : module isostatique

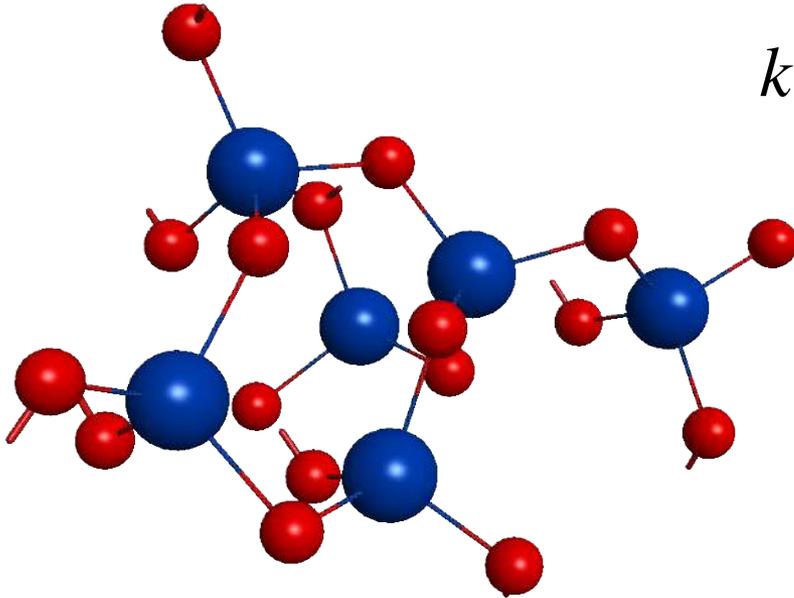
$$k = \frac{E}{3(1 - 2\nu)}$$



1 GPa = 0,1 tonnes/mm<sup>2</sup>  
 200 GPa = 20 tonnes/mm<sup>2</sup>

$$\epsilon = 0,1\% \rightarrow \sigma = E \times \epsilon = 200 \text{ GPa} \times 0.001 = 200 \text{ MPa} = 20 \text{ kg/mm}^2$$

Ravinder, R., Sridhara, K. H., Bishnoi, S., Grover, H. S., Bauchy, M., Kodamana, H., & Krishnan, N. A. (2020). Deep learning aided rational design of oxide glasses. *Materials Horizons*, 7(7), 1819-1827.



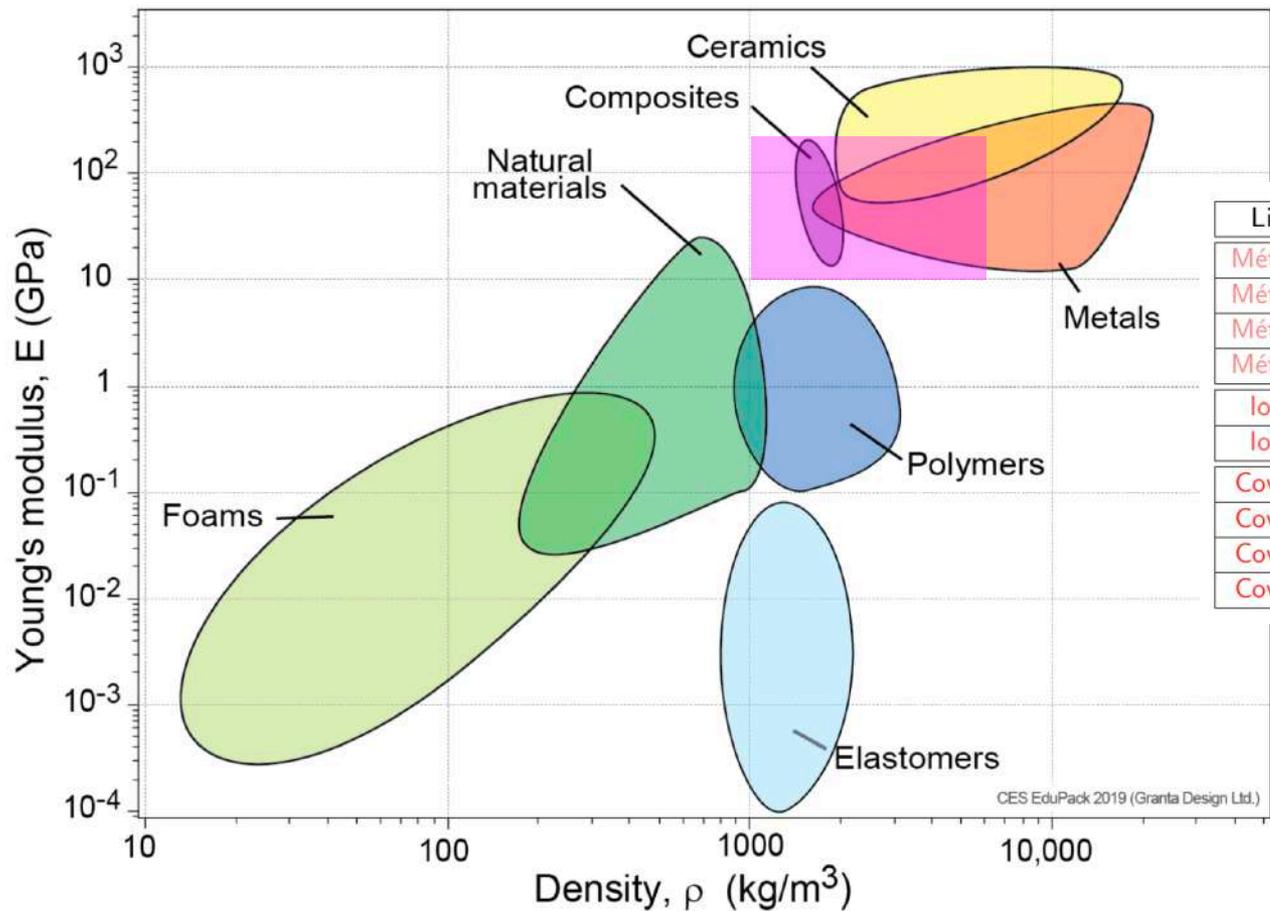
$$k = - \frac{P}{\Delta V/V} \rightarrow Pa \rightarrow J \cdot m^{-3}$$

Densité d'énergie

$$k \propto \frac{E_B}{r_e^3}$$

Plus l'énergie par unité de volume est grande plus les modules d'élasticité sont grands:

- Augmenter l'énergie de liaison.
- Augmenter le nombre de liaisons par unité de volume/atome.



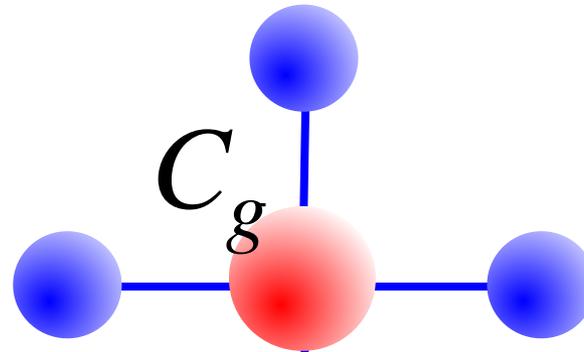
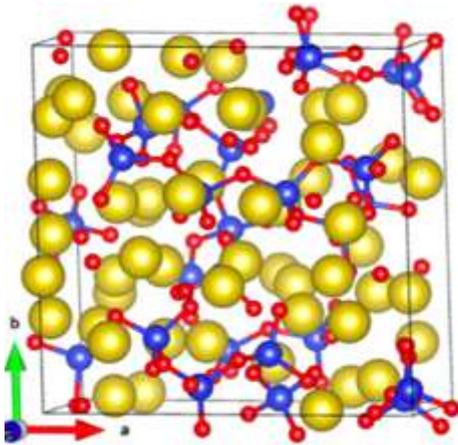
Liaison	Atomes	Energie de liaisons (kJ/mol)
Métallique	Fe-Fe	134
Métallique	Co-Co	164
Métallique	Cu-Cu	190
Métallique	Ti-Ti	243
Ionique	Na-Cl	410
Ionique	Li-Cl	464
Covalente	Ge-Ge	272
Covalente	Ge-Si	297
Covalente	H-H	432
Covalente	N-N	941

## Origine physique

$$E = 2 \times G \times C_g$$

densité d'empilement atomique du verre

énergie de dissociation du cristal/unité de volume



volume occupé par les atomes/volume du verre

Com- pounds	$G_i$ ( $\text{kJ} \times \text{m}^{-3}$ $\times 10^{-6}$ )	$V_i$ ( $\text{m}^3 \times$
Al <sub>2</sub> O <sub>3</sub>	133.80	21.4
CaO	63.80	9.4
SiO <sub>2</sub>	64.40	14.0
Na <sub>2</sub> O	37.20	11.2



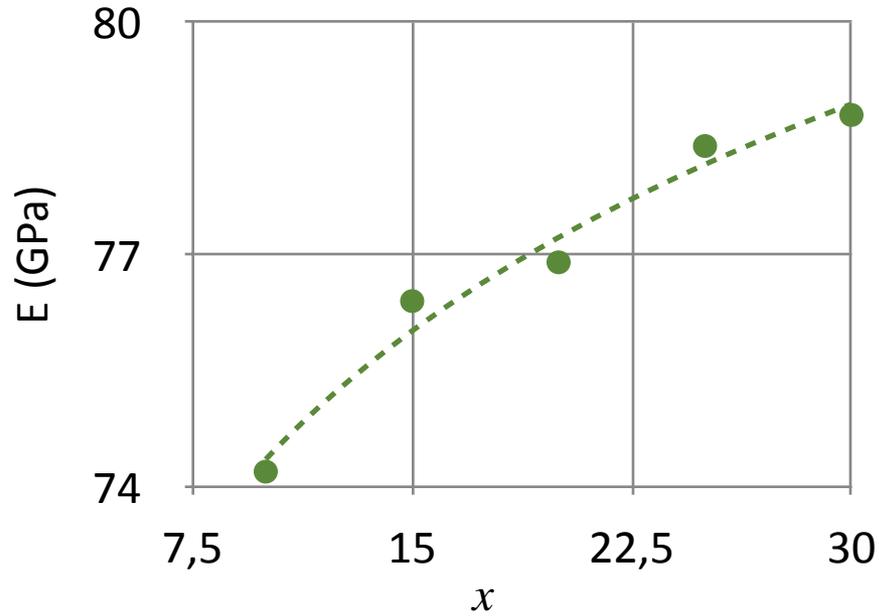
Oxyde (cristal)  
Coordinnence définie

$$G = \sum_i x_i \times G_i$$

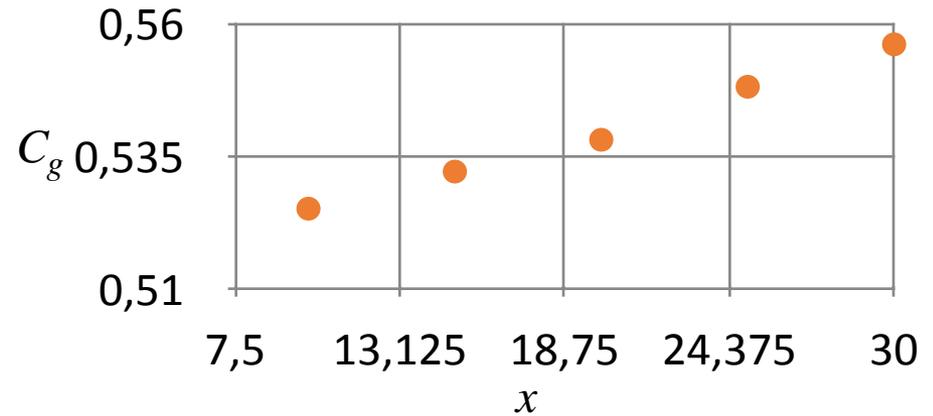
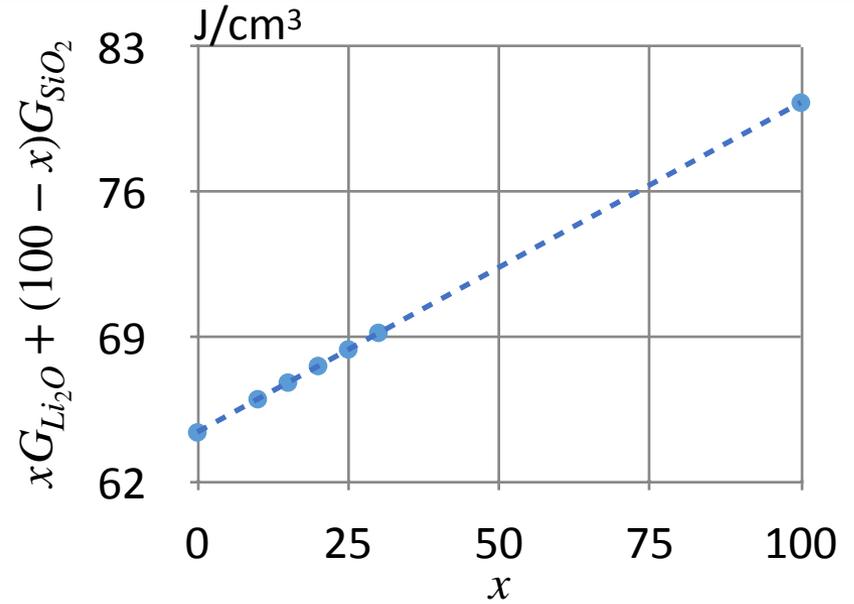
Rocherulle, J., Ecolivet, C., Poulain, M., Verdier, P., & Laurent, Y. (1989). Journal of Non-crystalline solids, 108(2), 187-193.

Makishima, A., & Mackenzie, J. D. (1973). Direct calculation of Young's modulus of glass. Journal of Non-Crystalline Solids, 12(1), 35-45.

## Origine physique



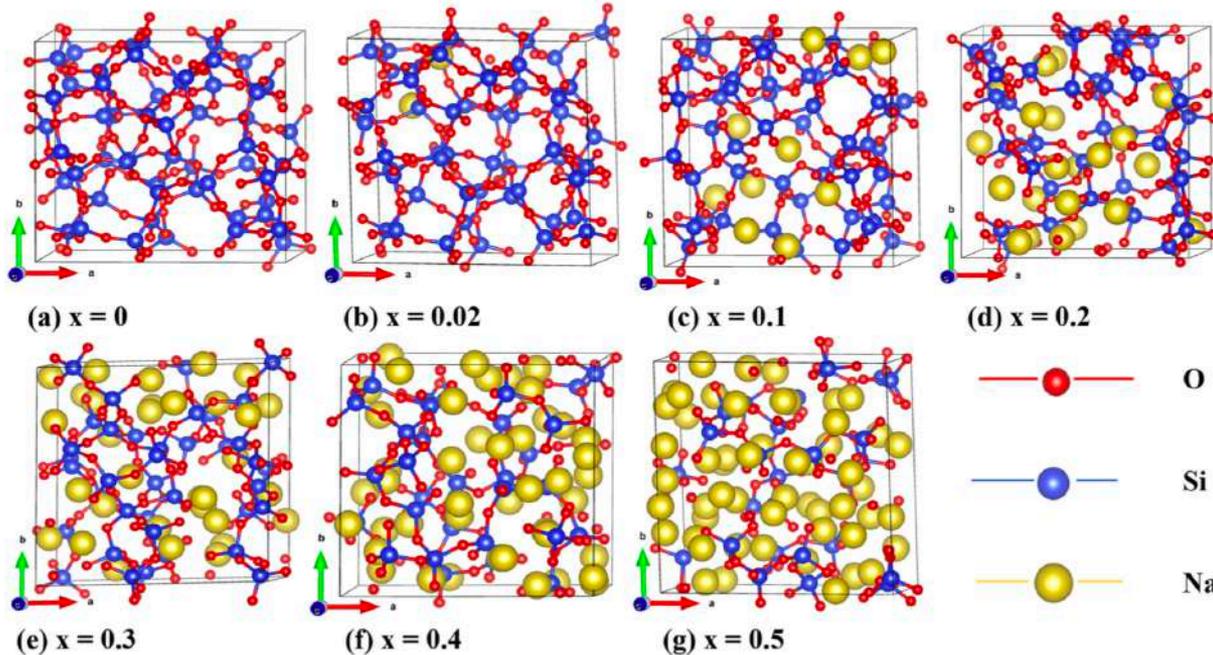
$$E = 2 \times G \times C_g$$



## Origine physique



Baral, K., & Ching, W. Y. (2017). Electronic structures and physical properties of  $\text{Na}_2\text{O}$  doped silicate glass. *Journal of Applied Physics*, 121(24), 245103.



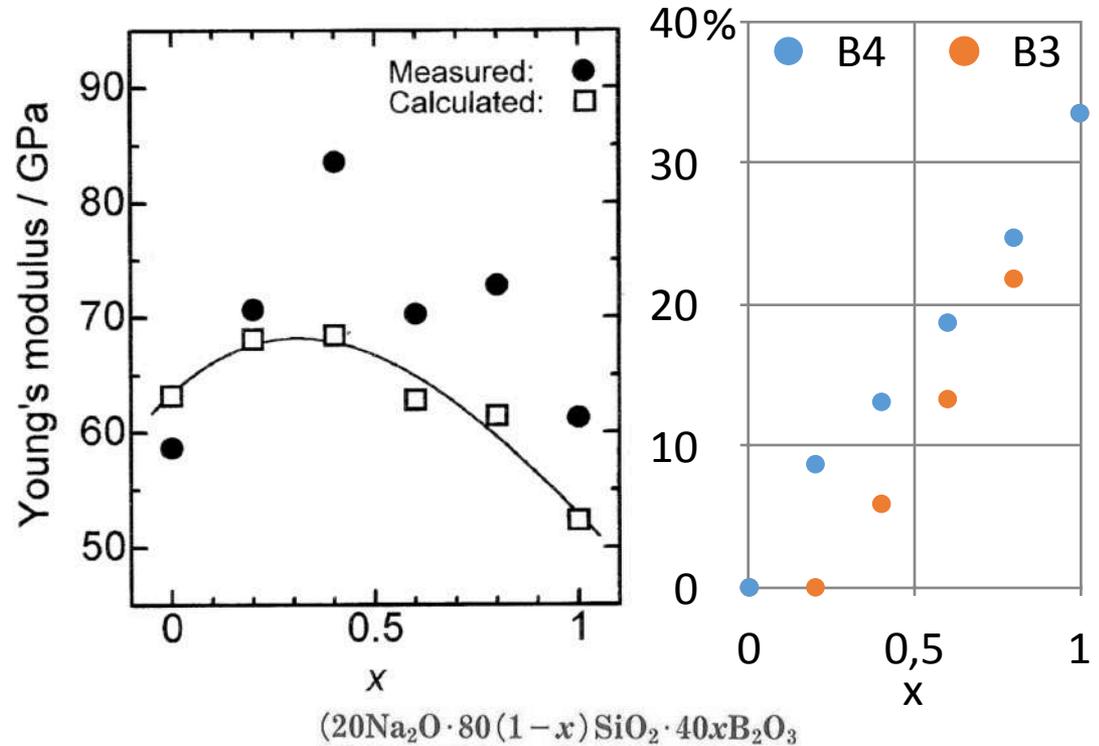
Même nombre d'atomes (162)  
Quasi-même volume

$x$

Rmq:  $(\text{SiO}_2)_{100-x}-(\text{Na}_2\text{O})_x \rightarrow E$  chute si  $x$  augmente,  $G_{\text{Na}_2\text{O}} = 37\text{kJ}/\text{cm}^3 < G_{\text{Li}_2\text{O}} = 80\text{kJ}/\text{cm}^3$

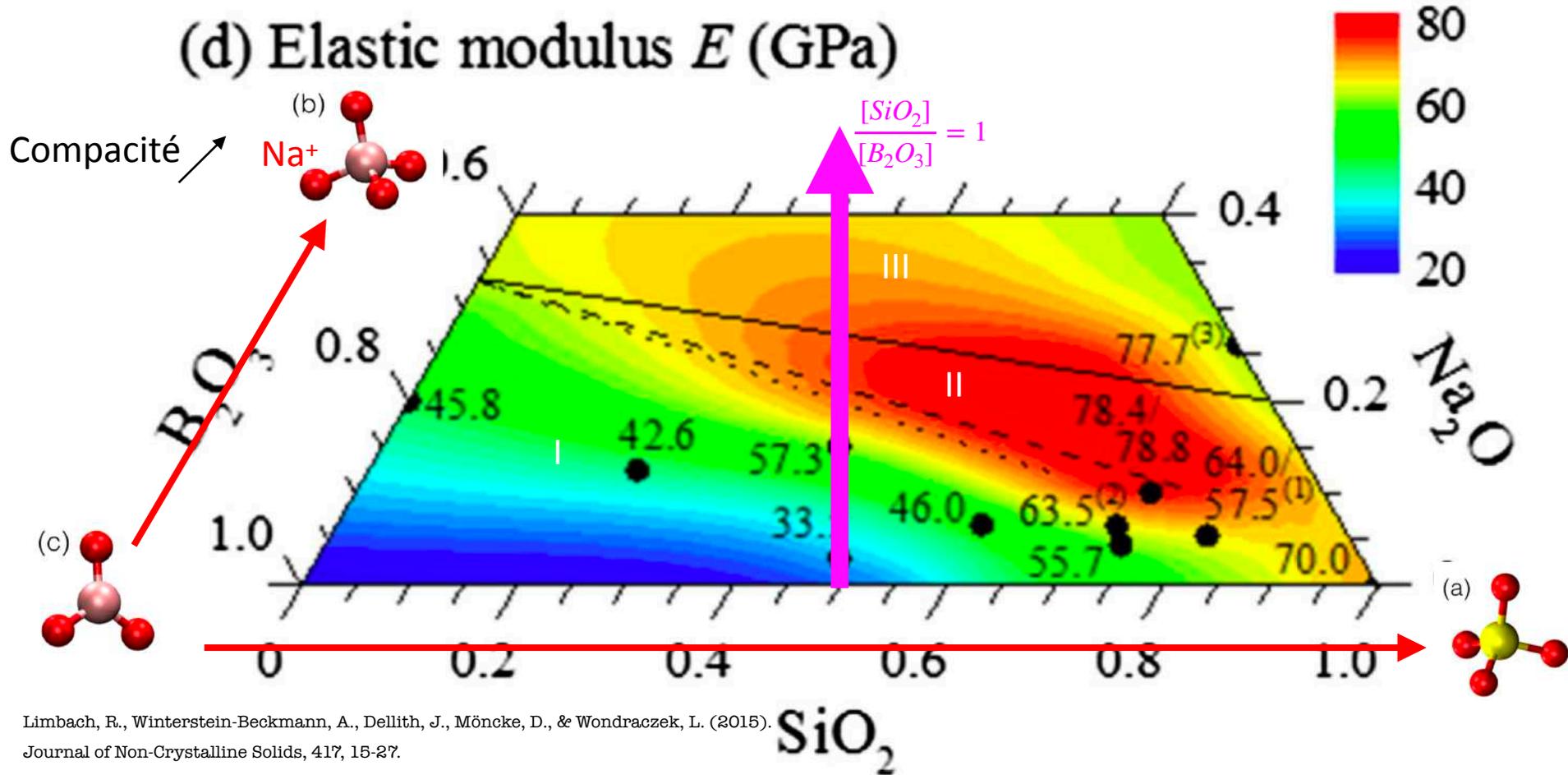
Borosilicate: mauvaise capacité de prédiction... coordinence du bore?

Oxide	$G_i$ / $\text{kJ cm}^{-3}$	$V_i$ / $\text{cm}^3 \text{mol}^{-1}$
$\text{Na}_2\text{O}$	31.9	11.2
$\text{B}_2\text{O}_3$ four-coordinated	82.8	20.8
$\text{B}_2\text{O}_3$ three-coordinated	15.6	20.8
$\text{SiO}_2$	68.0	14.0



YOSHIDA, S., TANAKA, H., HAYASHI, T., MATSUOKA, J., & SOGA, N. (2001). Scratch resistance of sodium borosilicate glass. *Journal of the Ceramic Society of Japan*, 109(1270), 511-515.

### (d) Elastic modulus $E$ (GPa)



Limbach, R., Winterstein-Beckmann, A., Dellith, J., Möncke, D., & Wondraczek, L. (2015).  
Journal of Non-Crystalline Solids, 417, 15-27.

Sodium = modificateur de réseau

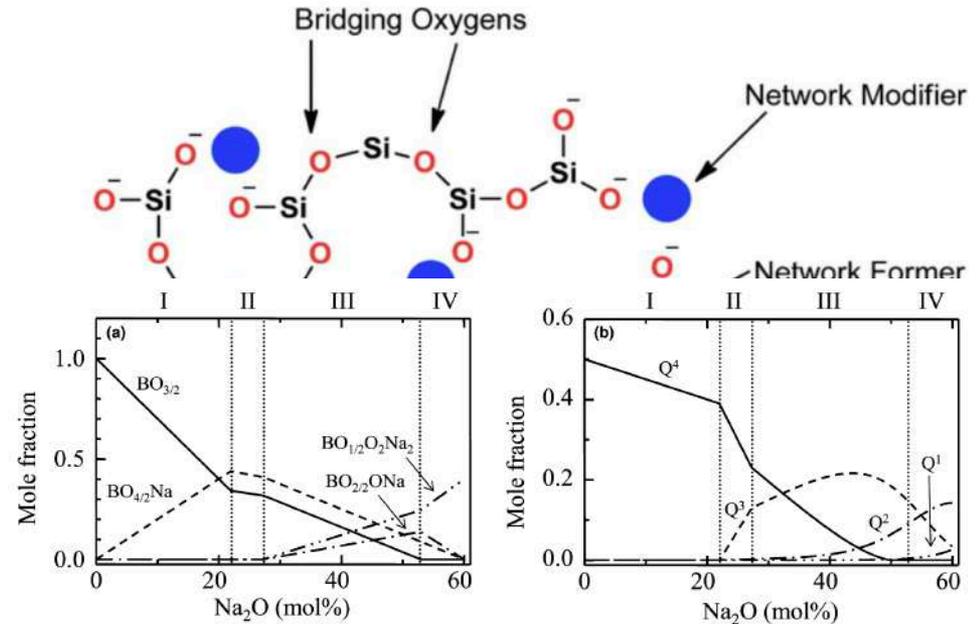
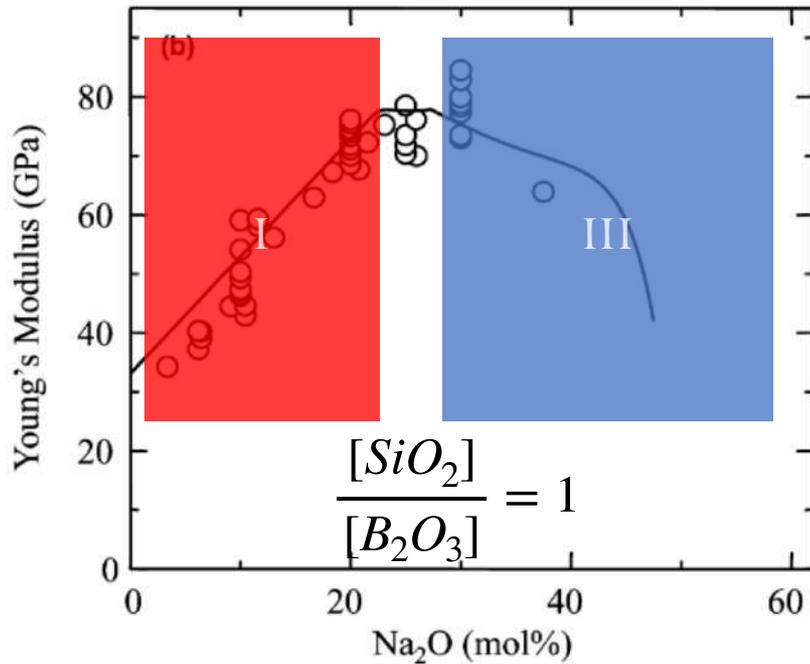


Fig. 2. Composition dependence of the mole fraction of (a) borate-related and (b) silicate-related units when [B<sub>2</sub>O<sub>3</sub>] is equal to [SiO<sub>2</sub>] in the Na<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glass system. Vertical dotted lines are the boundaries between Regions I, II, III, and IV.

