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Formation and evolution of bubbles in ascending magmas: Insight from decompression experiments in the systems rhyolite-H_2O and basalt-CO_2

Didier LAPORTE

In collaboration with: Ariel PROVOST, Nicolas CLUZEL, Mohirisa HAMADA,
Manon HARDIAGON, Catherine MOURTADA-BONNEFOI

ClerVolc Centre Clermontois de Recherche sur le Volcanisme

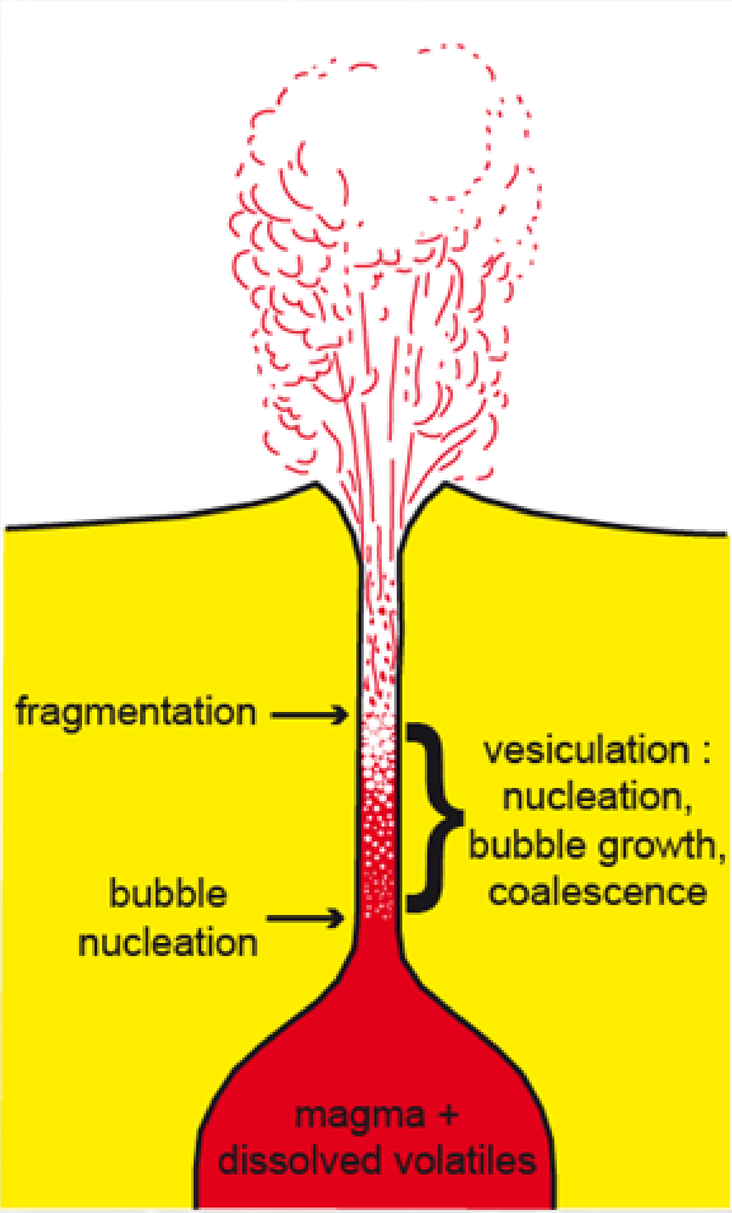
lmv Laboratoire Magmas et Volcans

AGENCE NATIONALE DE LA RECHERCHE ANR

I. Introduction: Importance of the kinetics of magma degassing

II. Effect of ascent rate on homogeneous bubble nucleation in the system rhyolite-H_2O

III. Homogeneous bubble nucleation in the system basalt-CO_2



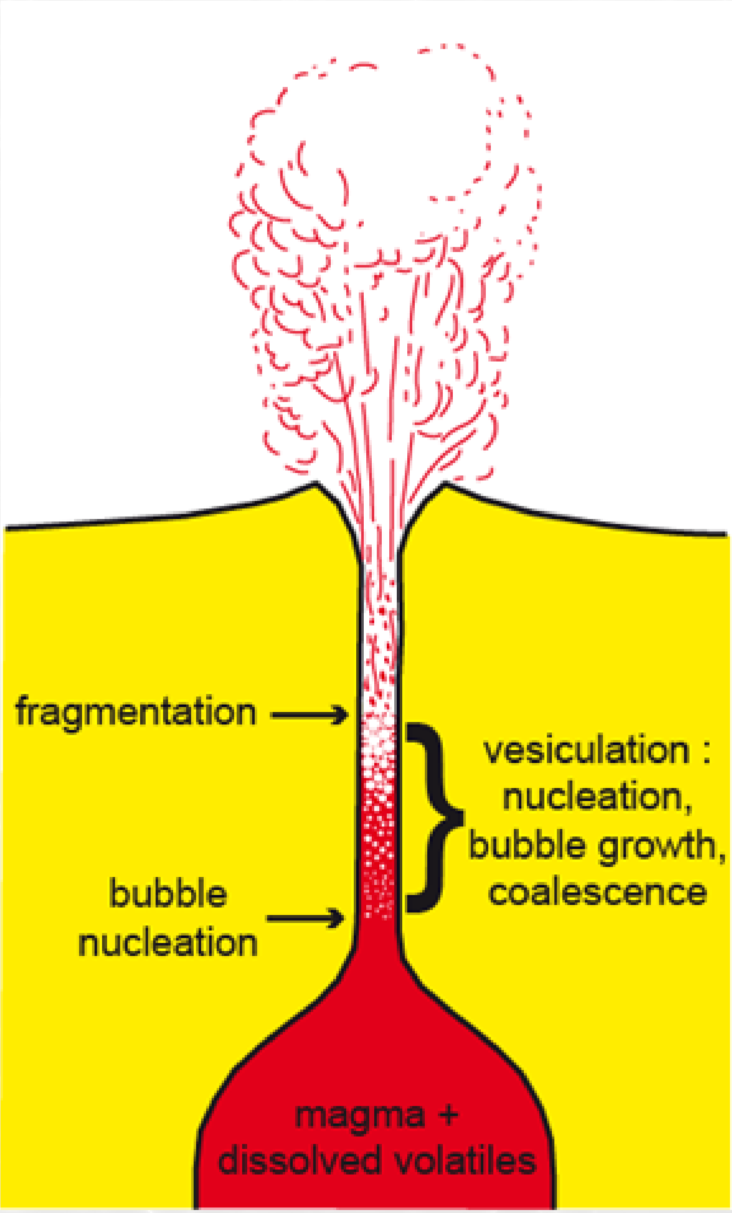
The importance of magma degassing:

⇒ Exsolution + expansion of volatiles = the main driving forces for magma ascent and volcanic eruptions

⇒ Magmas release huge amounts of volatiles (H_2O, CO_2, SO_2) into the atmosphere:

  ⇒ Impact on weather and long-term climate → mass extinctions…

  ⇒ Formation and composition of planetary atmospheres

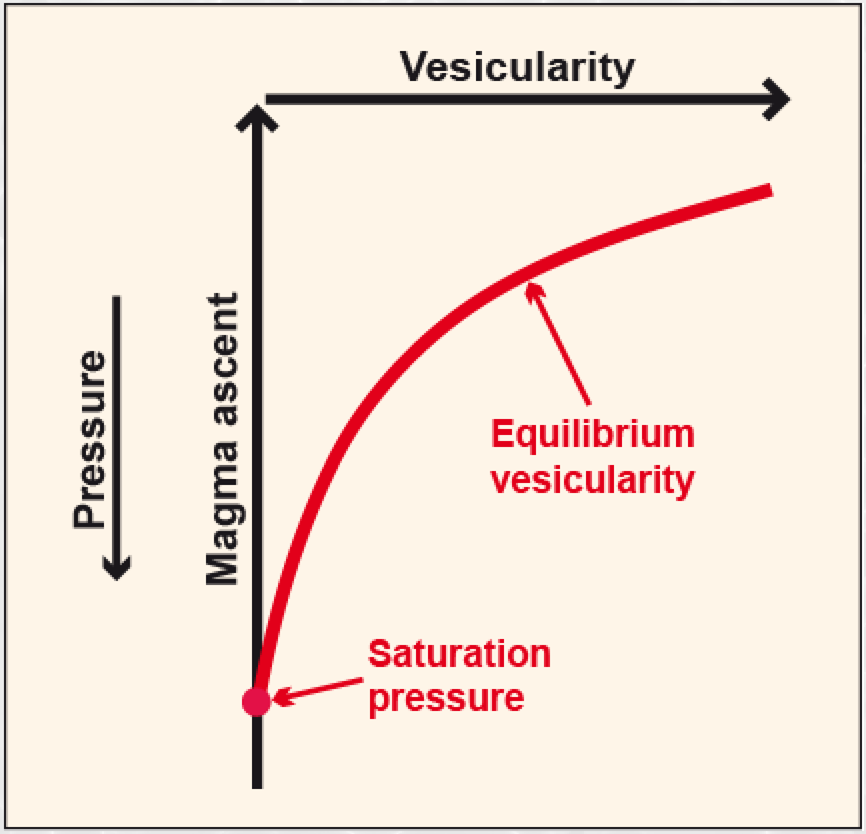


⇒ This talk will focus on processes occurring during magma ascent, specially on the first stage of degassing: bubble nucleation

⇒ Pressures of bubble nucleation, P_N?

⇒ Bubble number densities, BND (numbers of bubbles formed per unit volume of liquid)?

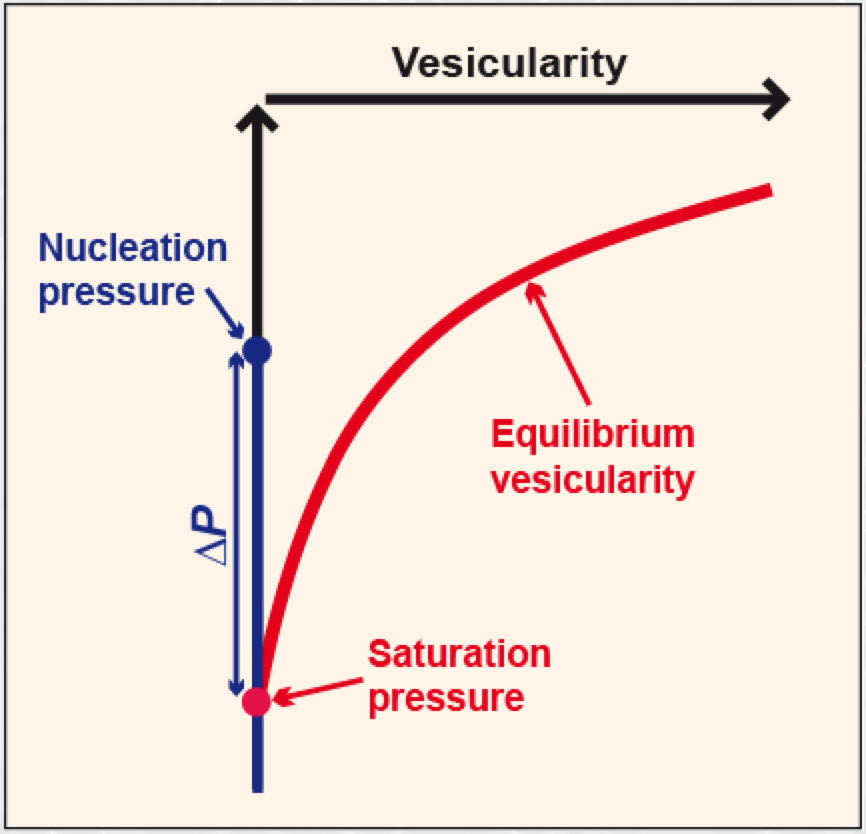
P_N and BND: control the kinetics of degassing



Equilibrium degassing

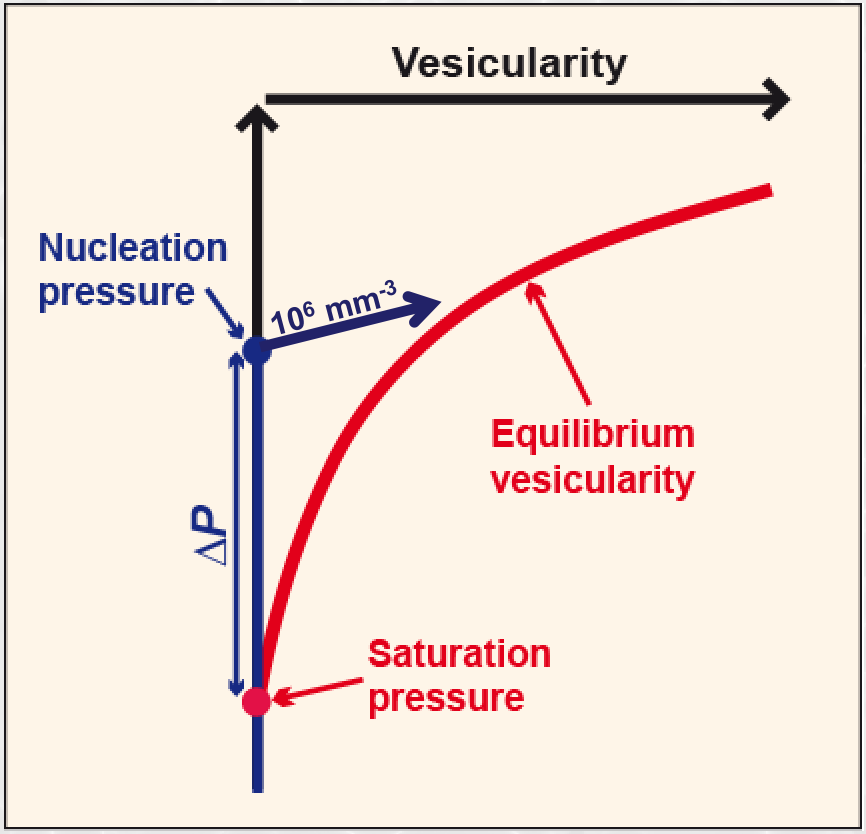
$$\text{Vesicularity} = \frac{\text{Volume of bubbles}}{\text{Total volume}}$$

P_N and BND: control the kinetics of degassing



1) Delayed bubble nucleation due to the effect of surface tension

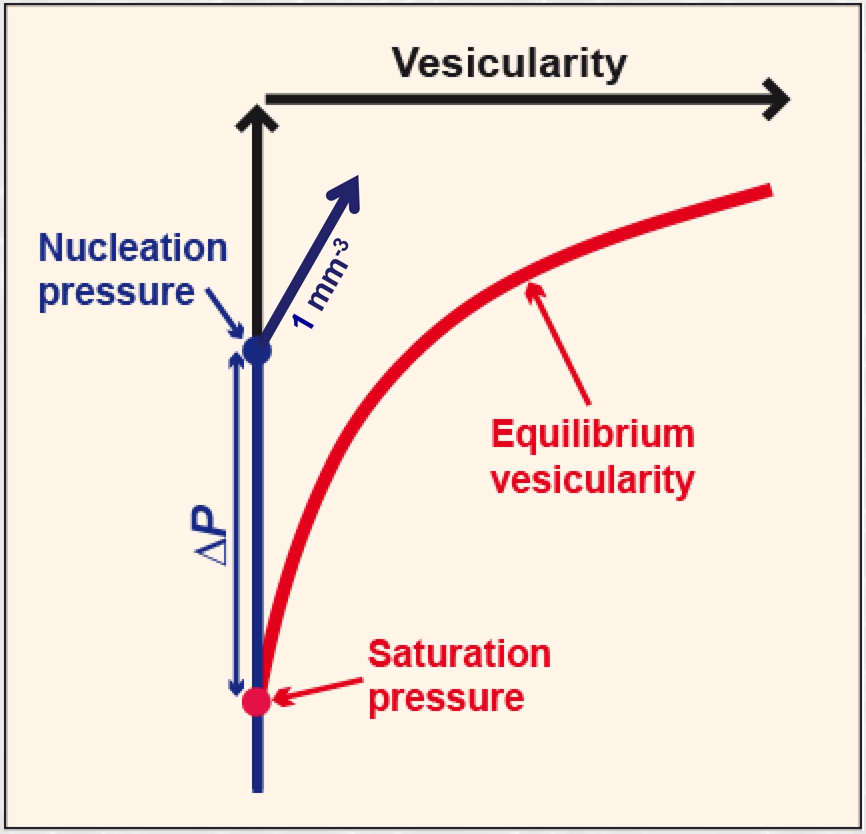
P_N and BND: control the kinetics of degassing



