

Modéliser la transition vitreuse

Bertrand Guillot

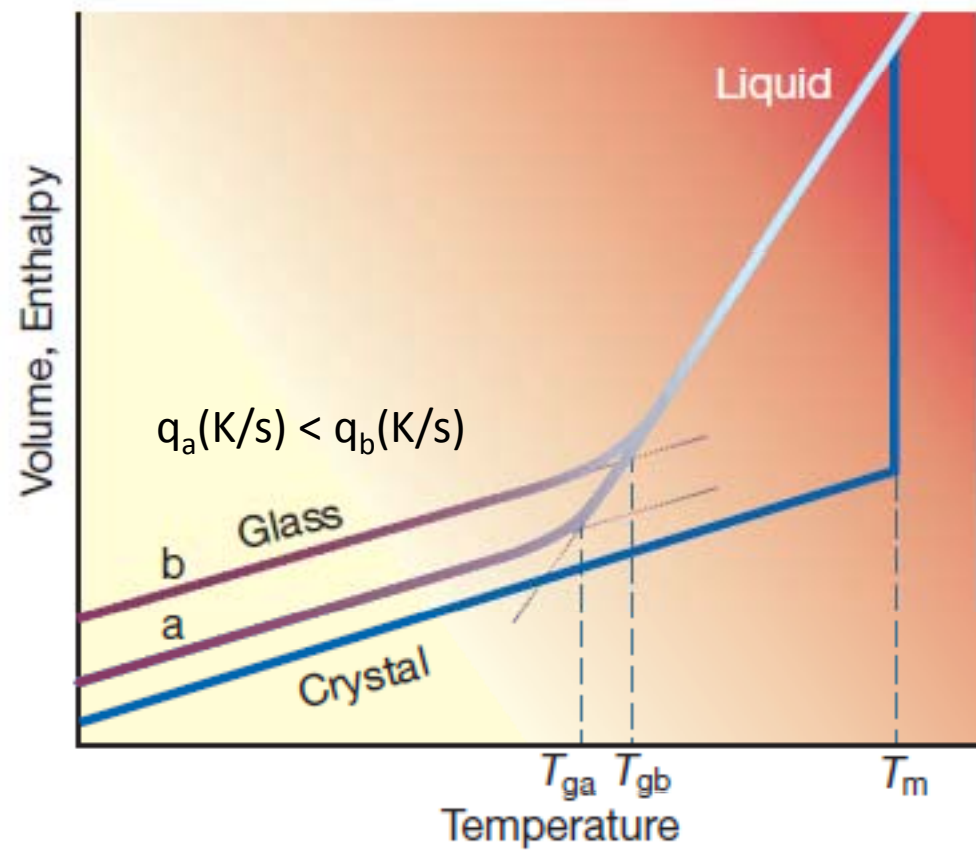
LPTMC, Université Pierre et Marie Curie (Paris 6), France



