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LA TECHNOLOGIE VERRIÈRE

Imaginer de nouvelles compositions de verre ?



Pourquoi se poser cette question?

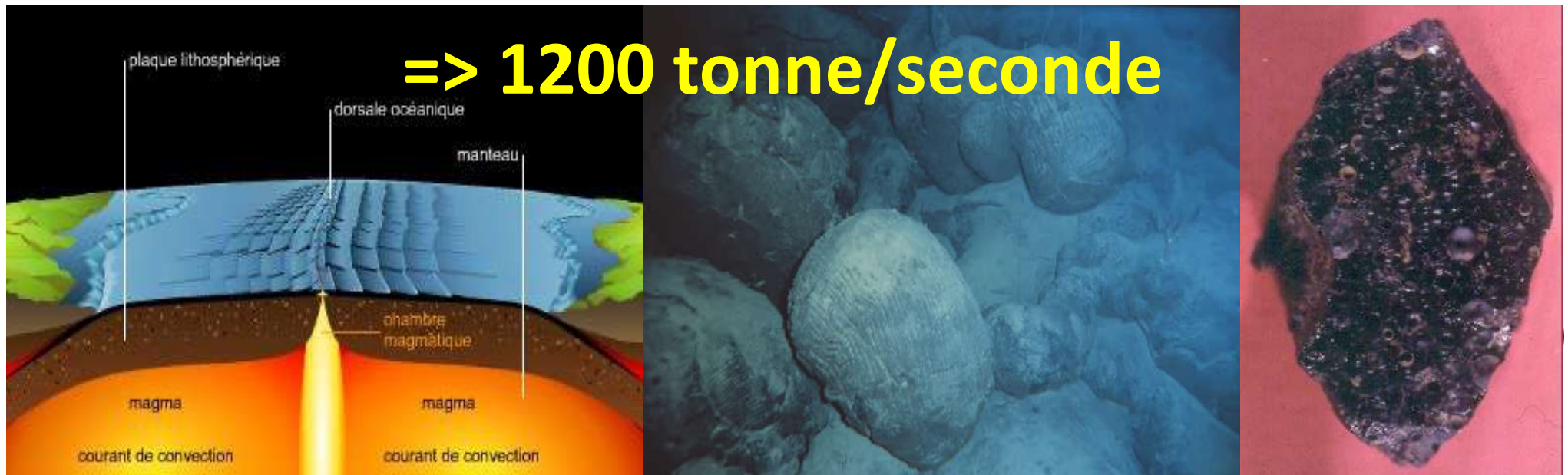
Volume du verre d'emballages (bouteilles, pots, flacons..) ~ 2,6 millions tonnes

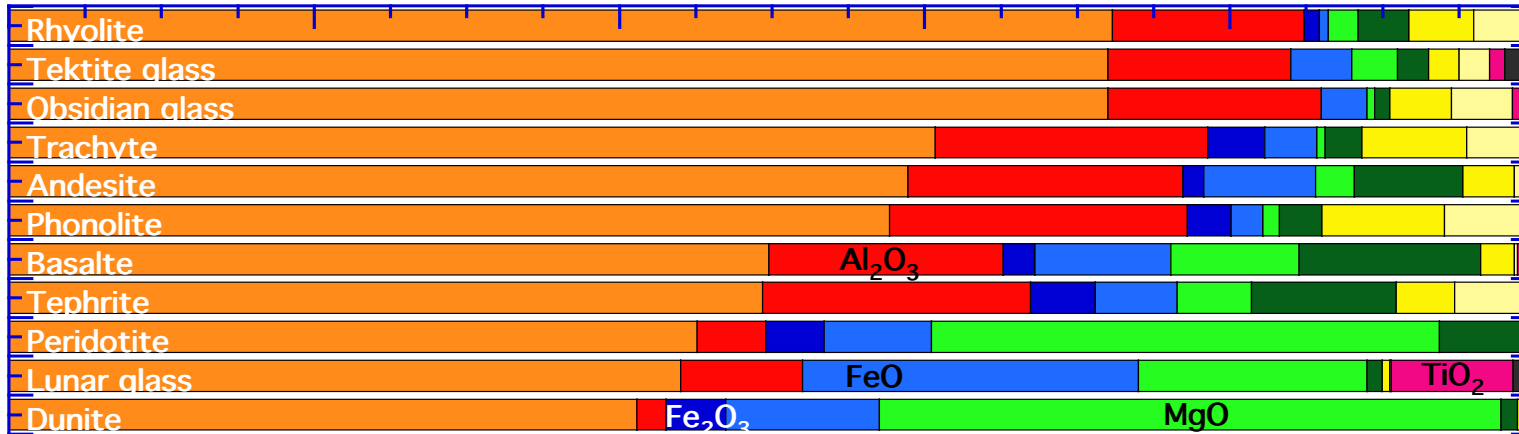
Volume de calcin ~ 2,2 millions tonnes

Quel est le plus grand producteur de verre au monde?

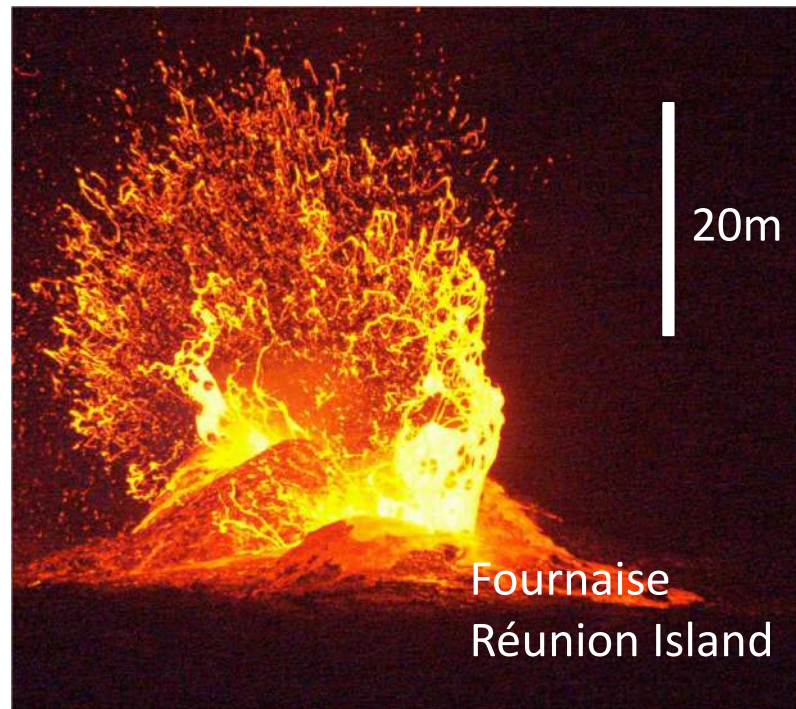
Industrie verrière : 140 millions de tonne par an
~72millions verre plat

La Terre : 37900 millions de tonne par an



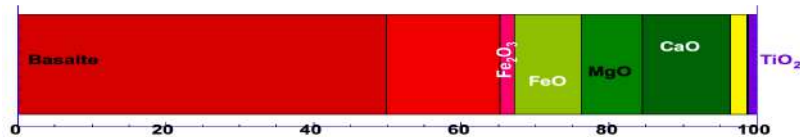
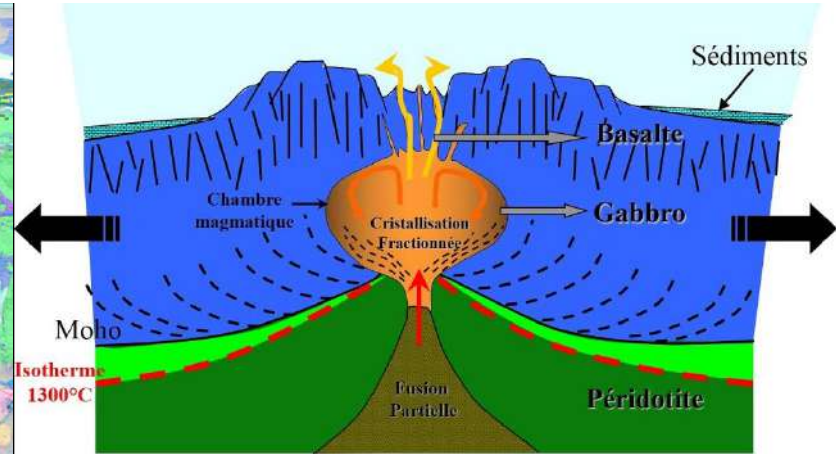
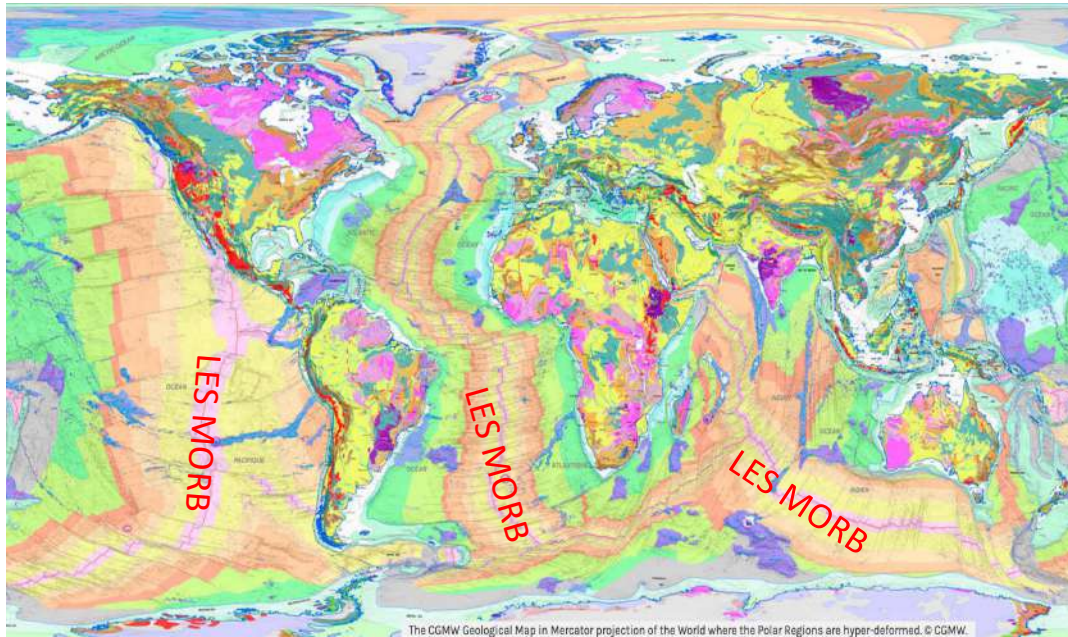


Mt. St. Helens, 1980; photo by M.P. Doukas, USGS

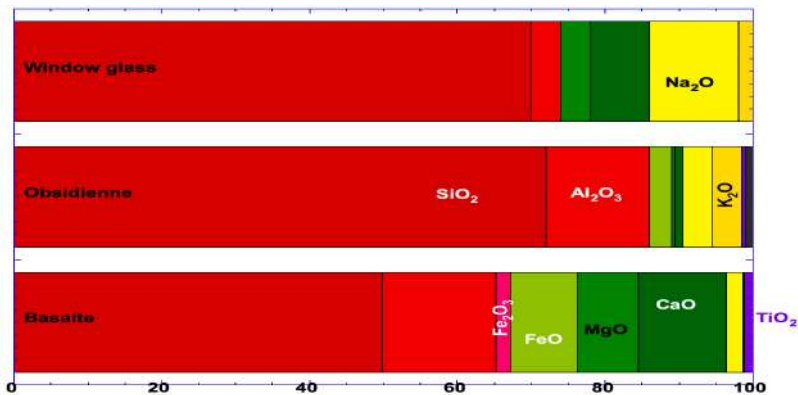
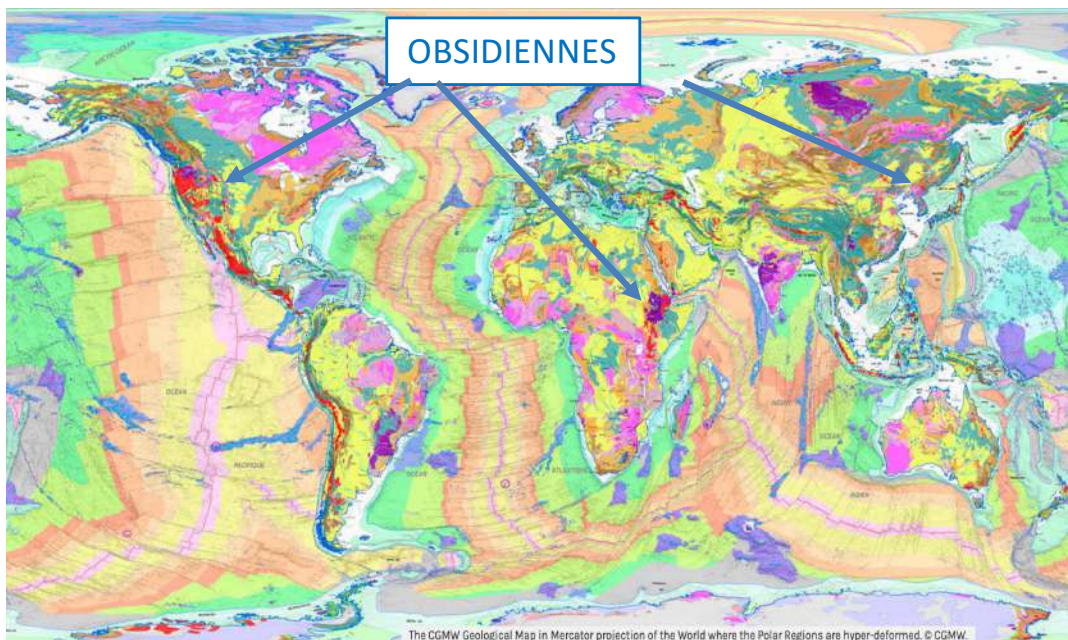


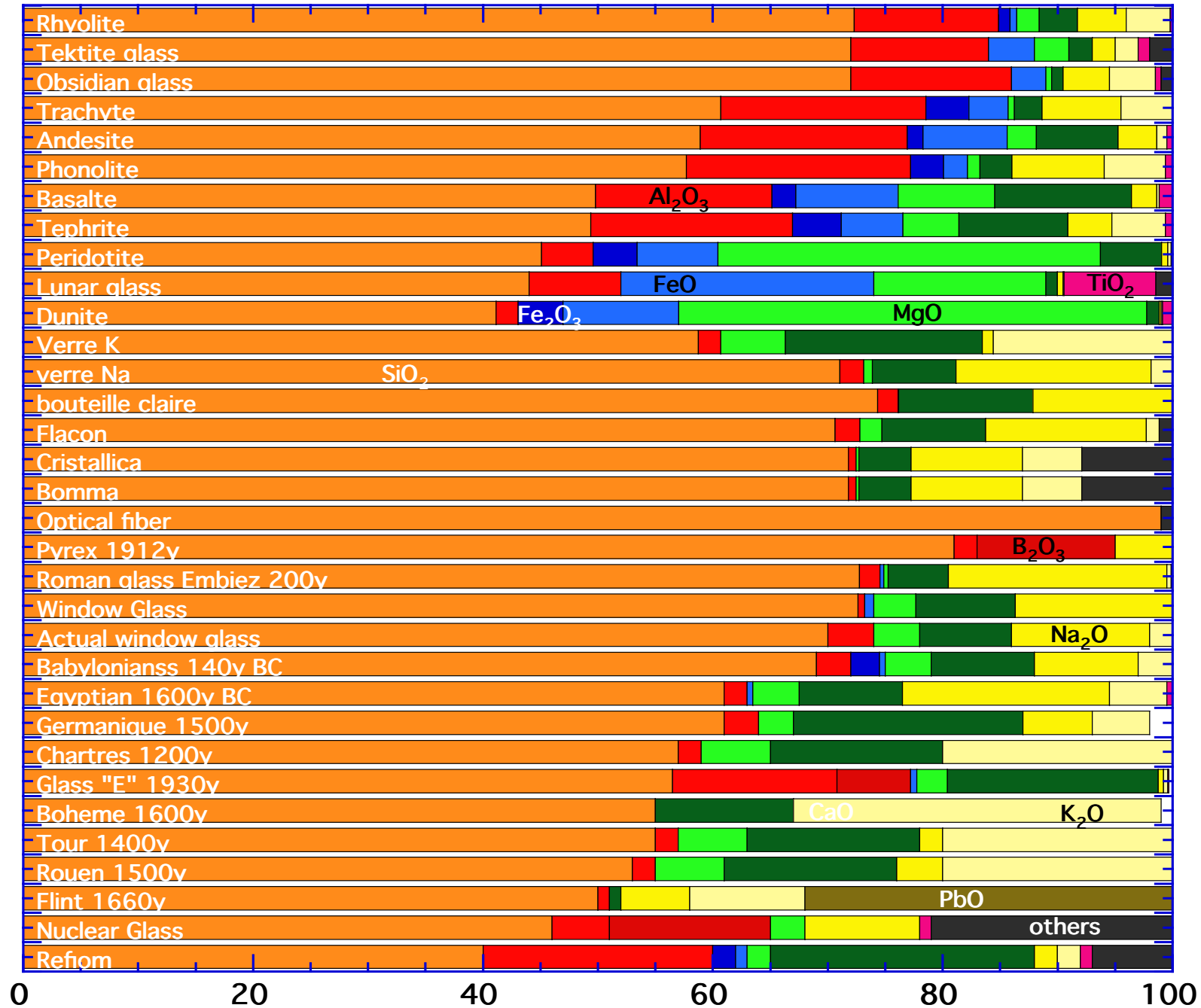
Fournaise
Réunion Island

✓ Où trouver du verre autour de nous ?



✓ Où trouver du verre autour de nous ?







Verre métallique



Laser glasses



Verre de phosphate

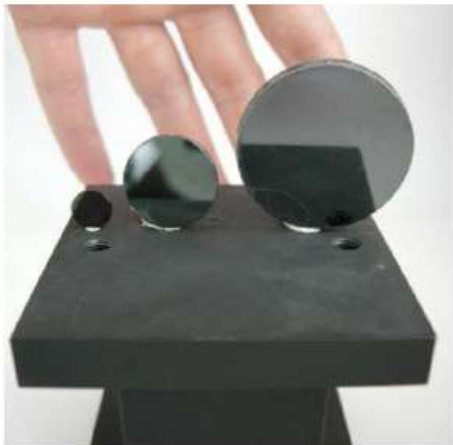


Image visible

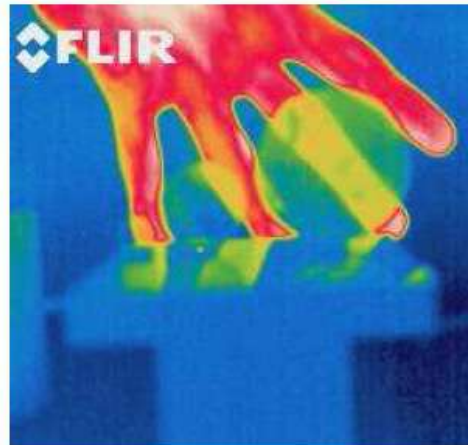


Image caméra thermique 8-12µm

Verre organique : le caramel



Source : écoles et ateliers UTSV, www.ustverre.fr

1 1.008* H hydrogen												2 4.003 He helium					
3 6.94* Li lithium	4 9.012 Be beryllium											5 10.81* B boron	6 12.01* C carbon	7 14.01* N nitrogen	8 16.00* O oxygen	9 19.00 F fluorine	10 20.18 Ne neon
11 22.99 Na sodium	12 24.31* Mg magnesium											13 26.98 Al aluminium	14 28.09* Si silicon	15 30.97 P phosphorus	16 32.06* S sulfur	17 35.45* Cl chlorine	18 39.95 Ar argon
19 39.10 K potassium	20 40.08 Ca calcium	21 44.96 Sc scandium	22 47.87 Ti titanium	23 50.94 V vanadium	24 52.00 Cr chromium	25 54.94 Mn manganese	26 55.85 Fe iron	27 58.93 Co cobalt	28 58.69 Ni nickel	29 63.55 Cu copper	30 65.38 Zn zinc	31 69.72 Ga gallium	32 72.63 Ge germanium	33 74.92 As arsenic	34 78.97 Se selenium	35 79.90* Br bromine	36 83.80 Kr krypton
37 85.47 Rb rubidium	38 87.62 Sr strontium	39 88.91 Y yttrium	40 91.22 Zr zirconium	41 92.91 Nb niobium	42 95.95* Mo molybdenum	43 [98] Tc technetium	44 101.1 Ru ruthenium	45 102.9 Rh rhodium	46 106.4 Pd palladium	47 107.9 Ag silver	48 112.4 Cd cadmium	49 114.8 In indium	50 118.7 Sn tin	51 121.8 Sb antimony	52 127.6 Te tellurium	53 126.9 I iodine	54 131.3 Xe xenon
55 132.9 Cs caesium	56 137.3 Ba barium	57-71 La lanthanum	72 178.5 Hf hafnium	73 180.9 Ta tantalum	74 183.8 W tungsten	75 186.2 Re rhenium	76 190.2 Os osmium	77 192.2 Ir iridium	78 195.1 Pt platinum	79 197.0 Au gold	80 200.6 Hg mercury	81 204.4 Tl thallium	82 207.2 Pb lead	83 209.0 Bi bismuth	84 [209] Po polonium	85 [210] At astatine	86 [222] Rn radon
87 [223] Fr francium	88 [226] Ra radium	89-103 Ac actinium	90 232.0 Th thorium	91 231.0 Pa protactinium	92 238.0 U uranium	93 [237] Np neptunium	94 [244] Pu plutonium	95 [243] Am americium	96 [247] Cm curium	97 [247] Bk berkelium	98 [251] Cf californium	99 [252] Es einsteinium	100 [257] Fm fermium	101 [258] Md mendelevium	102 [259] No nobelium	103 [266] Lr lawrencium	
		57 138.9 La lanthanum	58 140.1 Ce cerium	59 140.9 Pr praseodymium	60 144.2 Nd neodymium	61 [145] Pm promethium	62 150.4 Sm samarium	63 152.0 Eu europium	64 157.3 Gd gadolinium	65 158.9 Tb terbium	66 162.5 Dy dysprosium	67 164.9 Ho holmium	68 167.3 Er erbium	69 168.9 Tm thulium	70 173.0 Yb ytterbium	71 175.0 Lu lutetium	

Formateur de réseau, FR
 Ligand
 Gaz
 Modificateur de réseau, MR
Ou compensateur de charge, CC
 Ligand ou FR
 Élément intermédiaire

Comptes Rendus
 Géoscience — Sciences de la Planète
 2022, Vol. 354, Special Issue S1, p. 1-14
<https://doi.org/10.5802/crgeos.171>

Glass, an ubiquitous material / *Le verre, un matériau omniprésente*

Glass, an ubiquitous material

Le verre, un matériau omniprésent

Daniel R. Neuville[✉]

- Tous les éléments et toutes les liaisons chimiques:
- covalentes
 - ioniques
 - métalliques
 - Van der Waal's
 - Hydrogène

=> Verre d'oxydes, de chalcogénures, métalliques, d'halures, organiques et toutes les combinaisons possible



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Qu'est ce qu'un verre ?



✓ Quelques grandes notions sur le verre : Structure et propriétés

Huang, S. Kurasch, A. Srivastava, V. Skakalova, J. Kotakoski, A.V. Krasheninnikov, R. Hovden, Q. Mao, J.C. Meyer, J. Smet, D.A. Muller, U. Kaiser: Direct imaging of a two-dimensional silica glass on graphene, Nano Lett. 12, 1081–1086 (2012)

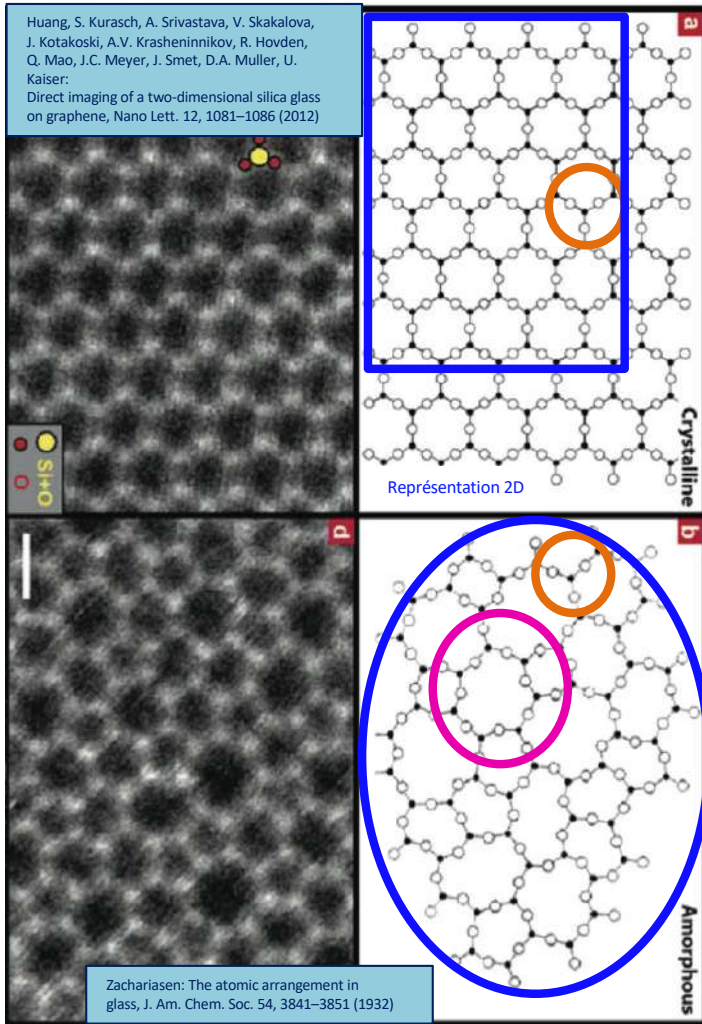
Représentation 2D

Crystalline

Zachariasen: The atomic arrangement in glass, J. Am. Chem. Soc. 54, 3841–3851 (1932)

Amorphous





Structure à courte distance :

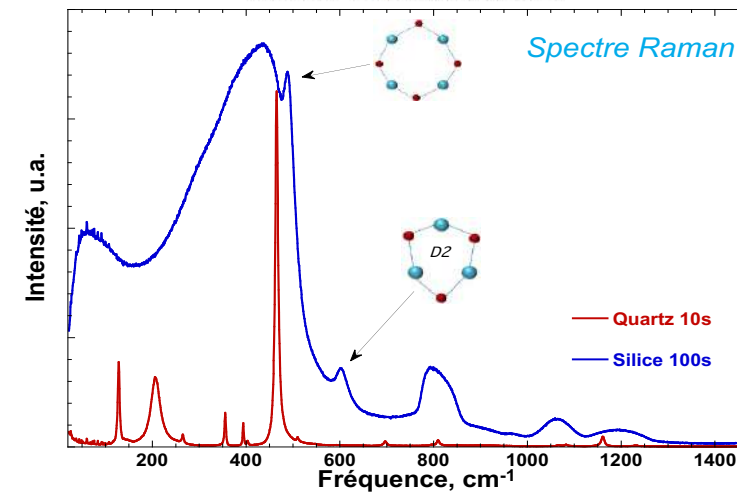
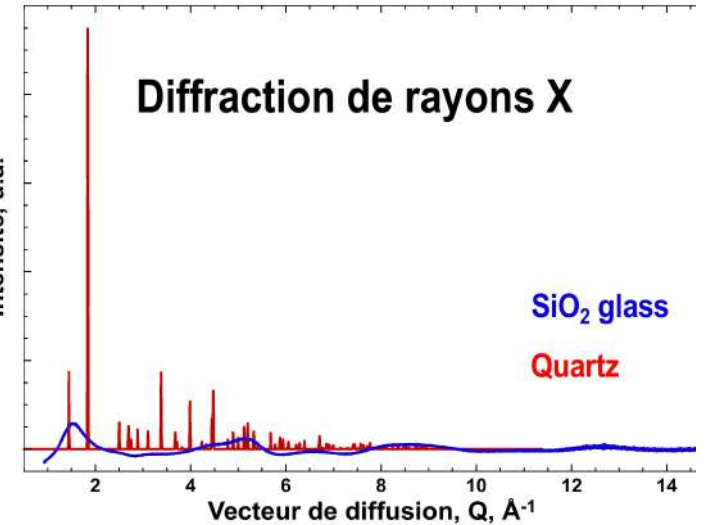
- coordinence, longueurs de liaisons, angles de liaisons

Structure à moyenne distance

- angles entre les unités de base
- connectivité entre les unités de base (liaisons par sommet, arête ...)
- dimensionnalité du réseau, anneaux

Structure à longue distance (pas périodique !):

