

Instantané de la mécanique des verres : plasticité - fissuration

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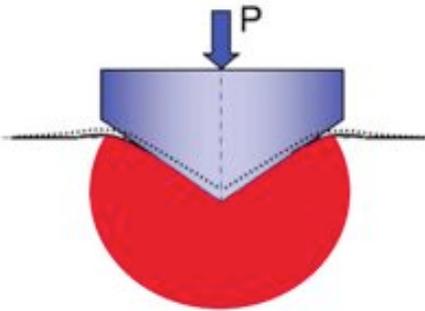
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<http://ipr.univ-rennes1.fr/>

Journées Plénières UST-GDR Verres

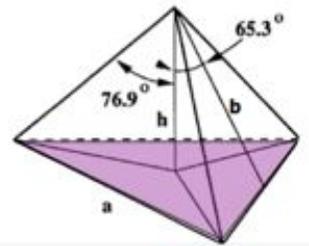
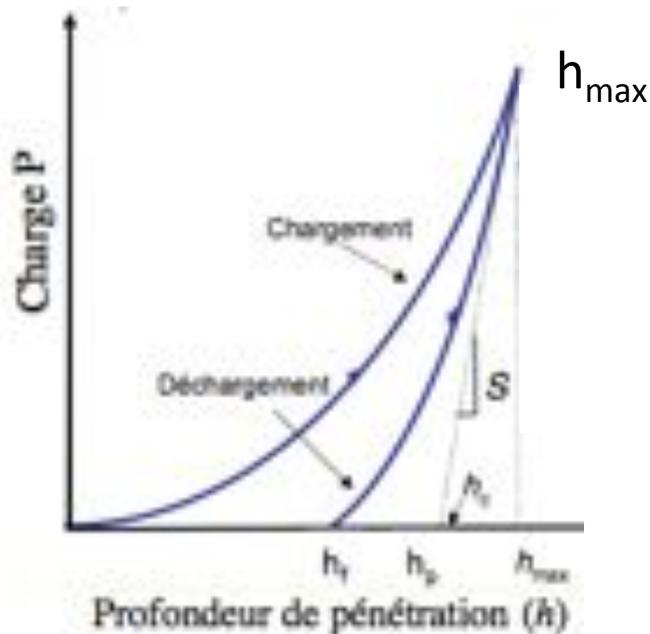
Dureté (H): Résistance qu'offre un matériau à la déformation plastique de sa surface par pénétration.



$$H = \frac{P}{A_c}$$

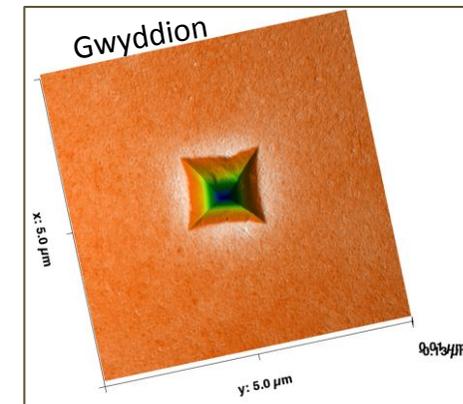
Charge appliquée (poids mort ou indentation instrumentée)

Aire de contact (mesure des dimensions ou indentation instrumentée (h_{max}))

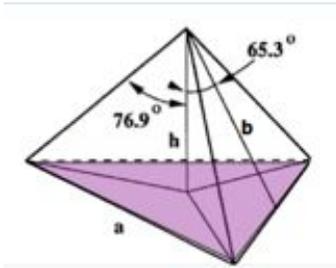


Berkovich
 $A_c = 24.56 h^2$
Vickers
 $A_c = 24.504 h^2$

Empreinte résiduelle



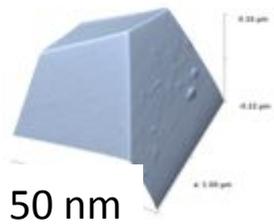
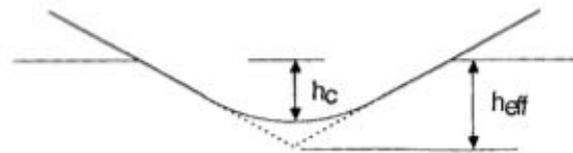
Empreinte résiduelle → plasticité



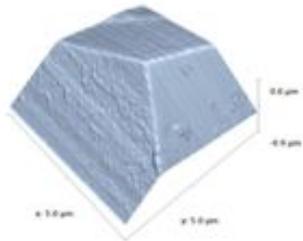
Tout le problème de H est dans la bonne estimation de A_c !

- Indenteur parfait?
- Comportement du matériau : bourrelets ou pas?

Réalité différente



50 nm

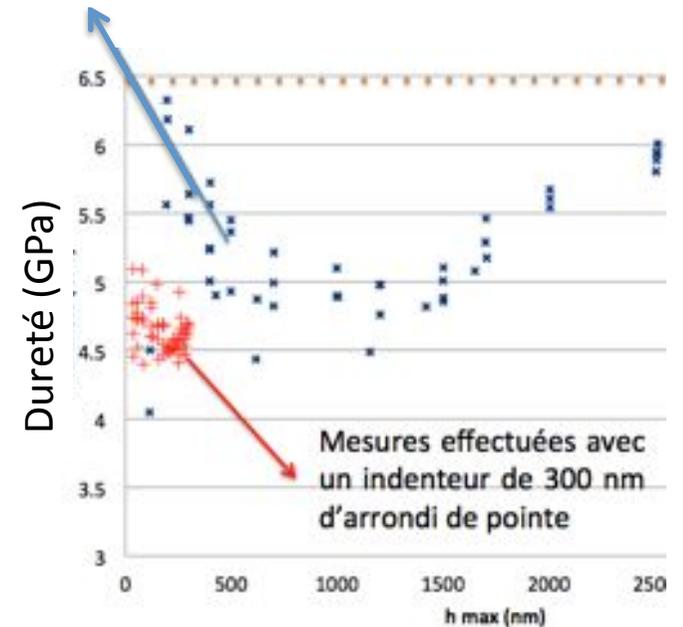


300 nm

Forme arrondie de la pointe = il manque un bout de l'indenteur

Indentation aux faibles charges \neq indentation pyramidale

Effet de l'arrondi de pointe ($r \approx 1.5 \mu\text{m}$)



Ténacité: Résistance qu'offre un matériau à la propagation d'une fissure.
 Pour un matériau élastique fragile : $K_{IC}=(2\gamma E)^{1/2}$



Contrainte à rupture: contrainte seuil pour laquelle la structure se casse de manière soudaine. Valeur extrêmement dépendante de l'état de surface (notion de maillon le plus faible).
 Pour le verre on caractérise avant tout le processus de fabrication des surfaces.

Loi de comportement: permet de définir le lien entre des grandeurs cinématiques (tenseur des déformation) et les grandeurs dynamiques (tenseur des contraintes).

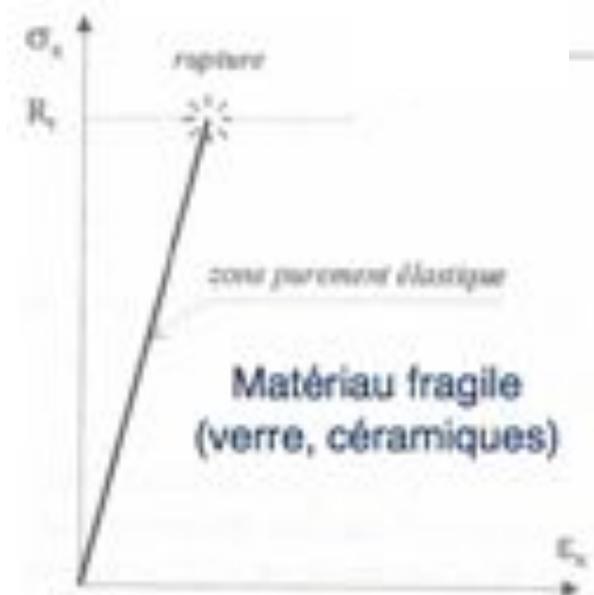
- Cas le plus simple: en élasticité c'est la loi de Hooke (18^{ème} siècle).
- Plasticité, viscosité

Pour le matériau verre

Essai de traction

Comportement élastique linéaire fragile

➔ Pas d'information sur la plasticité



Pour le verre: la seule information sera une loi de comportement élastique (Young et Poisson) et la caractérisation indirect du processus de préparation des surfaces de votre échantillon (contrainte à rupture)

Plasticité dans les verres ➔ essai de compression

Contrainte à rupture: théorique estimée de 35 GPa.

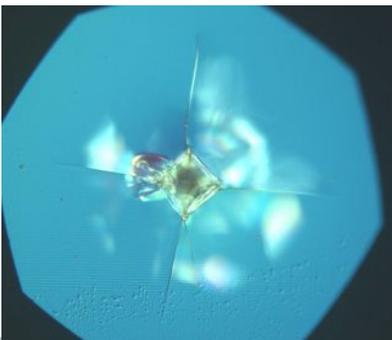
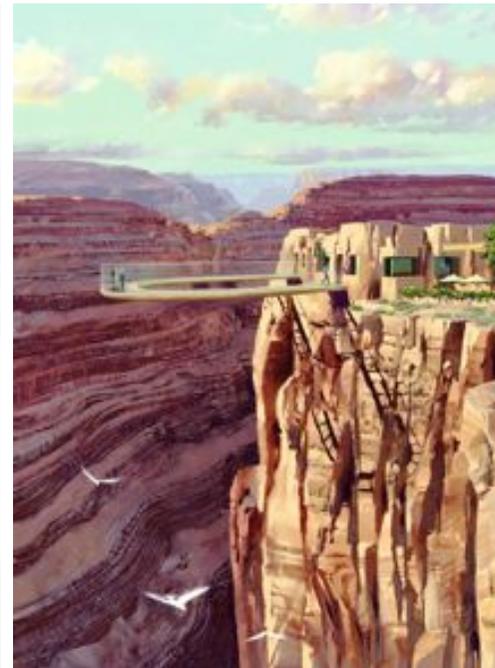
Valeur mesurée la plus élevée: 14 GPa fibre de silice à la température de N2

Valeurs mesurées pour des massifs : qq 10 de MPa.

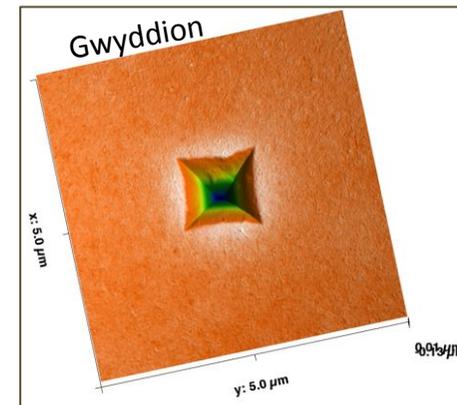
Pb1: Sensibilité à l'endommagement de surface;

Pb2 : Faible ténacité 0,1 to 1 MPa.m^{1/2}. Une fois le défaut créé (nano micro fissure), la tenue en service de l'objet est sérieusement compromise.

Pb3 : Interaction avec l'environnement, phénomène de croissance sous critique de la fissure



Plasticité dans les verres Peter (1970),
Yamane et McKenzie (1974)



contribution de 3 facteurs :

L'écoulement par cisaillement : déplacement de matière à iso volume;

La densification: déformation permanente ne conservant pas le volume;

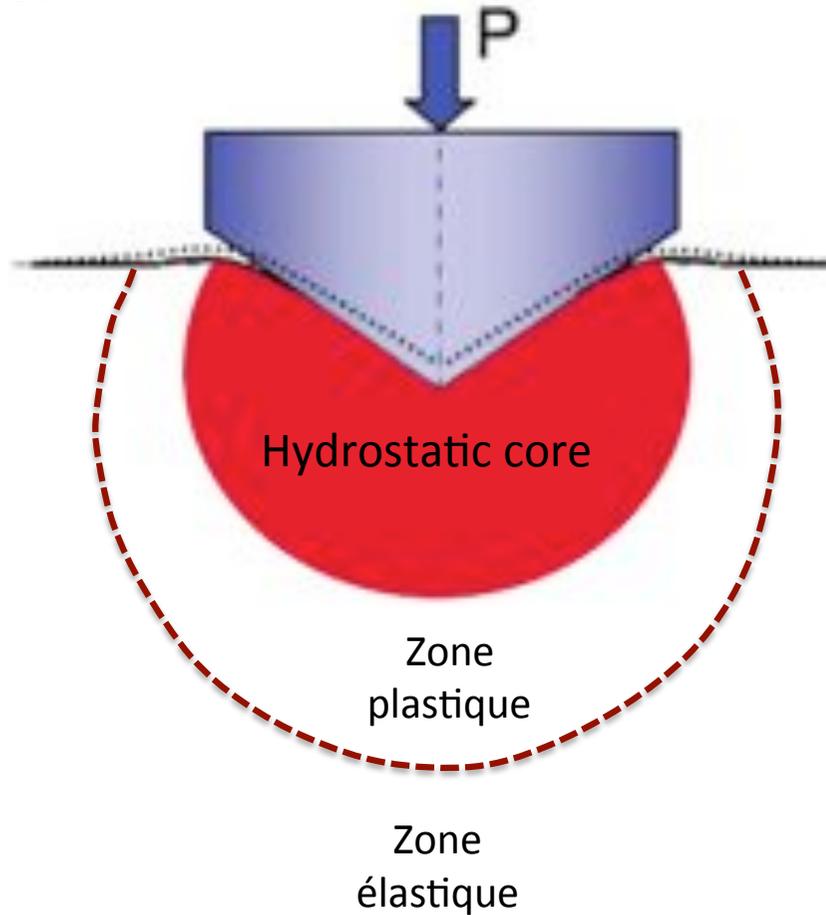
L'élasticité: déplacement de matière réversible dont une partie peut rester bloquée.

K.W. Peter, Densification and flow phenomena of glass in indentation experiments, JNCS, 5, (2), 1970, 103-11

Yamane, M., & Mackenzie, J. D. (1974) Vicker's Hardness of glass, JNCS 15 (2), 153-164.

Que cherchons nous?

Modèle d'expansion de cavité sphérique de Johnson (1970)



- Taille et forme de la zone plastique (densifiée)
- Paysage (tau de densification, gradients locaux?)
- Changement structuraux associés: (hydrostatique, cisaillement, couplages)



Modèle permettant de décrire le comportement mécanique des verres



Accès au champ de contrainte
=> Seuil de fissuration, Propagation

M. Matta et al.
(2006), IJSS, 43, 20,
5994

Approches développées par la communauté pour étudier la plasticité des verres et comprendre l'endommagement sous contact

Loi de comportement

Modélisations numériques:

MD Lyon, Marcoule
 MED Bordeaux
 MEF St Etienne, Lorient, Annecy

Chargement mécanique simple

Essais hydrostatique

Enclume diamant

Lyon, Clermont Ferrand,...

Compatibilité
 Échelles d'espace et de temps

Recalage / à l'expérimentation

Modifications structurales

Microscopies Raman – Brillouin

Variation de module élastique

→ Cartographie de densification permanente

Sonde chimique de la plasticité

Paris, Montpellier, Lyon, Rennes

Chargement mécanique complexe:

Hydrostatique + cisaillement

Indentation, rayage

Paris, Montpellier, Rennes

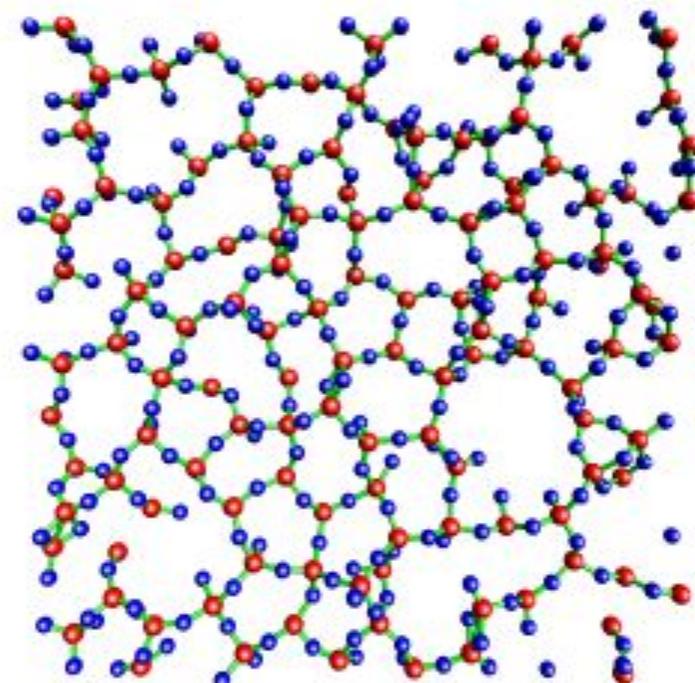
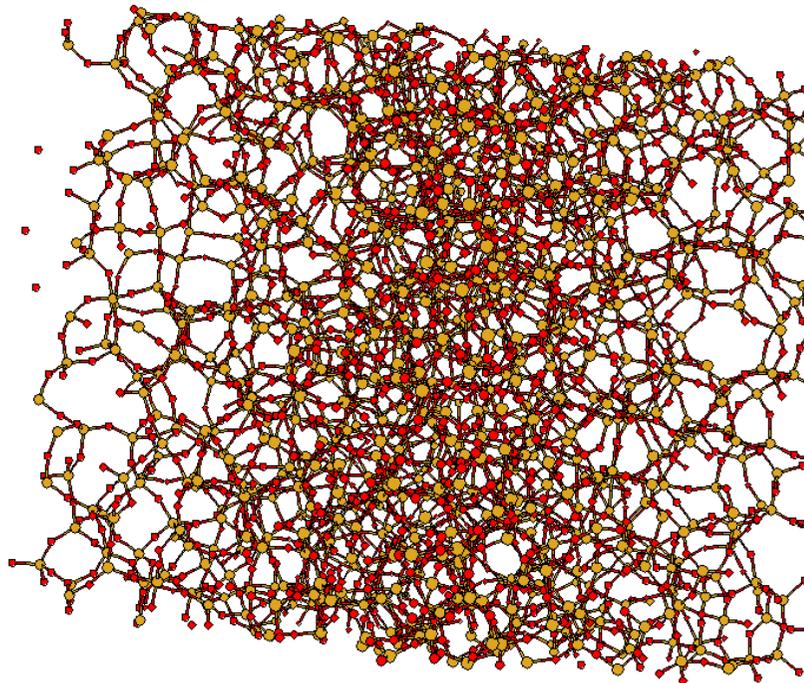
Ingénierie du chargement mécanique