Inoue, H., Masuno, A., Watanabe, Y., Suzuki, K., & Iseda, T. (2012). *Journal of the American Ceramic Society*, 95(1), 211-216.

## Ça sert à quoi l'élasticité d'un verre?

### Fibres de verres pour composite:

On veut un module de Young **élevé**.  
et une masse volumique faible.

Rigidité spécifique élevée  $\frac{E}{\rho}$

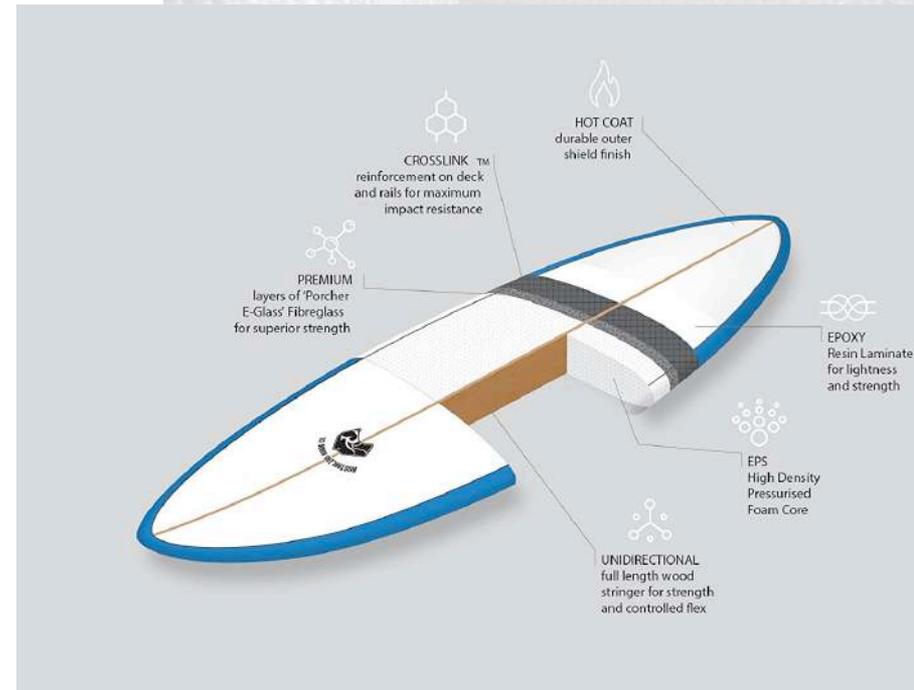
Fibre E:  $E=72 \text{ GPa}$ ,  $\rho = 2,54 \text{ kg/m}^3$

Fibre S:  $E=89 \text{ GPa}$ ,  $\rho = 2,53 \text{ kg/m}^3$

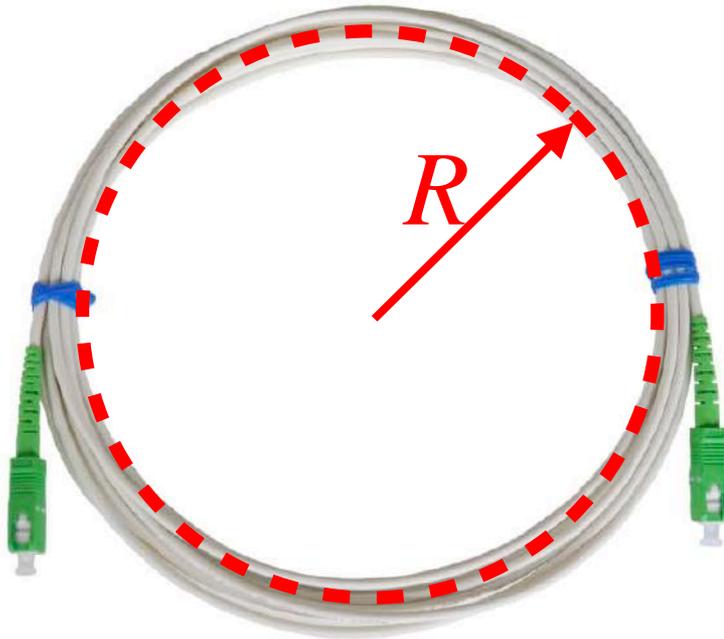
*E-glass: SiO<sub>2</sub>: 52-60%, Al<sub>2</sub>O<sub>3</sub>:12-15%, CaO: 22-23% (wt)*

*S-Glass: SiO<sub>2</sub>: 64-66%, Al<sub>2</sub>O<sub>3</sub>:24-26%, MgO: 8-12% (wt)*

Epoxy:  $E=3-4 \text{ GPa}$ ,  $\rho = 1,1 \text{ kg/m}^3$



Ça sert à quoi l'élasticité d'un verre?



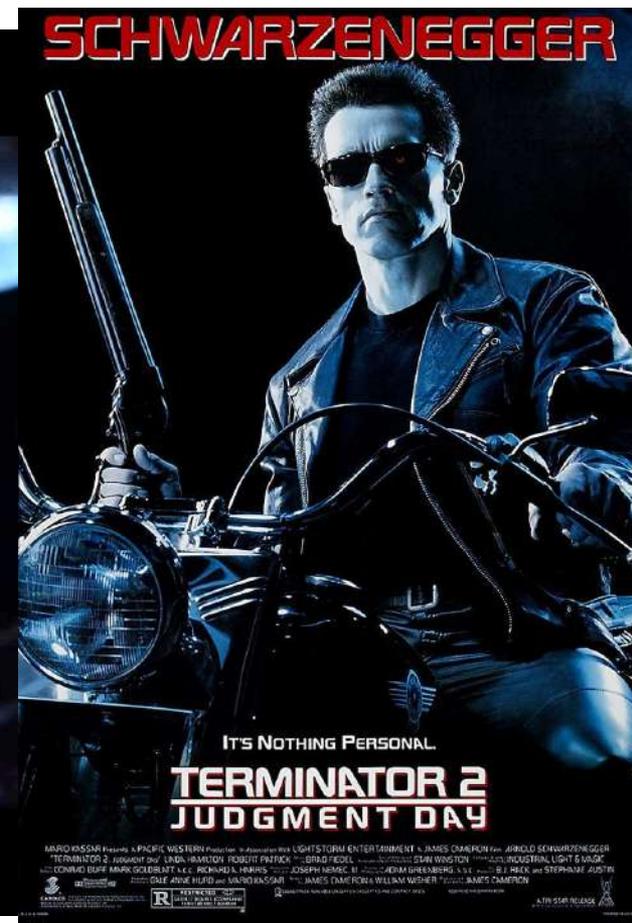
$$\sigma = E \times \epsilon$$

$$\epsilon = \frac{D}{2R} \quad D: \text{diamètre de fibre}$$



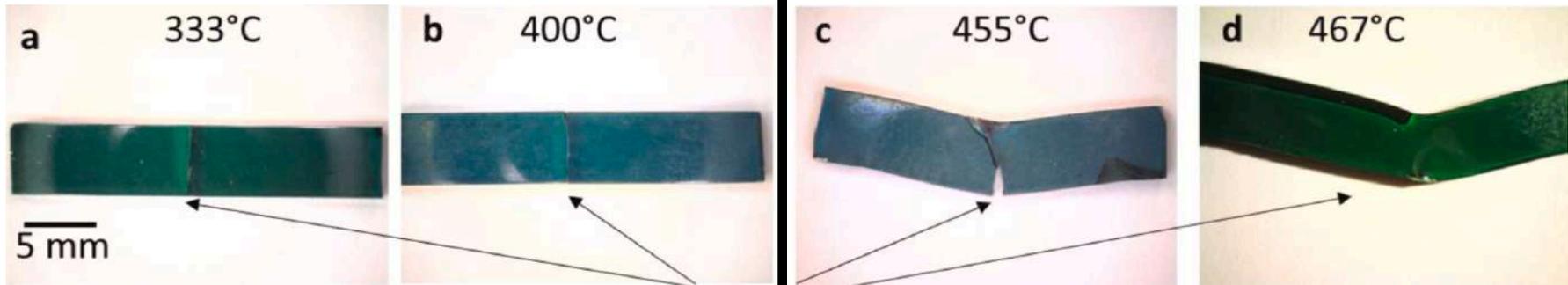
# Fragilité







## Définitions



# Fragile

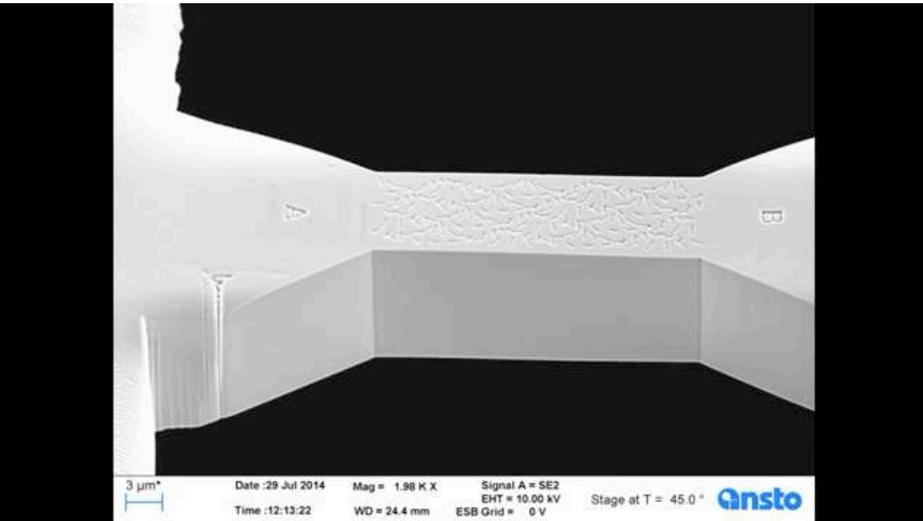
*Je peux re-  
coller les  
morceaux*

Transition  
Vitreuse

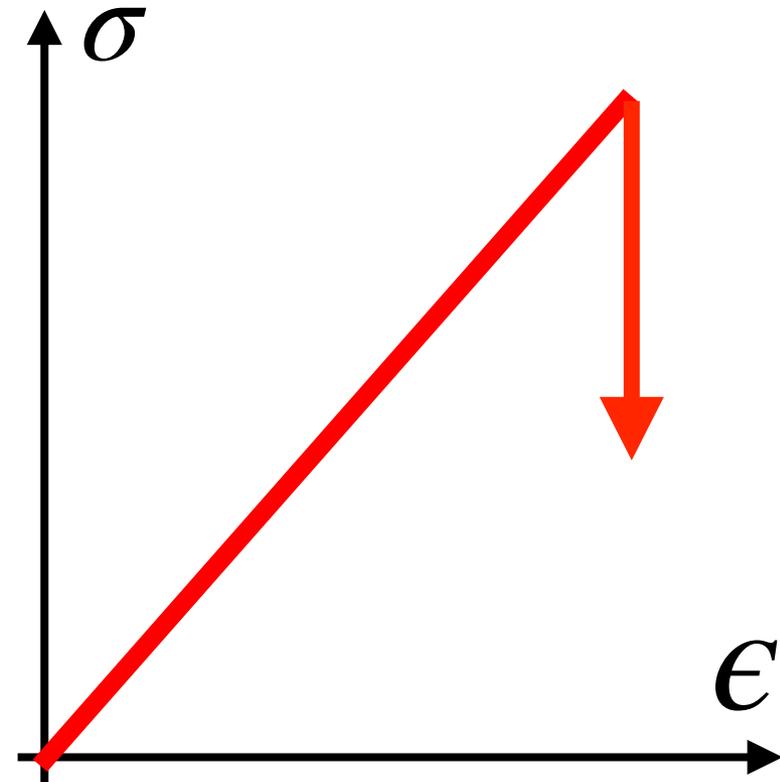
# Ductile

*Je ne peux pas  
re-coller les  
morceaux*

## D'où vient la ductilité?

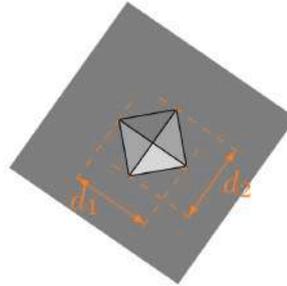
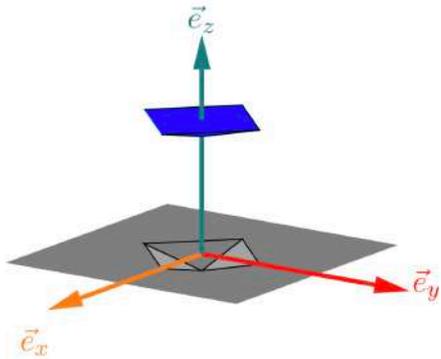


Ductilité:  
accumulation de déplacements  
atomiques locaux



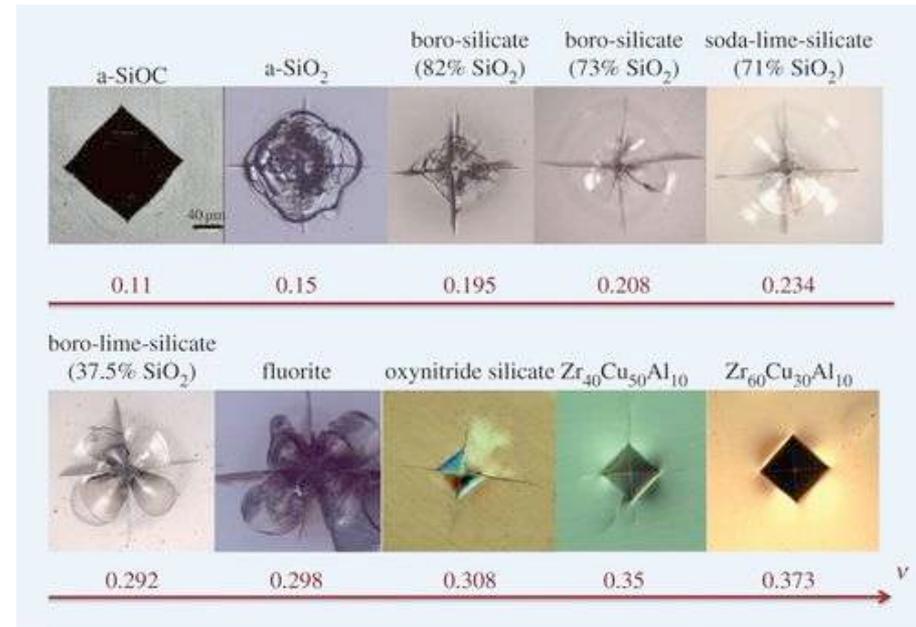
Verre:  
liaisons trop fortes,  
atomes trop désordonnés

## Dureté



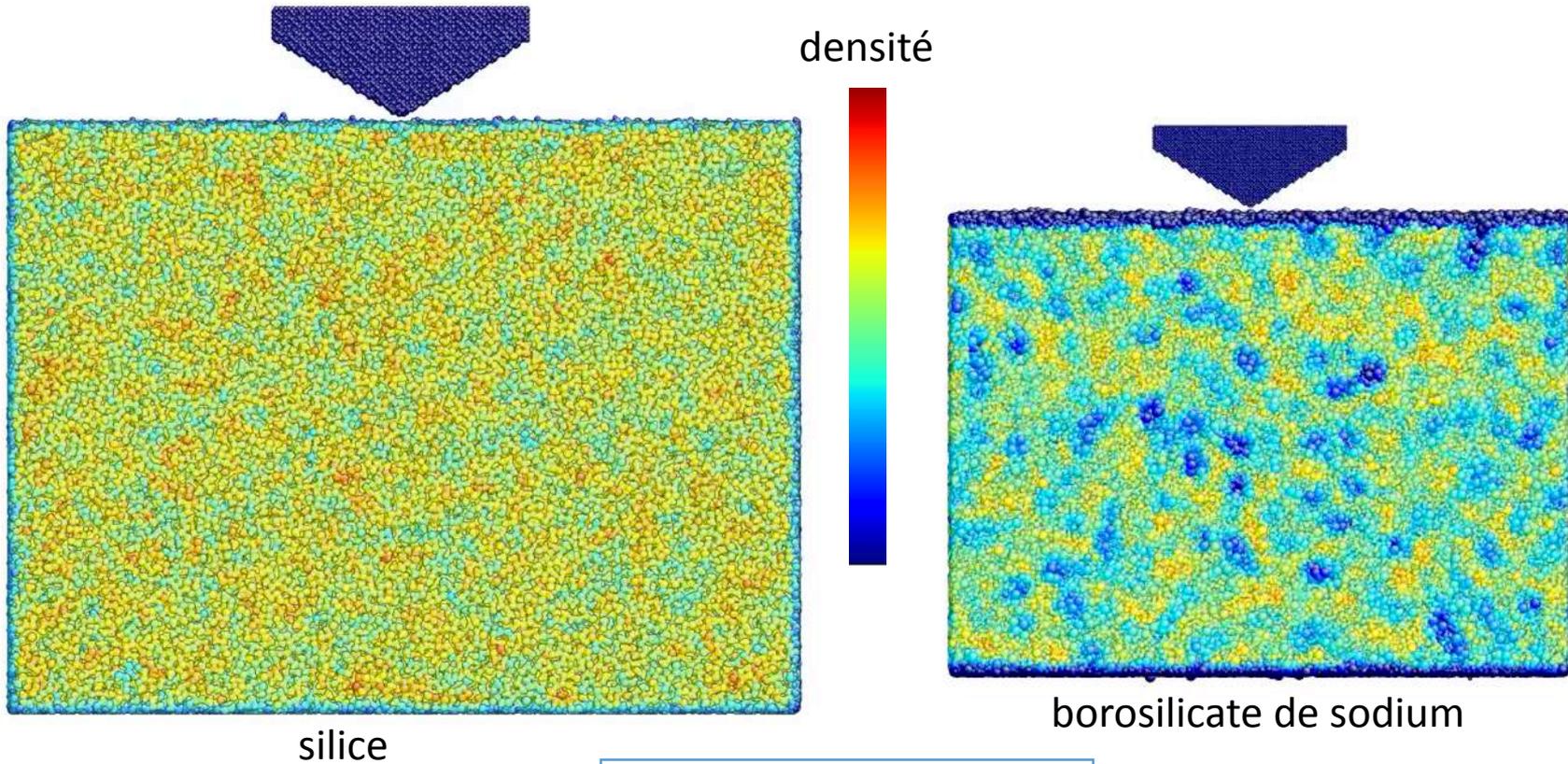
$$d = \frac{d_1 + d_2}{2}$$

$$HV = \frac{F}{S_{empreinte}}$$



Fragile... en traction!

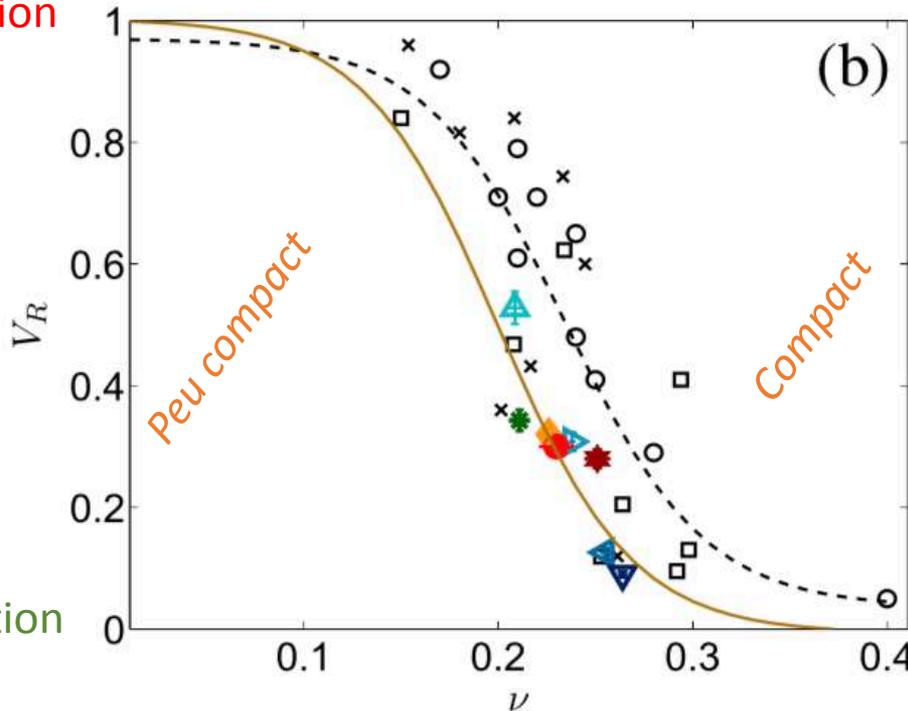
## Fragile... en traction!



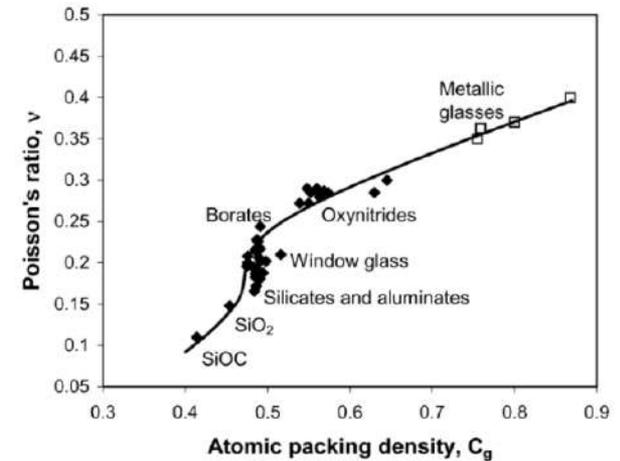
youtube: Dimitrios Kilymis

forte densification

Contribution de changement de volume à la formation d'empreinte de dureté



faible densification

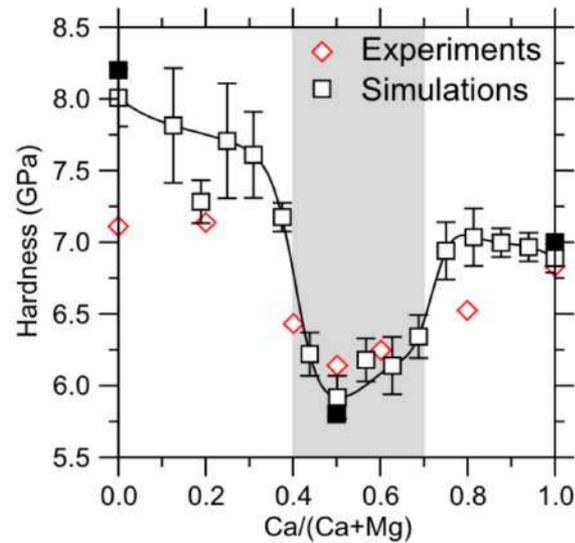


T. Rouxel, Elastic properties of glasses : A multiscale approach, C.R. Mécanique vol 334, p 743, 2006

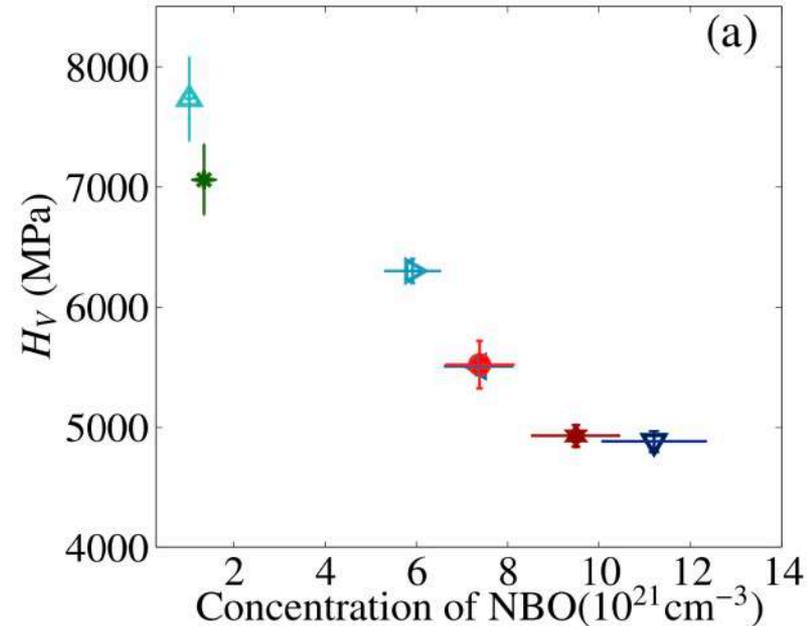
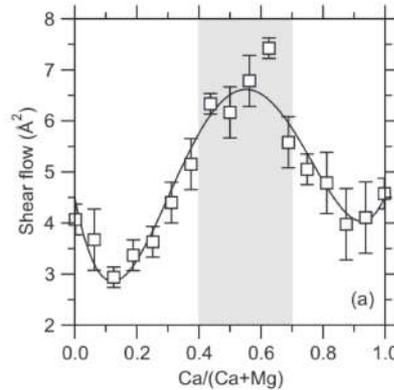
Barlet, M., Delaye, J. M., Charpentier, T., Gennisson, M., Bonamy, D., Rouxel, T., & Rountree, C. L. (2015).

