Rare gases adsorption in v-SiO_2 at high pressure

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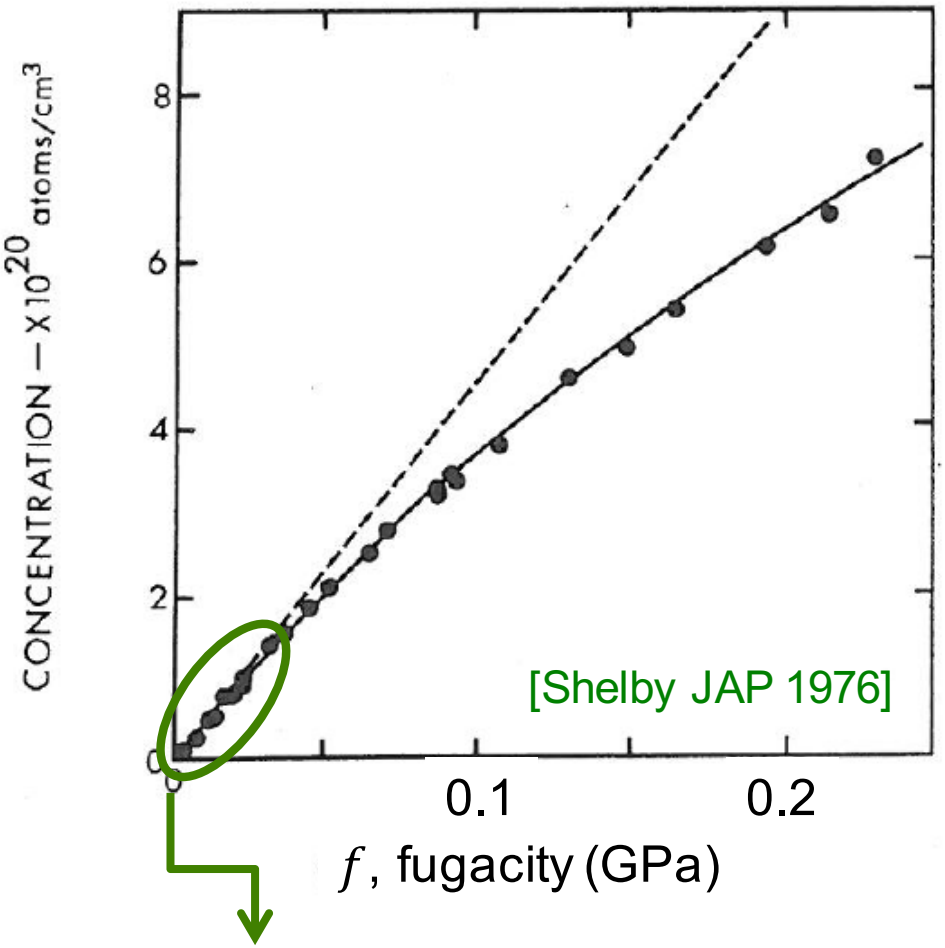
Helium solubility in v-SiO_2



At low pressure: Henry's law

Saturation effect
→ finite limiting value of C

Langmuir isotherm adsorption model :

$$C = \frac{Kf}{1+Kf} N_s$$

N_s: number density of solubility sites

For Helium:

- N_S ~ 2.3 x 10^{21} at./cm^3
  (0.1 mol / mol SiO_2)
- P_{sat} ~ 0.5 GPa

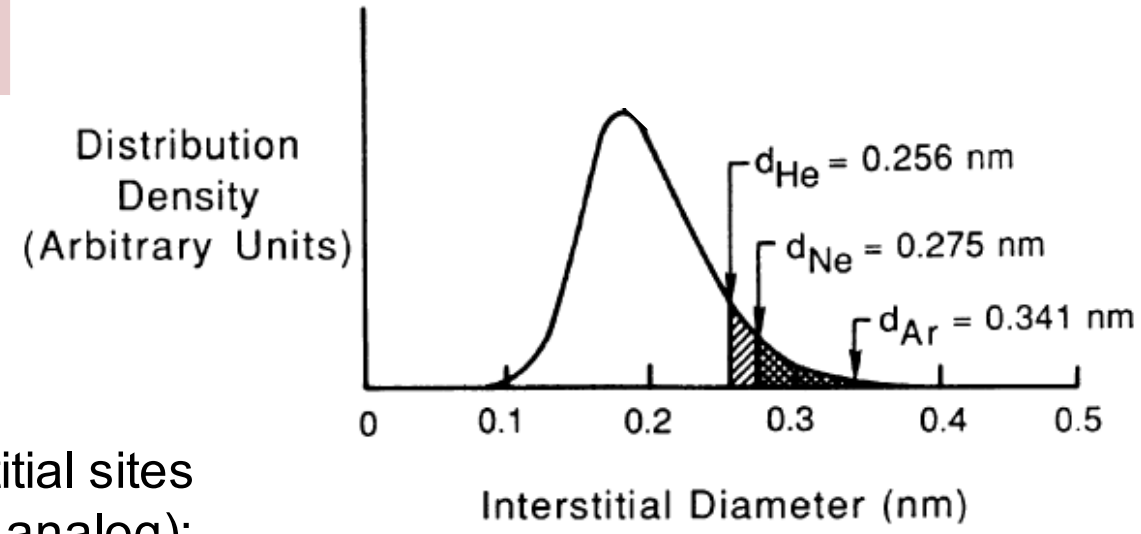
Rare gases solubility in v-SiO_2

Maximum concentration of adsorbed gas

Gas	Atomic dia. (nm)	N_S (at./cm^3)
He	0.256	2.3×10^{21} (0.1 at./SiO_2)
Ne	0.275	1.3×10^{21} (0.06 at./SiO_2)
Ar	0.341	1.1×10^{20} (0.005 at./SiO_2)

Shelby JAP (1976)
Nakayama & Shackelford JNCS (1990)

Log-normal distribution of interstitial void sizes



Shackelford JNCS 1978
Chan & Elliott PRB 1991

Total density of interstitial sites (based on cristobalite analog):
$\sim 2.2\times10^{22}$ at./cm^3

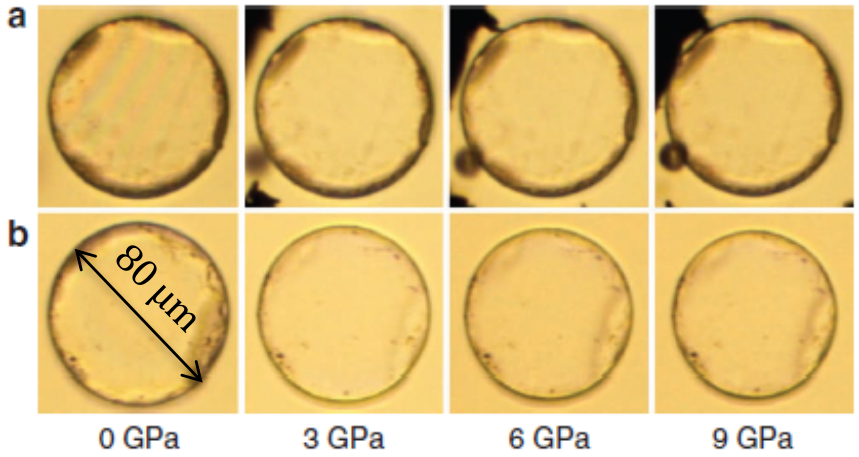
nature COMMUNICATIONS

Helium penetrates into silica glass and reduces its compressibility

DOI:10.1038/ncomms1343

Tomoko Sato[1], Nobumasa Funamori[2] & Takehiko Yagi[1]

