



Les applications de la microscopie électronique à balayage à l'étude des verres

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³ GREMI-CNRS, Université d'Orléans





*Pointe de flèche en
obsidienne 4000 avant JC
(musée de Sartène en Corse)*



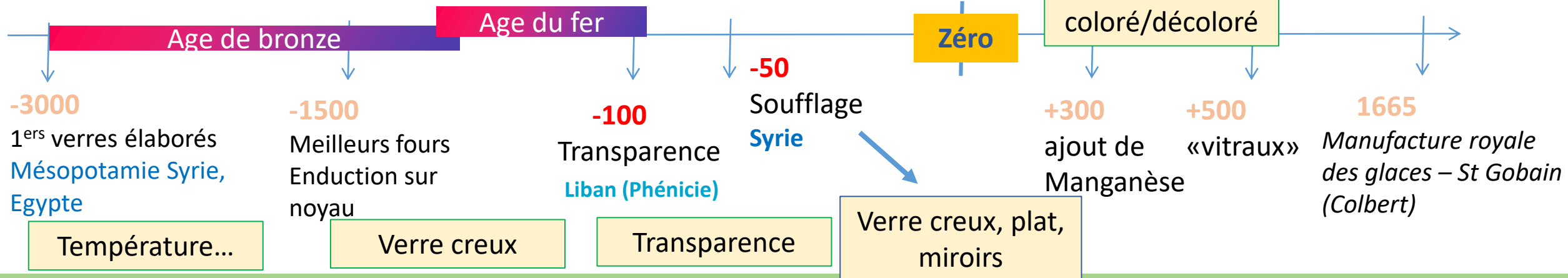
*Verre à vitre H. 51 cm; larg. 45,5 cm
Pompéi - SAP, inv. 18031 - I^{er} siècle apr. J.-C.*

Verre **opaque**
coloré bleu, vert

Verre **translucide** bleu-
vert, **verre creux**

Verre **transparent**

Mésopotamie : berceau du verre





Equilibre 

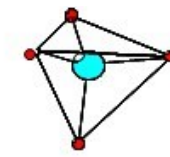
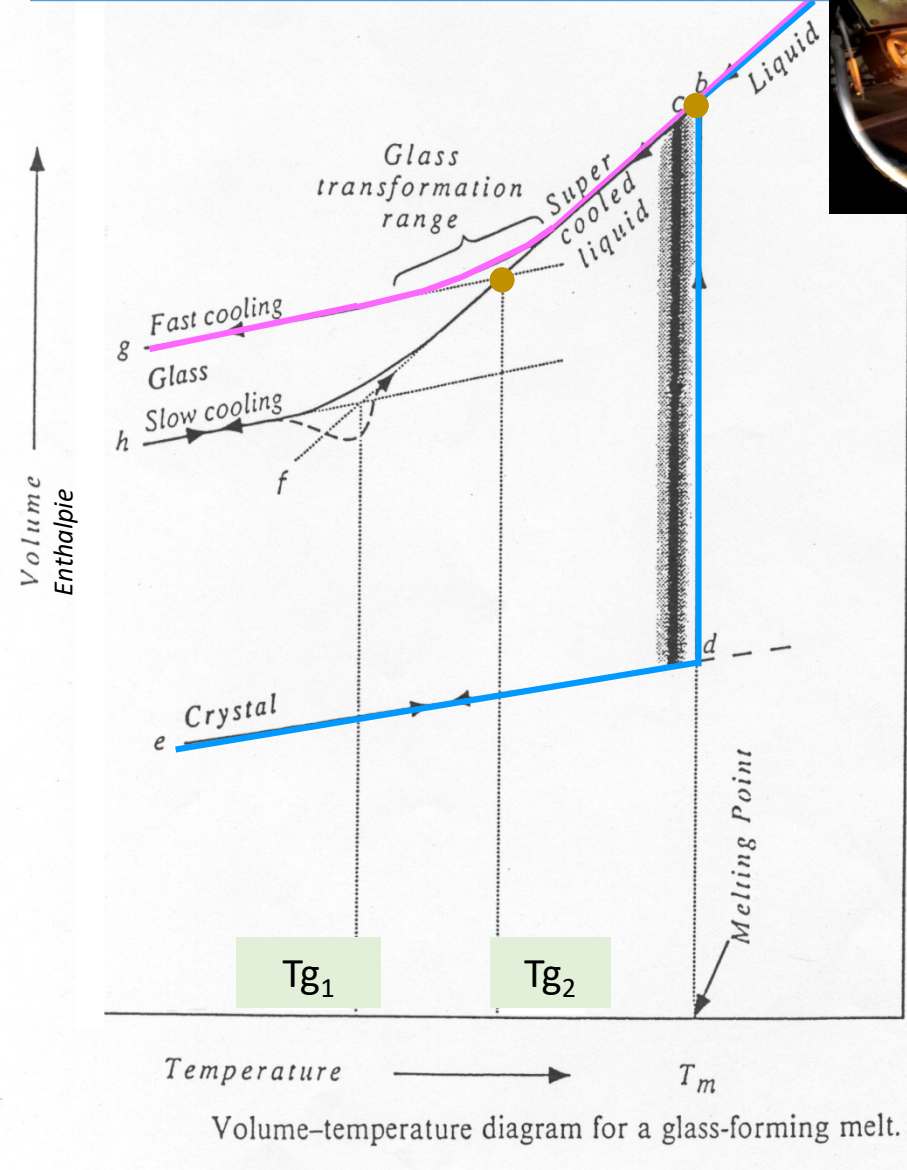
Silice cristalline:
Quartz