- séparation de phase
- inhomogénéité





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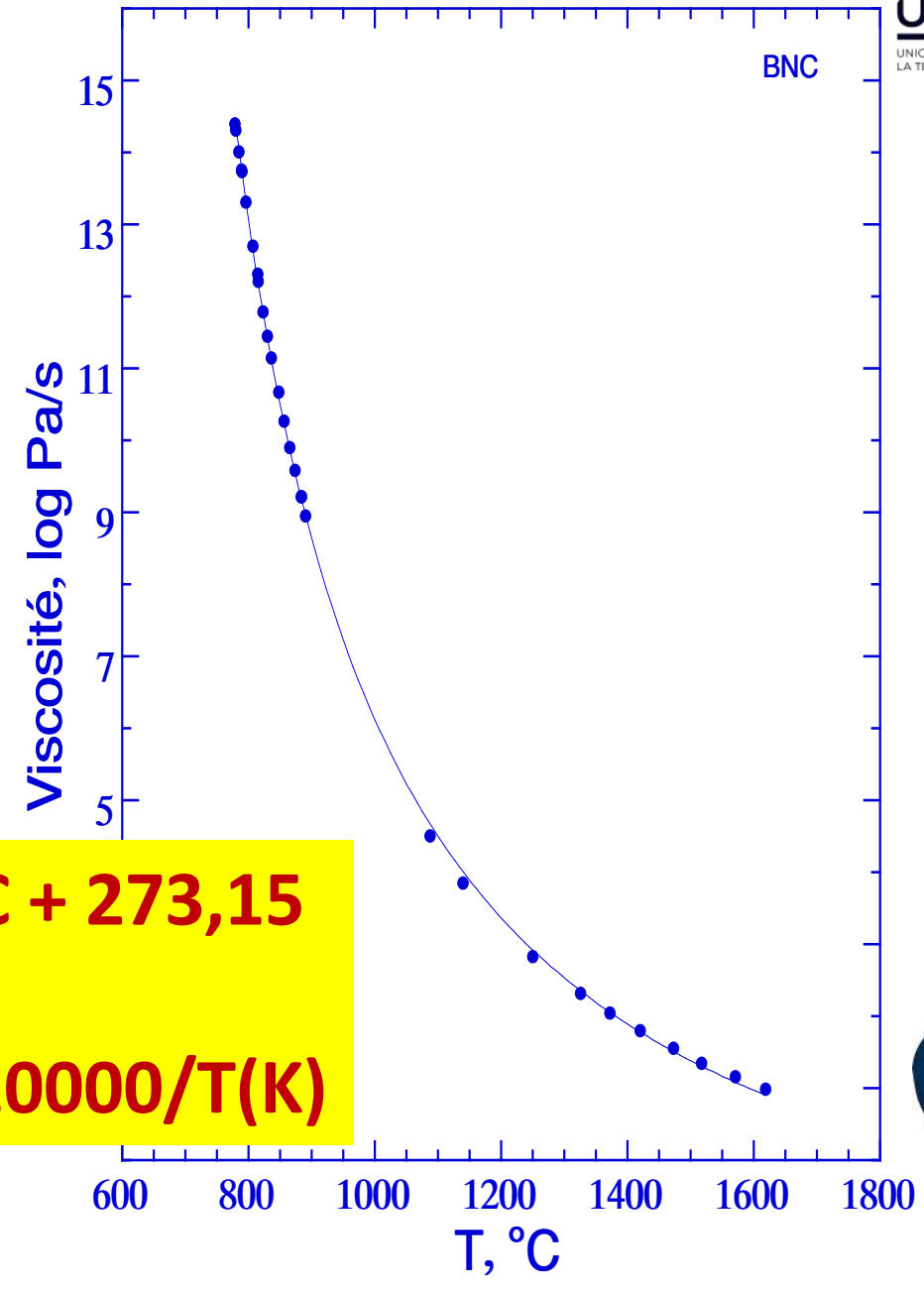
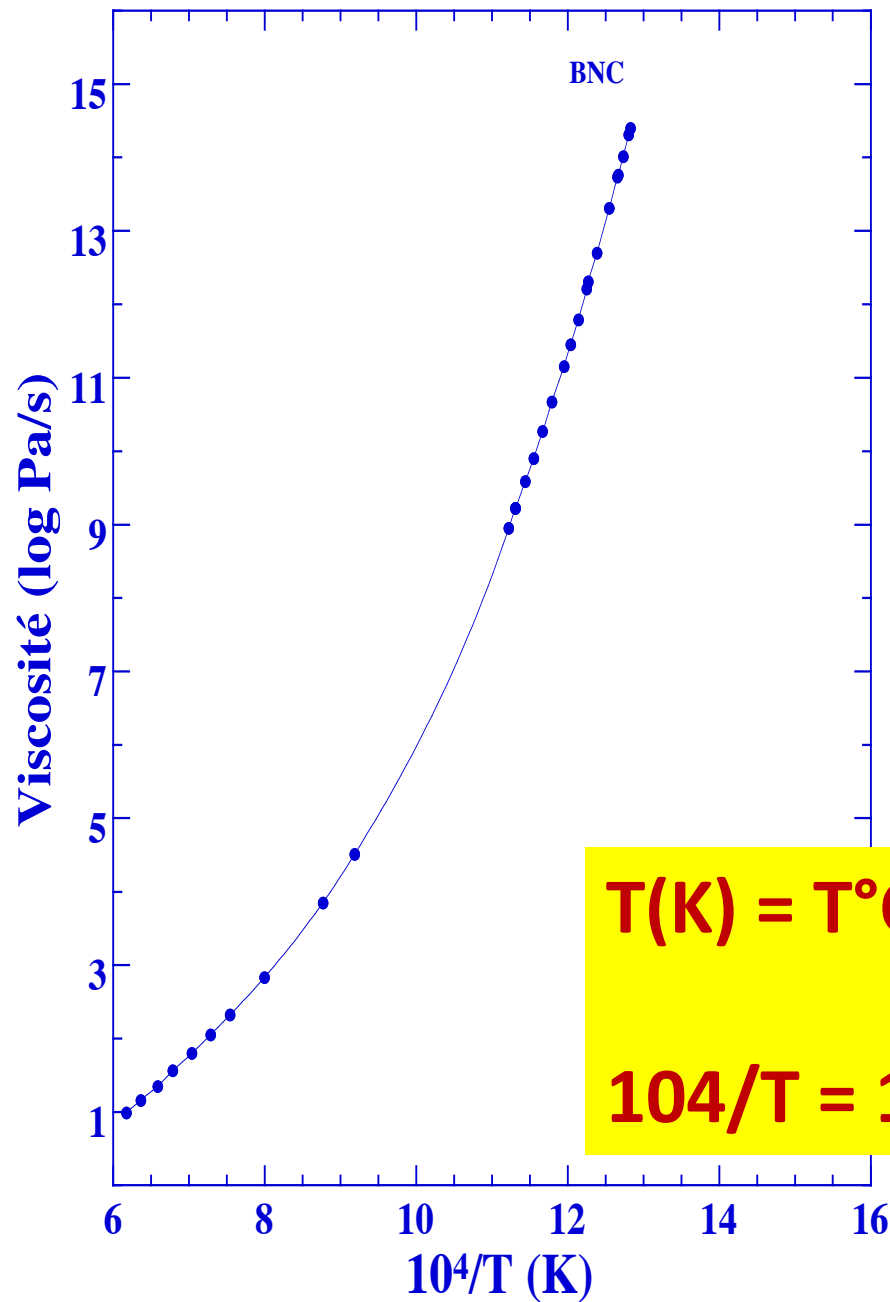
Qu'elle est la principale propriété d'un verre ?



Grand nombre -> difficile à mesurer



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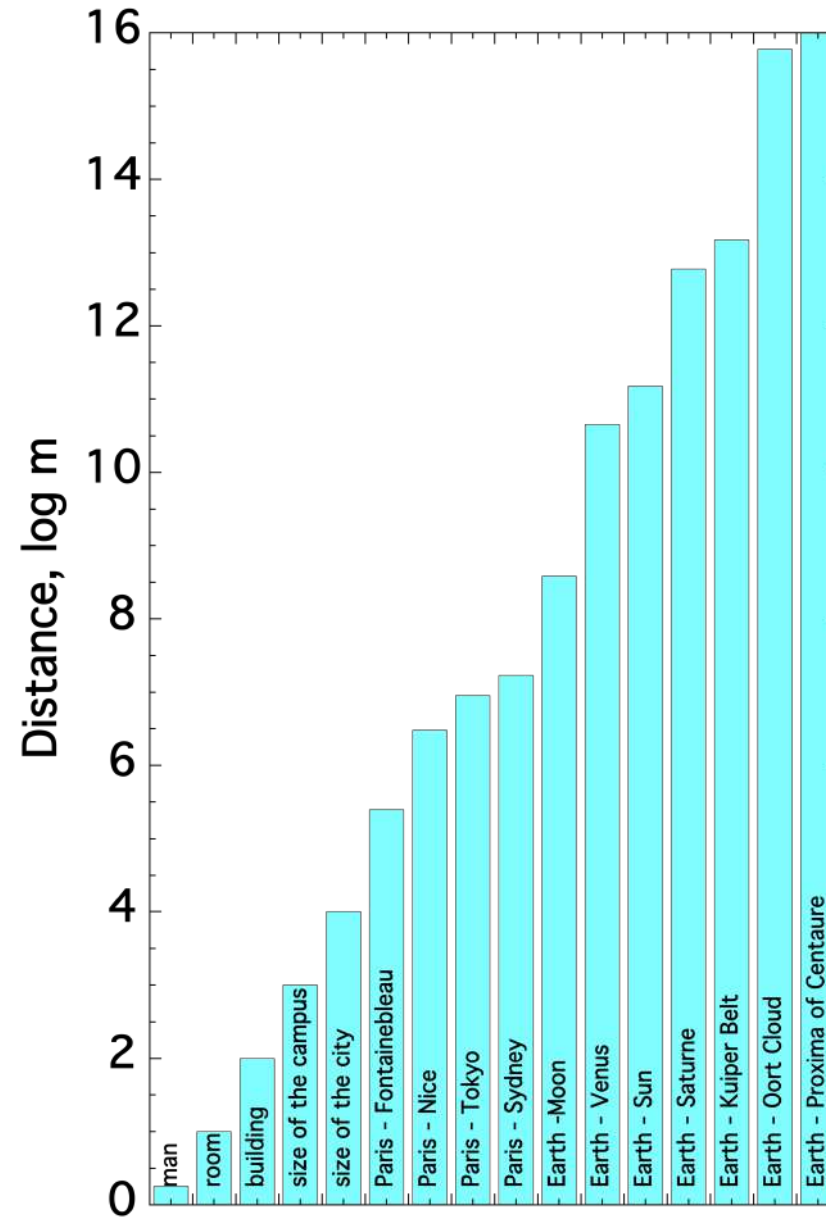
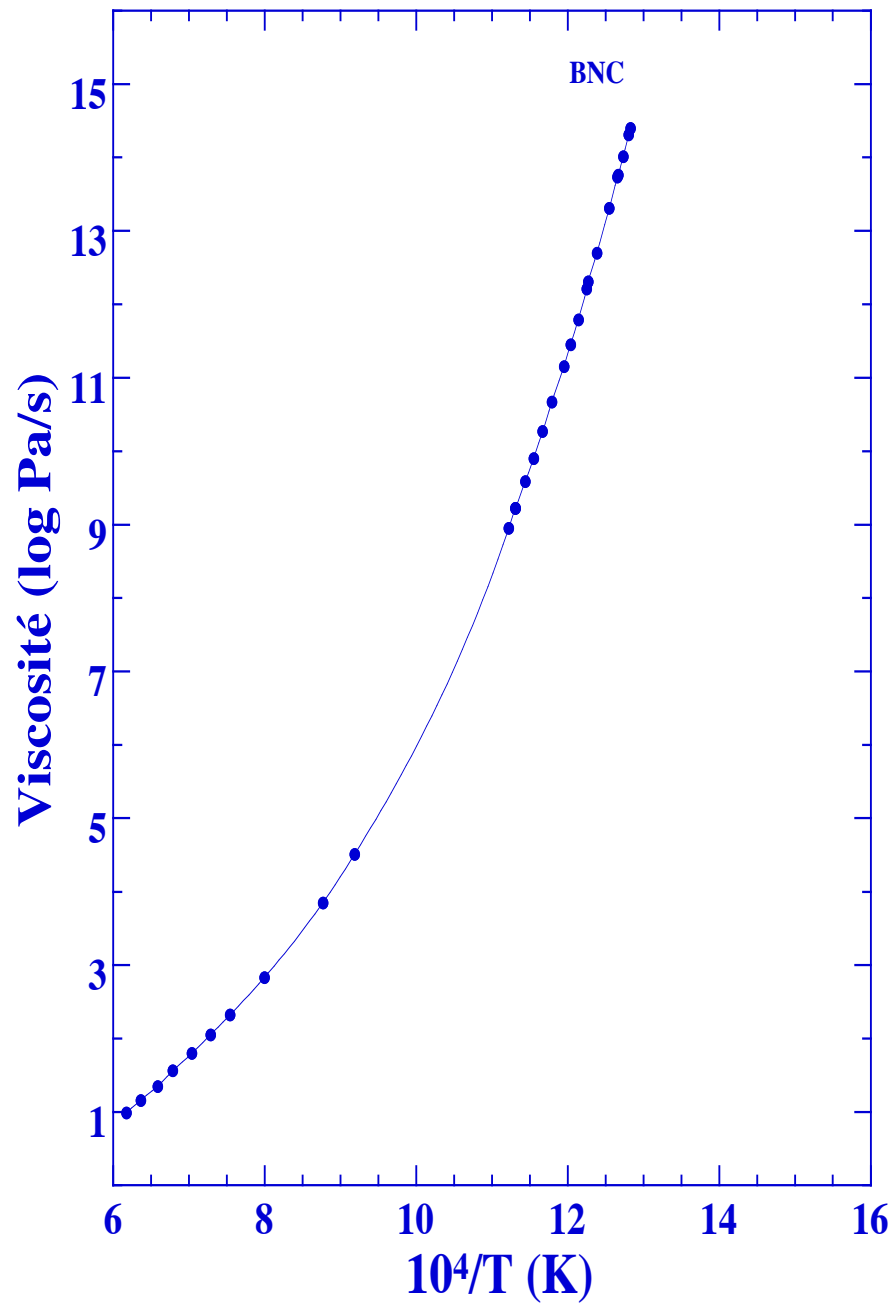
$T(K) = T^{\circ}C + 273,15$
 $10^4/T = 10000/T(K)$

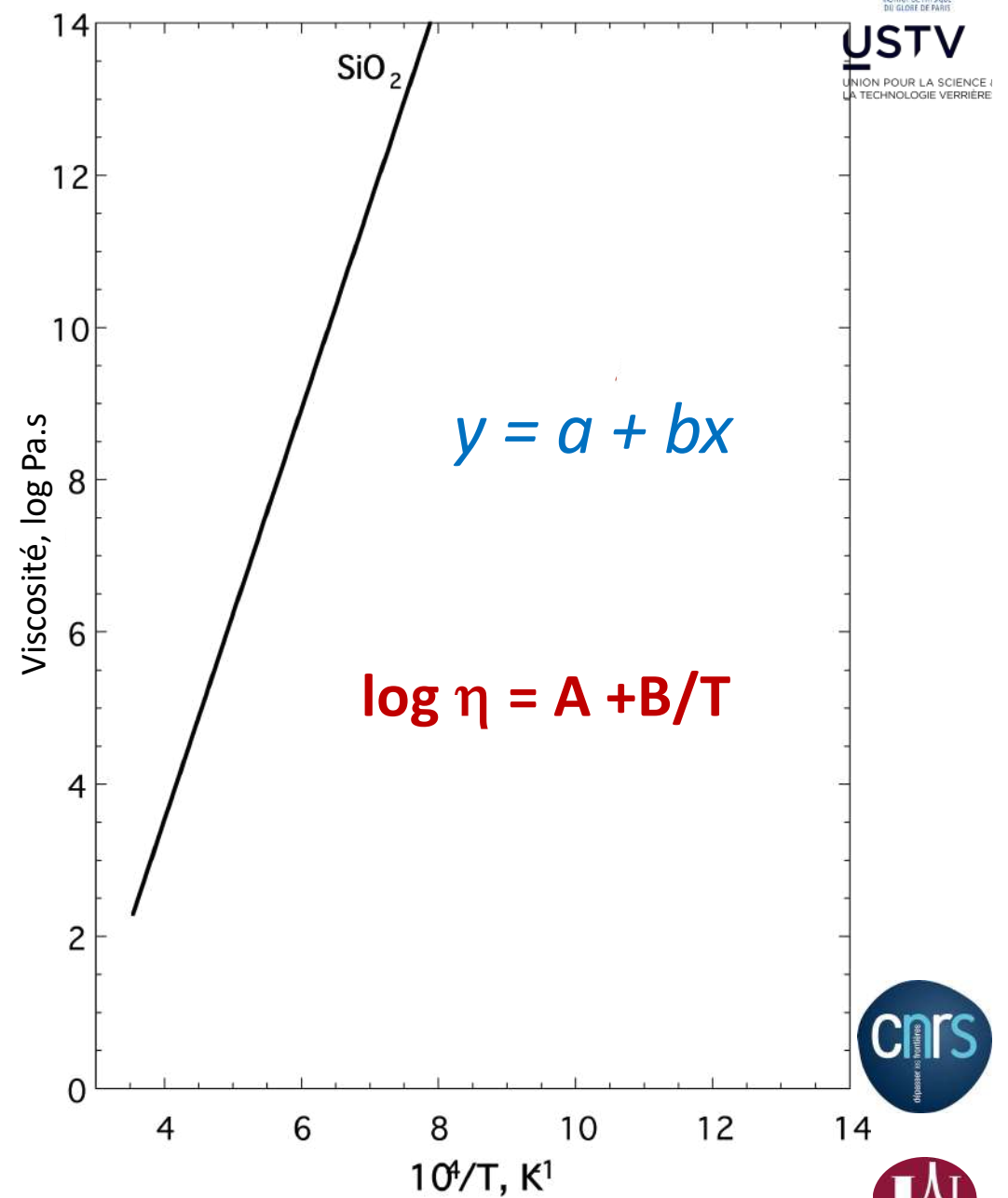
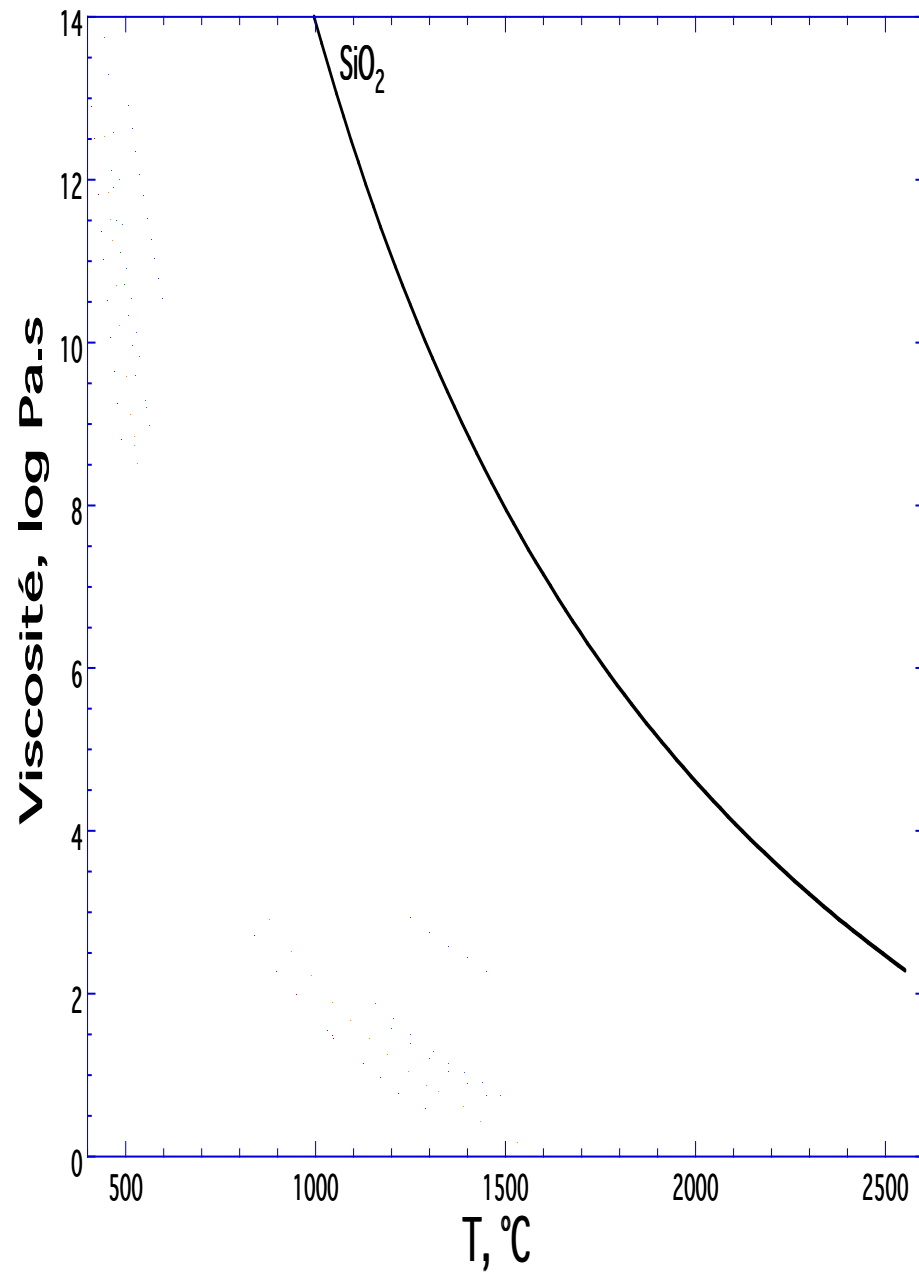


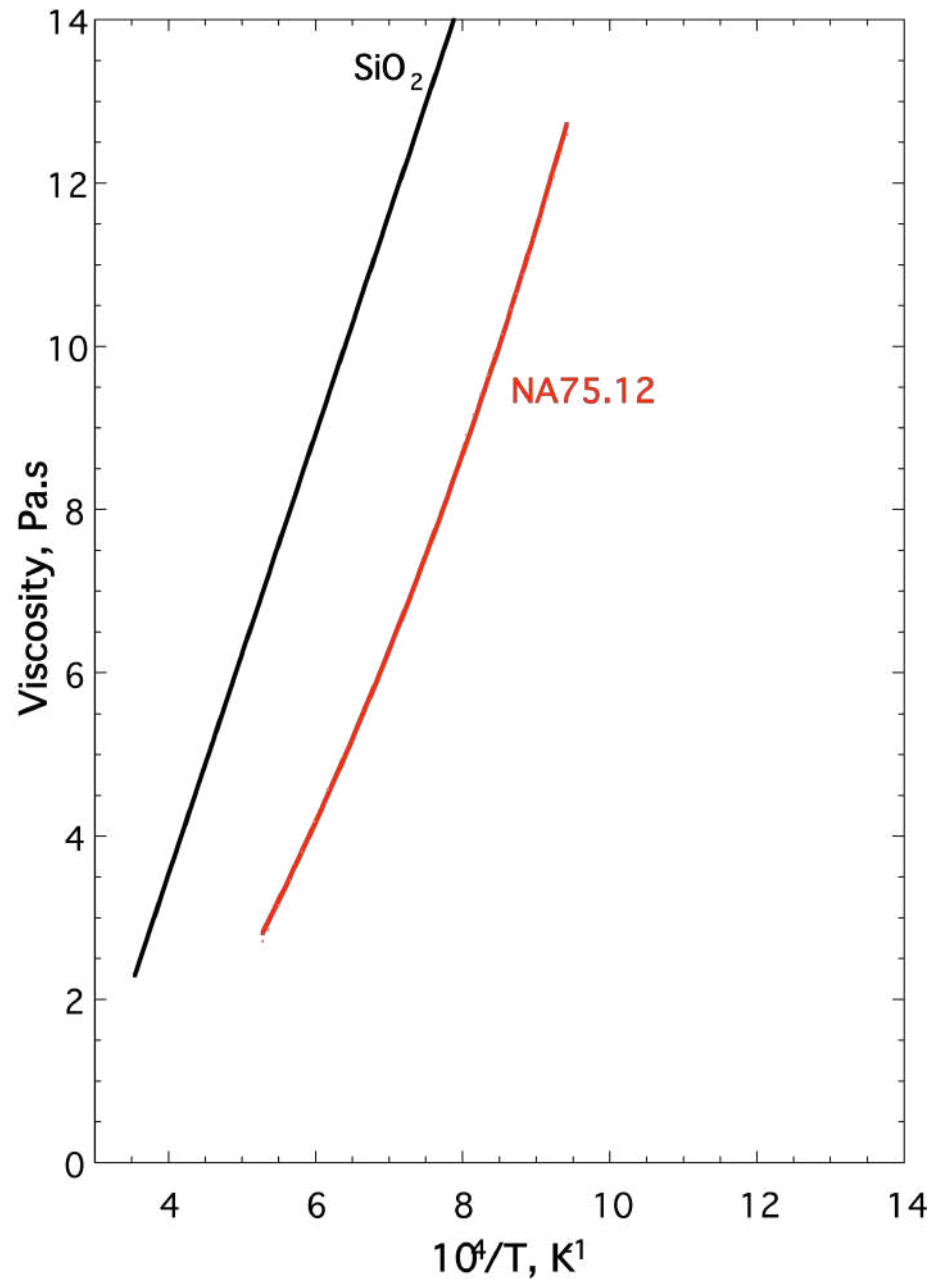
Grand nombre -> difficile à mesurer



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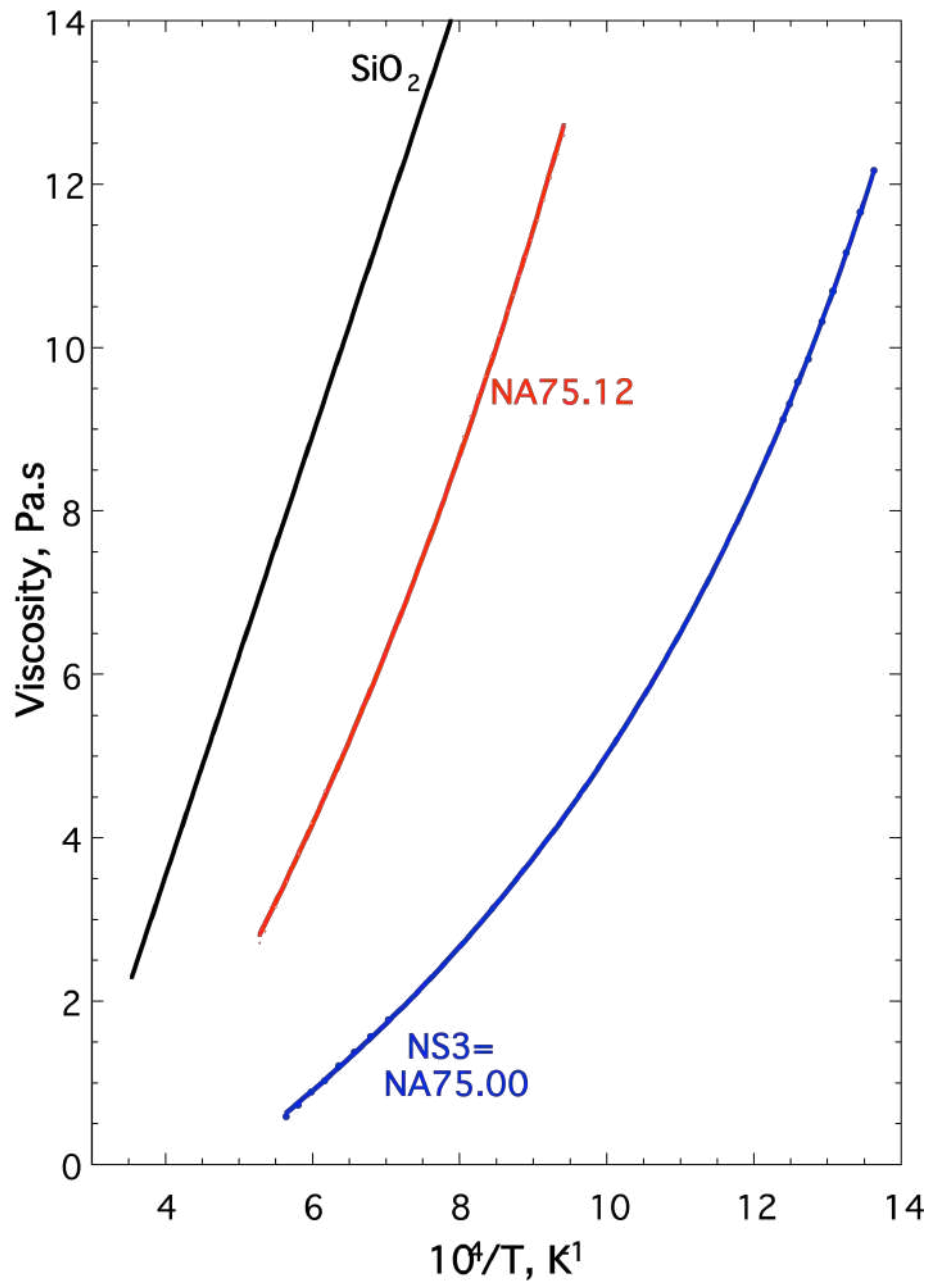




Modèle d'Arrhénus

$$\log \eta = A + B/T \quad (1)$$

Mais, cette loi ne fonctionne que pour quelques systèmes silicatés, SiO_2 , $NaAlSi_3O_8$ (NA75.12)...