2) BND controls the efficiency of degassing:

Large BND ⇒ degassing close to equilibrium

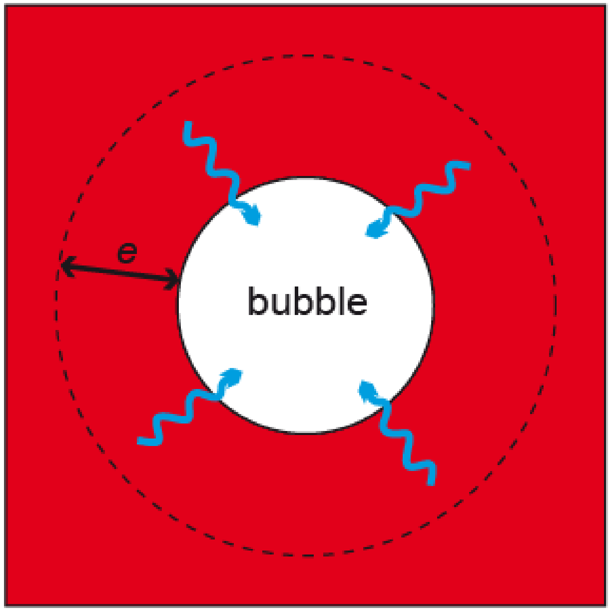
P_N and BND: control the kinetics of degassing



2) BND controls the efficiency of degassing:

Small BND ⇒ disequilibrium degassing

Importance of the number density of bubbles, *N* : diffusion length scale e vs. mean bubble-to-bubble distance *d*

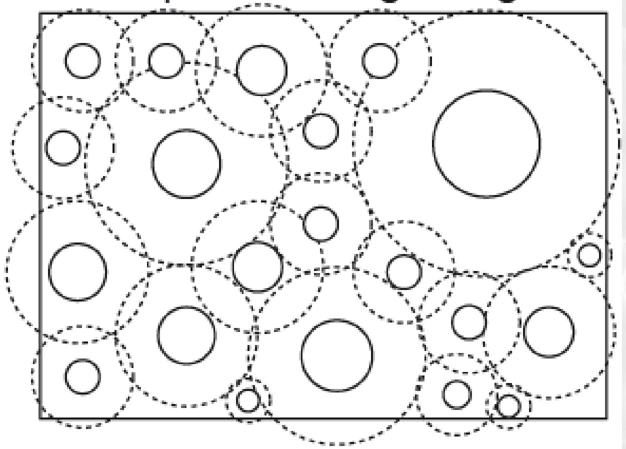


$$e = \sqrt{2D\,t}$$

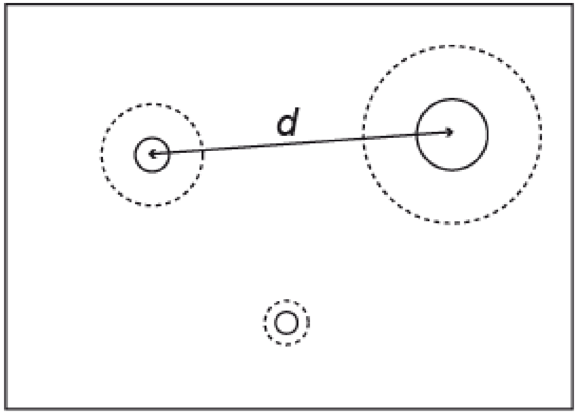
e: length scale of diffusion of volatile components
D : diffusion coefficient (for water : 10^{-11} m^2/s)
t : time scale of vesiculation (*t* = 100-10000 s)

e = 0.05-0.5 mm

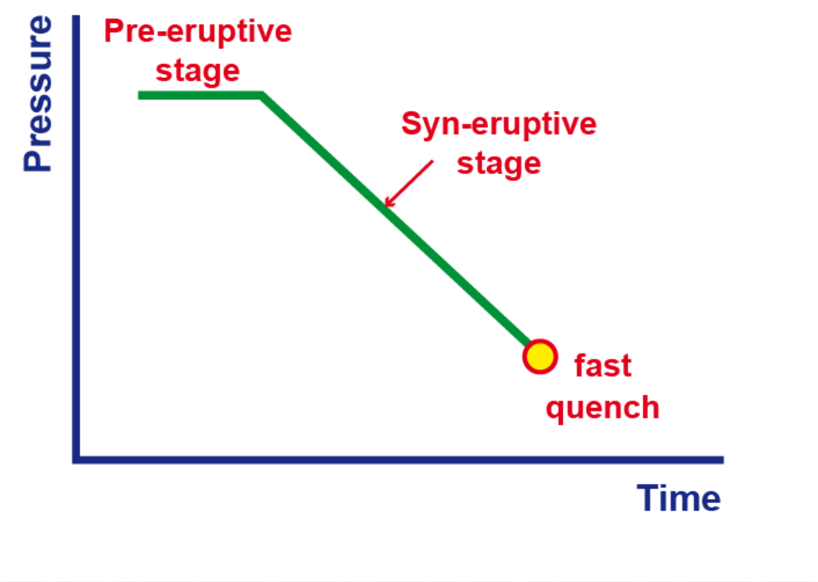
Large *N* : *d* << 2*e*
equilibrium degassing

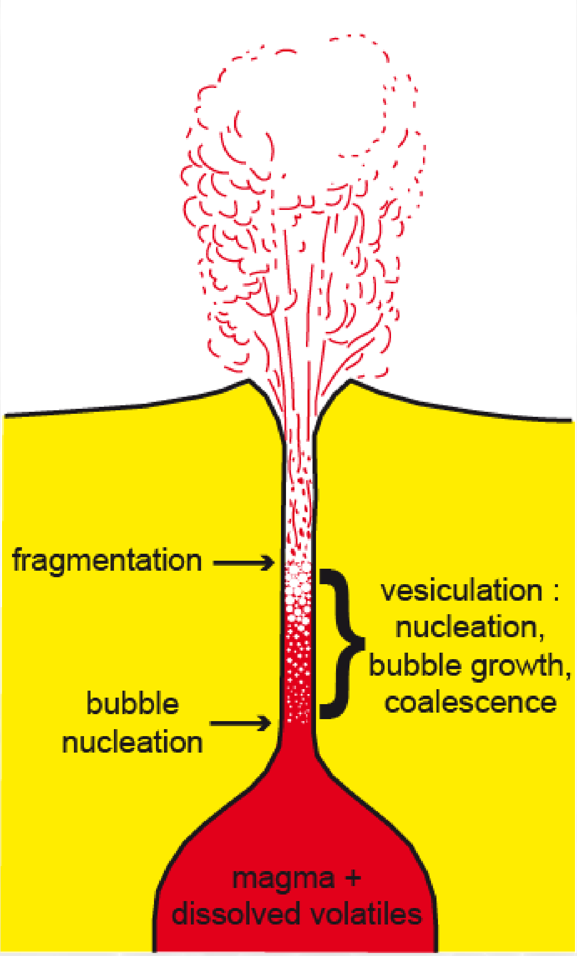


Small *N* : *d* >> 2*e*
disequilibrium degassing



Magma ascent and degassing can be simulated in the laboratory by running decompression experiments at high pressure and temperature

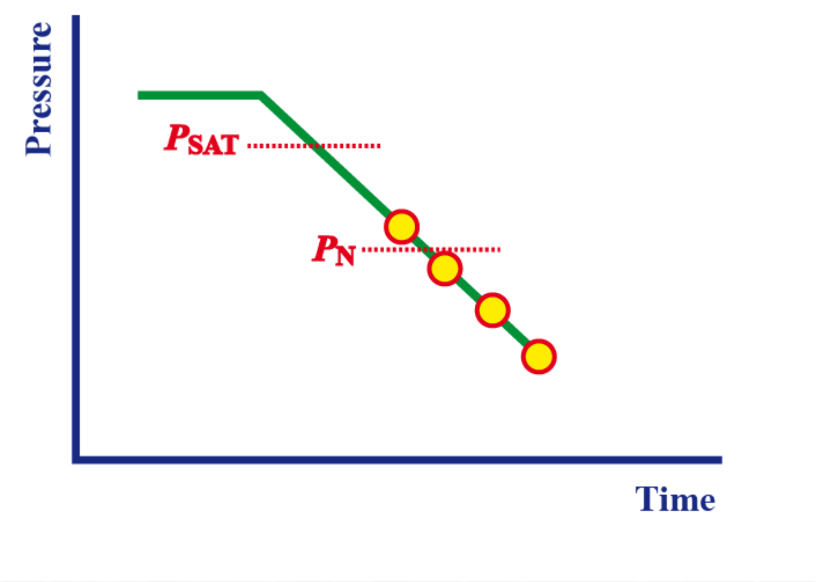


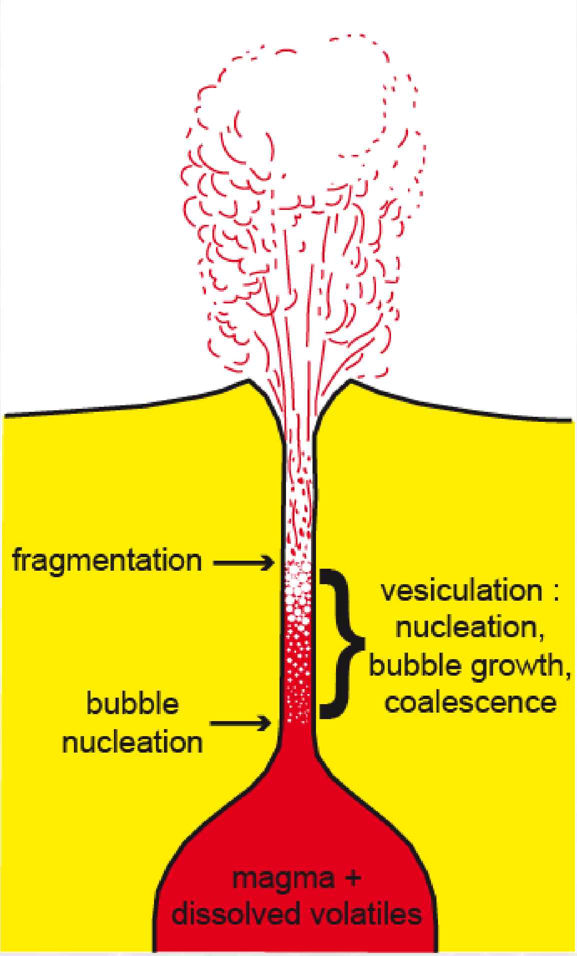


Experiments quenched at different *P*:

⇒ bracket the nucleation pressure

⇒ follow the evolution of the main textural and chemical parameters





I. Introduction: Importance of the kinetics of magma degassing

II. Effect of ascent rate on homogeneous bubble nucleation in the system rhyolite-H_2O

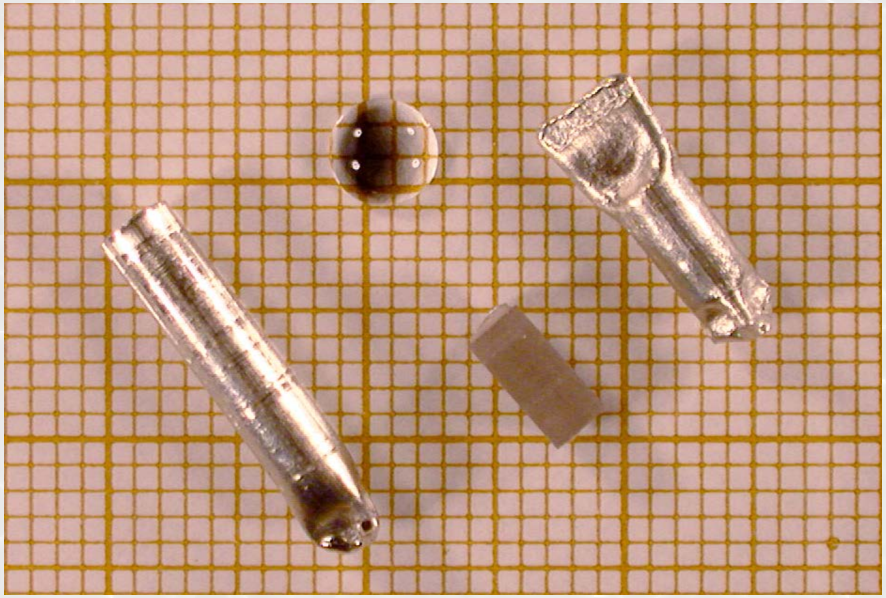
III. Homogeneous bubble nucleation in the system basalt-CO_2

⇒ Starting material = cores drilled into a rhyolitic obsidian

⇒ Saturated in water before decompression

SiO_2	**76.51**
Al_2O_3	**12.56**
Fe_2O_3	**0.78**
MgO	**0.01**
CaO	**0.25**
Na_2O	**4.47**
K_2O	**4.24**
TiO_2	**0.03**
MnO	**0.07**
H_2O	**1.39**
CO_2	**200 ppm**
Cl	**634 ppm**
F	**710 ppm**
S	**< 100 ppm**

⇒ 2.5 mm O.D. cylinder



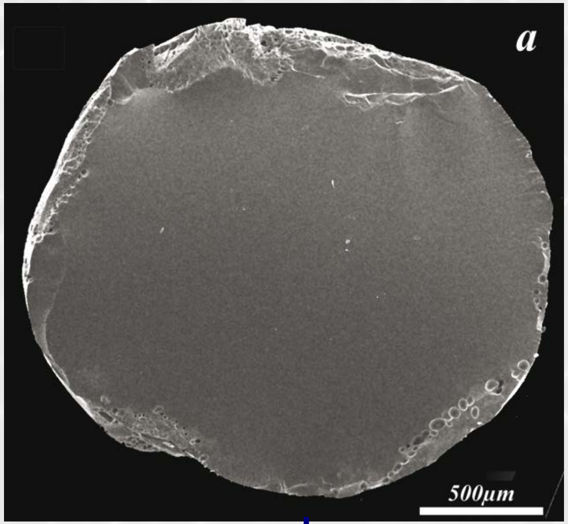
⇒ System: rhyolite + ≈ 7% H_2O; T = 800°C; P_{SAT} □ 240 MPa (Mourtada-Bonnefoi and Laporte, 2004; Hamada et al., 2010)