Etat cristallisé:
ordonné

La silice: SiO_2

Thermodynamique



$R_{(\text{Si-O})} = 1,61 \text{ \AA}$
O-Si-O de $109,5^\circ$


• O • Si

Silice amorphe:

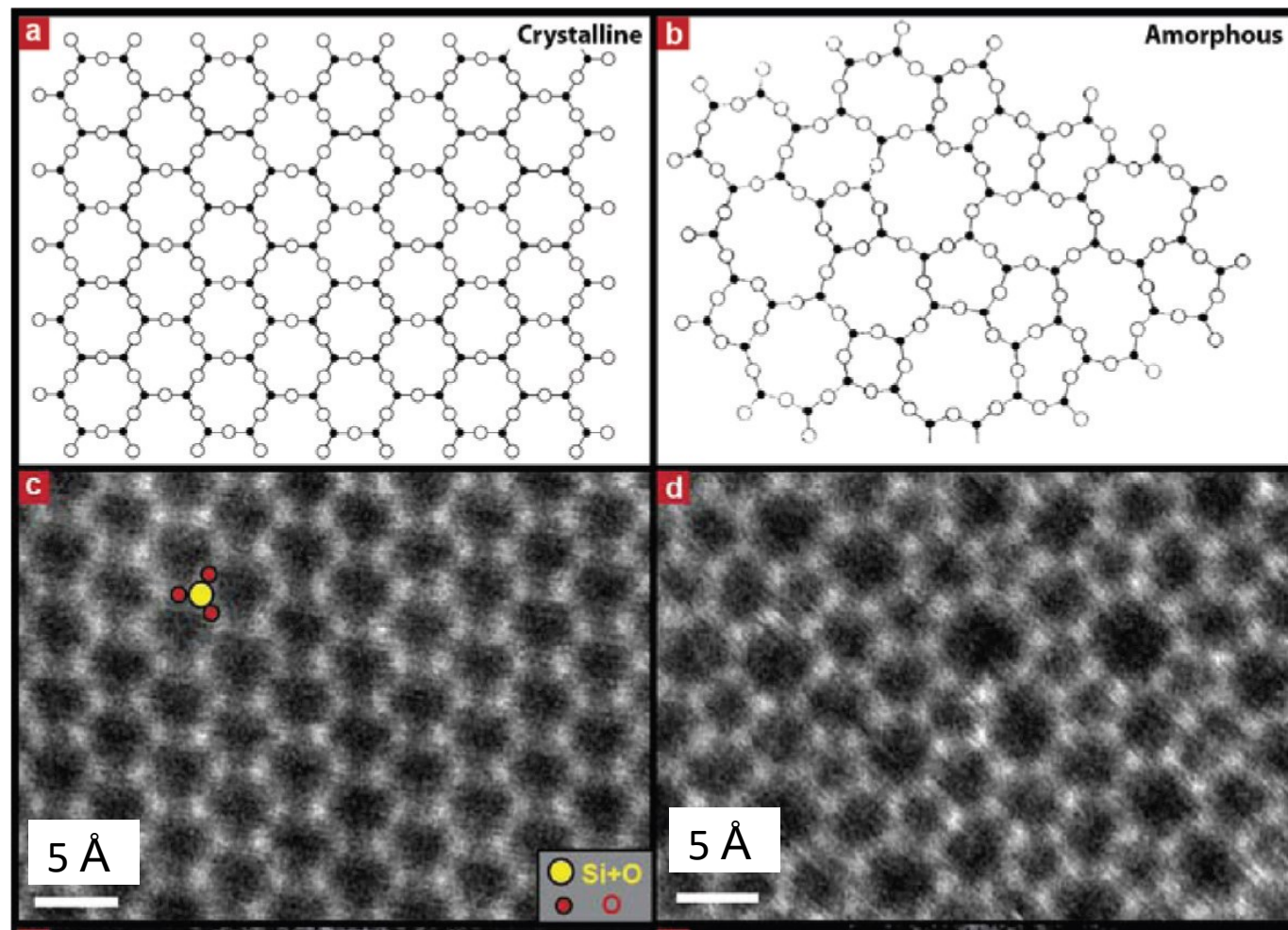
Verre de silice



Etat vitreux:
désordonné ou
amorphe

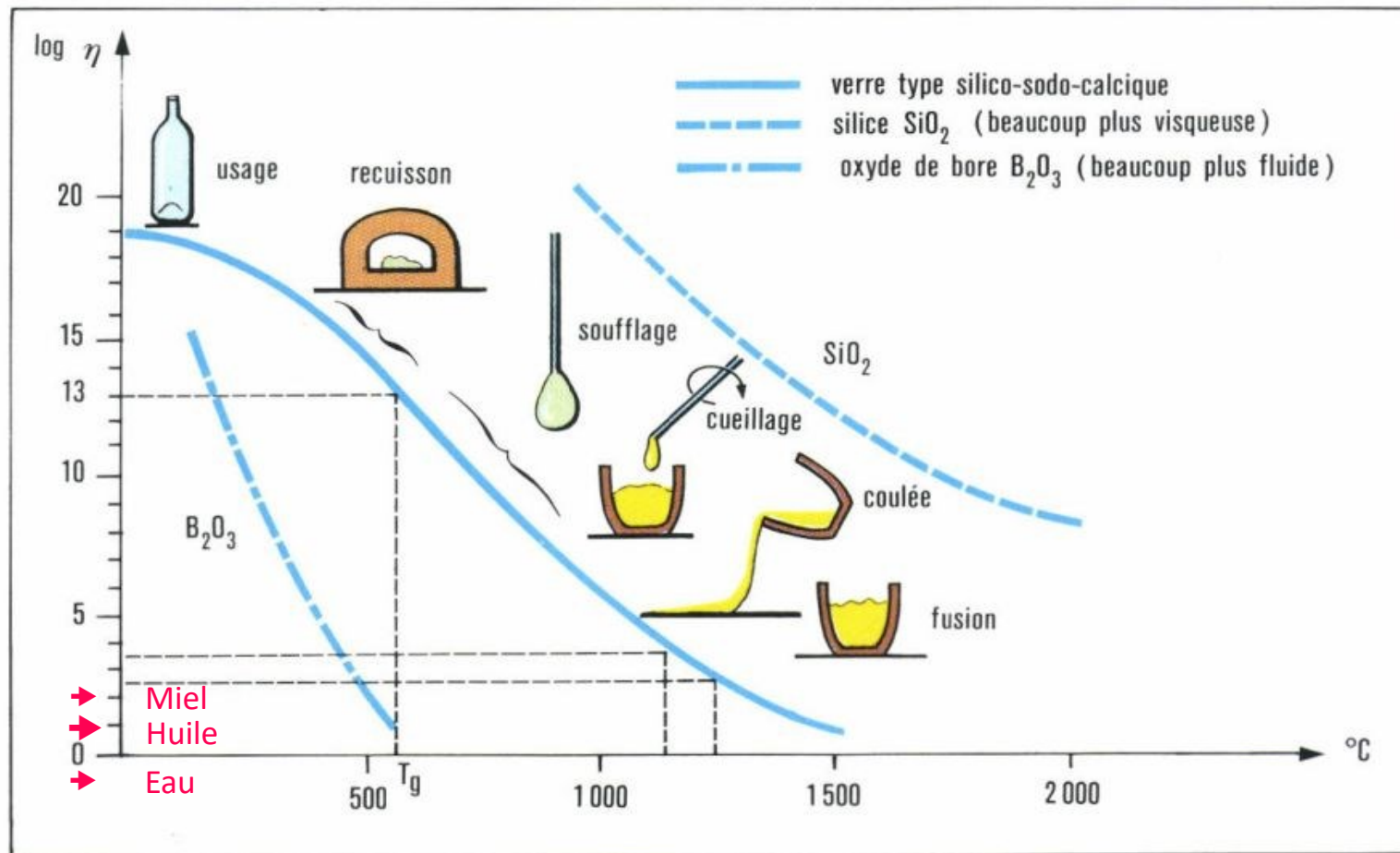
Hors équilibre 



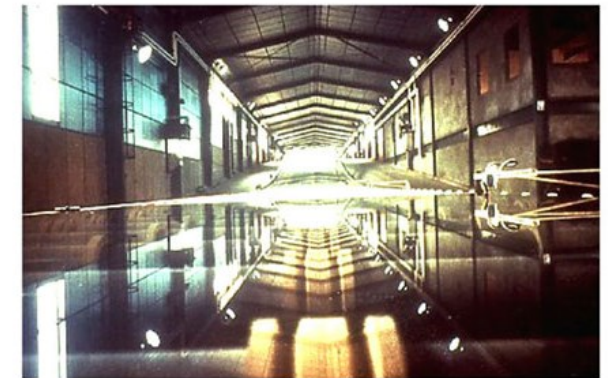


a et b: modèle de **Zachariasen** (1906-1979) de la silice cristalline et amorphe à 2 D;