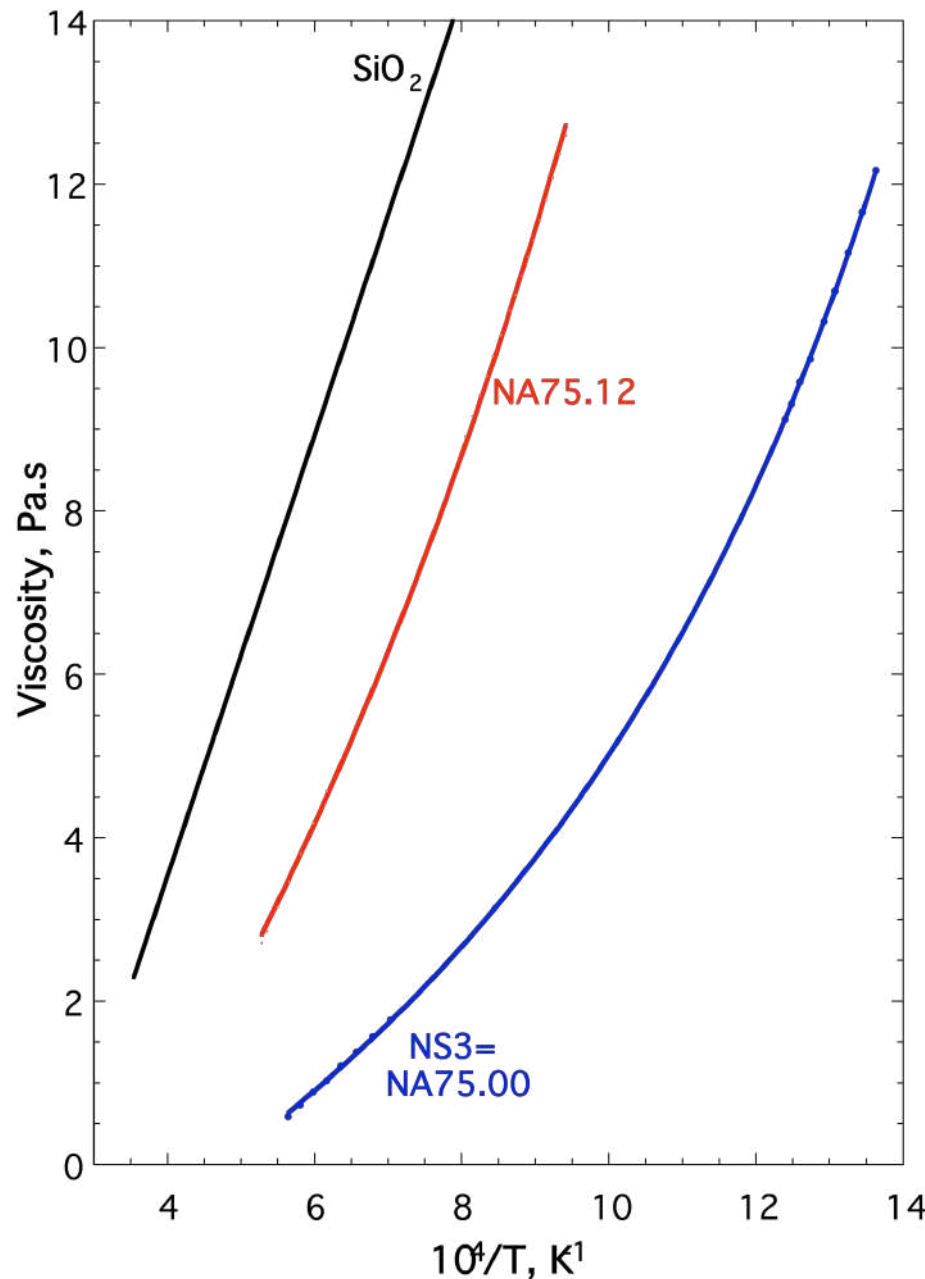


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Mais... cette loi ne fonctionne que pour quelques systèmes silicatés, SiO₂, NaAlSi₃O₈ (NA75.12)...

Dans le cas d'un silicate de sodium, NS3, l'énergie d'activation est de 2000kJ/mol à 1000K et de 300kJ/mol à 1800K, donc l'équation (1) ne peut pas reproduire correctement des changements continus lorsque la température varie.



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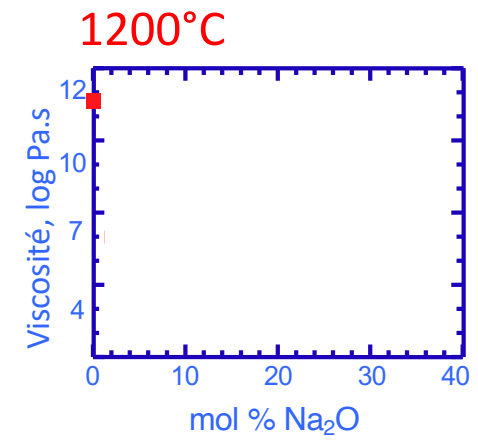
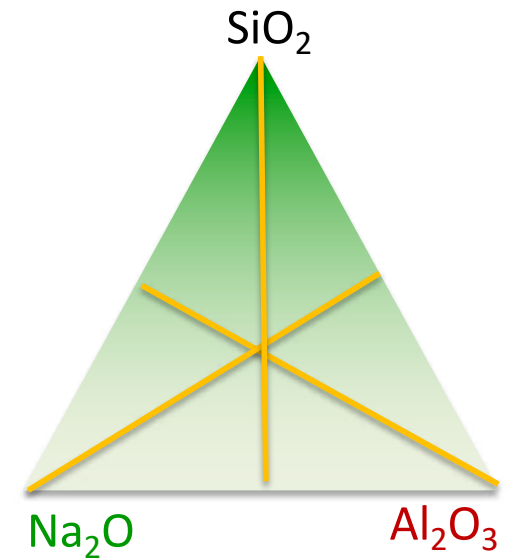
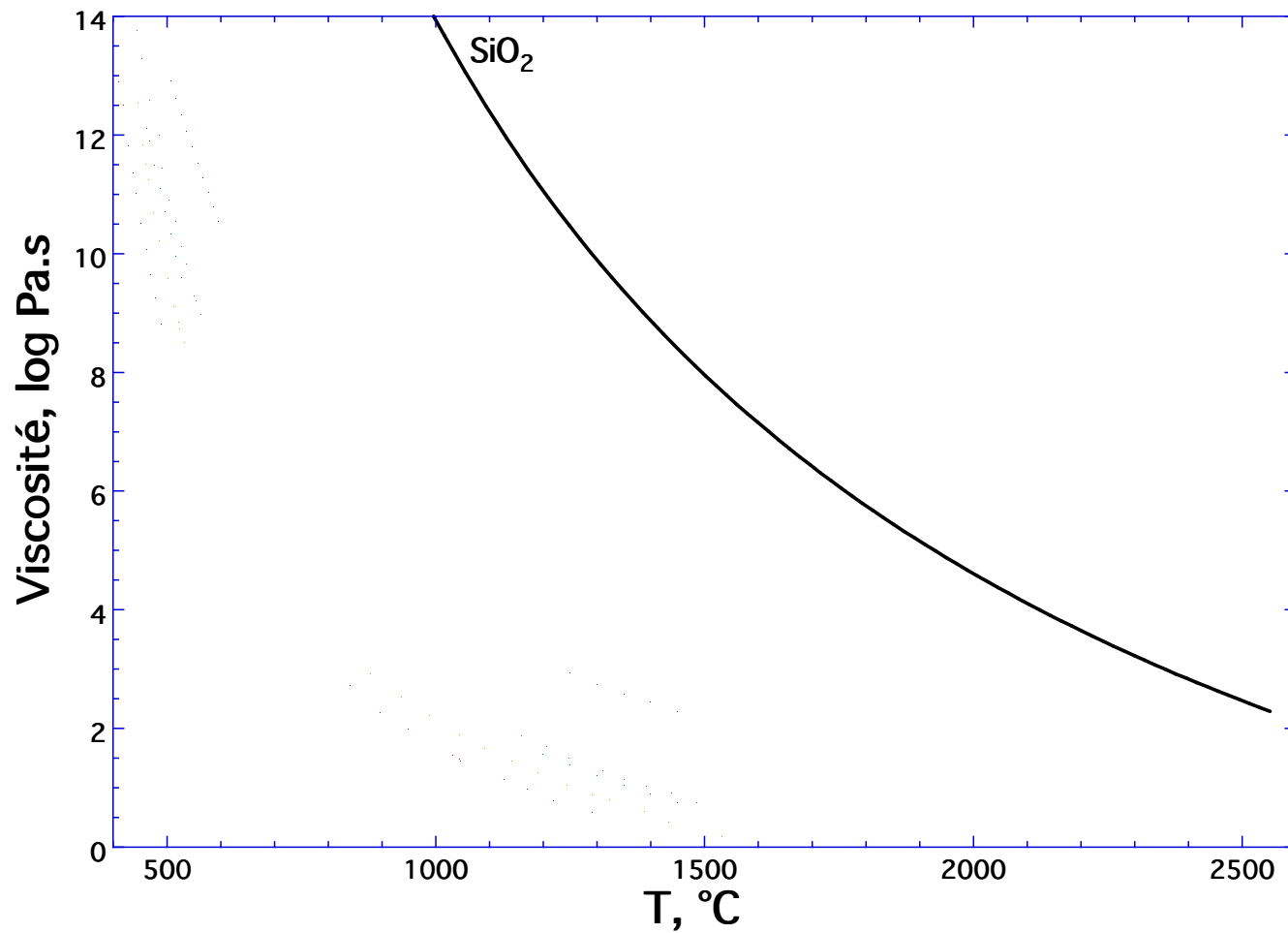
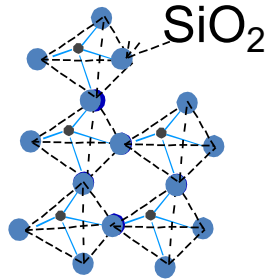
Modèle Tamman-Vogel-Fulcher, TVF

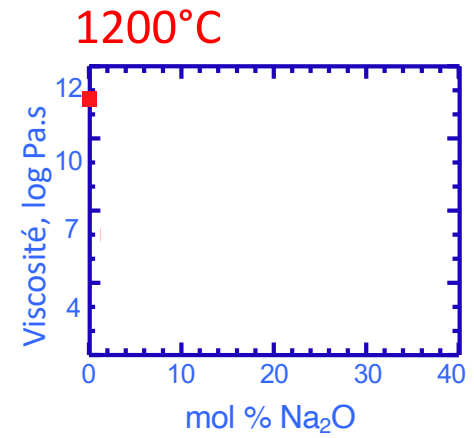
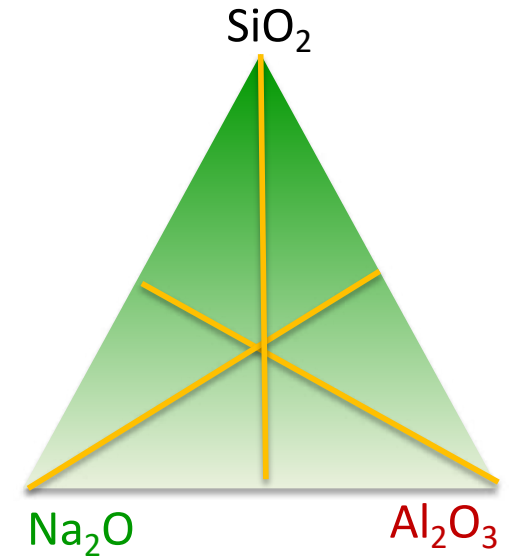
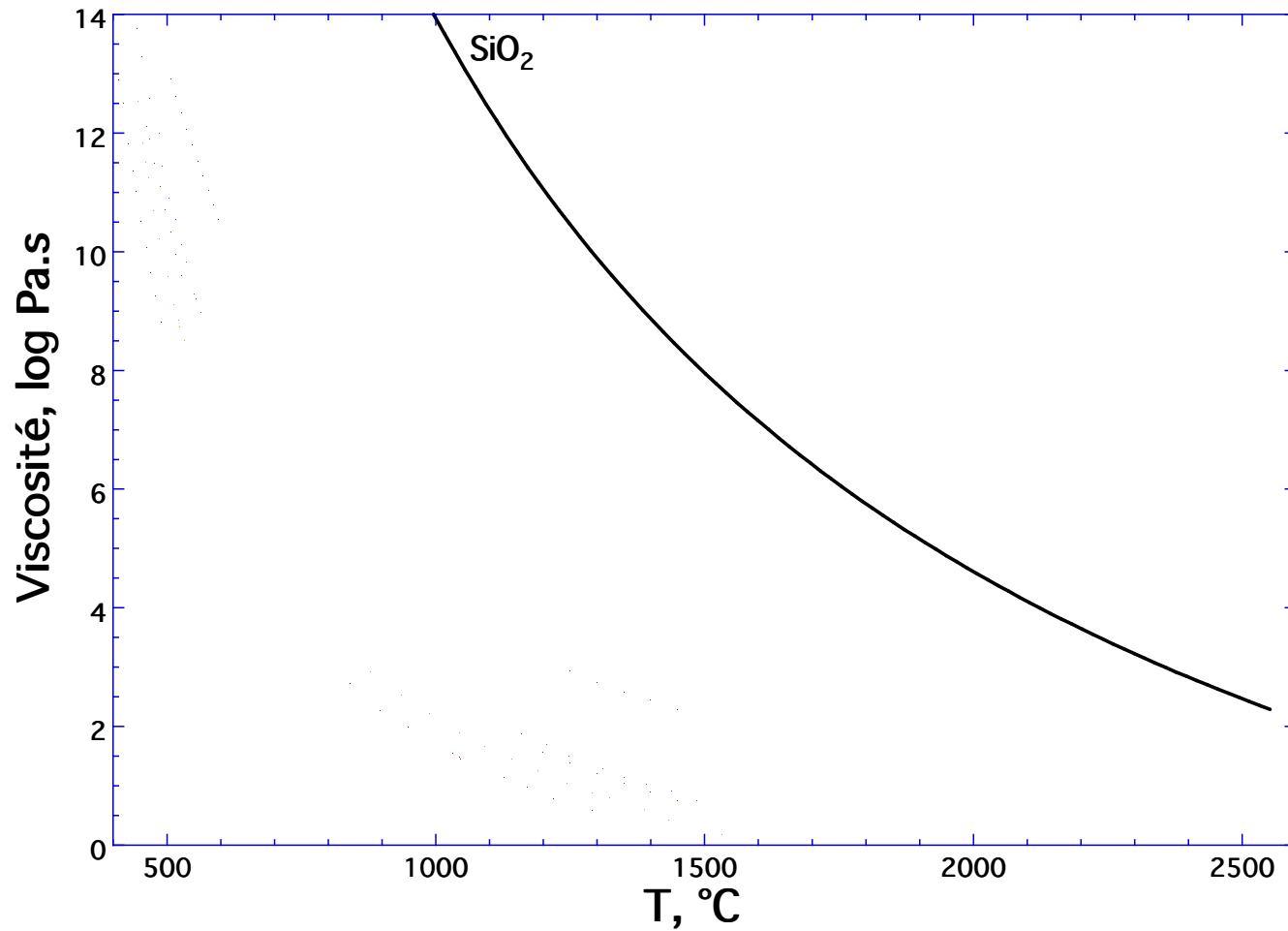
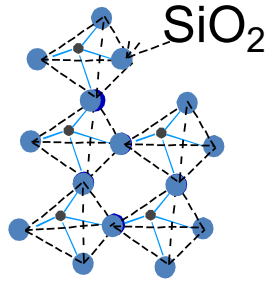
$$\text{Log } \eta = A + B/(T - T_1)$$

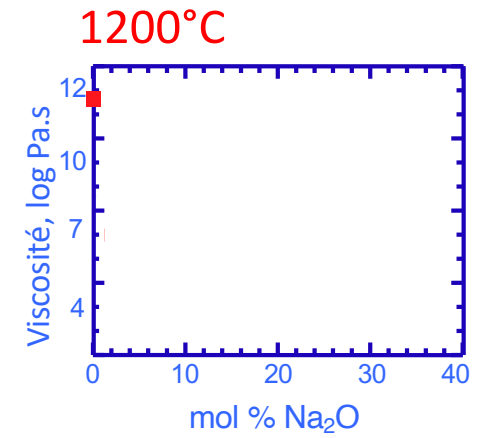
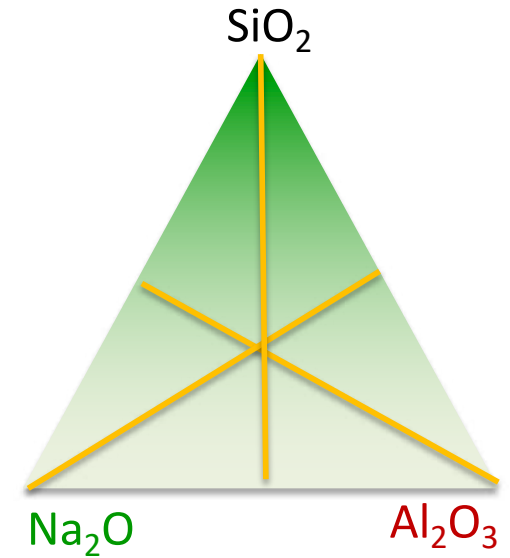
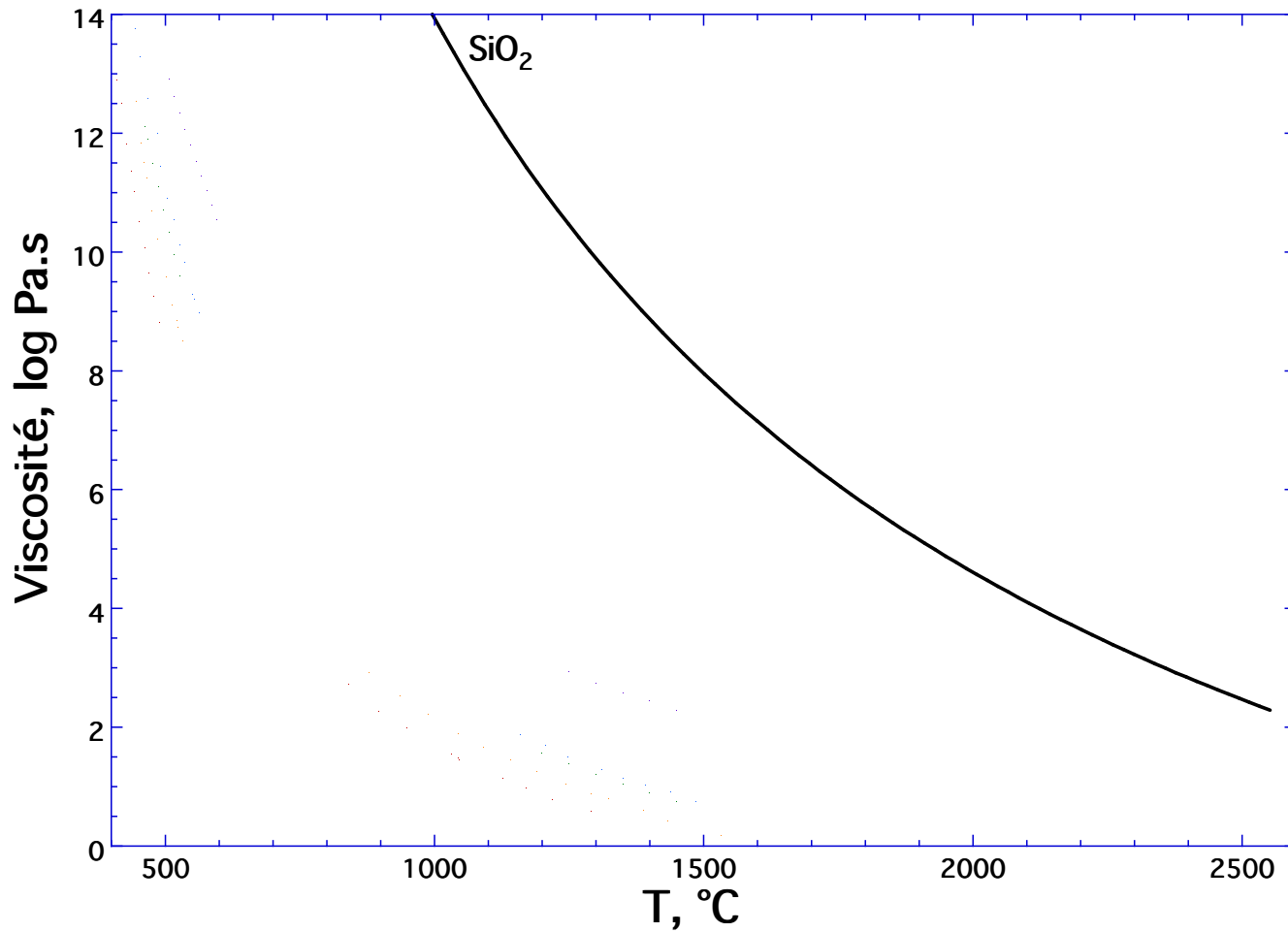
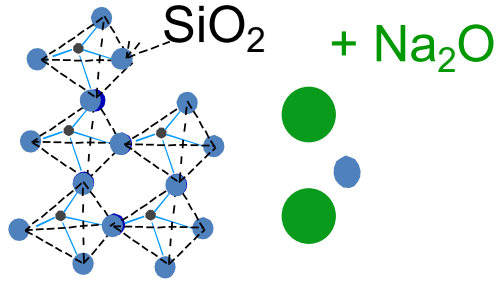
A, B, T₁ sont des paramètres ajustables empiriques qui permettent de reproduire les données.

A sans signification

B peut correspondre à une énergie d'activation



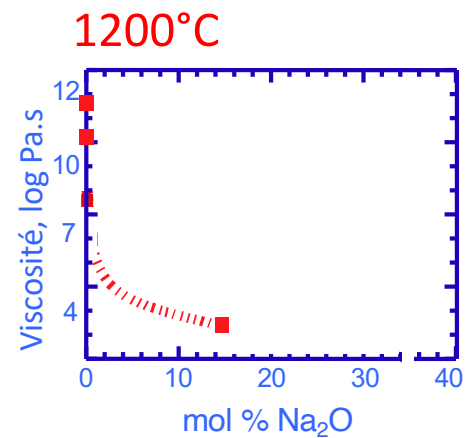
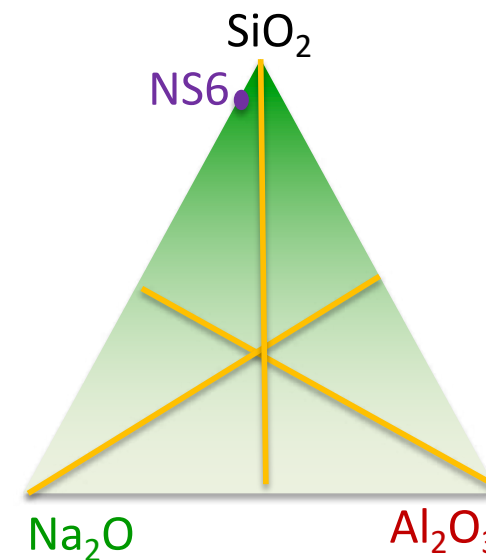
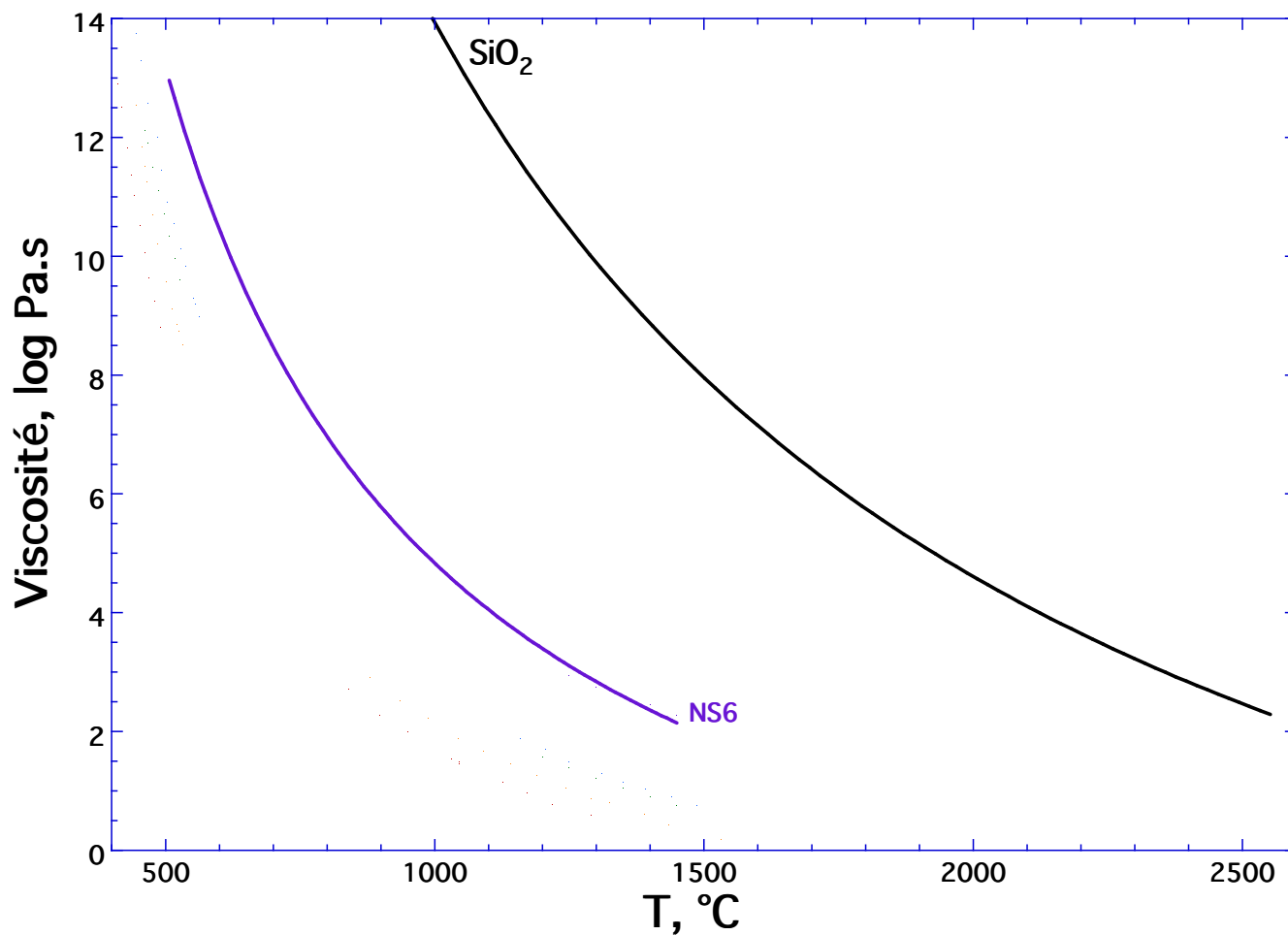
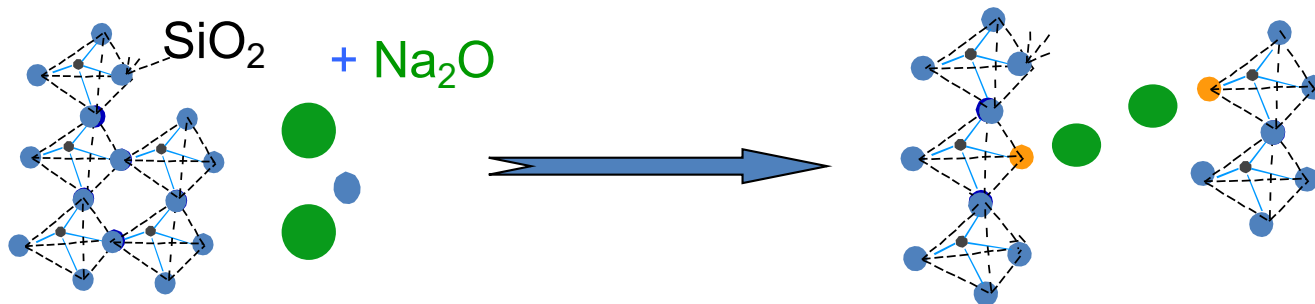