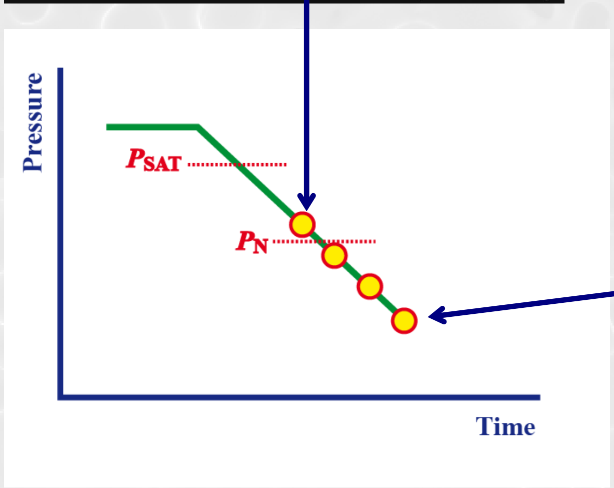
⇒ Decompression rates from 0.0278 to 90 MPa/s to quantify the effect of ascent rate on the kinetics of homogeneous bubble nucleation

⇒ 1 MPa/s (10 bar/s) is equivalent to an ascent rate of 40 m/s (for a liquid density of 2500 kg/m^3)

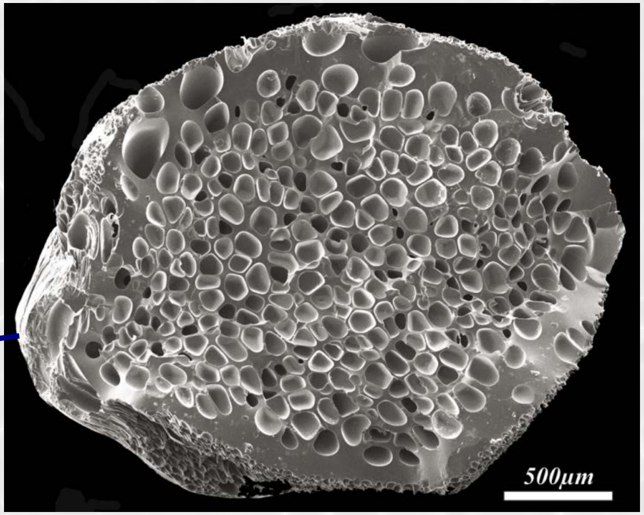
Nucleation pressures

No bubbles : $P > P_N$





Bubbly core : $P \leq P_N$



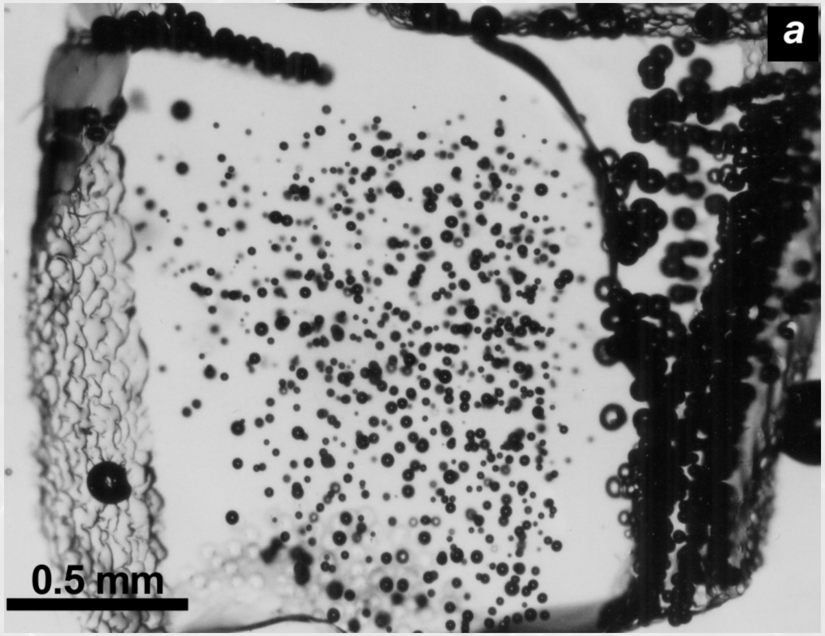
- ☐ $P_N = 90 \pm 2$ MPa in all series $\Rightarrow \Delta P$ (= P_{SAT} - P_N) = 150 MPa
- ☐ ΔP very large in the case of homogeneous bubble nucleation, and only very slightly dependent of decompression rate

Textural parameters

#A2

1 MPa/s

P_f = 79.2 MPa

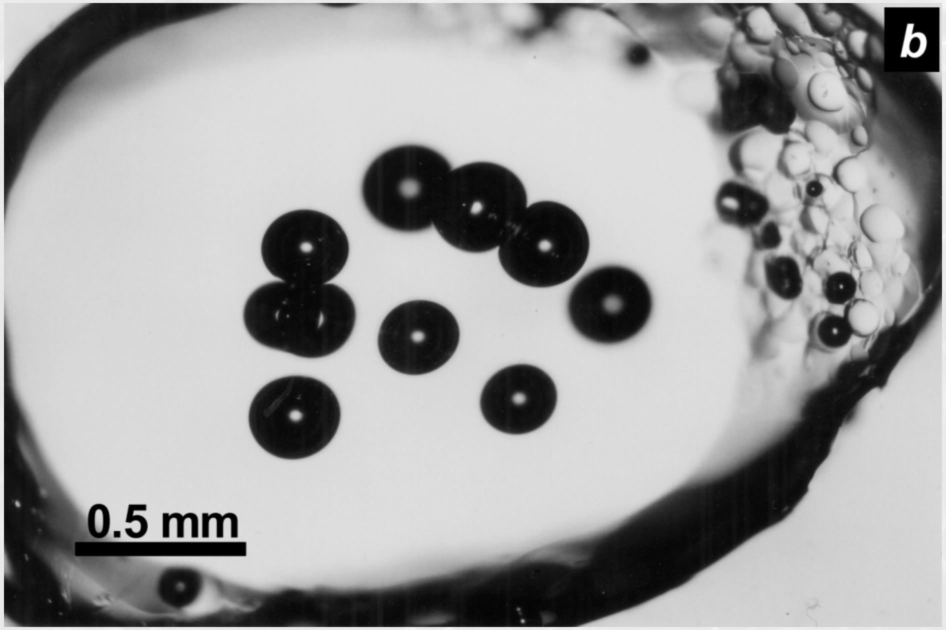


d = 23.1 μm, N = 2300 mm^{-3}

#C8

0.0278 MPa/s

P_f = 79.5 MPa

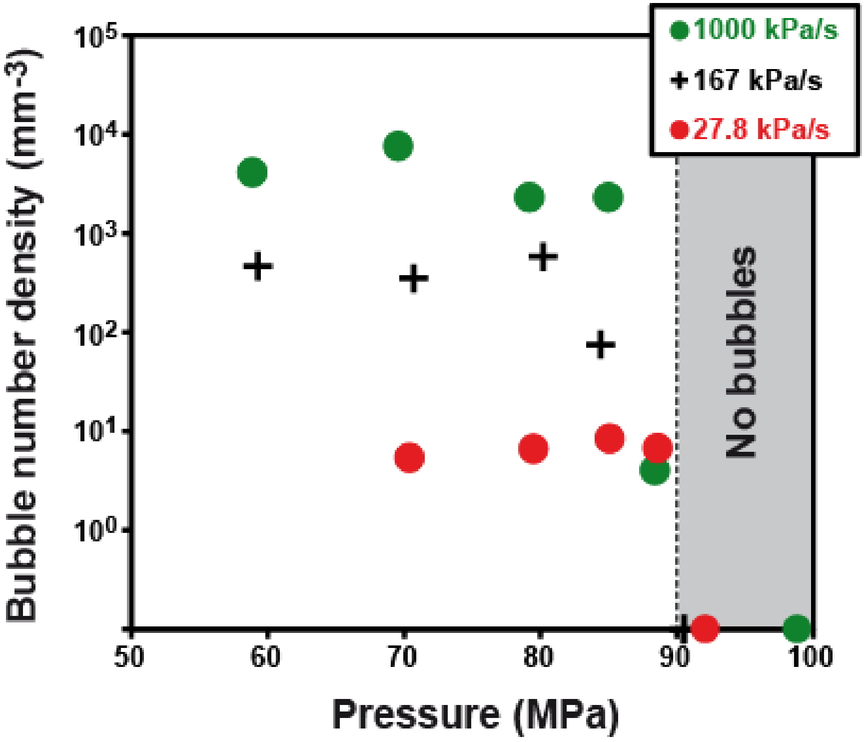


d = 258 μm, N = 6.6 mm^{-3}

Strong variations of bubble number density N and mean bubble diameter d as a function of decompression rate

Textural parameters

⇒ Below P_N, BND rapidly reaches a stationary value very sensitive to |dP/dt|.



Classical theory of nucleation:

Calculation of surface tension coefficient, σ_{LG} (N/m), from the nucleation pressure P_N

Hirth et al., 1970; Hurwitz and Navon, 1994; Cluzel et al., 2008

$$\boxed{J = J_0 \, e^{-\frac{16\pi\sigma_{\mathrm{LG}}^{3}}{3kT\left(P_{\mathrm{G}}^{*} - P_{\mathrm{L}}\right)^{2}}}}$$

$$\boxed{J_0 = \frac{2\Omega_{\mathrm{L}} n_0^{2} D_{\mathrm{H2O}}}{a_0}\sqrt{\frac{\sigma_{\mathrm{LG}}}{kT}}}$$

- Temperature
- Ω_L: volume of a H_2O molecule in the liquid (0.8 to 3.4×10^{29} m^{-3})
- n_0: number of H_2O molecules per m^3 of liquid
- a_0: distance between H_2O molecules
- D_{H2O} : diffusion coefficient (1.5×10^{-11} m^2/s)
- σ_{LG}: the unknown parameter (0.03-0.13 N/m)

Classical theory of nucleation:

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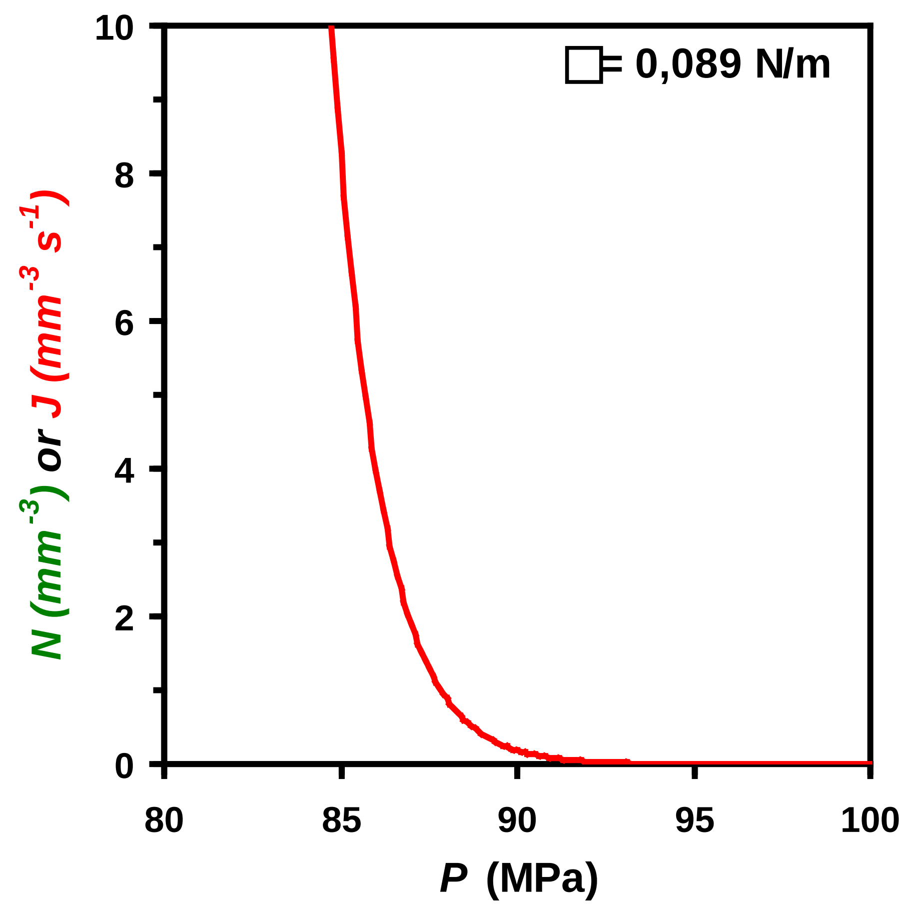

(1) Compute J as a function of P_L for a given σ_{LG}

(2) Integrate J over time to obtain the BND, N, for a given $|dP/dt|$

(3) Compute P_N (assuming that nucleation is detected when the BND exceeds 1 mm^{-3})

(4) Adjust σ_{LG} until the P_N computed matches the experimental value

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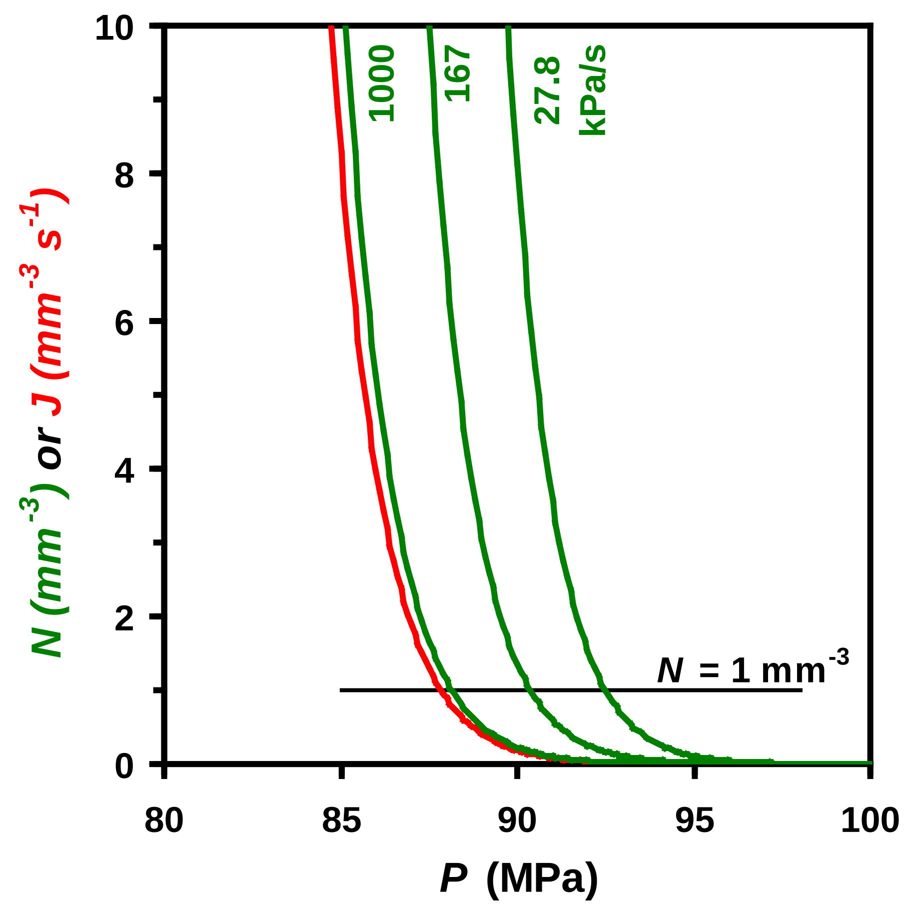