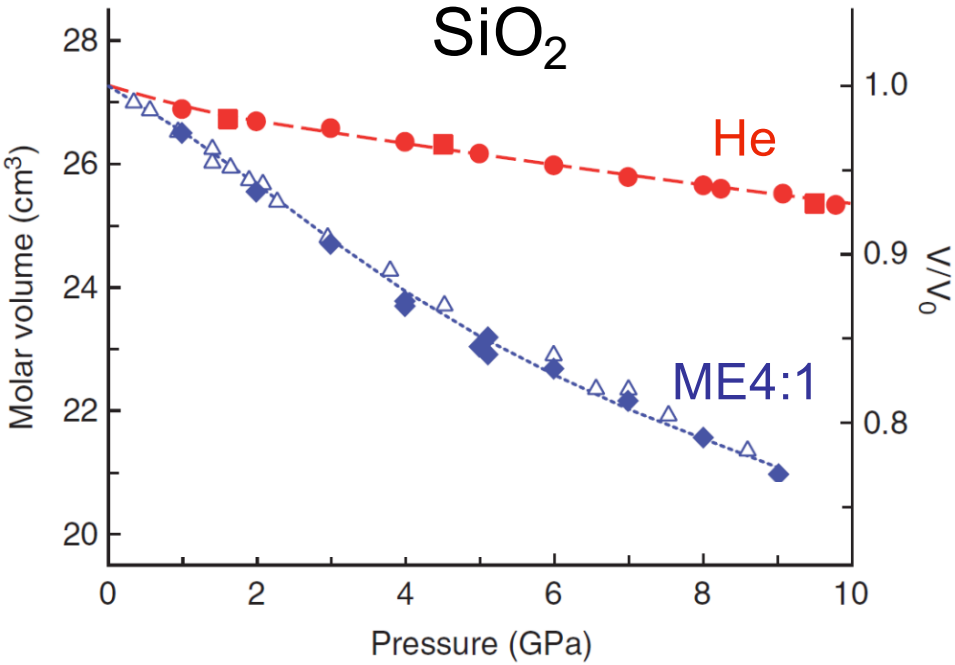
[Sato et al. Nature Comm. 2011
& Shen et al. PNAS 2011]



He

ME4:1

V(P)



He solubility much higher
than that predicted by Langmuir model

Rare gases adsorption in v-SiO_2 by Brillouin spectroscopy

1) huge amount of He and Ne atoms could be adsorbed

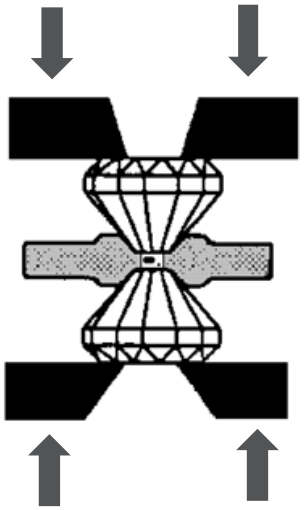
2) swelling of the silica network upon adsorption

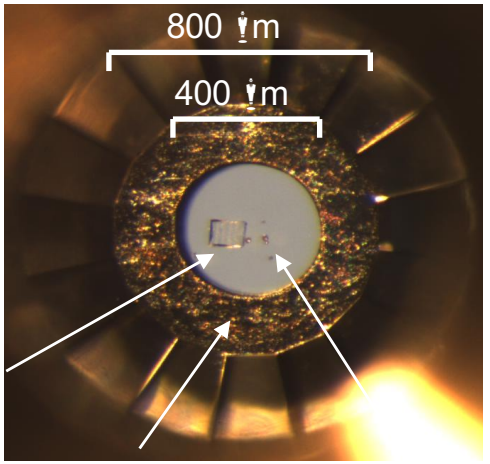
3) adsorption-desorption kinetics

4) applicability of a poro-mechanical approach

in situ high pressure Brillouin measurements

- Diamond Anvil Cell (0 - 10 GPa, 300 K)





v-SiO_2 sample

gasket (Re)
thickness ~ 200 µm

ruby
(pressure gauge)

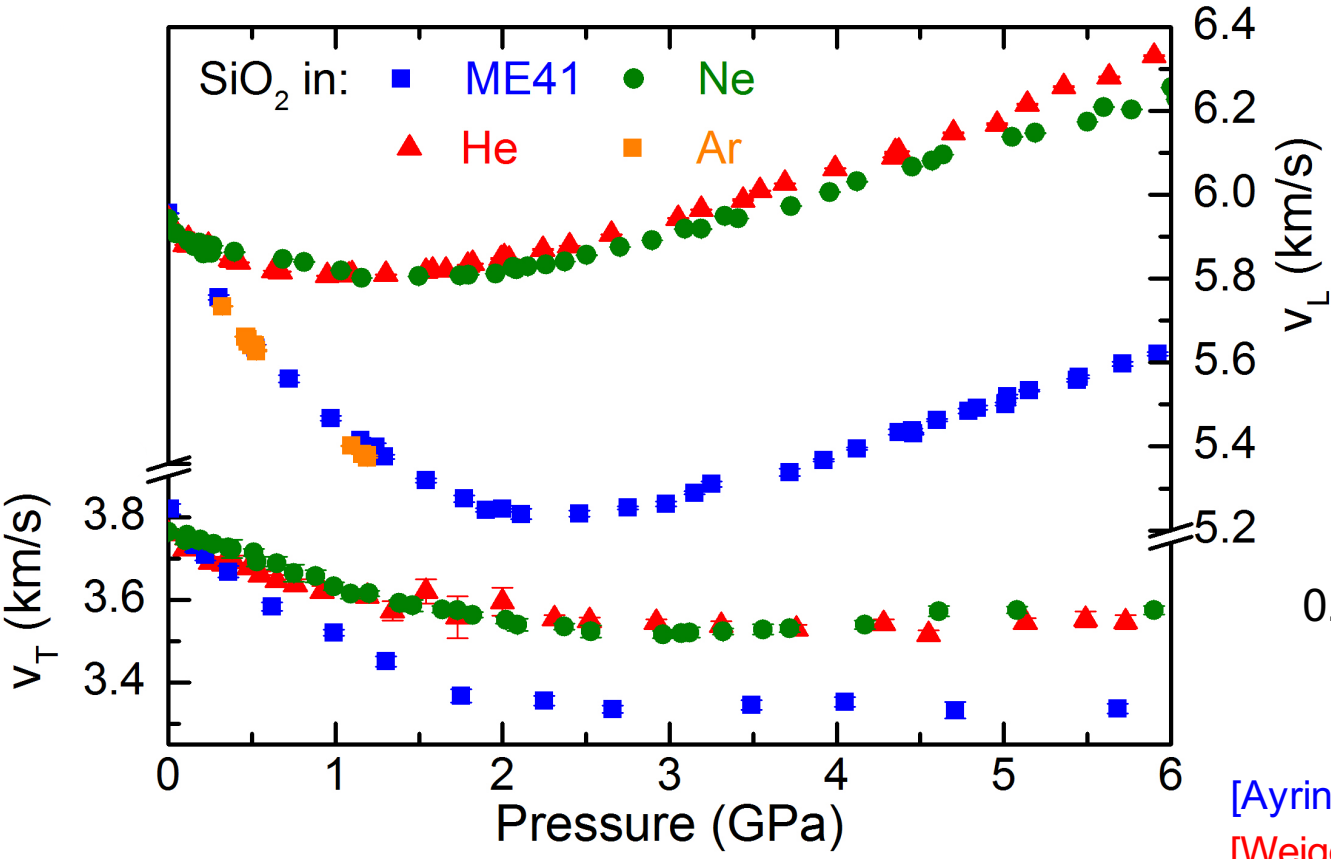
Pressurizing fluid :