Silicate vitreux de sodium



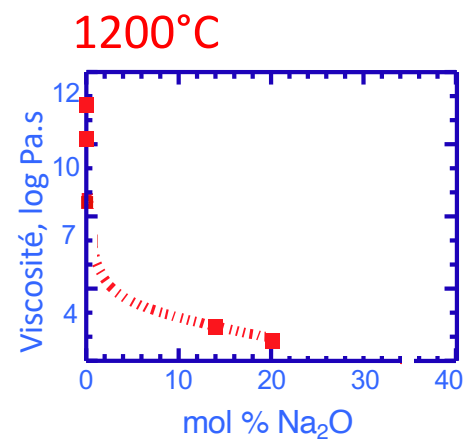
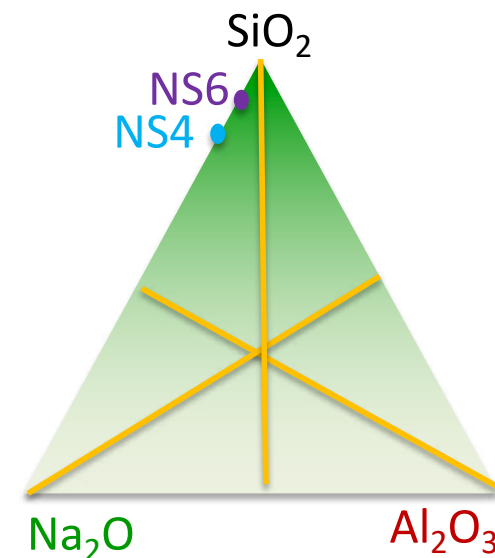
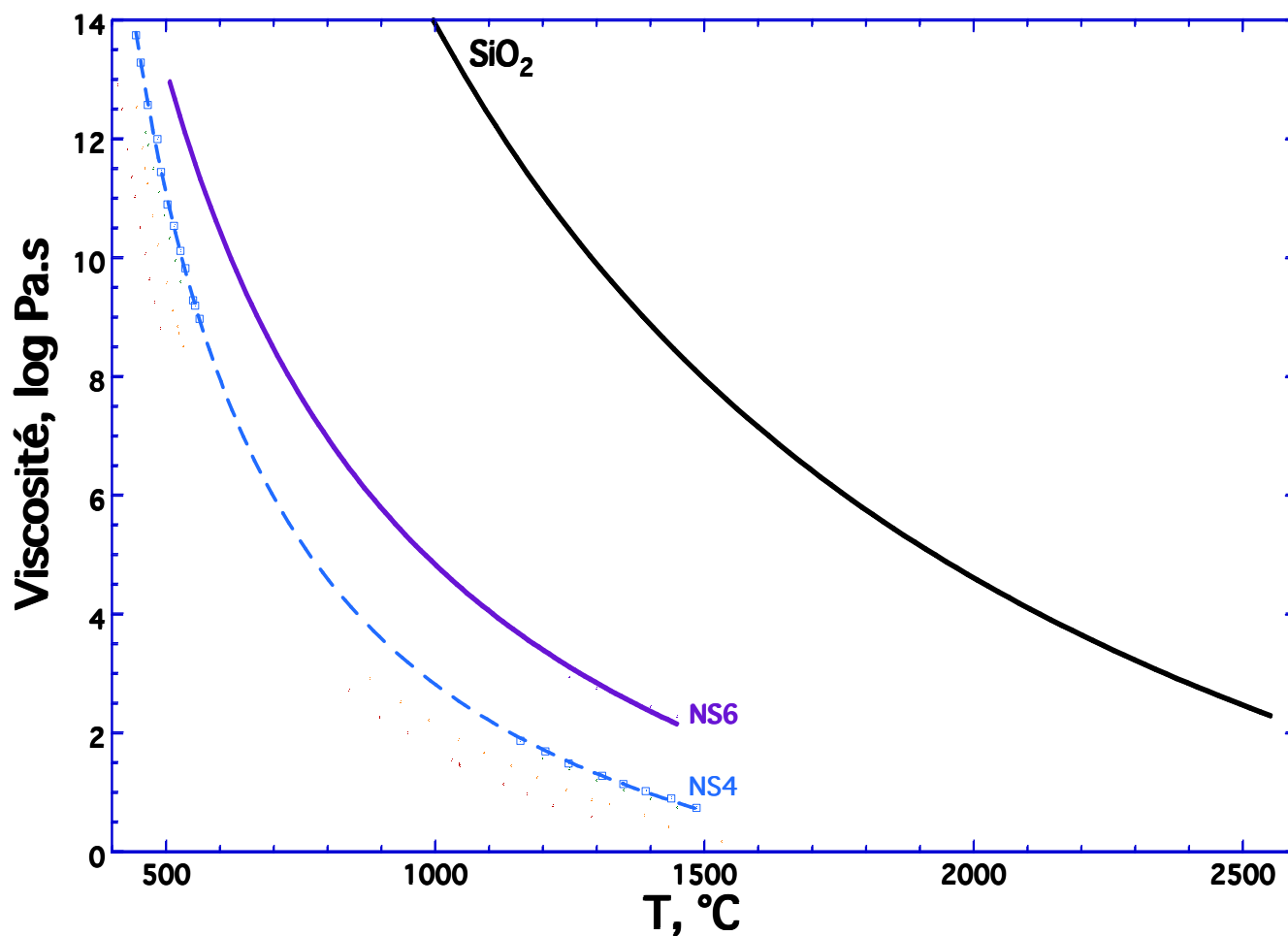
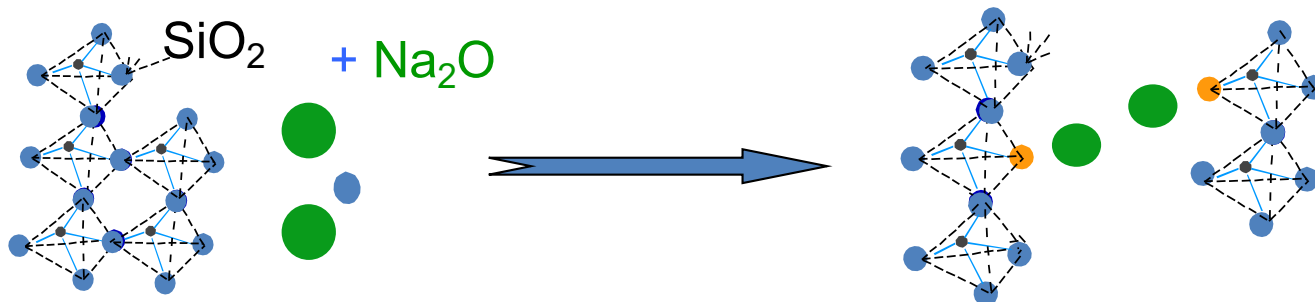
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Silicate vitreux de sodium



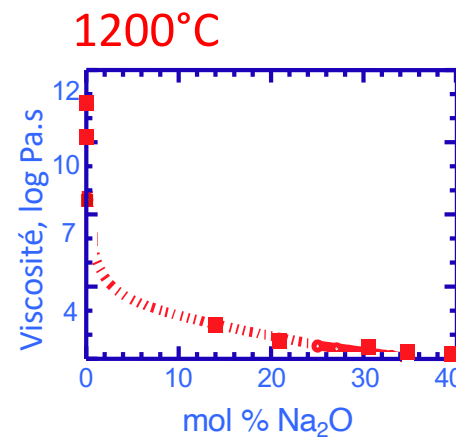
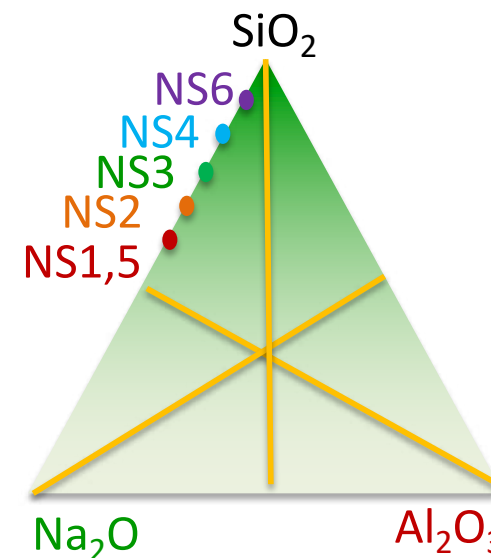
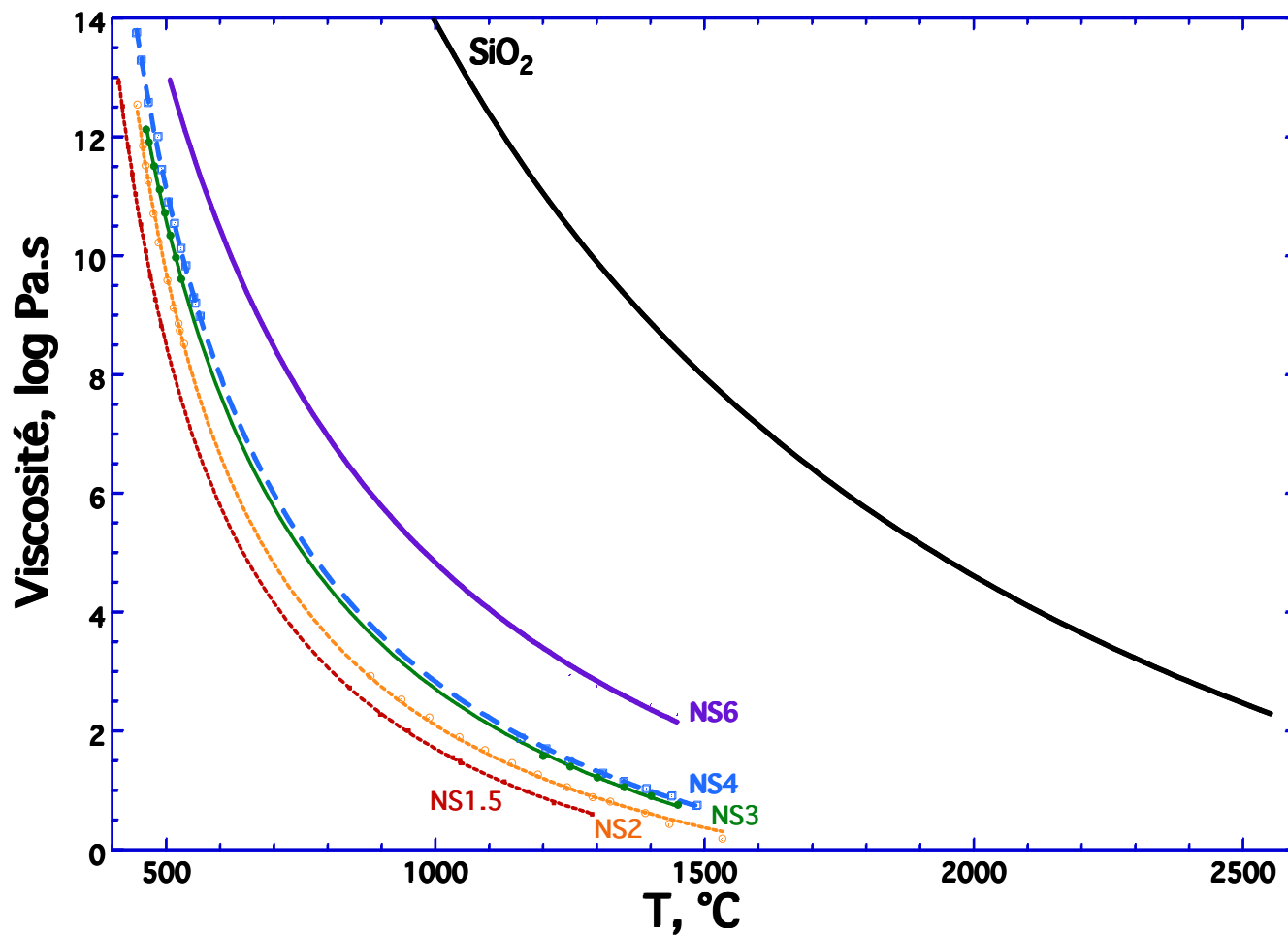
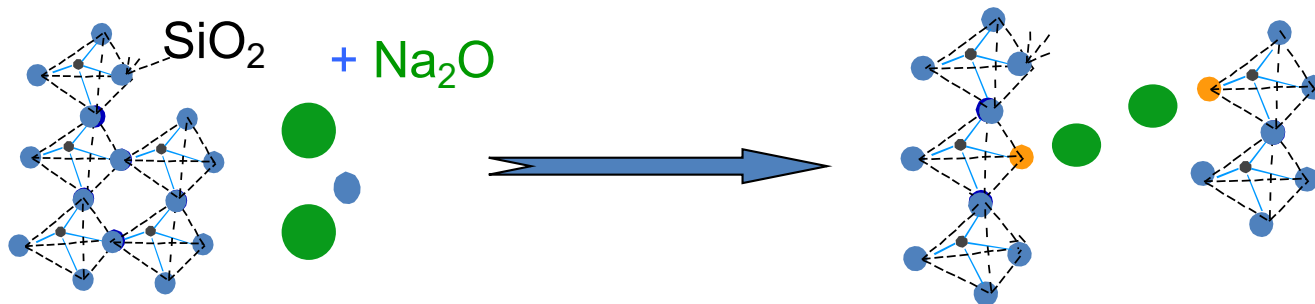
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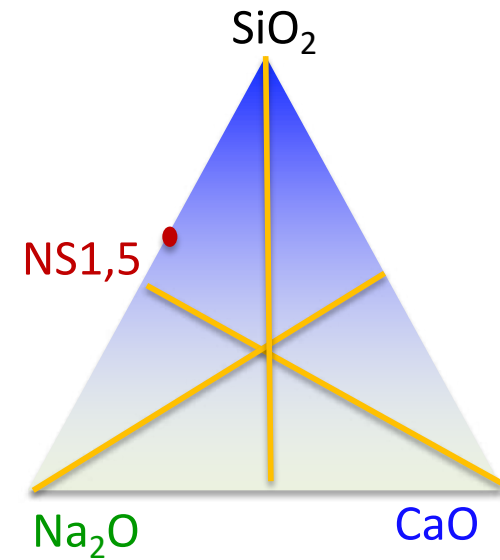
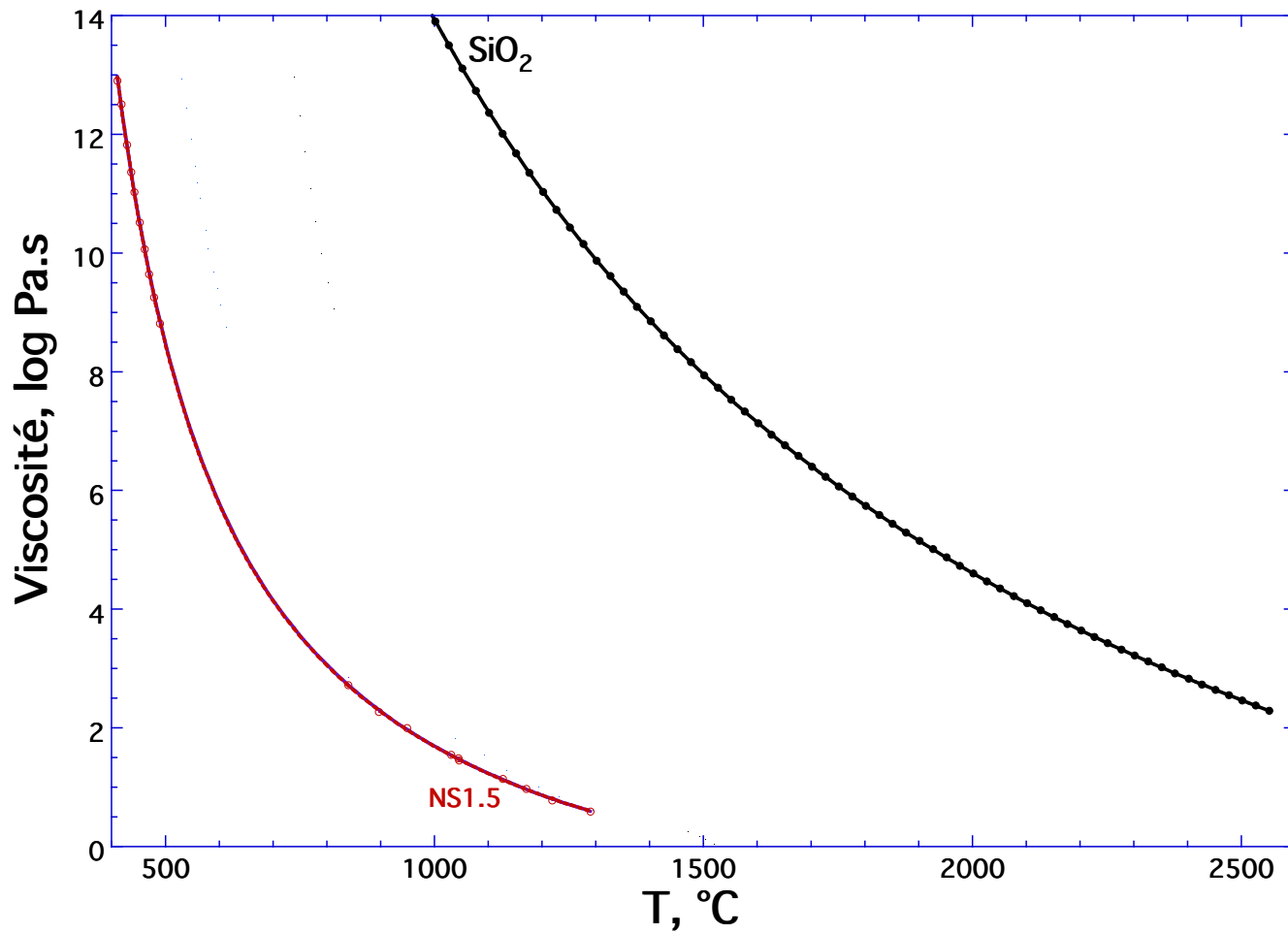
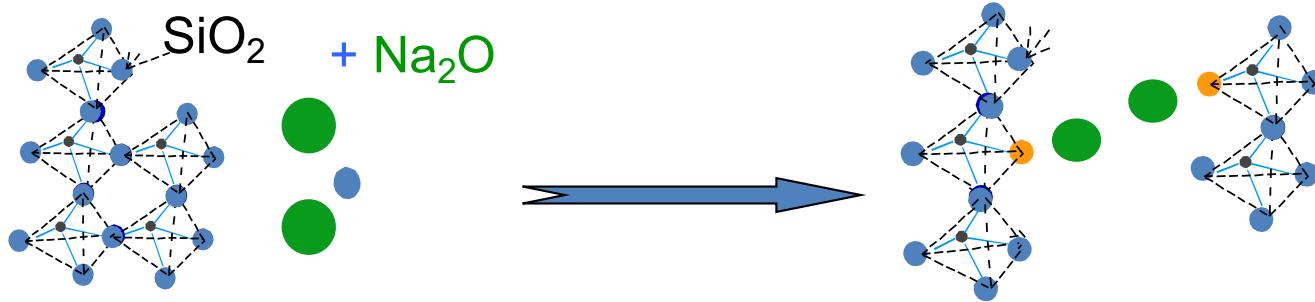
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Silicate vitreux de sodium



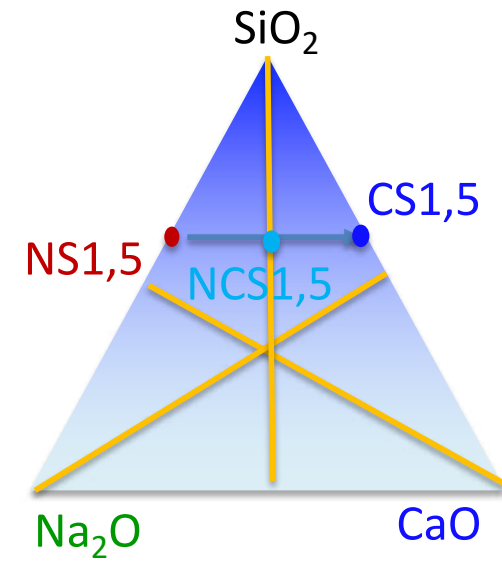
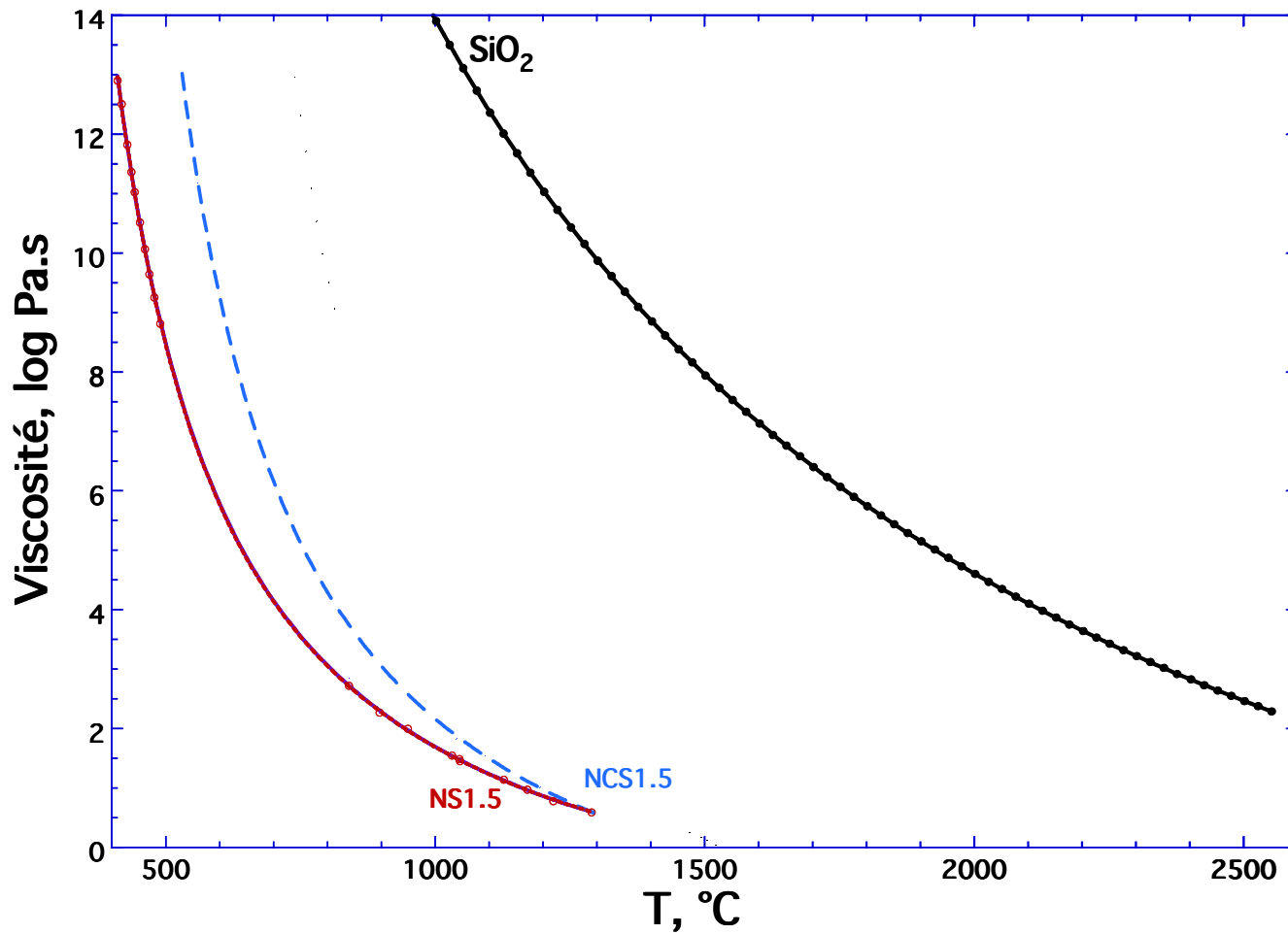
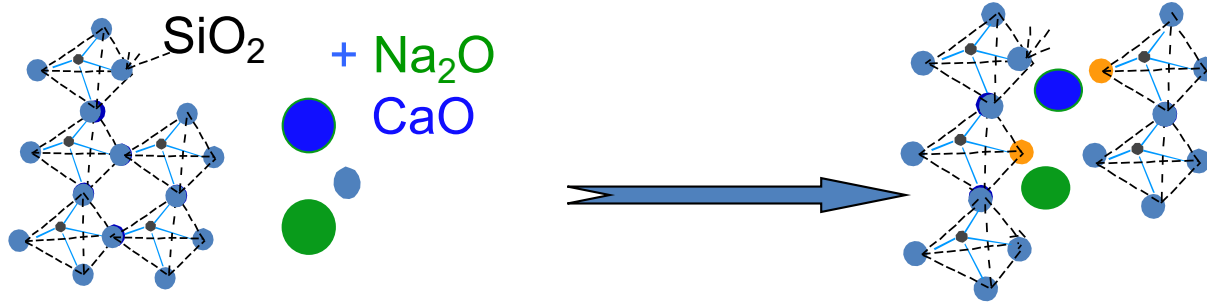
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Silicate vitreux de calcium et sodium