(1) Compute *J* as a function of P_L for a given σ_{LG}

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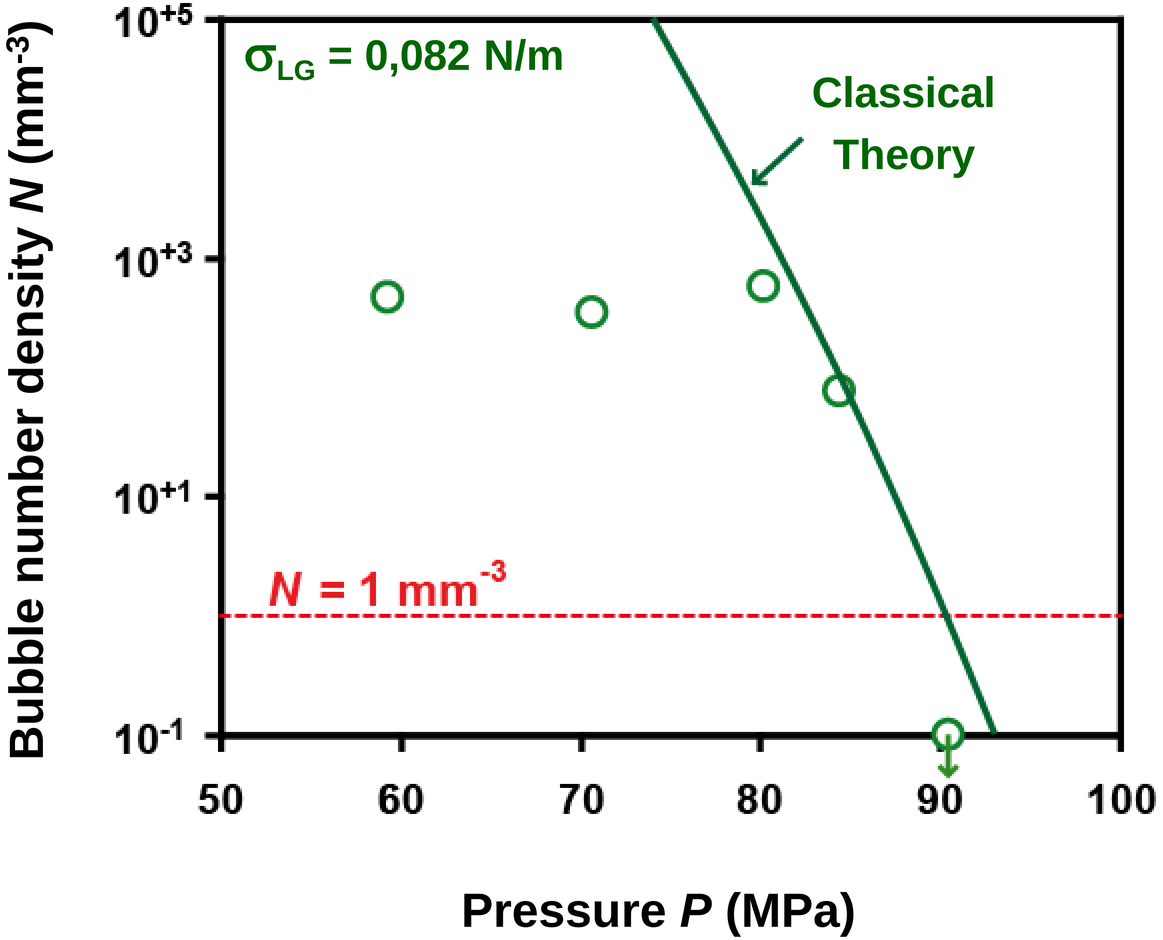
(4) Adjust σ_{LG} until the P_N computed matches the experimental value



$\Rightarrow$ We compute $P_N \approx 90$ MPa for $\sigma_{LG} = 0.082$ N/m

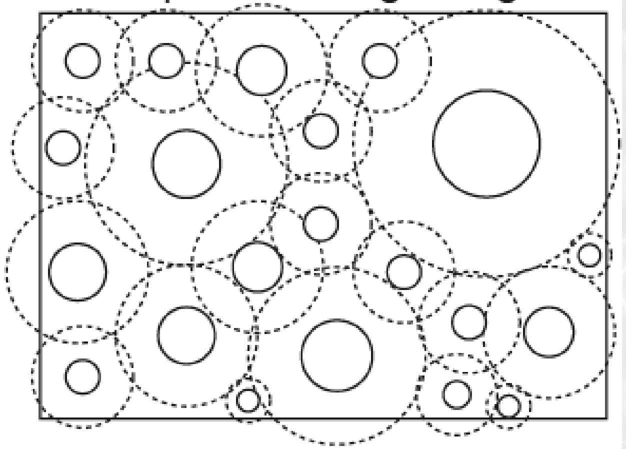
$\Rightarrow$ In good agreement with direct measurement of σ_{LG} : 0.087 N/m (Bagdassarov et al., 2000)

$\Rightarrow$ At some point, the nucleation rate drops…

Importance of the number density of bubbles, *N* : diffusion length scale e vs. mean bubble-to-bubble distance *d*

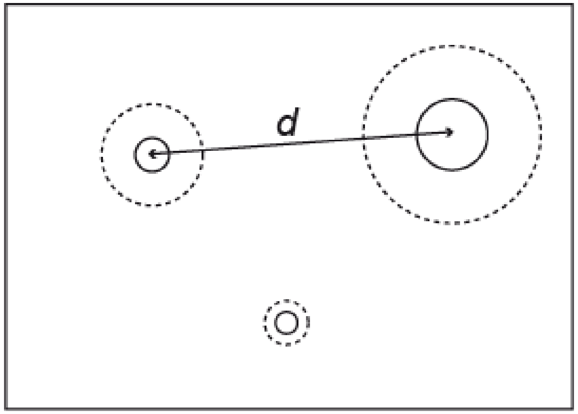
Diffusive bubble growth dominates: N stationary

Large *N* : *d* << 2*e*
equilibrium degassing



Nucleation dominates

Small *N* : *d* >> 2*e*
disequilibrium degassing



Competition between nucleation and diffusive growth of bubbles (Toramaru 1995, 2006) :

⇒ numerical simulation of the ascent and vesiculation of magmas ⇒ 2 steps:

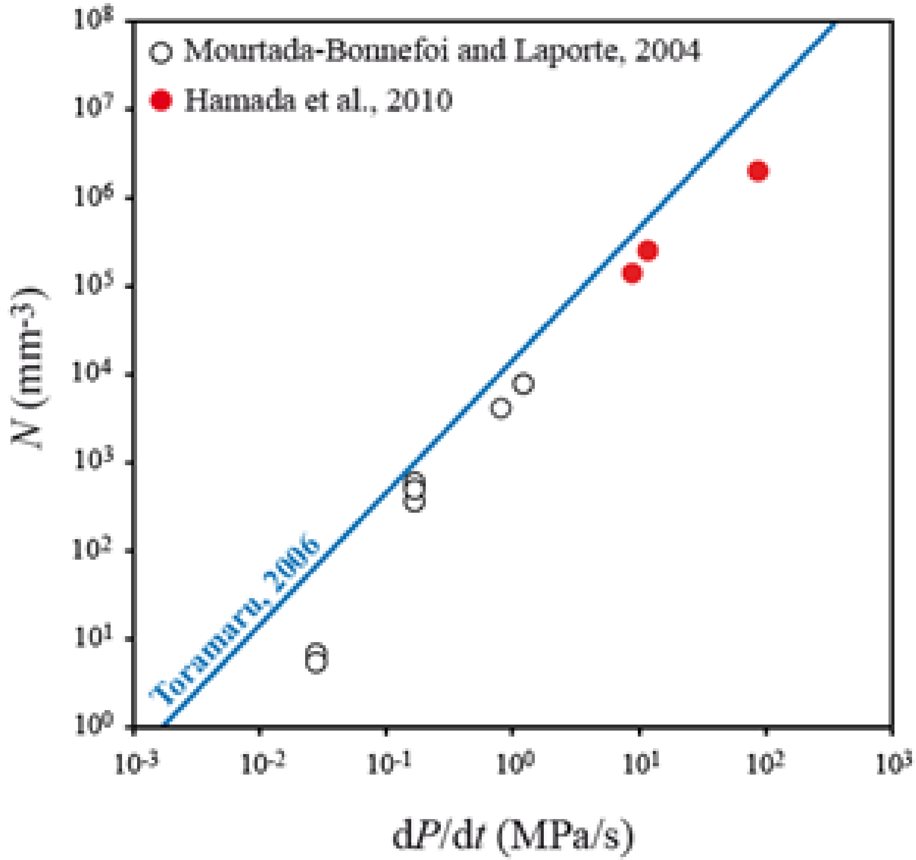
(1) a nucleation step of very short duration

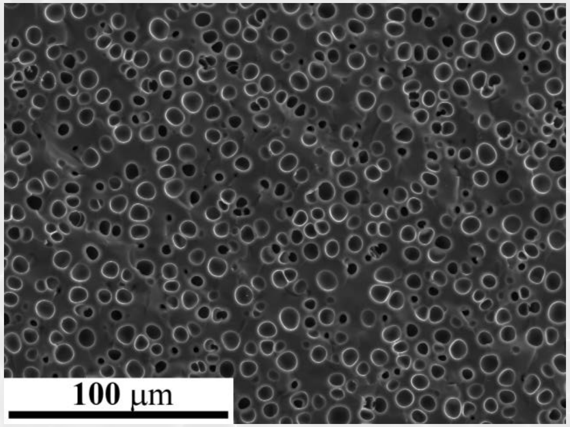
(2) a step dominated by diffusive bubble growth, in which BND is stationary = N_{STAT}

$$\boxed{N_{\mathrm{STAT}}} \approx 34 \cdot C_0 \left(\frac{16\pi\gamma_{\mathrm{LG}}^3}{3kTP_{\mathrm{SAT}}^2}\right)^{-2} \left(\frac{\Omega_{\mathrm{L}} P_{\mathrm{SAT}}}{kT}\right)^{-1/4} \left(\frac{kTC_0 D_{\mathrm{H2O}} P_{\mathrm{SAT}}^2}{4\gamma_{\mathrm{LG}}^2 \boxed{\left|dP/dt\right|}}\right)^{-3/2}$$

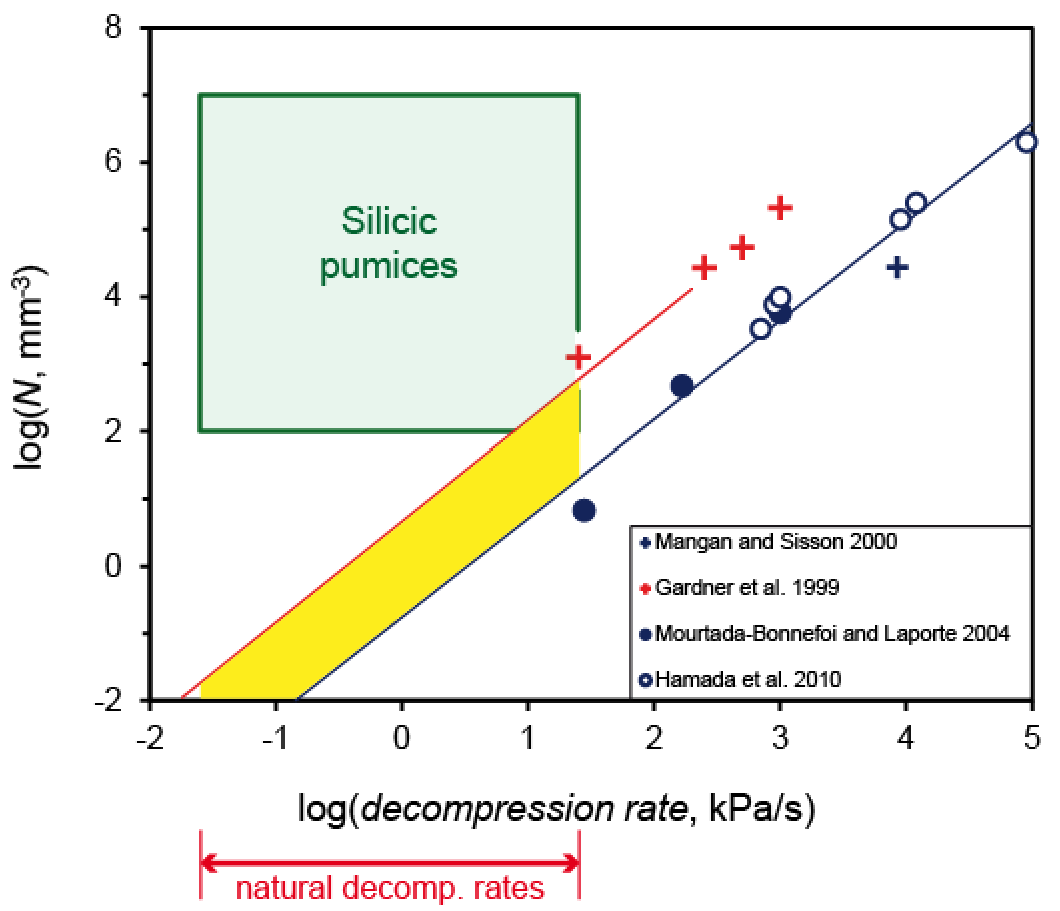
N_{STAT} is strongly sensitive to decompression rate = the Bubble Number Density Decompression Ratemeter (Toramaru, 2006)

0.0278 MPa/s ⇒ N ~ 7 mm^{-3}



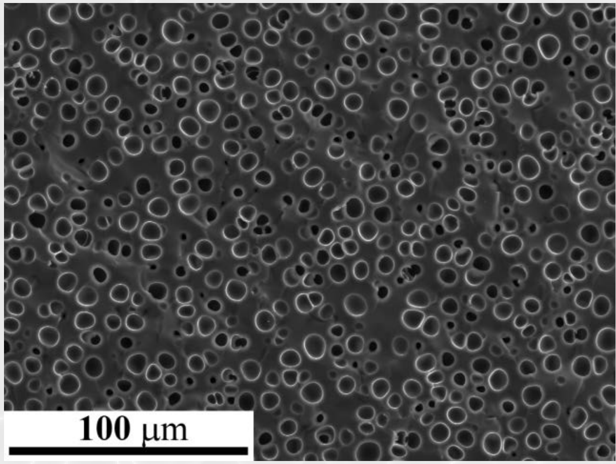


90 MPa/s ⇒ N ~ 2x10^{6} mm^{-3}

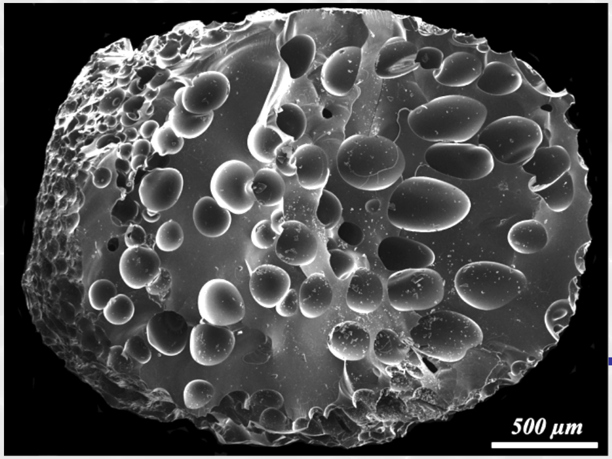


- Application: interpretation of BNDs in natural volcanic pumices

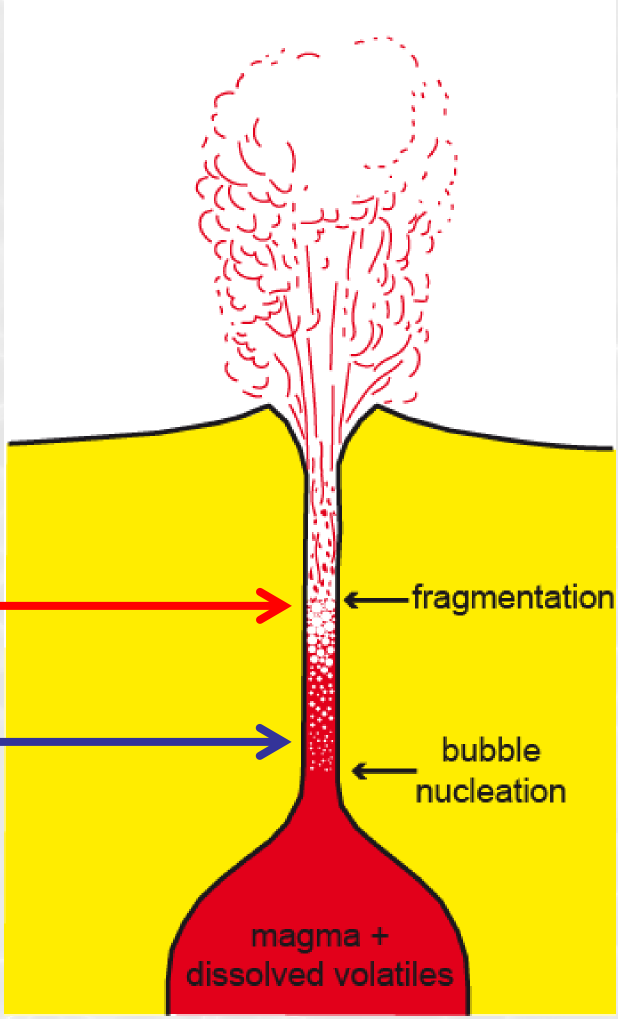
- Bubble number densities in natural pumices are orders of magnitude above extrapolated BNDs: 10^2-10^7 mm^{-3} (= 10^{11} to 10^{16} bubbles /m^3).