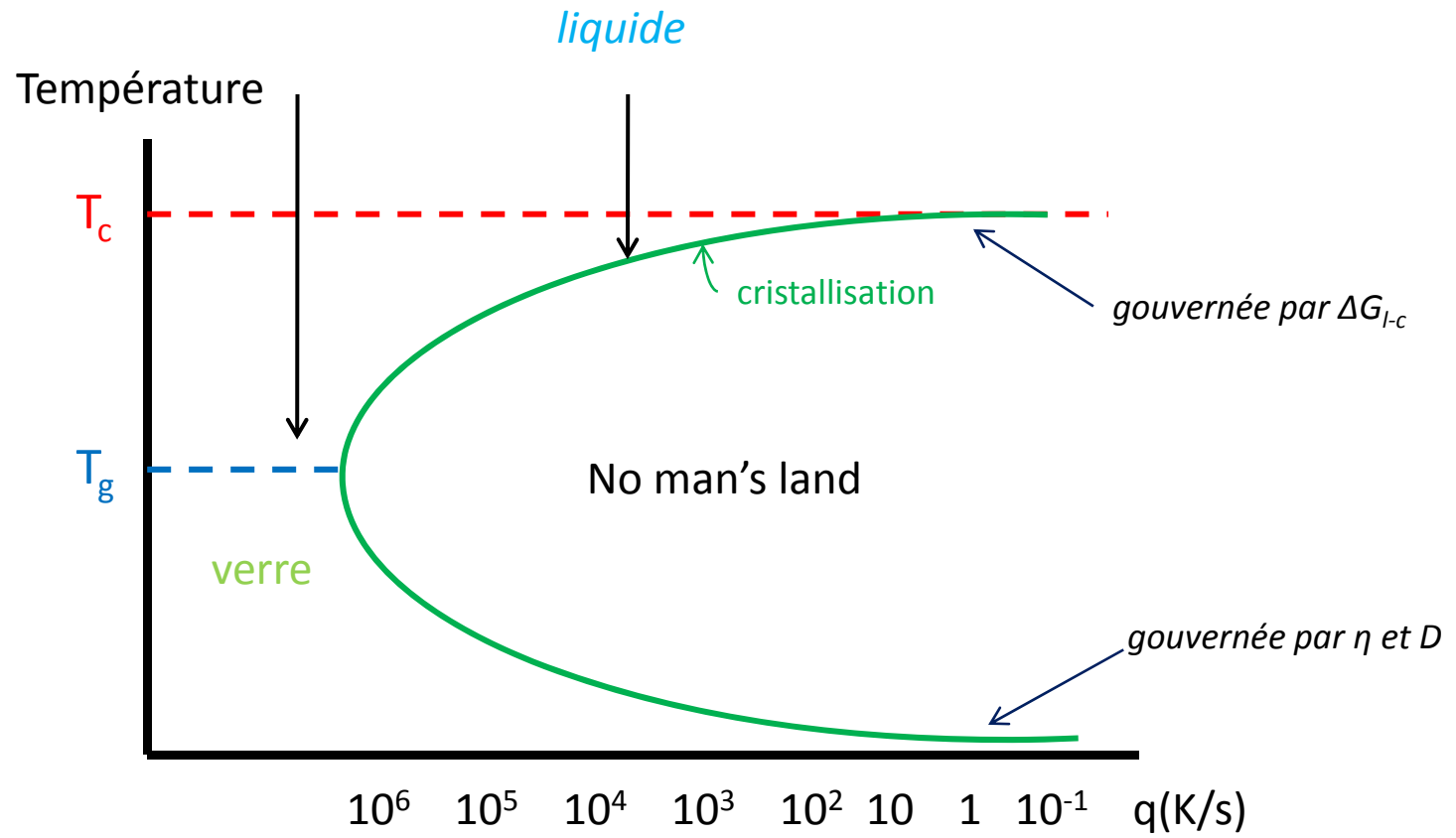
Obsidienne



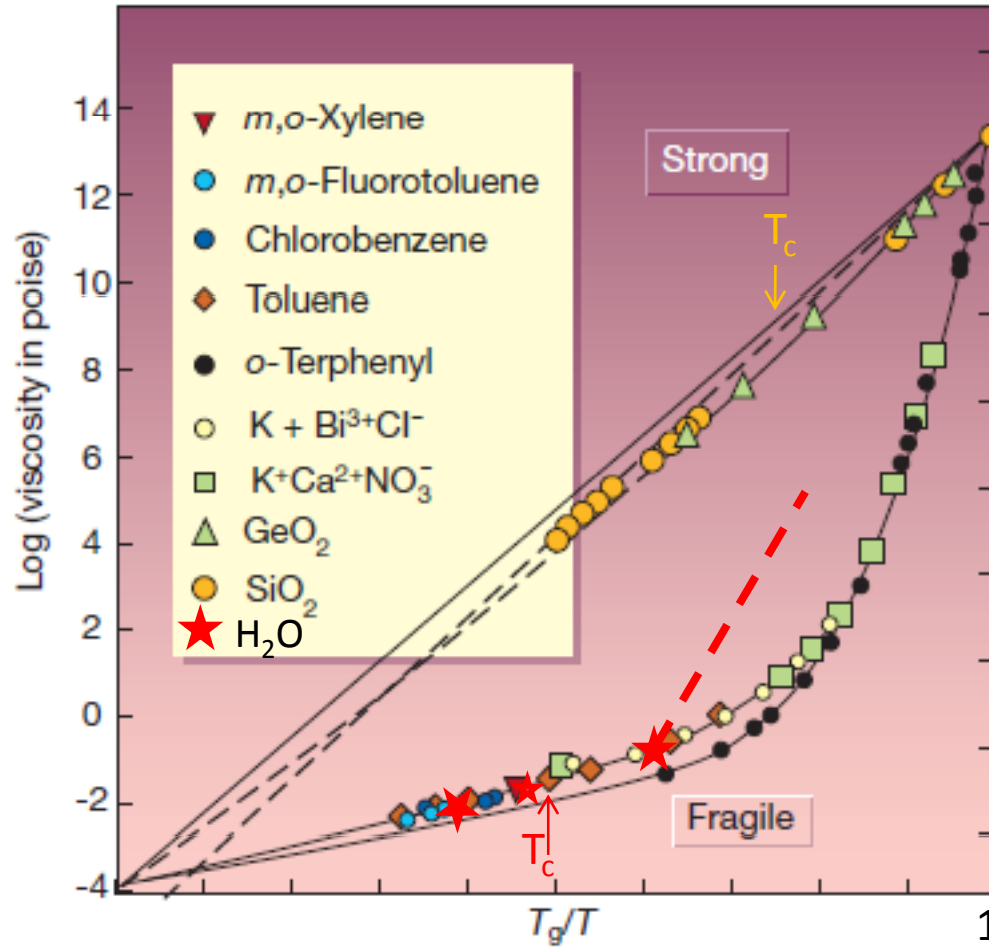
Basalte de dorsale océanique

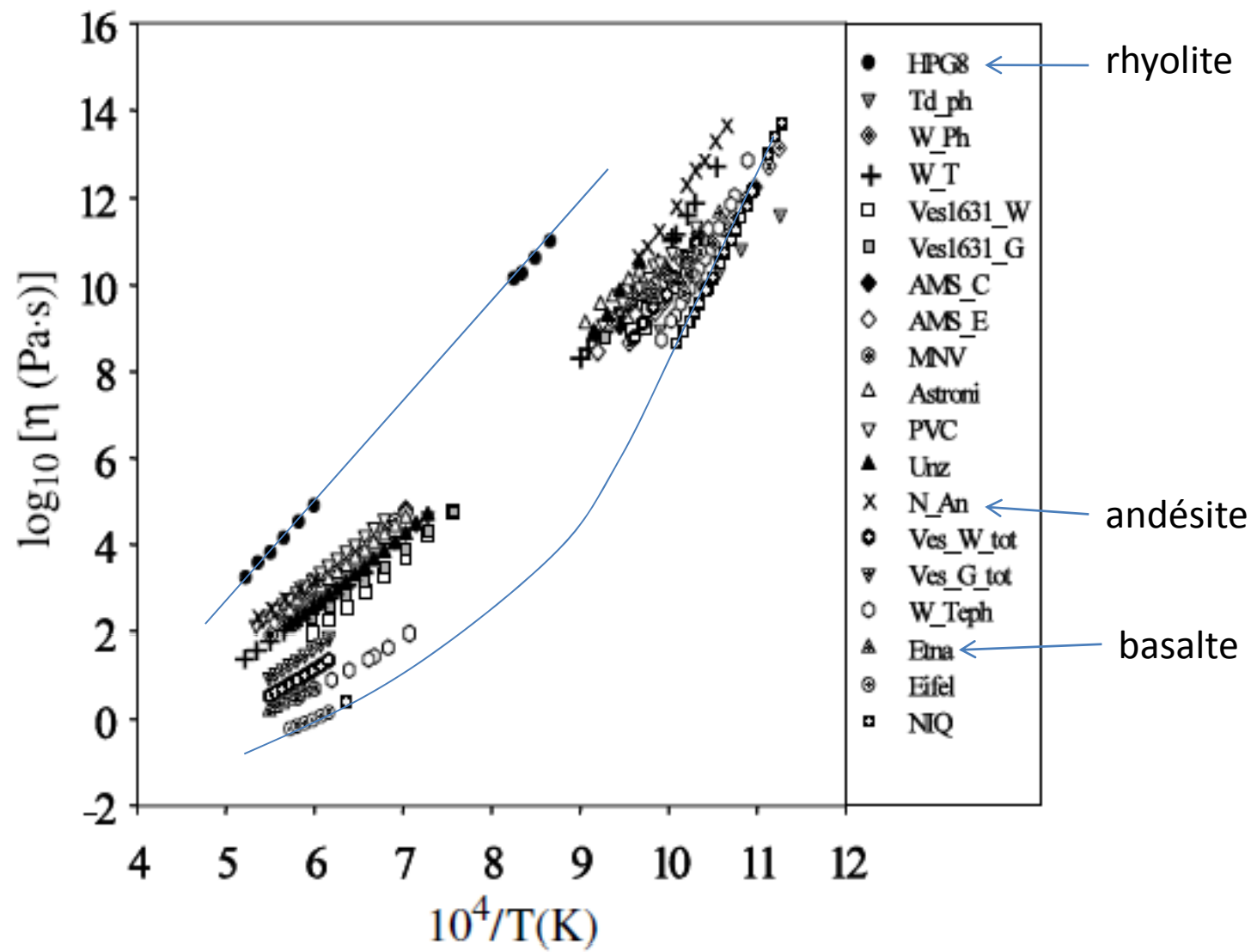


Courbe de transformation temps-température

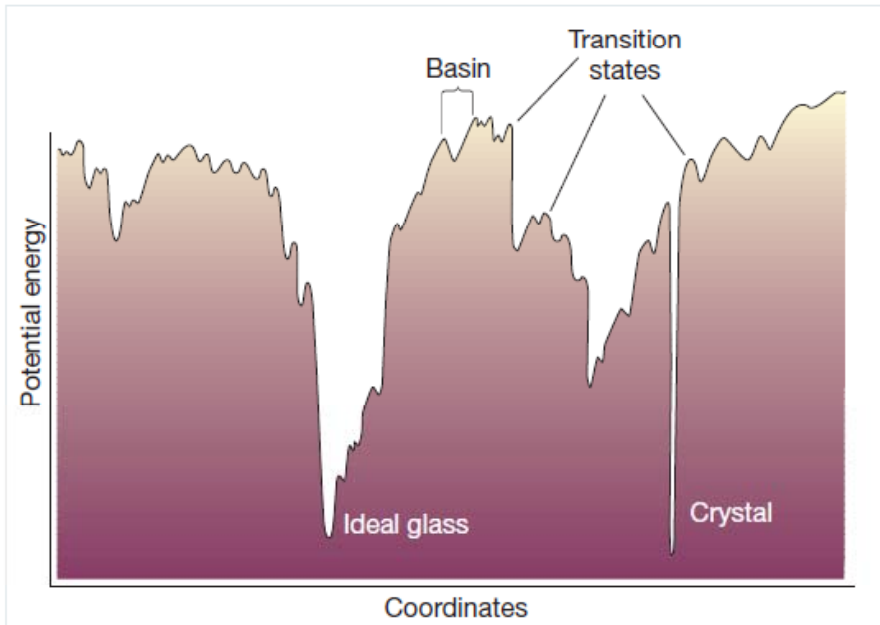


$\text{Log } \eta = A + B/(T-T_0)$ $T_0 \sim 0$ pour les liquides forts
 $0 < T_0 < T_g$ pour les liquides fragiles

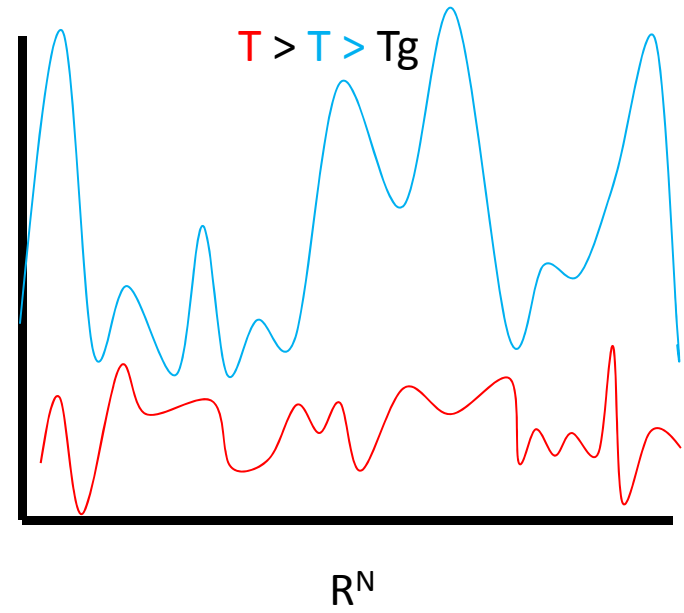




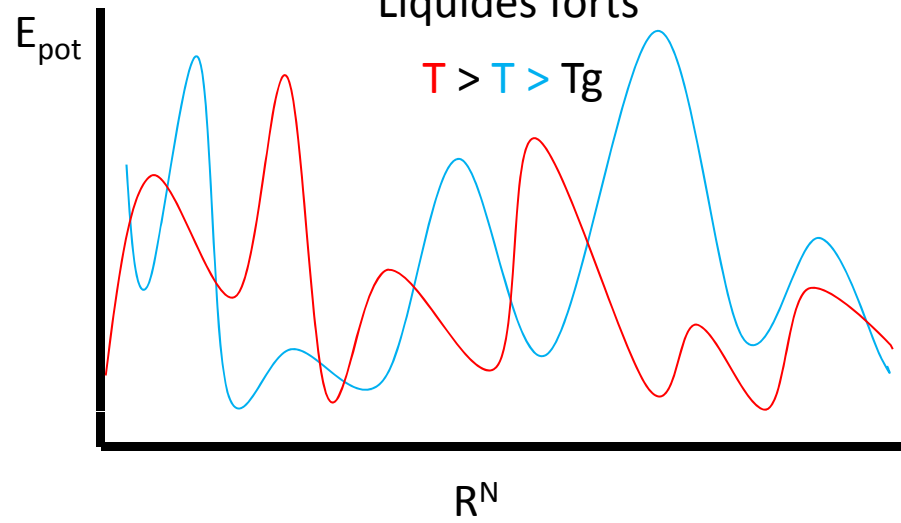
Paysage énergétique

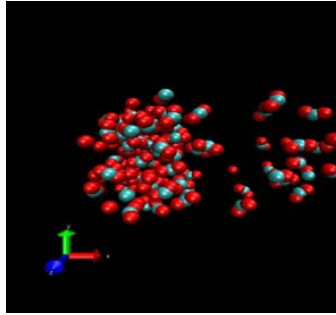


Liquides fragiles



Liquides forts





$N = 10^3 - 10^4$ atomes



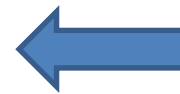
Champ de forces
 $U_{\text{pot}} = \sum u_{ij} + \sum u_{ijk} + \dots$