- rare gas: He, Ne, Ar
- alcoholic mixture: ME 4:1

- Brillouin Light Scattering
  (inelastic scattering of light caused by the elastic waves of matter)

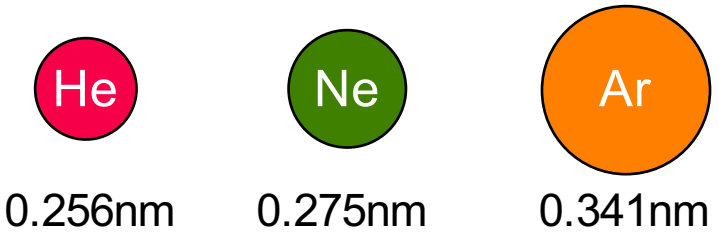
→ - sound velocities: $v_L(P)$, $v_T(P)$
- refractive index: $n(P)$

Sound velocities by Brillouin light scattering



- Min. around 2GPa strongly reduced

Atomic diameters :



[Ayrinhac et al. PRB 2011]
[Weigel et al. PRL 2012]
[Coasne, Weigel et al. JPC (2014)]

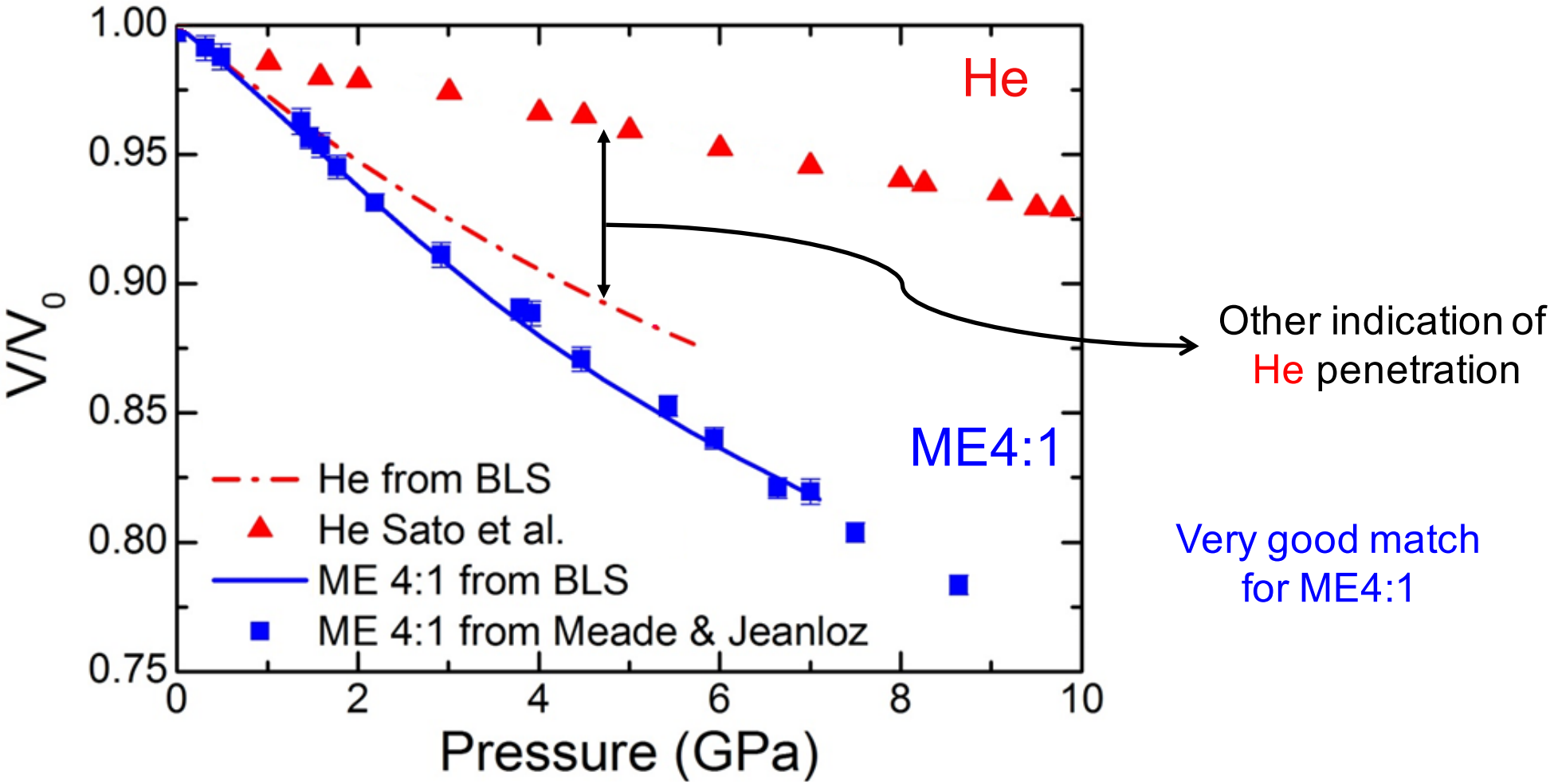
Volume variations from sound velocities

$$\chi = B^{-1} = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,n}$$

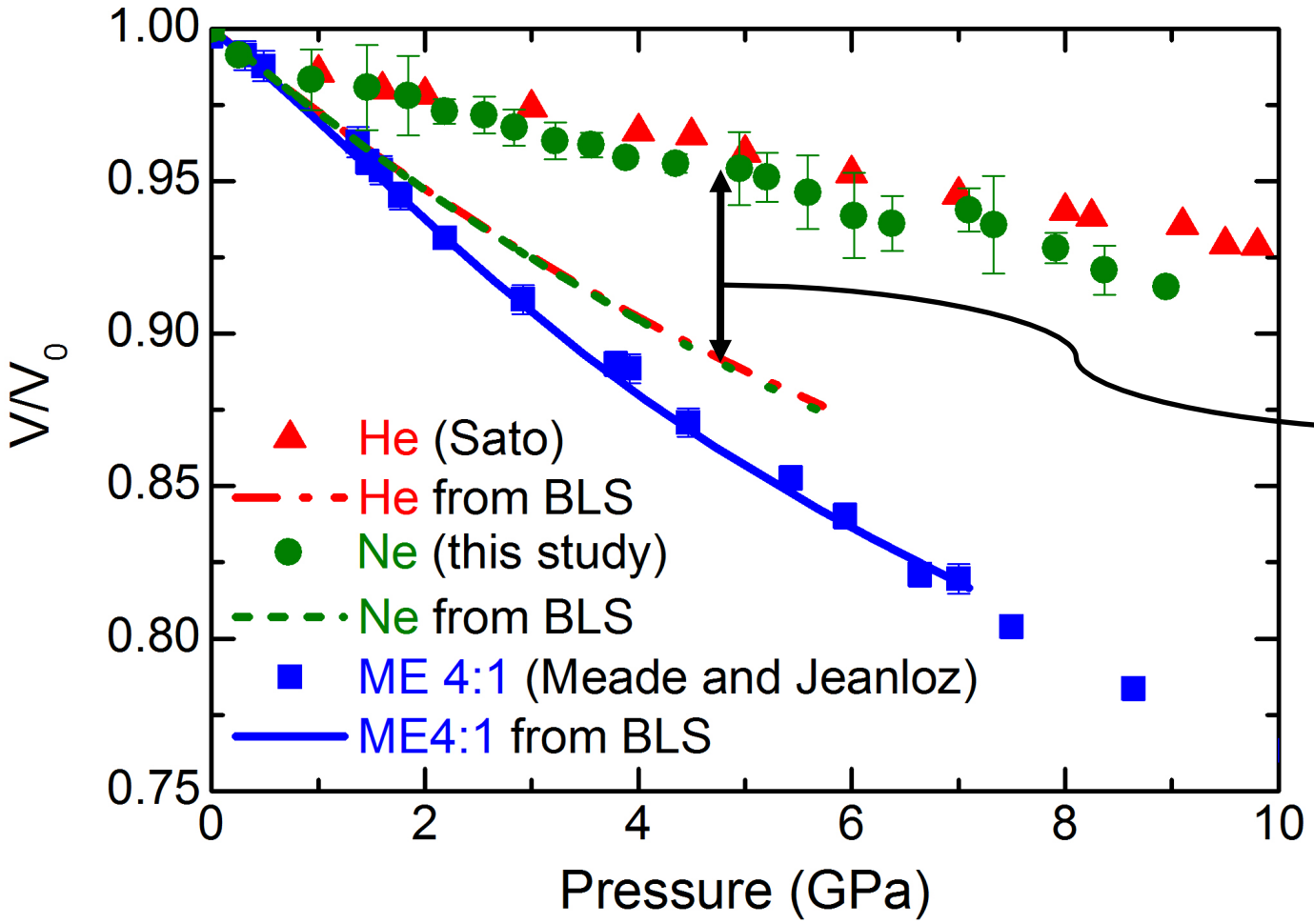
$$B = \rho\left(v_{LA}^2 - \frac{4}{3}v_{TA}^2\right)$$