2nd nucleation event under extreme decompression rates at the fragmentation level (≥ 10 MPa/s) ⇒ BND up to 10^6 mm^{-3}.



Deep nucleation in the conduit at low |dP/dt| ⇒ BND ≤ 100 mm^{-3}



Homogeneous bubble nucleation in rhyolitic liquids: Summary

☐ Only one nucleation event of short duration marked by a fast increase of bubble number density; then BND is nearly stationary.

☐ Homogeneous bubble nucleation strongly delayed (P_{SAT}-P_N = 150 MPa)

☐ Early stages of nucleation well described by the classical theory.

☐ Very strong correlation between bubble number density and decompression rate: the measurement of bubble number density in natural pumice samples is a potential tool to estimate the ascent rate of magmas.

I. Introduction: Importance of the kinetics of magma degassing

II. Effect of ascent rate on homogeneous bubble nucleation in the system rhyolite-H_2O

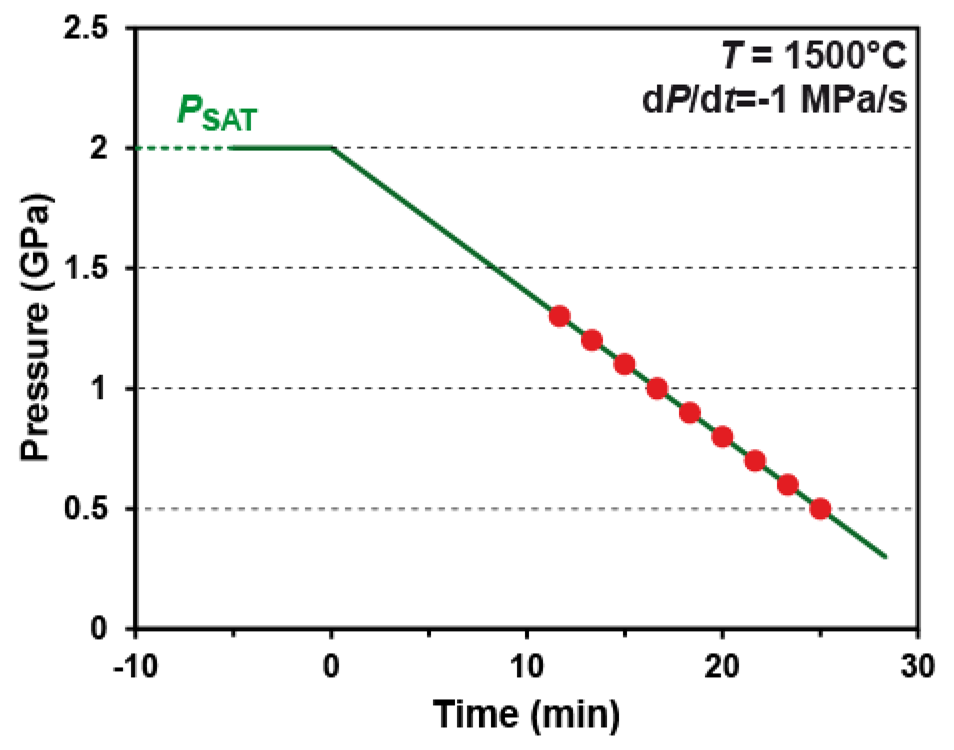
III. Homogeneous bubble nucleation in the system basalt-CO_2

System: synthetic basalt (CMAS-Na) saturated in CO_2 at 2 GPa-1500°C

C_0 = 1.6 wt. % CO_2

$|dP/dt|$ = 1 MPa/s, with quench pressures down to 0.5 GPa

CMAS-Na (wt %)	
SiO_2	49.25
Al_2O_3	19.41
MgO	16.40
CaO	12.83
Na_2O	2.11



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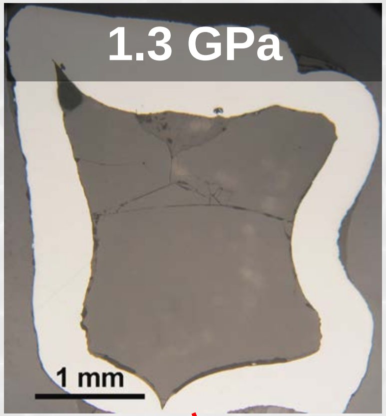
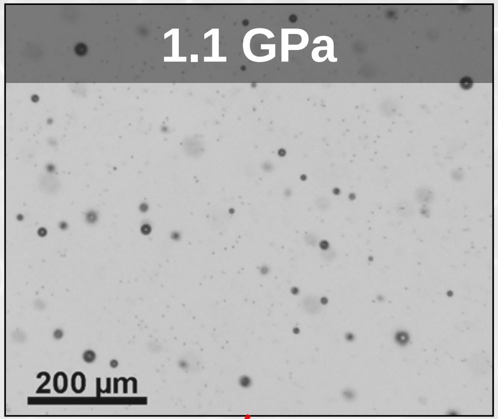
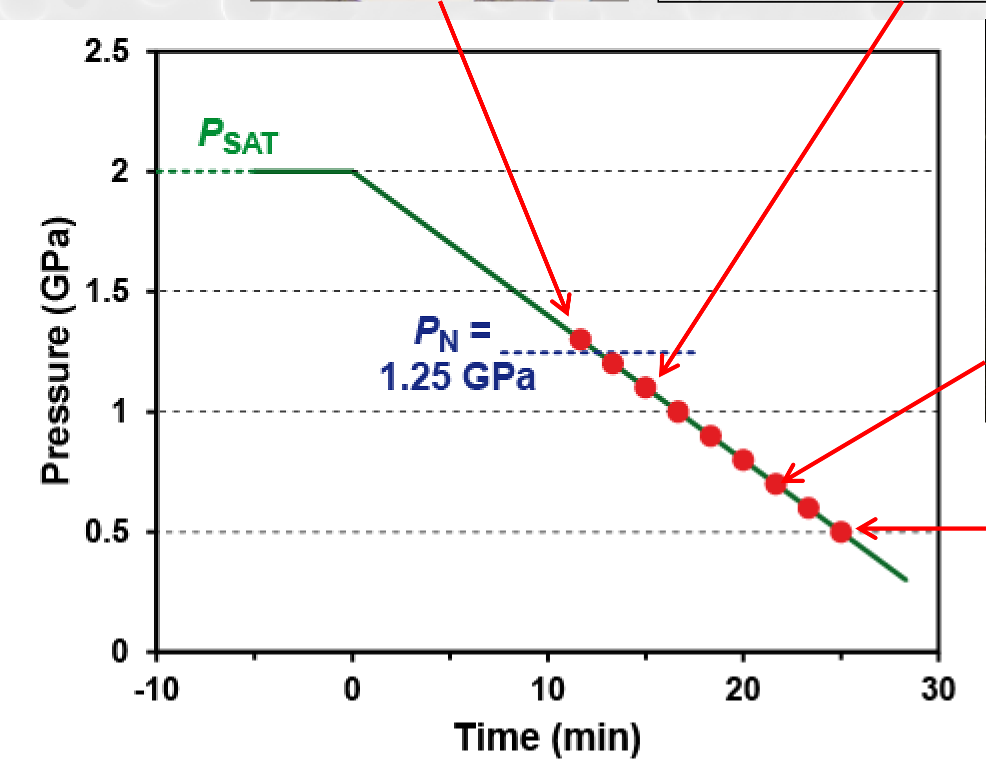
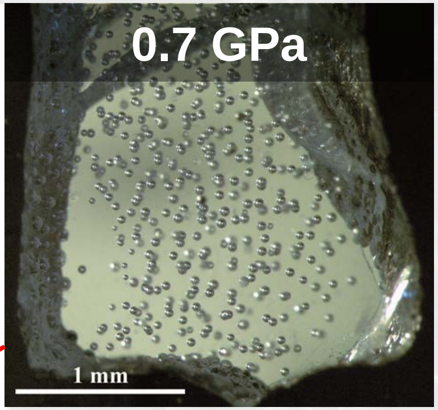




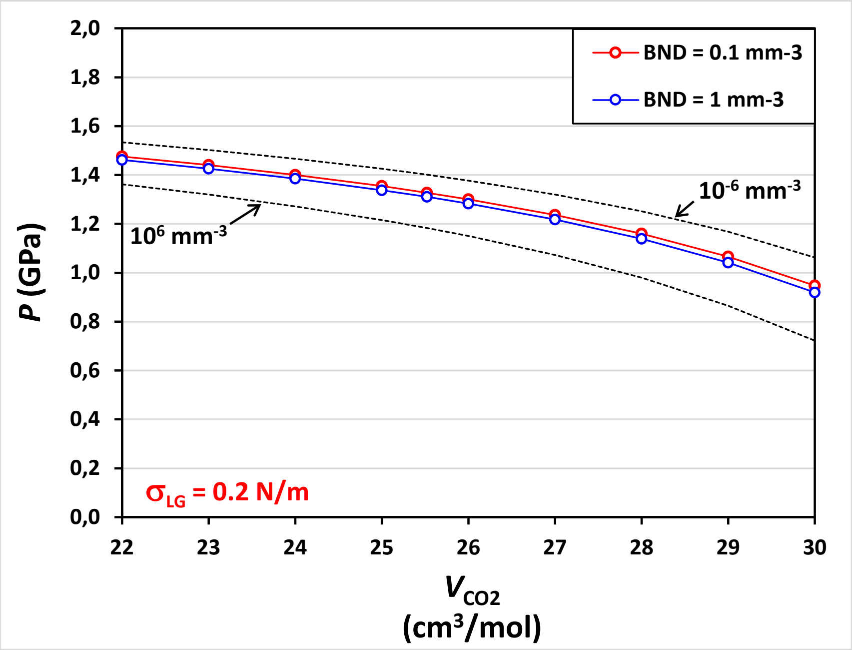




⇒ High supersaturation required for homogeneous bubble nucleation in the system basalt-CO_2: ΔP = 0,75 GPa

Calculation of surface tension coefficient σ_{LG} (N/m) from nucleation pressure (P_N = 1.25 ± 0,05 GPa) using classical nucleation theory

- Temperature: 1773 K; P_{SAT} = 2 GPa
- CO_2 solubility at P_{SAT} (1.6 wt %) and CO_2 speciation (% molecular CO_2; Guillot & Sator, 2011; Konschak & Keppler, 2014)
- D_{CO2} : diffusion coefficient (1×10^{-10} m^2/s; Guillot & Sator, 2011)
- V_{CO2}: molar volume of CO_2 in the liquid (23-28 cm^3/mol: Liu & Lange, 2003)



P_N decreases from 1.43 GPa (@ 23 cm^3/mol) to 1.14 GPa (@ 28 cm^3/mol)

Calculation of surface tension coefficient σ_{LG} (N/m) from nucleation pressure ($P_N = 1.25 \pm 0,05$ GPa) using classical nucleation theory

- Temperature: 1773 K; $P_{SAT} = 2$ GPa
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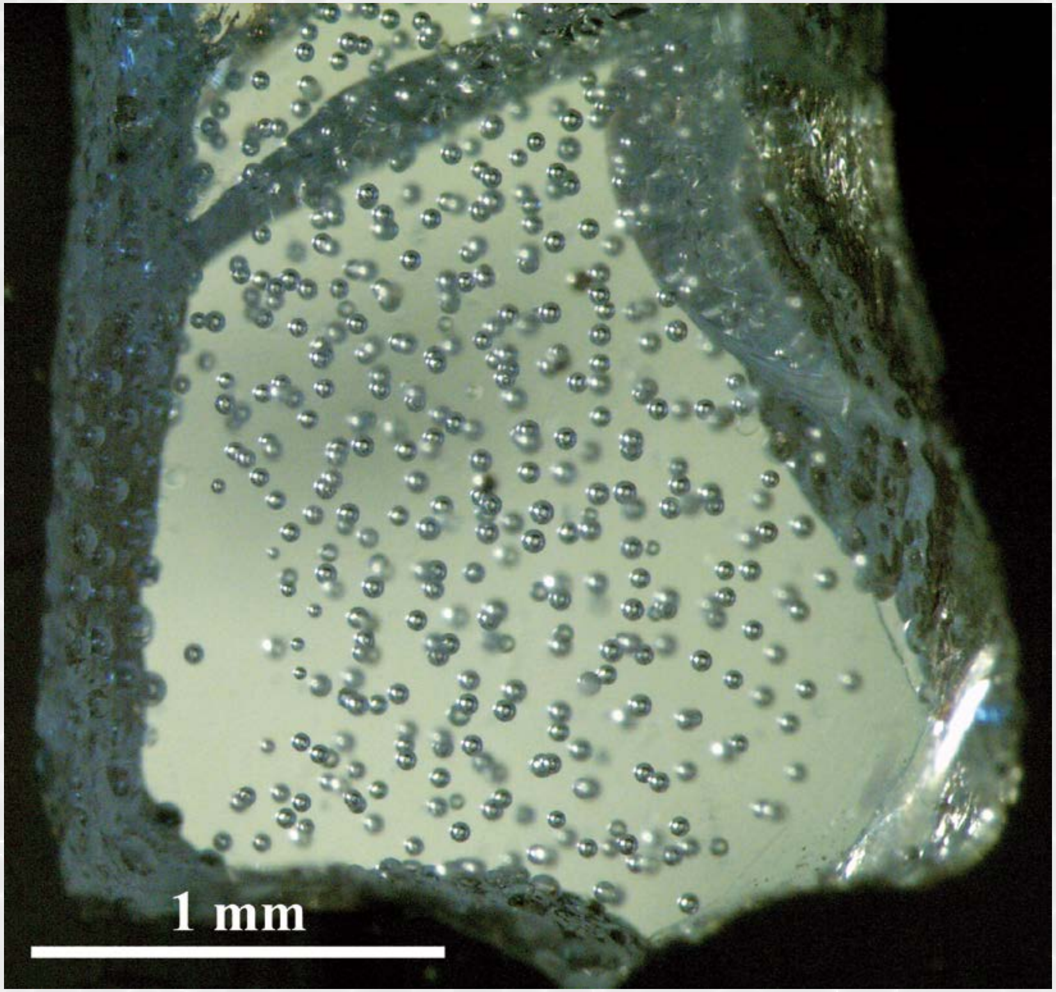
Taking into account uncertainties on V_{CO2} and P_N, we obtain:

$$\sigma_{LG} = 0.21 \pm 0.03 \text{ N/m}$$

P = 0.7 GPa



Homogeneous nucleation texture: bubbles of uniform size (30 to 60 µm) with a uniform spatial distribution