 c et d: ADF-STEM (*Annular Dark Field – Scanning TEM Microscopy*): film de silice sur support graphène
 (P. Y. Huang, *Nano Letters*, 2012, 12, 1081-1086)

Variation de la viscosité η des verres en fonction de la température.



BAIN D'ETAIN DU PROCEDE FLOAT



Source : Saint-Gob

Verre plat : procédé float / verre flotté
(invention: Pilkington **1952**) Bain d'étain à 600°C

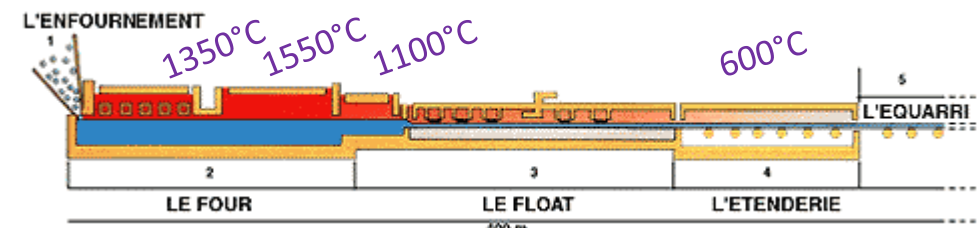
$T_g \gg 10^{13}$ poise = 10^{12} Pa.s

3 zones:

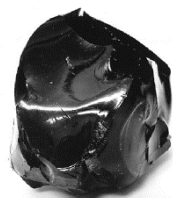
Fusion: 1300 – 1400°C

Affinage: 1450 – 1550°C

Braise: 1000 – 1200°C



<https://www.dumaine.fr/VerreFabrication.php>



INTERET DU MEB DANS L'ETUDE DU VERRE?



CEMHTI/IRAMAT
Microscope Environnemental
PHILIPS XL40 ESEM

Plateforme MACLE-CVL (2021)
JEOL JSM-IT800
Canon à effet de champ
Détecteur SBED



Vérifier son homogénéité!!!