Hardness and toughness of sodium borosilicate glasses via Vickers's indentations. Journal of Non-Crystalline Solids, 417, 66-79.

## Dureté vs structure



CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-Na<sub>2</sub>O

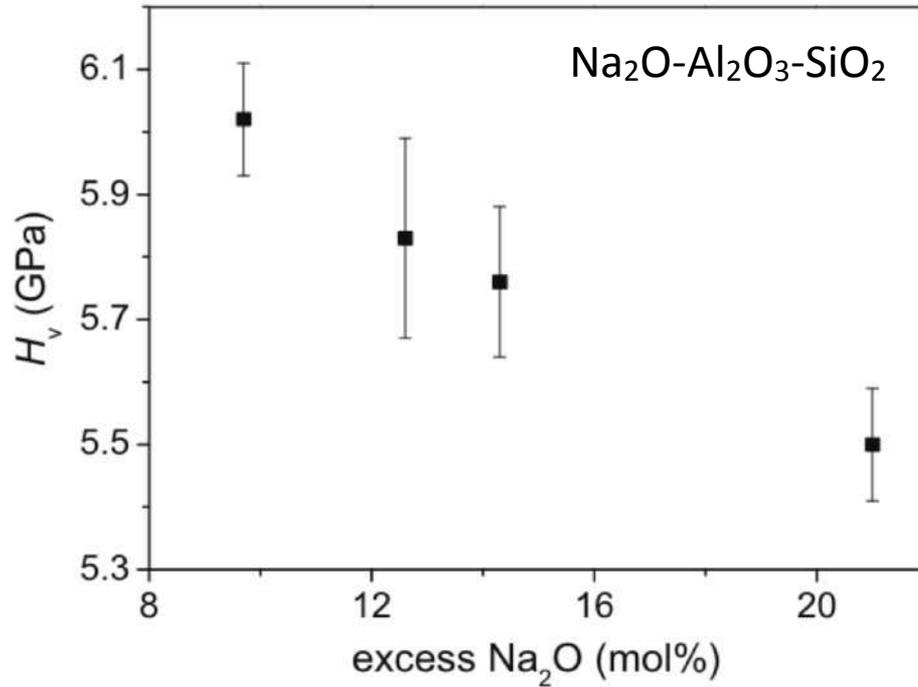


Yu, Y., Wang, M., Krishnan, N. A., Smedskjaer, M. M., Vargheese, K. D., Mauro, J. C., ... & Bauchy, M. (2018). Hardness of silicate glasses: Atomic-scale origin of the mixed modifier effect. *Journal of Non-Crystalline Solids*, 489, 16-21.

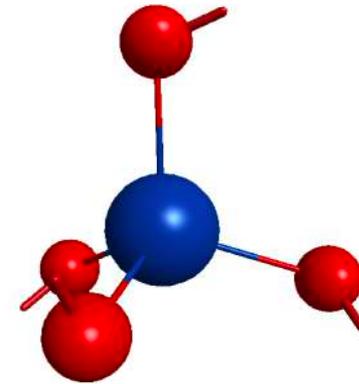
Barlet, M., Delaye, J. M., Charpentier, T., Gennisson, M., Bonamy, D., Rouxel, T., & Rountree, C. L. (2015).

Hardness and toughness of sodium borosilicate glasses via Vickers's indentations. *Journal of Non-Crystalline Solids*, 417, 66-79.

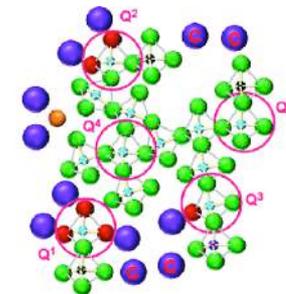
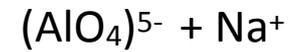
## Dureté vs structure



Smedskjaer, M. M., Jensen, M., & Yue, Y. (2010). Effect of thermal history and chemical composition on hardness of silicate glasses. *Journal of non-crystalline solids*, 356(18-19), 893-897.



Si et Al en tétraèdre:



Sreenivasan, H., Cao, et al. (2020). *PLoS One*, 15(12), e0244621

Sodium	Bridging oxygen	Silicon
Non-bridging oxygen	Free oxygen	Aluminum

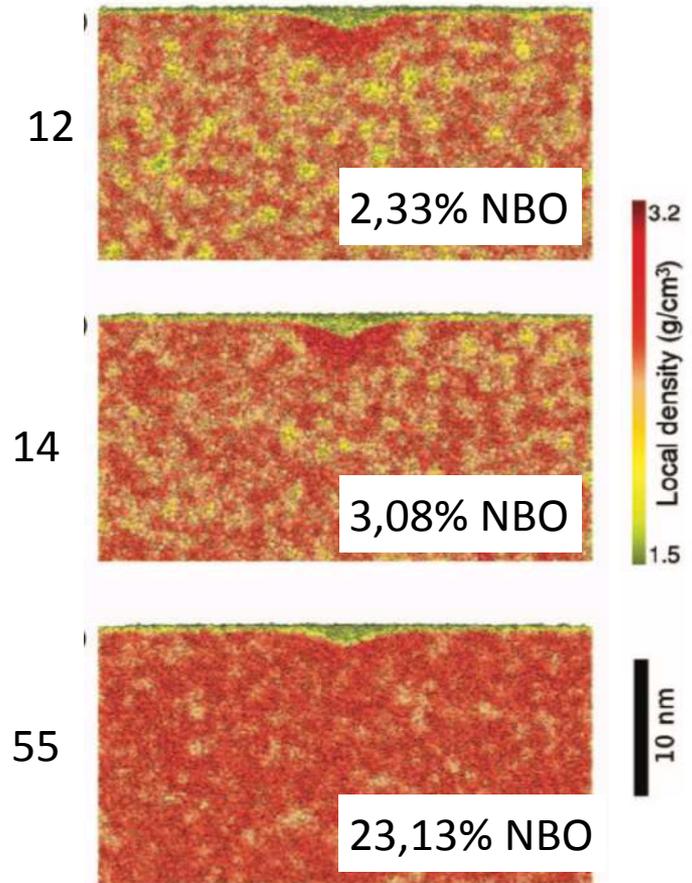
### Tendances générales:

Faible compacité = peu de NBO = densification

*Mais très covalent:  
densification demande une très forte pression*

Beaucoup de NBO: peu de densification,  
mais fort écoulement par cisaillement,  
demande une contrainte de cisaillement  
relativement faible

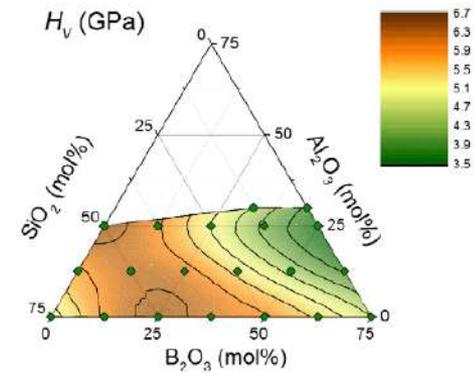
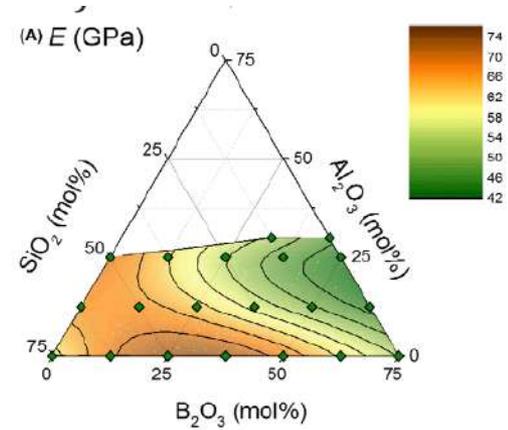
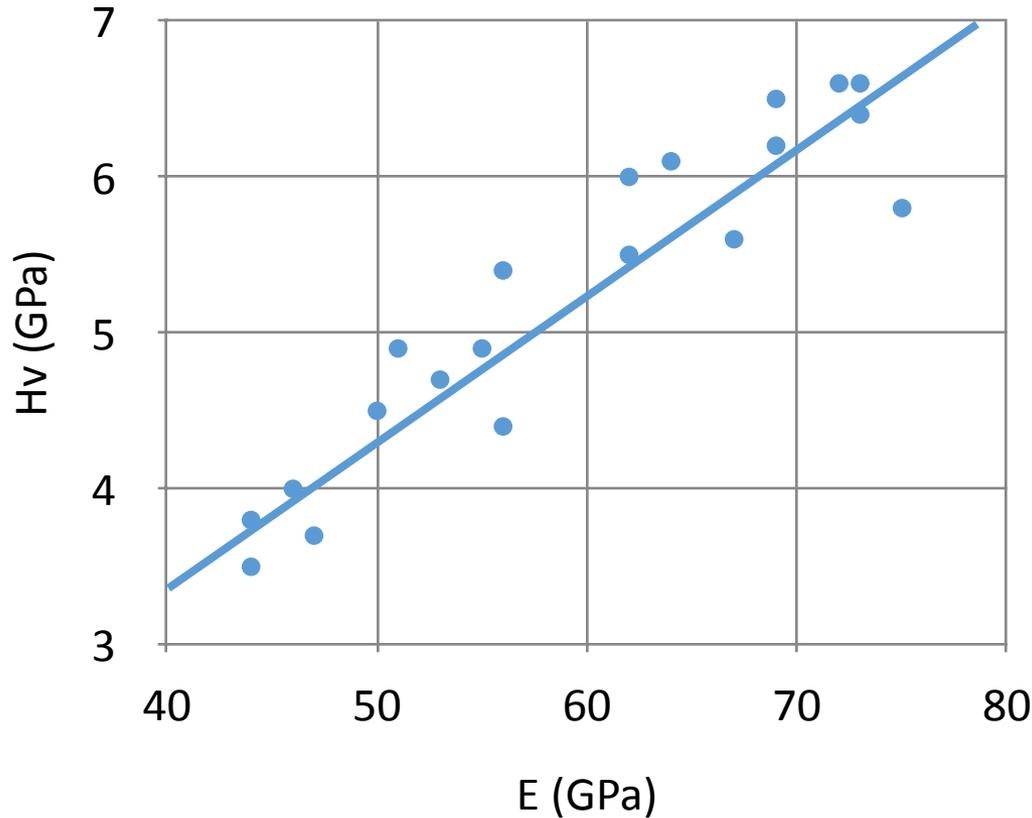
	SiO <sub>2</sub> (%)	B <sub>2</sub> O <sub>3</sub> (%)	Na <sub>2</sub> O (%)
SBN12	59.66	28.14	12.20
SBN14	67.73	18.04	14.23
SBN55	55.30	14.71	29.99



Kilymis, D. A., & Delaye, J. M. (2014). Deformation mechanisms during nanoindentation of sodium borosilicate glasses of nuclear interest. The Journal of Chemical Physics, 141(1), 014504.

## Dureté vs élasticité

Alumino-Boro-Silicate +25%sodium

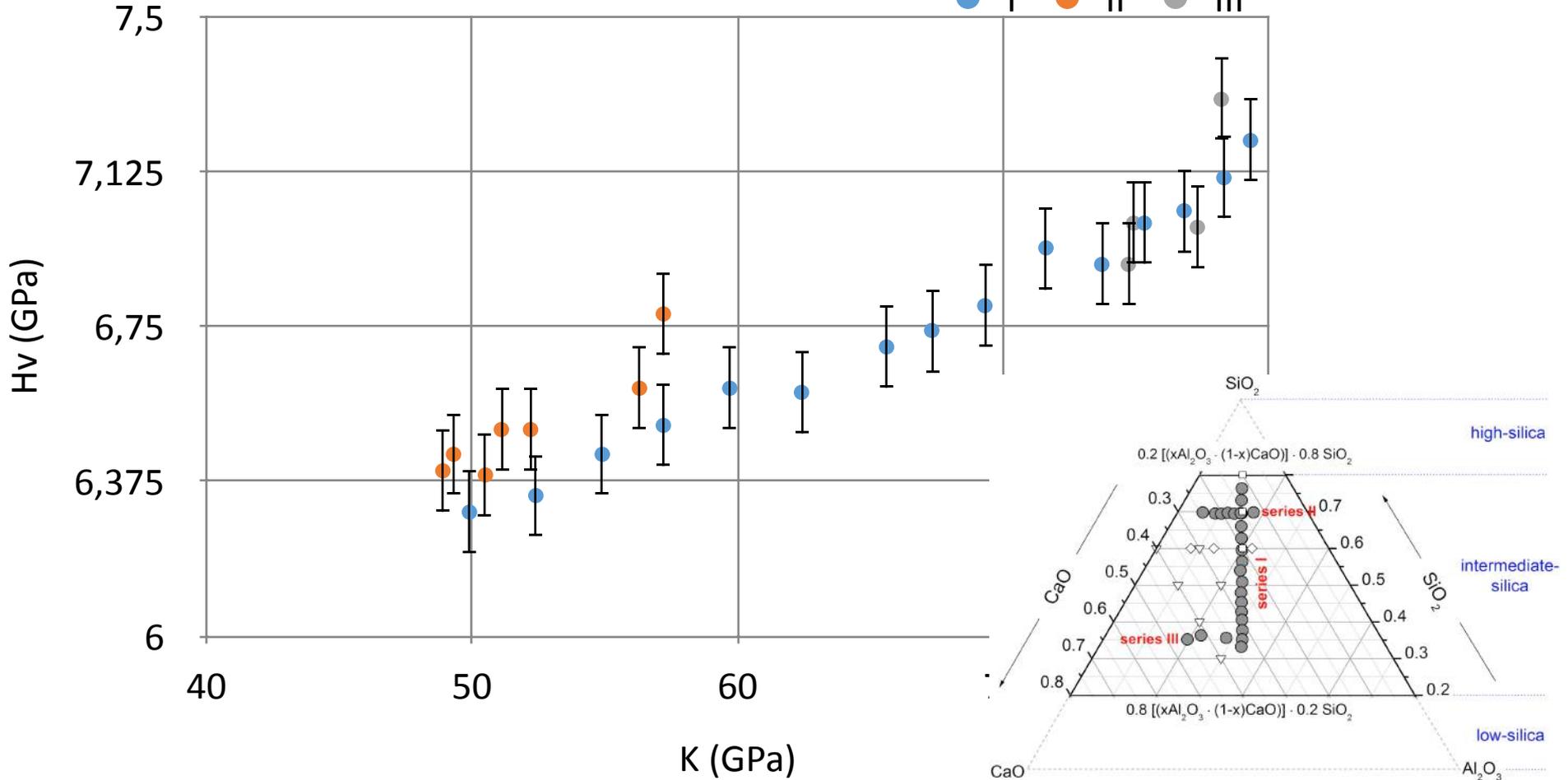


Januchta, K., To, T., Bødker, M. S., Rouxel, T., & Smedskjaer, M. M. (2019). Elasticity, hardness, and fracture toughness of sodium aluminoborosilicate glasses. *Journal of the American Ceramic Society*, 102(8), 4520-4537.

## Dureté vs élasticité

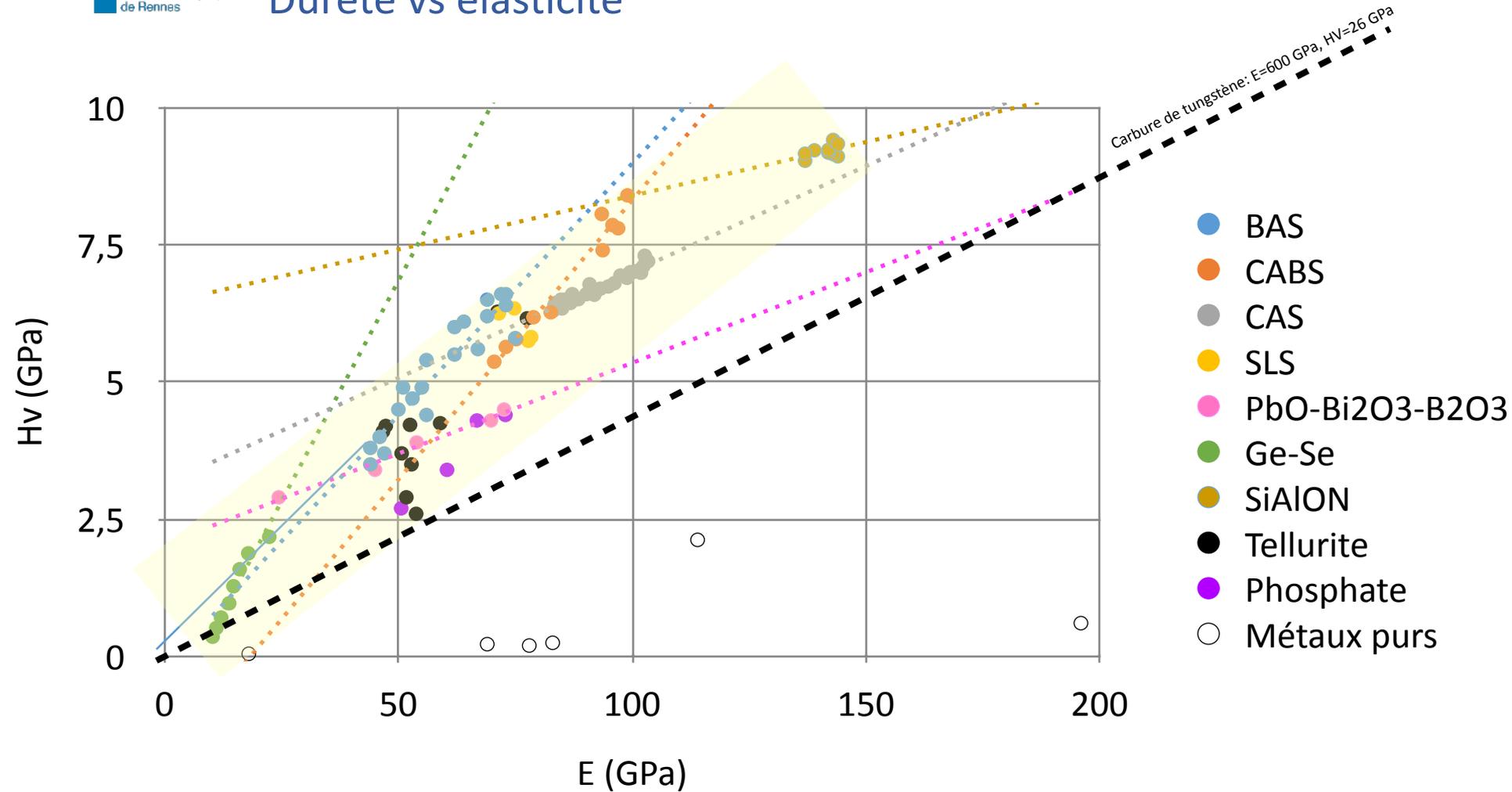
Séries:

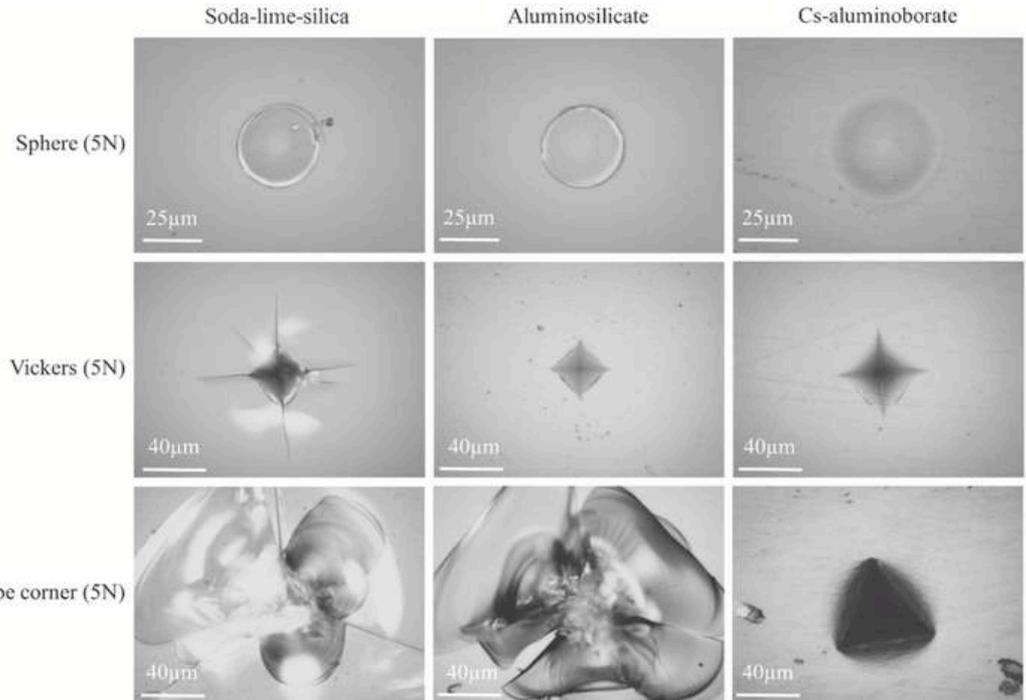
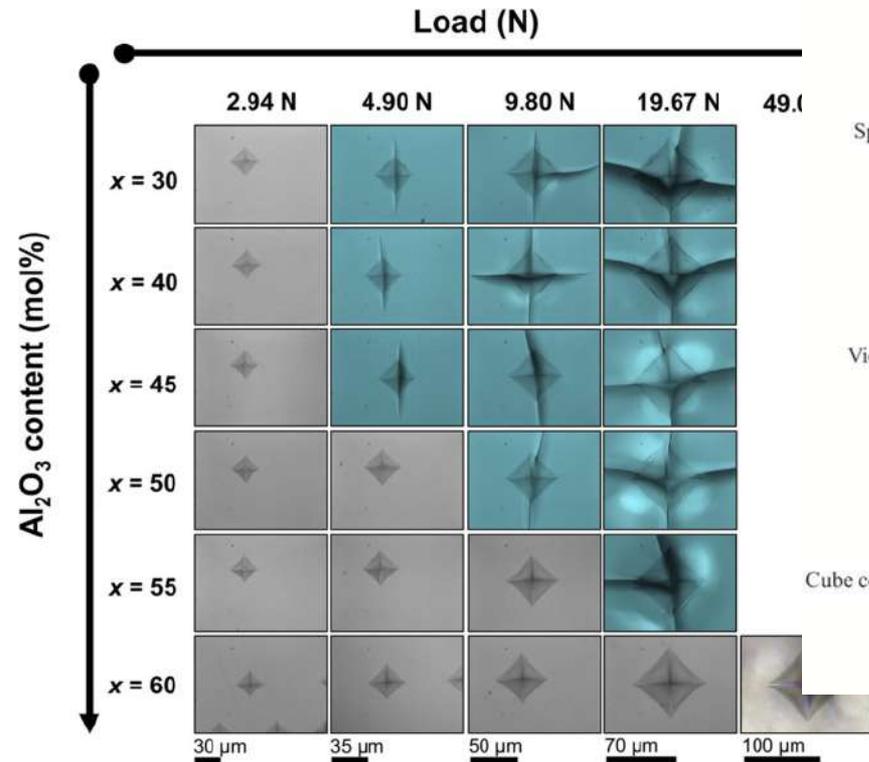
- I
- II
- III



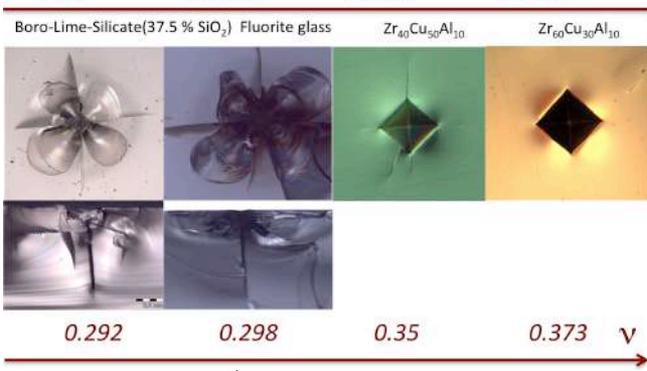
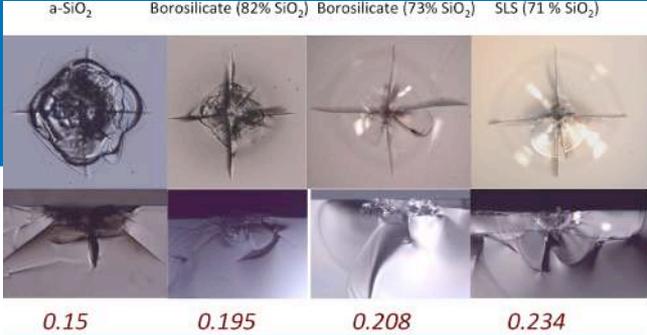
Pönitzsch, A., Nofz, M., Wondraczek, L., & Deubener, J. (2016). Journal of non-crystalline solids, 434, 1-12.