Micro piliers

Paris

Atomic structure of glass : silica

No dislocations, no LRO but MRO and SRO, a lot of free volume 30 %



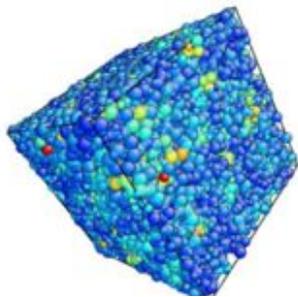
Amorphous silica (SiO₂)

University of Florida: Quantum Theory Project

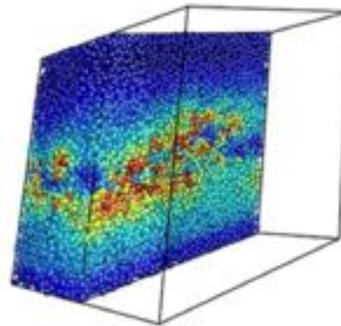


Origine structurelle de la déformation plastique :

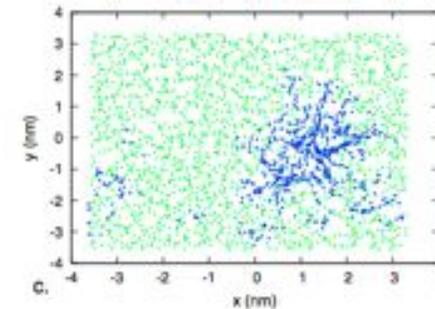
- **Propose des mécanismes physiques possibles de déformation**
Forte localisation des évènements plastiques (réorganisation locale de la matière)
Redistribution locale des contraintes
- **Possibilité de varier à volonté les conditions de chargement (P, S, P+S)**
- Difficile à vérifier expérimentalement ... quoique Raman?
- Comparaison quantitative avec l'expérimentation : pb échelle de temps, d'espace



compression



cisaillement



Intensité des déplacements non affine (écart à un comportement homogène)

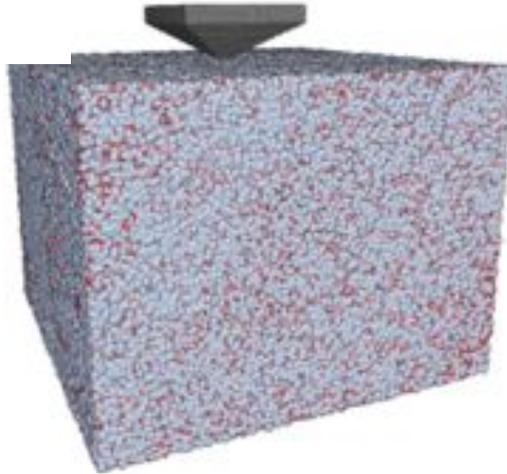
C. Fusco et al. P. Rev. E (2010), 82, 066116

B. Mantisi et al. E. Phys. J. B., (2012), 85, 304



Tend vers les EF

Essais d'indentation:



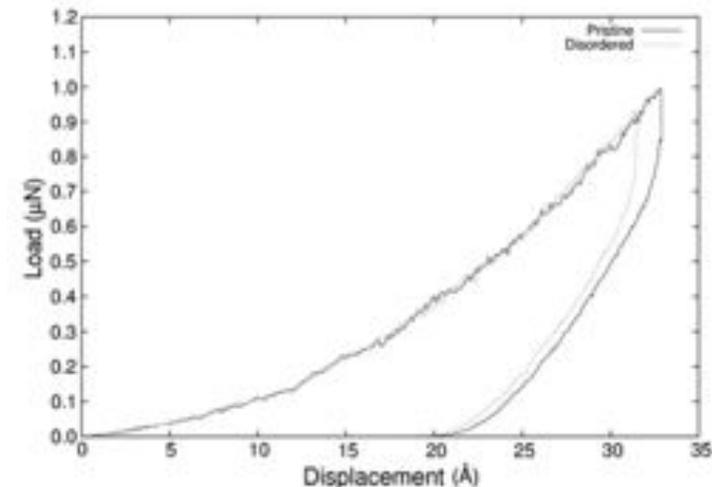
Indentation Vickers/ SiO₂

Zone plastique sous chargement max



8 nm

Courbe d'indentation



Vis à vis de l'expérience réelle?
Échelle d'espace (ok) si dans régime de similarité géométrique de l'indentation et loin d'un **V.E.R.**

Echelle de temps: 850 ps v.s. 20 s !?!

D.A. Kilymis, J.M. Delaye, JNCS (2013), 382, 87

Densification under high level of hydrostatic pressure (up to 30 GPa)

(1953) P. W. Bridgman and I. Simon, J. Appl. Phys.,
existence of a threshold below which no permanent densification is observed

(1963) J. D. Mackenzie, J. Am. Ceram. Soc. 46

Effect of temperature effect of shear on densification, curing of densification(initial volume recovery by TT.

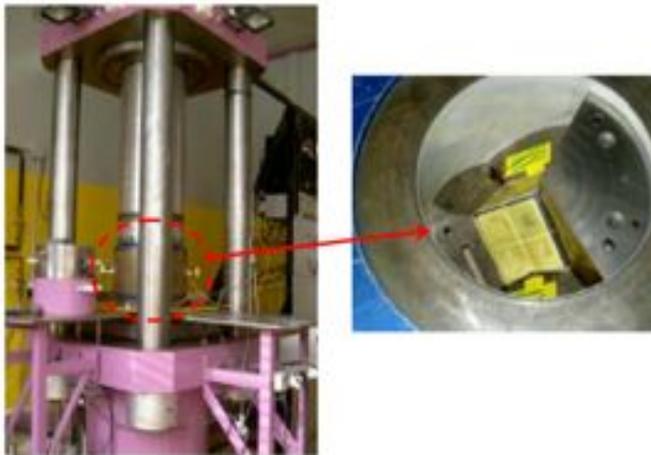
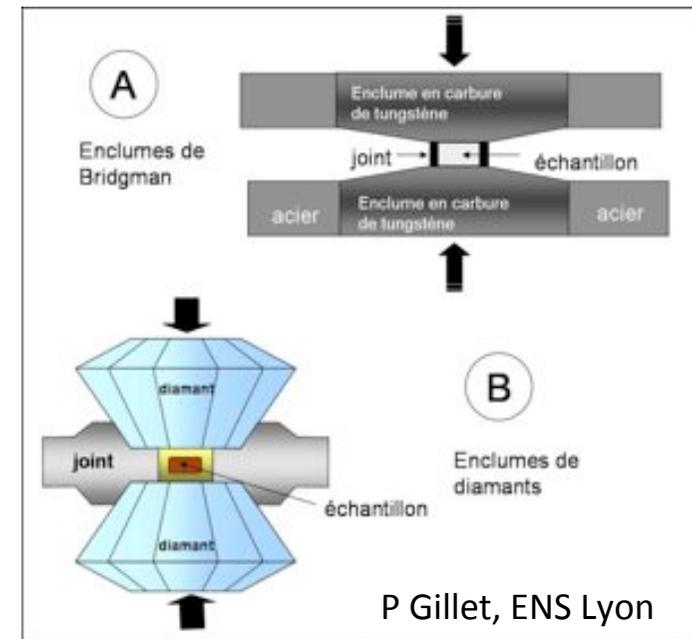
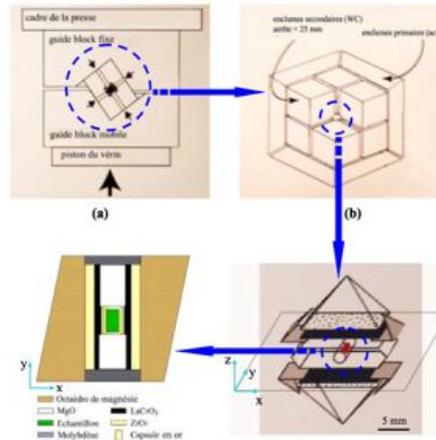


Figure II. 1 : Le vérin 1000 tonnes de la presse multi-enclumes.



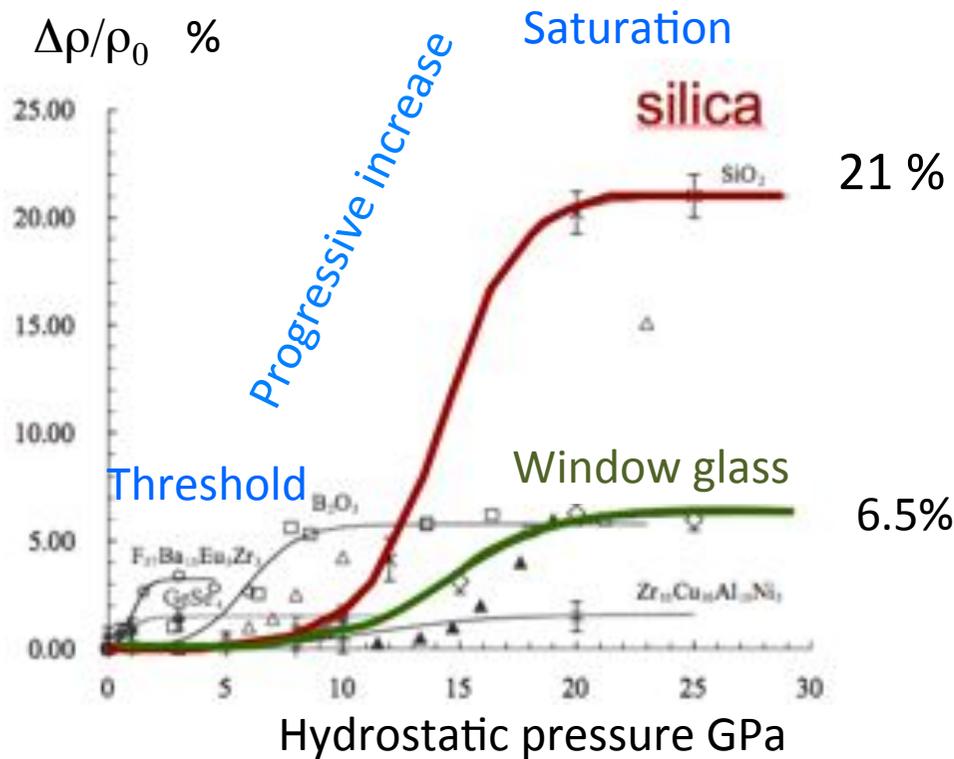
Multi anvil system, octahedral mounting

Hui Ji PhD thesis

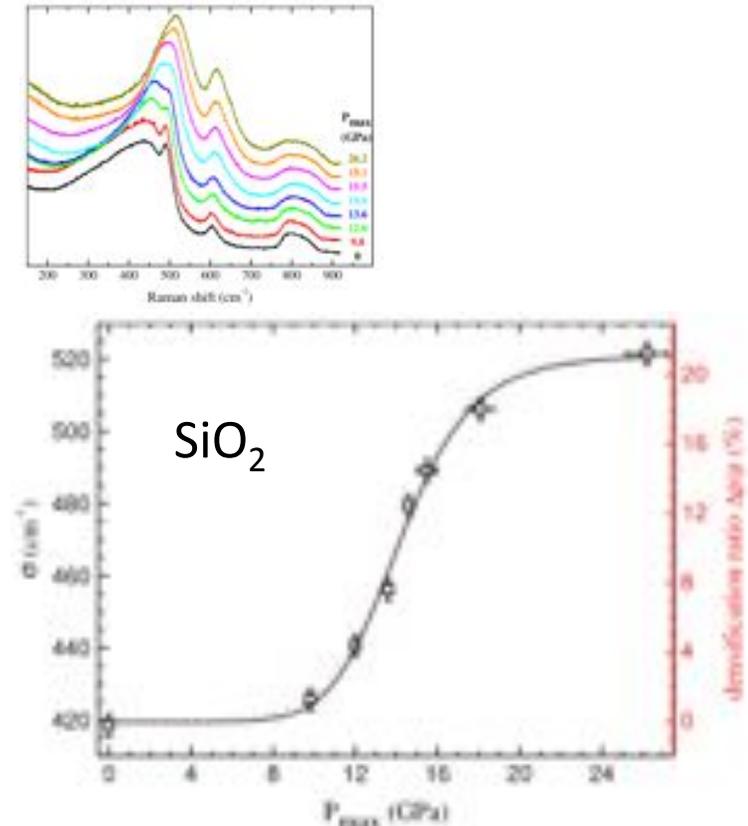
Rouzel Advanced Materials Research Vols. 39-40 (2008)

Cellule à enclume diamant

(1953) P. W. Bridgman and I. Simon, J. Appl. Phys.,
 existence of a threshold below which no permanent densification is observed
 (1963) J. D. Mackenzie, J. Am. Ceram. Soc. 46

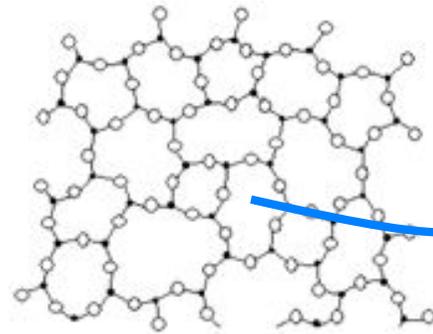


Rouxel et al. Phys. Rev. Let. (2008)



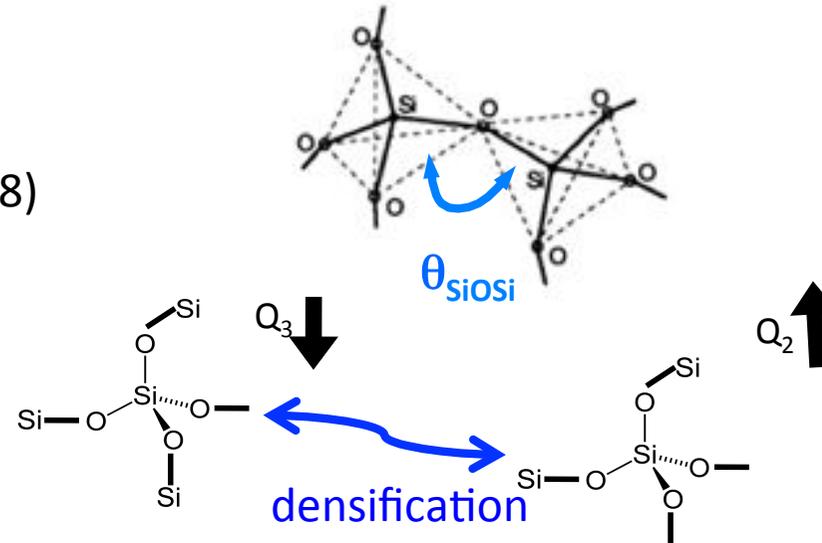
T. Deschamps et al., J. Phys: Cond. Matter, 25 (2013), 25402.

Raman spectroscopy



n-folded rings (2-8)

Zachariasen (1932)



Silica: [Hehlen 2010] Decrease of the SiOSi inter tetrahedral mean bond angle

But all the n-folded rings (2-8) are not equally affected, the smaller the lesser $\Delta\theta_{\text{SiOSi}}$ (3 and 4 folded are weakly affected by densification : $-0,5^\circ$)

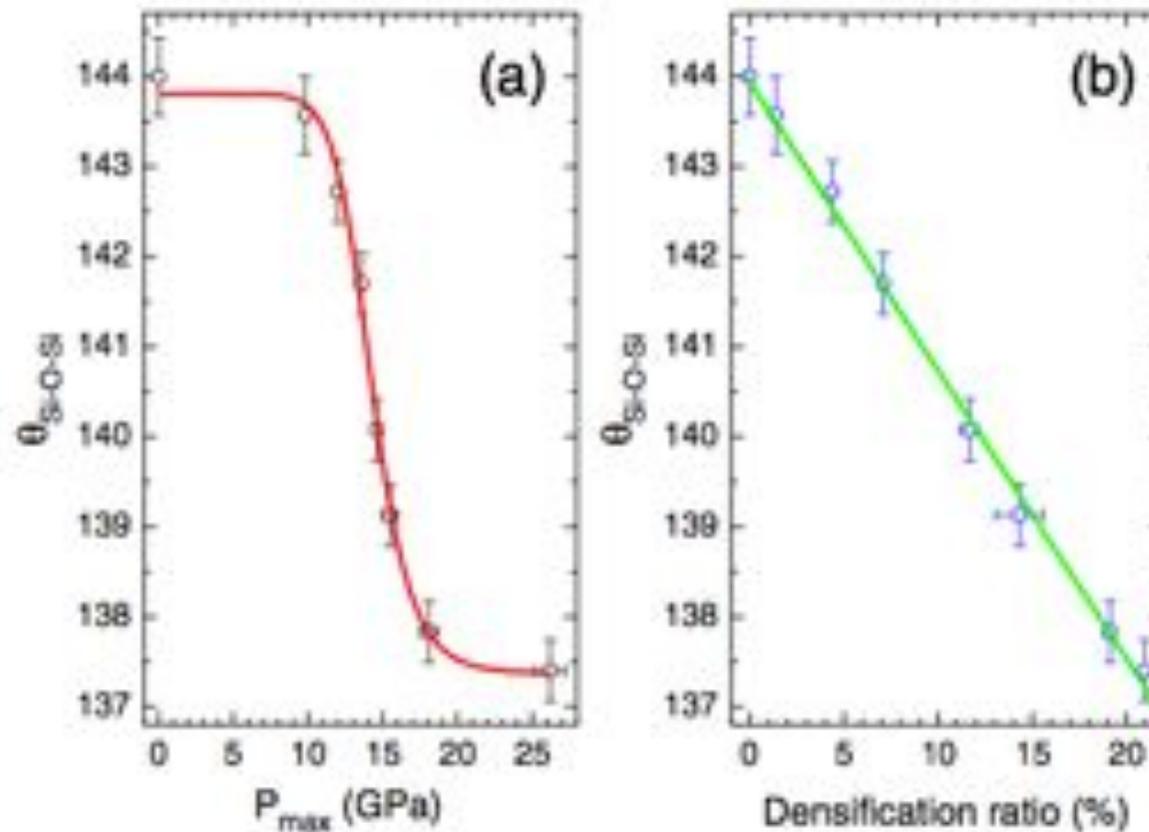
Change of mean angle value is progressively increasing with the level of densification. $\Delta\theta_{\text{SiOSi}} = -5.7^\circ$ at saturation.