$$\rho V = \text{cste}$$

$$\frac{V(P)}{V_0} = \left[1 + \frac{1}{\rho_0}\int_{P_0}^{P} \frac{dP}{v_{LA}^2(P) - \frac{4}{3}v_{TA}^2(P)}\right]^{-1}$$



Volume variations from sound velocities



Indication of
He/Ne penetration:

Very good match
for ME4:1

Estimate of the adsorbed He/Ne quantity

From optical index

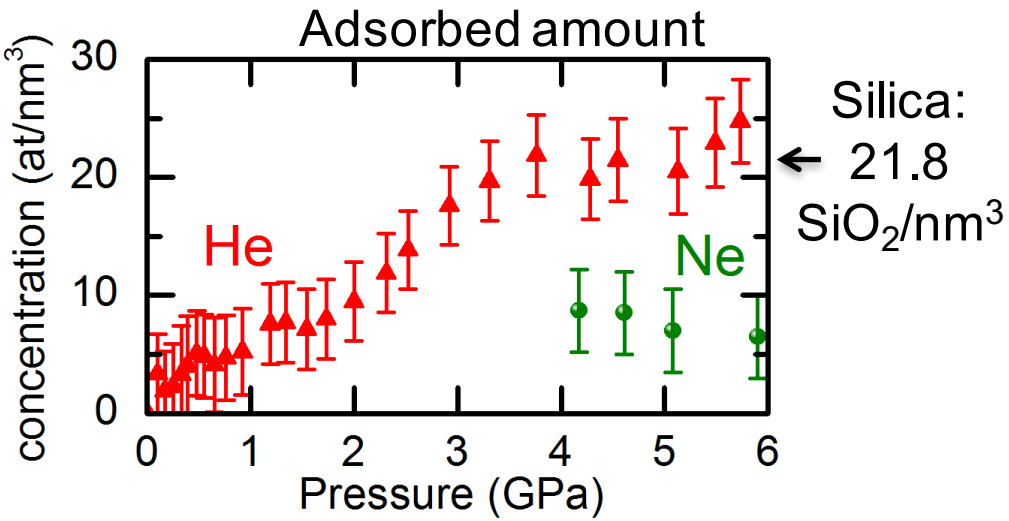
$$3\varepsilon_0 \frac{n^2-1}{n^2+2} = N_{SiO_2}\alpha_{SiO_2} + N_{Fluid}\alpha_{Fluid}$$

available from observed volume change in He or Ne

?

polarisability of the silica skeleton

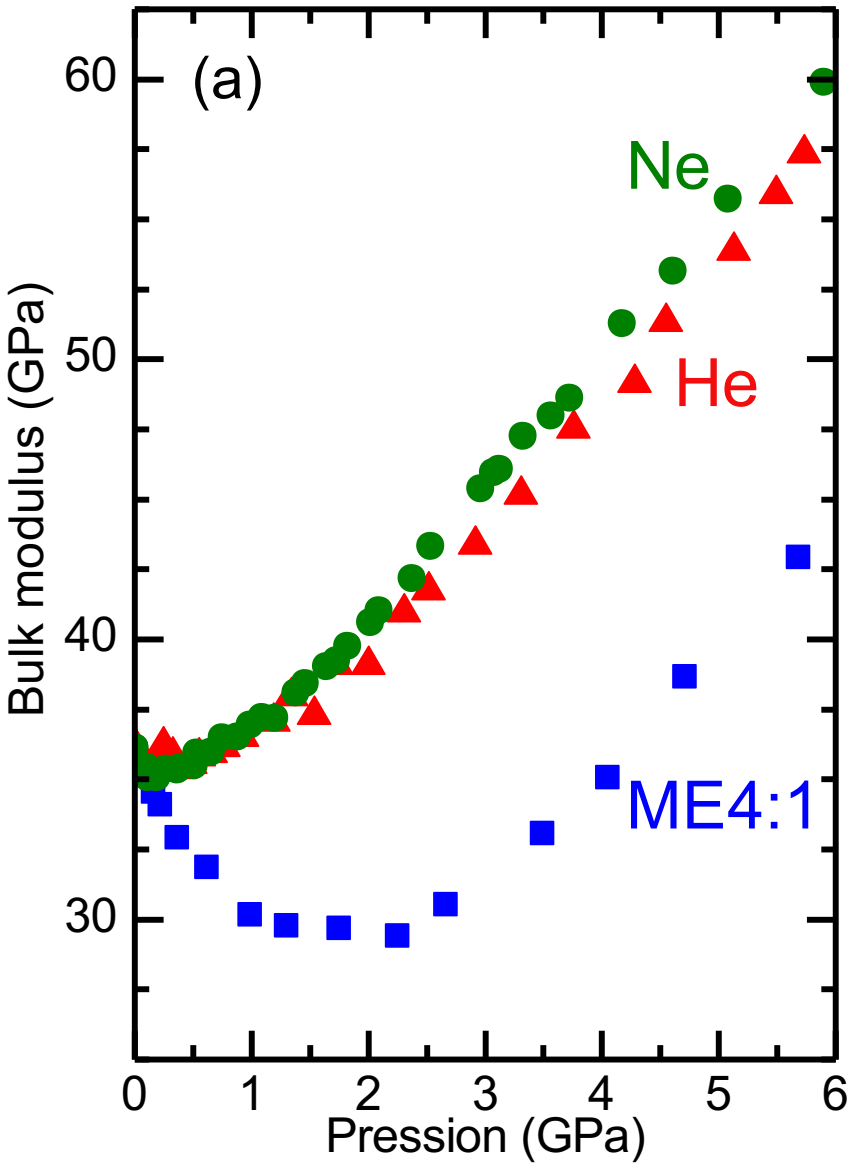
$$\alpha_{He} = \varepsilon_0 2.6\times10^{-24}\,\mathrm{cm}^3$$
$$\alpha_{Ne} = \varepsilon_0 4.7\times10^{-24}\,\mathrm{cm}^3$$



↗1 at. He / SiO_2 !