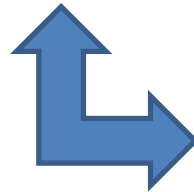
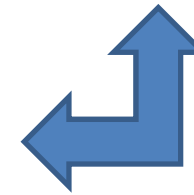
Dynamique moléculaire
 $m_i a_i = \sum f_{ij}$
Pas d'intégration $\sim 10^{-15}$ s

principe ergodique
moyenne temporelle pour les grandeurs
d'équilibre

$$\langle A \rangle = (1/N) \sum A_i \text{ pour } M \text{ pas } (M = 10^{7-8})$$



À chaque pas d'intégration:
une configuration des atomes



Propriétés thermodynamiques
ensemble:
microcanonique (N,V,E)
canonique (N,V,T) ou (N,P,T)

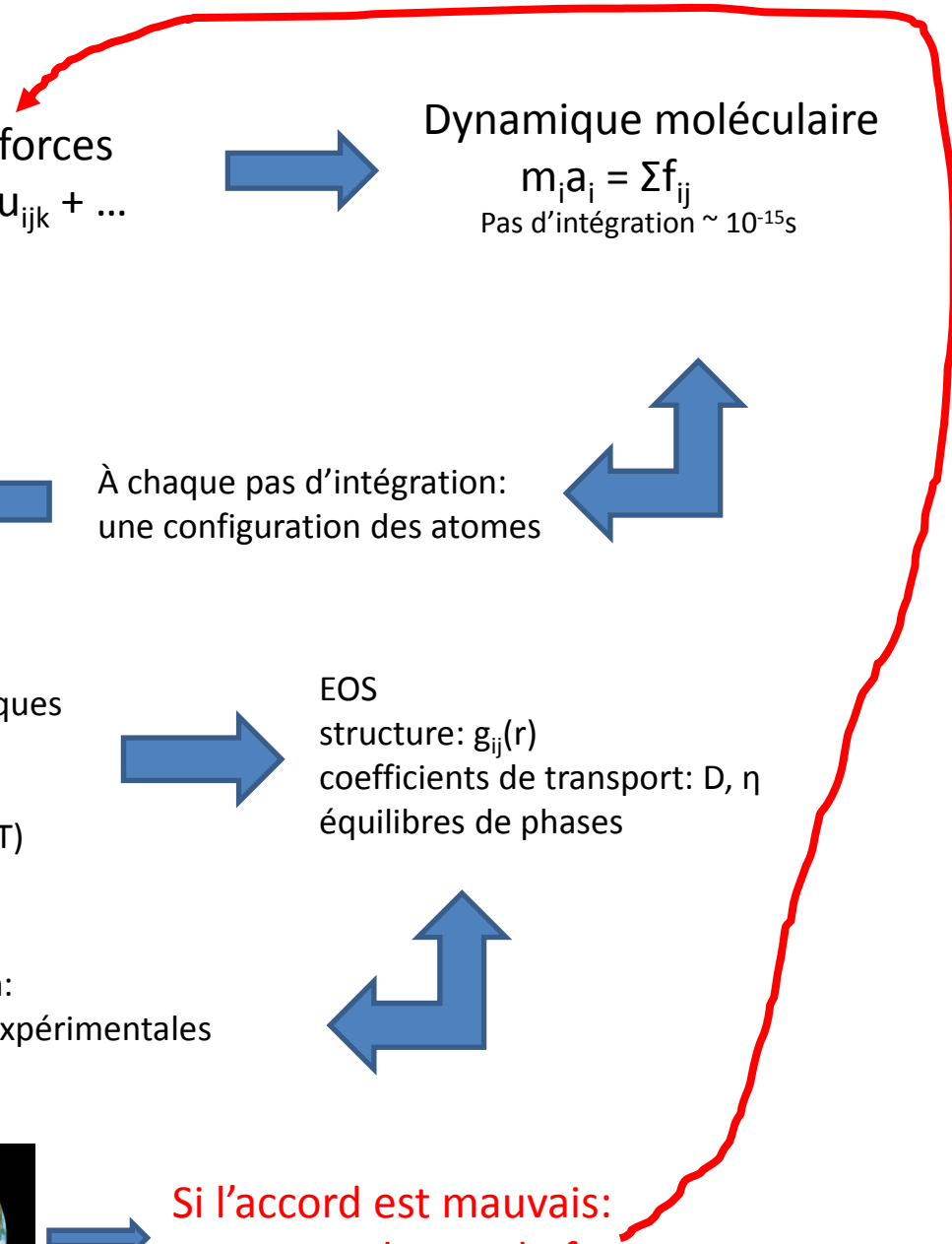


EOS
structure: $g_{ij}(r)$
coefficients de transport: D, η
équilibres de phases

étape de validation:
comparaison avec les données expérimentales



Si l'accord est mauvais:
retour au champ de forces



Quelques données clés des simulations ...

Les ressources informatiques sont limitées \longrightarrow $N=1000$ atomes, $t_{\max} \sim 1000$ ns

$$D_{\min} = \langle R_{\min}^2 \rangle / 6t_{\max} = 2 \cdot 10^{-14} \text{ m}^2/\text{s} \text{ pour un déplacement carré moyen de } 10 \text{ \AA}^2$$

$$\text{D'où (d'après Eyring)} \quad \eta_{\max} = k_B T / \lambda D_{\min} = 3000 \text{ Pa}\cdot\text{s} \quad (!!)$$

\uparrow
 $\lambda = 2.8 \text{ \AA}$ pour les silicates

$$\text{Vérification: (d'après Maxwell)} \quad \tau_{\text{relax}} = \eta / G_{\infty} = 100 - 1000 \text{ ns}$$

\uparrow
avec $G_{\infty} = 0.3 - 3 \cdot 10^{10} \text{ Pa}$

Remarque : à T_g , $\eta \sim 10^{12} \text{ Pa}\cdot\text{s}$ il faudrait une simulation de 300 s

Vitesse de trempe la plus lente: $1000 \text{ K} / 1000 \text{ ns} = 10^9 \text{ K/s}$
est-ce bien raisonnable ?