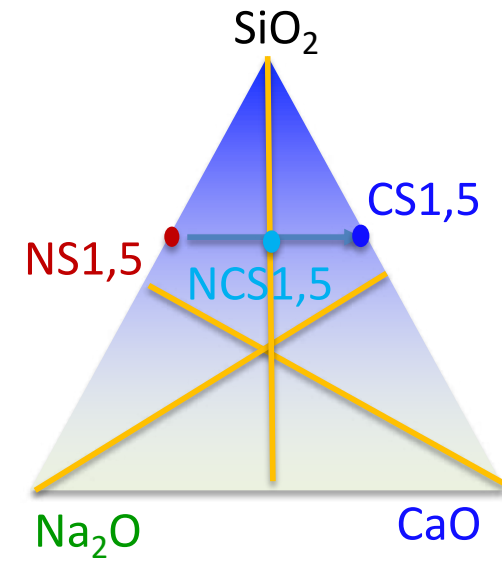
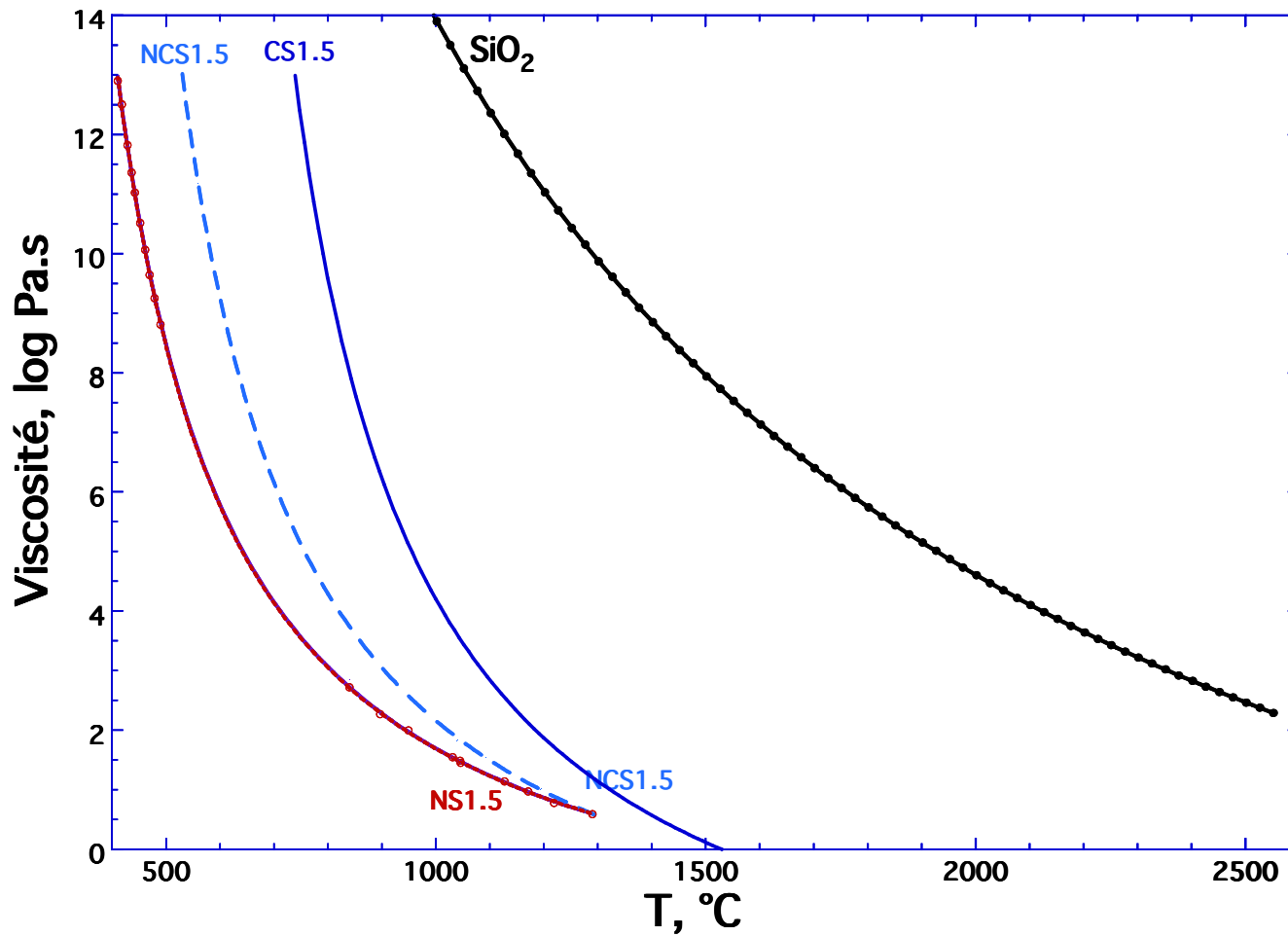
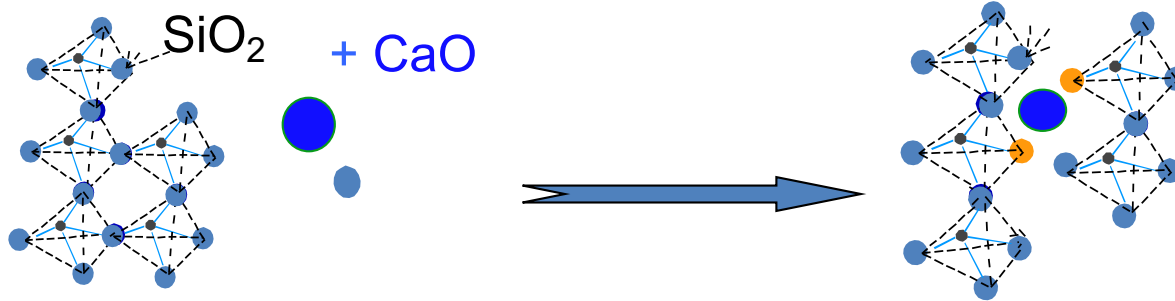
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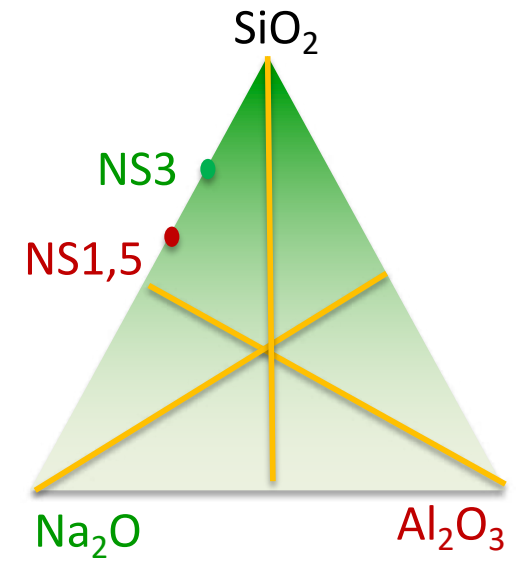
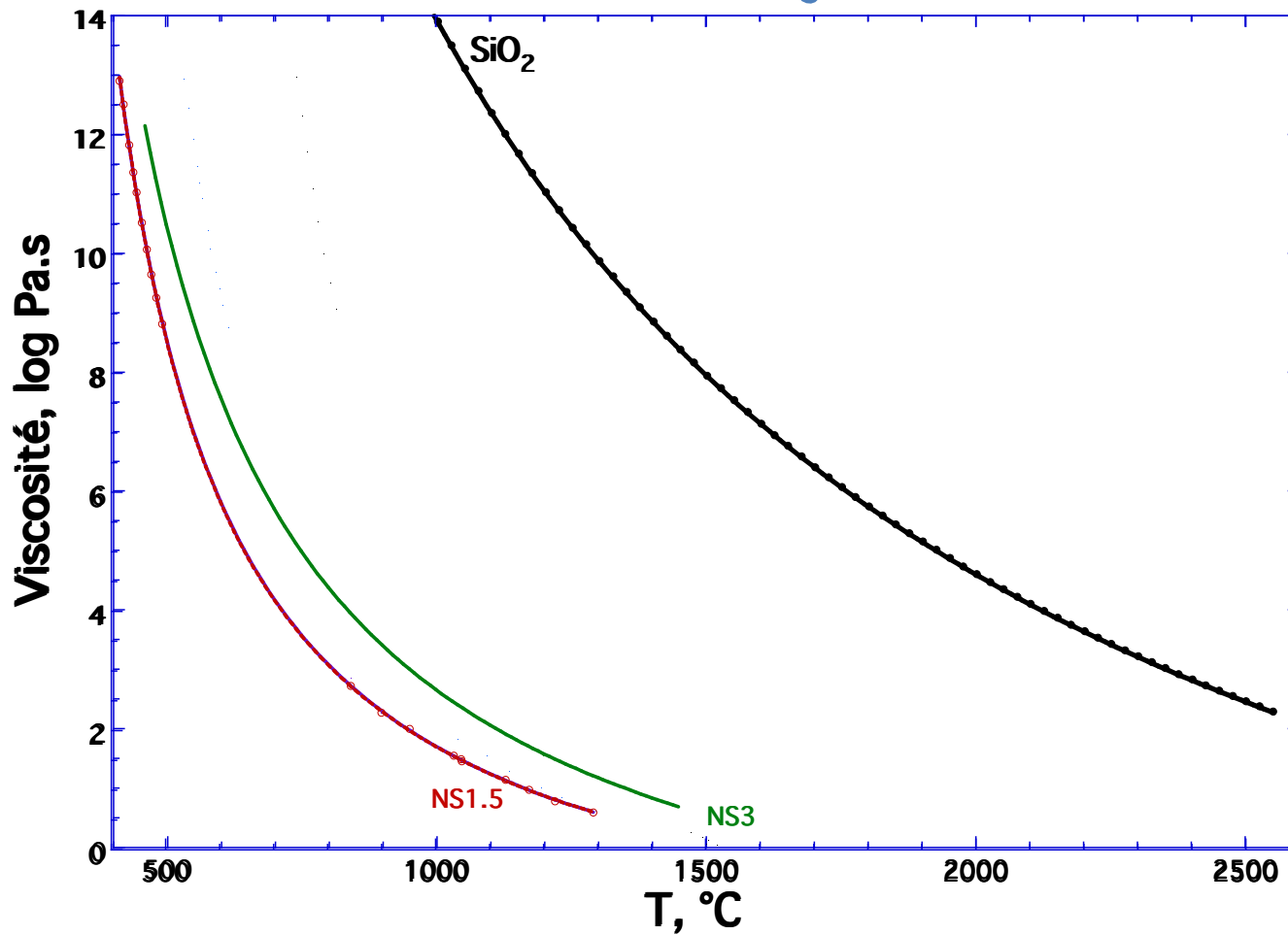
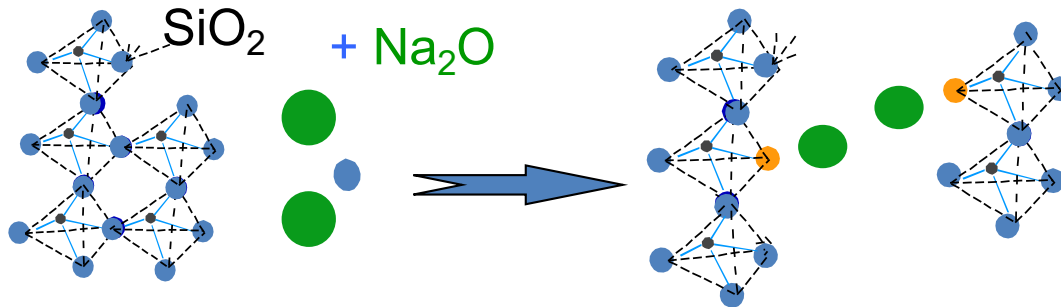


Silicate vitreux de calcium et sodium



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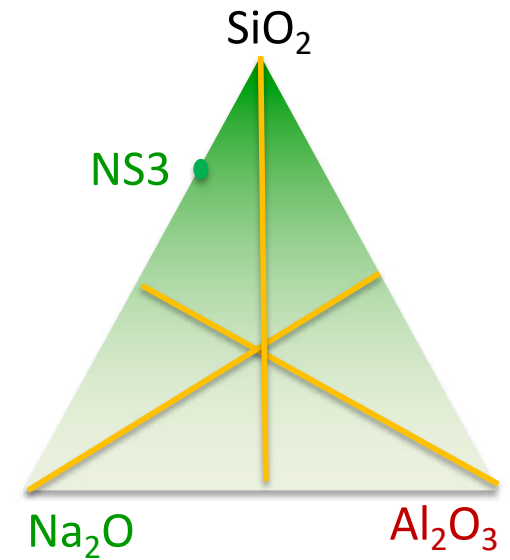
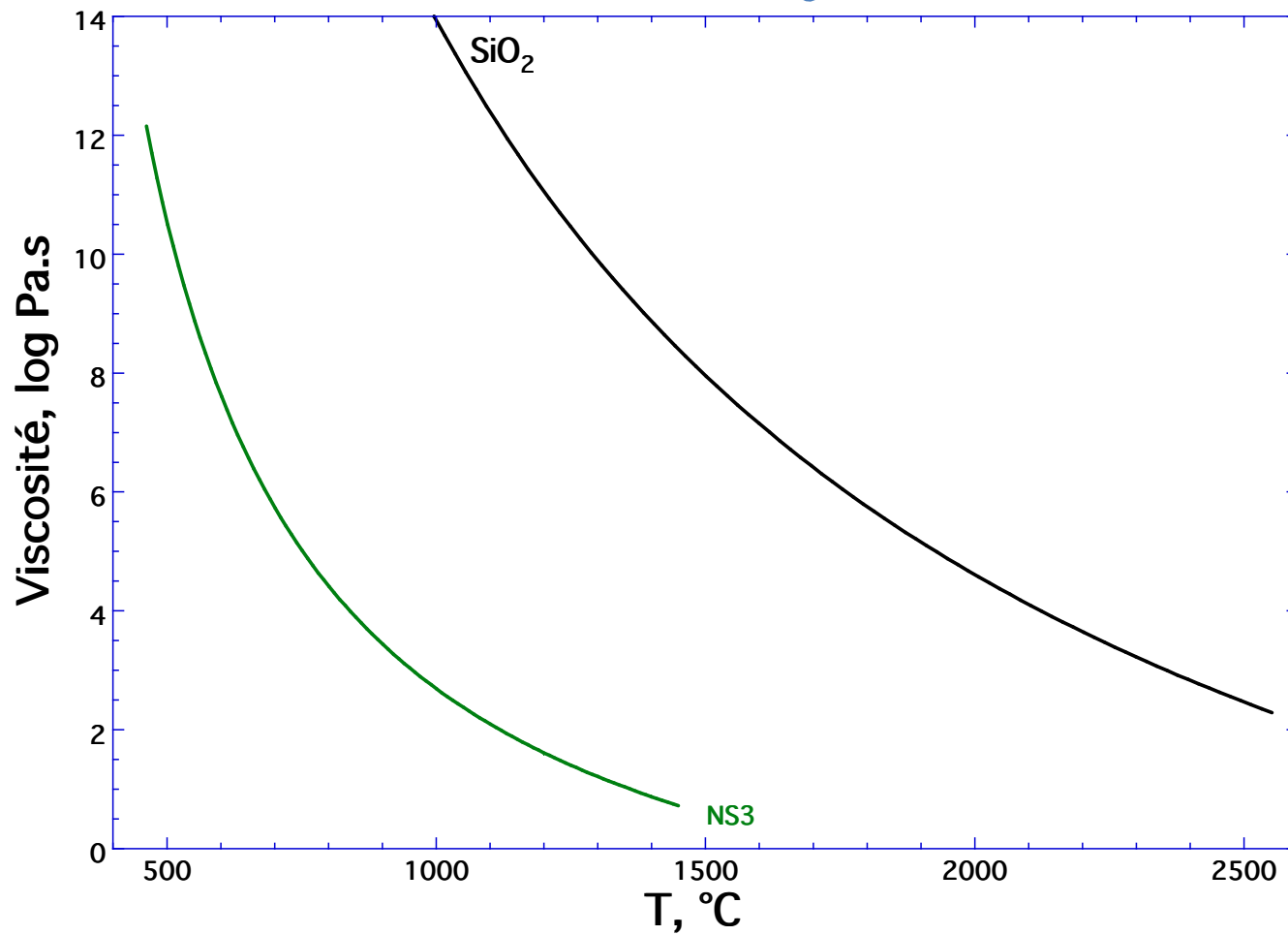
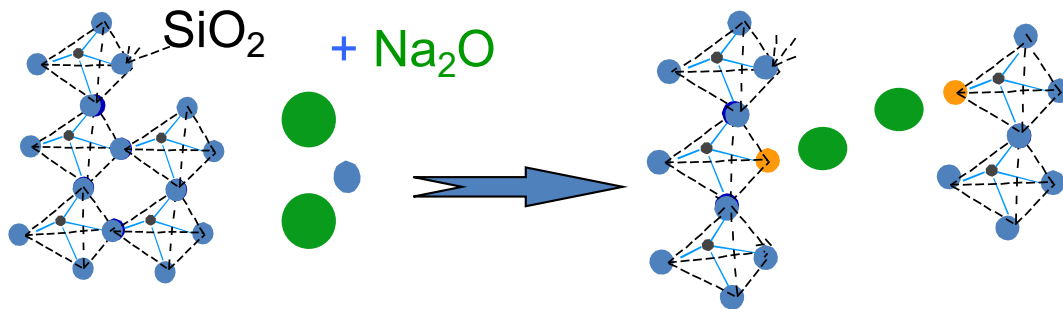




Aluminosilicate vitreux de sodium



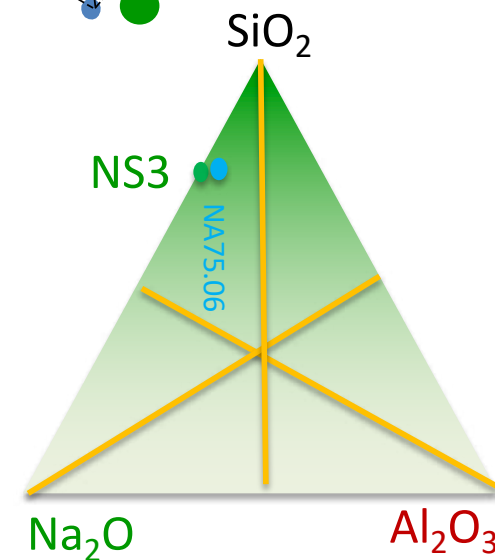
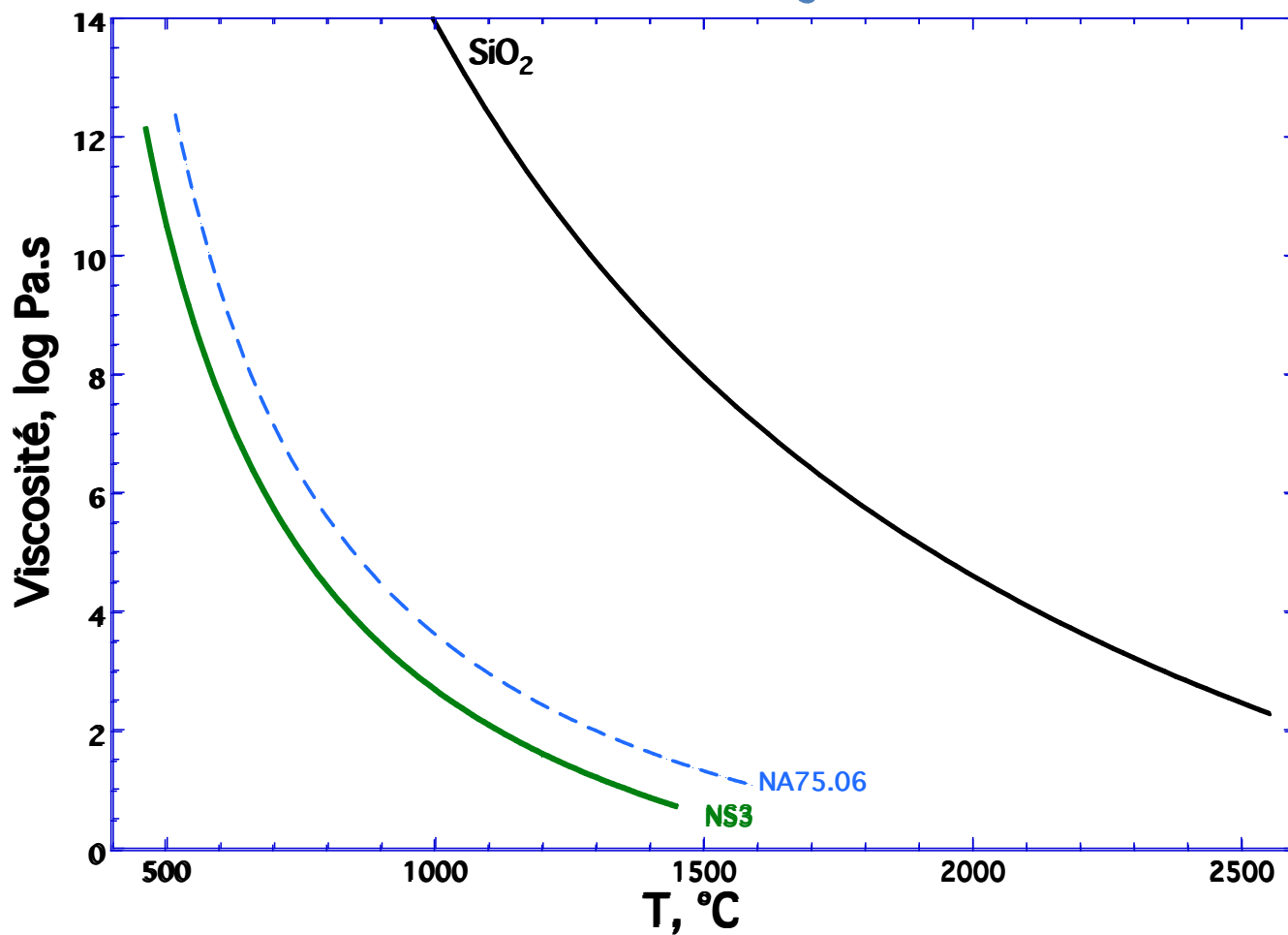
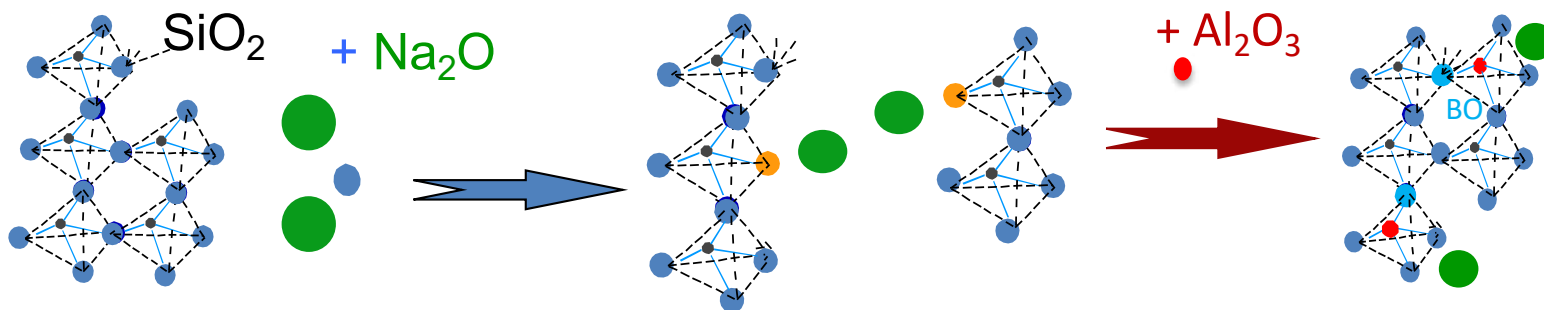
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Aluminosilicate vitreux de sodium



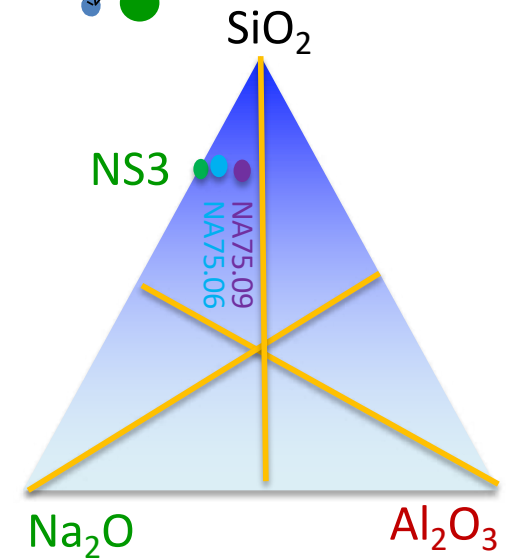
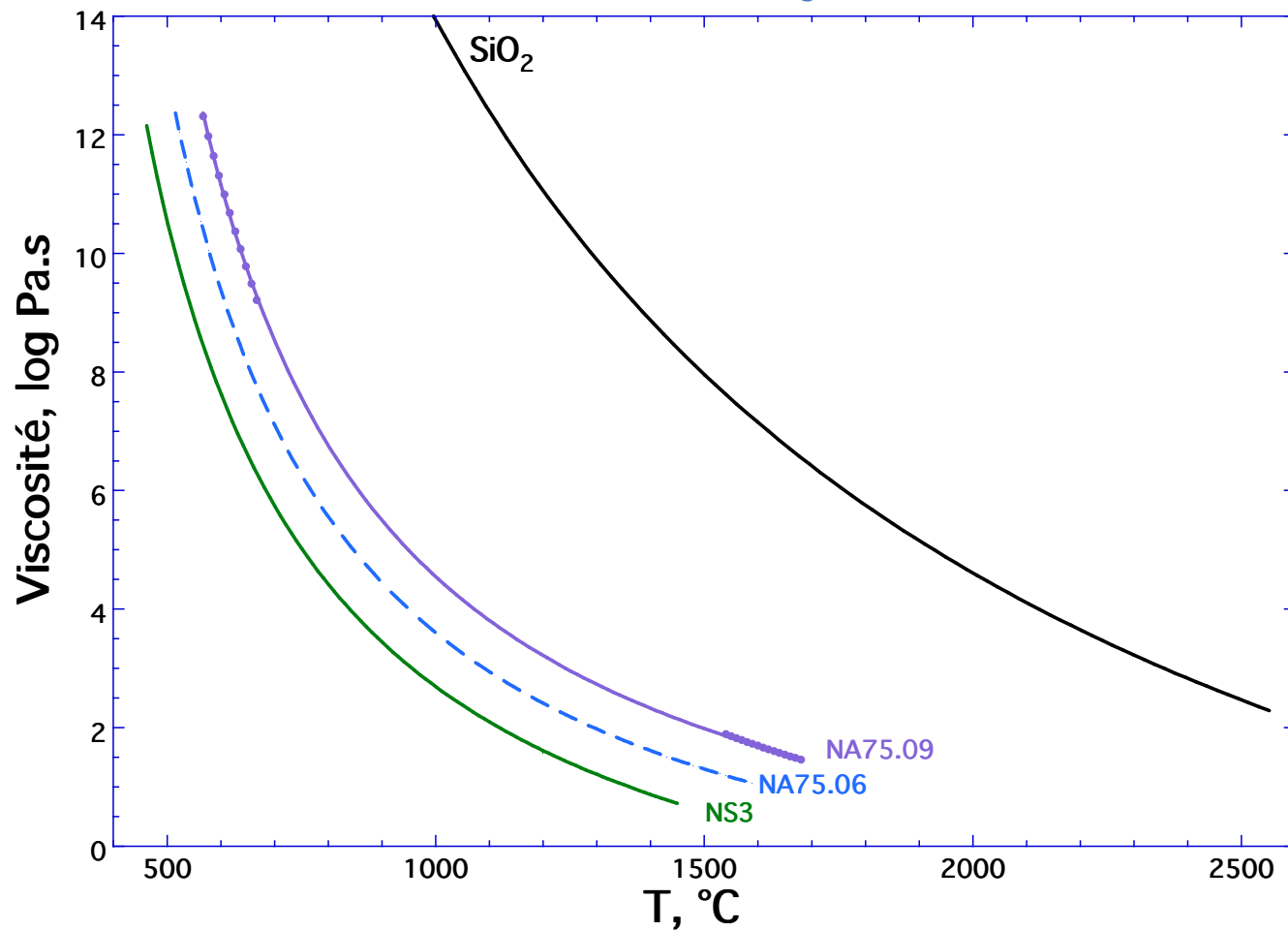
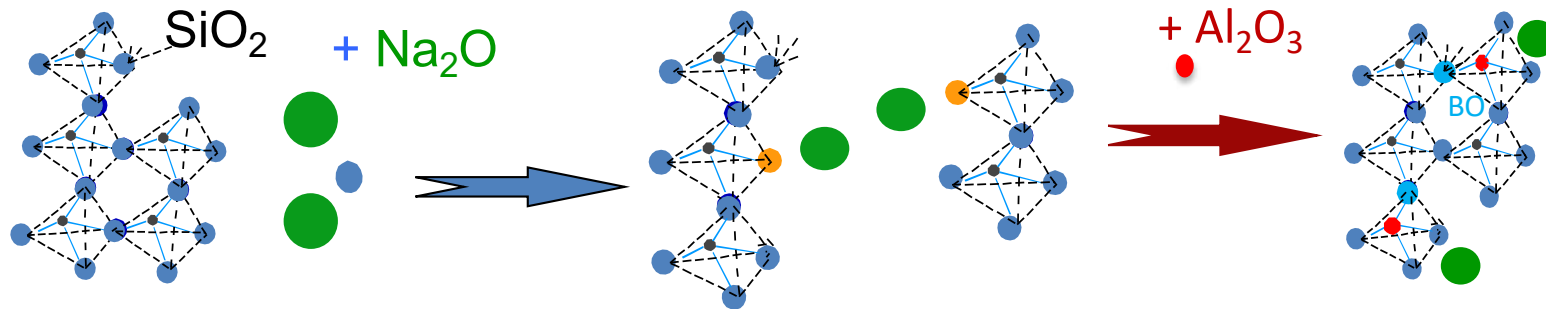
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Aluminosilicate vitreux de sodium



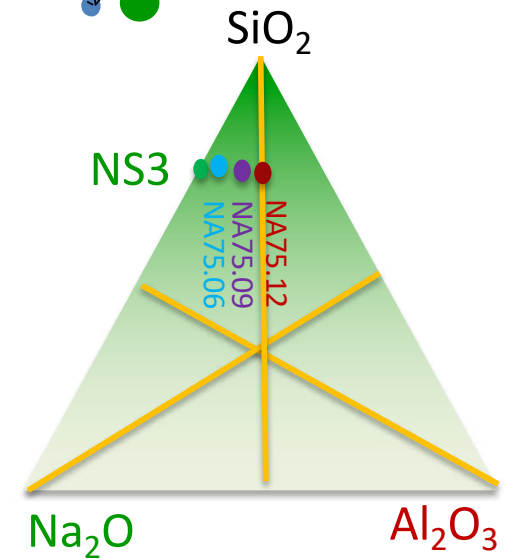
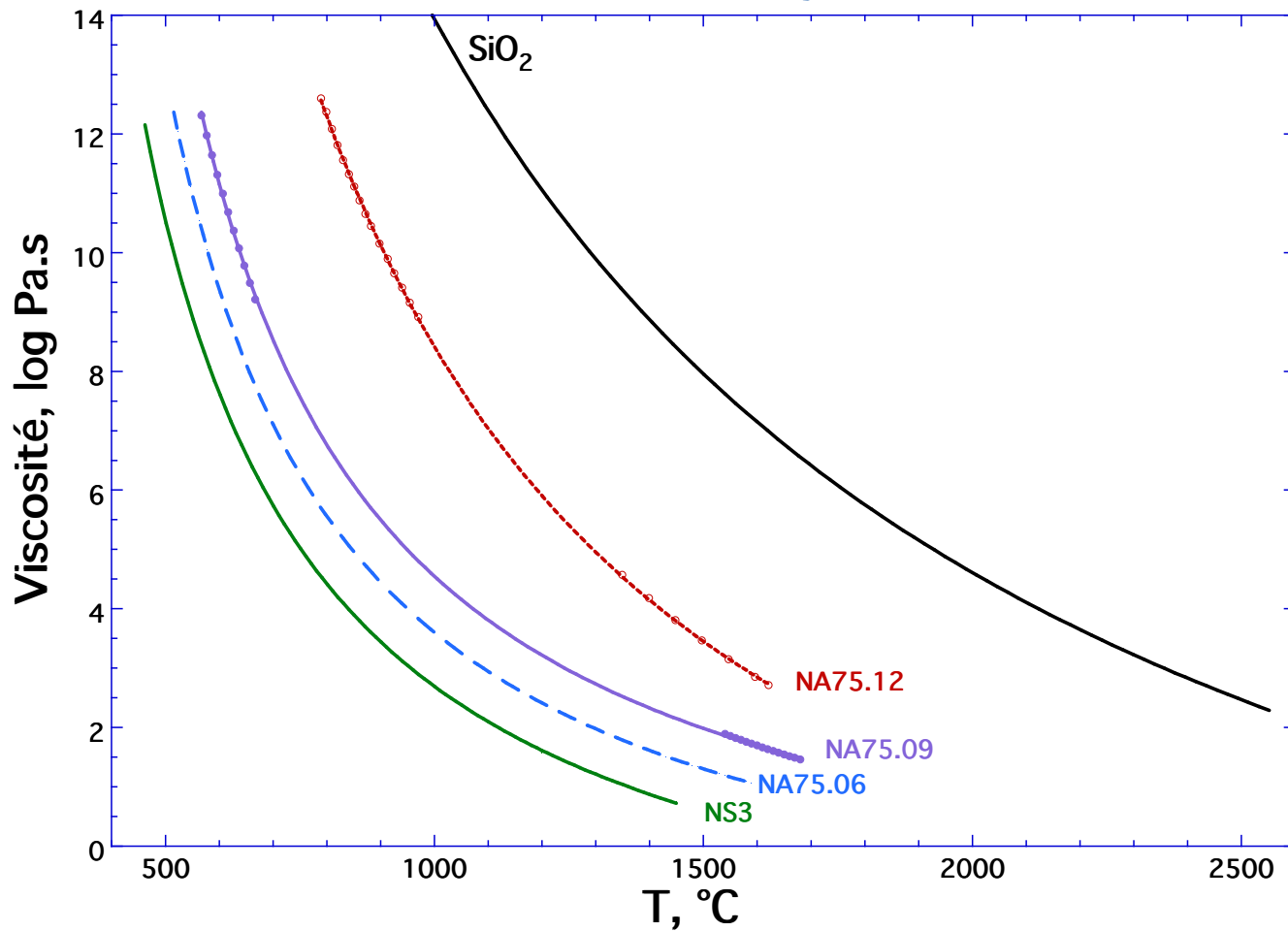
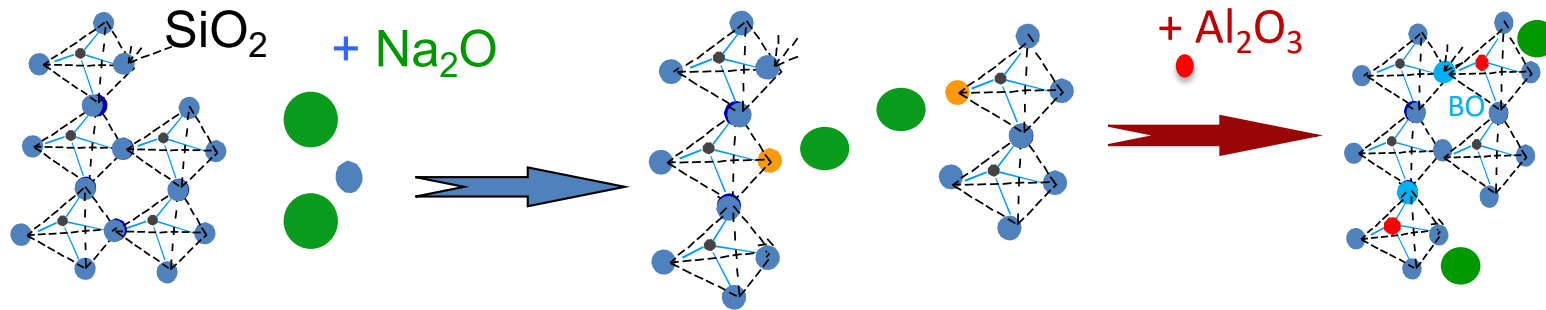
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Aluminosilicate vitreux de sodium