[Coasne, Weigel et al. JPC (2014)]

Bulk modulus



$$B = \rho\left(\mathrm{v}_L^2 - \frac{4}{3}\mathrm{v}_T^2\right)$$

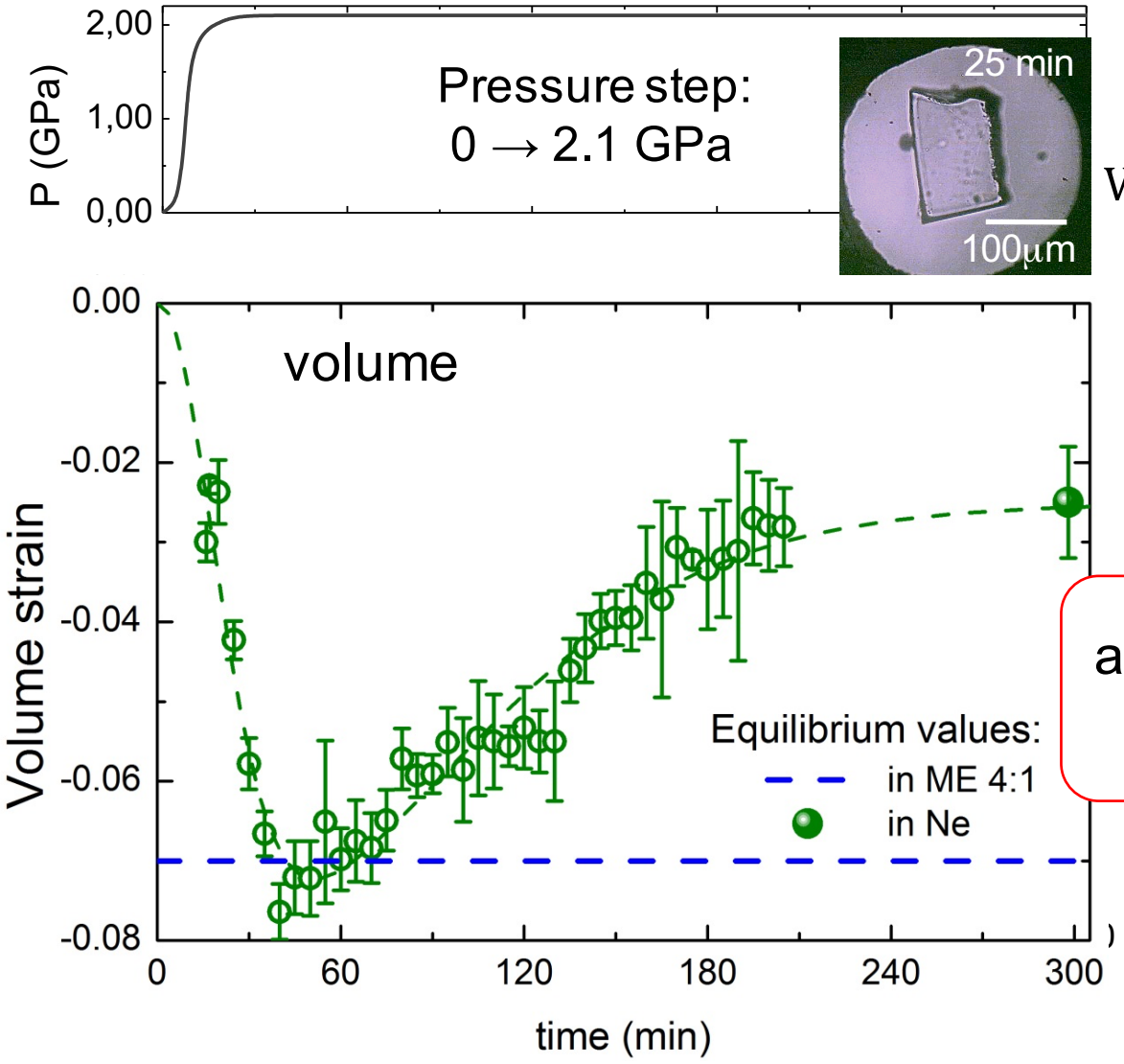
- Anomalous min. of B completely suppressed in He and Ne

  local structural changes making the network more compliant no longer allowed

  the rare gas atoms penetrate into the interstitial voids and prevent their collapse

Ne adsorption kinetics

Response to a fast pressure step ?



Diffusion coeff. at ambient P

$D_{He} \approx 2{,}9.10^{-8}\ cm^2.s^{-1}$

$D_{Ne} \approx 10^{-12}\ cm^2.s^{-1}$

[Shelby, 1976]

$$V(P) = S(P)^{3/2}$$

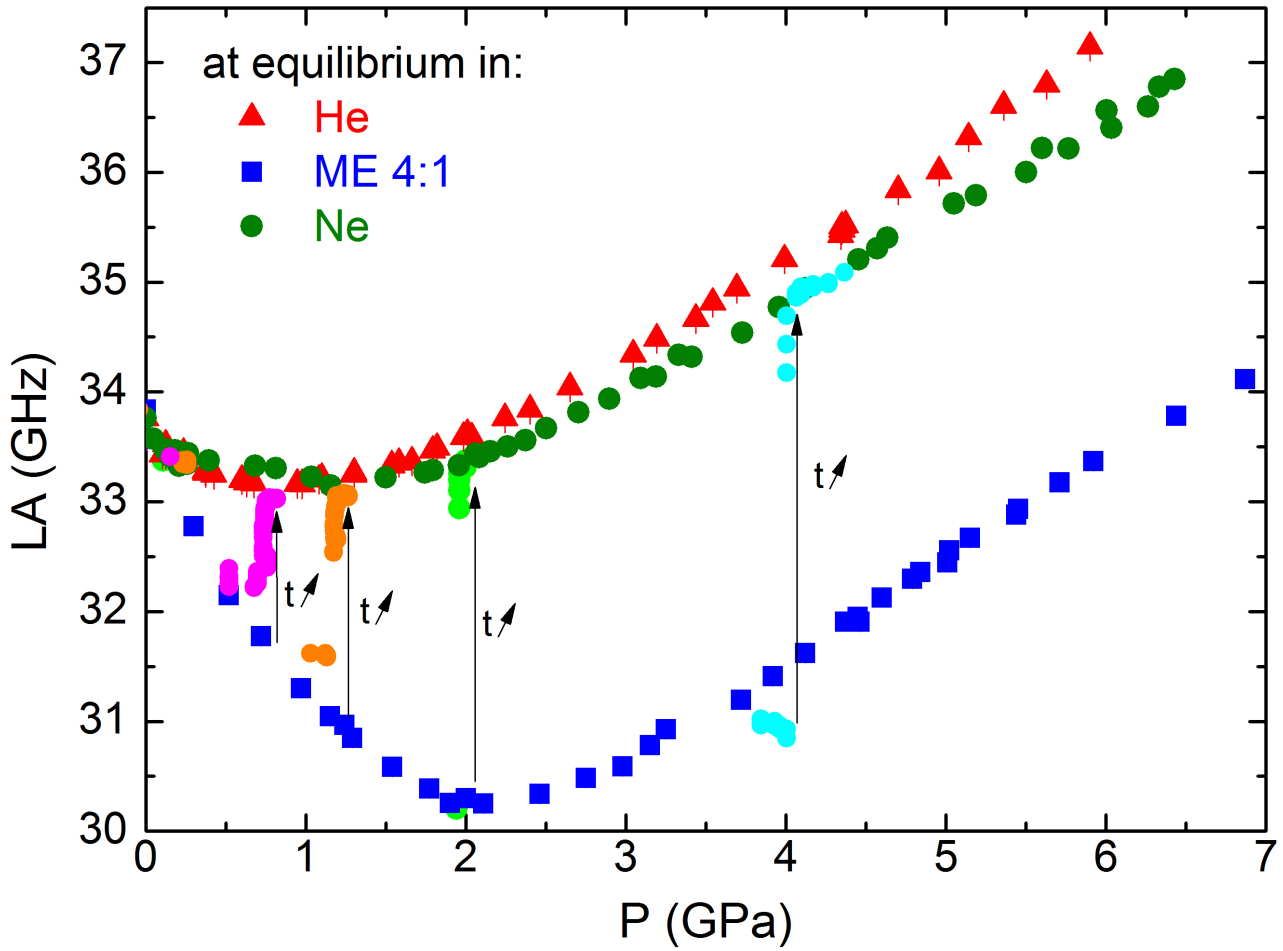
adsorption-induced swelling of the SiO_2 network