Window glass: [Deschamps 2011] : Decrease of the SiOSi mean bond angle

And loss of connectivity $Q_3 \rightarrow Q_2$

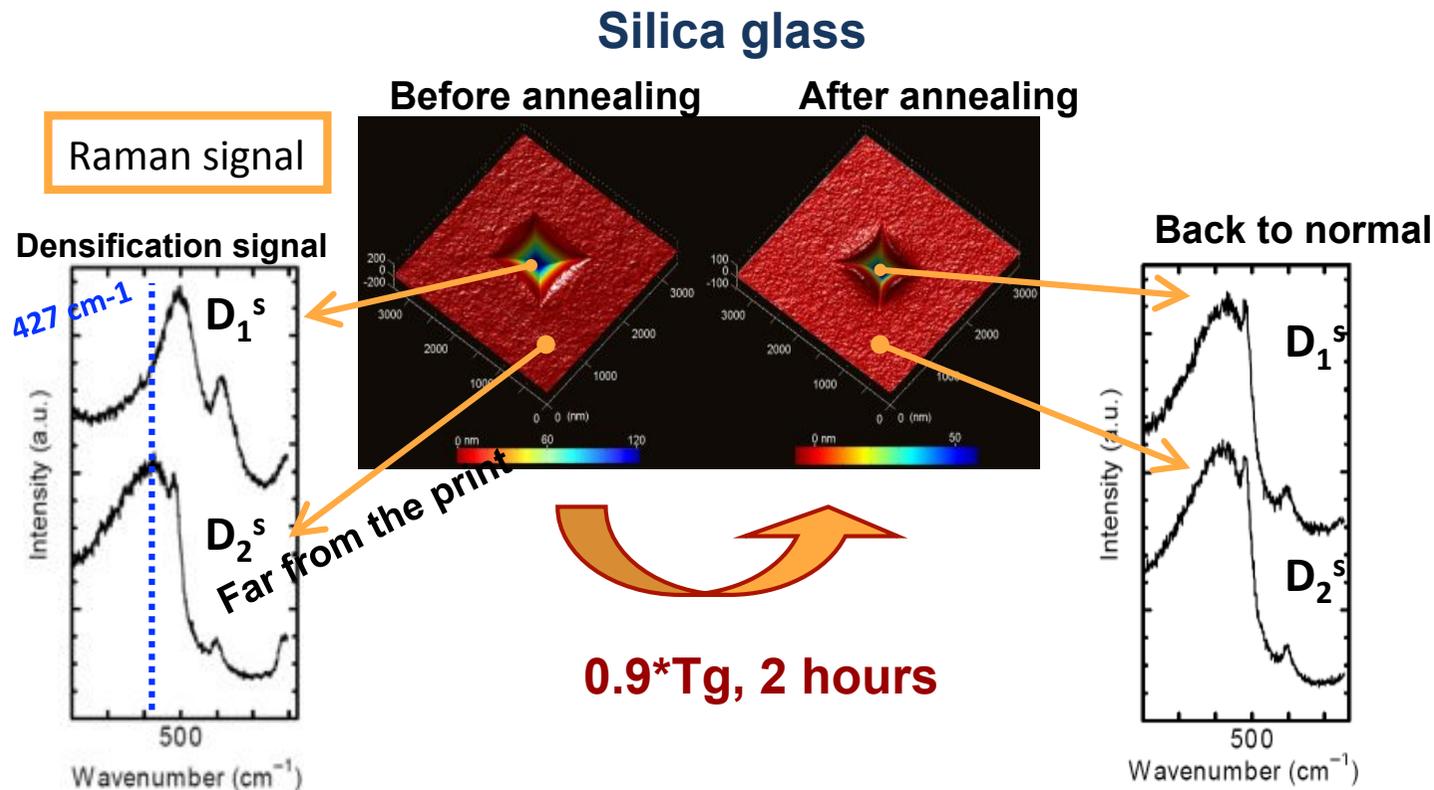
Possible clustering of mobile ions (Na^+) (MD simulation)

- Spectroscopie Raman: globalement, variation progressive des changements structuraux avec le niveau de pression hydrostatique.
- Forte corrélation entre SiOSi et le tau de densification



C. Sonnevile, T. Deschamps, C. Martinet, D. de Ligny, A. Mermet, and B. Champagnon, Polyamorphic transitions in silica glass, Journal of Non-Crystalline Solids, (2013)

- Densified glass has a Raman signature
- Densification may be cured!! by a proper thermal treatment ($0.9 \cdot T_g$ (K), 2 hours) [Mackenzie(1963), Neely & Mackenzie (1968), Yoshida (2001, 2005, 2007)]



Confocal Raman Spectroscopy as a 3D probe for mapping the zone affected by densification at indentation site

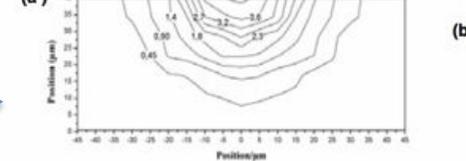
[Raman study: Satoshi Y., GOMD 2009, Vancouver on 1 N indentations, AFM pictures: Niu Y-F, Guin J-P LARMAUR]



Vickers indentation on window glass,
20 N



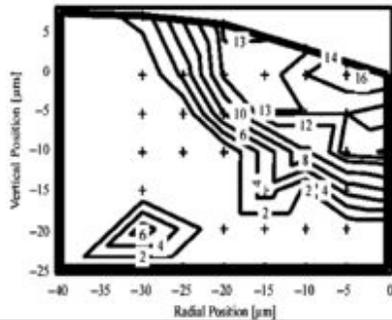
[A. Kassir-Bodon (2012)]



$$\Delta\rho/\rho_0 \%$$

Permanent densification ratio mapping

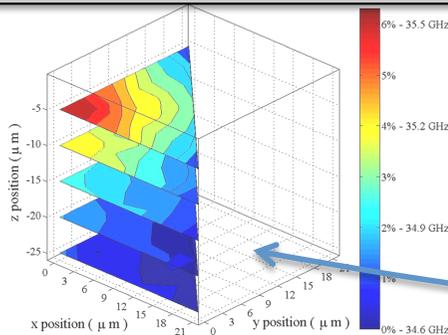
Micro Raman spectroscopy



Silica glass, Vickers indentation, 20 N.

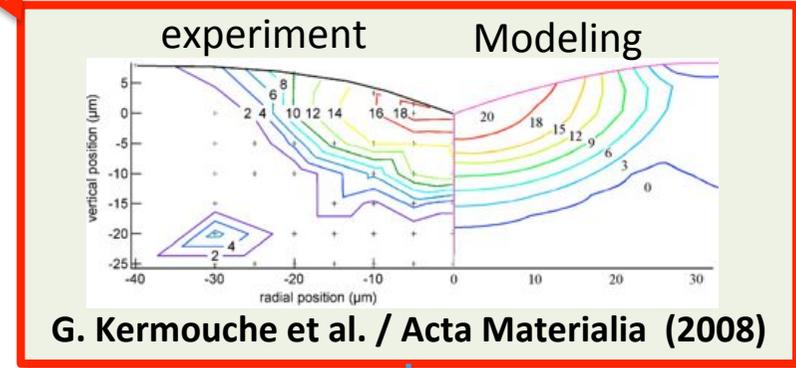
[Perriot (2006)]

Micro Brillouin spectroscopy



Window glass, Vickers Indentation, 20 N

[B. Rufflé et al. (2012)]



G. Kermouche et al. / Acta Materialia (2008)

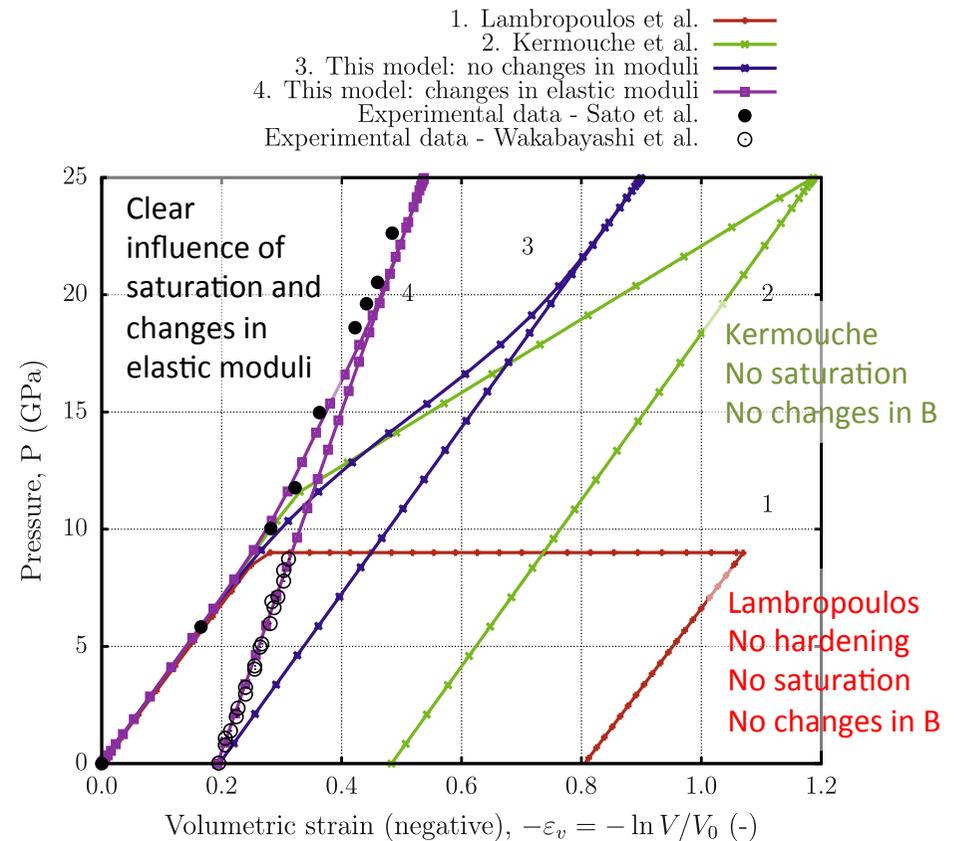
Loi de comportement !

PROBLEM : spatial resolution of those spectroscopies is about 1 μm → a large densified zone must be obtained thus high indentation loads must be used → plasticity plus damage. ATTENTION!

Constitutive law : modeling of a simple hydrostatic loading silica glass

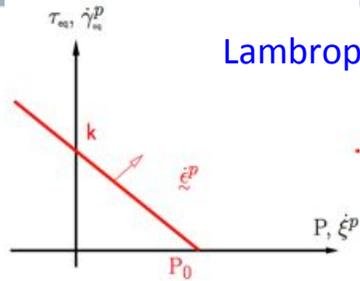
2 constitutive laws have been proposed in the literature : Lambropoulos, Kermouche. None of them describes properly a hydrostatic compression test! (l'essai le plus simple).

Sato et al., Phys Rev Lett 2008;
Wakabayashi et al., Phys Rev B (2011);
Lambropoulos et al. J Amer Ceram Soc 1997;
Kermouche et al. Acta Mater 2008;



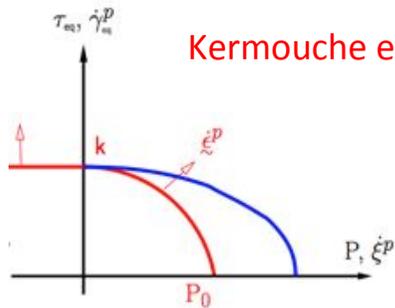
Keryvin et Al. Acta Mat 62 (2014) 250-257

First constitutive law describing appropriately a pure hydrostatic testing of SiO₂ : 2014 !!!



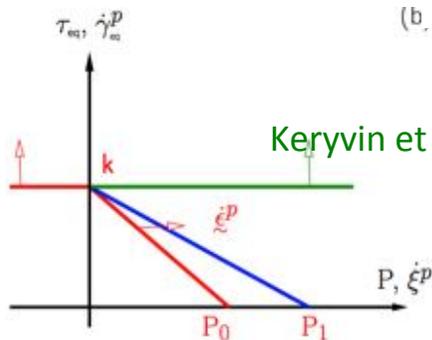
Lambropoulos et al. J Am. Ceram Soc (1997)

Modèle associé,
critère de plasticité linéaire
Pas de saturation



Kermouche et al. Acta Mater. (2004).

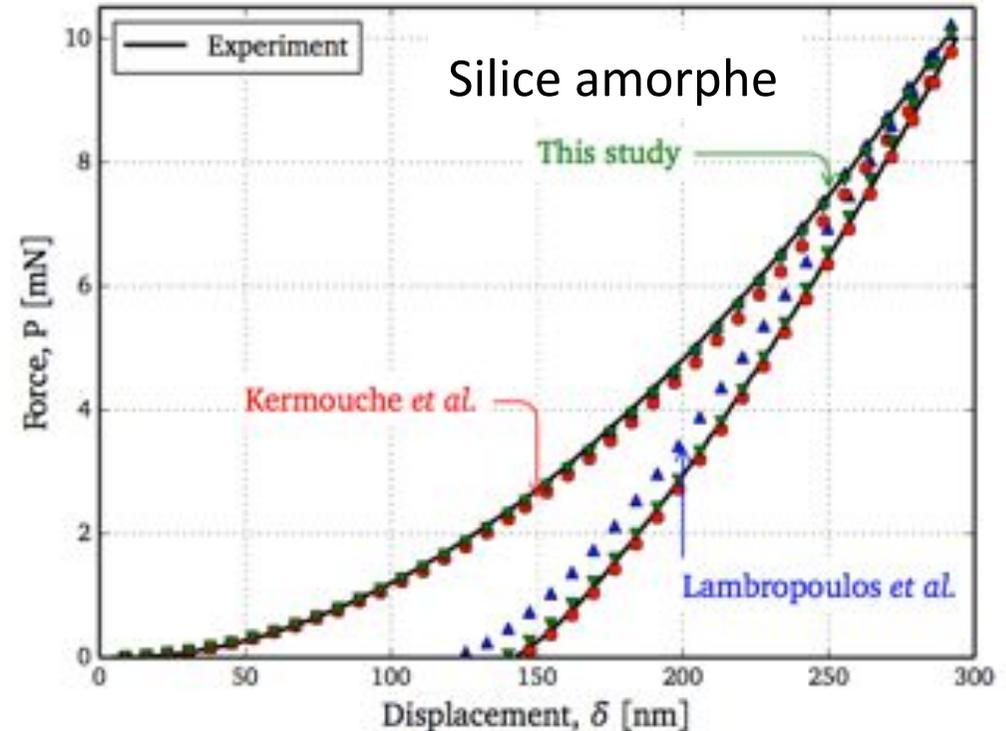
Modèle associé,
Critère de plasticité elliptique
avec un accroissement de la
limite élastique avec le tau de
densification. Pas de
saturation.



Keryvin et al. Acta Mat. (2014) modifiée,

Modèle séquentiel à
écoulement plastique non
associé

Il nous reste la courbe d'indentation!



Indentation Berkovich, 10 mN

PROBLEM : 3 really different constitutive laws are able to fit almost perfectly a 10 mN experimental Berkovich indentation curve. Load-displacement curve is not discriminatory!

Est on coincé?