P = 0.5 GPa

Bubble accumulation and coalescence at the top due to buoyancy-driven bubble rise

Hadamard-Rybcynski law: velocity *V* of a bubble of radius *R* in a liquid of viscosity μ (Bottinga and Javoy, 1990):

$$V = \frac{(\rho_M - \rho_G)R^2 g}{3\mu}$$

Distance traveled by a bubble between *P* = 0.7 GPa and *P* = 0.5 GPa (Δ*t* = 200 s)

Bubble diameter (μm)	Distance (mm)
10	0.08
30	0.74
60	2.94
100	8.18

ρ_M = 2600 kg/m^3; ρ_G = 1400 kg/m^3; μ = 0.24 Pa.s; g = 9.81 m/s^2

Application to natural systems:

Bubble diameter (cm)	Velocity (m/s)
0.1	1.5×10^{-4}
1	1.5×10^{-2}
10	1.5

In basalts, bubbles rise at velocities that are not negligible in comparison to magma ascent rates (0.1-1 m/s for MORBs), specially for diameters > 1 cm:

open-system degassing…

$\rho_M = 2800\ kg/m^3$; $\rho_G = 1000\ kg/m^3$; $\mu = 10$ Pa.s; $g = 9.81\ m/s^2$

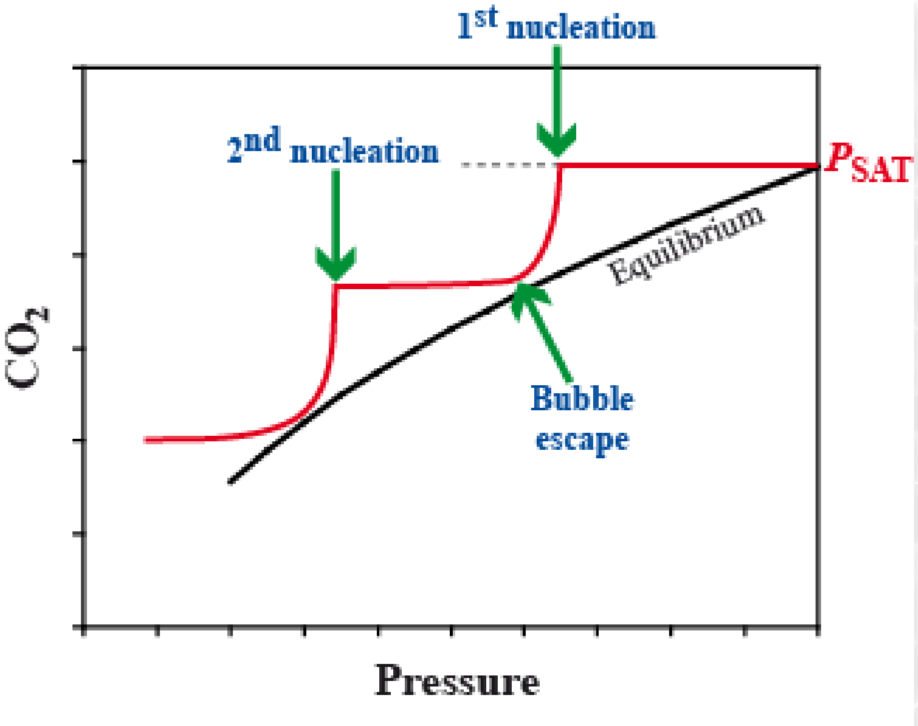
Homogeneous bubble nucleation in the system basalt-CO_2: Summary

❑ Bubble nucleation in the system basalt-CO_2 is strongly delayed ($\Delta P = 0.75$ GPa) due to high surface tension coefficient (0.21 ± 0.03 N/m).

❑ Vesiculation of basaltic magmas is affected by bubble buoyancy even at the early stages.

❑ After bubble escape, CO_2 super-saturation will increase and may lead to a second nucleation event.

❑ Correlation between BND and ascent rate at the nucleation stage presumably erased by bubble rise.



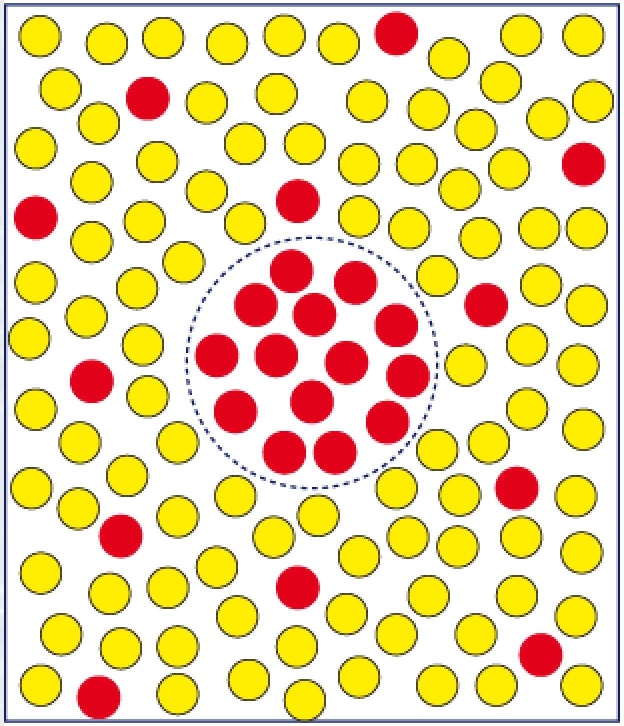
Some research perspectives

❑ Only very few experimental studies on basalt degassing (Le Gall, 2015): need for more work in this direction.

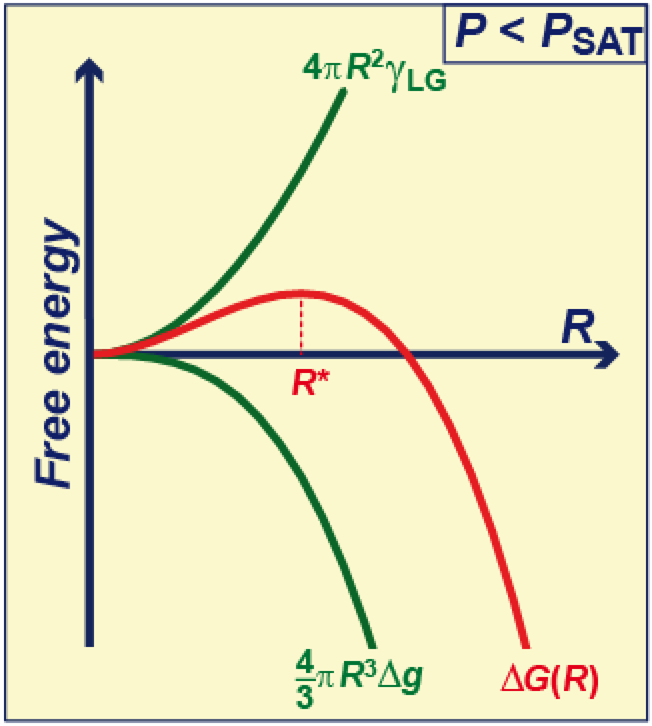
❑ Theoretical and experimental studies on bubble nucleation and growth in silicate liquids with two or more volatile components (H_2O, CO_2, SO_2, noble gases, etc.):

  ❑ models of bubble nucleation in the presence of two volatiles.
  ❑ diffusive fractionation of volatile components during bubble growth.

Homogeneous bubble nucleation: Classical theory



Bubble nucleus of radius *R*



Δg : free energy of vaporization (J/m^3)

γ_{LG}: coefficient of interficial energy (J/m^2)

(γ_{LG} is equivalent to surface tension)

Classical theory of nucleation:

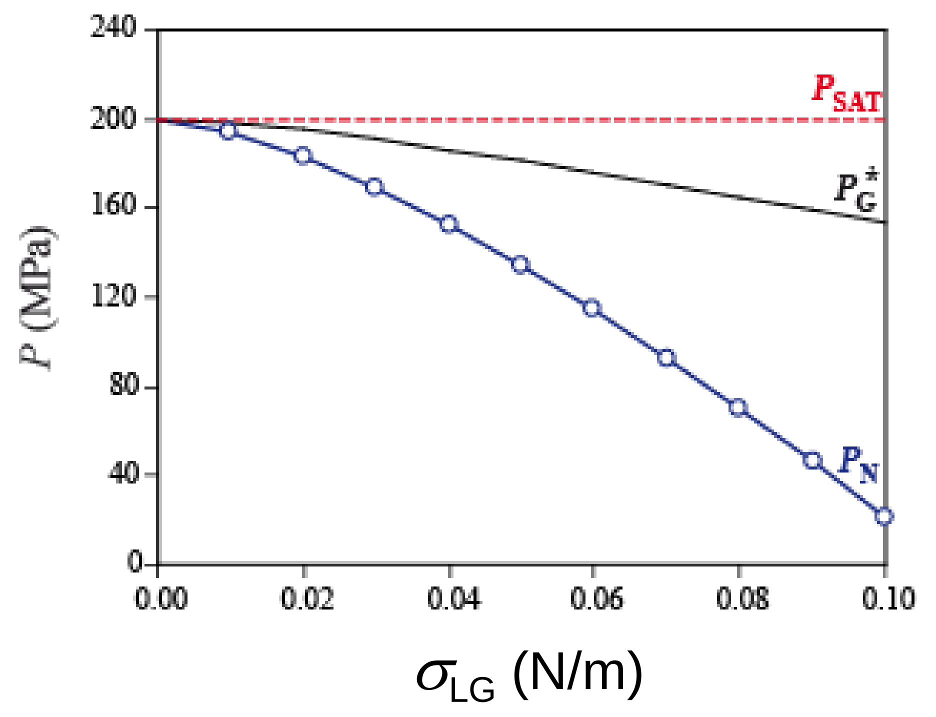
Calculation of surface tension coefficient, σ_{LG} (N/m), from the nucleation pressure P_N

Hirth et al., 1970; Hurwitz and Navon, 1994; Cluzel et al., 2008

P_{SAT} = 200 MPa

T = 800°C

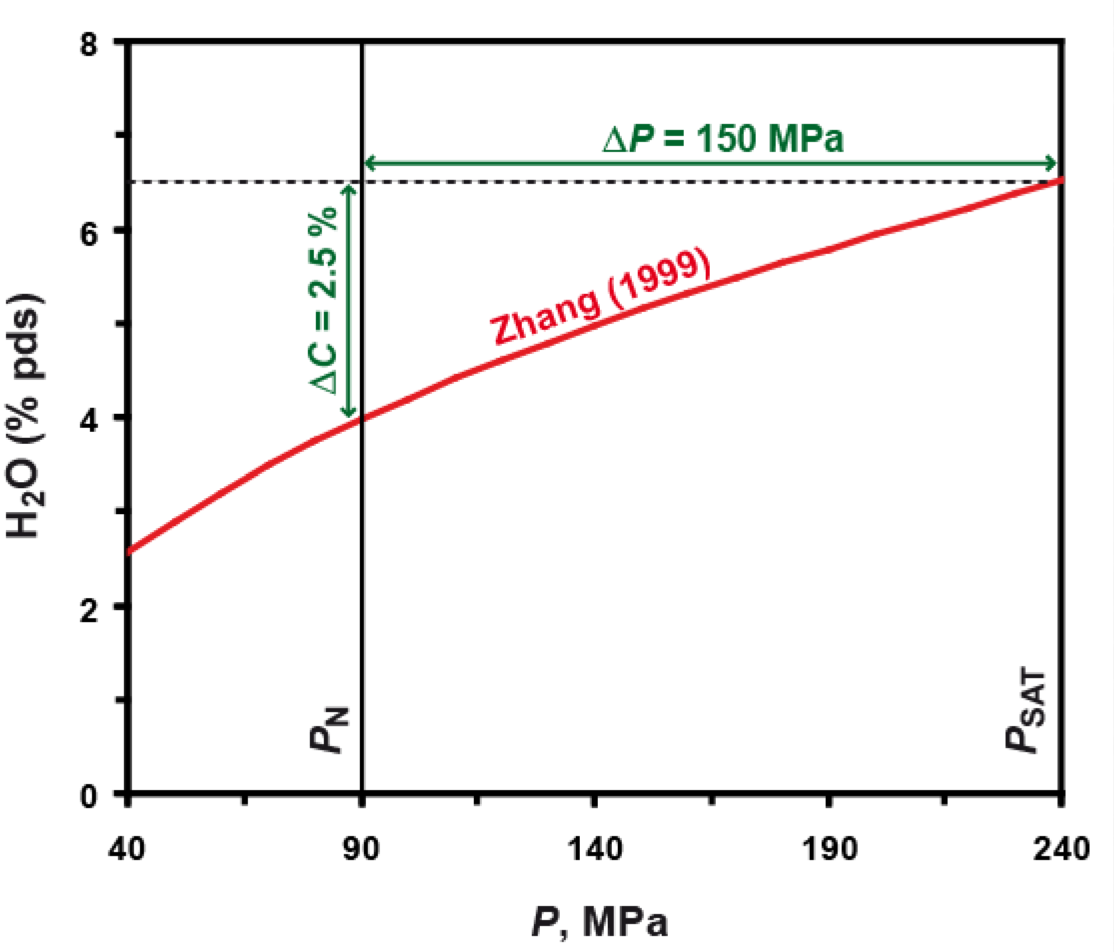
$|dP/dt|$= 1 kPa/s



Cluzel et al. (2008)

- Externally-heated pressure vessel for automatic decompression
- *P* and *T* up to 200-300 MPa, 800-900°C
- Possible to simulate the ascent of silicic magmas in volcanic conduits: 1 mm/s to 10 m/s, that is 0.025 kPa/s to 250 kPa/s (≈ 1 bar/hr to 2.5 bar/s)

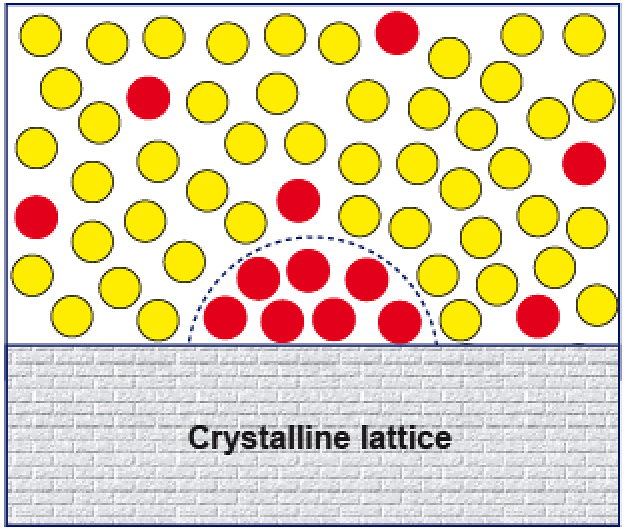
- Internally-heated pressure vessel for automatic decompression:
- *P* and *T* up to 1 GPa-1450°C ⇒ Ascent and degassing of basaltic magmas