## Dureté vs élasticité

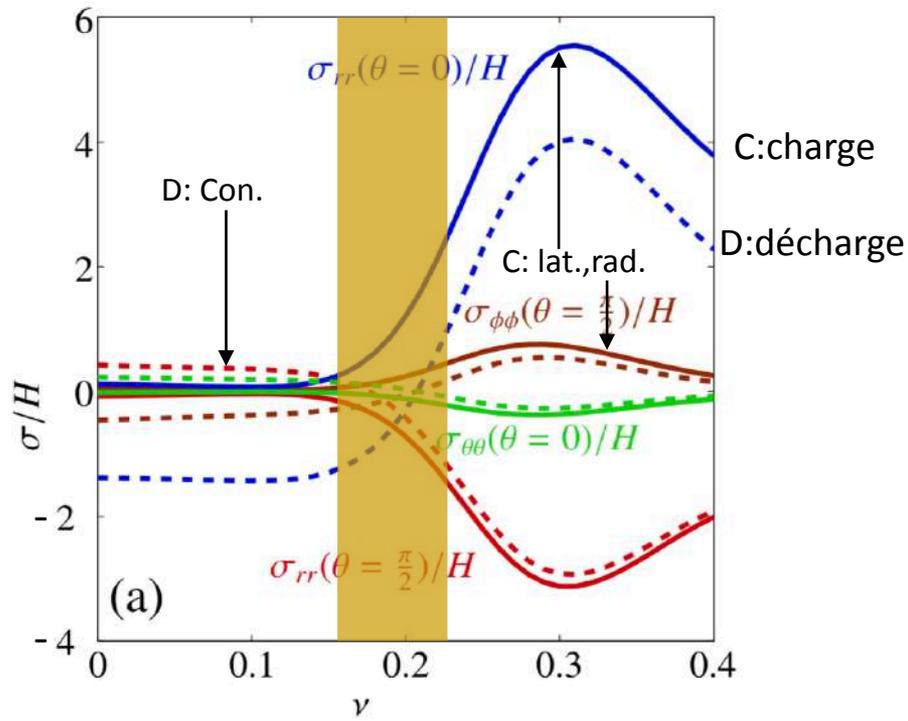
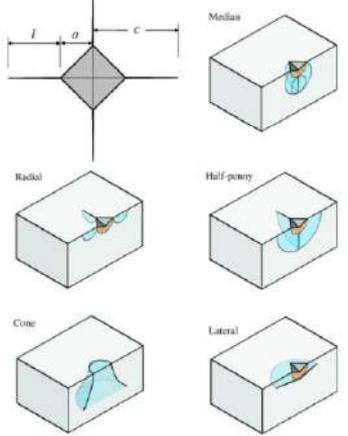
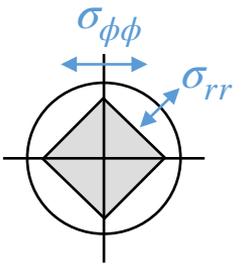




Januchta, K., Stepniewska, M., Jensen, L. R., Zhang, Y., Somers, M. A., Bauchy, M., ... & Smedskjaer, M. M. (2019) *Advanced Science*, 6(18), 1901281.



# ement de surface



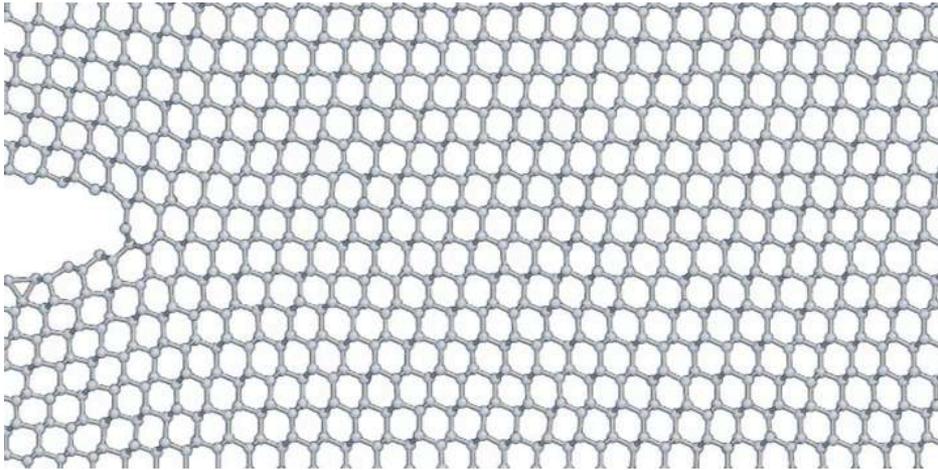
Barlet, M., Delaye, J. M., Charpentier, T., Gennisson, M., Bonamy, D., Rouxel, T., & Rountree, C. L. (2015).  
 Hardness and toughness of sodium borosilicate glasses via Vickers's indentations. *Journal of Non-Crystalline Solids*, 417, 66-79.

K.I. Schiffmann, Determination of fracture toughness of bulk materials and thin films by nanoindentation: comparison of different models, *Philosophical Magazine*. 91 (2011) 1163-1178

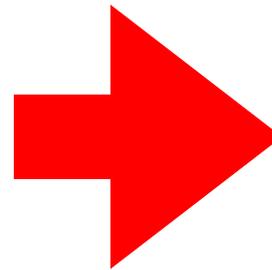
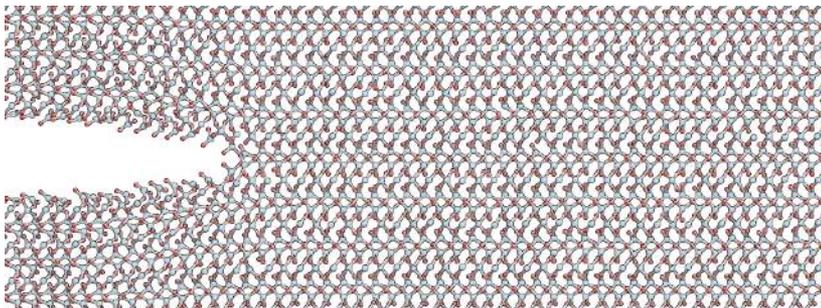
# Fissuration



## Fissuration?



<https://libatoms.github.io>



Liaisons par m<sup>2</sup>

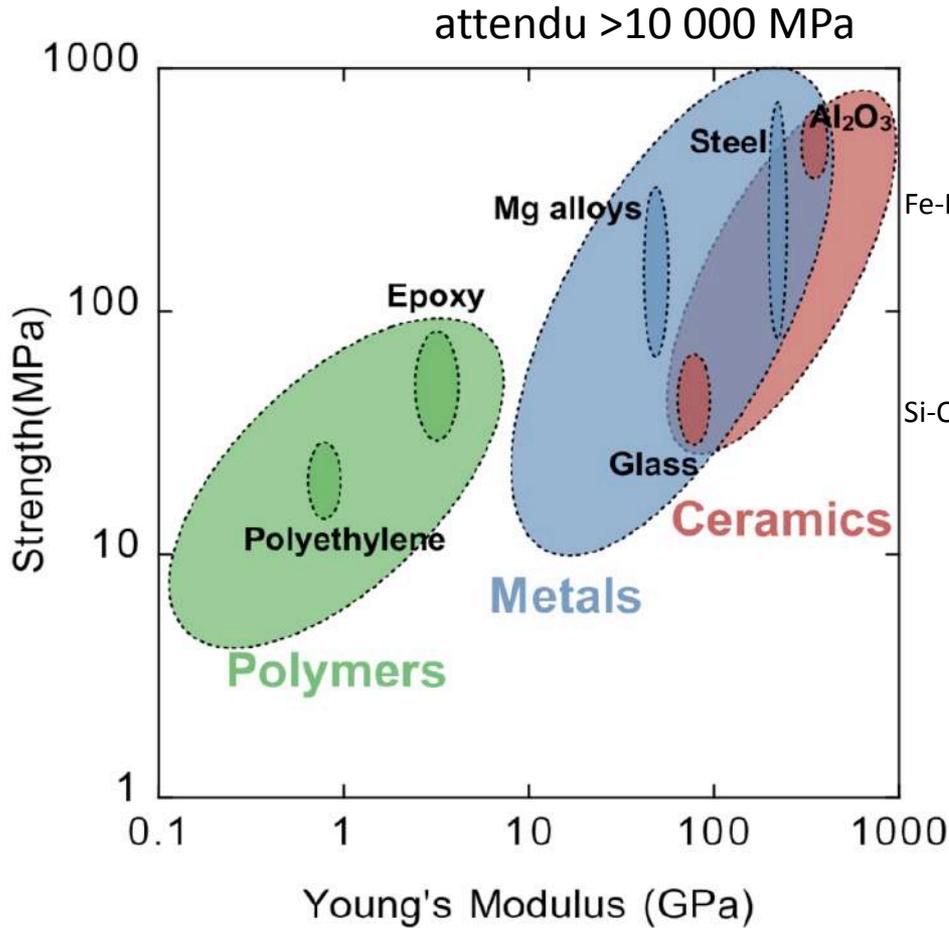
Energie de liaison

Energie Mécanique

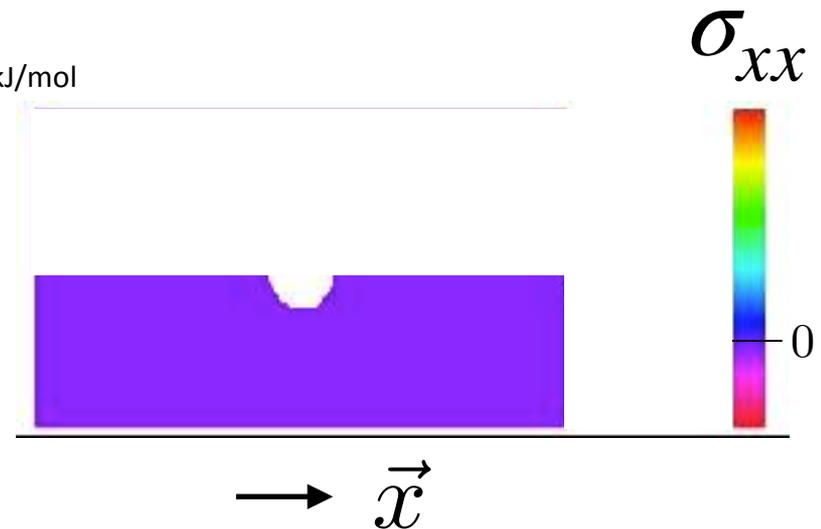
Verre de silice en traction:

$$\sigma_R = 15 - 20 \text{ GPa}$$

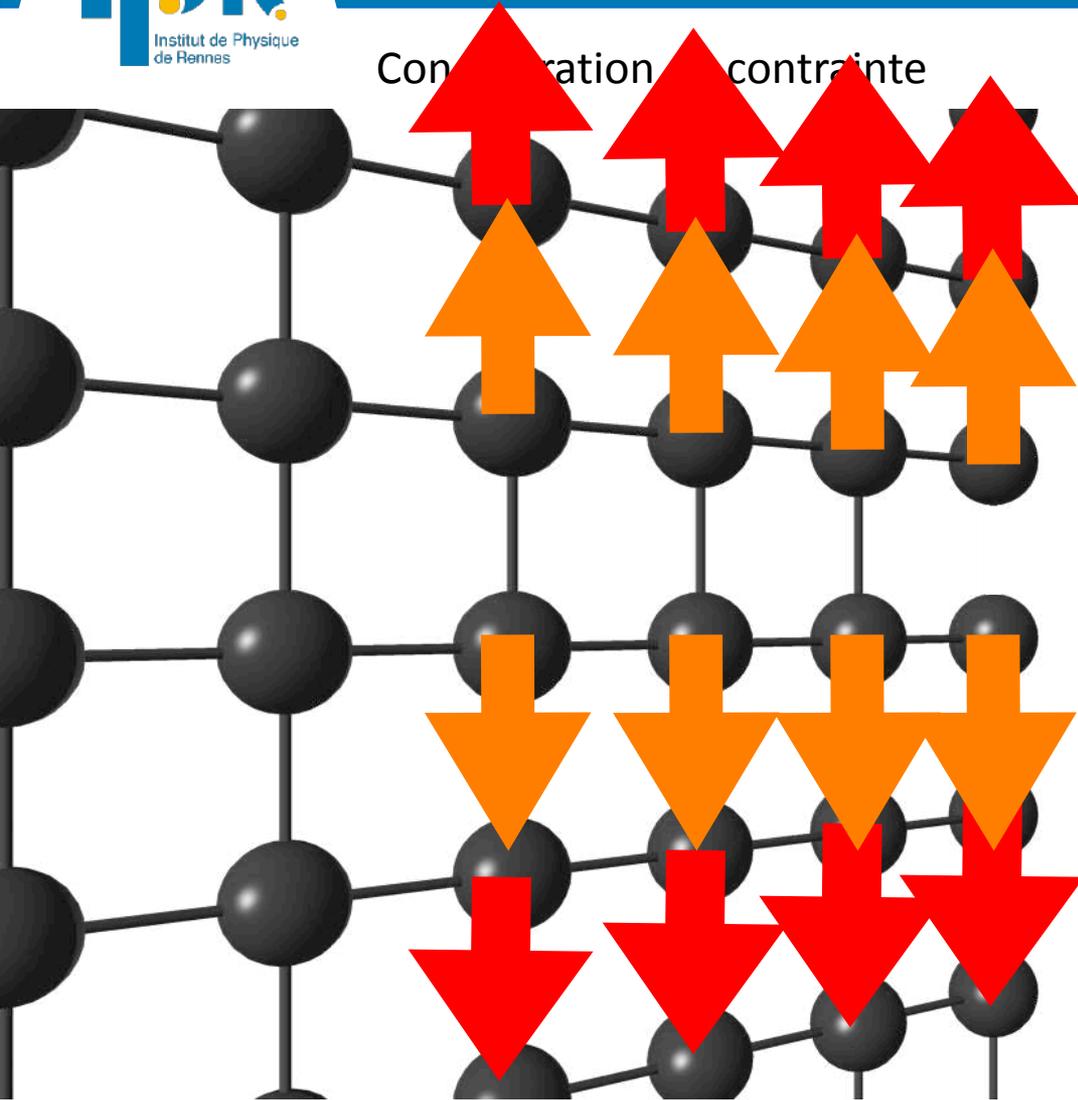
## Contrainte à rupture



Présence de défauts  
à la surface du verre



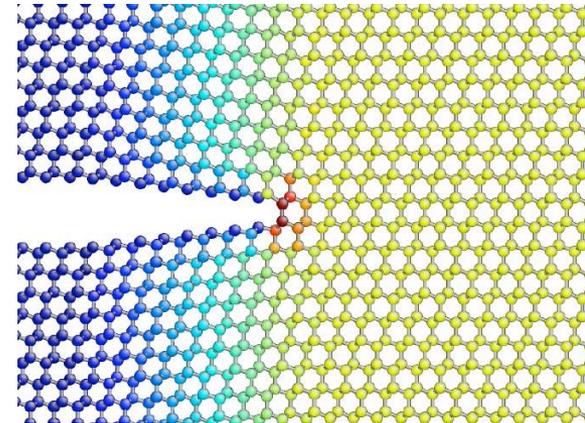
Concentration de contrainte



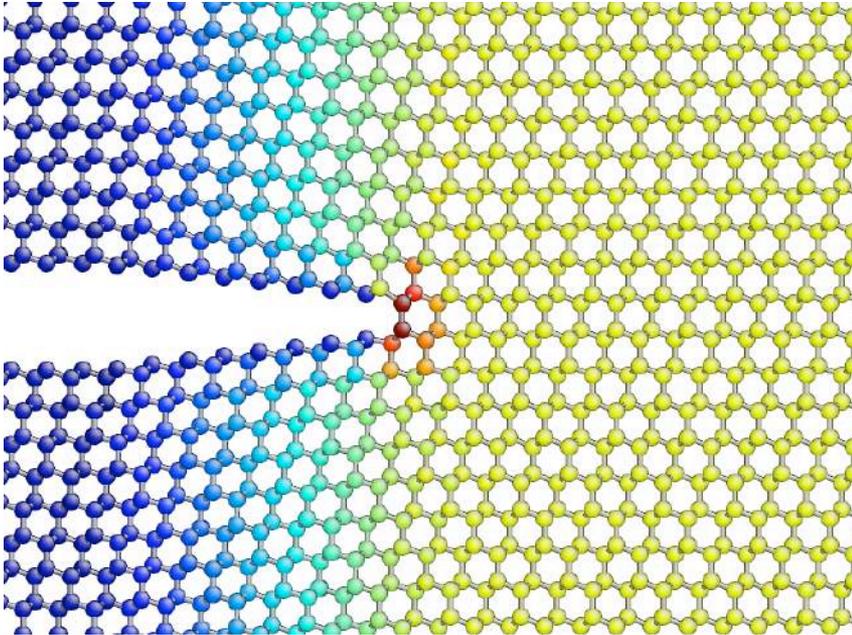
Report des "forces" d'une liaison vers la voisine...

Complicé à prédire!

Géométrie du réseau,  
type de liaisons...



## Concentration de contrainte



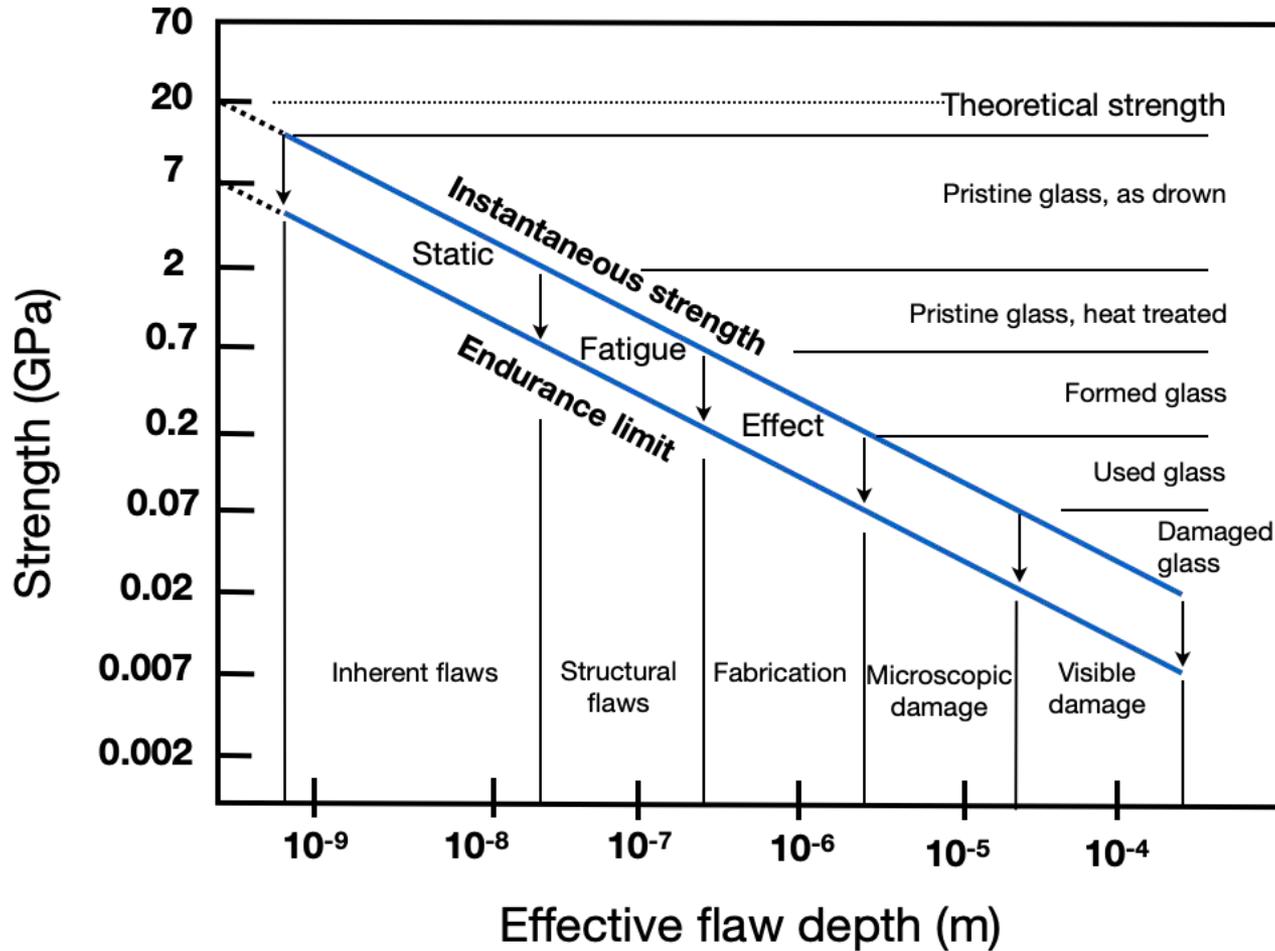
Contrainte à rupture  
de fibres de silice  
"sans défauts"

12-14 GPa

C.R. Kurkjian et al. / Journal of Non-Crystalline Solids 316 (2003) 114-124

<https://libatoms.github.io>

## Rôle des défauts



fibres

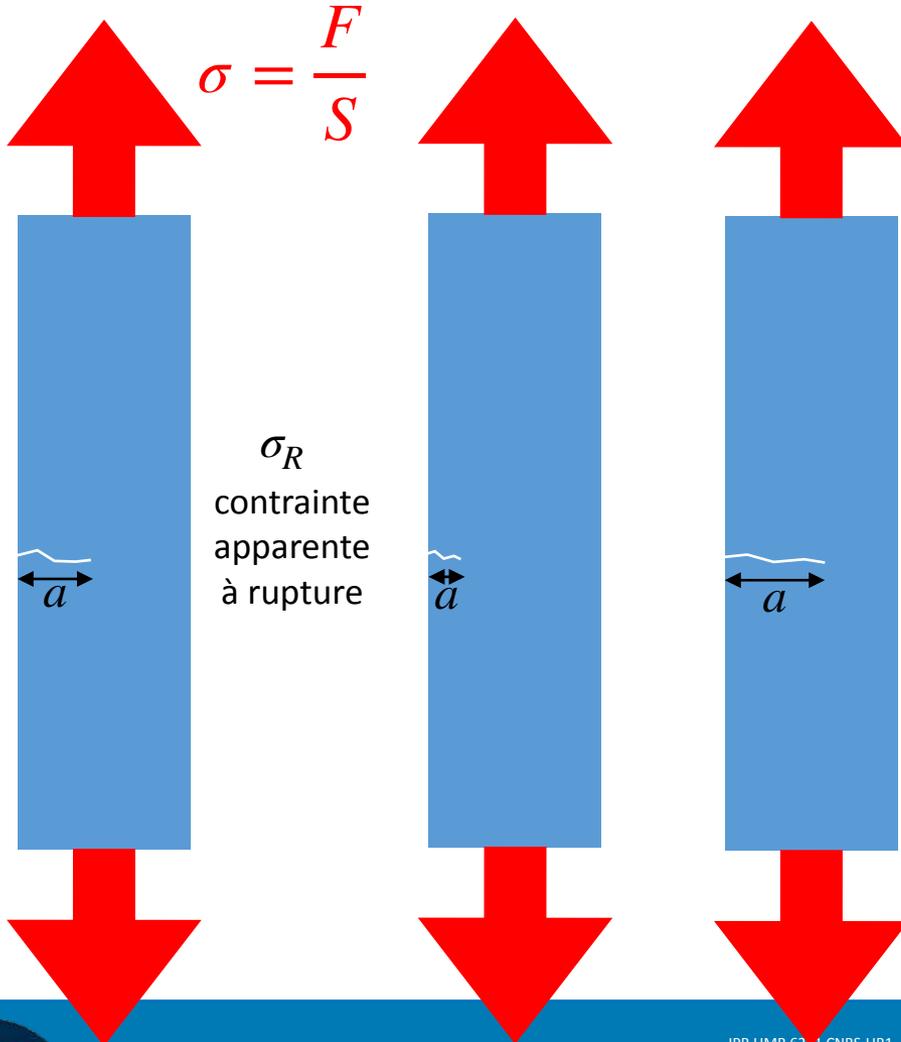
défaut lors de la fabrication

défaut lors de la mise en forme

nettoyage

impacts

## Expérience de Griffith: Ténacité



$$\sigma_R \times \sqrt{a} = Cste$$

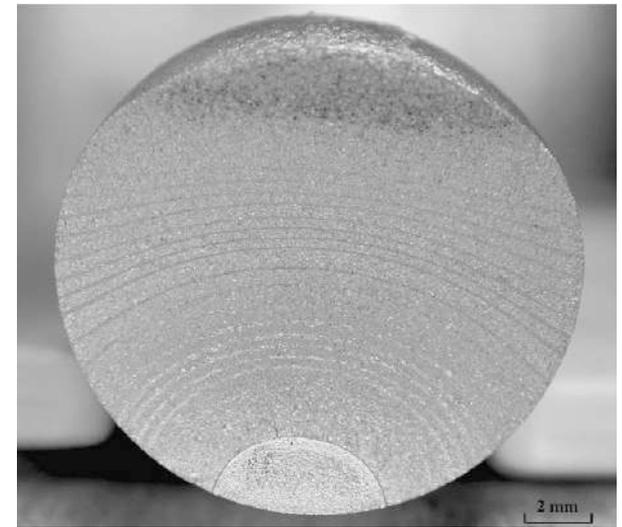
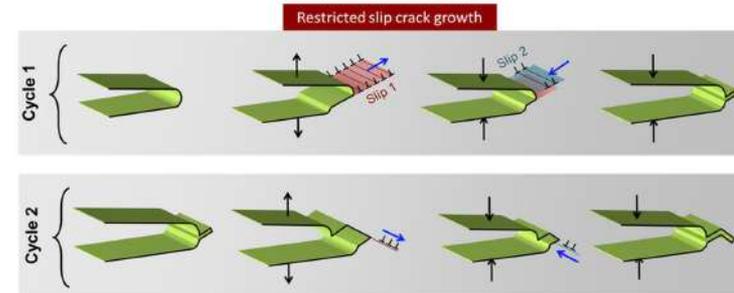
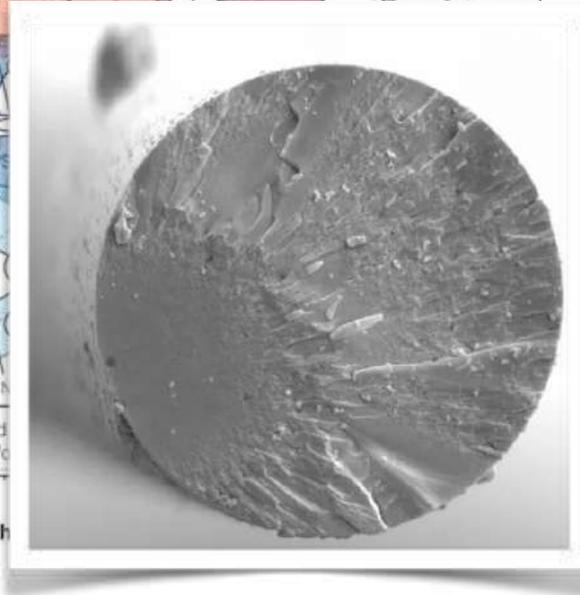
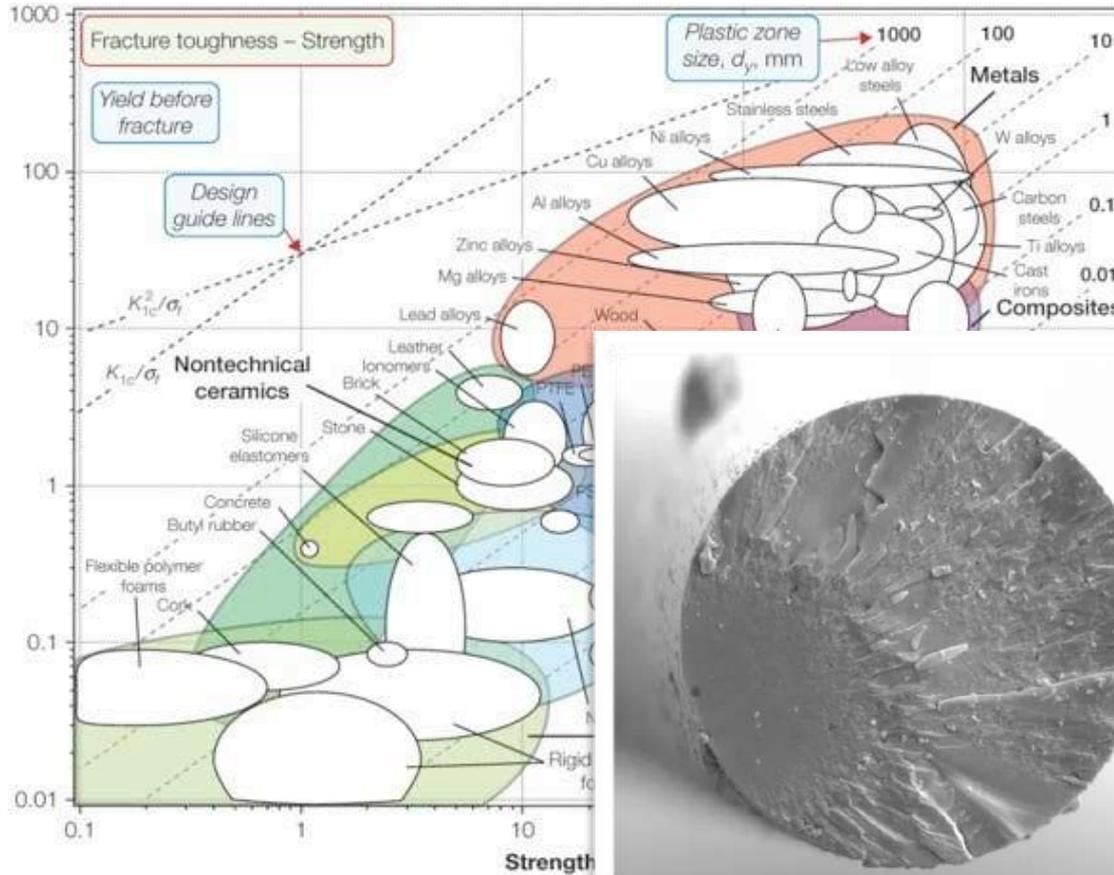
La "ténacité"

$$K_{IC}$$

$$MPa \cdot \sqrt{m}$$

## Ténacité

## Matériau ductile



Shin, C. S., & Cai, C. Q. (2004).