Ne adsorption kinetics

Response to fast pressure steps from ambient to :

- 0.8 GPa
- 1.2 GPa
- 2 GPa
- 4 GPa

LA Brillouin frequency



- In the early stages:
  equil. value in ME4:1
- Final stages:
  equil. value in Ne

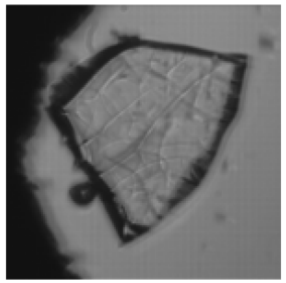
Equilibration time:
@ 0.8 GPa :10h
@ 1.2 GPa: 3.5h
@ 2GPa: 2h
@ 4GPa: 1.5h

Adsorption - desorption

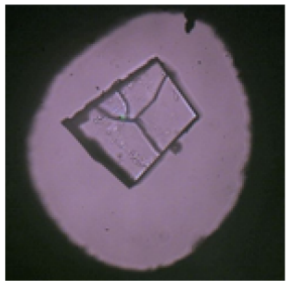
Adsorption : ΔP^{+} = +0,8 GPa

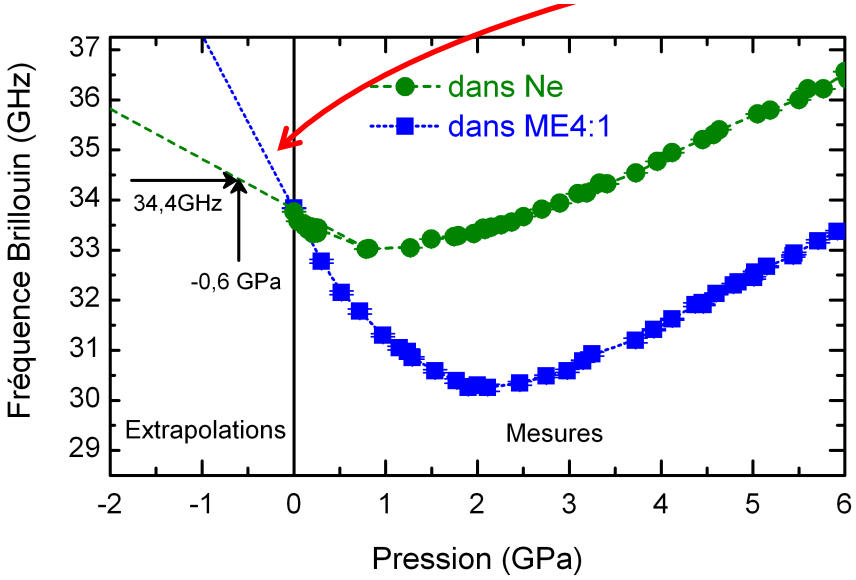
Desorption : ΔP^{-} = -0,8 GPa

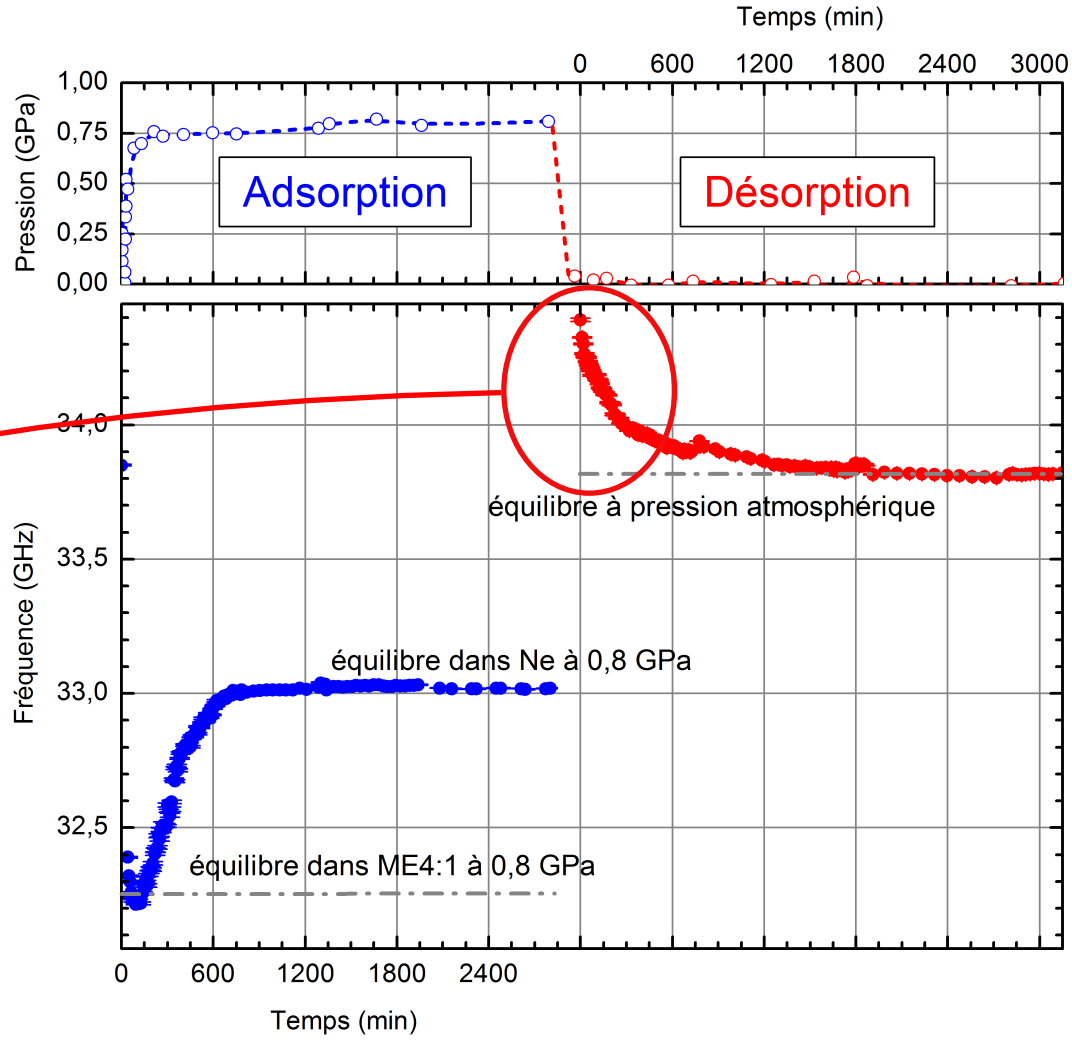
ΔP^{-} = -4,3 GPa



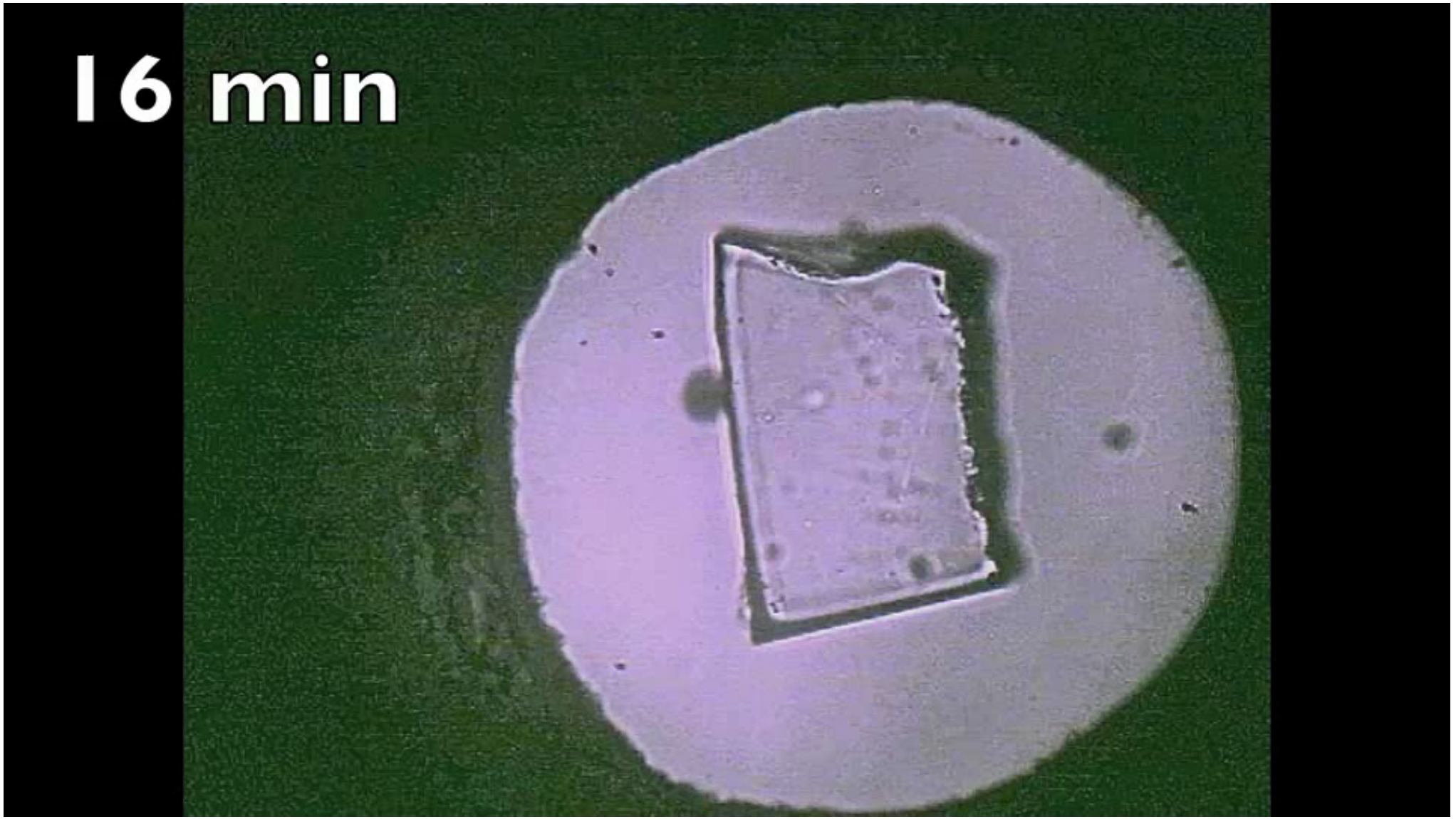
ΔP^{-} = -9,0 GPa





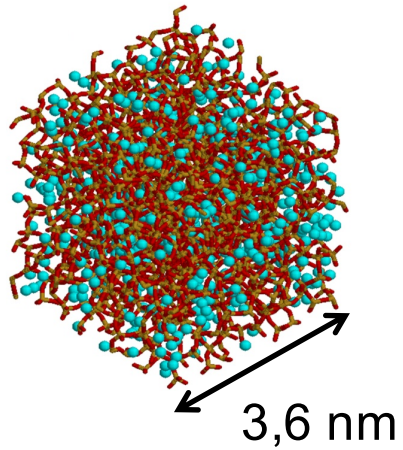


Ne diffusion edge (pressure step: 0 → 2.1 GPa)



Poromechanics

GCMC simulation in the frame of poromechanics
to probe the deformation of v-SiO_2 upon adsorption