Nucleation occurs when the liquid contains 2.5 wt. % H_2O in excess of the solubility value: very large degree of volatile supersaturation ΔC

III. The effect of crystals: Heterogeneous bubble nucleation in silicic melts

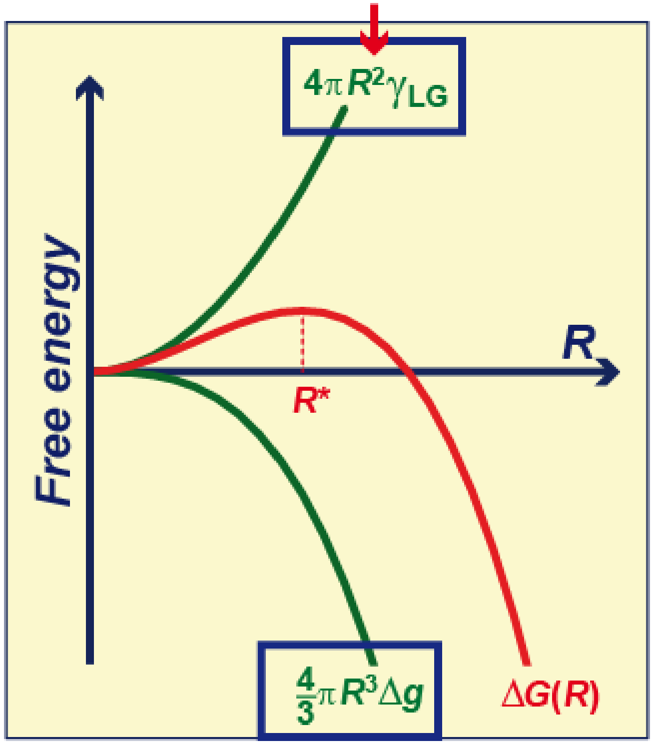
- Nucleation on a substrate (« heterogeneous ») easier than in the liquid (« homogeneous »): Bubble nucleation on Fe-Ti oxides requires a supersaturation pressure of only 5-10 MPa (Hurwitz and Navon, 1994)



Bubble nucleus on a crystal face

Low γ_{SG} = good substrate

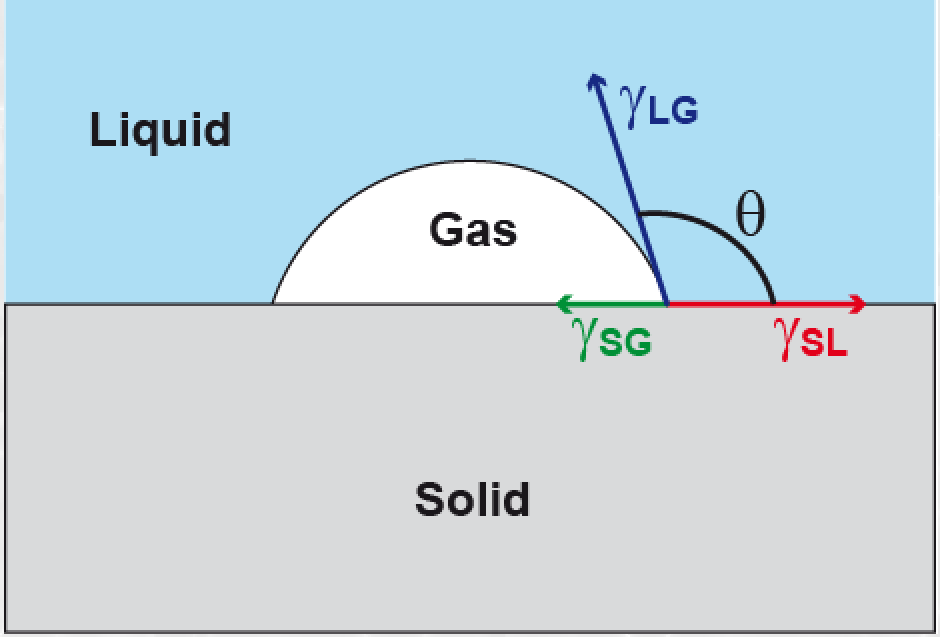
Terms in γ_{LG}, γ_{SL} and γ_{SG}



- ❑ Nucleation on a substrate (« heterogeneous ») easier than in the liquid (« homogeneous »): Bubble nucleation on Fe-Ti oxides requires a supersaturation pressure of only 5-10 MPa (Hurwitz and Navon, 1994)

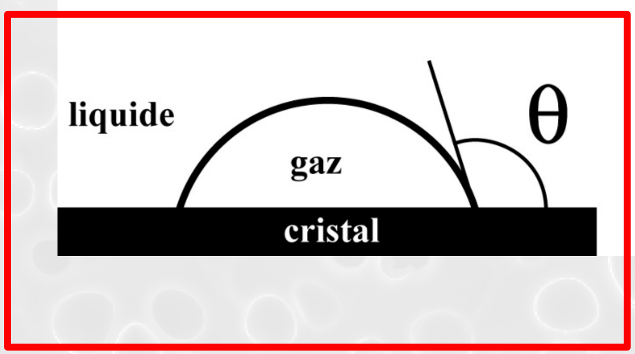
- ❑ What are the good mineral substrates for heterogeneous bubble nucleation?

- ❑ What are the parameters controlling the number density of bubbles in the case of heterogeneous nucleation?



Theory: contact angle of a nucleus on a crystal face

$$\boxed{\gamma_{SG} - \gamma_{SL} = \gamma_{LG} \cdot \cos\theta}$$



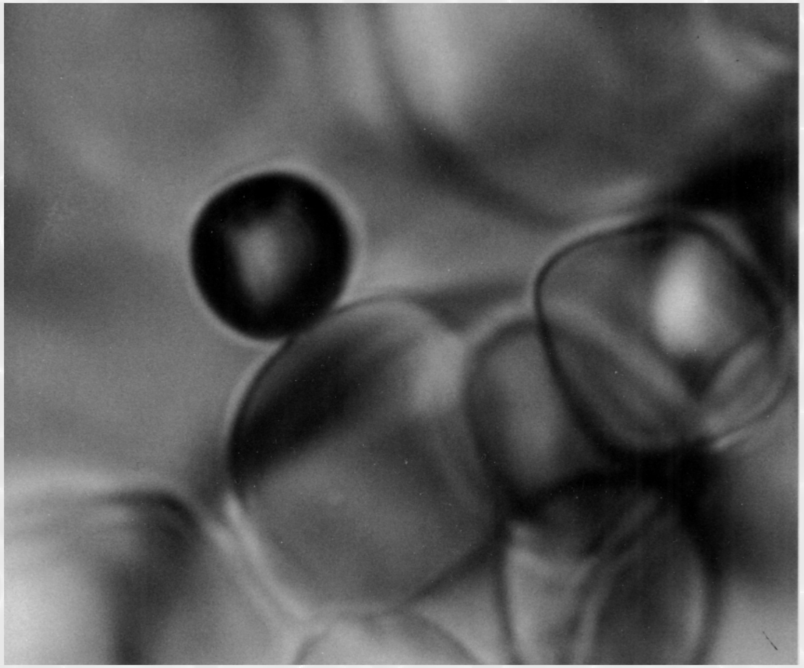
$\theta \gg 90° \Rightarrow \gamma_{SG}$ small relative to $\gamma_{SL} \Rightarrow$ good for bubble nucleation

$$\Delta P_{\text{Heterogeneous}} = \sqrt{\phi} \cdot \Delta P_{\text{Homogeneous}}$$

$$\phi = \frac{(2 - \cos\theta)(1 + \cos\theta)^2}{4}$$

Exercise no. 3

Compute the nucleation pressure for a rhyolitic liquid saturated in water at *P* = 240 MPa and *T* = 800°C in the presence of quartz (θ = 24°; photo) or in the presence of magnetite (θ = 150°). The nucleation pressure in the absence of crystals is equal to P_N = 90 MPa.



Water bubble on quartz

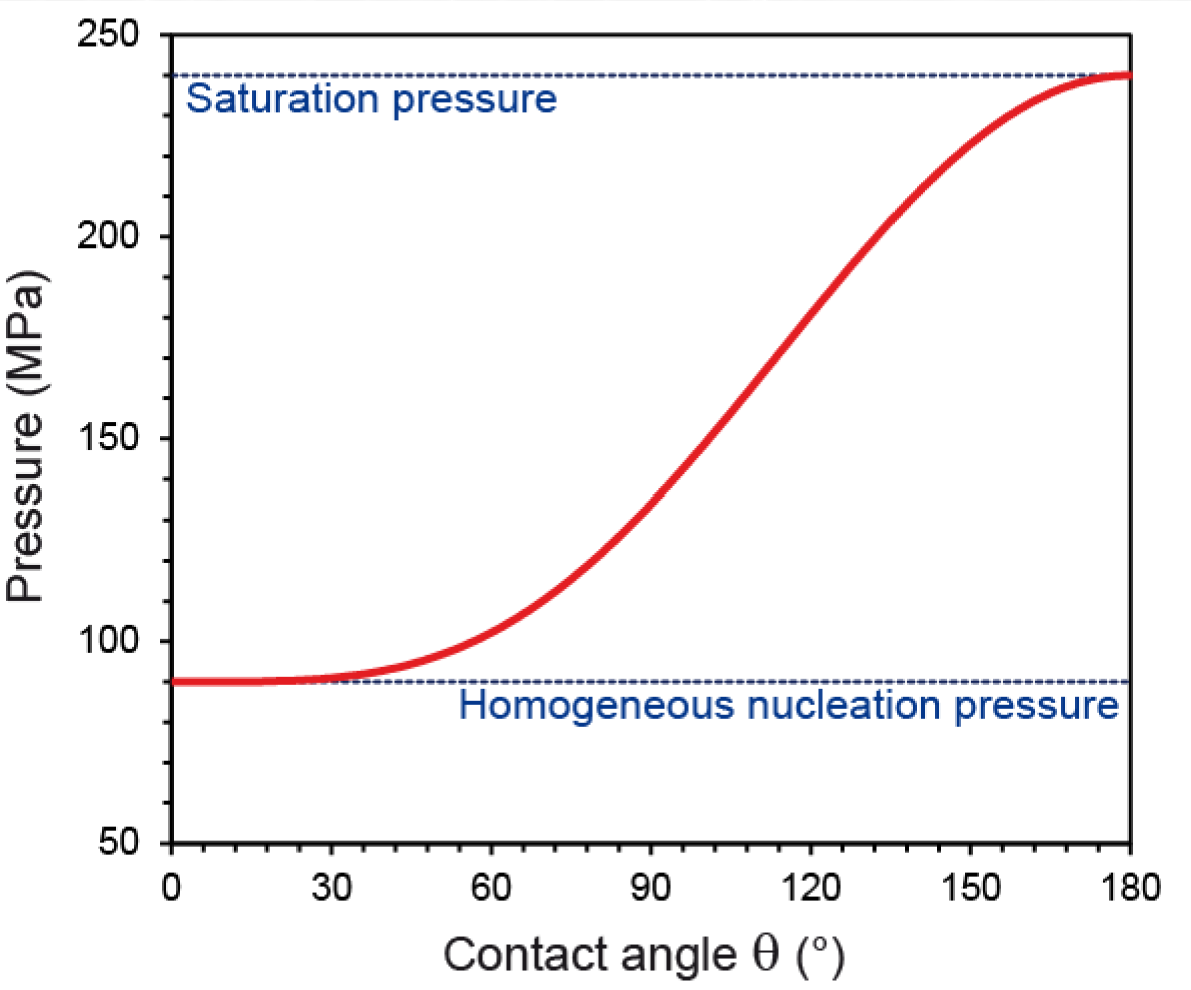
⇒ $\Delta P_{\text{homogeneous}} = P_{\text{SAT}} – P_{\text{N}} = 240 – 90 = 150$ MPa

⇒ Case of quartz:

- $\theta = 24° \Rightarrow \sqrt{\emptyset} = 0{,}997$
- $\Delta P_{\text{quartz}} = 0{,}997 \times 150 = 149{,}6$ MPa
- the nucleation pressure on quartz is 90,4 MPa: almost equal to the pressure of homogeneous nucleation!

⇒ Case of magnetite:

- $\theta = 150° \Rightarrow \sqrt{\emptyset} = 0{,}113$
- $\Delta P_{\text{magnetite}} = 0{,}113 \times 150 = 17$ MPa
- The nucleation pressure on magnetite is 223 MPa: just slightly less than the saturation pressure.



Strong reduction of the nucleation pressure only for $\theta \gg 90°$

$$\Delta P_{\text{Heterogeneous}} = \sqrt{\phi} \cdot \Delta P_{\text{Homogeneous}}$$

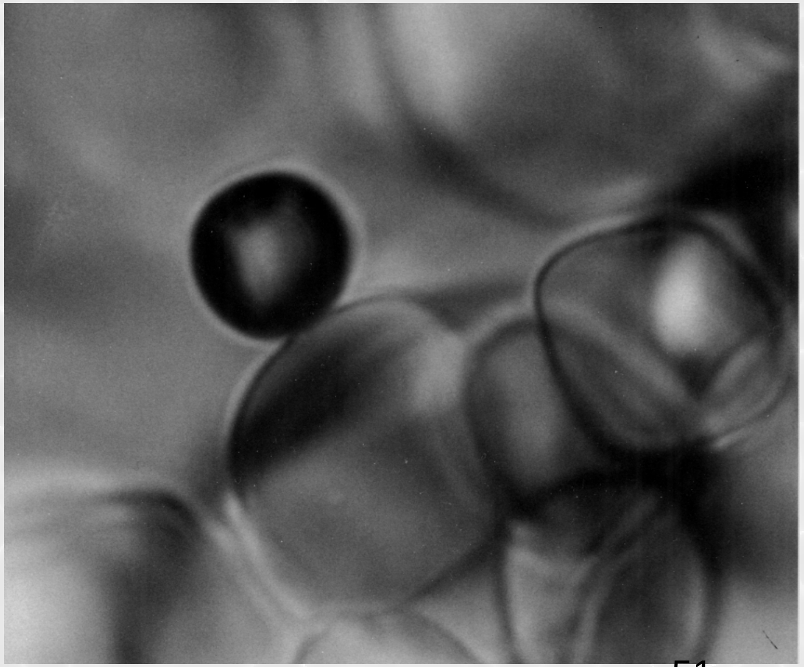
$$\phi = \frac{(2 - \cos\theta)(1 + \cos\theta)^2}{4}$$

For most species: $\theta \ll 90°$

For instance quartz: θ = 24 ° → $\sqrt{\phi}$ = 0,997

⇒ During magma ascent, heterogeneous bubble nucleation on quartz would occur just a few MPa before homogeneous nucleation.