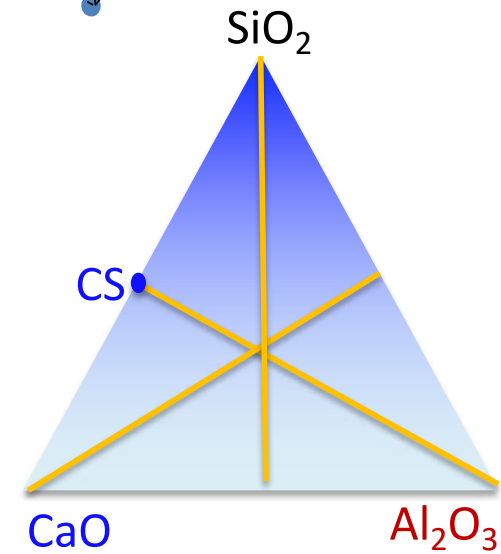
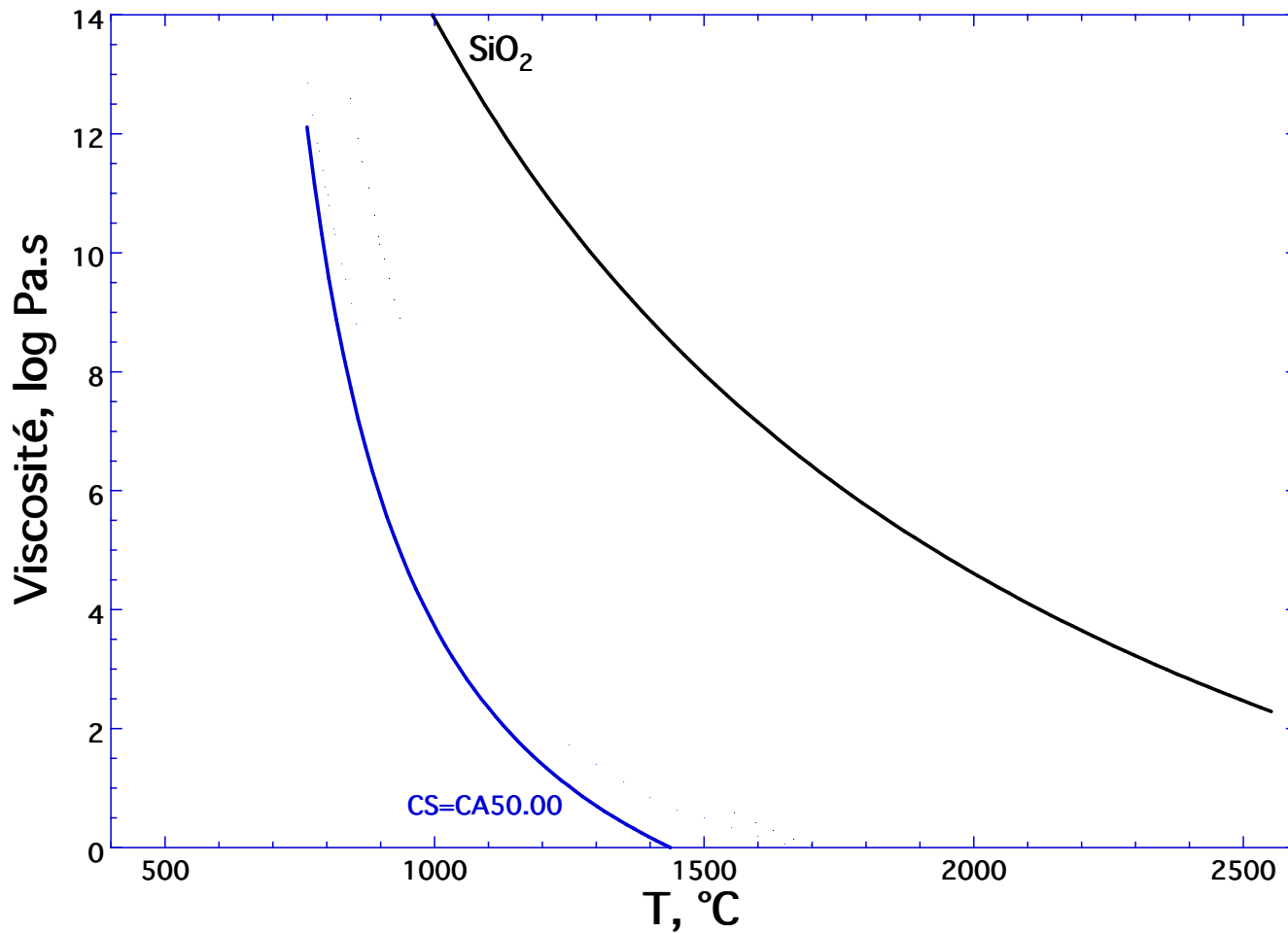
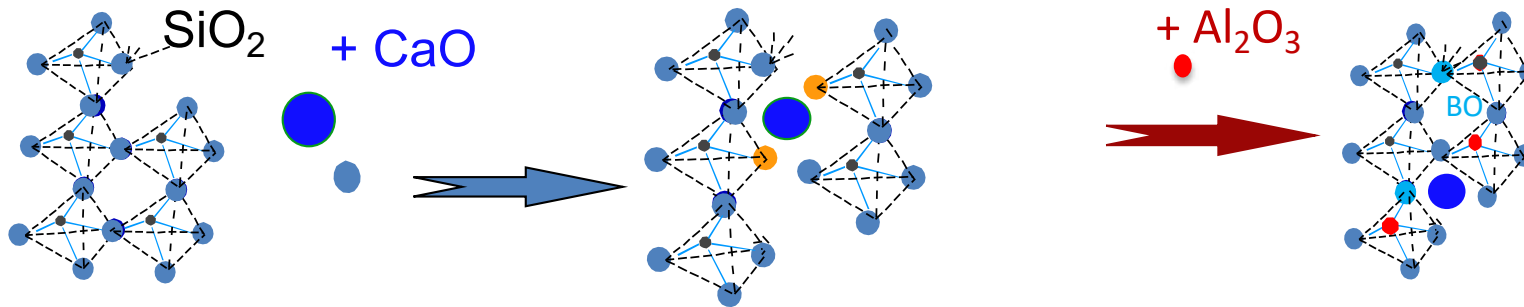
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Aluminosilicate vitreux de calcium



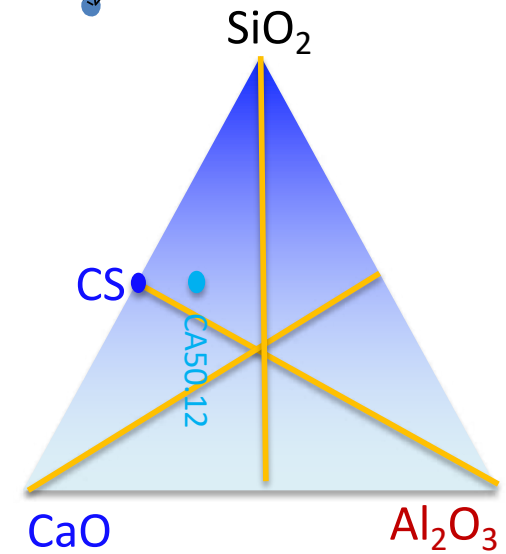
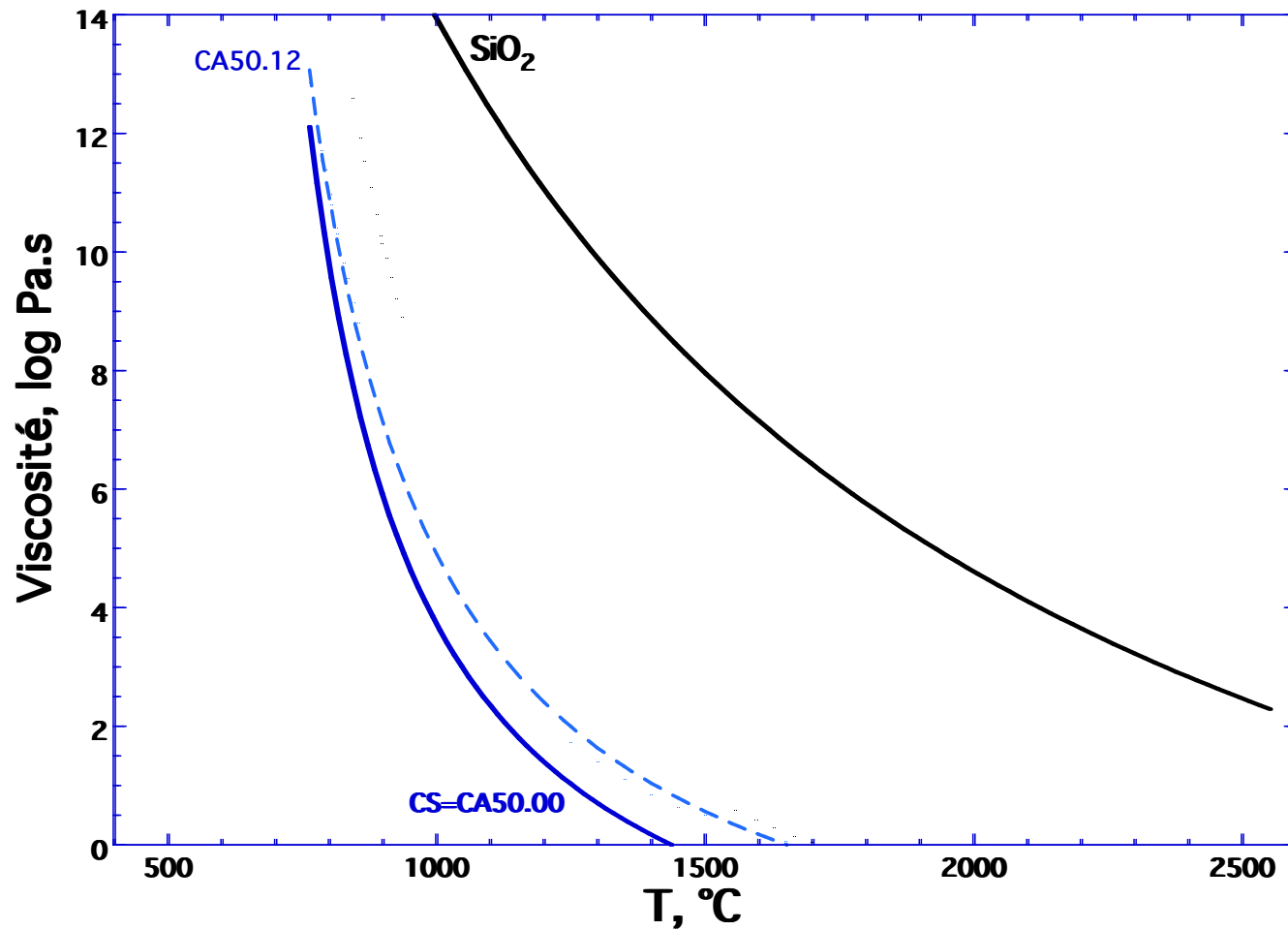
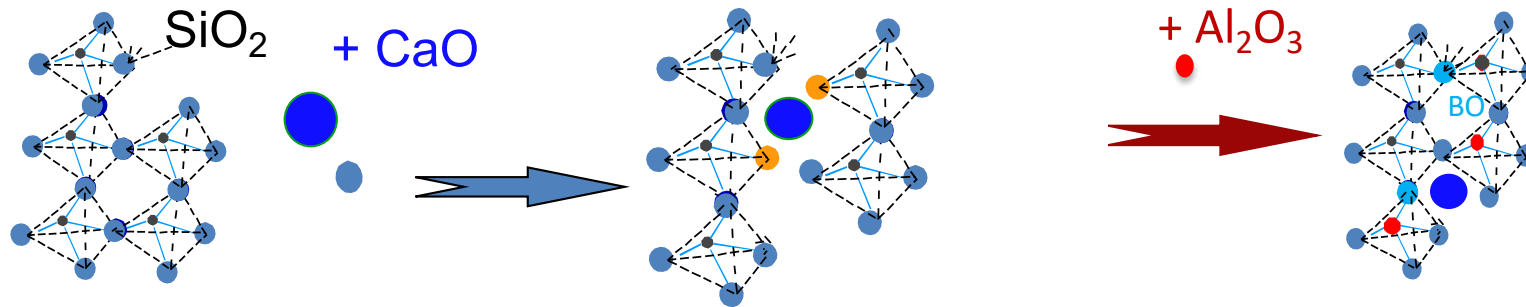
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Aluminosilicate vitreux de calcium



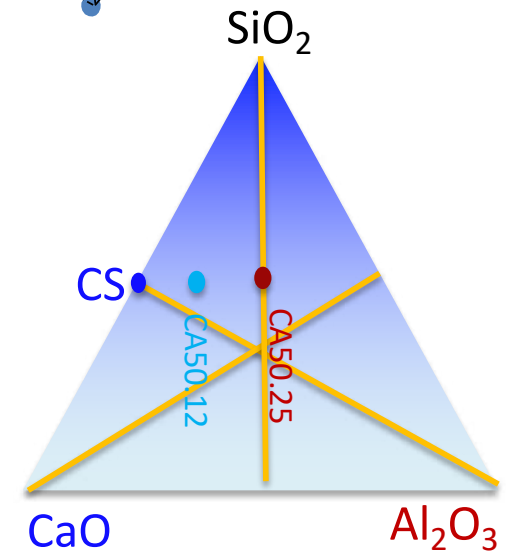
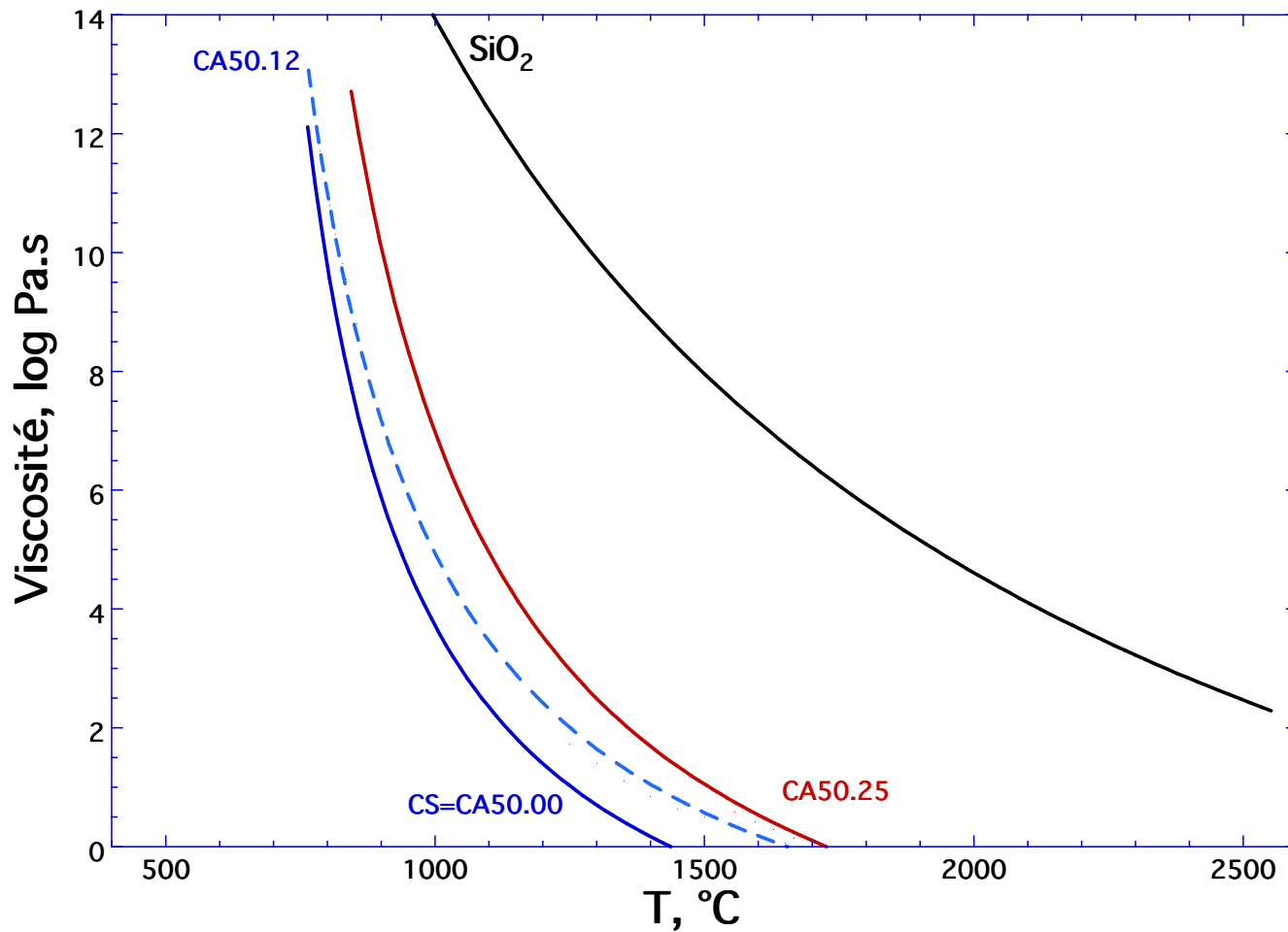
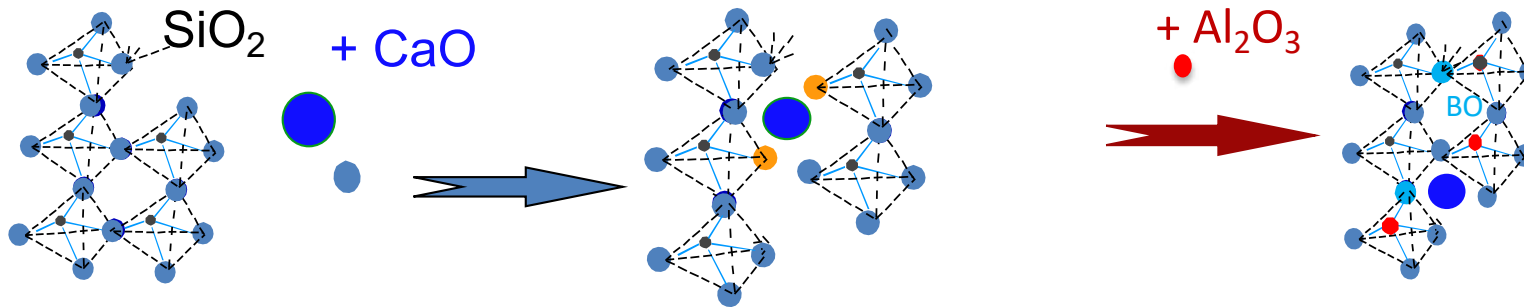
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Aluminosilicate vitreux de calcium



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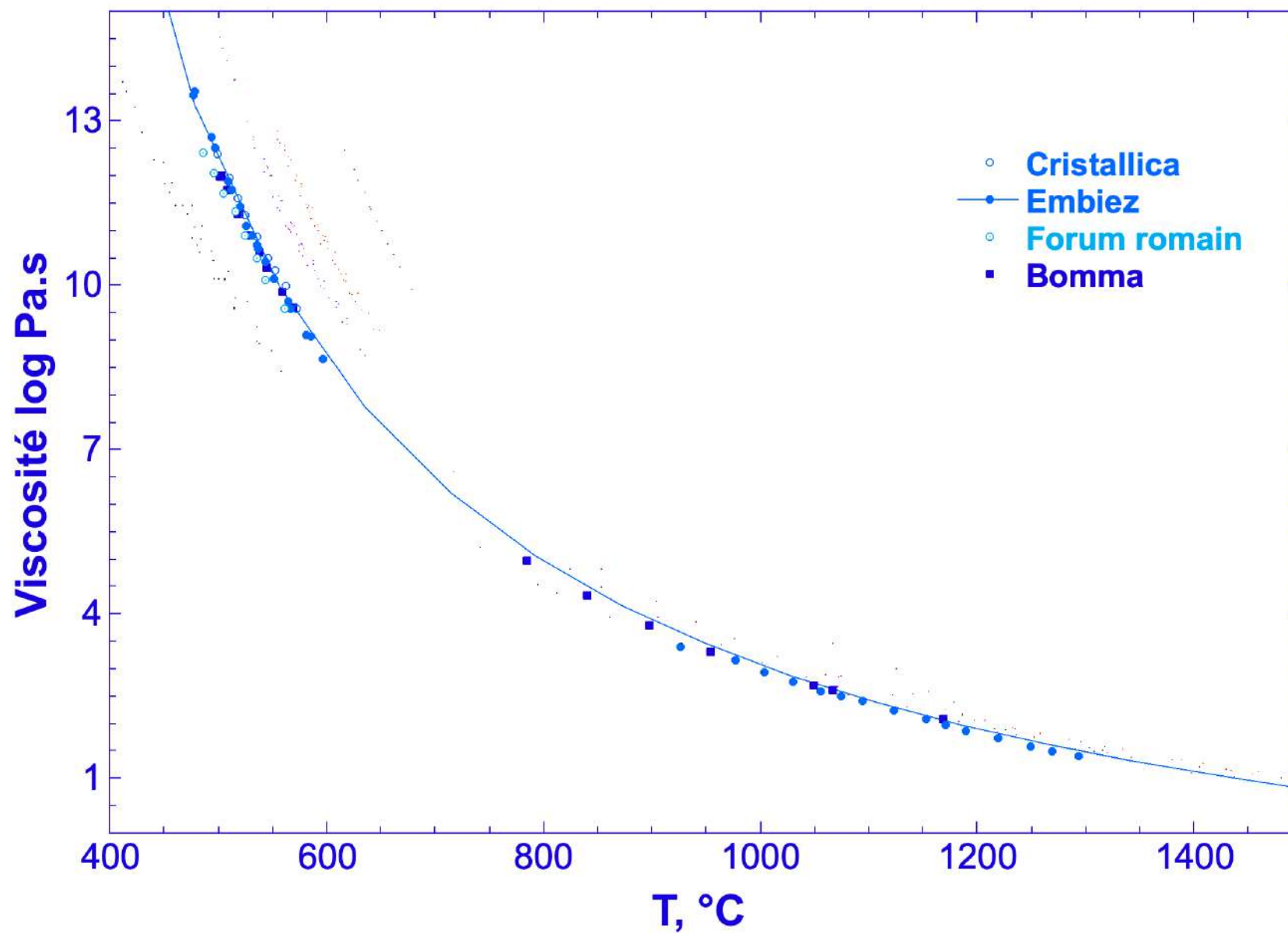
Si⁴⁺ : formateur de réseau : très forte viscosité.

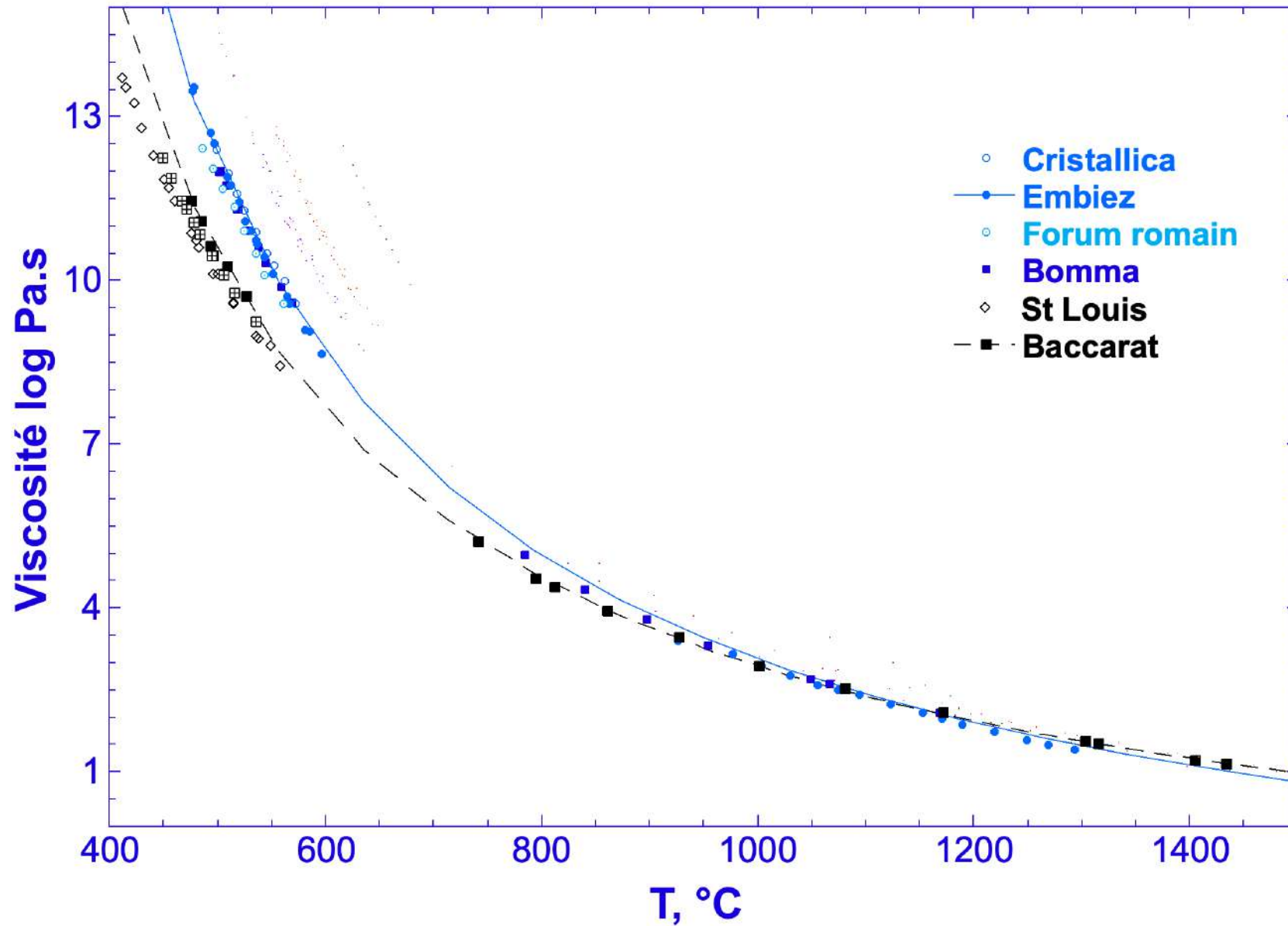
O : Oxygène : connection entre les Si en créant des oxygènes pontants.