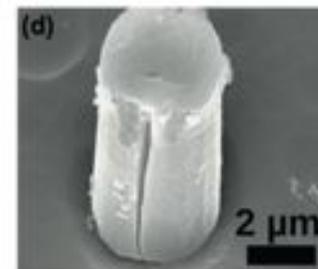
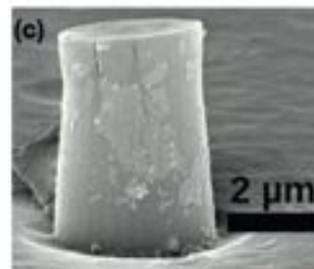
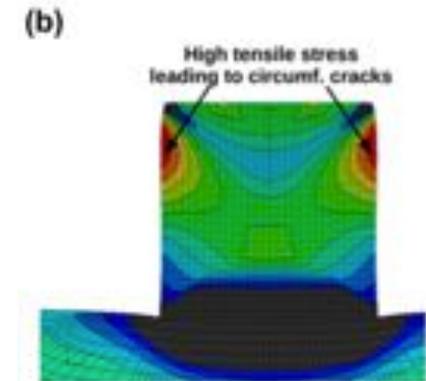
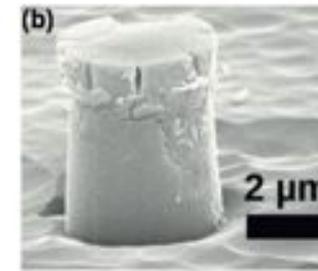
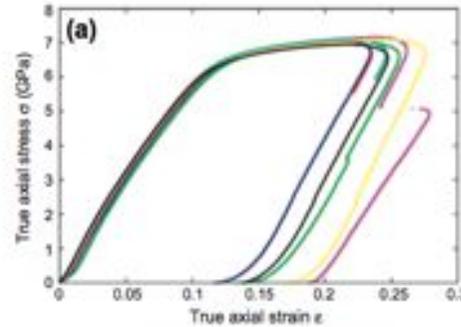
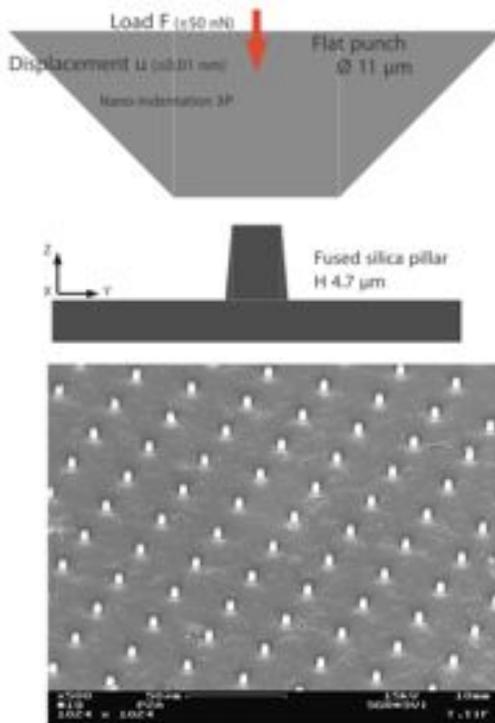
- 1) Utiliser d'autres essais mécaniques (essais sur piliers)
- 2) Utiliser l'indentation aux faible charges (mN) mais trouver un moyen d'obtenir des informations sur la zone plastique;

Intérêt:

Hydrostatique = pauvre (pas de cisaillement)

Indentation (riche) hydrostatique + cisaillement mais complexe

Micro pilier : «proche» d'un essai de compression uni axial, limitation de l'effet hydrostatique de confinement élastique présent en indentation (matériau infini entourant la zone plastique)



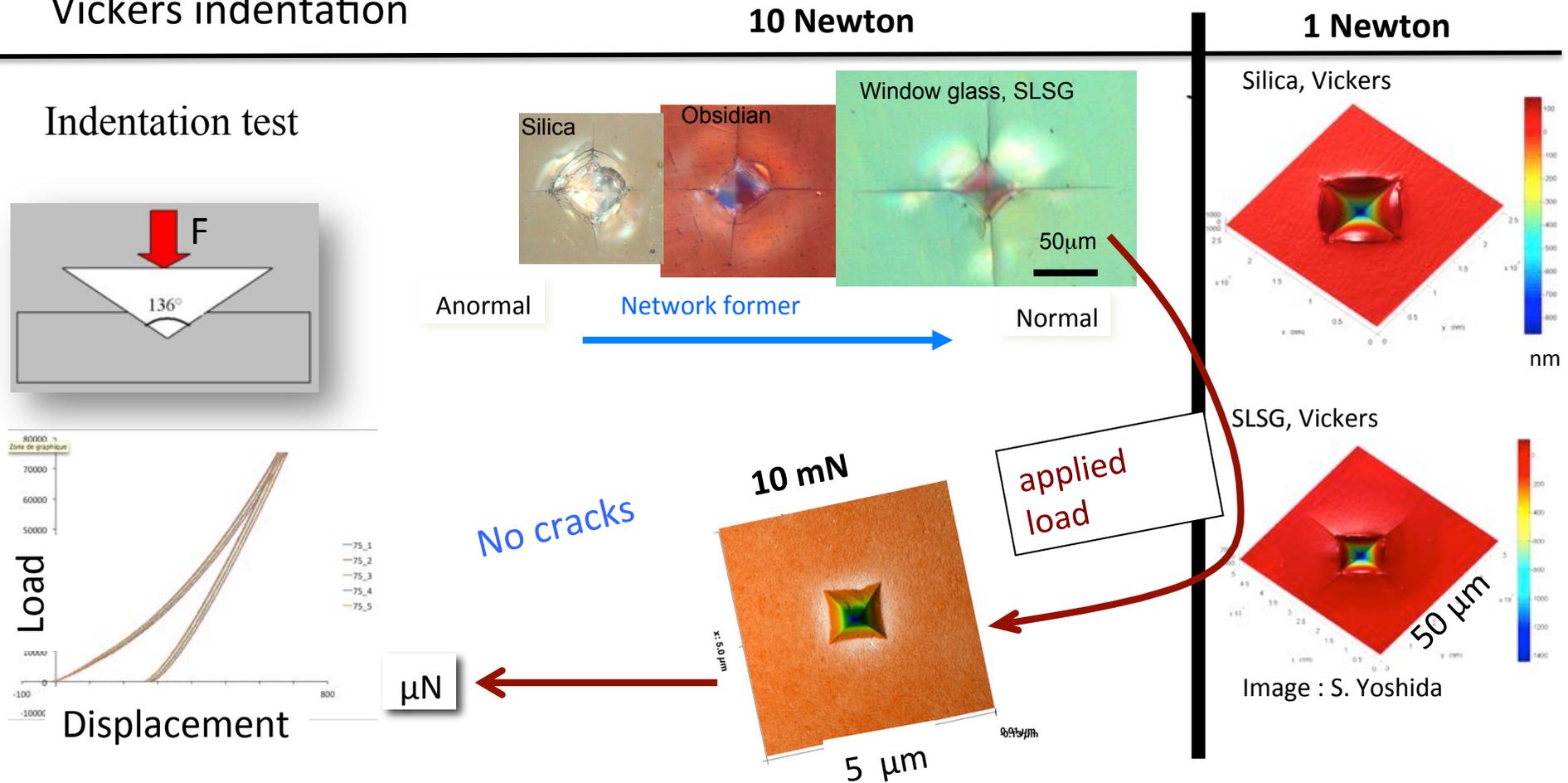
R. Lacroix, et al., *Plastic deformation and residual stresses in amorphous silica pillars under uniaxial loading*, *Acta Mat.*, 60 (2012), 5555.

R. Lacroix et al., *Mi- cropillar testing of amorphous silica*, *International Journal of Applied Glass Science*, 3 (2012), 36

Plasticity and surface damage : indentation as an efficient tool

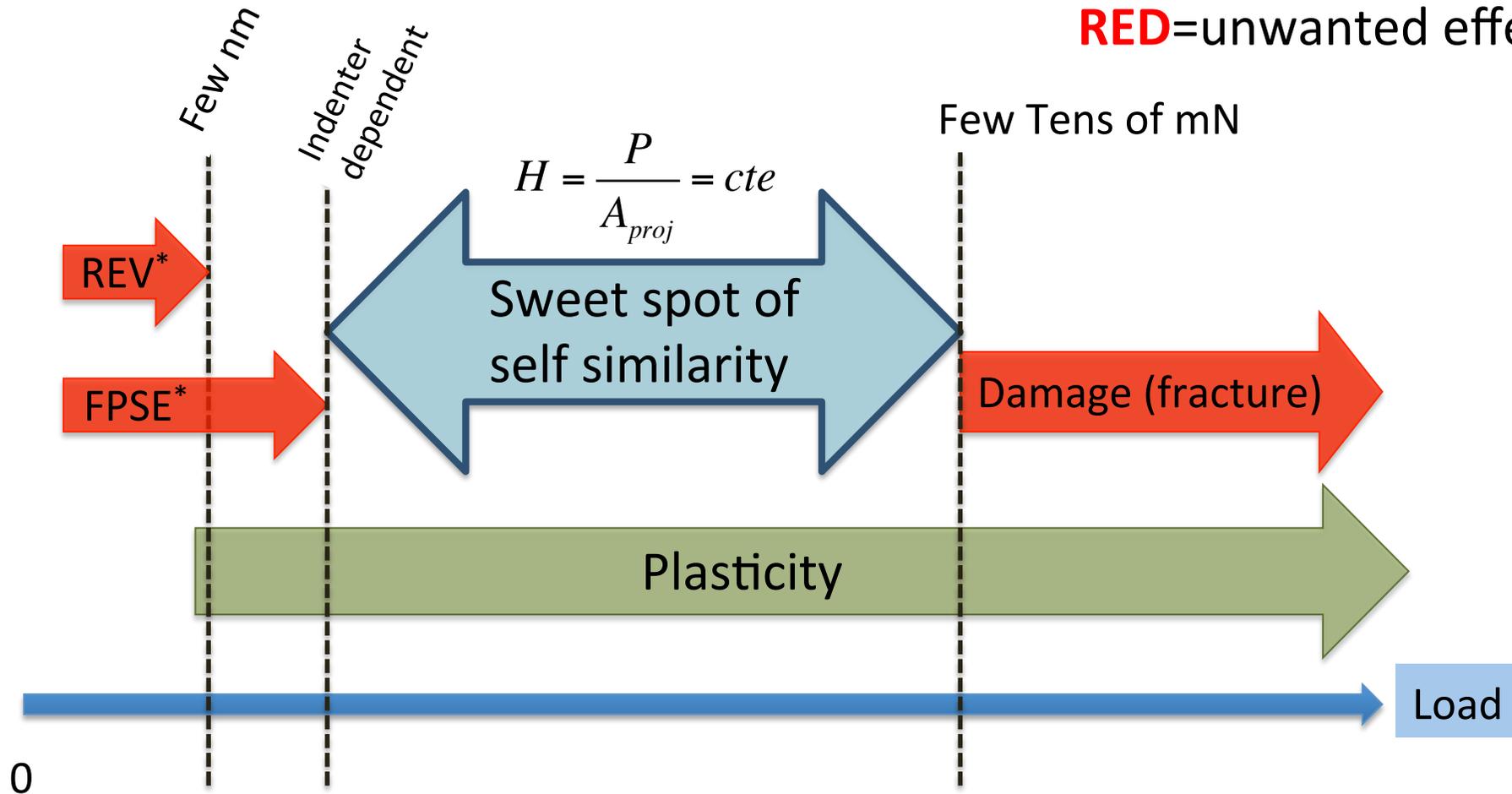
- Indentation behavior and cracking systems are composition dependent

Vickers indentation





RED=unwanted effects

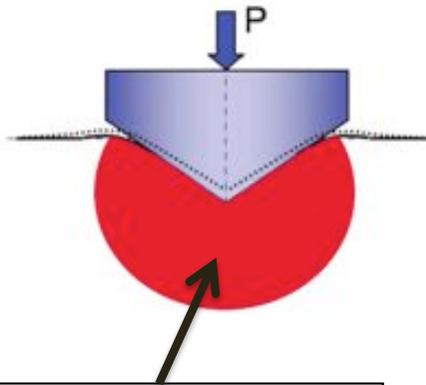


FPSE: Finite probe size effect

REV (representative elementary volume)

Problem : sub micrometer size plastic zone at indentation site.
How to probe it?

While indenting

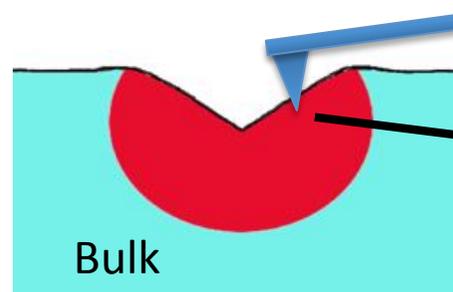


Permanently deformed zone shear flow + densification

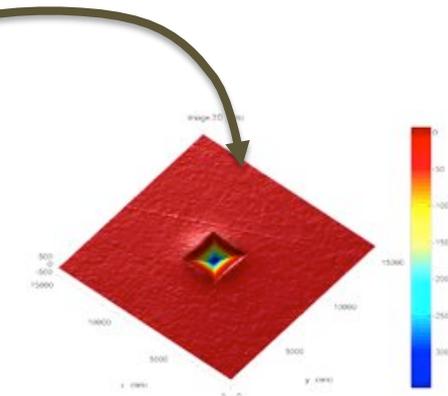
Starting grant
QUIC GLASS (2007-2012)



Atomic force microscopy



Shape?
Size?
Nature?



How does it work?

Densification → structural modifications → Impact on local chemical reactivity?

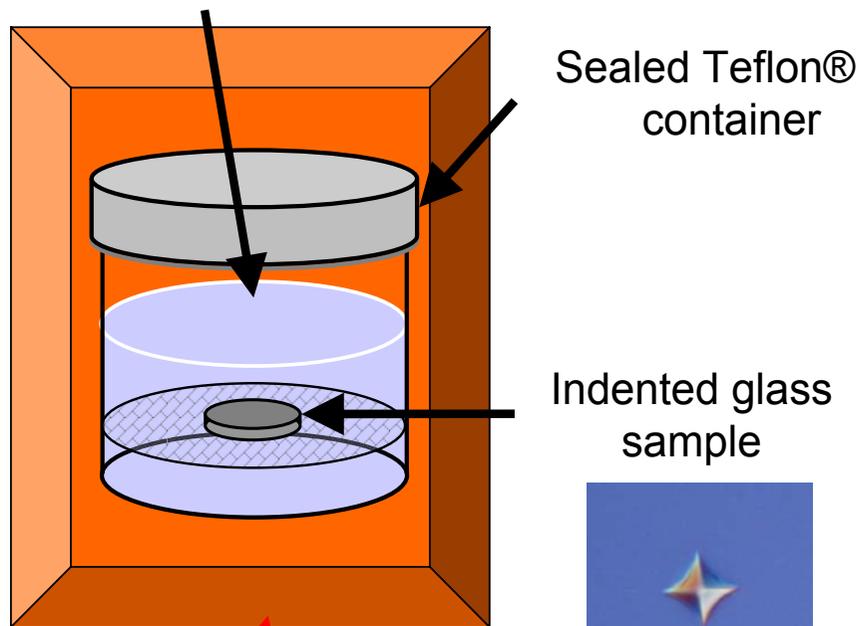
Reactivité : θSiOSi décroît → une chute drastique de la résistance à la réaction d'hydrolyse de la liaison Si-O [Michalske 1984, Yip 2006]

Perte de connectivité → moins de liaisons à hydrolyser par unité de volume

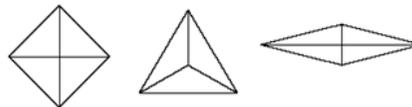
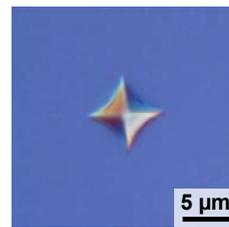
Les changements structuraux décrits ci-dessus sont en parfait accord avec une augmentation de la vitesse de dissolution du verre densifié.