International Journal of fracture, 129(3), 239-264.

# Fatigue statique



Rupture

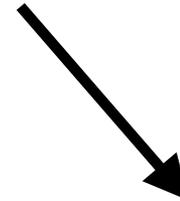
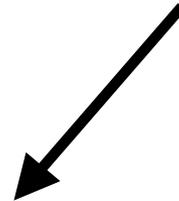
$$\sigma = \frac{F}{S}$$



$$\sigma_R \sqrt{a} = K_{IC}$$

facteur d'intensité de contrainte:

$$\sigma \sqrt{a} = K_I$$



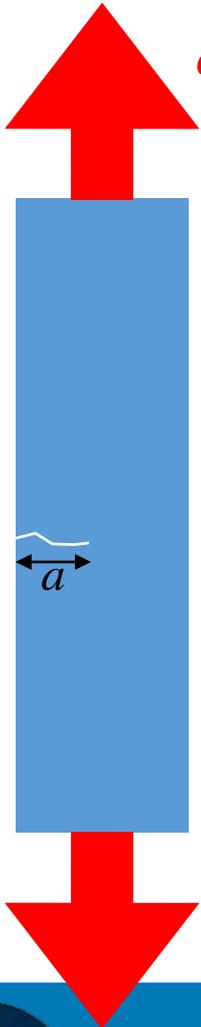
$$K_I < K_{IC}$$

Pas de rupture

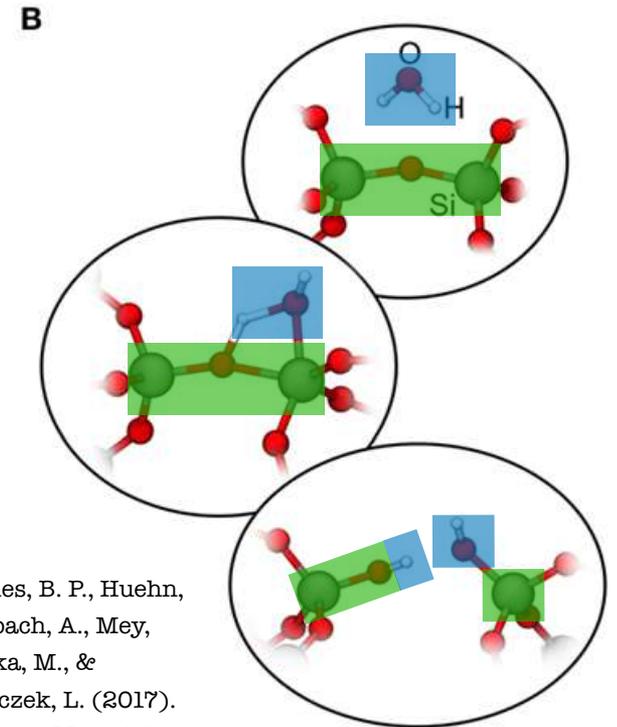
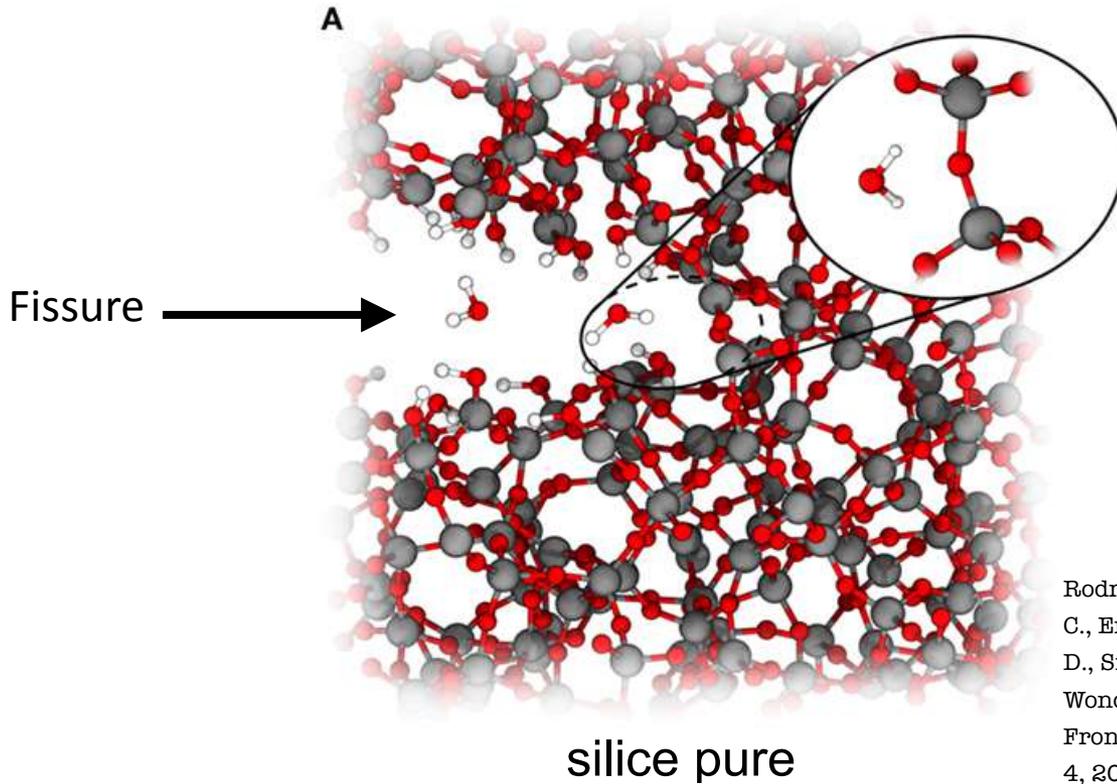
$$K_I \geq K_{IC}$$

Rupture

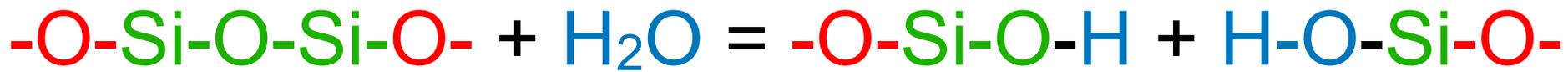
## Binaire?



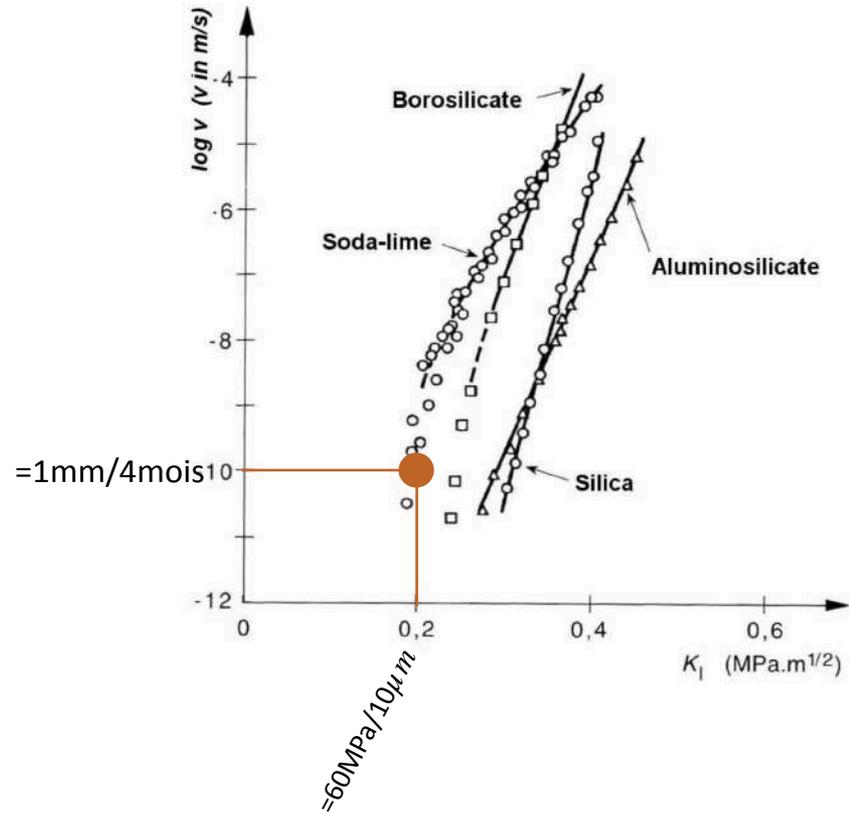
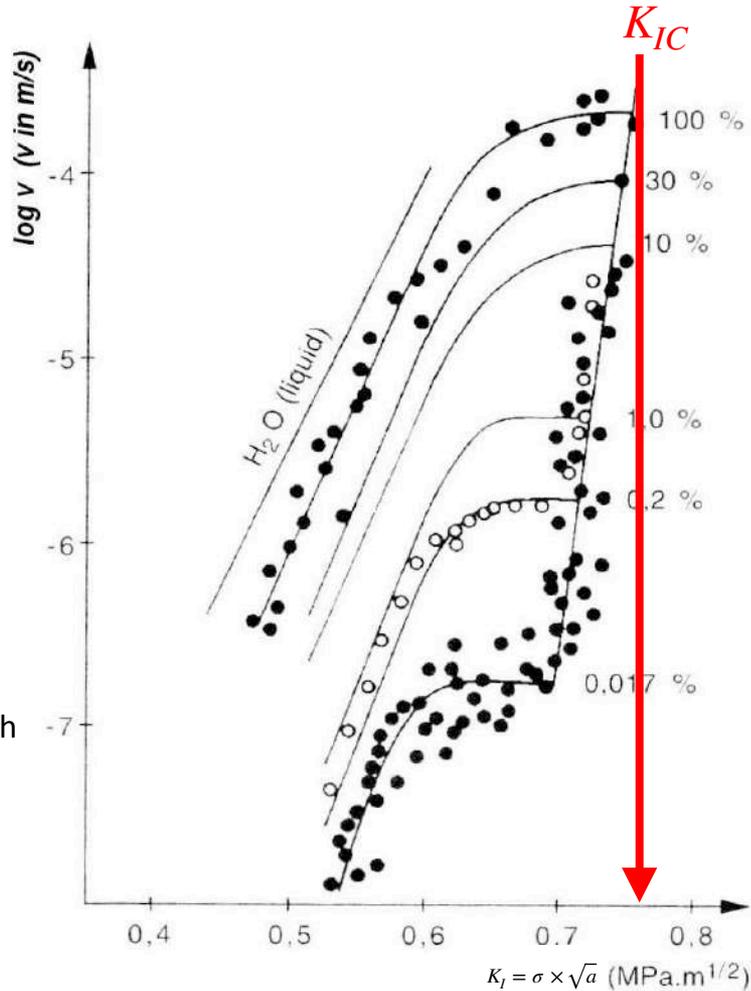
## Corrosion sous contrainte



Rodrigues, B. P., Huehn, C., Erlebach, A., Mey, D., Sierka, M., & Wondraczek, L. (2017). *Frontiers in Materials*, 4, 20.



## Propagation sous-critique

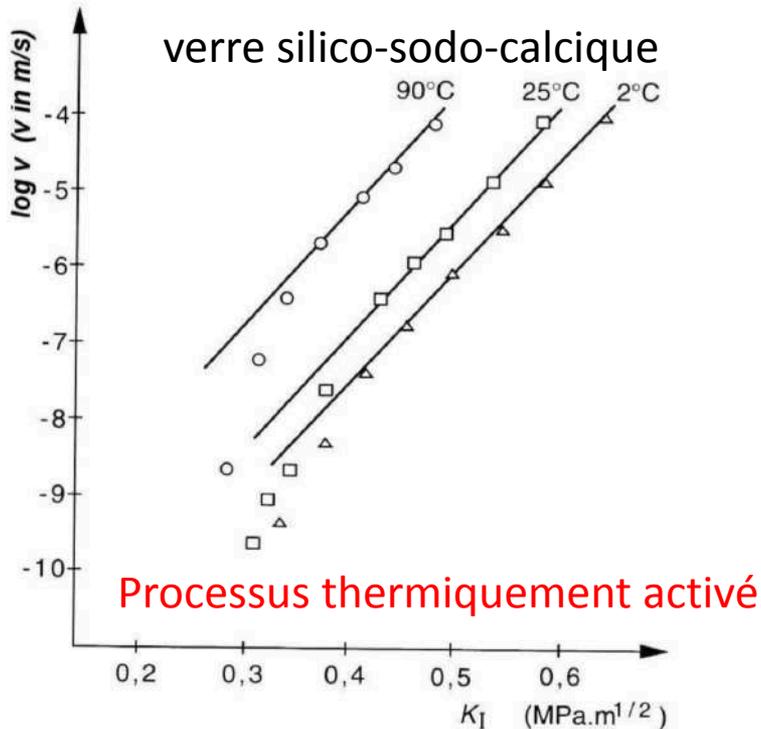


Wiederhorn S M 1967 J. Am. Ceram. Soc. 50 407-14

Wiederhorn S M 1969 J. Am. Ceram. Soc. 52 99-105

Wiederhorn S M and Bolz L H 1970 J. Am. Ceram. Soc. 53 543-8

## Propagation sous-critique



Contre-intuitif:

Plus un verre est étiré lentement... plus sa contrainte à rupture est faible!



=contrainte  
+humidité  
+temps

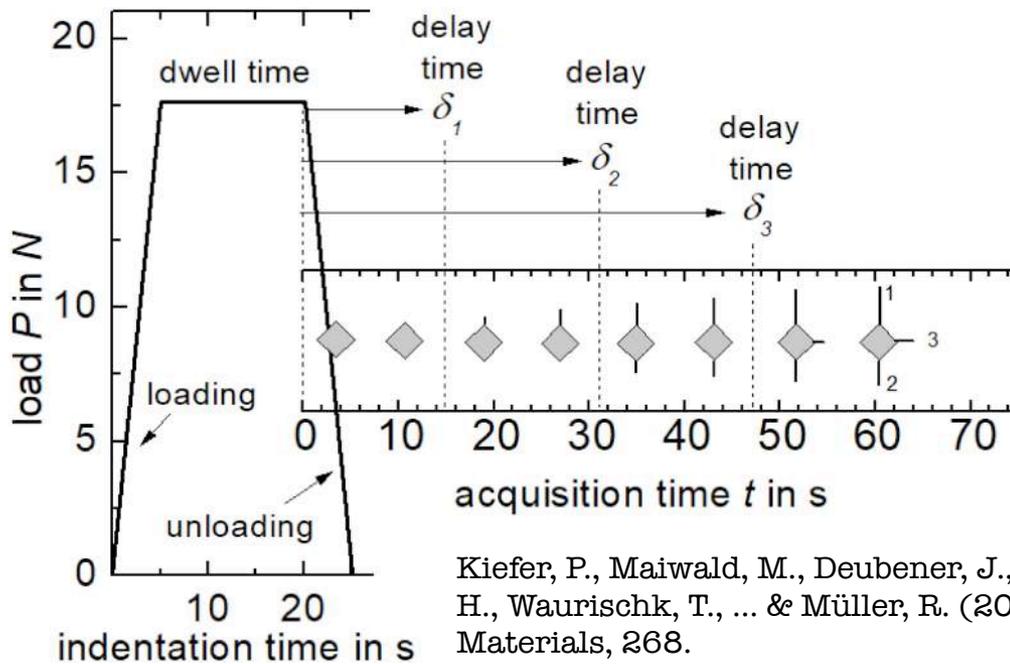
Elle peut casser spontanément  
au bout de 1 mois, 1 an, 1 siècle...

Wiederhorn S M 1967 J. Am. Ceram. Soc. 50 407-14

Wiederhorn S M 1969 J. Am. Ceram. Soc. 52 99-105

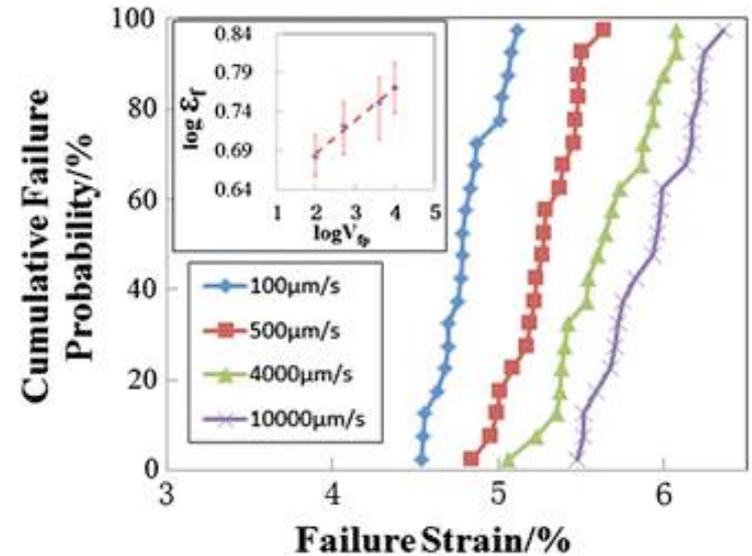
Wiederhorn S M and Bolz L H 1970 J. Am. Ceram. Soc. 53 543-8

## Initiation et propagation sous-critique



Kiefer, P., Maiwald, M., Deubener, J., Balzer, R., Behrens, H., Waurischk, T., ... & Müller, R. (2020). *Frontiers in Materials*, 268.

E-glass fibers

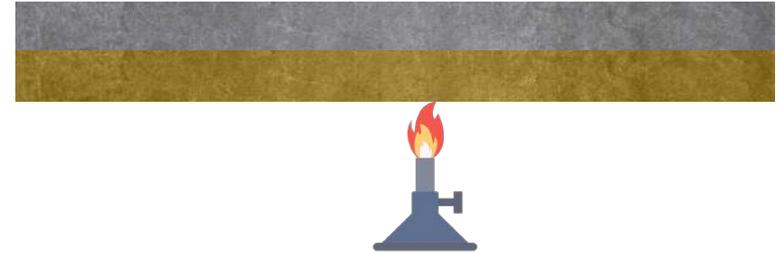
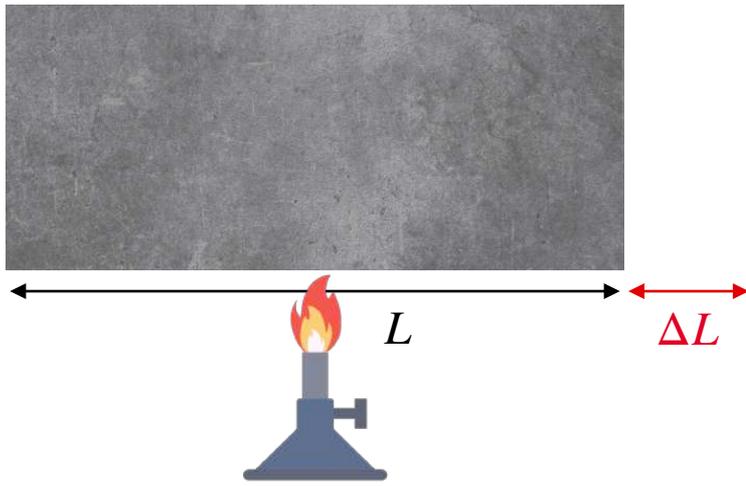


Wang, Q., Brow, R. K., Li, H., & Ronchetto, E. A. (2016). *Journal of materials science*, 51(5), 2404-2410.

# Contraintes thermiques



## Dilatation



$$\frac{\Delta L}{L} = \alpha \times \Delta T$$

## Dilatation

vitro-céramique LAS

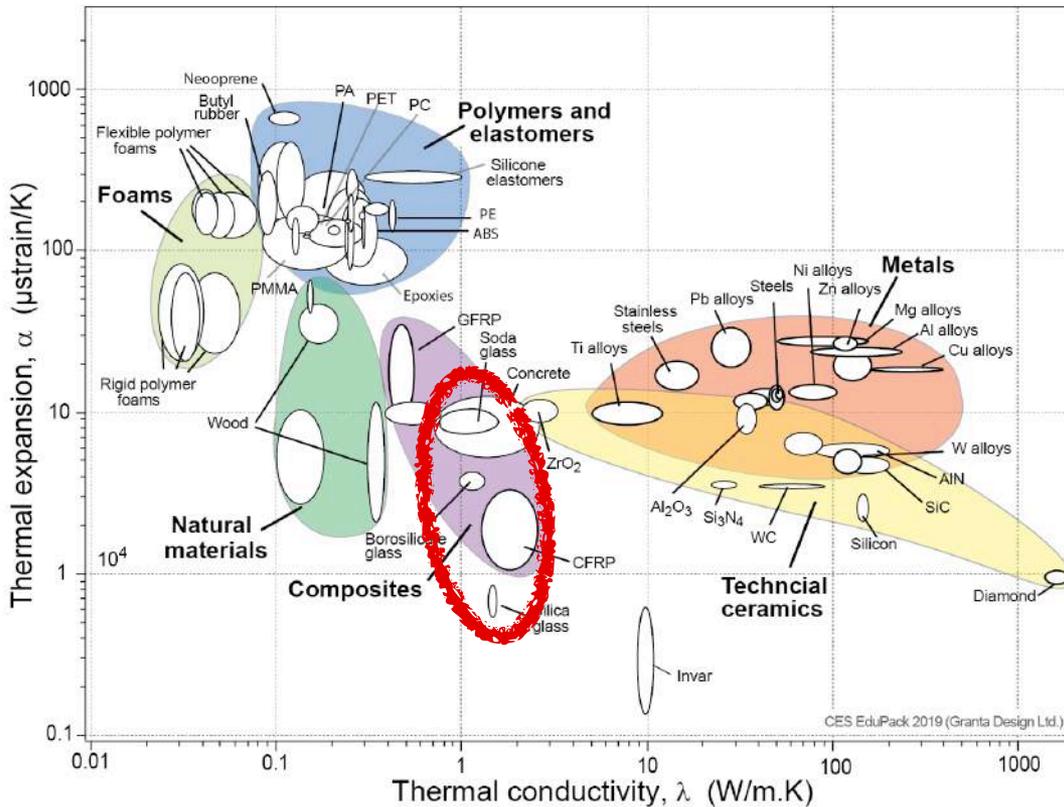
Glass	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Li <sub>2</sub> O	MgO	ZnO	K <sub>2</sub> O	Na <sub>2</sub> O	TiO <sub>2</sub>	ZrO <sub>2</sub>	As <sub>2</sub> O <sub>3</sub>
Po	67.5	17.2	8.7	1.7	1.2	0.3	0.2	2	1	0.2

$$\alpha < -5 \times 10^{-6} / K$$

**Alumino-silicate de sodium:**

100°C=0,1% de déformation

Autant que 70 MPa!