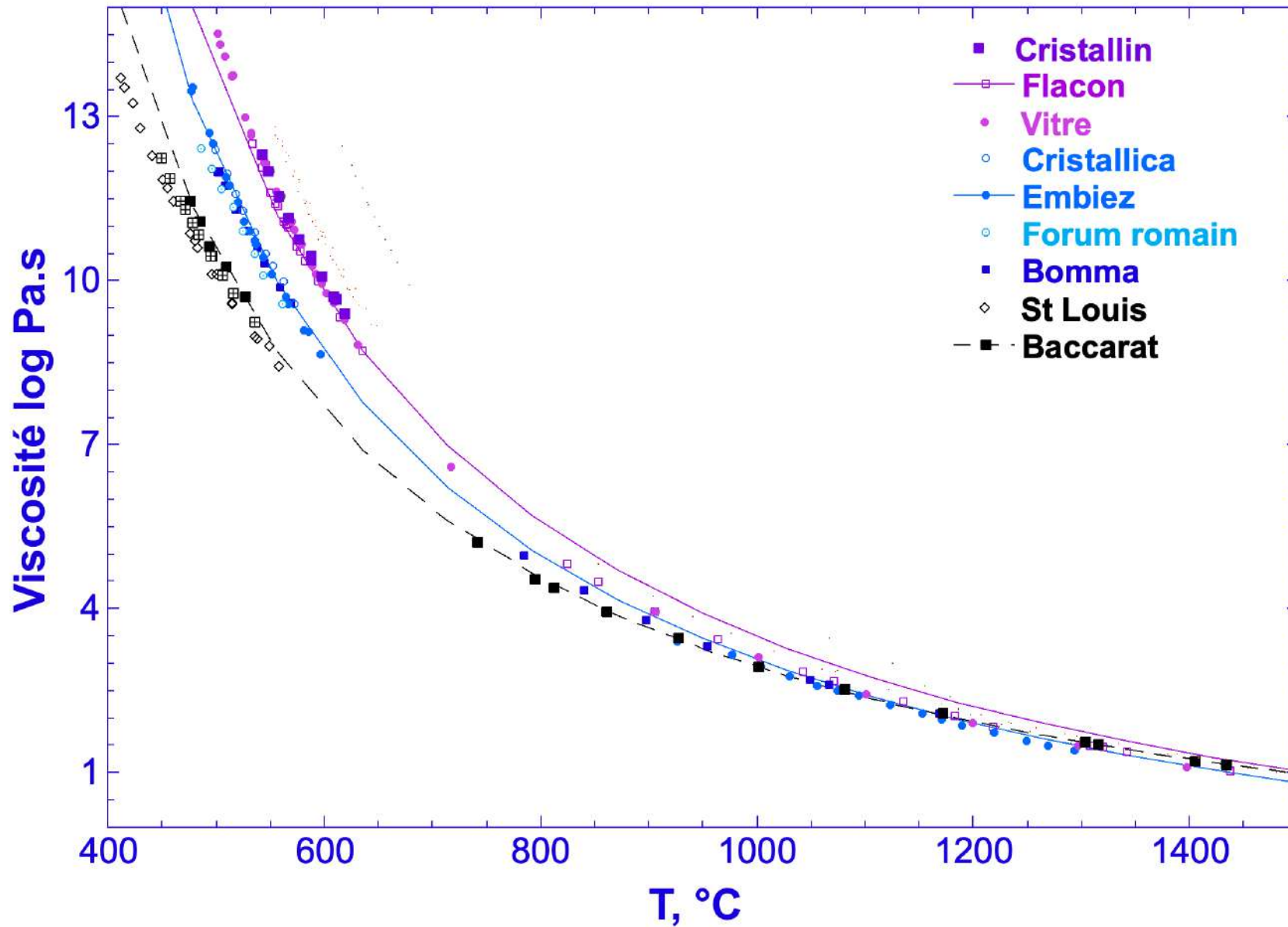
Na⁺ : casse les connections entre les Si : plus Na augmente et plus viscosité diminue.

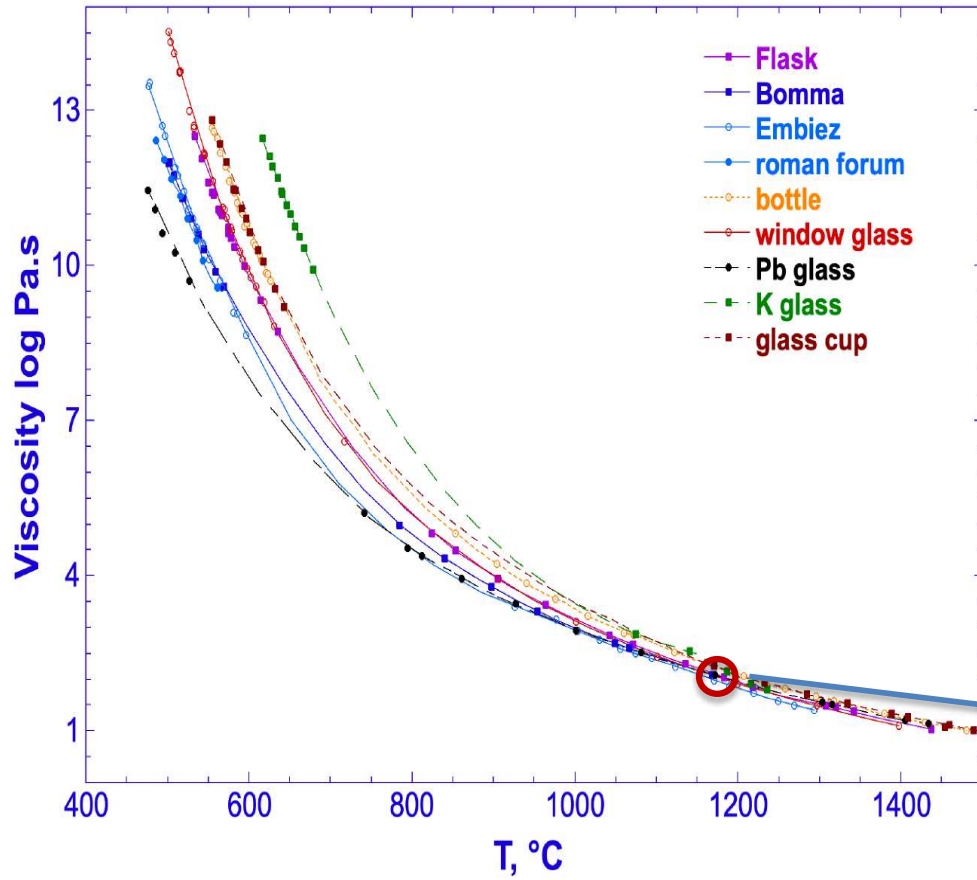
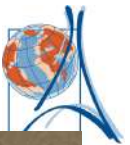
Ca²⁺ : stabilise le réseau, mais casse les connections entre Si, faible viscosité mais moins faible qu'avec Na.

Al³⁺ : reconstruit le réseau car il prend la charge + de Na ou 2+ de Ca qui ne casse plus le réseau, la connection du réseau augmente et la viscosité aussi.

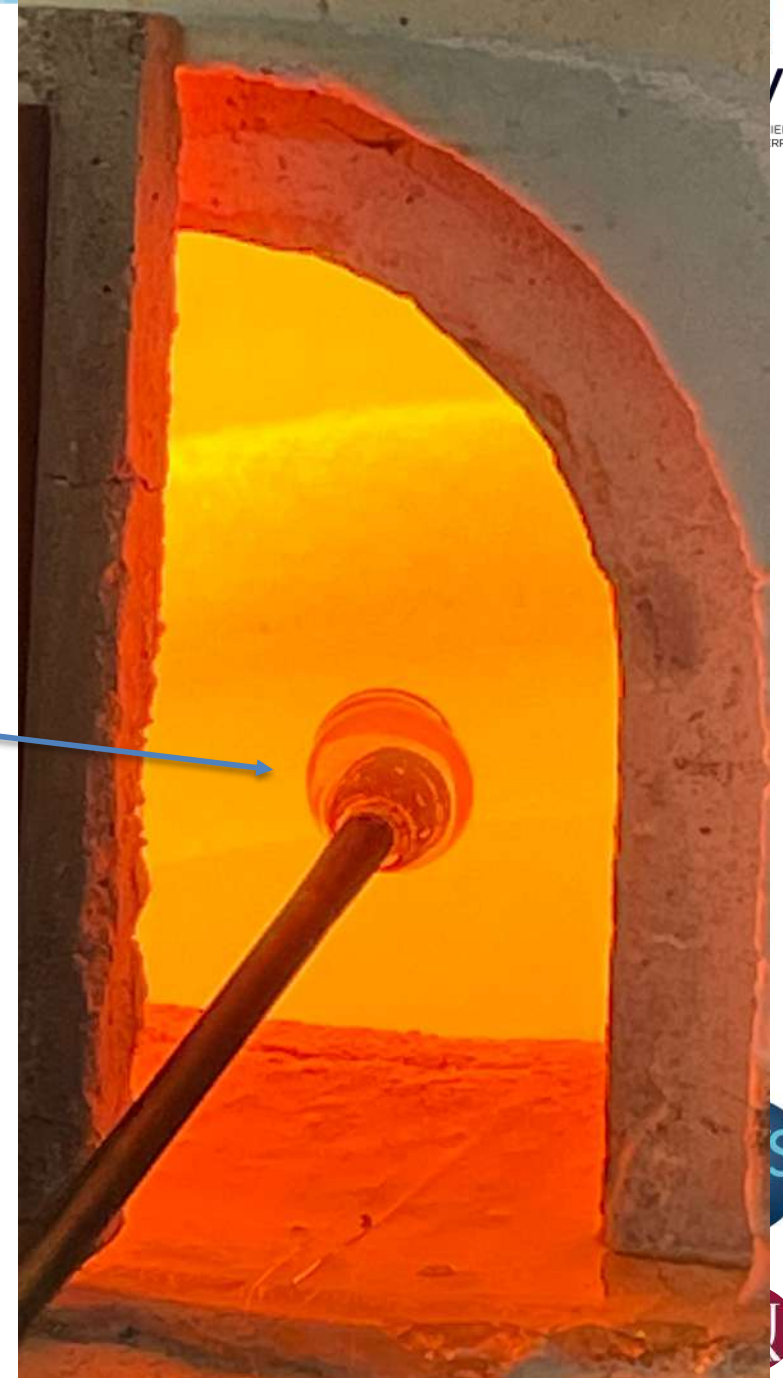


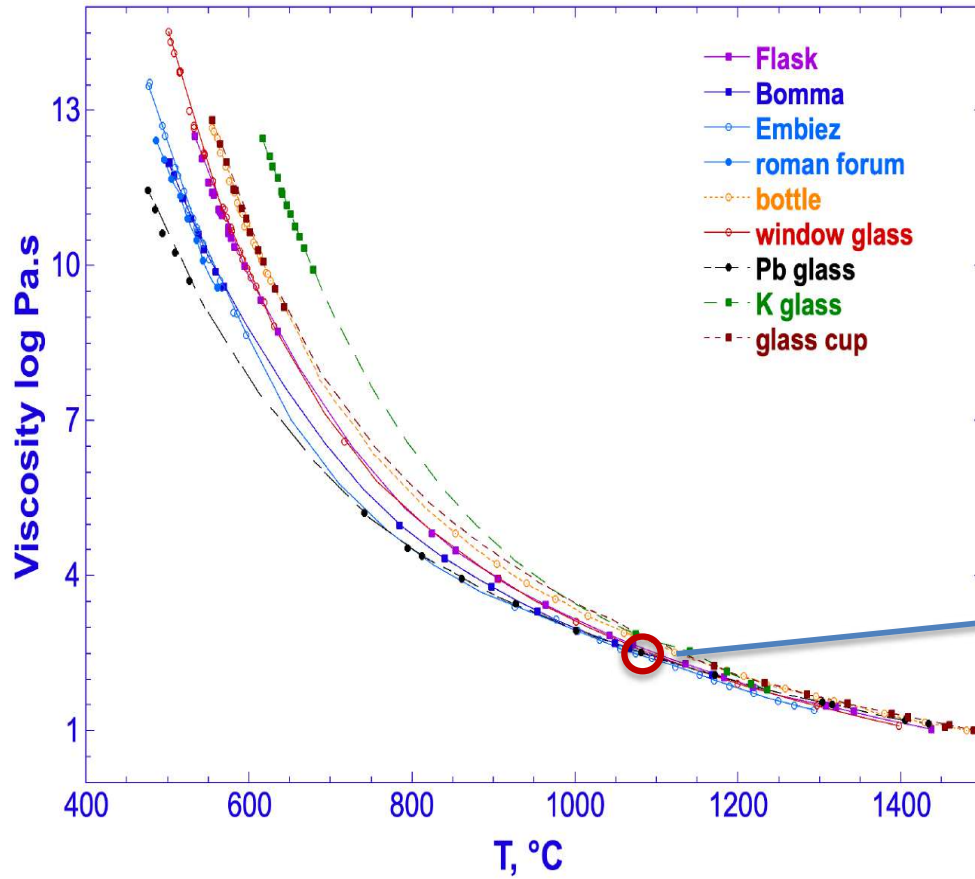
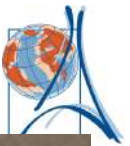