0.1 N NaOH solution
($S/V \approx 8 \text{ m}^{-1}$)

S: surface of the sample
V: volume of the solution

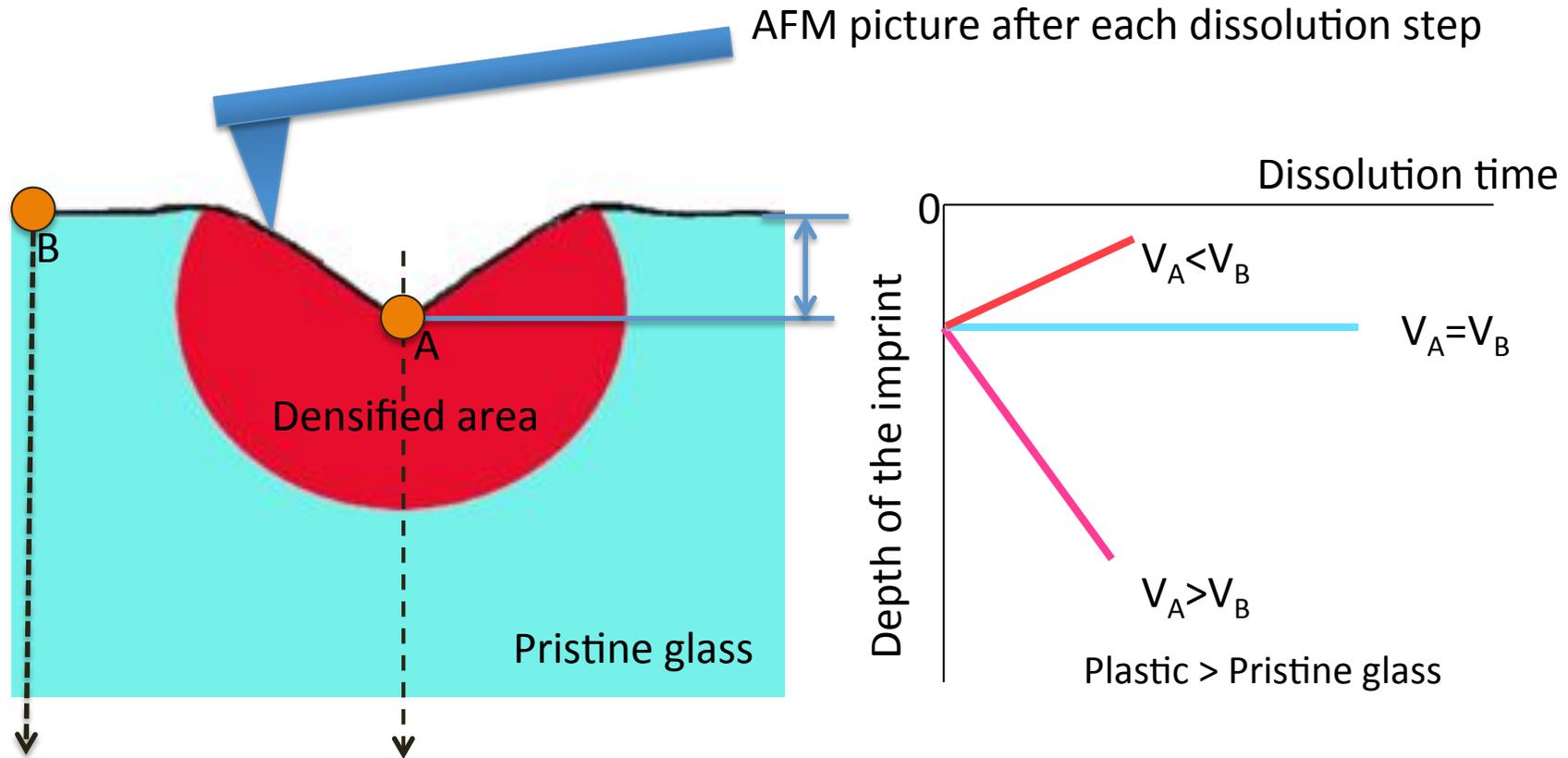


Thermo regulated furnace
(80 ± 1) °C



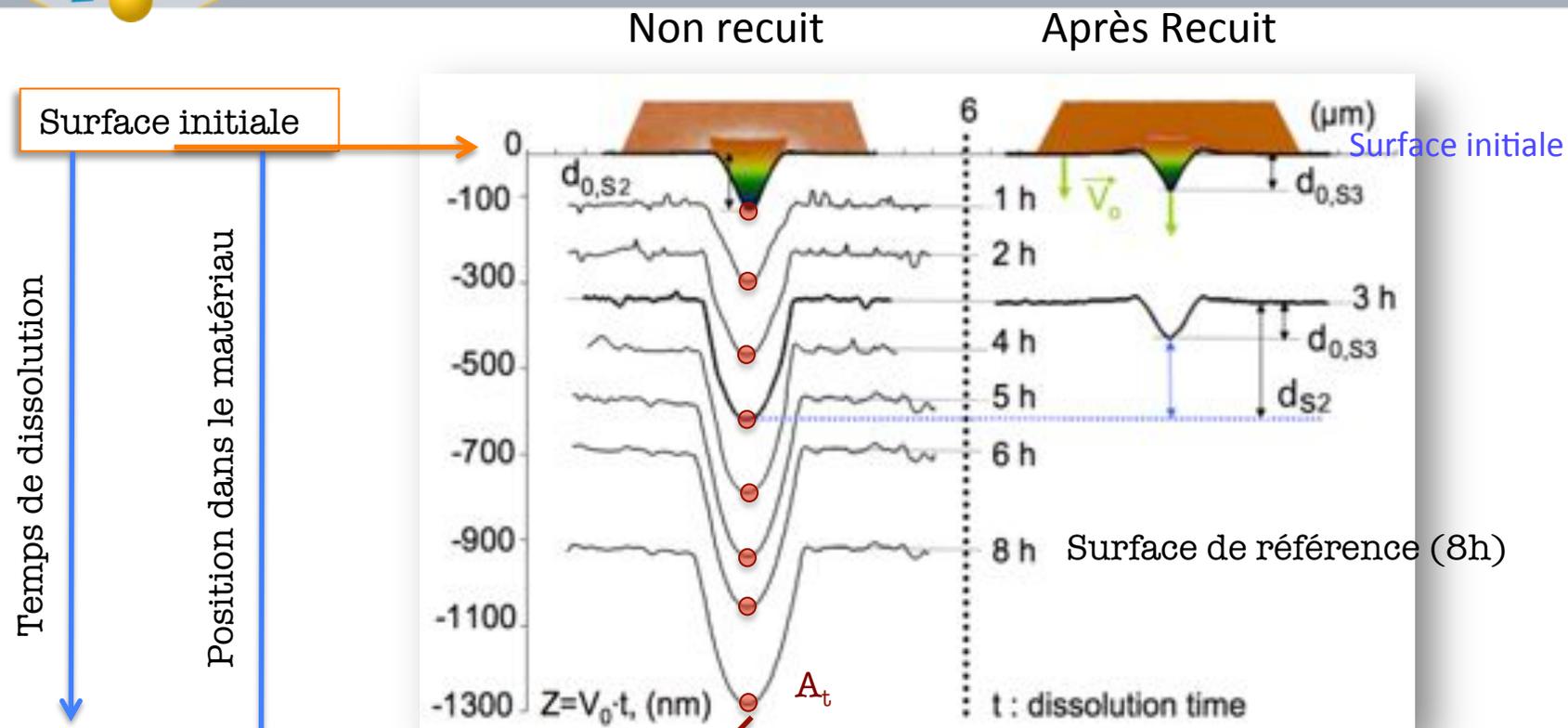
1. Conditions de dissolution congruente (Doremus 1982)
2. échantillon blanc pour la mesure de V_0 la vitesse de dissolution du verre relaxé dans la même solution
3. Échantillon indenté et imagé par AFM.

Evolution of the indentation imprint (depth, morphology) through dissolution steps.



If the dissolution rate in A (densified area at the bottom of the imprint) is faster than in B (free surface) then the imprint depth after dissolution step will increase

Suivit d'empreintes d'indentations : exemple Vickers 10 mN, VAV

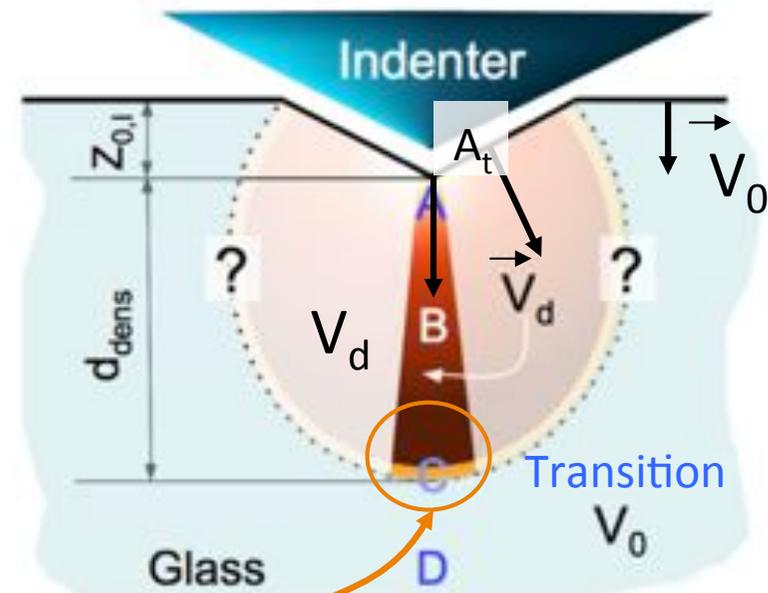
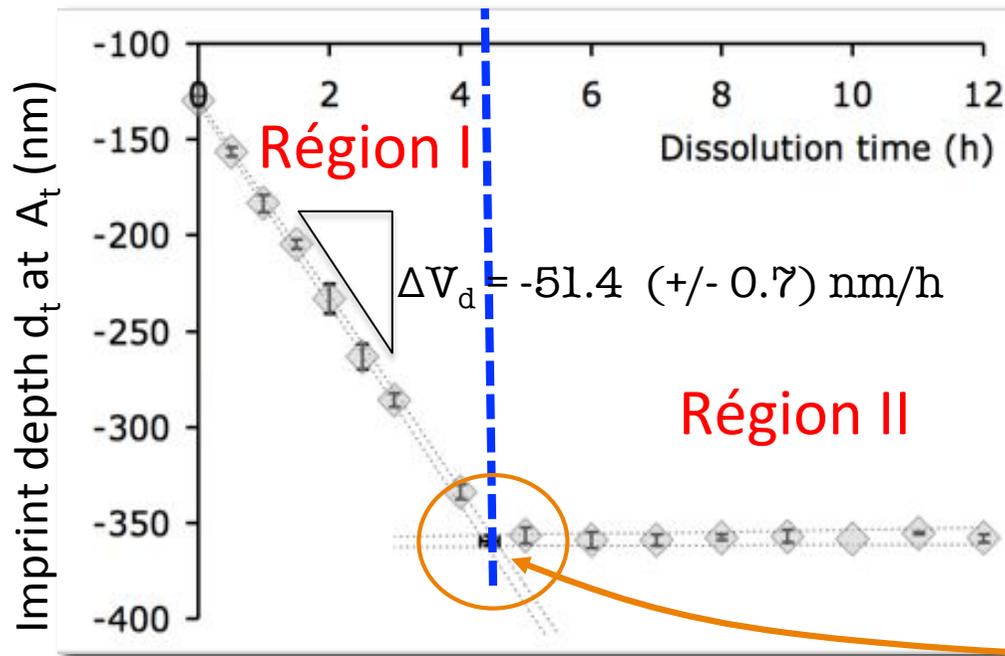


Nécessite la mesure de V_0
la vitesse de dissolution
du verre relaxé

Le suivi de l'altitude du point A_t à la surface de référence donne la vitesse de dissolution relative entre le fond de l'empreinte et la surface de référence.

$V=V_0$ en tout point de la surface $\Rightarrow d_t=d_0 = \text{constante}$
 $V>V_0$ en A_t et V_0 ailleurs $\Rightarrow d_t>d_0$ pour $t>0$ et est une fonction croissante de t

Niu Y-F, Han K., Guin J-P, Langmuir, 28, 10733 (2012)



Two different regions :

Région I : increase of imprint depth = enhanced dissolution rate at the bottom of the print.

Région II: plateau = same dissolution rate at the free surface and in A_t the bottom of the imprint.

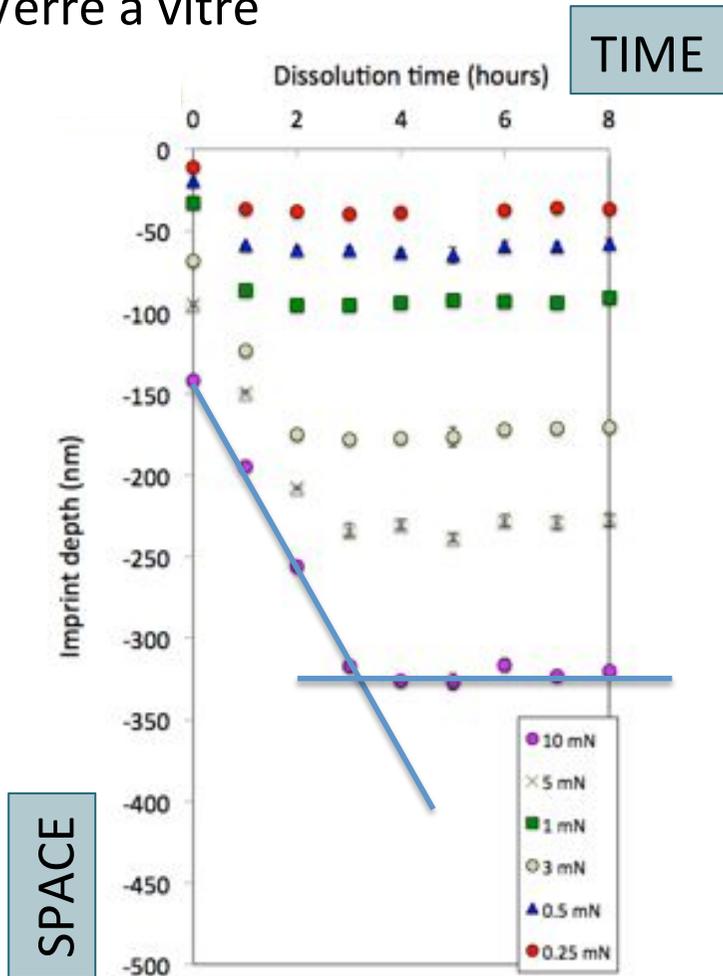
$$d_{\text{dens}} = V_{\text{densified}} \times t^* = (V_0 + \Delta V_d) \cdot t^*$$

Thickness of the plastic zone under the indenter apex

Niu Y-F, Han K., Guin J-P, Langmuir, 28, 10733 (2012)

Indentation Berkovich de 0.25 à 10 mN sur un échantillon de verre → même pas de temps pour toute les charges

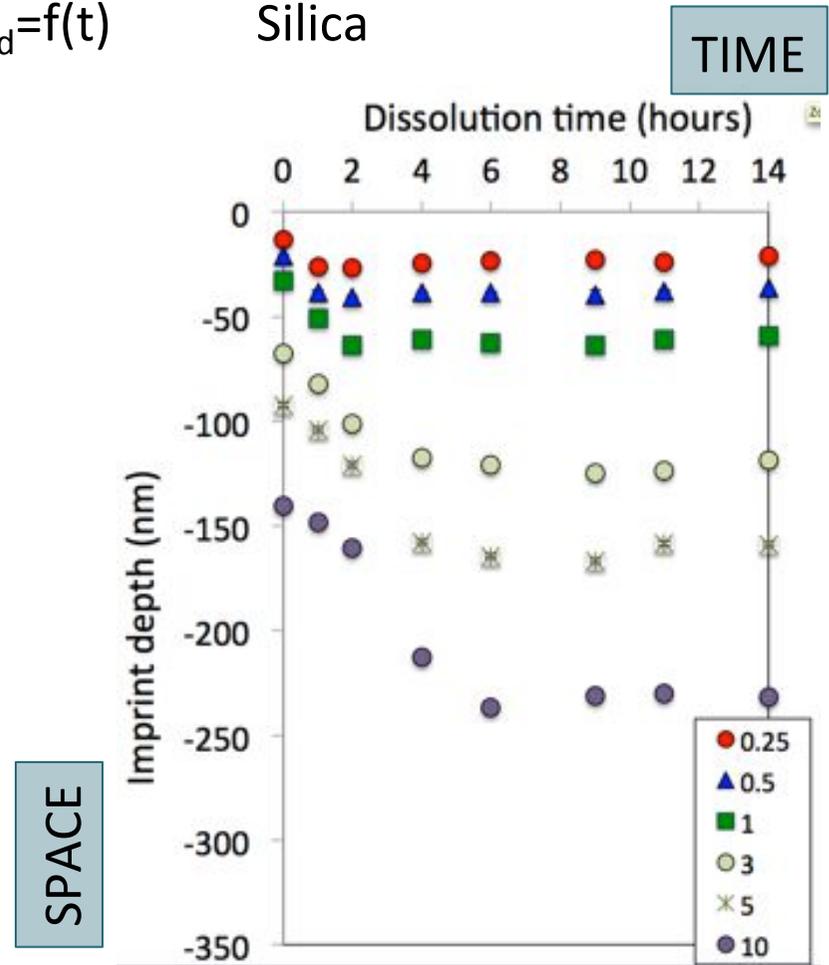
Verre à vitre



Courbes $h_d=f(t)$

2 régions distinctes
RI et RII

Silica



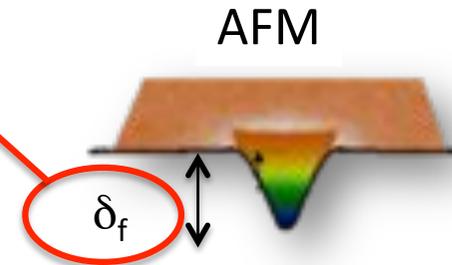
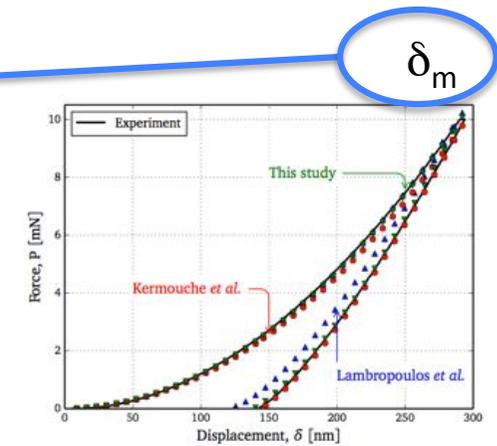
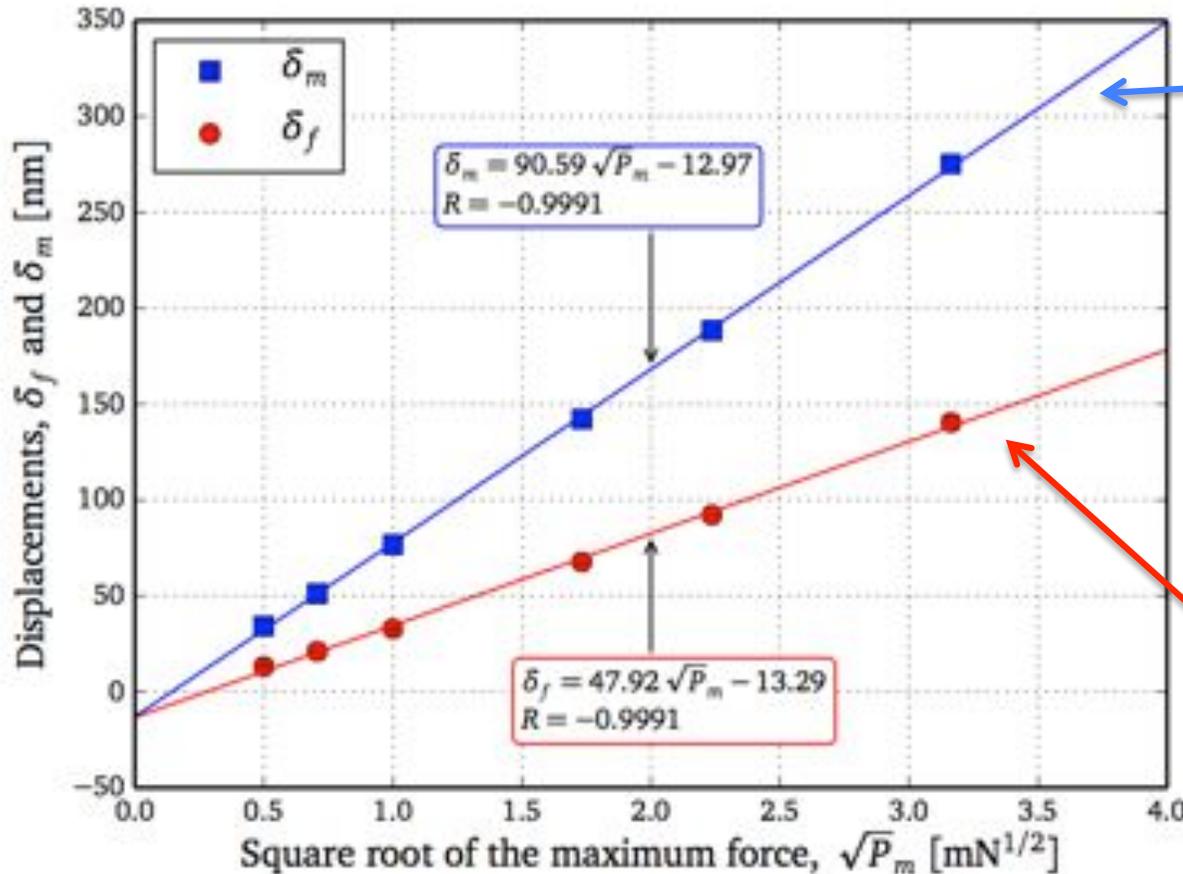
Due to experimental constraint data sampling is poor for low indentation loads!