⇒ The same holds for plagioclase (Mangan and Sisson, 2005; Gardner, 2007)



Water bubble **on quartz**

$$\Delta P_{\text{Heterogeneous}} = \sqrt{\phi} \cdot \Delta P_{\text{Homogeneous}}$$

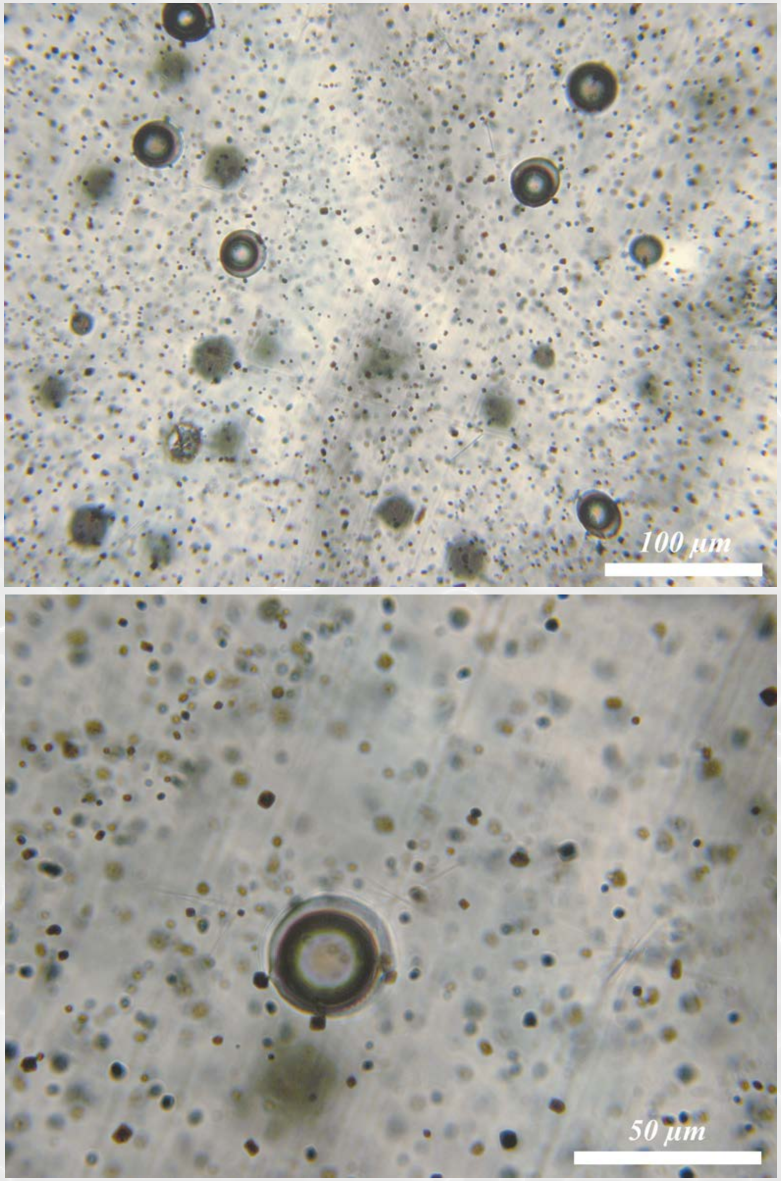
$$\phi = \frac{(2 - \cos\theta)(1 + \cos\theta)^2}{4}$$

⇒ Only magnetite has a contact angle $\theta \gg 90°$: from 140° (Cluzel, 2007) to 160° (Hurwitz and Navon, 1994)

⇒ Very low Δ*P* in the presence of magnetite: down to 5-10 MPa (Hurwitz and Navon, 1994; Gardner and Denis, 2004…)

⇒ Contact angles θ not known for many mineral species…

❑ Case 1: large number of crystals N_{XL}



Run ATHO#14: P_L = 100 MPa

⇒ System rhyolite-magnetite-H_2O saturated with water at 200 MPa-825°C (Cluzel, 2007)

⇒ Heterogeneous bubble nucleation at ΔP = 30-40 MPa

⇒ 2800 bulles/mm^3 versus $N_{XL} = 2 \cdot 10^5$ magnetites/mm^3 ⇒ Bubble number density is not controlled by crystal number density.

Heterogeneous bubble nucleation in rhyolitic liquids: Summary

- Possible to have deep bubble nucleation (at low ΔP) on magnetite. For many other minerals, heterogeneous nucleation requires a large ΔP.

- Importance of deep nucleation depends on the abundance of magnetite microphenocrysts at the pre-eruptive stage:

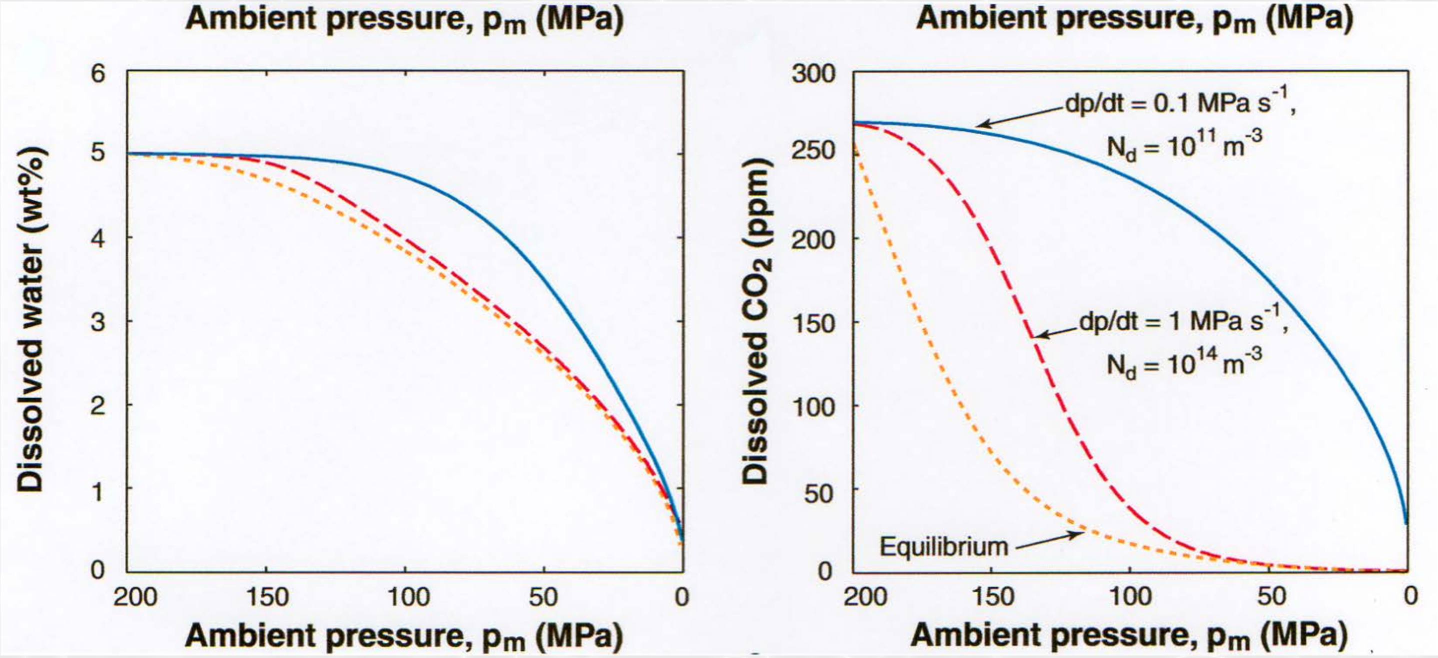
  ⇒ 1-100 mm^{-3} (Cashman, 1988; Gualda and Rivers, 2006)?

- If N_{XL} is large, same kinetics as for homogeneous bubble nucleation with a strong correlation between bubble number density and decompression rate: BND in natural pumice samples can be used as a decompression ratemeter.

- Need to better know the abundance of crystals at the onset of magma ascent (that is, before degassing-induced crystallization).

Diffusive fractionation of H_2O and CO_2 in ascending rhyolitic melt

$D_{H2O} \approx 10^{-11}$ m^2/s $\approx 10^* D_{CO2}$



Initial state:

T = 850°C

P_{SAT} = 200 MPa

H_2O = 5 wt. %

CO_2 = 268 ppm

Evolution of H_2O (left) and CO_2 (right) dissolved into the melt with decreasing P (from Gonnermann and Manga, 2007):

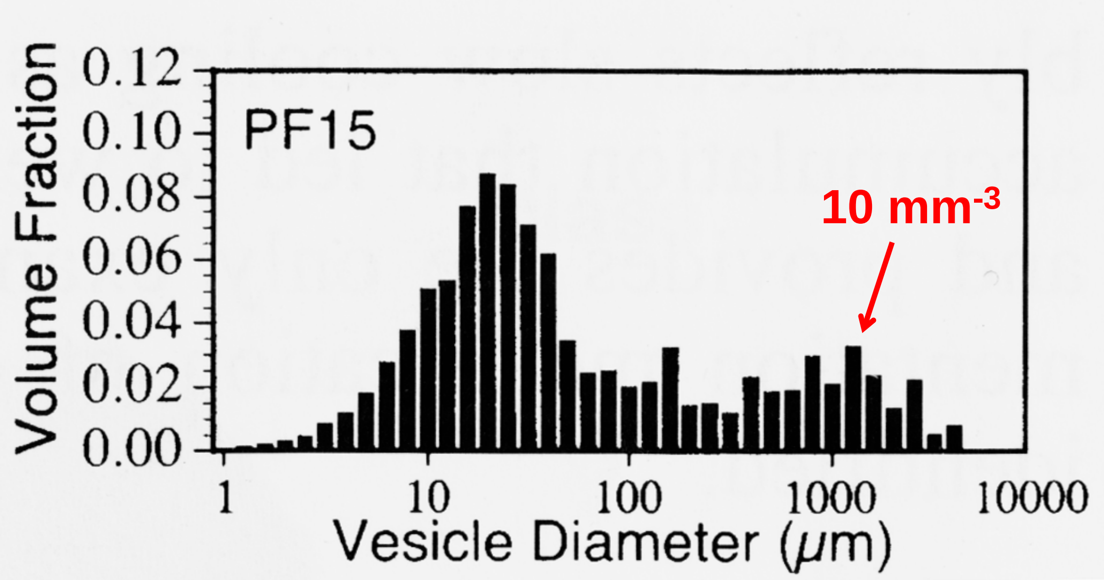
⇒ both CO_2 and H_2O in the liquid (blue curves) are above their equilibrium values (orange)

⇒ the liquid is strongly enriched in CO_2 (the slow diffusing species) relative to H_2O.

Diffusive fractionation between slow and fast diffusing volatile species

= a tool to estimate the time-scale of degassing

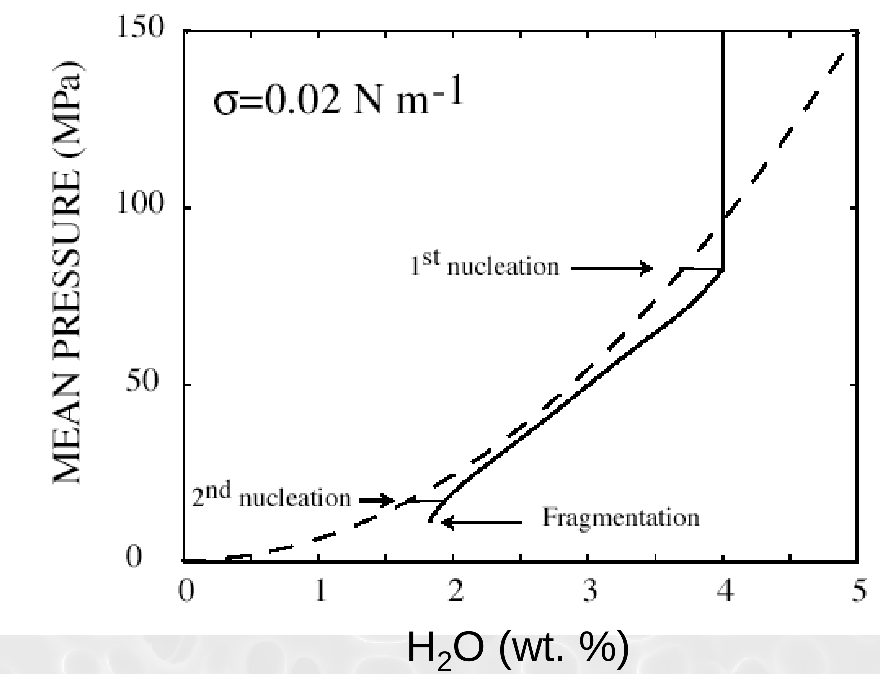
	FAST	SLOW
Major volatiles	H_2O	CO_2
	H_2O	S
	H_2O	F, Cl
Noble gases	He	Ar
Light elements	Li	B
Isotopes	^{6}Li	^{7}Li
	^{12}C	^{13}C

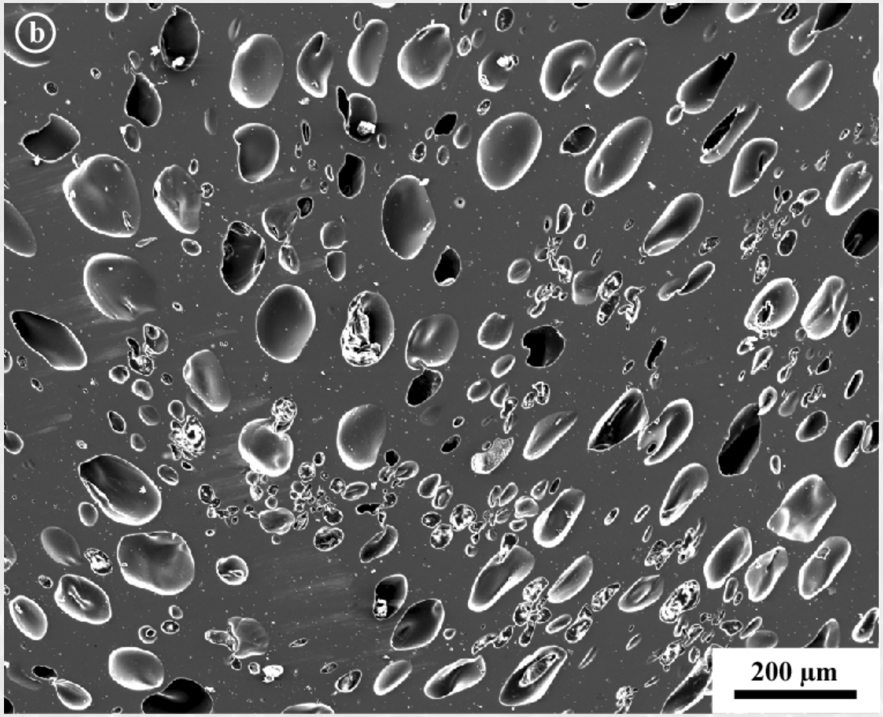


Bubble size distribution in a pumice from Mount Mazama (Crater Lake), Oregon (Klug et al., 2002):

⇒ total bubble number density ≈ 10^7 mm^{-3} (mostly < 100 μm)

⇒ number density of large bubbles (300-4000 μm) ≈ 10 mm^{-3}





Massol and Koyaguchi (2005) :

⇒ Numerical simulations of ascent and vesiculation of magmas

⇒ Decompression rates > 10 MPa/s close to the fragmentation level

⇒ Increase of the degree of water super-saturation at low *P* ⇒ 2nd nucleation

Cluzel (PhD 2007) :

⇒ System rhyolite-magnetite-H_2O with P_{SAT} = 200 MPa and T = 825°C

⇒ Textural record of a 2nd nucleation event in the run quenched at 40.2 MPa