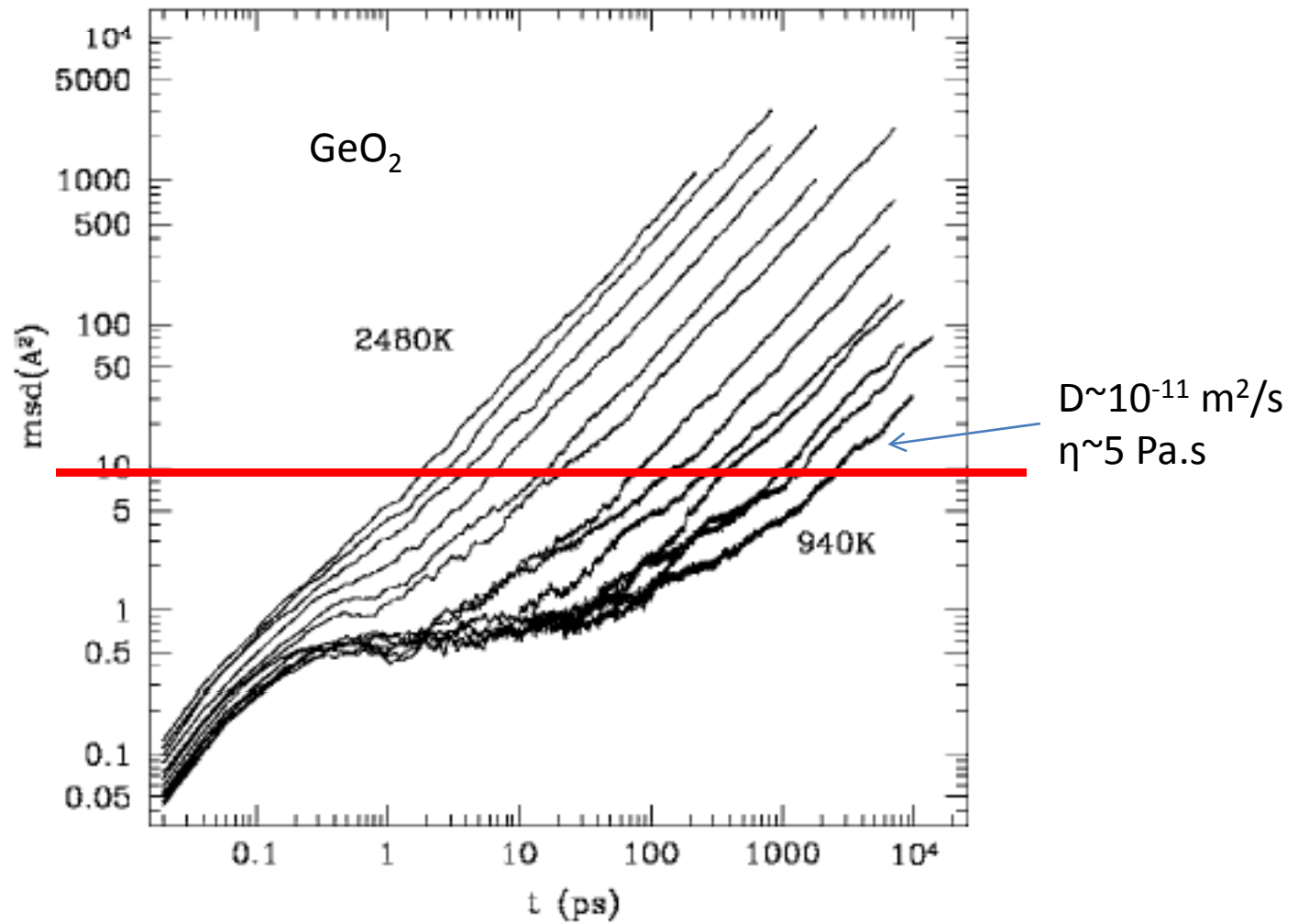
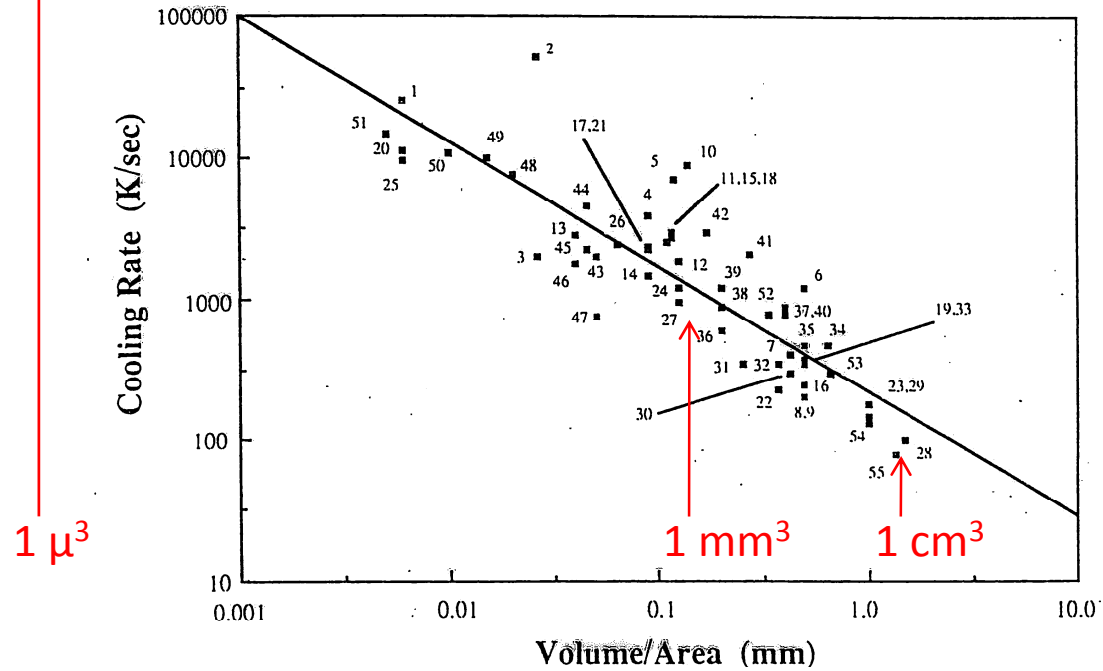


FIG. 4. Time dependence of the mean-squared displacement of oxygen for different temperatures ranging from 2500 to 920 K.

$\sim 10^6$ K/s pour l'eau

d'après Zasadzinski, J. Microsc. 150 (1988), 137



Pour un échantillon nanométrique $(20 \text{ \AA})^3$ de basalte le calcul donne 10^9 K/s (!)

ρ

$$U_{ij} = U_{ij}^{EX} + U_{ij}^{ES} + U_{ij}^{Disp}$$

U_{ij}^{EX} = énergie de répulsion ($\sim e^{-r/\rho}$)

U_{ij}^{ES} = interaction électrostatique ($\sim q_i q_j / r$)

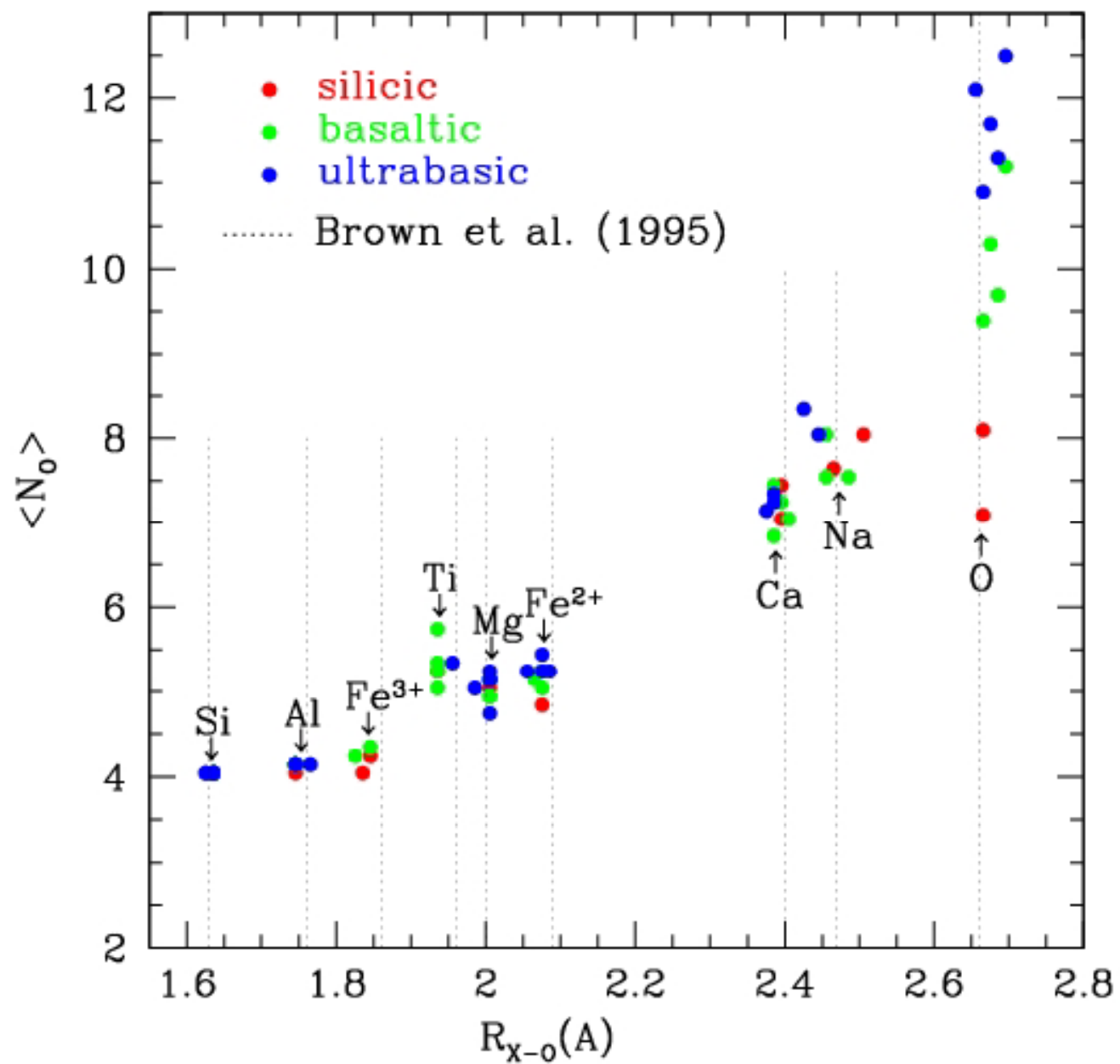
U_{ij}^{Disp} = énergie de dispersion ($\sim -1/r^6$)

	z(e)	B(kJ/mol)	$\rho(\text{Å})$	C(A⁶kJ/mol)
O	-0.945	870570.0	0.265	8210.17
Si	1.89	4853815.5	0.161	4467.07
Ti	1.89	4836495.0	0.178	4467.07
Al	1.4175	2753544.3	0.172	3336.26
Fe³⁺	1.4175	773840.0	0.190	0.0
Fe²⁺	0.945	1257488.6	0.190	0.0
Mg	0.945	3150507.4	0.178	2632.22
Ca	0.945	15019679.1	0.178	4077.45
Na	0.4725	11607587.5	0.170	0.0
K	0.4725	220447.4	0.290	0.0