δ_m : maximal penetration depth of the indenter at P_{max} (from the nano indenteur)

δ_f : post indentation residual imprint depth (mesurée par AFM)

Silice, Berkovich

Nano indenteur



→ Indentation self similar regime validated!

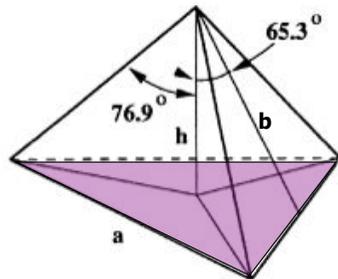
Indentation self similar regime? : what ever is the load H remains constant!

- 1) Indenter geometry is self similar: A_{proj} scales with h (penetration depth).
As long as one stays far from the finite size of the probe tip.
- 2) Material : if far from any REV (representative elementary volume) consideration regarding plasticity and as long as only plasticity is involved (no fracture for example).

Berkovich indenter:

$$A_{proj} = 3\sqrt{3}h^2 \tan^2 65.3^\circ = 24.56h^2$$

In the self similar regime



$$H = \frac{P}{A_{proj}} = cte = \frac{P}{24.56 \cdot h^2} \quad \text{thus}$$

$$P = cte \cdot h^2$$

$$h = cte \cdot P^{1/2}$$

➔ Any length scale associated to the indentation process should scale with $P^{1/2}$

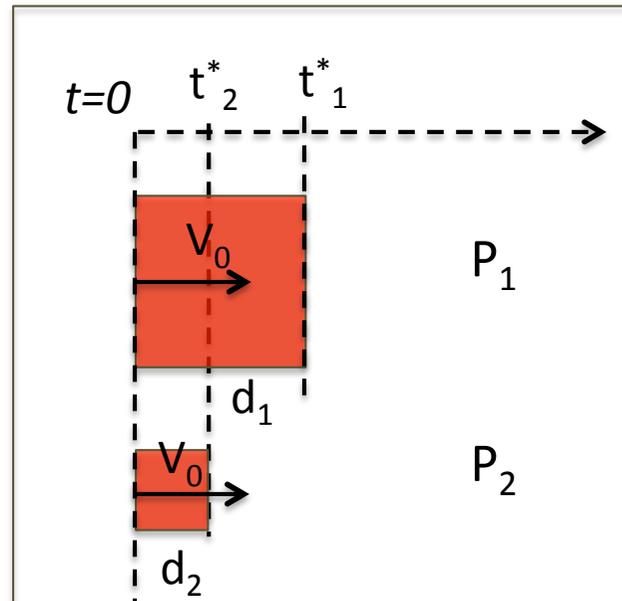
Space and time dimensions: In the geometrical similar regime

◆ Space:

From hardness
définition

$$H = \frac{P}{A_{proj}} = cte = \frac{P}{24.56 \cdot h^2} \rightarrow \frac{P}{h^2} = cte = \frac{P_i}{h_i^2}$$

◆ Time



t^* : time to go
through the red
space at a speed V_0

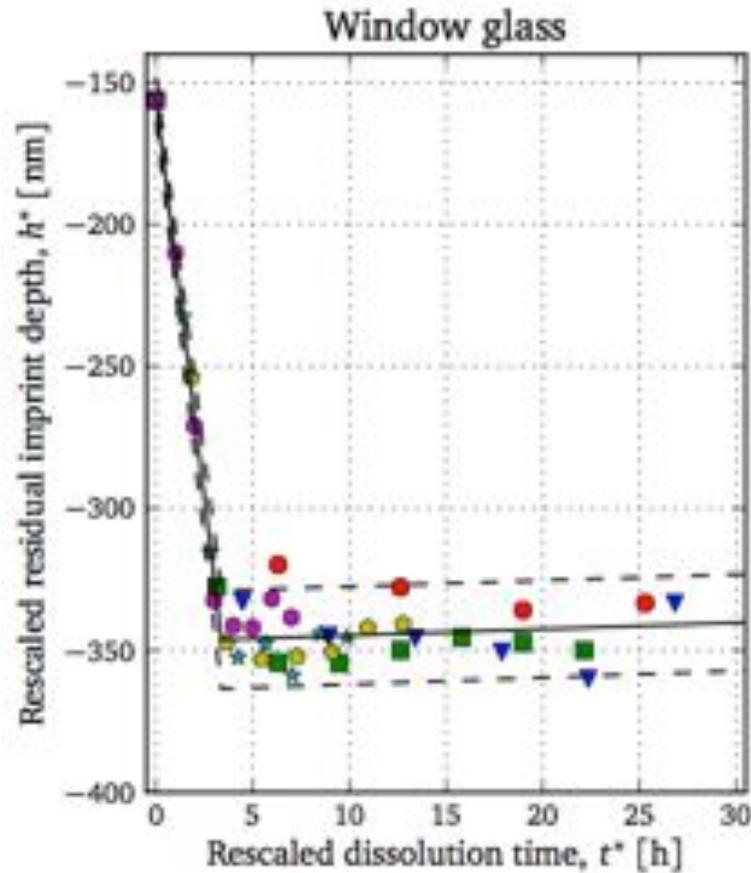
$$V_0 = \frac{h_1}{t_1^*} = \frac{h_2}{t_2^*} = cte$$

Thus we show that

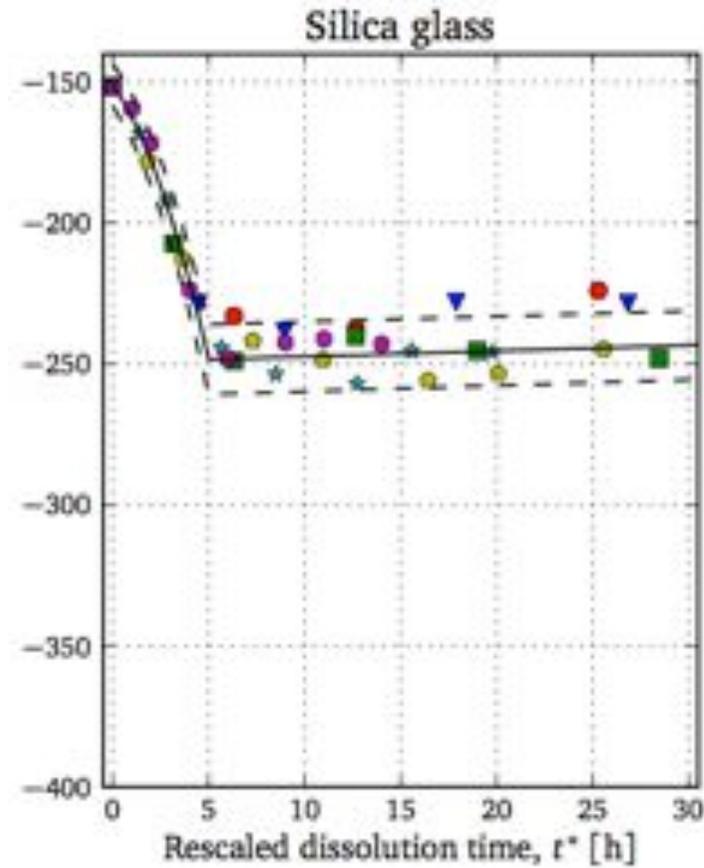
$$\frac{t}{\sqrt{P}} = cte = \frac{t_i}{\sqrt{P_i}}$$

The curves, Imprint depth versus dissolution time, may be rescaled both in space and time scales so that all the curves should collapse into a single one.

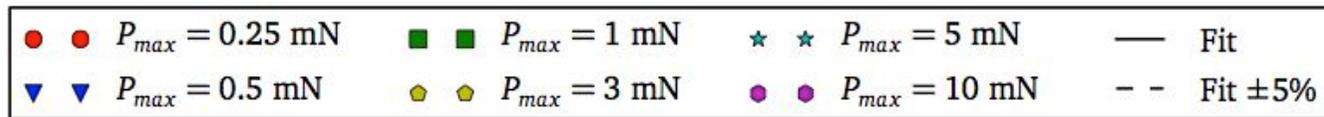
Charge servant de référence : 10 mN



- 5%
+ 5%

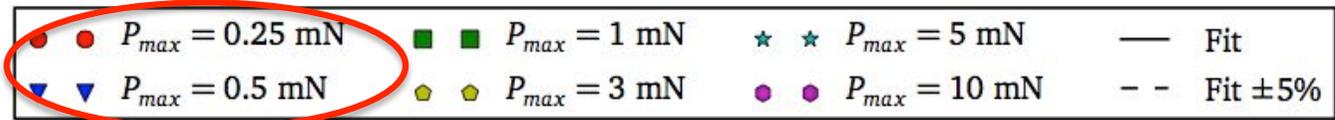
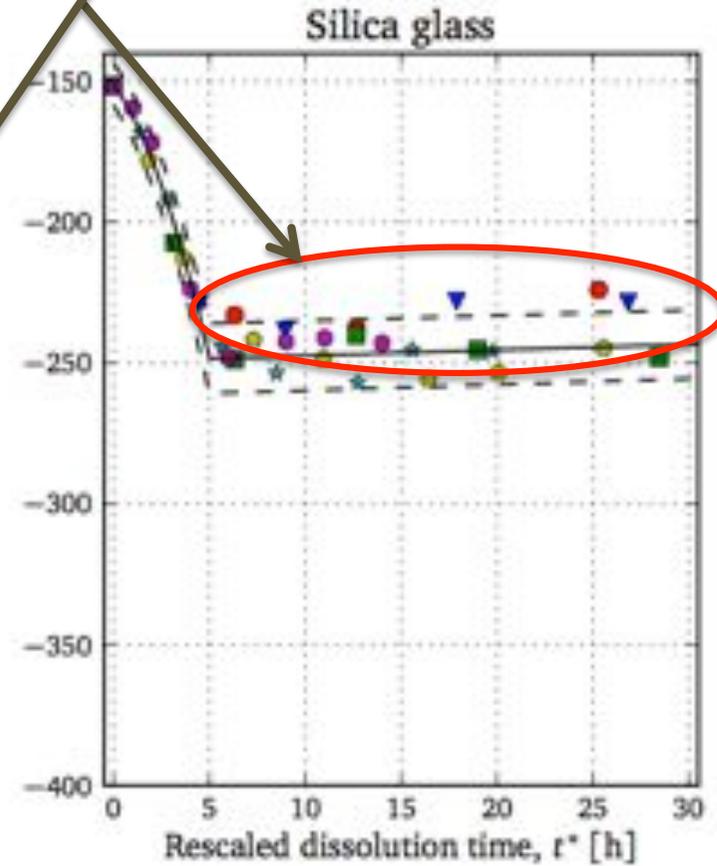
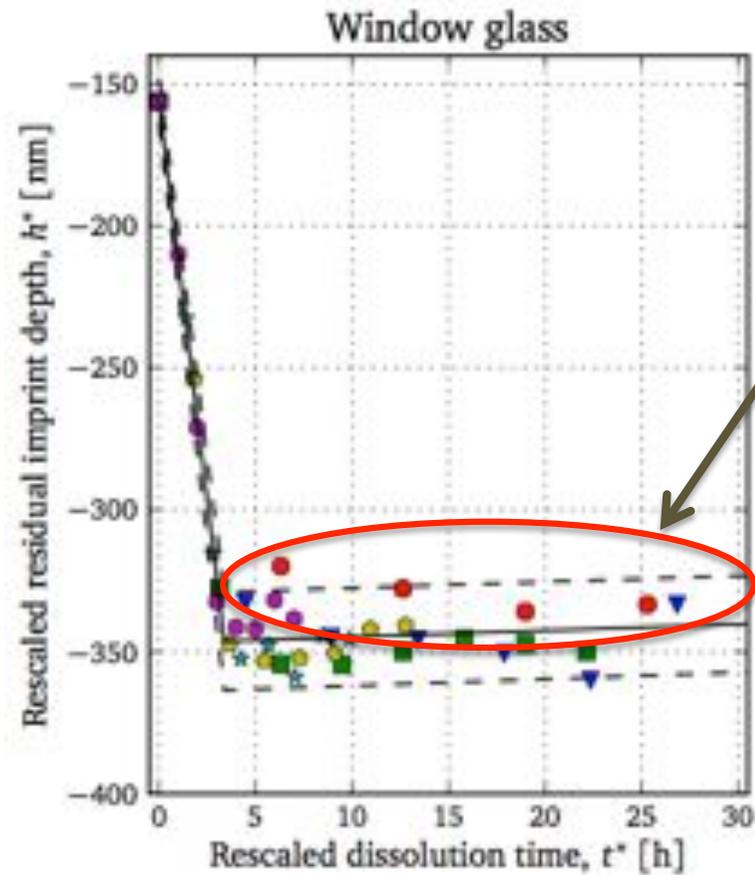


- 5%
+ 5%



Conclusion : it works, all the curves collapse into a single one: de 250 μN à 10 mN.

Tiny finite probe size effect on the position of the plateau



Extraire des paramètres permettant un dialogue avec les modélisations numériques

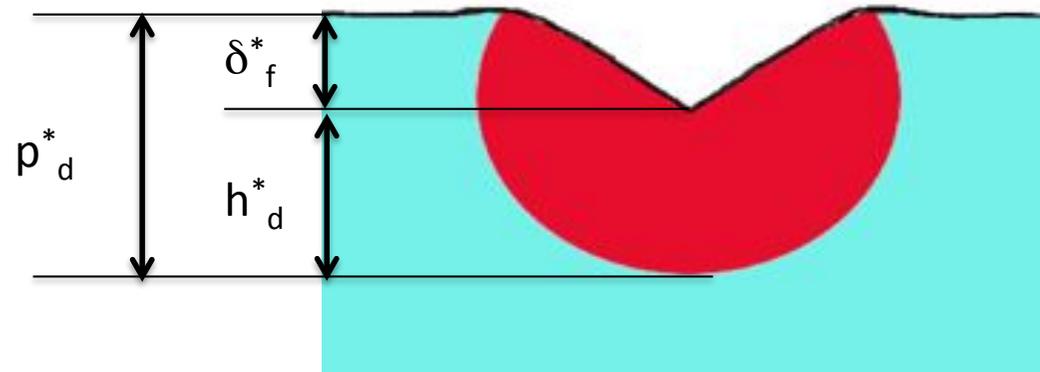
δ_f^* : post indentation imprint depth (AFM)

δ_m^* : max penetration depth at Pmax

h_d^* : thickness of the plastic zone under the point of contact

p_d^* : depth, under the pristine surface, where the boundary of the plastic zone may be found ($\delta_f^* + h_d^*$)

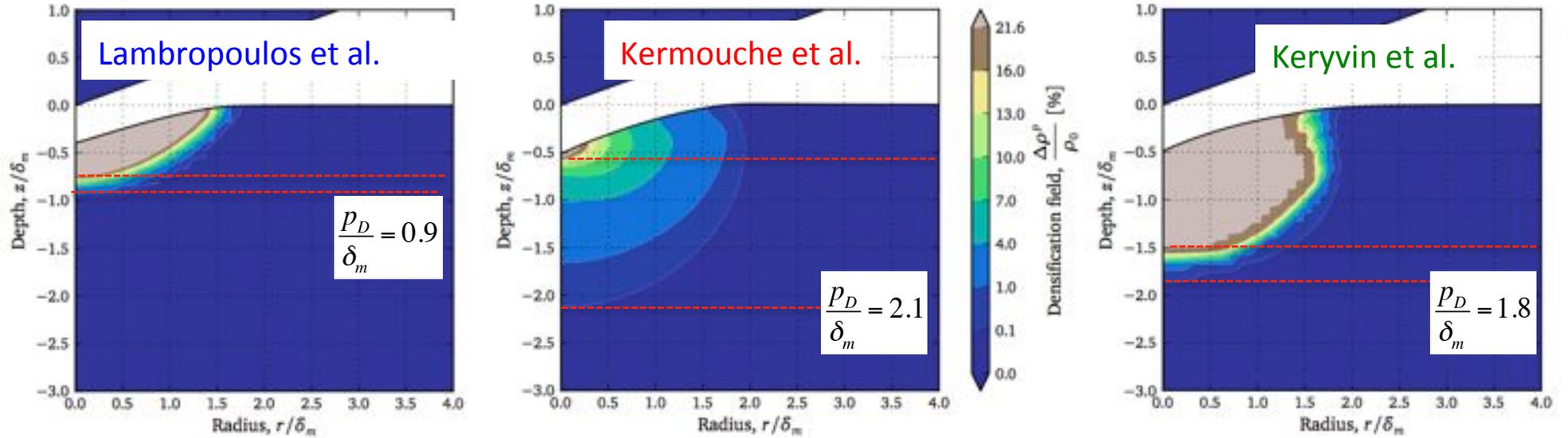
p_d^*/δ_m^* : example of an non dimensional parameter used in numerical modeling.