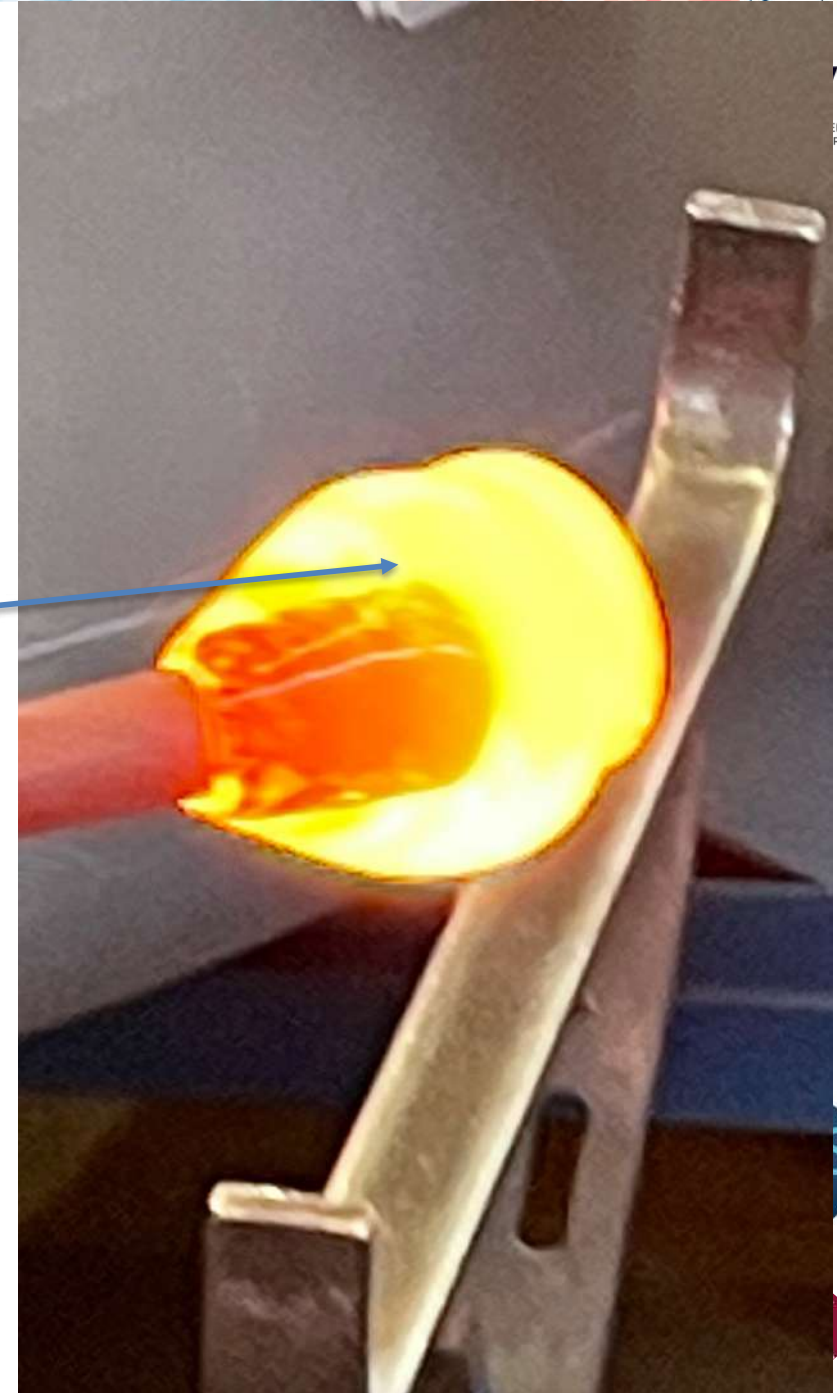


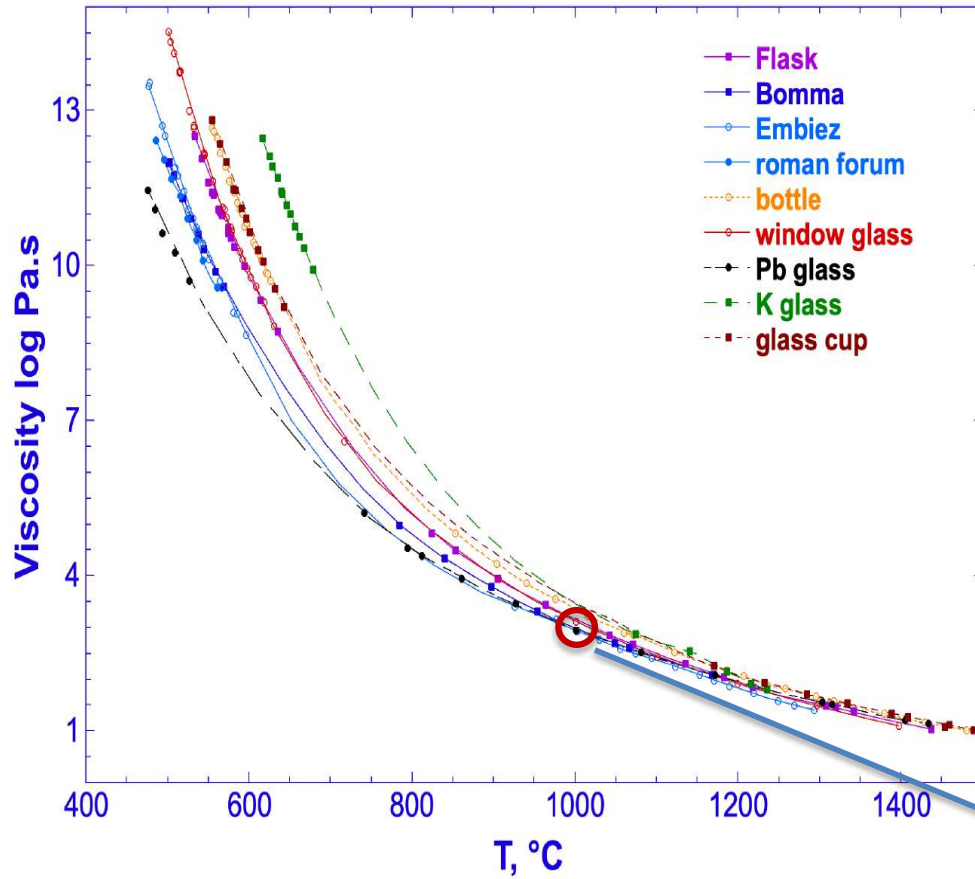
1150°C => ~2 log Pa.s





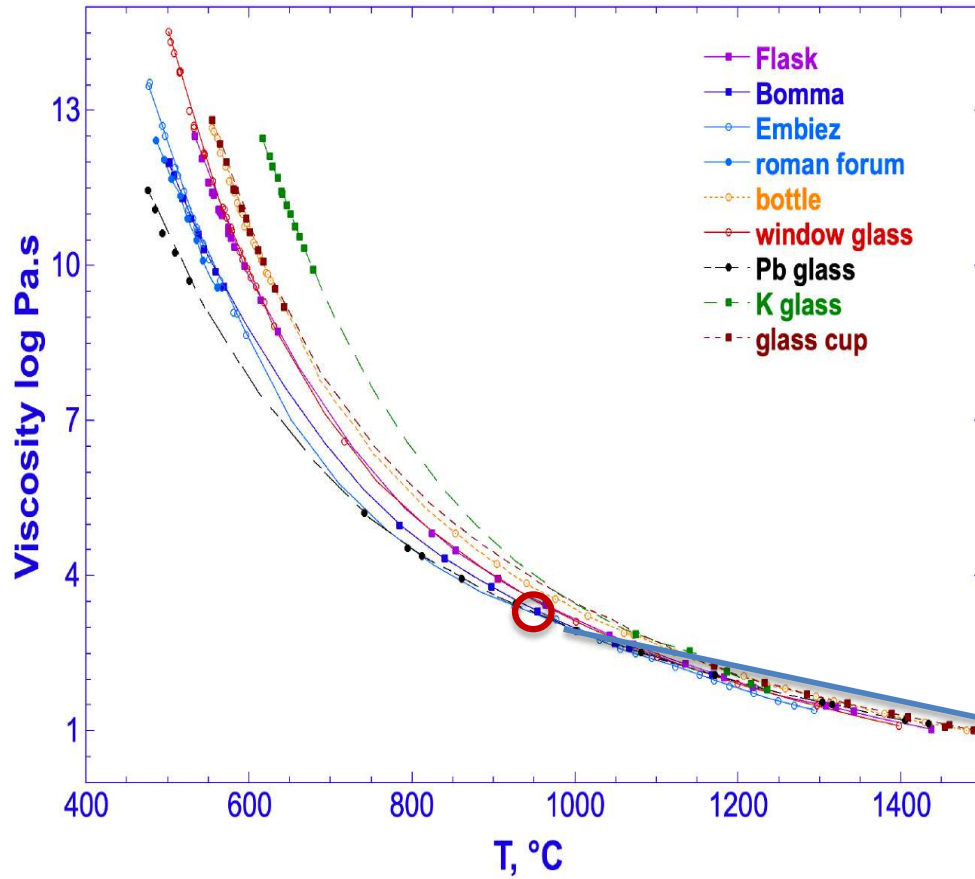
1060°C => ~2,6 log Pa.s





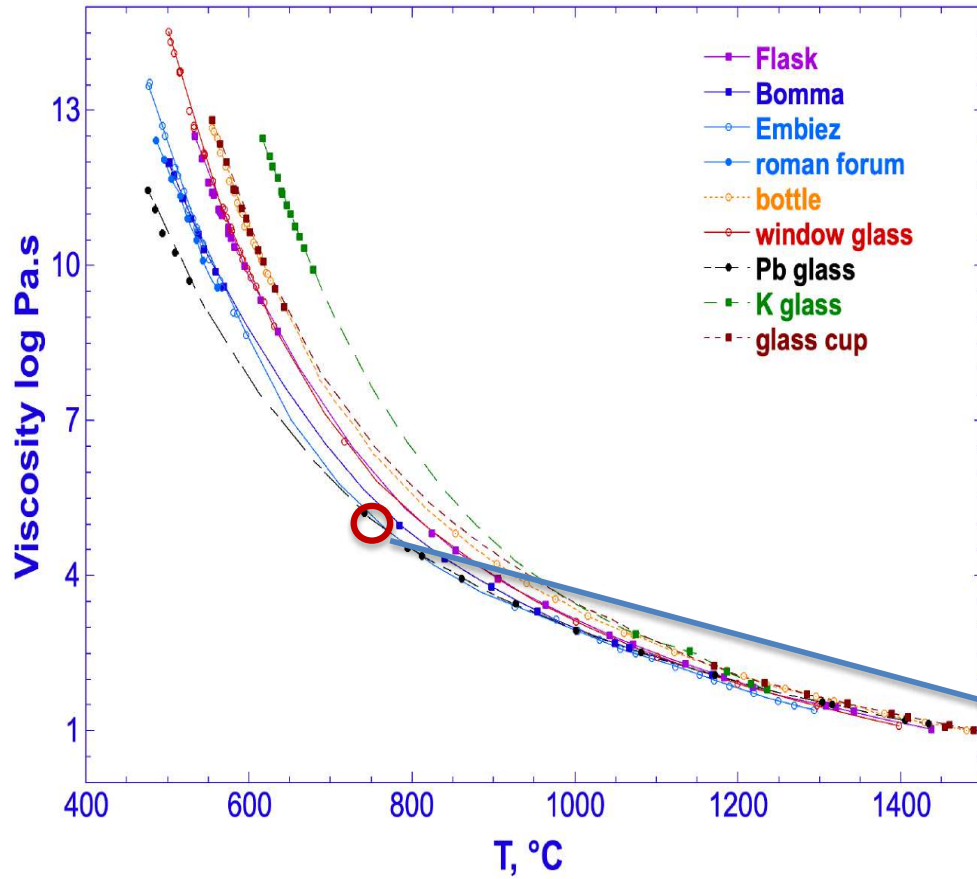
1060°C => ~3,2 log Pa.s





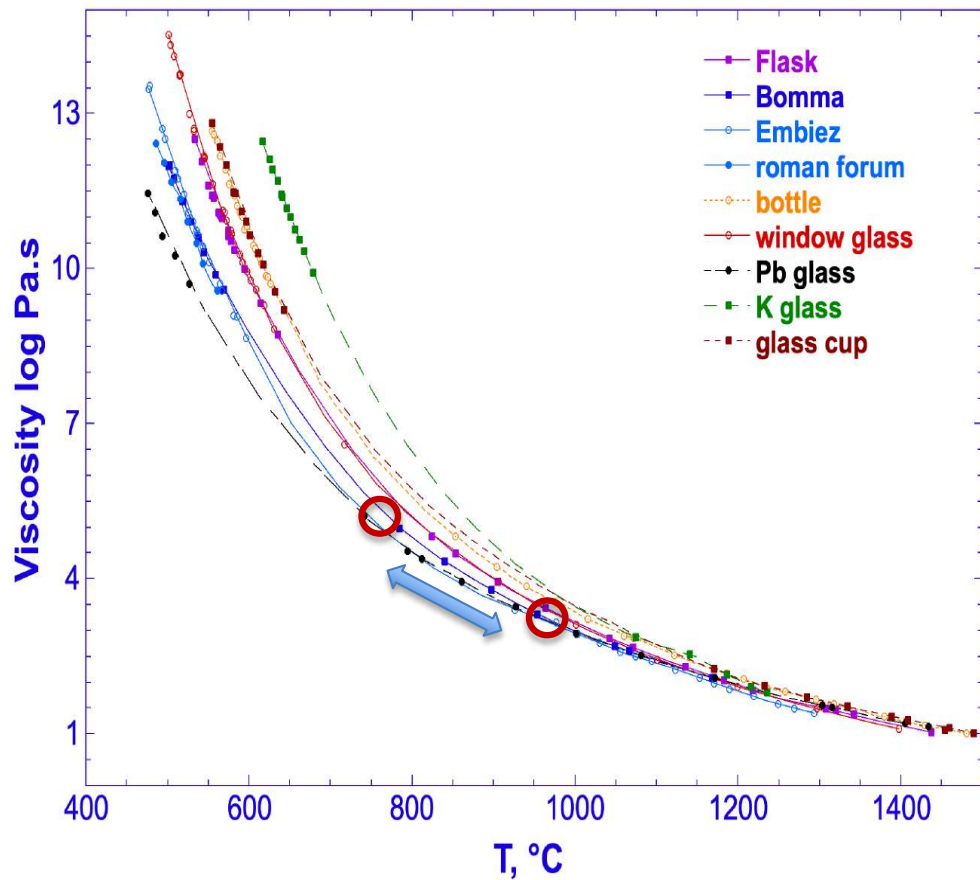
950°C => ~3,6 log Pa.s





720°C => ~5,3 log Pa.s



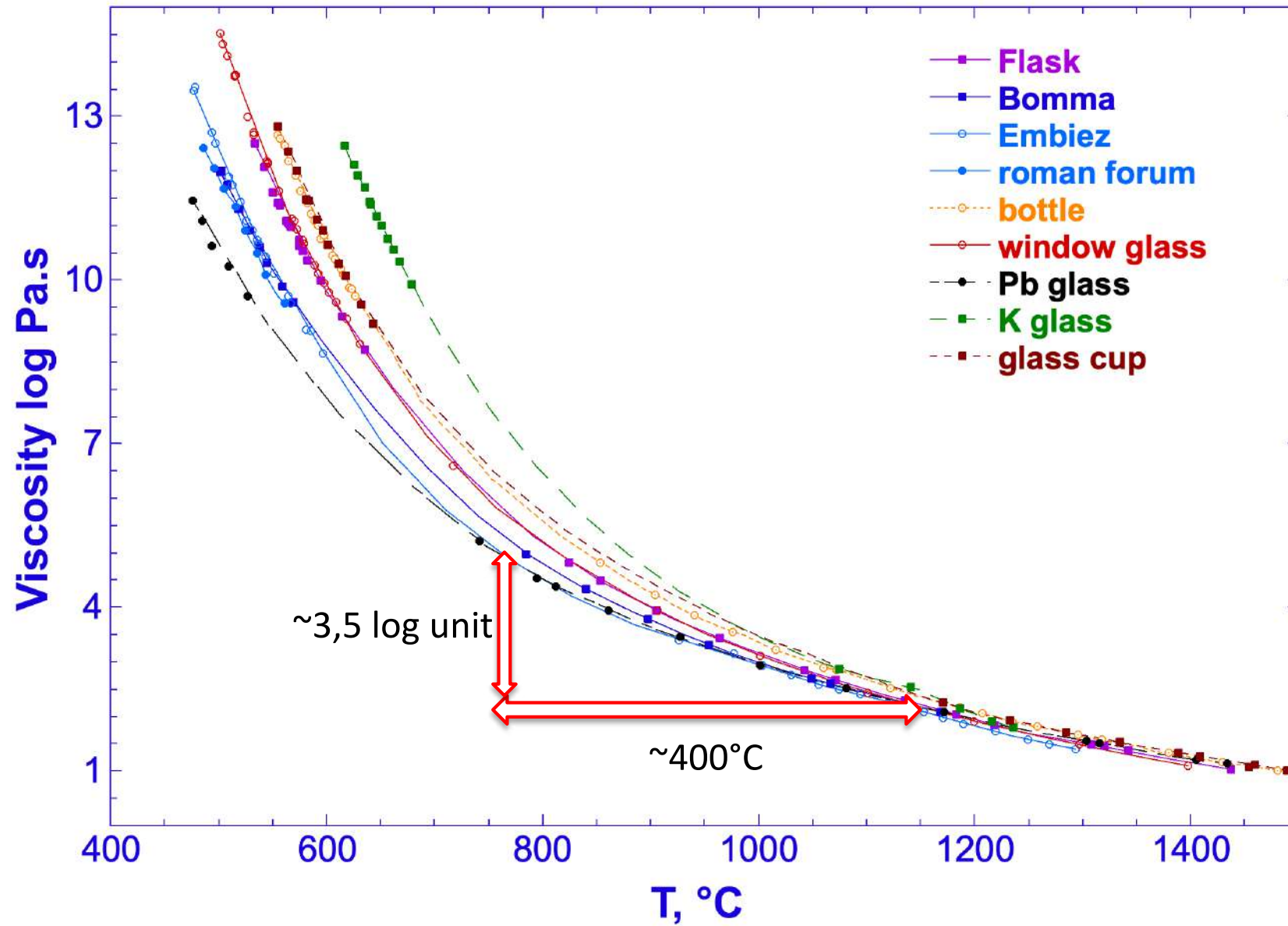


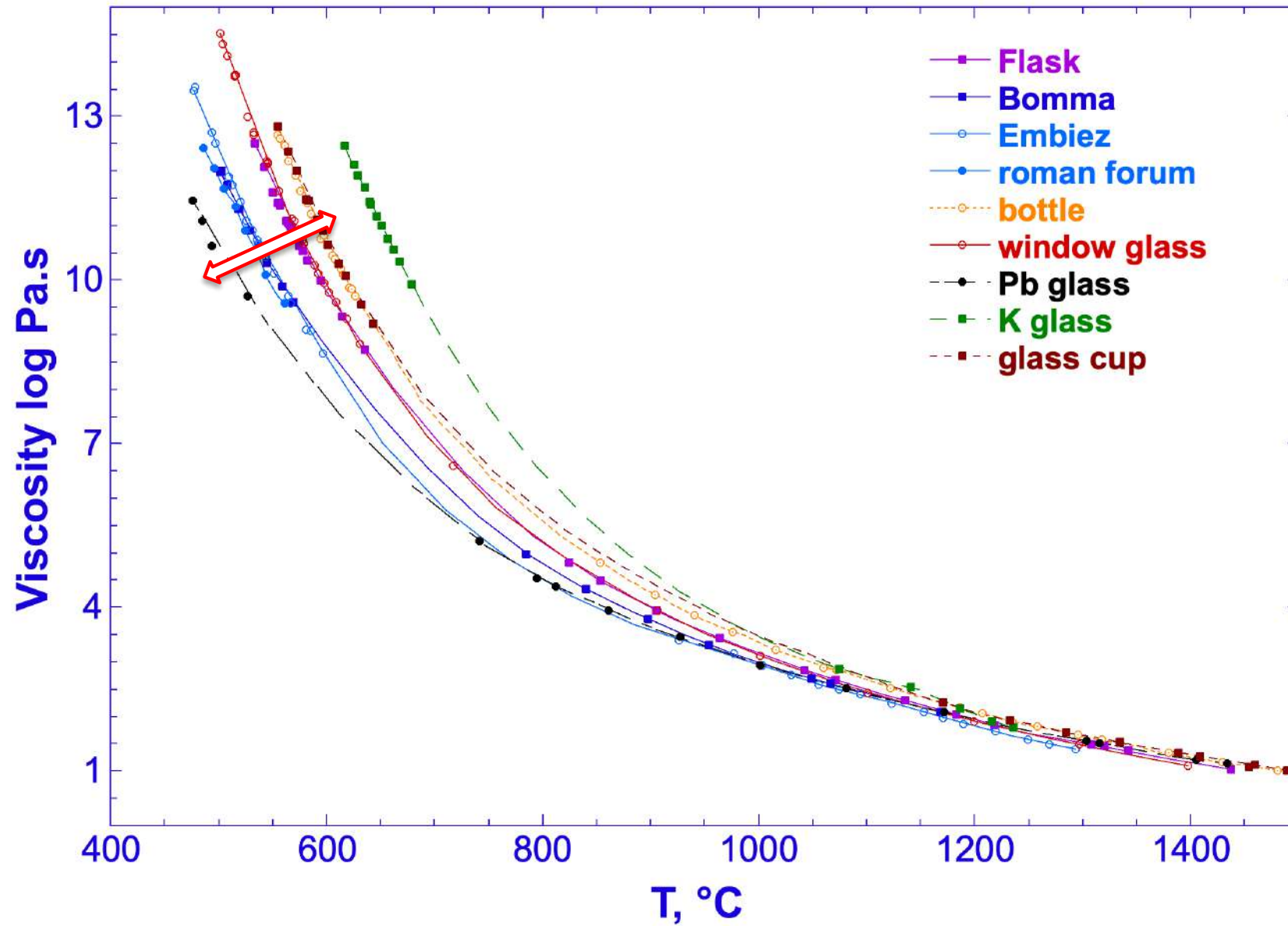
950°C => ~3,6 log Pa.s

720°C => ~5,3 log Pa.s





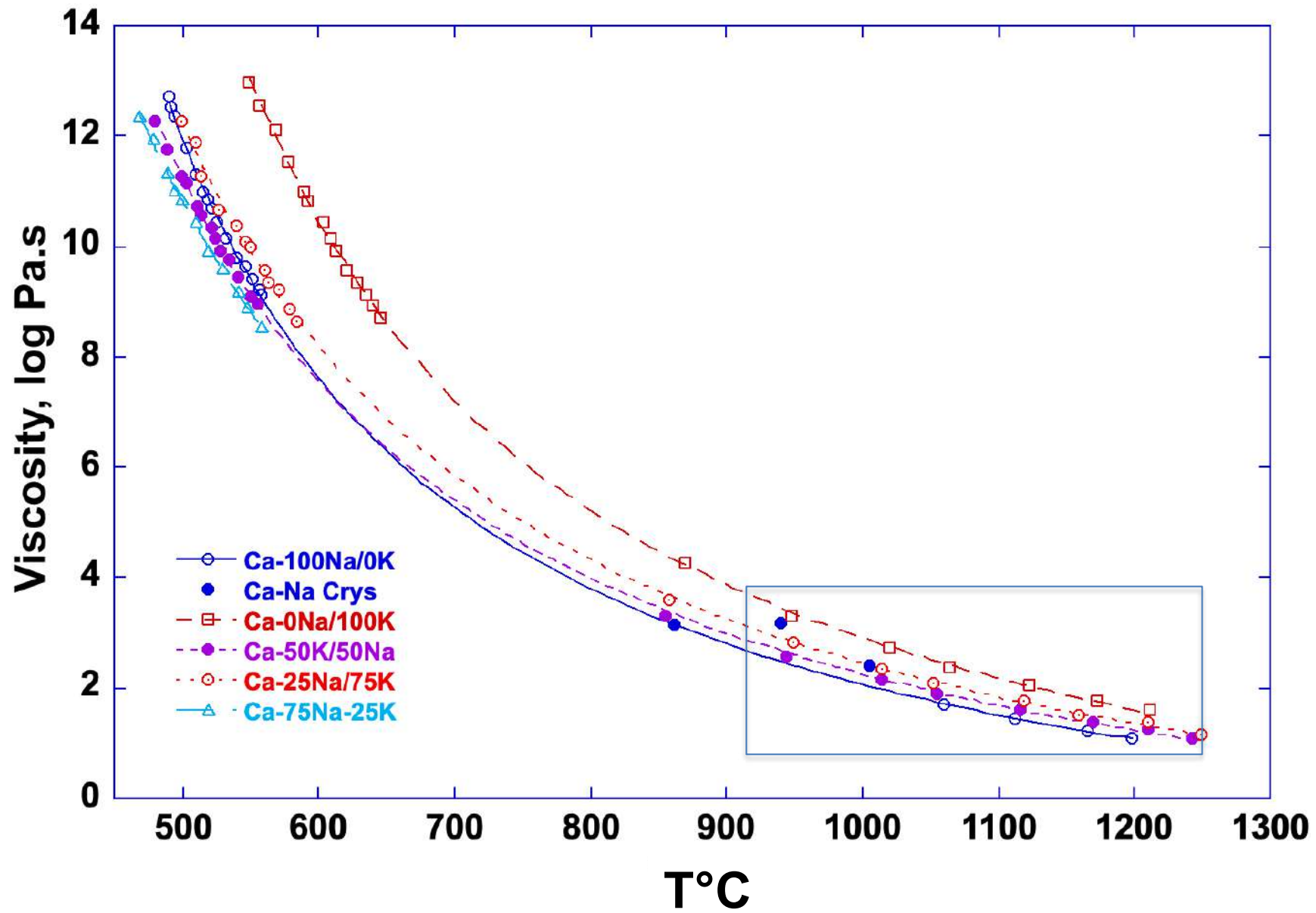


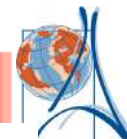


	SiO ₂	CaO	Na ₂ O	K ₂ O	K/(Na+K)	A	B	T1	Tg K	Tg°C
Ca-100Na/0K	65	11	24	0	0	-2,5658	3403,9	538,42	772,1	499,0
Ca-75Na/25K	65	11	18	6	0,25	-3,0085	4144,7	472,58	748,7	475,6
Ca-50Na/50K	65	11	12	12	0,5	-2,7799	3930,9	492,43	758,4	485,2
Ca-25Na/75K	65	11	6	18	0,75	-2,9839	4246,9	493,13	776,6	503,4
Ca-0Na/100K	65	11	0	24	1	-3,0338	4244,9	558,58	840,9	567,8



ALICIA VAN HAM-MEERT ET MAYA DAUSSIN

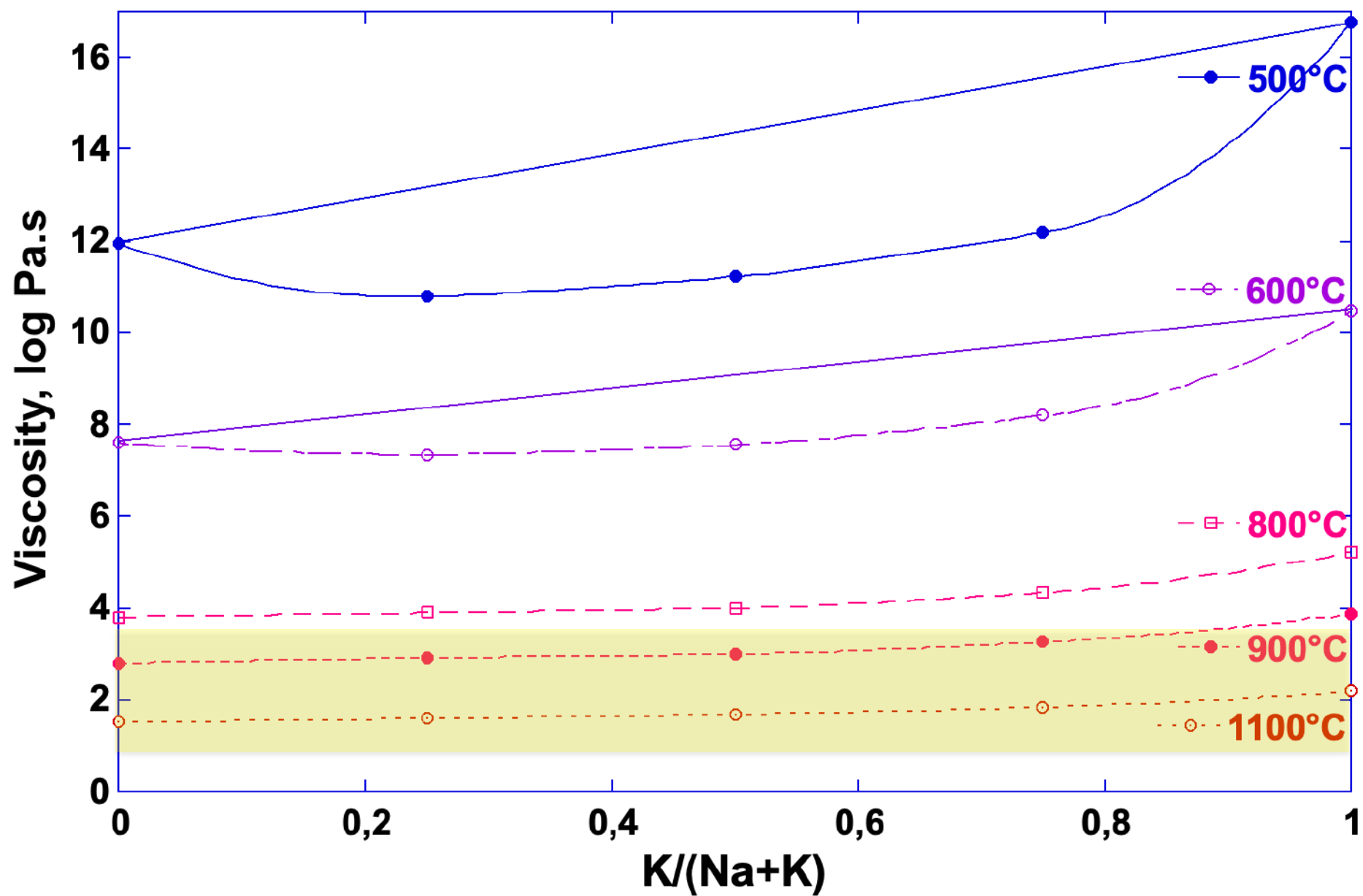




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GÉNÉRALISTE DE PARIS

ITV

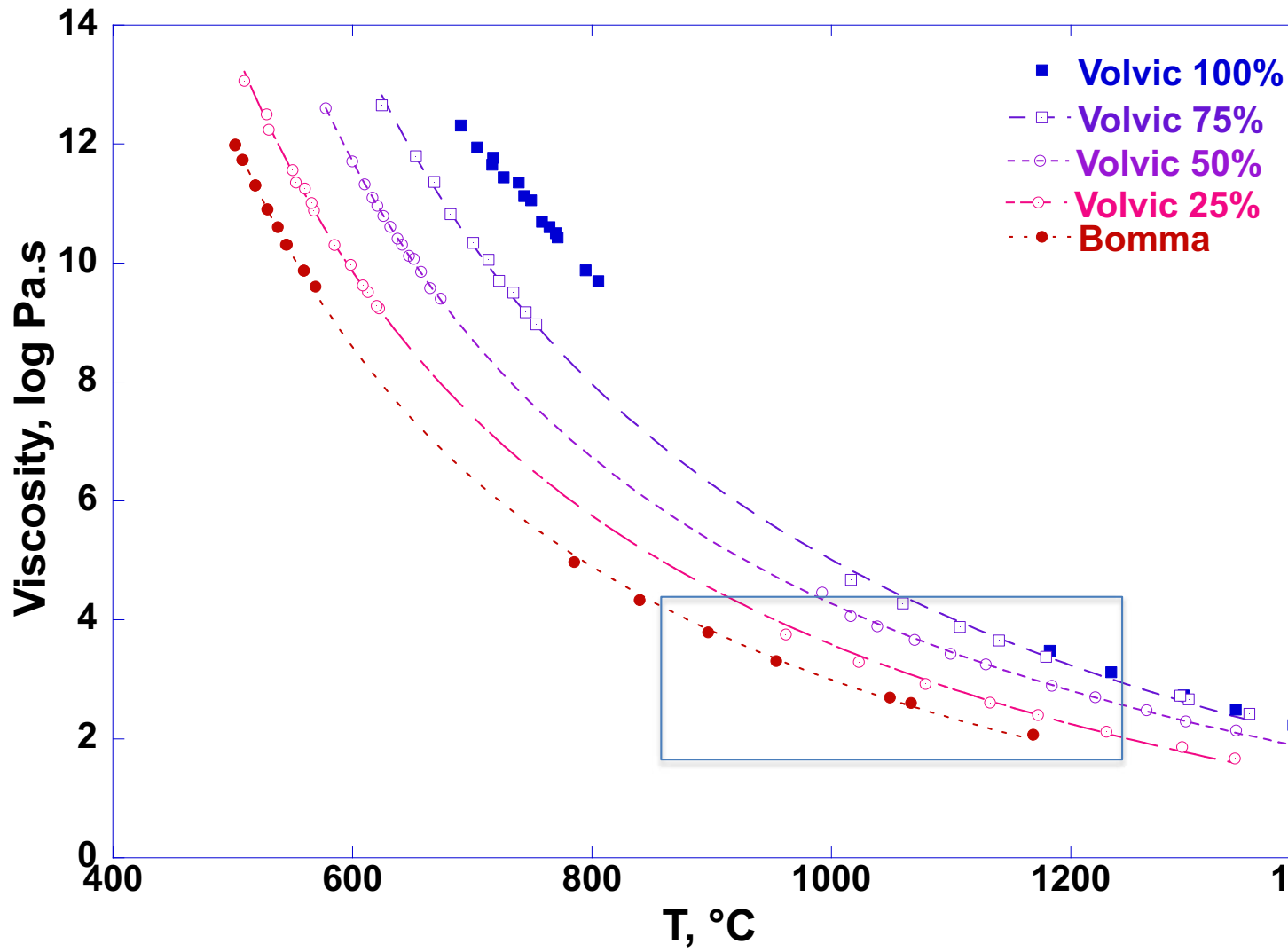
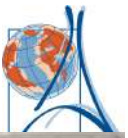
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Que faut-il faire pour développer de nouvelles compositions de verre?

=> Trouver une composition qui présente un palier de travail comparable compositions précédentes !

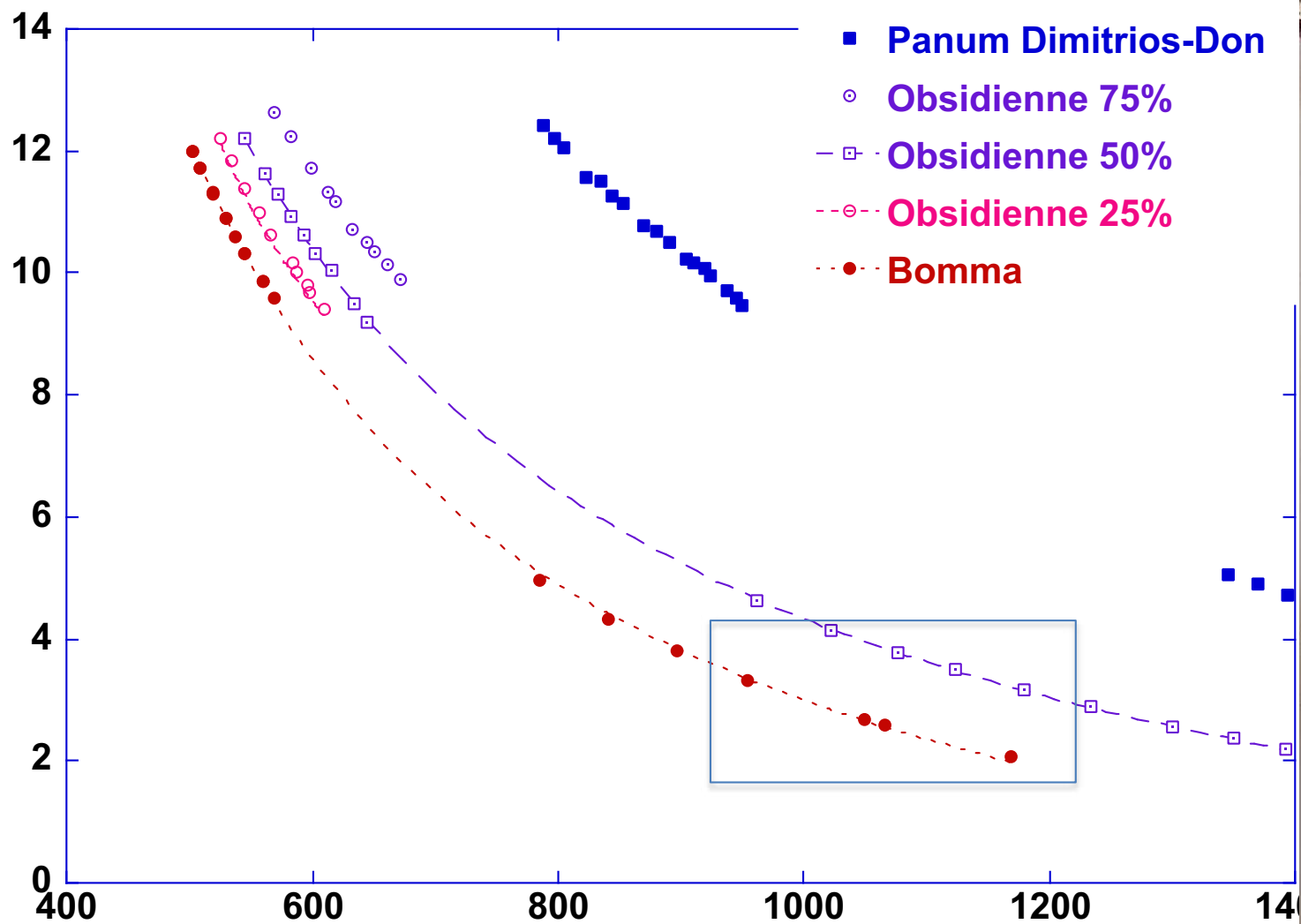
	SiO₂	Al₂O₃	Na ₂ O	K ₂ O	MgO	CaO	BaO	ZnO	Ce ₂ O ₃	Sb ₂ O ₃	SO ₂	P ₂ O ₅	TiO ₂	FeO
Bomma	71,79	0,68	9,68	5,18	0,23	4,54	3,6	1,04	0,28	0,66	0,05	0,01	0	0
basalte	44,73	13,74	2,85	1,77	11,23	8,92	0,05	0	0,02	0,14	0,01	0,61	2,02	10,37
andesite- Volvic	55,73	18,35	3,26	3,53	1,88	4,57	0,11	0	0,04	0,02	0,02	0,15	1,16	5,92
obsidienne	71,57	14,43	4,06	3,9	0	0,06	0,02	0,07	0,03	0,02	0,01	0	0,02	0,93

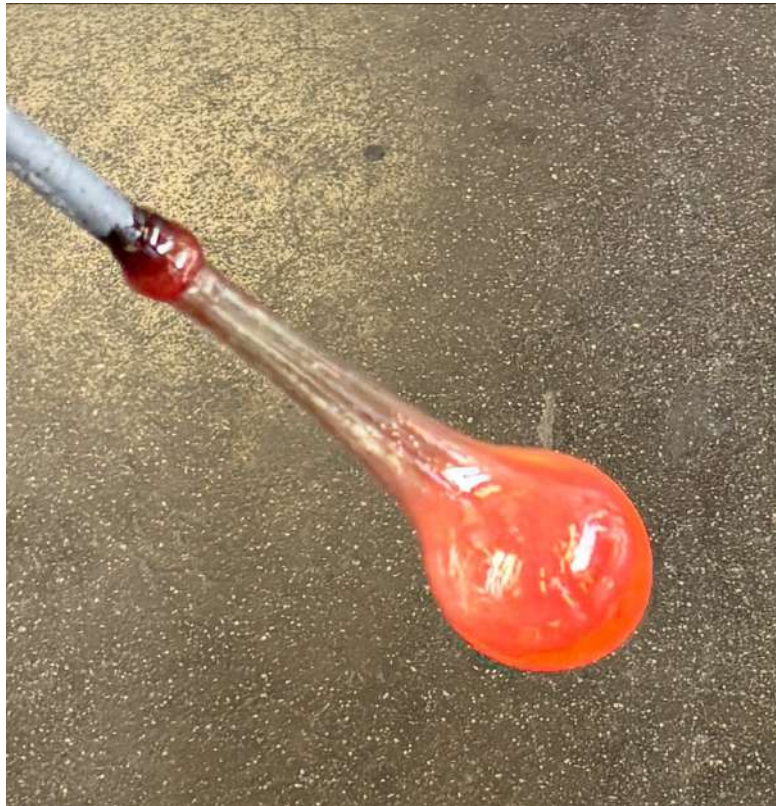




50%Volvic-50%Bomma

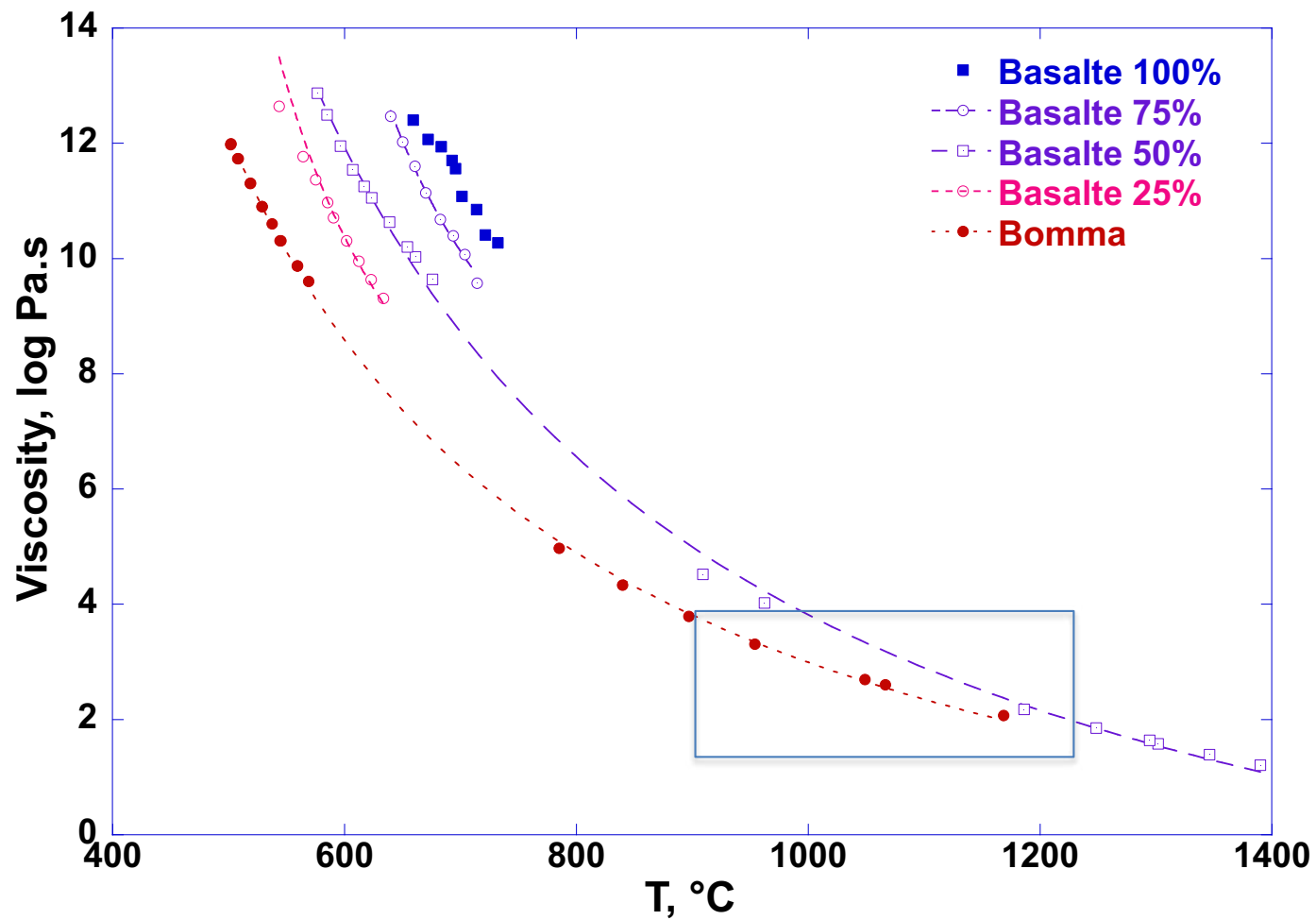






25%obsidienne-75%Bomma





1) Geste verrier : palier de travail long $\sim 3,5$ log pour 400°C

2) Nouvelles compositions = possible si répondez aux gestes verriers



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Merci