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MultiScale Material Science for Energy and Environment
LiPhy Grenoble

Poromechanics

- Classical poroelasticity (macropores, fluid molecules in their bulk state)

$$\sigma = B\epsilon - bP$$
$$\varphi = \phi - \phi_0 = b\epsilon + \frac{P}{N}$$
$$s_{ij} = 2Ge_{ij}$$

Biot (1941), Coussy (2004)

- Generalized poroelasticity (micro and mesopores, confined fluid molecules)

$$\sigma = B\epsilon - \frac{\partial}{\partial \epsilon}\left[\int_0^P n\, V_b\, dp\right]_{P,e_{ij}}$$

Brochard et al. JMPS **60**, 606 (2012)

$n(\epsilon, p)$: amount of fluid atoms adsorbed at given p and ϵ

DAC conditions: $\boldsymbol{\sigma = -P}$
(so-called "unjacketed" conditions)

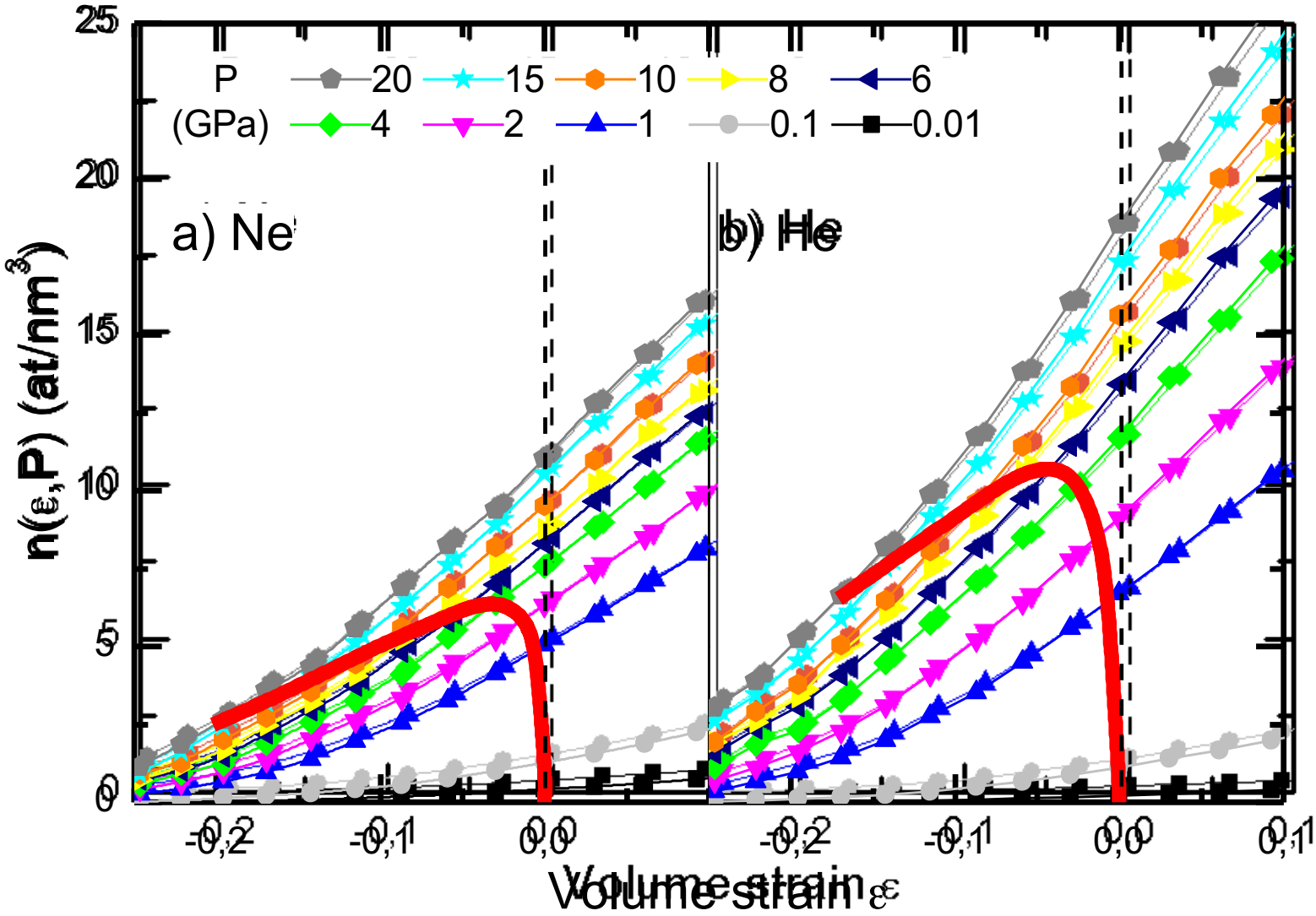
$$\epsilon^u(P) = -\frac{P}{B} + \frac{1}{B}\int_0^P \left.\frac{\partial n}{\partial \epsilon}\right|_{\epsilon^u} V_b(p)dp$$