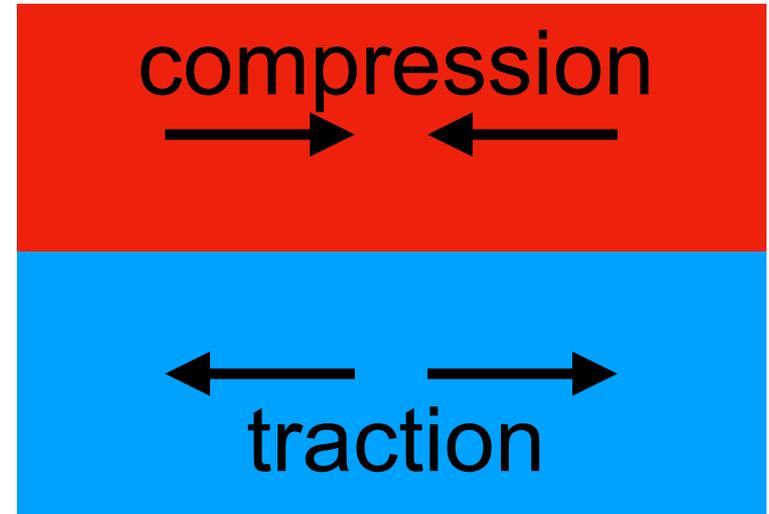
## Choc thermique

chaud



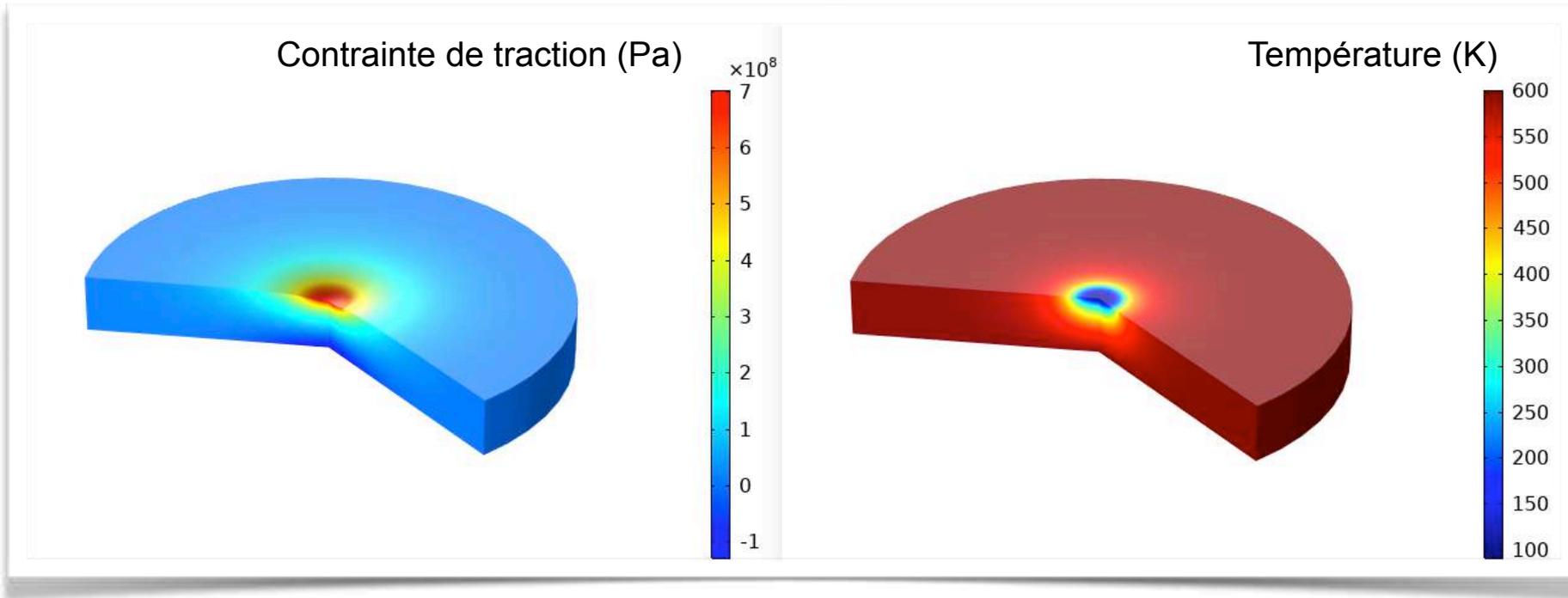
chaud

chaud



froid

## Choc thermique

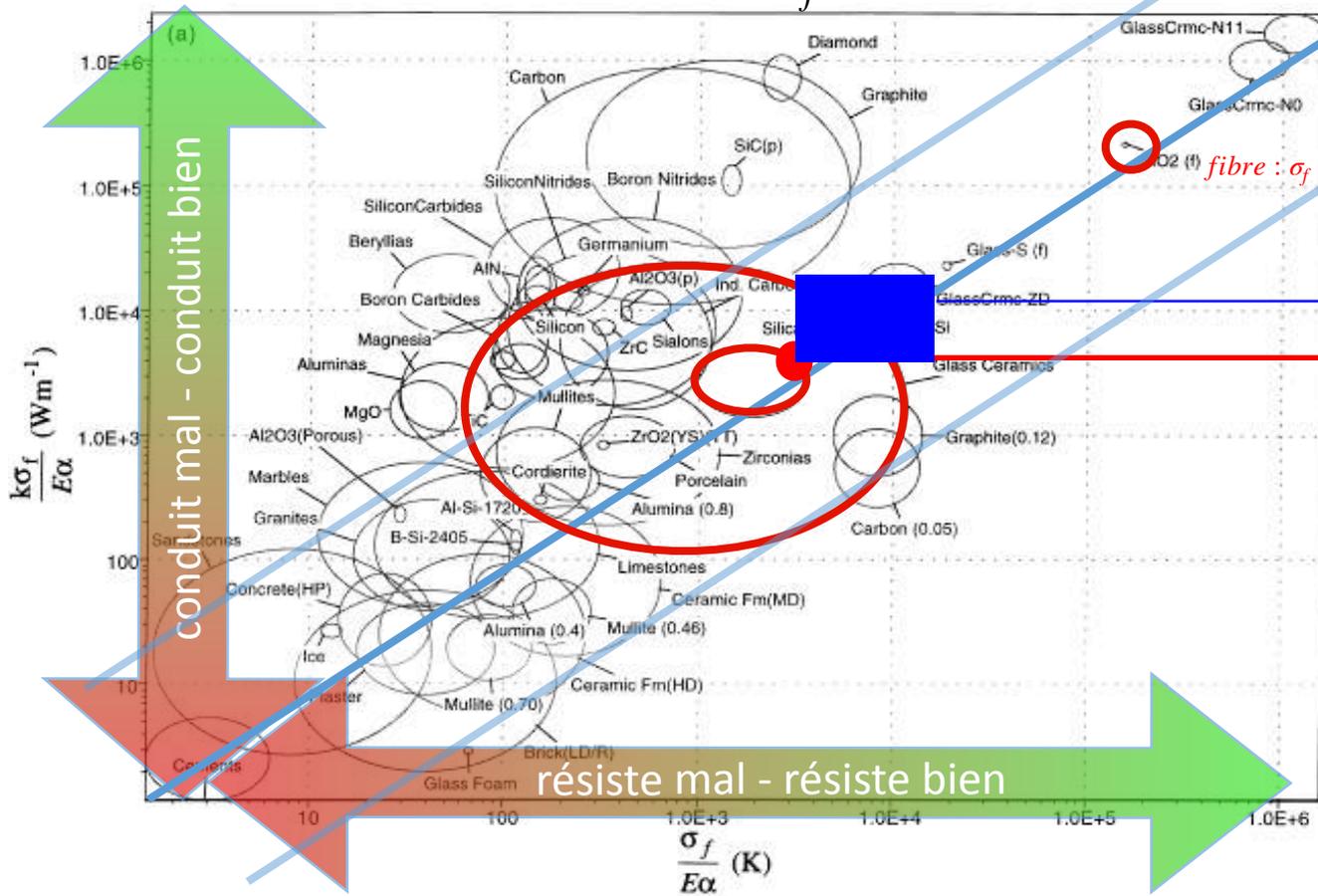


Une forte hétérogénéité de température entraîne une forte hétérogénéité de dilatation, donc des fortes contraintes.

$$\sigma \propto E \times \alpha \times \Delta T$$

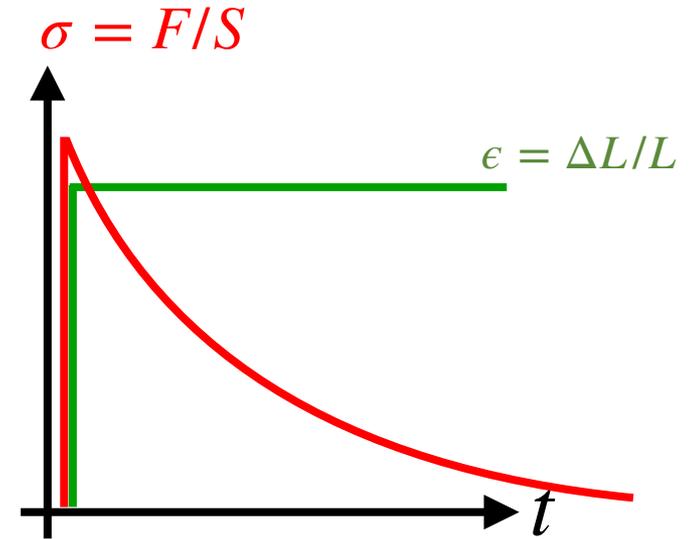
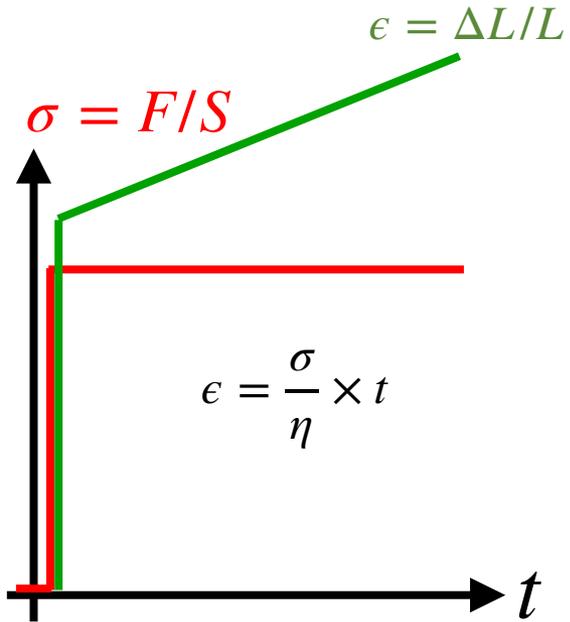
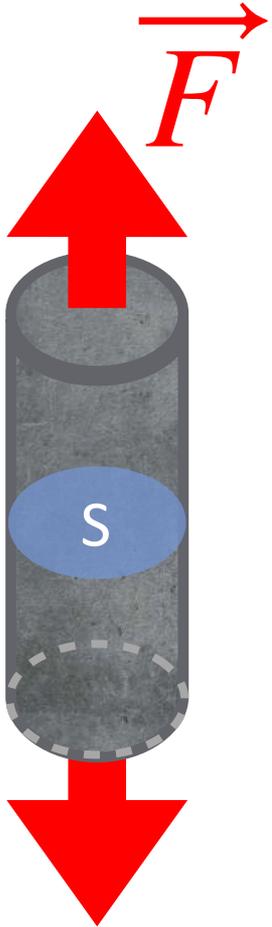
## Choc thermique

$k$ : conductivité thermique,  $\sigma_f$ : contrainte à rupture



Lu, T. J., & Fleck, N. A. (1998). The thermal shock resistance of solids. Acta materialia, 46(13), 4755-4768.

## Relaxation de contrainte

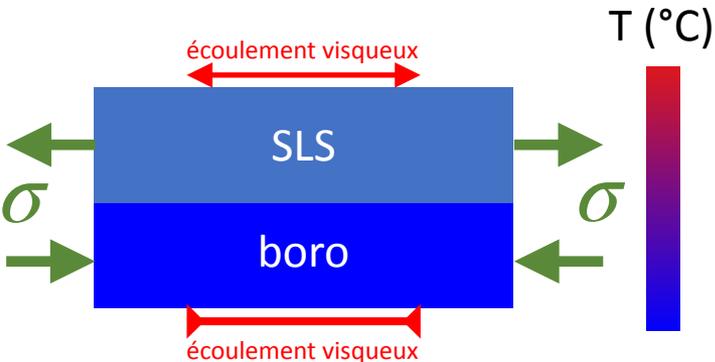


La contrainte "relaxe"  
par écoulement visqueux.

## Assemblage risqué...

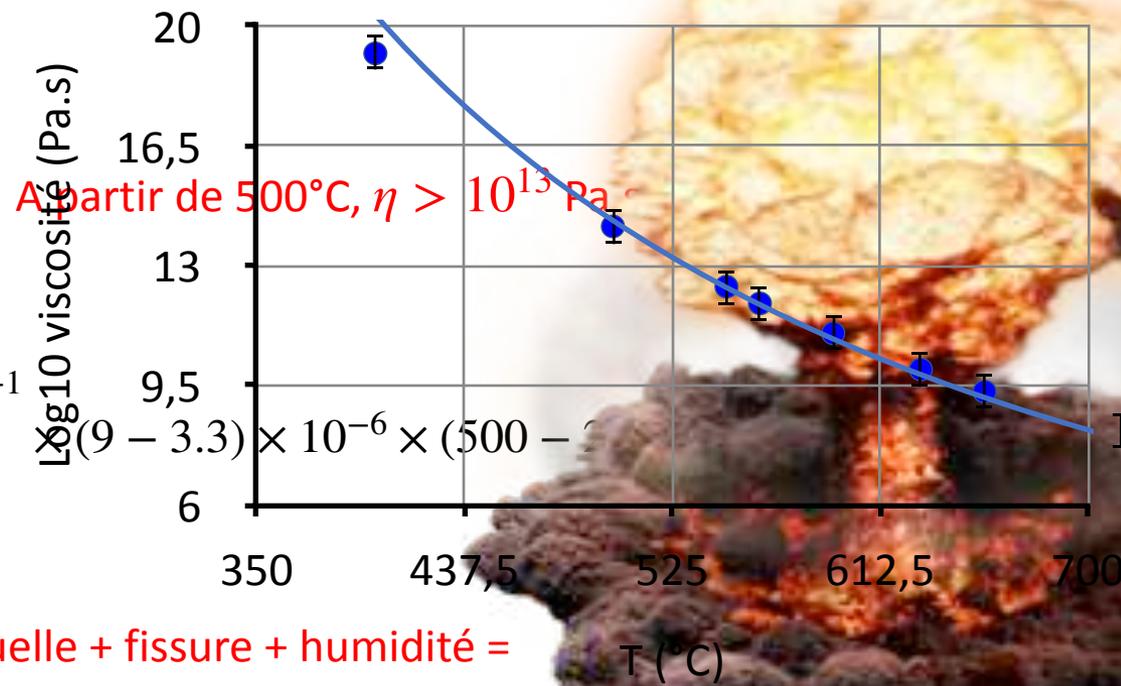
Borosilicate (Pyrex<sup>®</sup>):  $\alpha = 3,3 \times 10^{-6}/K$ ,  $T_g=565^\circ C$ ,  $E=64$  GPa

silico-sodo-calcique:  $\alpha = 9 \times 10^{-6}/K$ ,  $T_g=550^\circ C$ ,  $E=72$  GPa



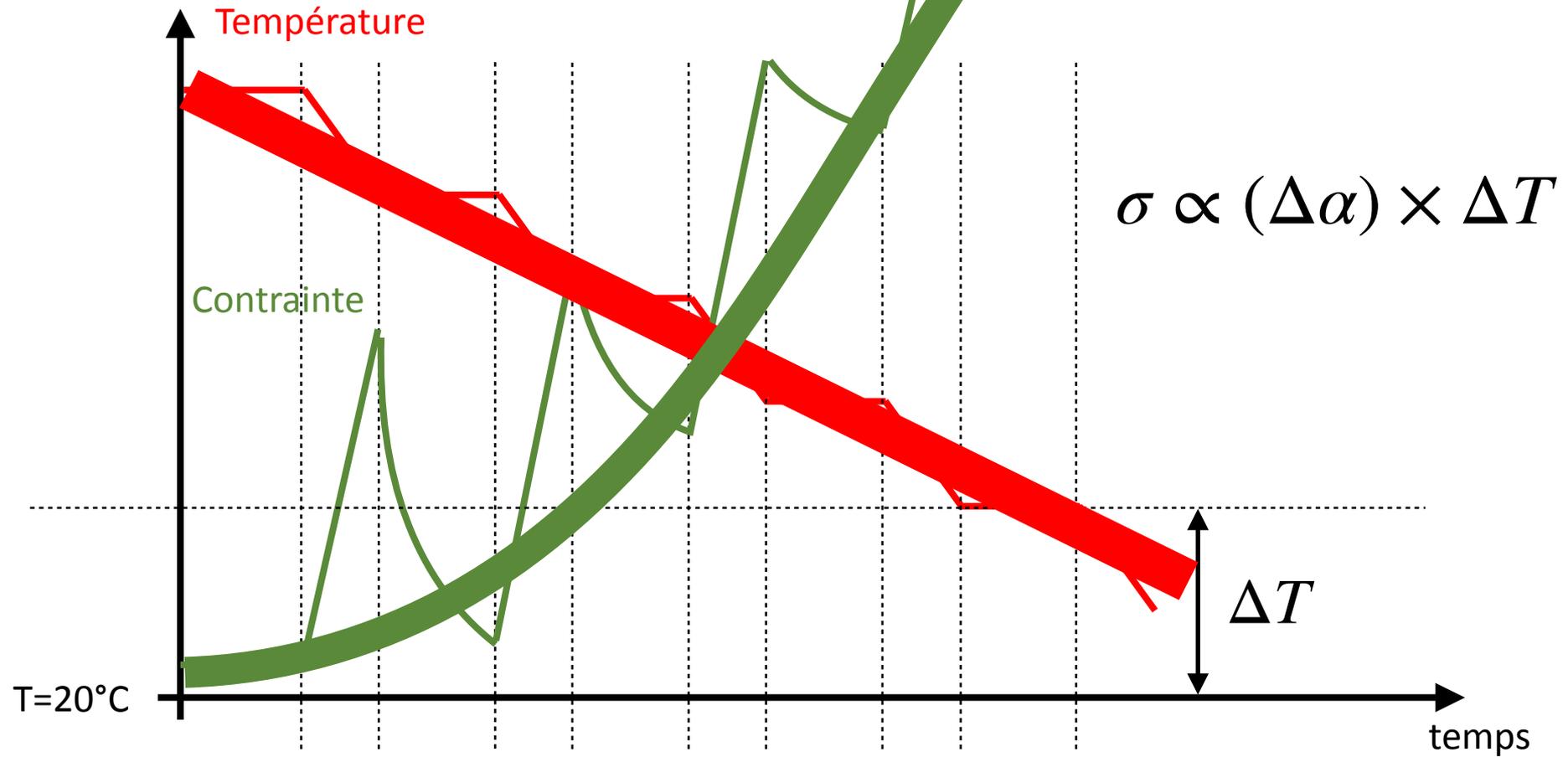
A 20°C: 
$$\sigma = \left( \frac{1}{64000} + \frac{1}{72000} \right)^{-1} \times (9 - 3.3) \times 10^{-6} \times (500 - T)$$

75 MPa si 400°C



Contrainte résiduelle + fissure + humidité =

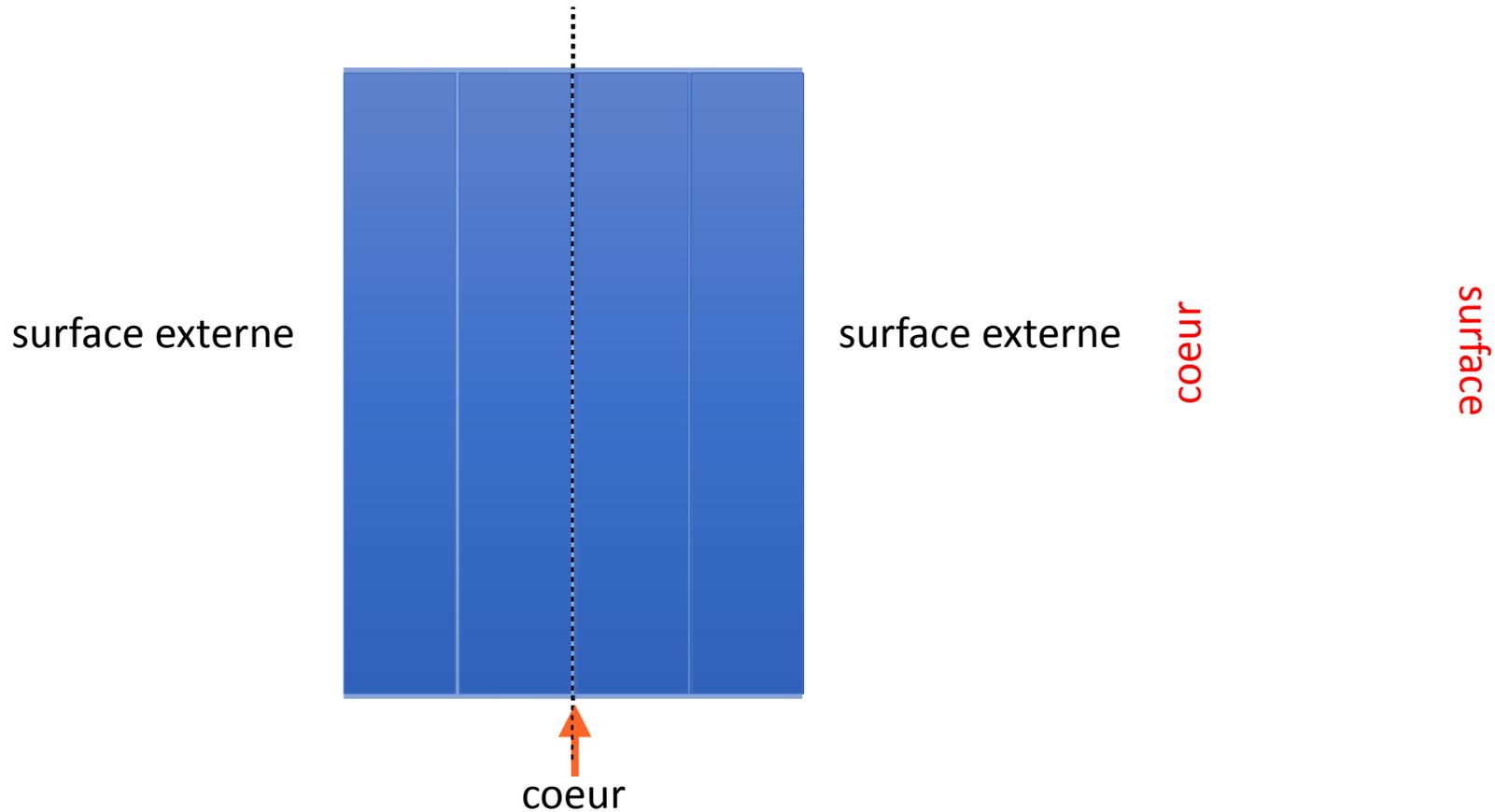
Assemblage risqué...