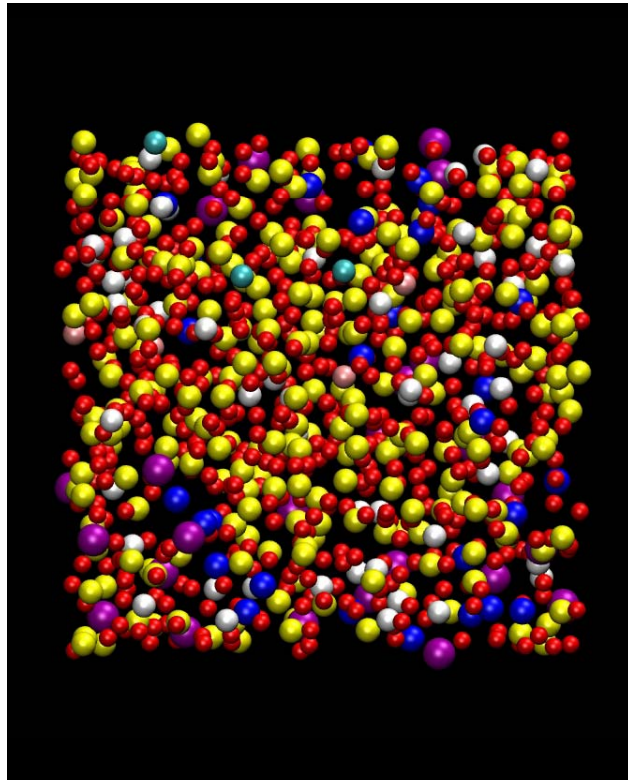
B. Guillot and N. Sator, GCA 71, 1249 (2007); GCA 71, 4538 (2007)

Chemical compositions (weight fraction) of the silicate melts investigated in this study

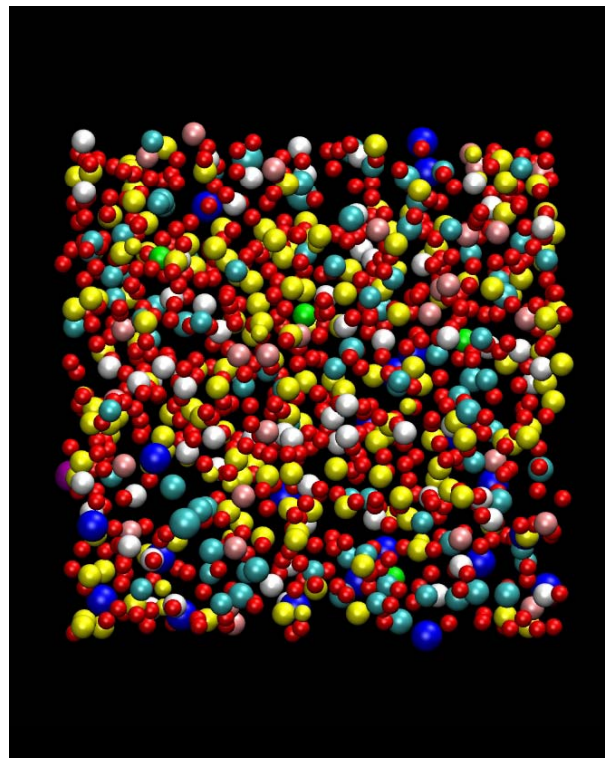
Silicate	SiO ₂ (wt%)	TiO ₂ (wt%)	Al ₂ O ₃ (wt%)	Fe ₂ O ₃ (wt%)	FeO (wt%)	MgO (wt%)	CaO (wt%)	Na ₂ O (wt%)	K ₂ O (wt%)	Total
Rhyolite (Ry)	74.51 (257)	0.10 (0)	13.25 (54)	0.32 (1)	1.28 (3)	0.08 (0)	0.75 (3)	4.15 (28)	5.64 (25)	100.08 (1000)
Andesite (And)	56.65 (203)	1.01 (3)	17.41 (73)	4.63 (12)	3.53 (11)	4.30 (23)	7.38 (28)	3.23 (22)	1.56 (7)	99.70 (998)
Basalt(MORB)	50.59 (185)	1.52 (4)	15.11 (65)	1.15 (3)	8.39 (26)	7.77 (42)	11.87 (47)	2.94 (21)	0.13 (1)	99.47 (1000)
Mars basalt (BM)	47.68 (176)	0.54 (1)	10.96 (48)	3.09 (9)	15.82 (49)	12.62 (69)	7.96 (31)	2.68 (19)	0.06 (0)	101.41 (1000)
Green glass (LG15)	48.00 (179)	0.26 (1)	7.74 (34)		16.50 (52)	18.20 (101)	8.57 (34)			99.27 (999)
Black glass (LG14)	34.00 (136)	16.40 (50)	4.60 (22)		24.50 (83)	13.30 (79)	6.90 (30)	0.23 (2)	0.16 (0)	100.09 (1000)
Komatiite (Ko)	46.73 (168)	0.31 (1)	6.30 (27)		10.76 (32)	28.42 (152)	6.29 (24)	0.85 (6)	0.13 (1)	99.79 (1001)
Peridotite (Pe)	45.10 (159)		2.80 (12)		10.40 (31)	38.40 (203)	3.40 (13)			100.10 (1001)
Olivine (Ol)	40.68 (142)		0.01 (0)		8.76 (25)	50.52 (262)	0.06 (0)			100.03 (1000)
Allende m. (All)	38.57 (147)	0.14 (0)	3.71 (17)		24.79 (79)	29.23 (166)	2.62 (11)	0.48 (3)		99.54 (1000)
Fayalite (Fa)	29.49 (143)				70.51 (286)					100.00 (1001)