volume strain can be *predicted* from adsorption isotherms

Adsorption isotherms

GCMC simulation of $n(\epsilon, P)$, ϵ and P being independent external variables
(CHIK potential for SiO_2 / LJ potential for He and Ne)

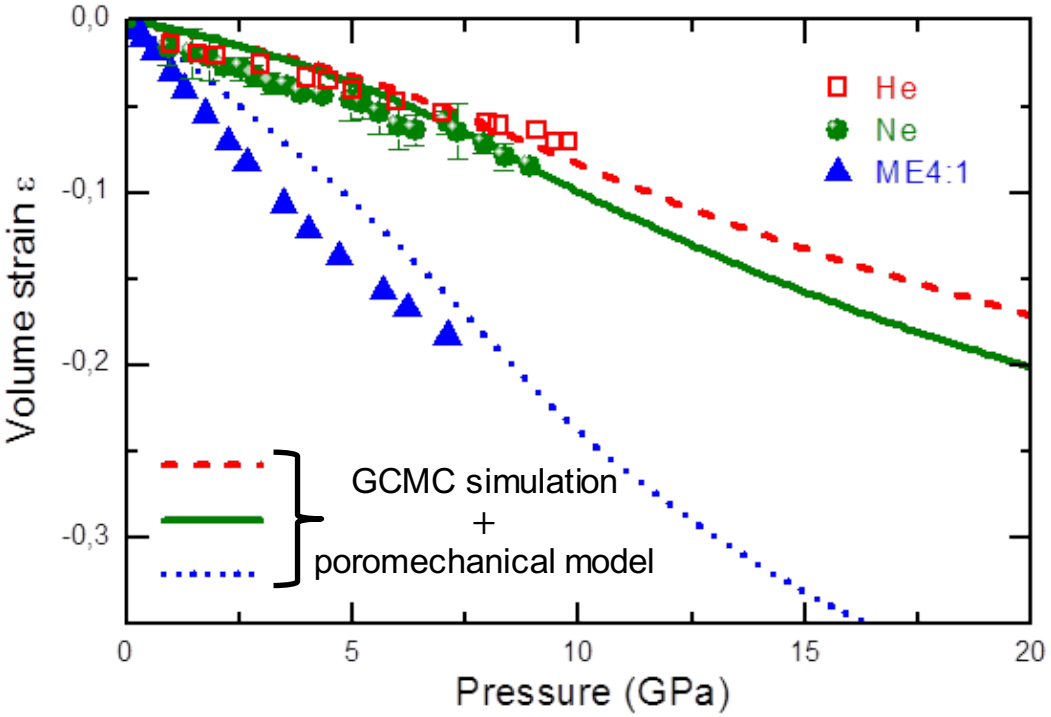
Silica:
21.8
SiO_2/nm^3



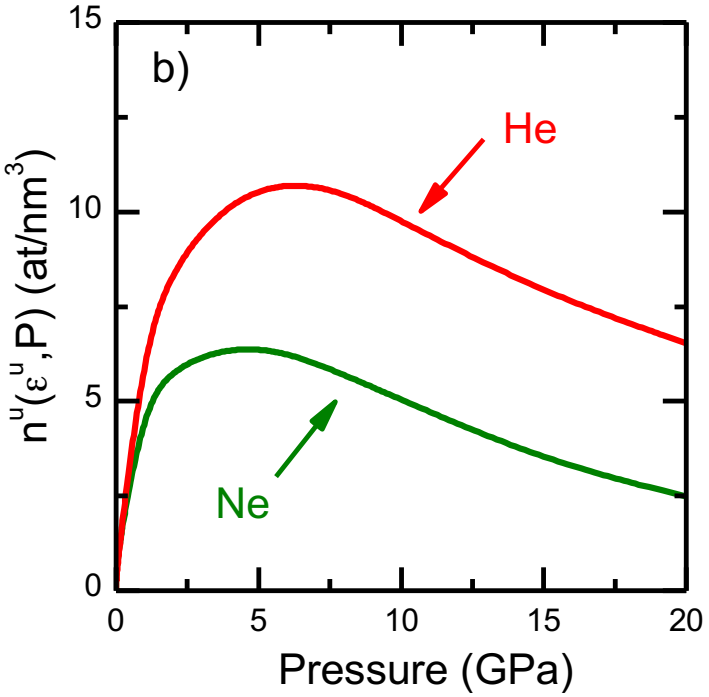
Red line: predictions of poromechanics for $\epsilon^u(P)$ and thus $n^u(P)$

Predictions of poromechanics for $\epsilon^u(P)$ and $n^u(P)$

$\epsilon^u(P)$



$n^u(P)$



from refractive index at 6 GPa:

$n^u \simeq 20 \pm 4$ at/nm^3 in He

$n^u \simeq 7 \pm 4$ at/nm^3 in Ne

Coasne, Weigel et al.
J. Phys. Chem. **B118**, 14519 (2014)

Summary

- Huge amount of incorporated He / Ne in v-SiO_2

  open and flexible structure of silica glass allowing gas atoms to distend the network

- Swelling of the silica network upon fluid adsorption

- Adsorption-desorption kinetics by Brillouin spectroscopy

- Poro-mechanical approach

Thank you for your attention!

Acknowledgements

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  - Sébastien CLEMENT and Rémy VIALLA
  - Christelle DUPAS

- Collaborations:
  - Alain Polian
  - Benoit Coasne
  - Julien Haines, Jerome Rouquette

$$\omega_1^2 = \frac{\alpha}{m}\cos^2(\theta/2) \qquad \omega_3^2 = \omega_1^2 + \frac{4\alpha}{3M} \qquad \omega_2^2 = \frac{\alpha}{m}\sin^2(\theta/2)$$

$m = 16$
$M = 28$