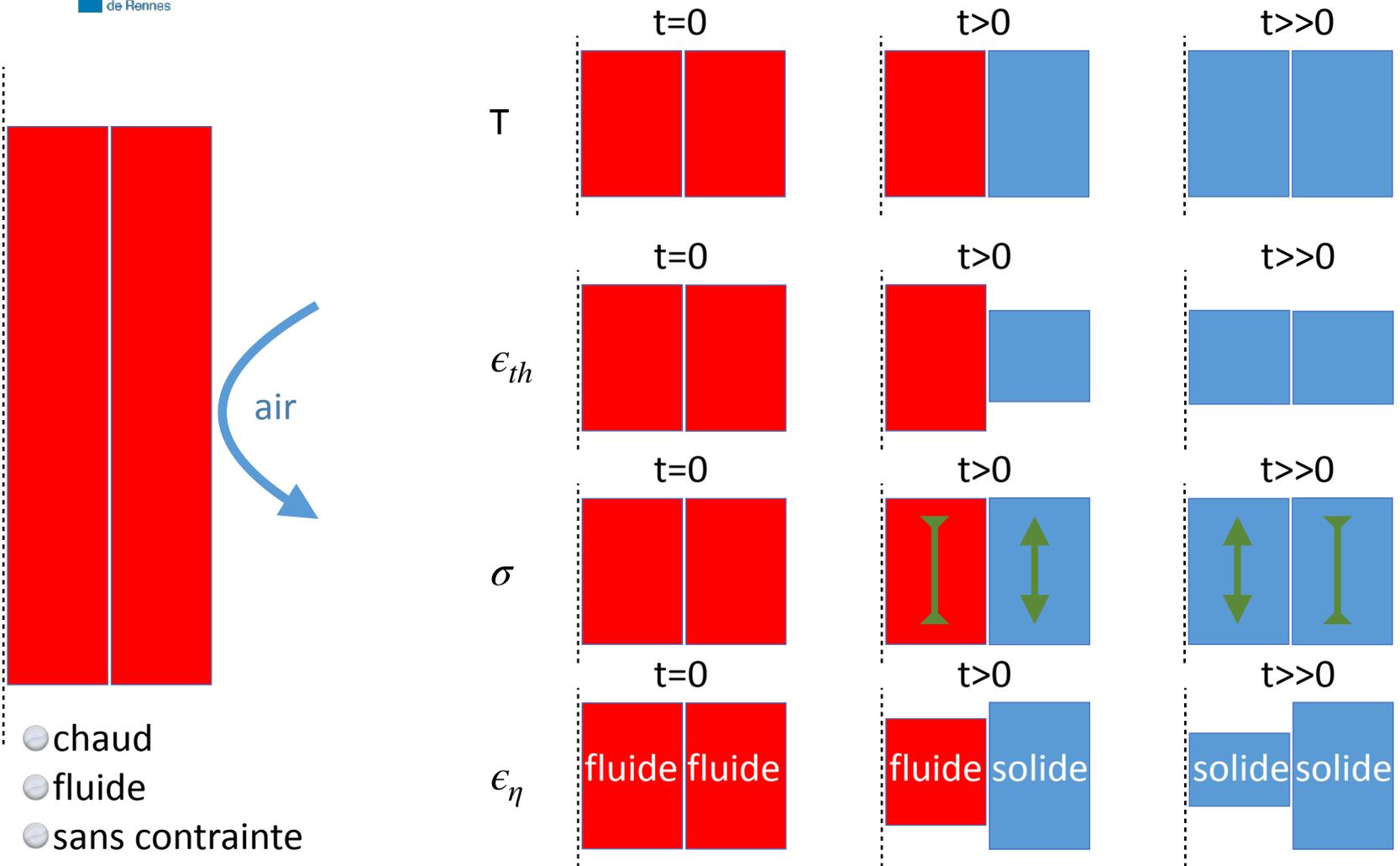


# Trempes thermiques



Modèle simple de la trempe thermique: 2x2 couches



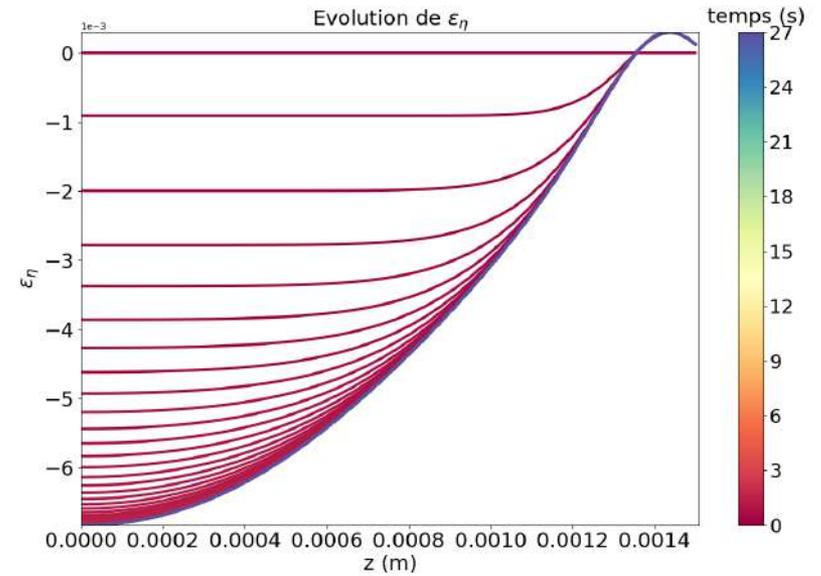
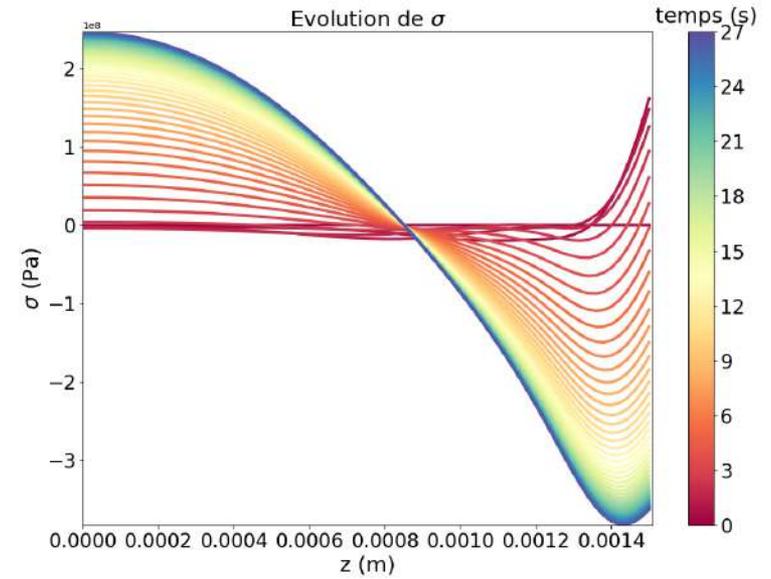
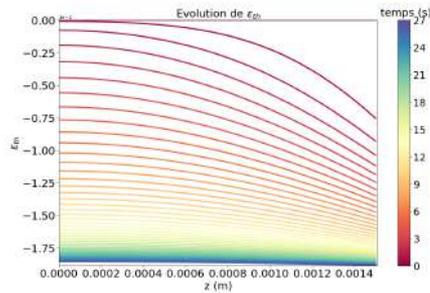
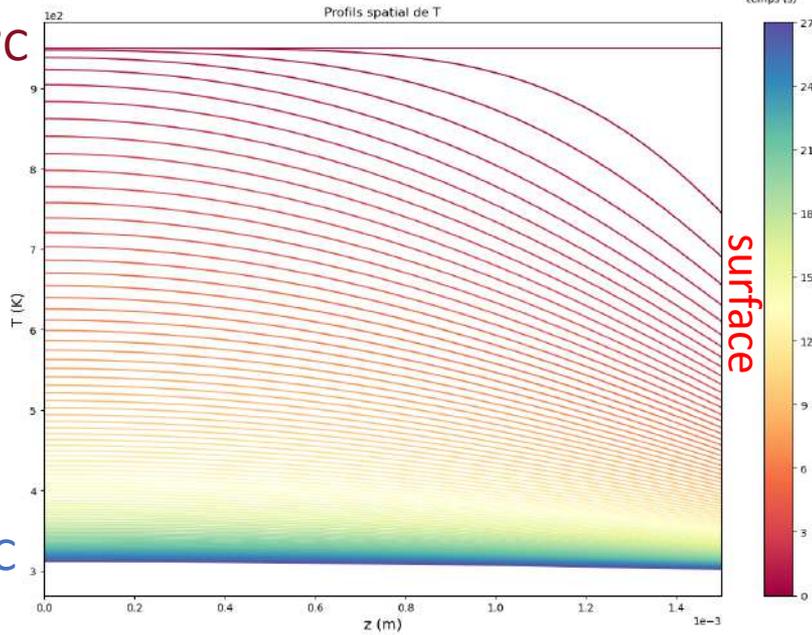


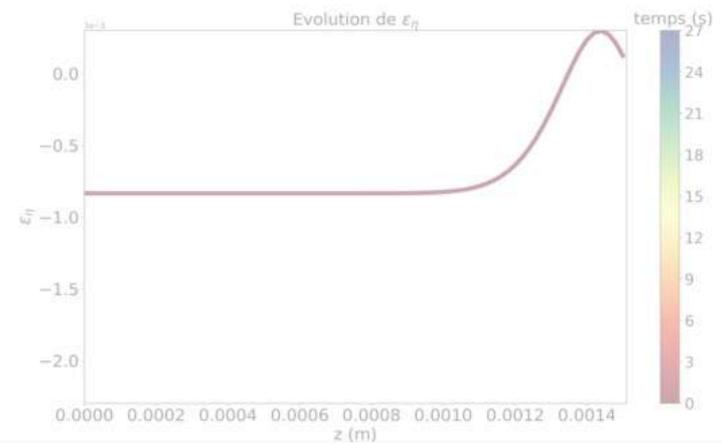
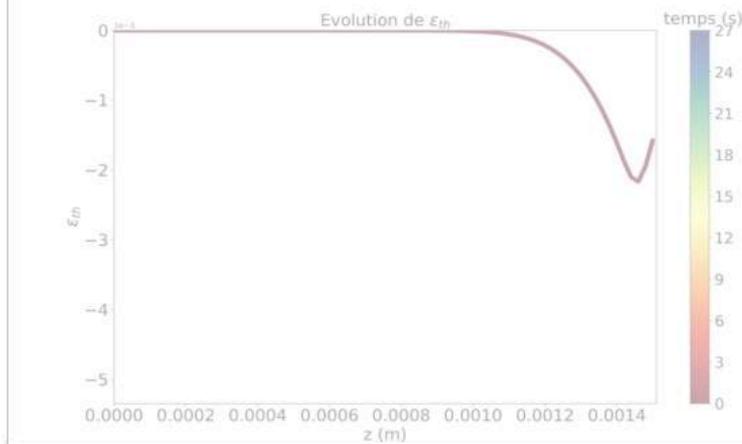
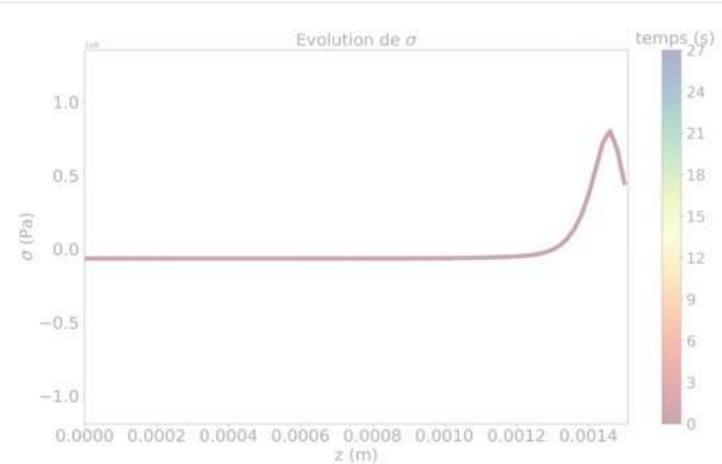
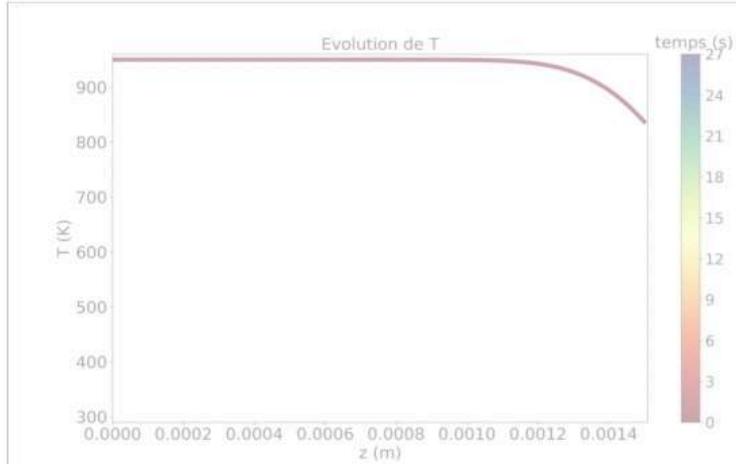
680°C

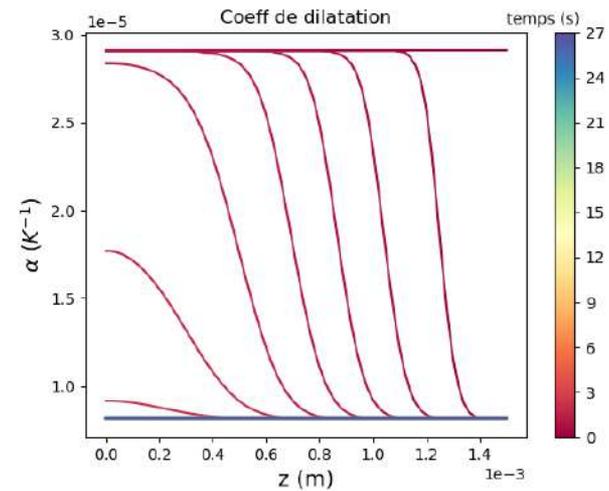
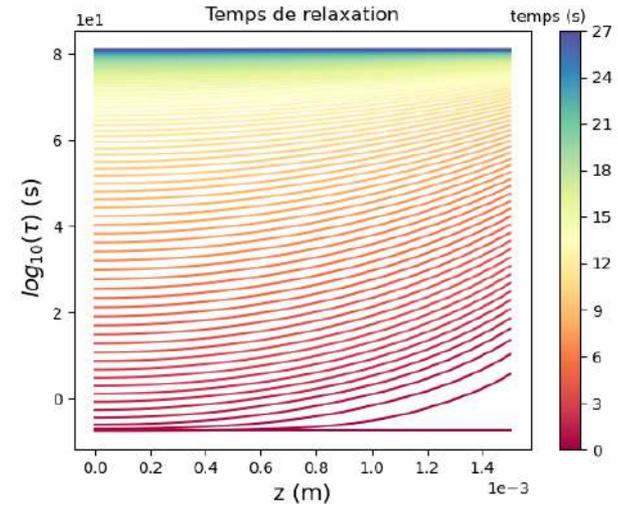
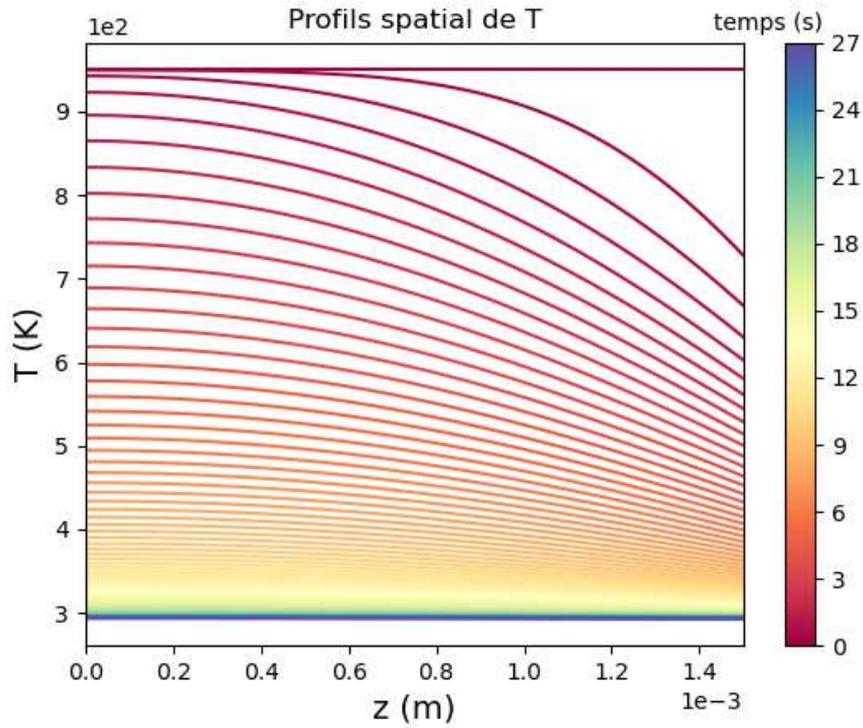
coeur

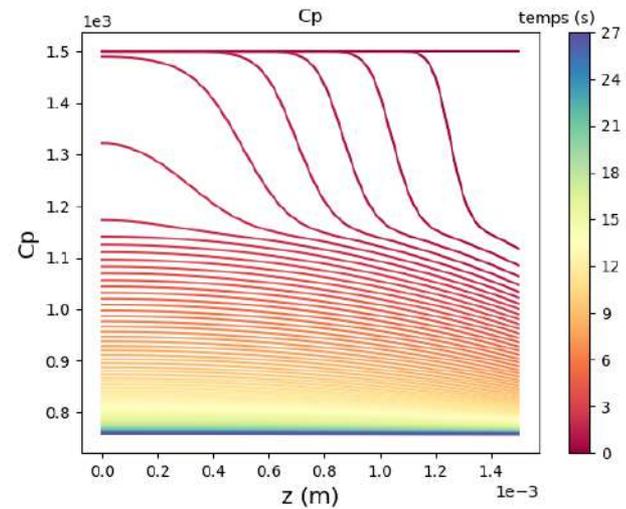
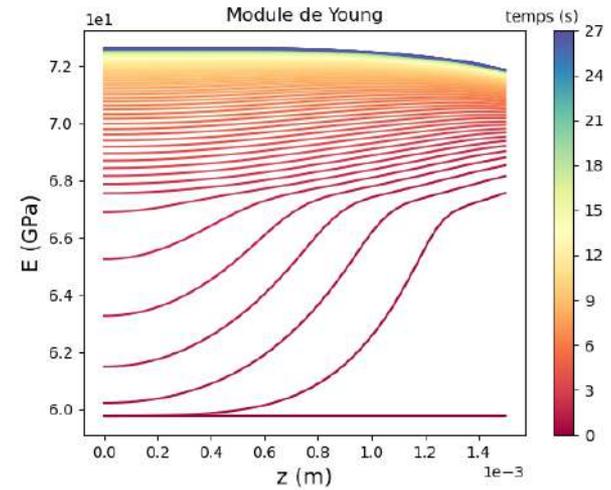
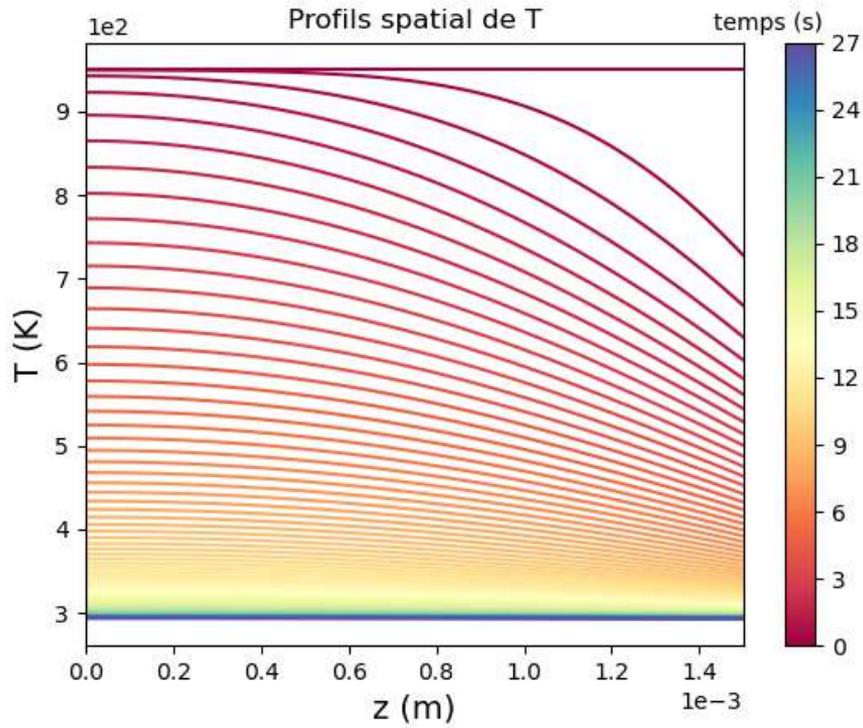
20°C

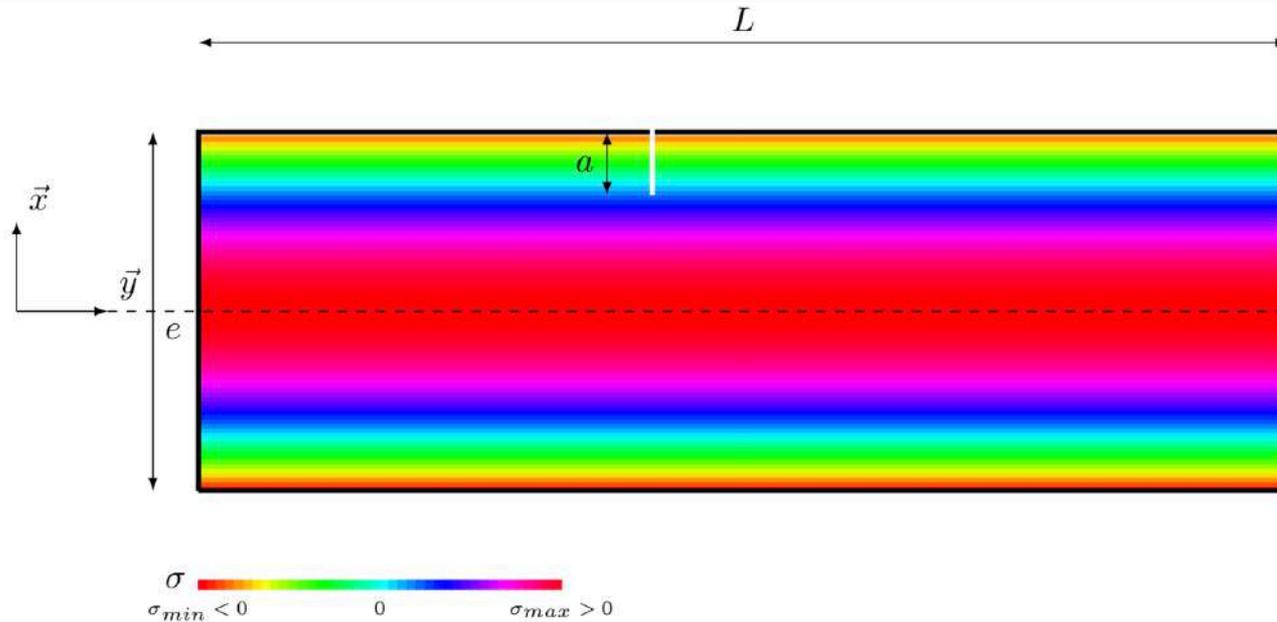
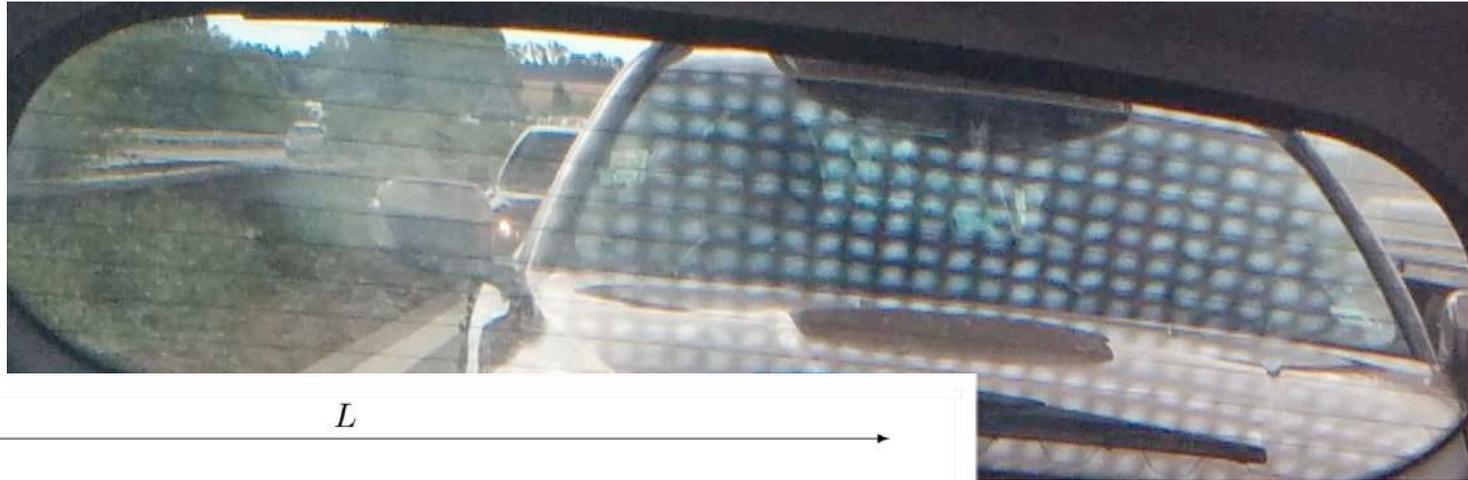
surface











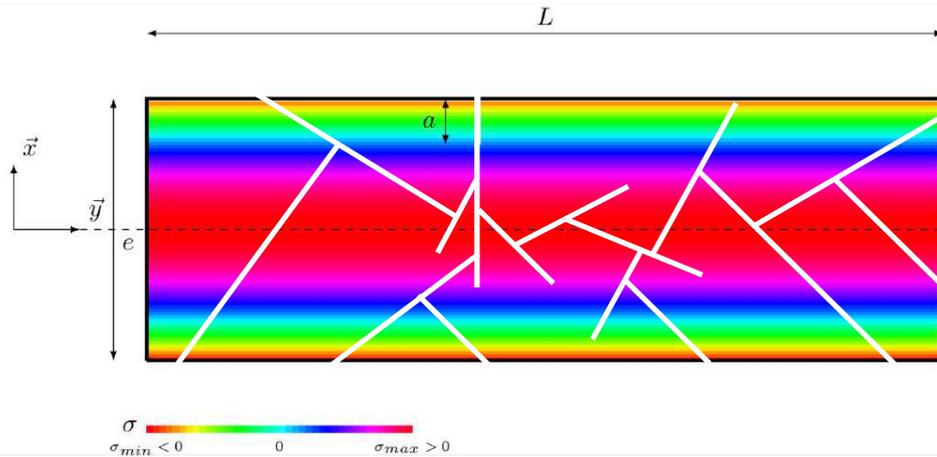
Fissure dans une zone  
de compression:

$$K_{IC} = \sigma_R \sqrt{a} \rightarrow \sigma_R = \frac{K_{IC}}{\sqrt{a}}$$

$$\sigma_R = \frac{K_{IC}}{\sqrt{a}} + \sigma_{th}$$

## Rupture d'un verre trempé thermique

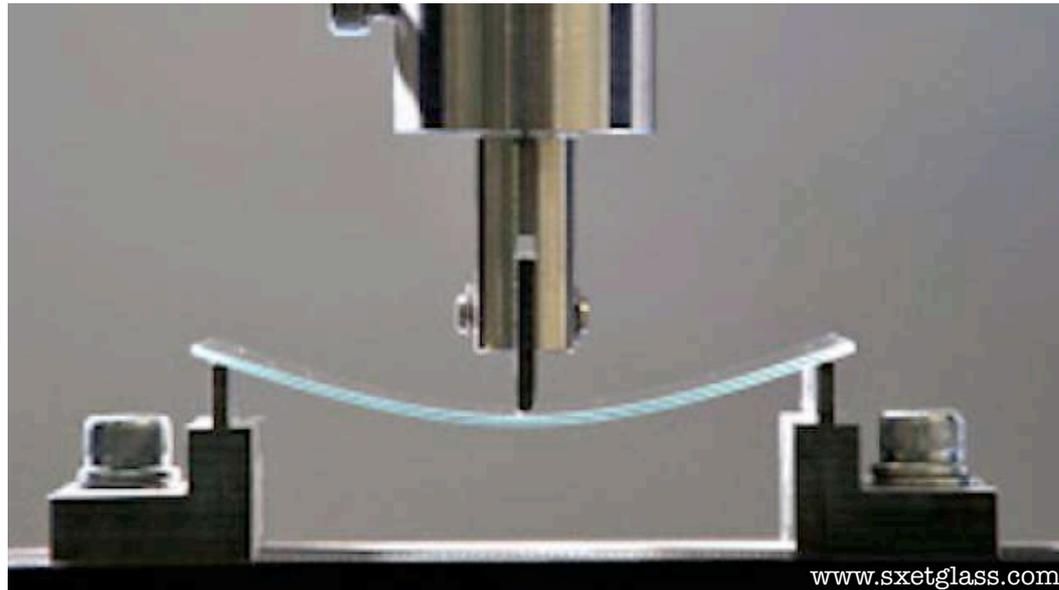
$$\sigma > \sigma_R = \frac{K_{IC}}{\sqrt{a}}$$

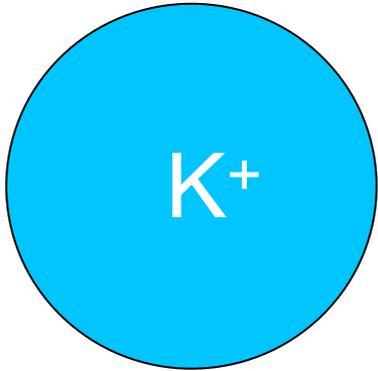
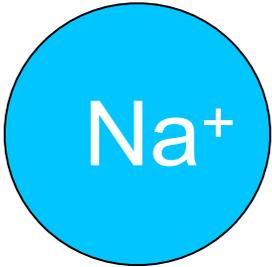


Il y a assez d'énergie mécanique pour casser énormément de liaisons.