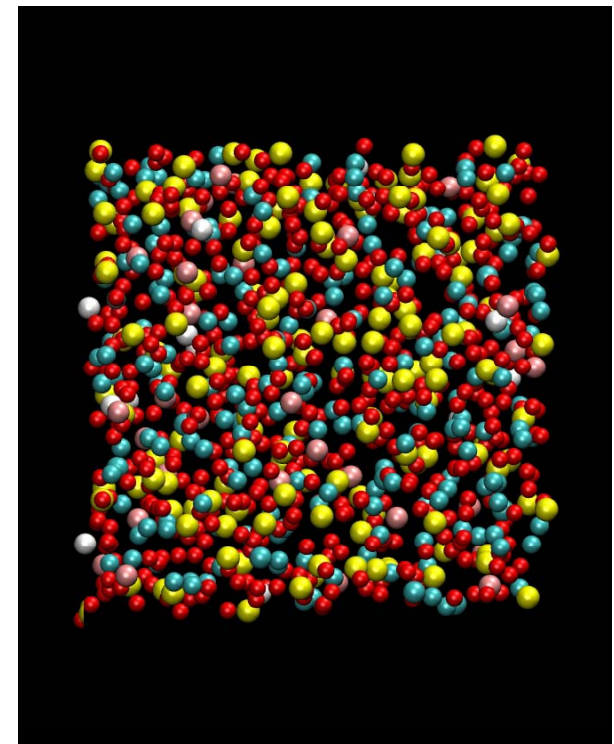
Rhyolite



MORB

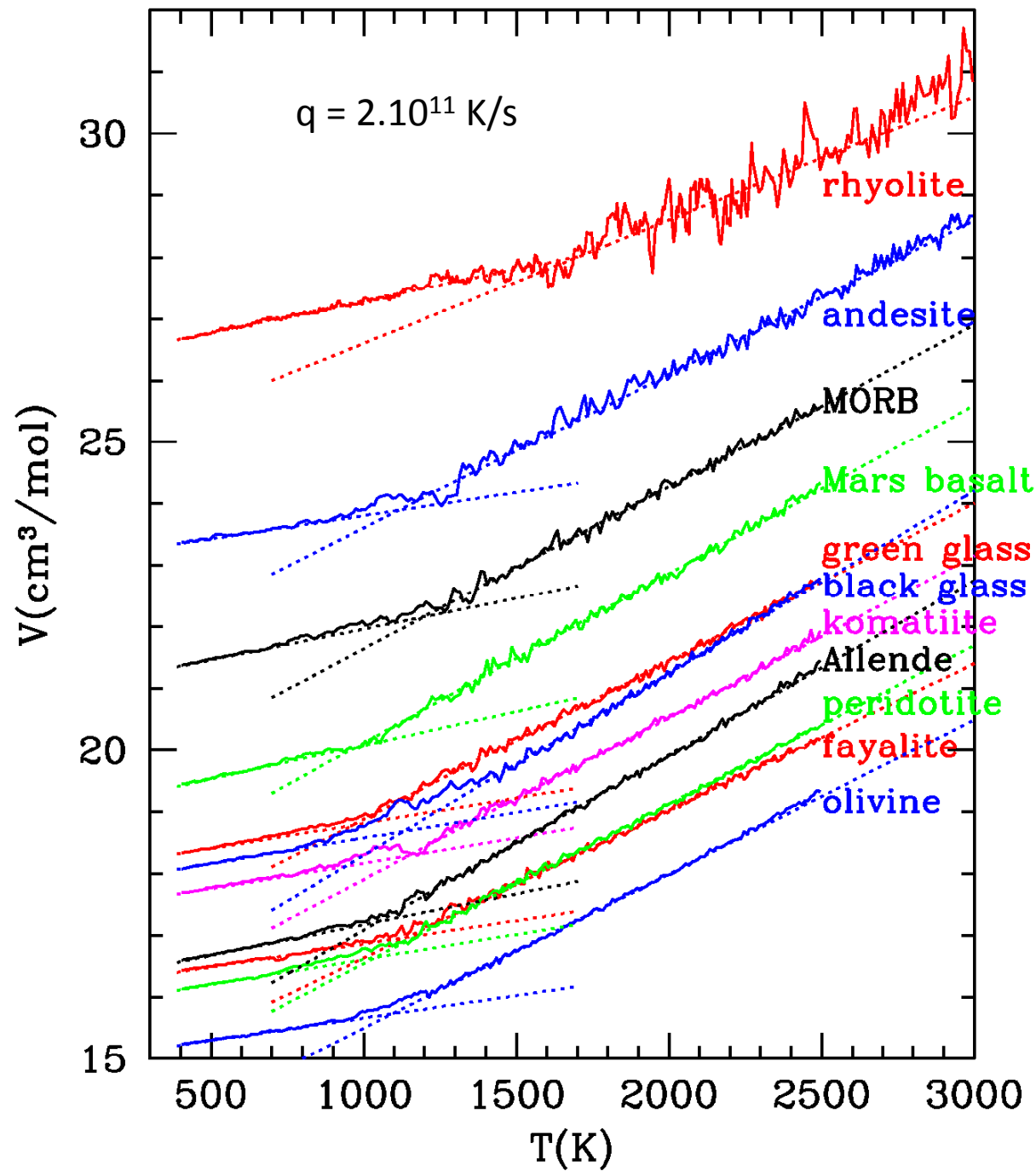


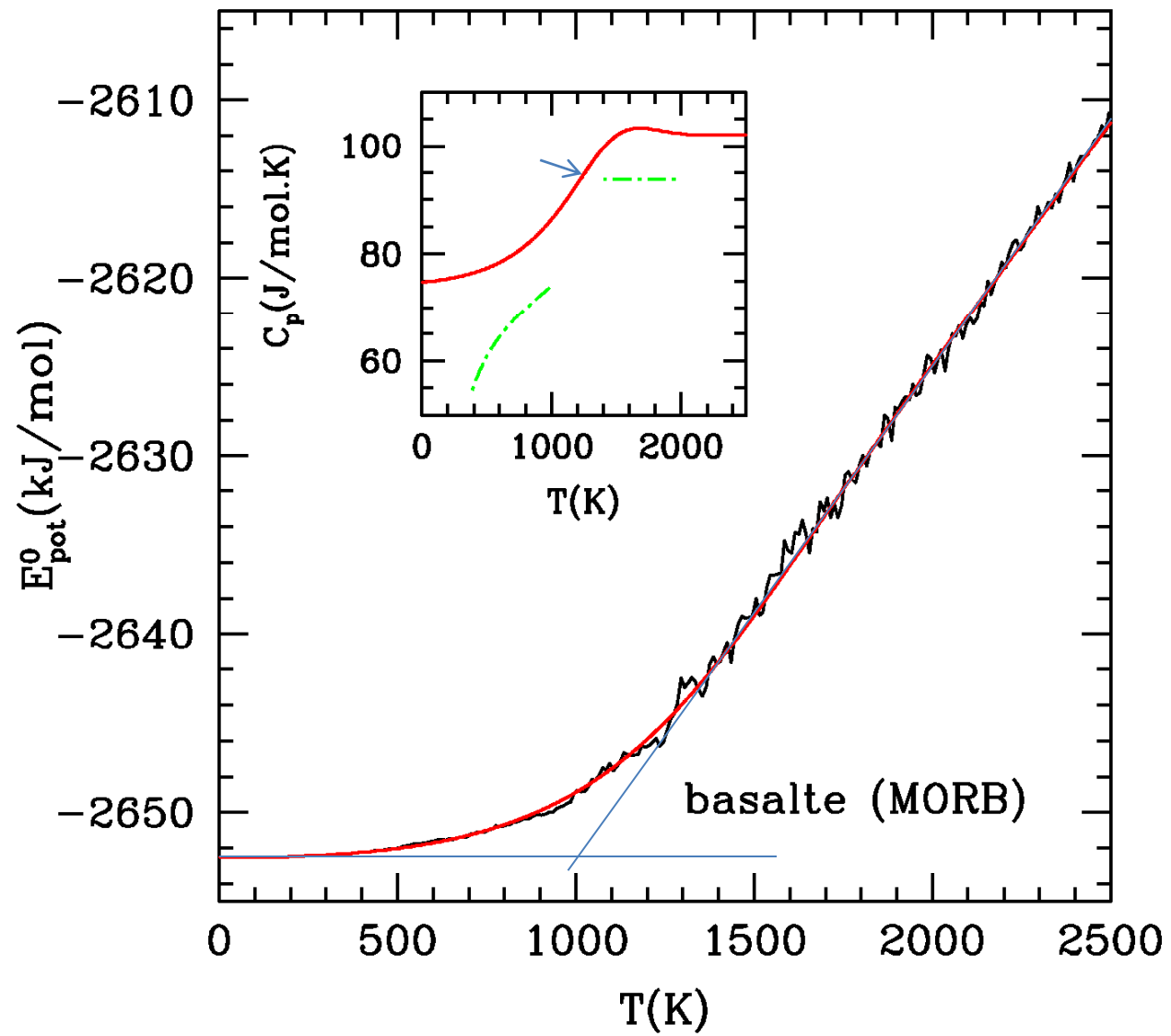
Peridotite

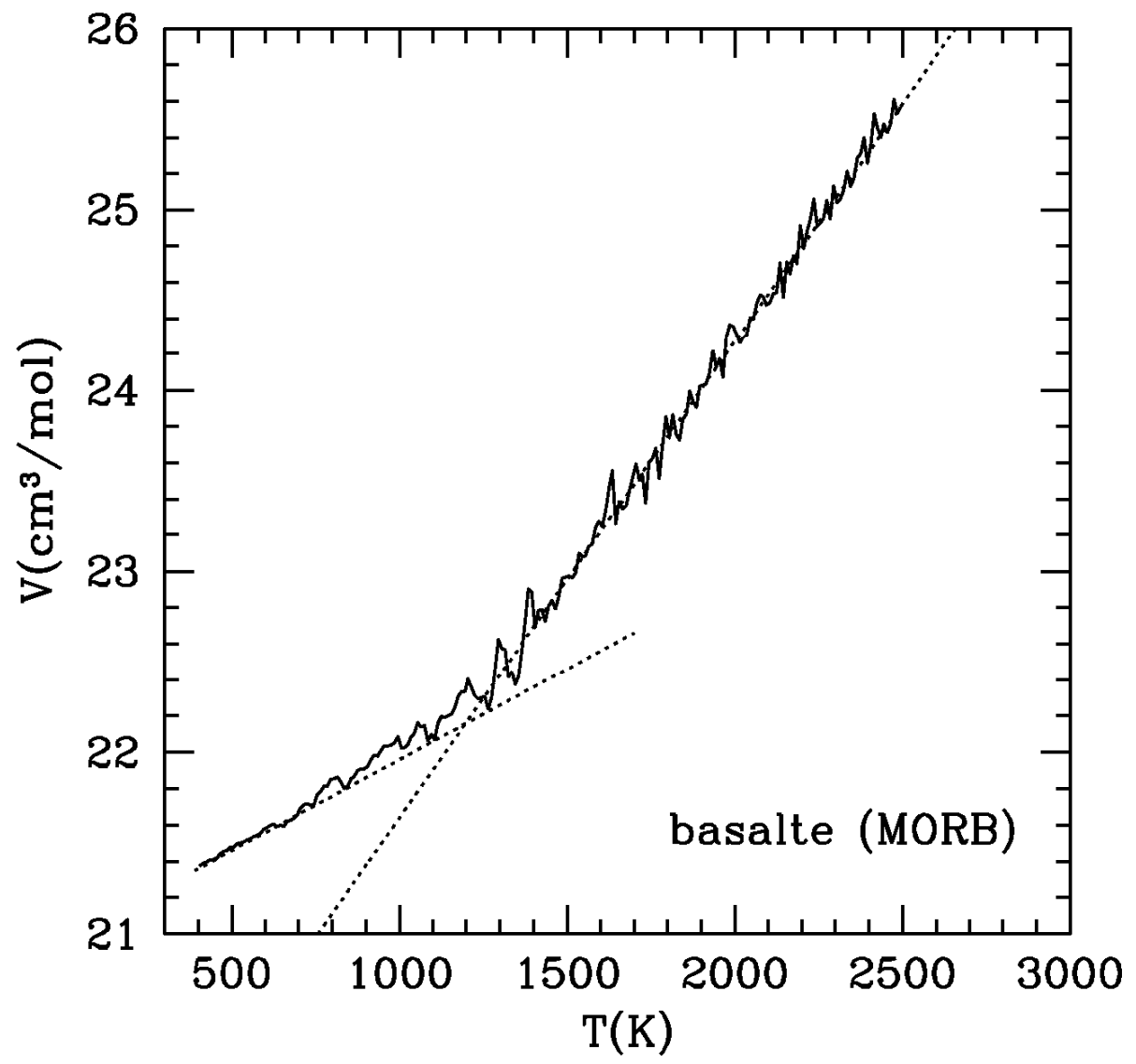


2273K, ~1 bar

O red	Mg light blue
Si yellow	Ca light blue
Ti green	Na blue
Al white	K purple
Fe pink	