** Signifie que ces valeurs sont calculées à partir des données expérimentales en prenant pour charge de référence 10 mN. Pour toute autre charge d'indentation P la valeur de ces paramètres peut être obtenue en appliquant le rapport $\sqrt{P[mN]}/10$*



Densification map obtained from FEM



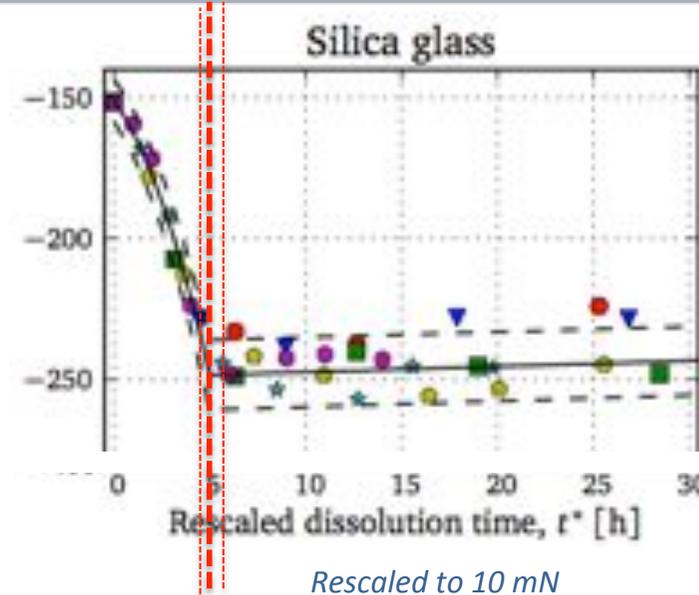
$$\frac{P_D}{\delta_m}$$

<i>Longueurs adimensionnées par δ_m</i>	Lambropoulos	Kermouche	Keryvin
Densification depth	0.9	2.1	1.8
Transition zone	0.2	1.6	0.35 – 0.4

From our experimental curves

$$\frac{p_D}{\delta_m} = 1.7_{1.5}^{2.1}$$

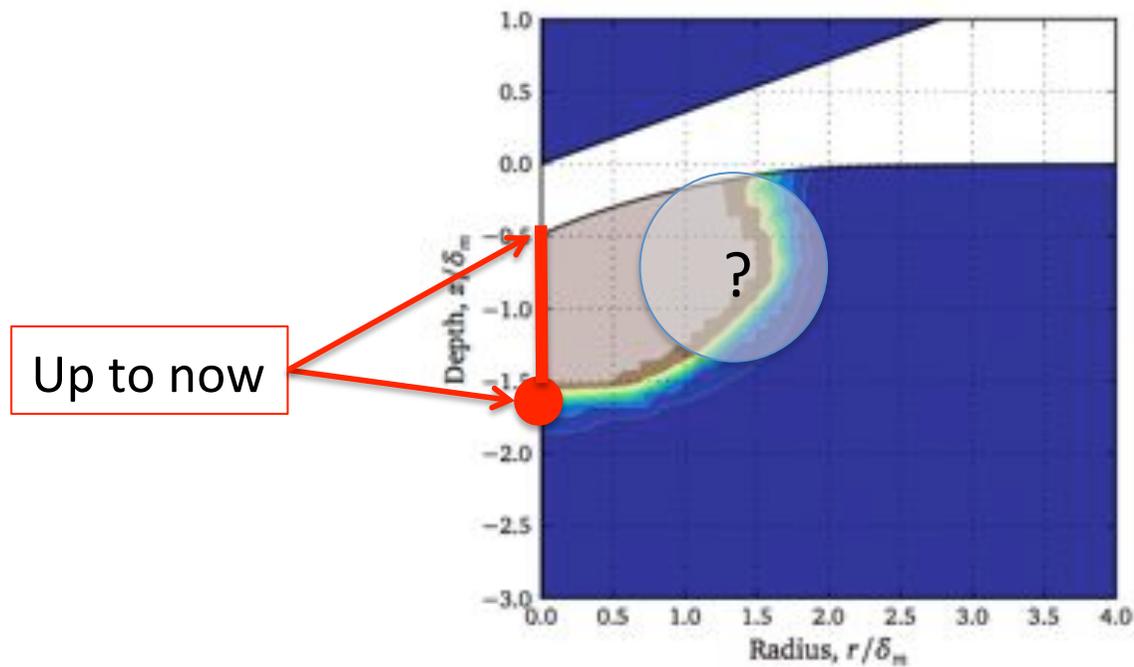
Épaisseur de la zone de transition de 0.35 (≈ 100 nm)



Longueurs adimensionnées par δ_m	Lambropoulos	Kermouche	Keryvin	Experiment
Densification depth	0.9	2.1	1.8	1.7
Transition zone	0.2	1.6	0.35 – 0.4	0.35 (max)

This densification chemical probe allows for discriminating constitutive laws where P-u curves don't. It is also a good way for checking the limit of the self similar regime, especially as ultra low load (finite probe size effect, REV).

Is the 1 D approach enough to discriminate between constitutive laws?

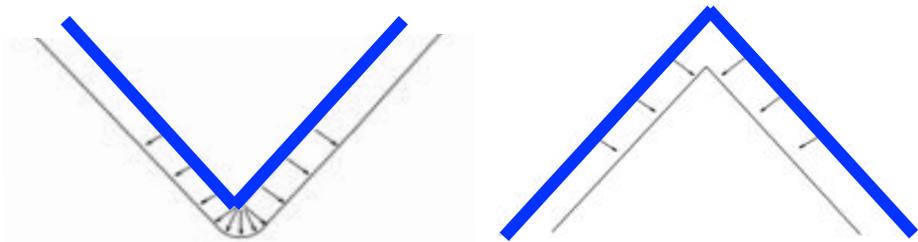
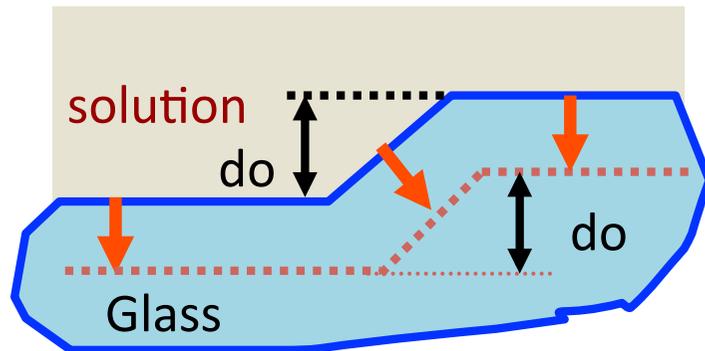


1) Shape evolution of surfaces through dissolution: dissolution vector applies normally to the surface at each point of the surface.

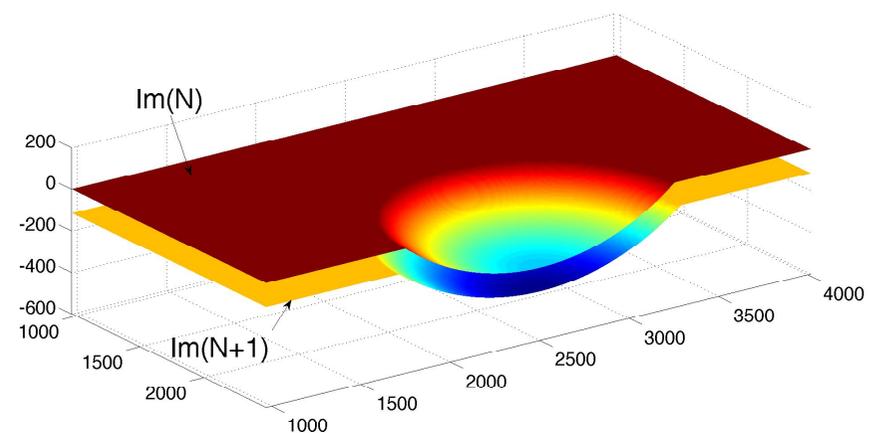
Mathematical formalism: level set functions or PDE, (Sethian 1982)

- 1: The dissolution vector applies normally to the surface for each considered point
- 2: Use of Huygens principle to deal with edges (inward or outward)

$$\phi_t + V_0 |\nabla \phi| = 0$$

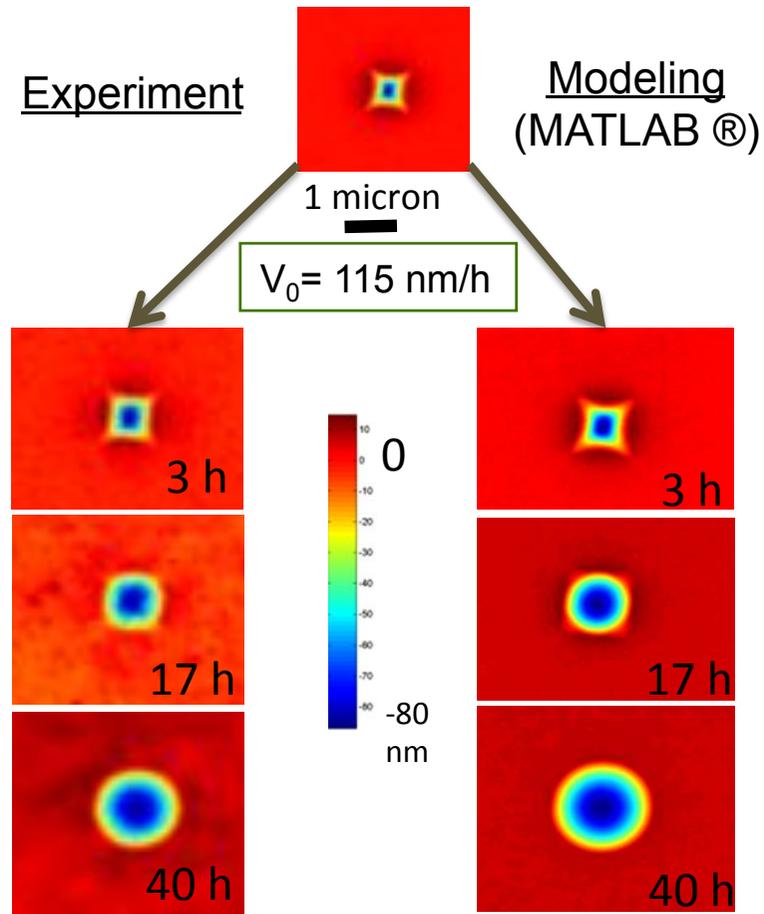


Reconstructing the matrix of dissolution vector from two AFM images of the same imprint taken at two different dissolution times



1) Evolution of surfaces through dissolution

Initial imprint: 10 mN, SLSG
 (after annealing = no densification effect)



It is possible to model the 3D shape evolution of a surface through congruent dissolution
 Yes a squared pyramid transforms into a spherical like shape through dissolution.

Champ des vitesses de dissolution reconstruit

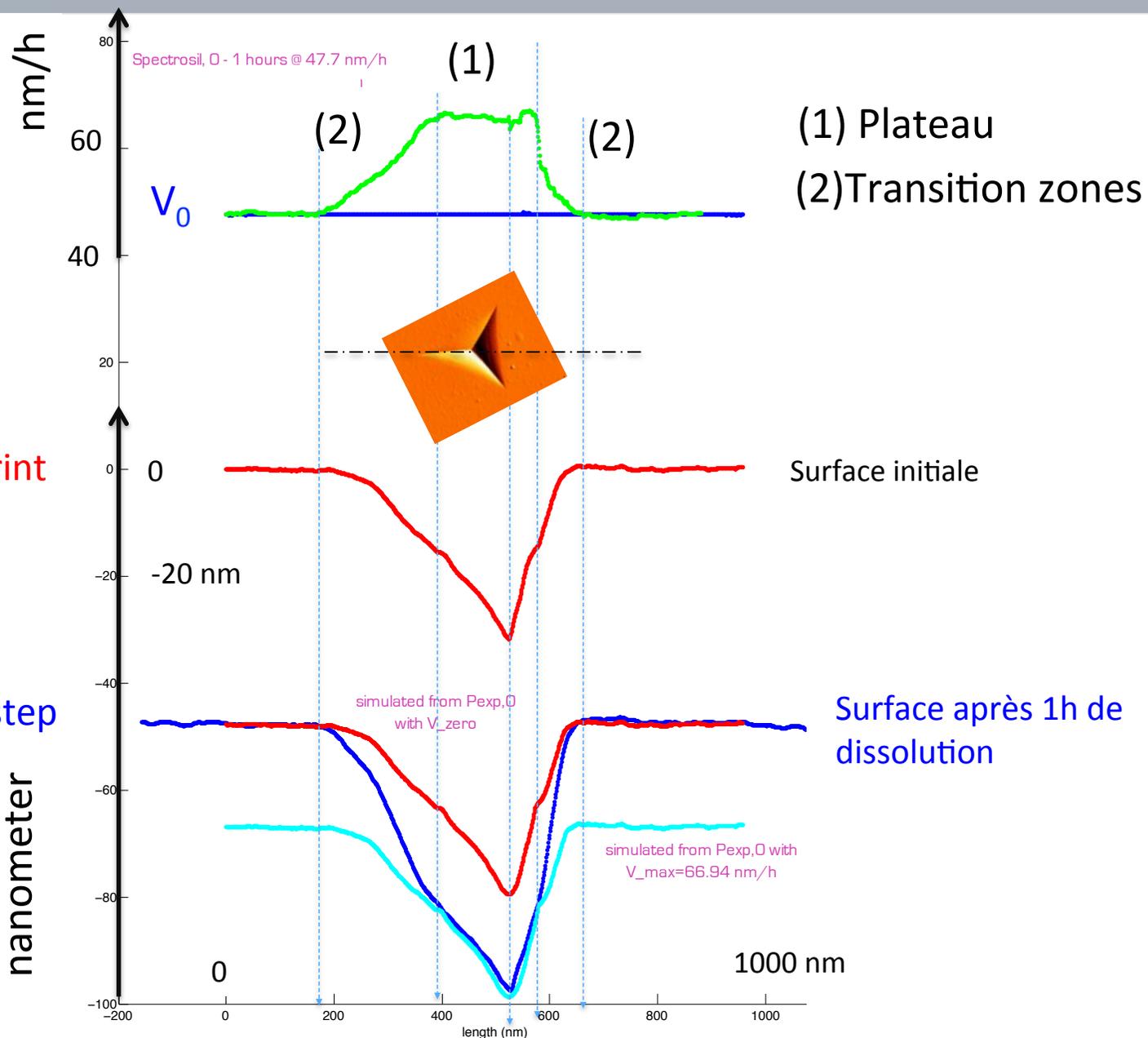
3

1

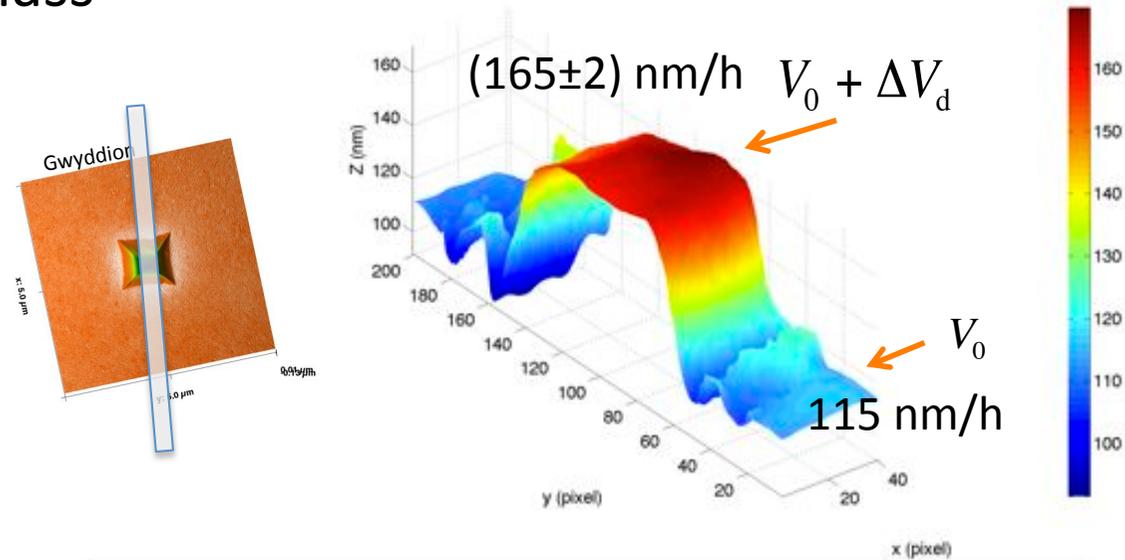
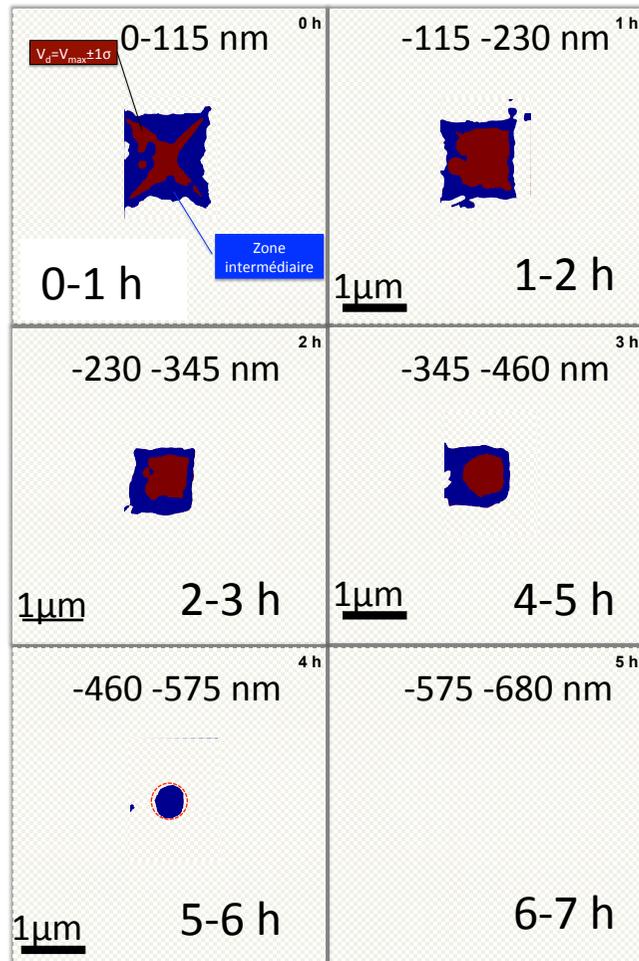
Pristine indentation imprint