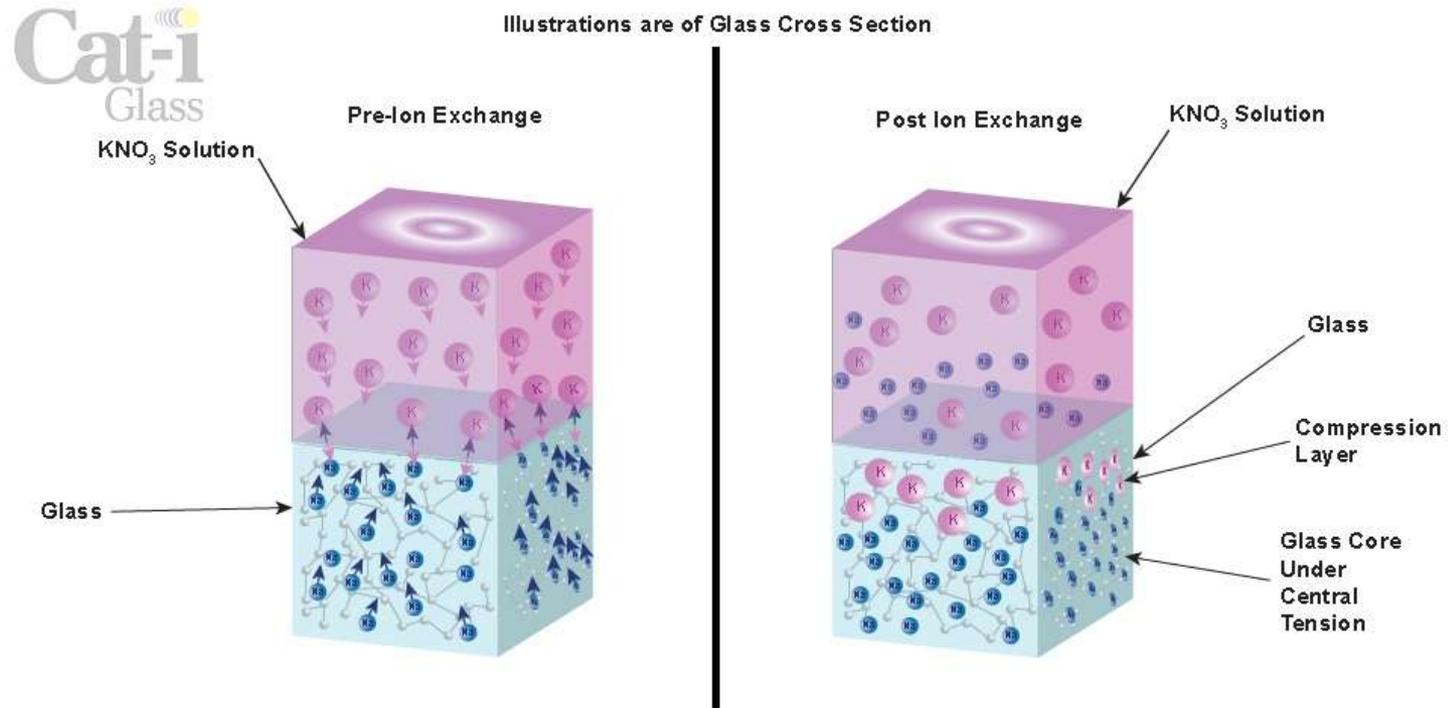
Grand coeff. de dilatation, épais (2mm), après découpe.

# Trempes chimiques

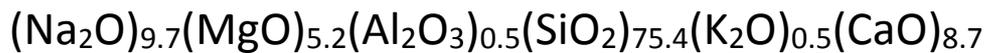




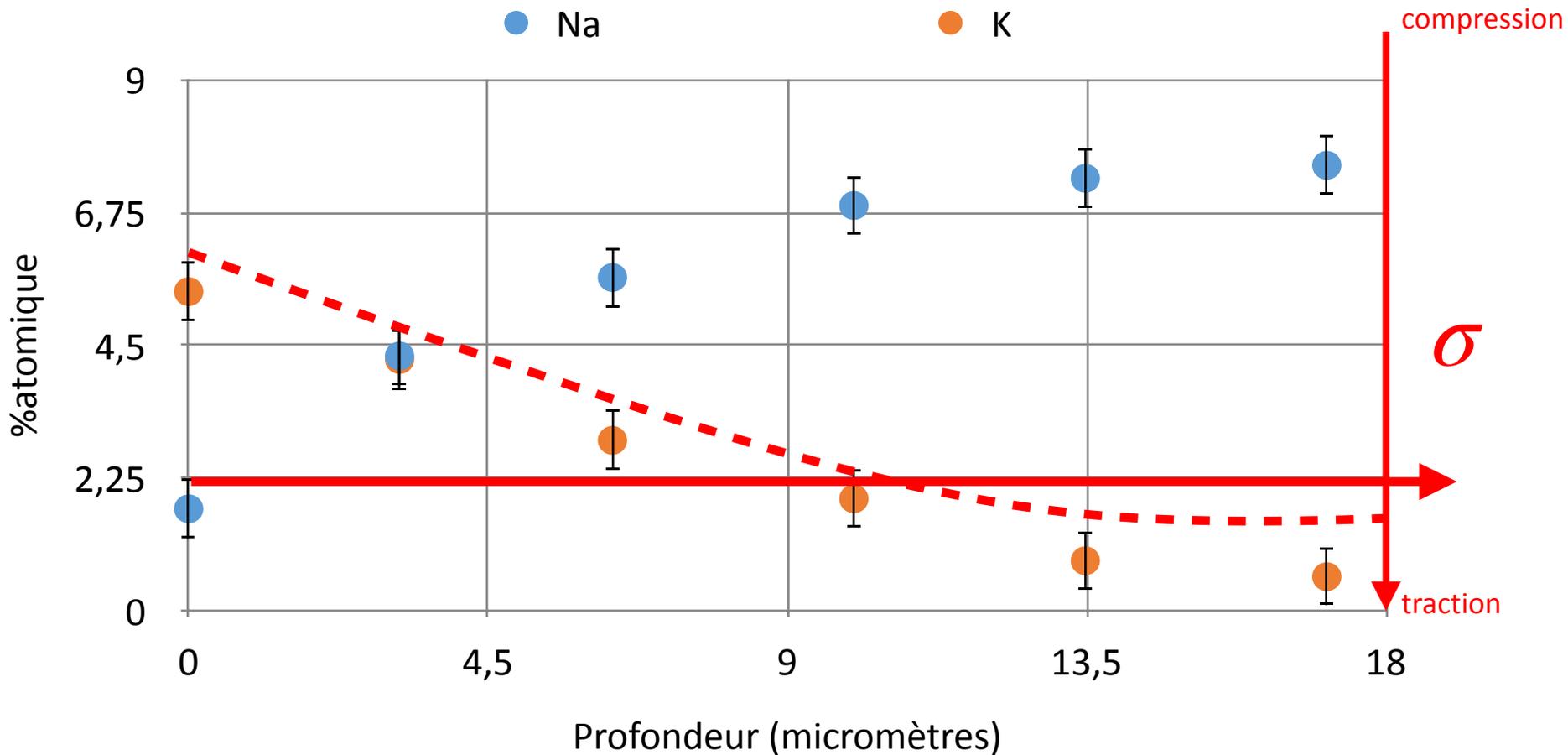
A l'échelle

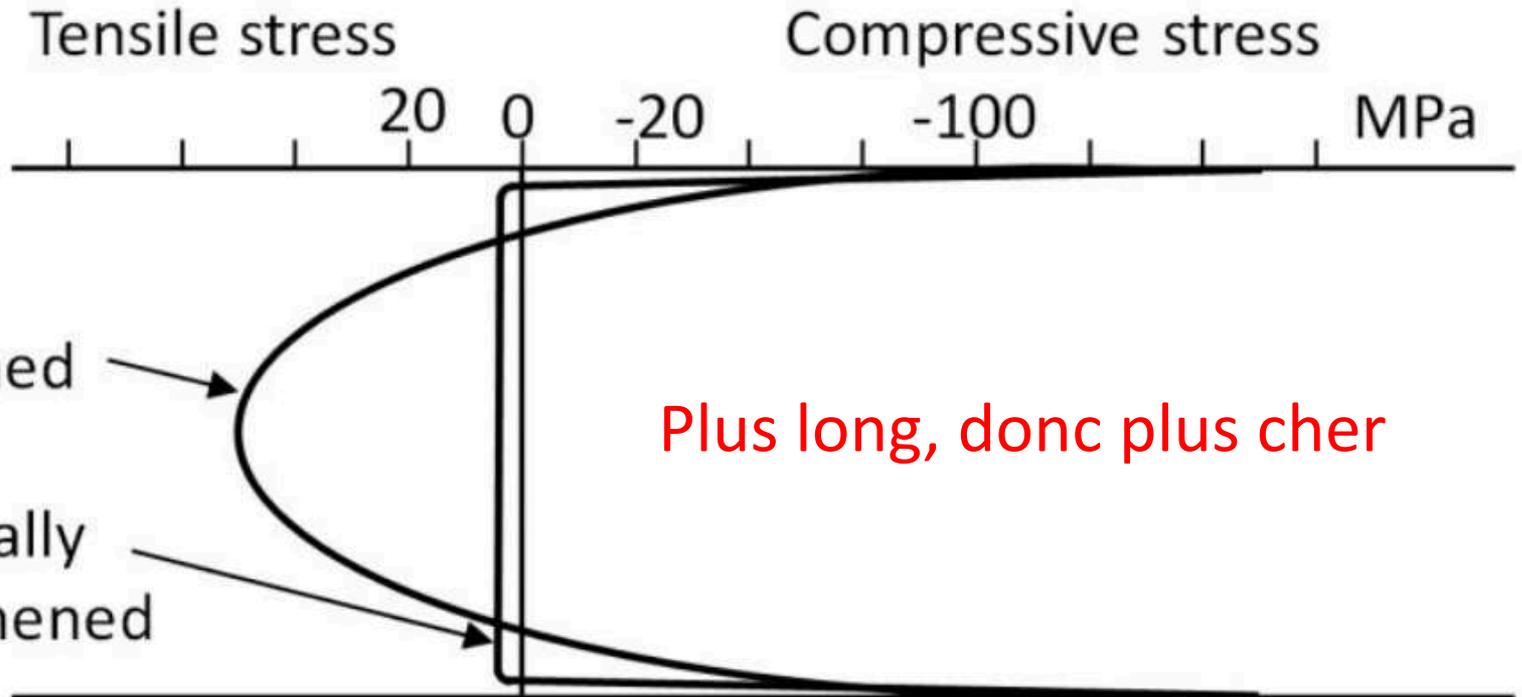


T: assez haute pour favoriser la diffusion  
pas trop haute pour ne pas relaxer la contrainte



T=410°C, 27h

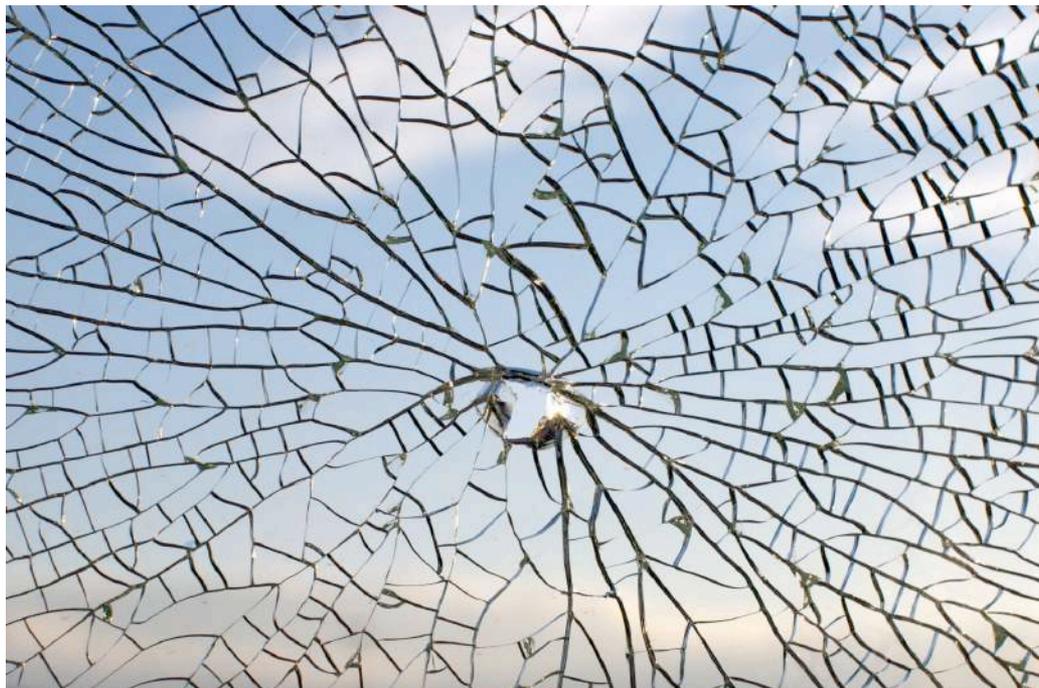




trempe thermique = +50 MPa

trempe chimique = +800 MPa

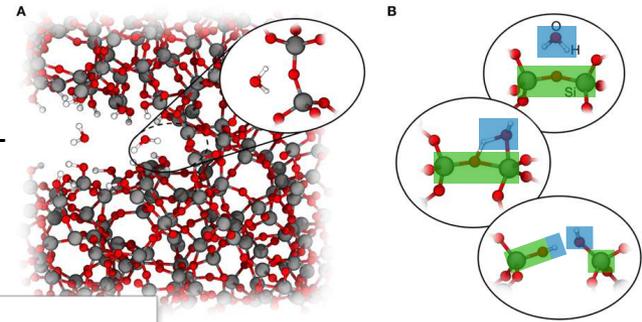
# Explosion spontanée



## Sur un verre non-trempé thermique

Il est mal recuit.

Contrainte résiduelle +



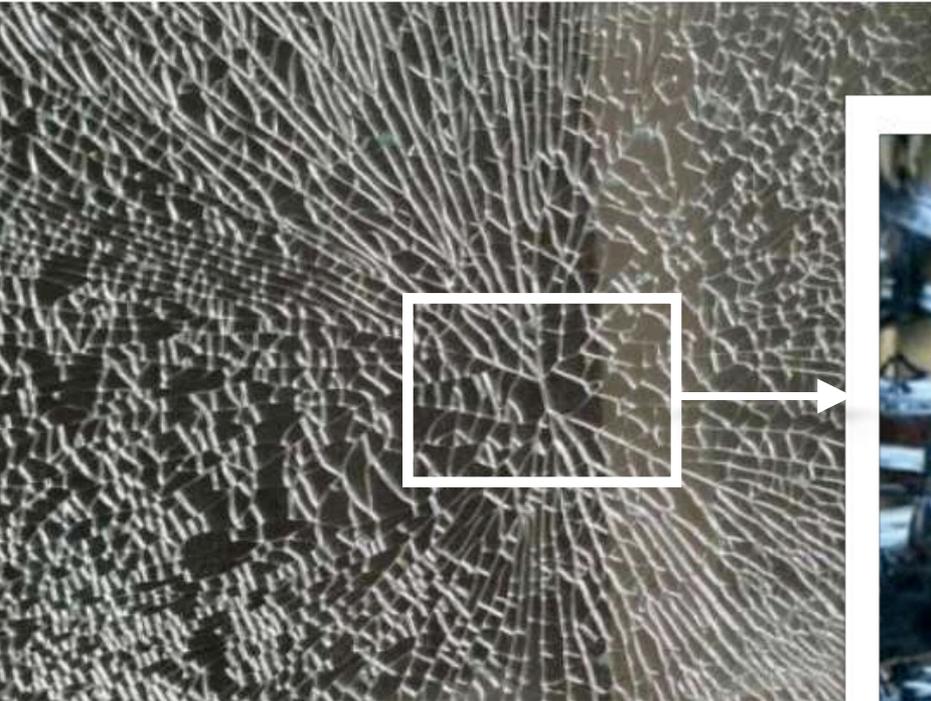
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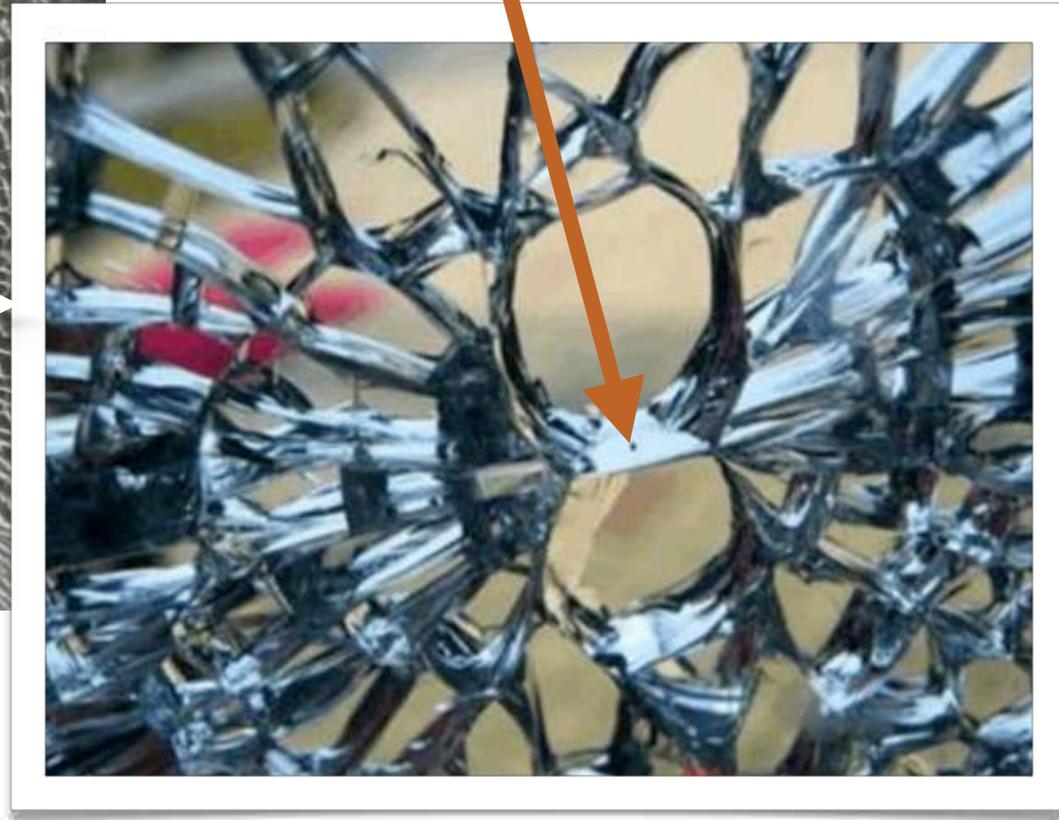
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User:Colin / Wikimedia Commons



NiS



[www.cnmorn.com/](http://www.cnmorn.com/)

Pour un verre trempé thermique

NiS: pollution rare des matières premières (calcite)

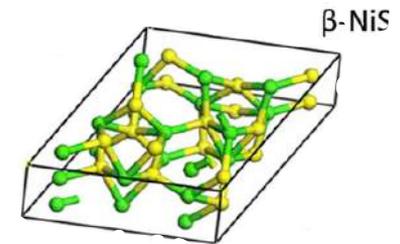
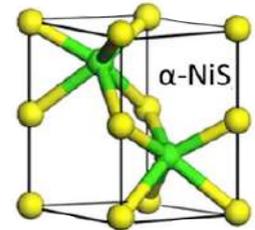
phase  $\beta$  (rhombo) stable jusqu'à 379°C, puis  $\alpha$  (hexa) à T supérieure avec réduction de 3 à 4% de volume

Trempe thermique = chauffe à  $T > 640^\circ\text{C}$  NiS passe en  $\alpha$

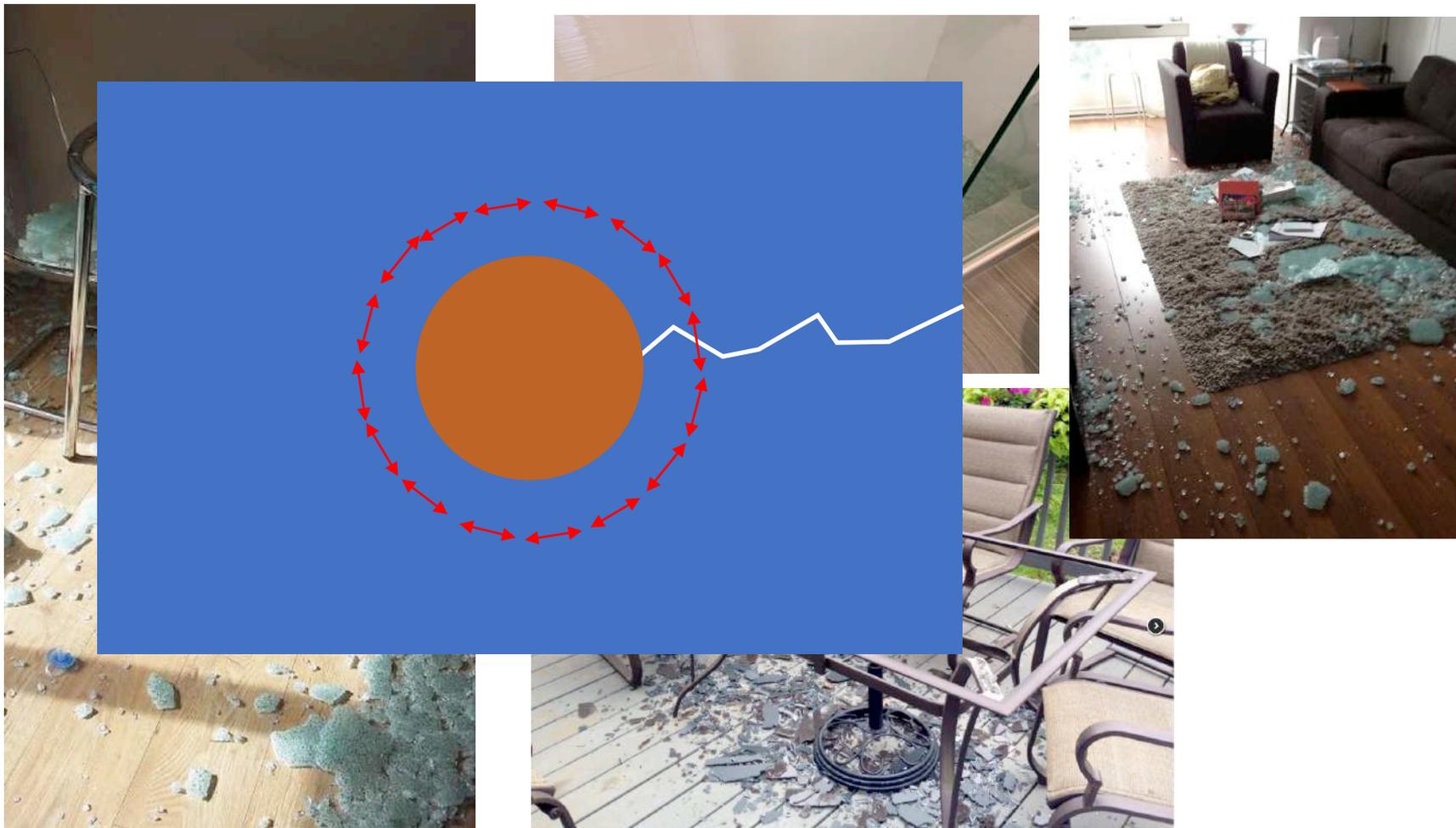
Trempe thermique = puis refroidissement rapide vers  $20^\circ\text{C}$

NiS reste en  $\alpha$ ... pas le temps de passer  $\beta$

NiS passe en  $\beta$  car il est métastable: gain de volume de 3%



3% de déformation dans un verre équivaut à  $>2$  GPa!



# Conclusion

- Module de Young assez moyen (WC:  $E=600 \text{ GPa}$ , Alumine  $>300 \text{ GPa}$ , Acier  $200 \text{ GPa}$ ):  
liaisons iono-covalentes, mais faible compacité
- Fragile: liaisons trop fortes pour permettre la plasticité en traction, mais en contrepartie une dureté élevée.
- Ténacité faible: silice amorphe  $0,8 \text{ MPa}\cdot\sqrt{m}$  - quartz  $1-1,2 \text{ MPa}\cdot\sqrt{m}$  (SiC, WC,  $\text{Al}_2\text{O}_3$ :  $3-5 \text{ MPa}\cdot\sqrt{m}$ , acier:  $10-100 \text{ MPa}\cdot\sqrt{m}$ )... propre aux liaisons iono-covalentes... et sensible à l'environnement
- Sensibles aux choses thermiques... mais viscoélastiques: renforcement par trempe thermique possible.

# LE VERRE

## SCIENCE ET TECHNOLOGIE

James Barton et  
Claude Guillemet