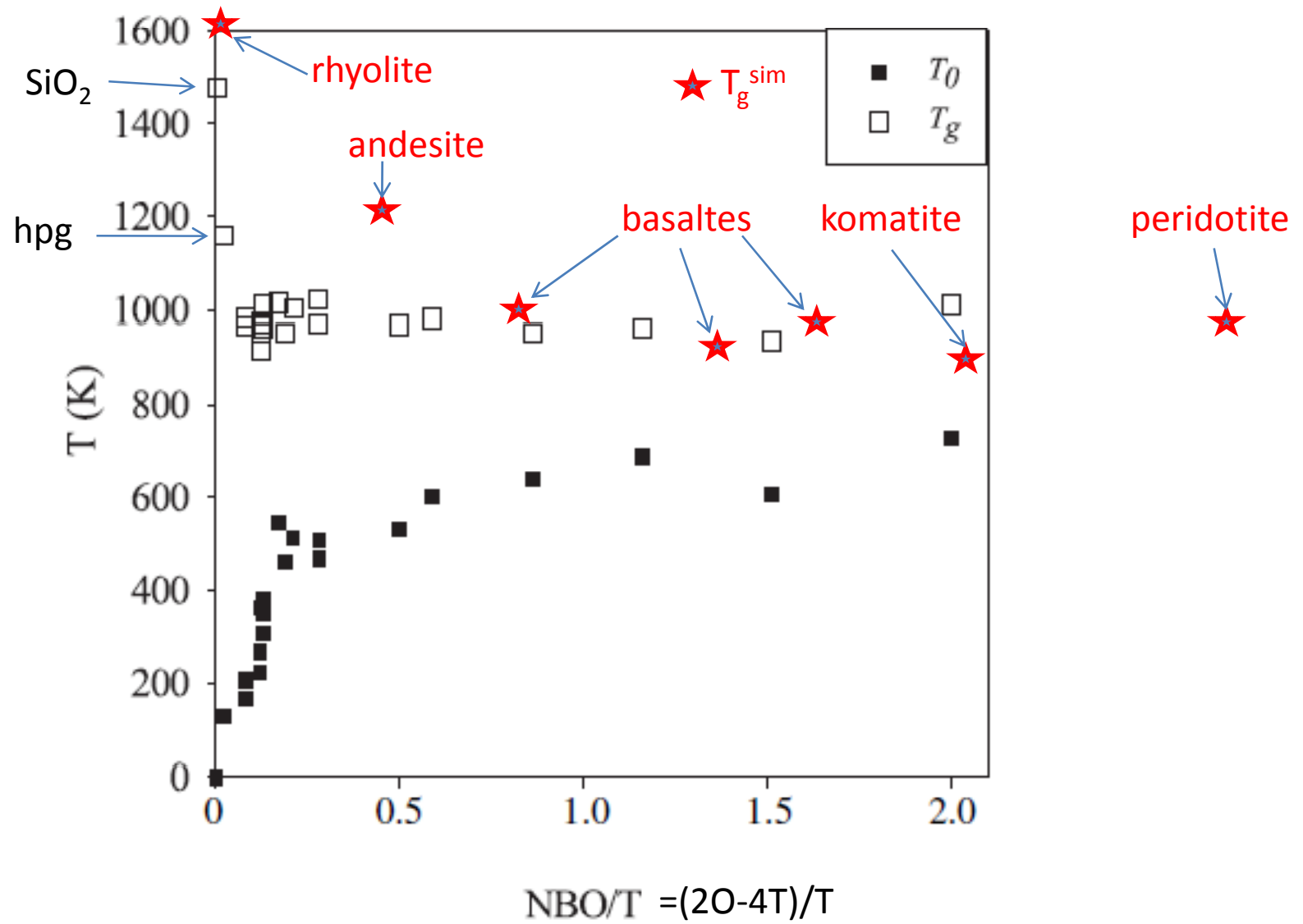




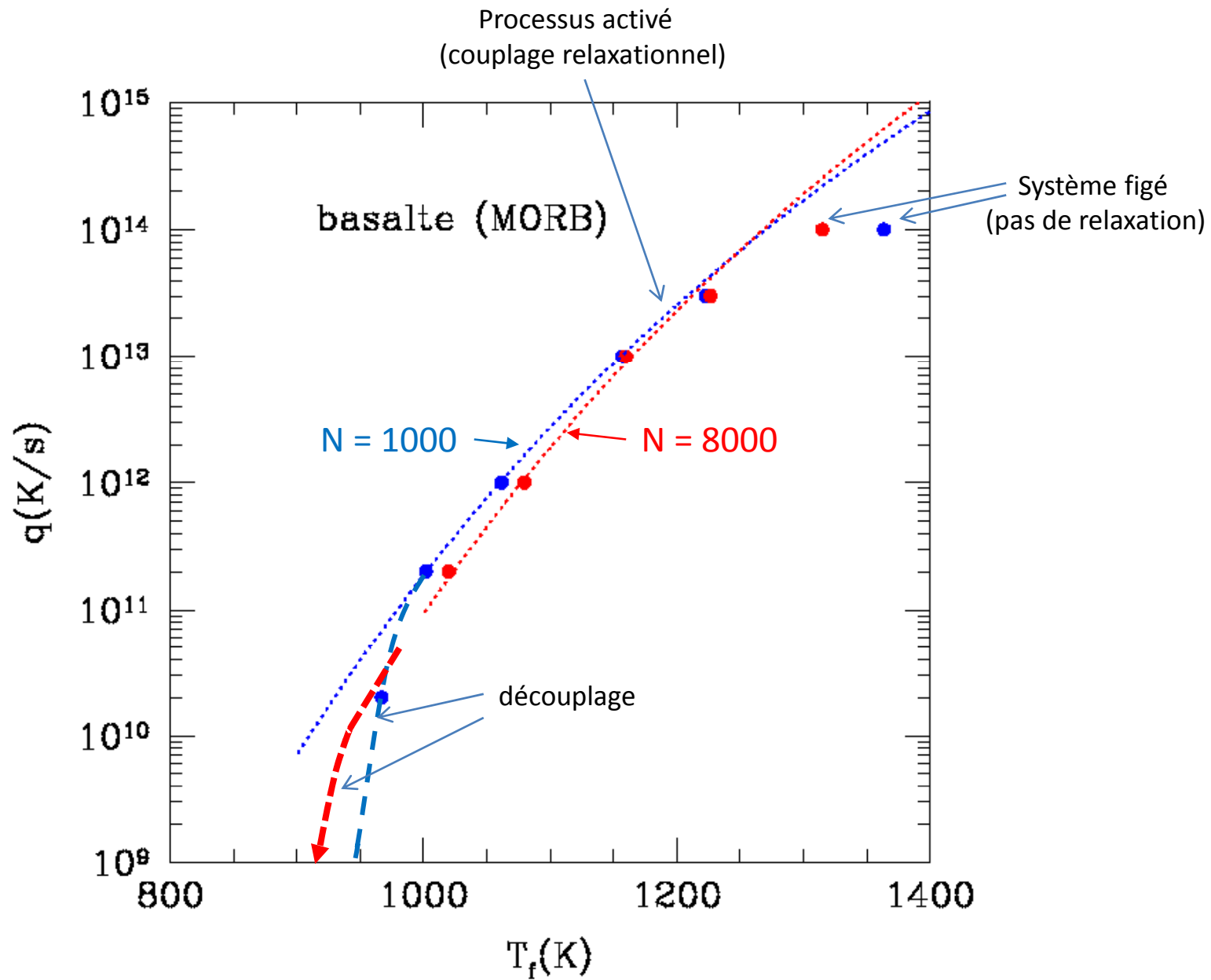


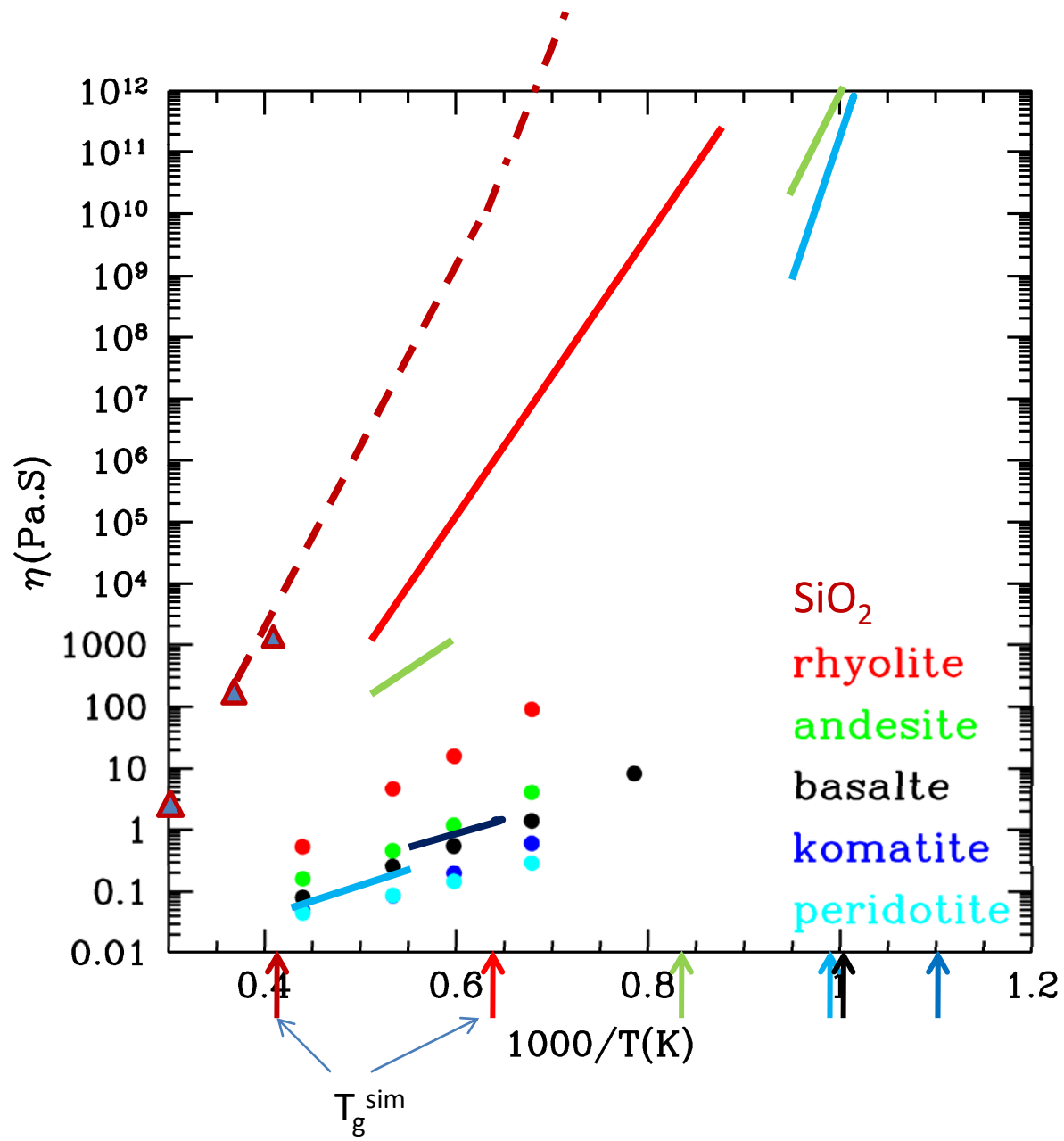
	$T_g(K) = (\text{dilatométrie; calorimétrie})$	T_g^{exp}
Rhyolite (74.5 wt%SiO ₂)	1500; 1600	1125
andesite (56.7 wt%SiO ₂)	1116; 1210	1013
MORB (50.6 wt%SiO ₂)	1178; 1000	950
Mars (47.7 wt%SiO ₂)	960; 940	
Lunar Glass 14 (34.0 wt%SiO ₂)	1126; 1020	
Lunar Glass 15 (48.0 wt%SiO ₂)	960; 990	
komatite (46.7 wt%SiO ₂)	1147; 900	~1000