2

After 1 hours dissolution step



Reconstruction of the densified zone under a 10 mN Vickers indentation on Window glass



Meaning of the Colors

At + or - 1 standard deviation

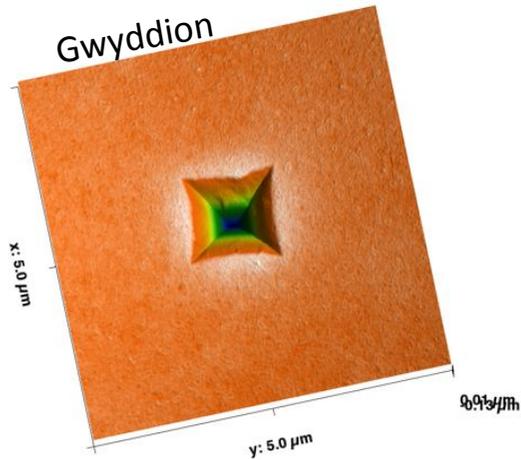
Red : 165 nm/h = fully densified

Blanc : 115 nm/h = not densified

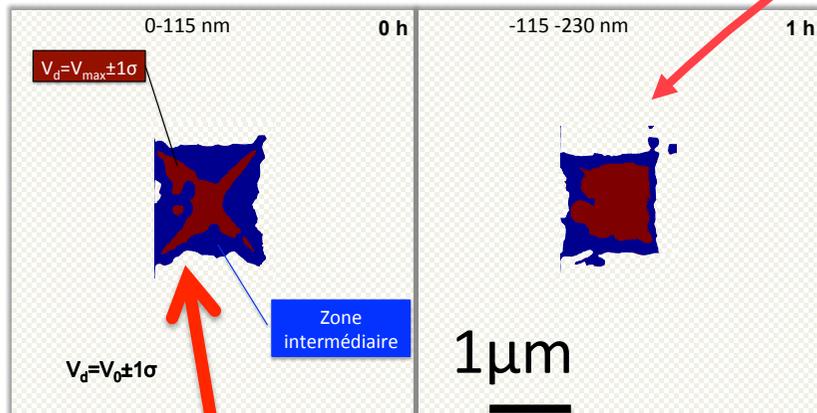
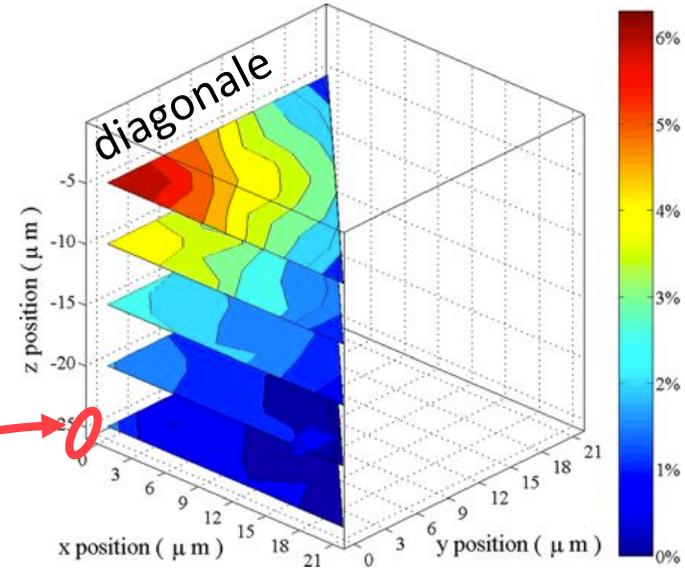
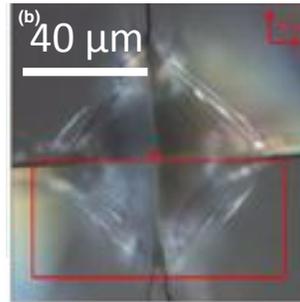
Blue: transition zone, from densified to less densified; from less densified to undensified; edge artefacts

comparaison with other techniques

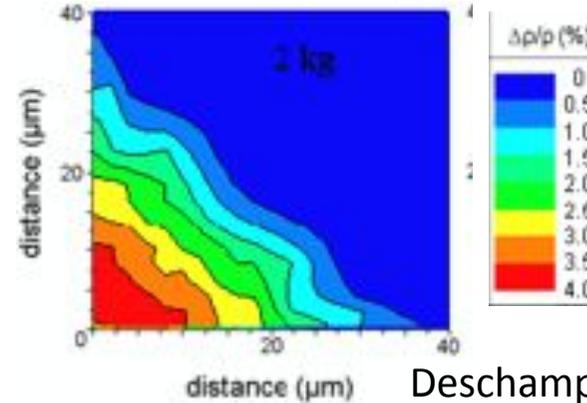
Brillouin spectroscopy, B. Rufflé et al. (2012)



20 N



Raman spectroscopy



20 N,
window glass

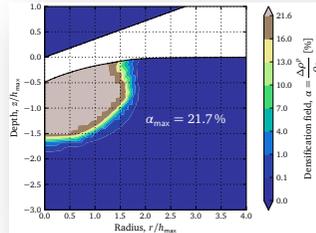
Deschamps et al. (2011)

Edge singularity effect on densification also observed with FEM.

A reliable experimental benchmark at a pertinent scale to study plasticity in glass

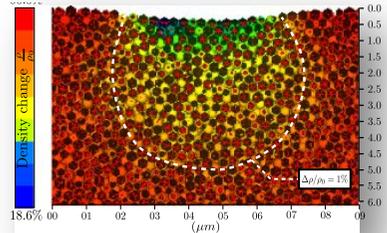
Numerical Modeling:

Finite element modeling



V. Keryvin et al., silice 2006, 2014

Discrete element method



M. Jebahi et al., silice, 2013

Molecular dynamic



D. A. Kilymis J-M. Delaye, silice, 2013

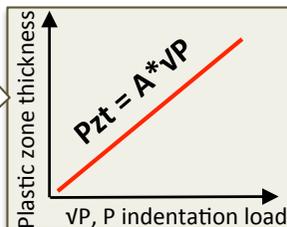
Plastic zone: size, shape, local gradients, crack nucleation



Validation of numerical hypotheses

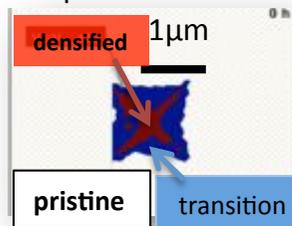
Experimental benchmark : chemical probe for plasticity

Thickness of the plastic zone sizes with indentation load



Geometrical similarity

3D mapping of the plastic zone



Nano crack 3D network

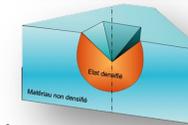
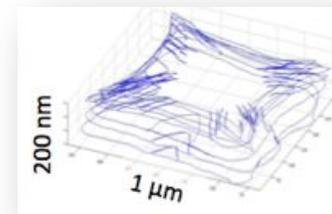
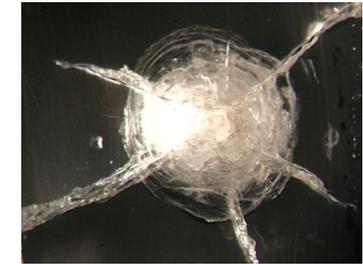
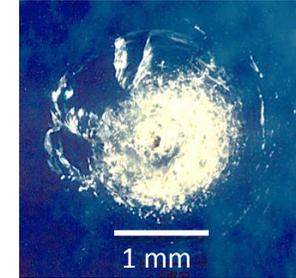


Illustration of the strategy developed in order to understand the coupling between densification and shear flow in glasses either at indentation sites or at scratches site.

ANR GLASS
(2014-2018)
IPR – PIMM
– CEA DAM
– I2M

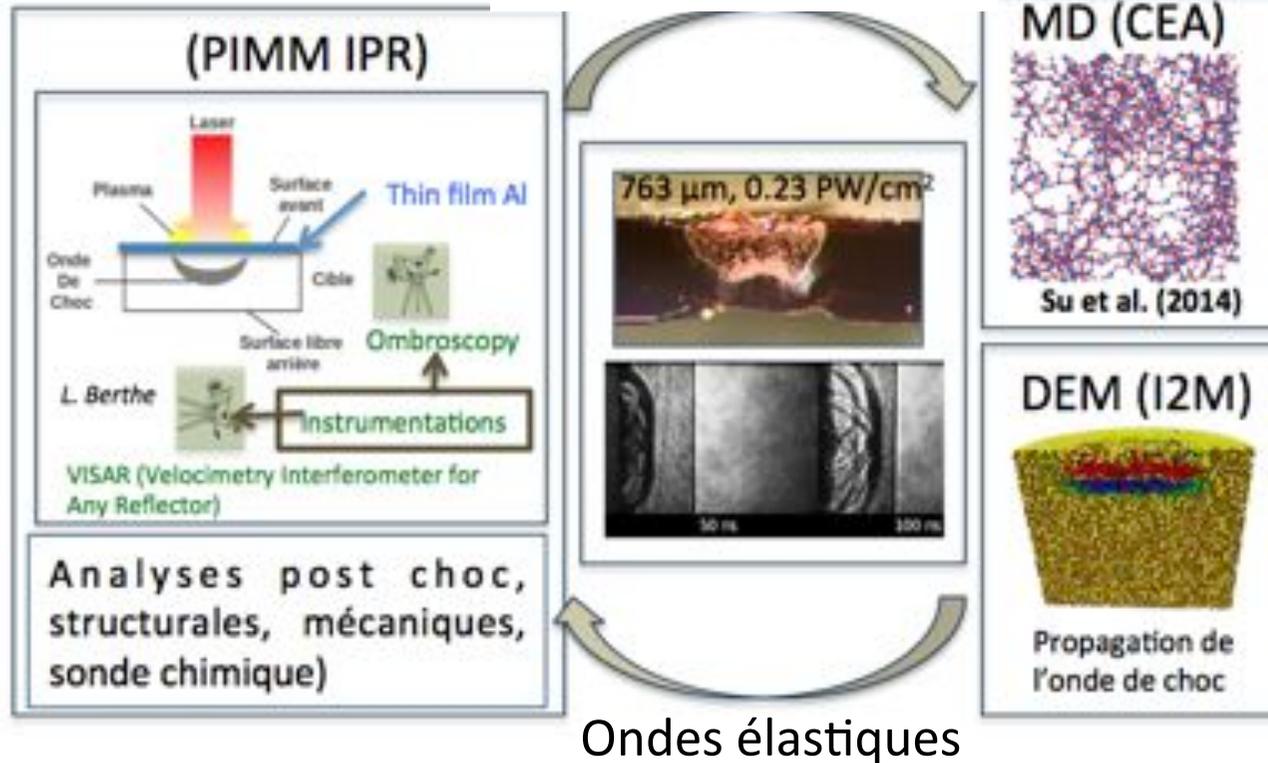
Loi de comportement (effet dynamique)
endommagement
**Expérience –modélisation : compatibilité
des échelles de temps et d'espace**



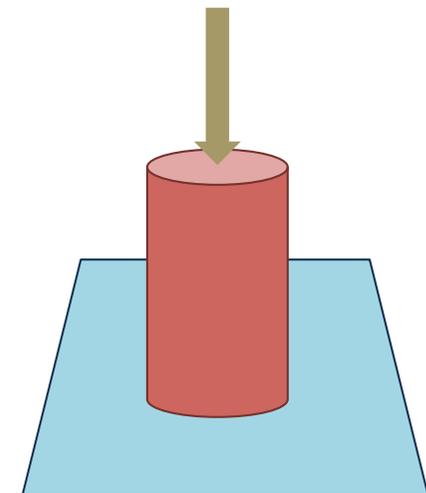
Elfie : $\approx 1.5 \text{ PW/cm}^2$



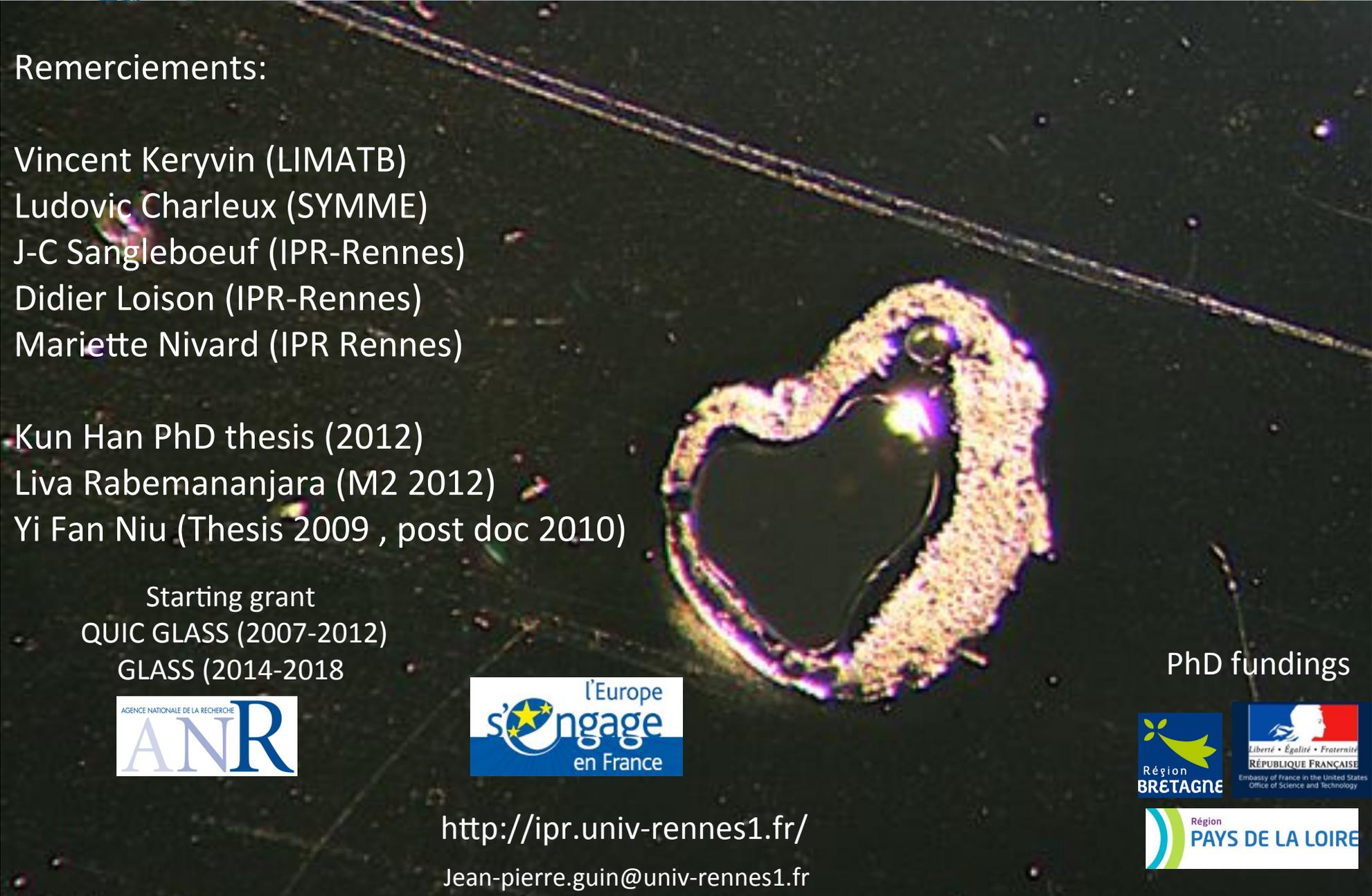
Plasticité en face avant



Géométrie idéale : top hat
Piston cylindrique/plan



Durée du chargement : de la ps à la ns pour plusieurs dizaines de GPa disponibles



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GLASS (2014-2018)



PhD fundings



<http://ipr.univ-rennes1.fr/>

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