peridotite (45.10 wt%SiO ₂)	1037; 1000	~1000
Allende (38.6 wt%SiO ₂)	1043; 900	
olivine (40.7 wt%SiO ₂)	1100; 1000	
fayalite (29.5 wt%SiO ₂)	1137; 1000	

D'après Giordano and Dingwell, J.Phys.: Condens. Matter 15 (2003) S945-954)

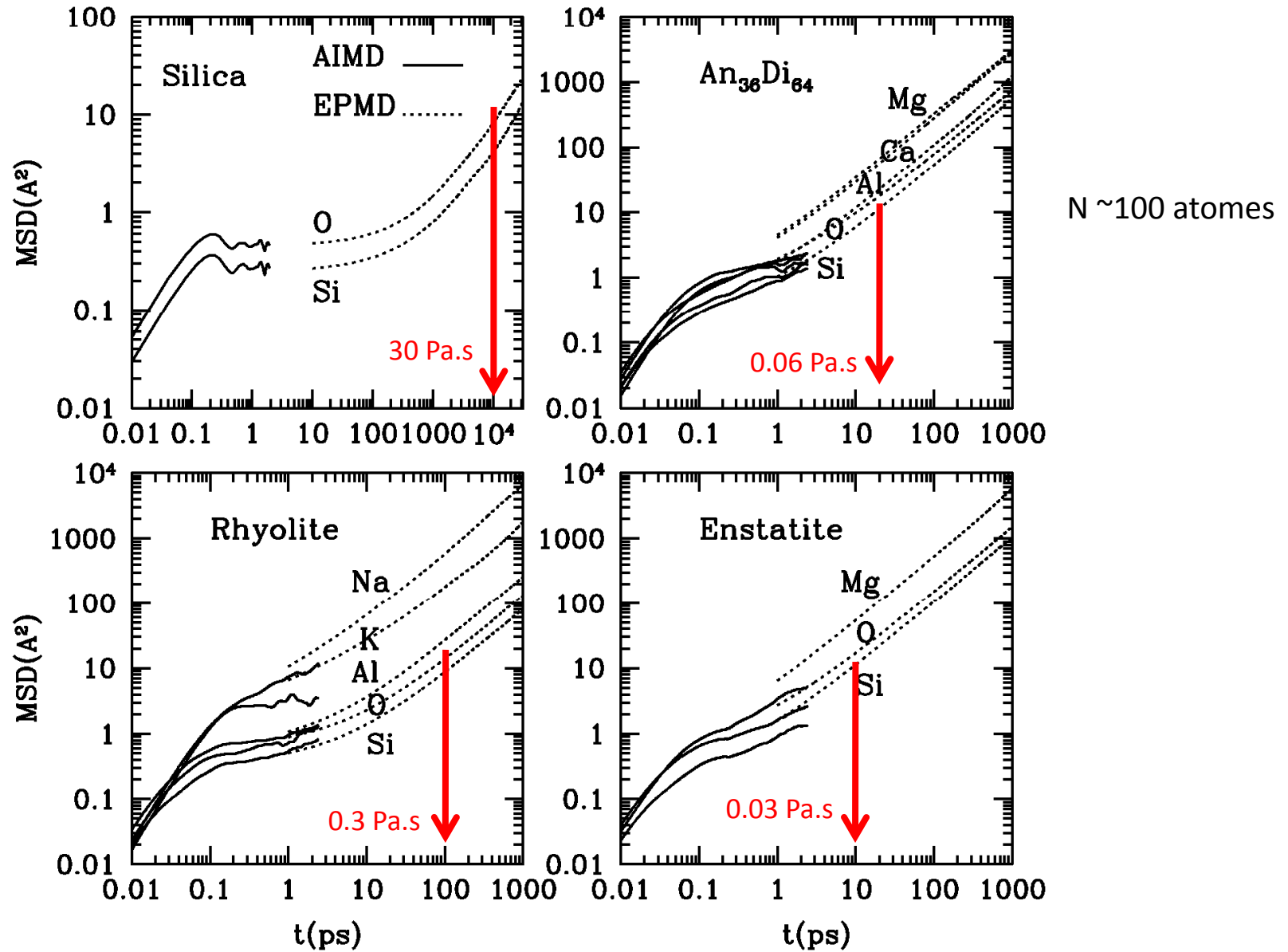


$$\text{Log } \eta = A + B/(T - T_0)$$





Calculer la viscosité (à 2000 °C) de la silice par simulation ab initio est hors de portée ... pour l'instant



N = 80 atoms
 $t_{\text{run}} = 70\text{-}200$ ps