Vérifier sa composition

Suivre une évolution chimique ou microstructurale du verre:

**SURFACE
COUPE**

**DURABILITE
CHIMIQUE**

PROBLEMES:
migration sous faisceau des alcalins....
Non detection du bore

PROBLEMES:
ISOLANT ► METALLISATION ☹
VIDE ► Désorption des espèces
hydratées de surface ☹

Vérifier un collage, une adhésion: **INTERFACES**

Technique de caractérisation non isolée:
Microsonde/ MET/ Spectroscopie RMN,
IR, Raman / Mesures optiques..

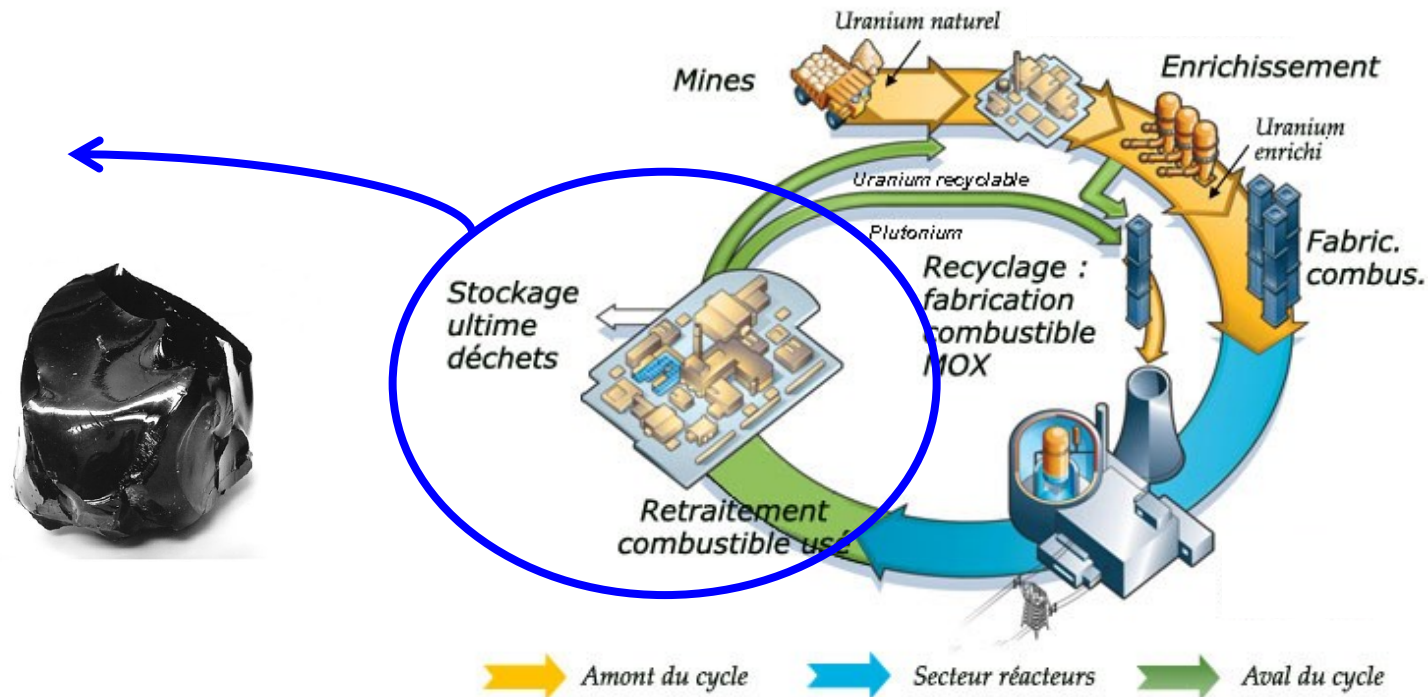
Exemples d'études

Verre nucléaire français (CEA – Orano)

Flacon pharmaceutique (ANR – Région CVL- SGD - LGC – CIRIMAT)

Nanotexturation du verre (ARD MATEX – GREMI)

Verre du patrimoine industriel et artisanal (Région CVL- Durelex® – Centre International du vitrail)



Matériau

- Taux de charge
- Homogénéité (teneur en terres rares ...)

Durabilité

- Résistant à l'altération
- Stabilité thermique
- Résistance à l'auto-irradiation...

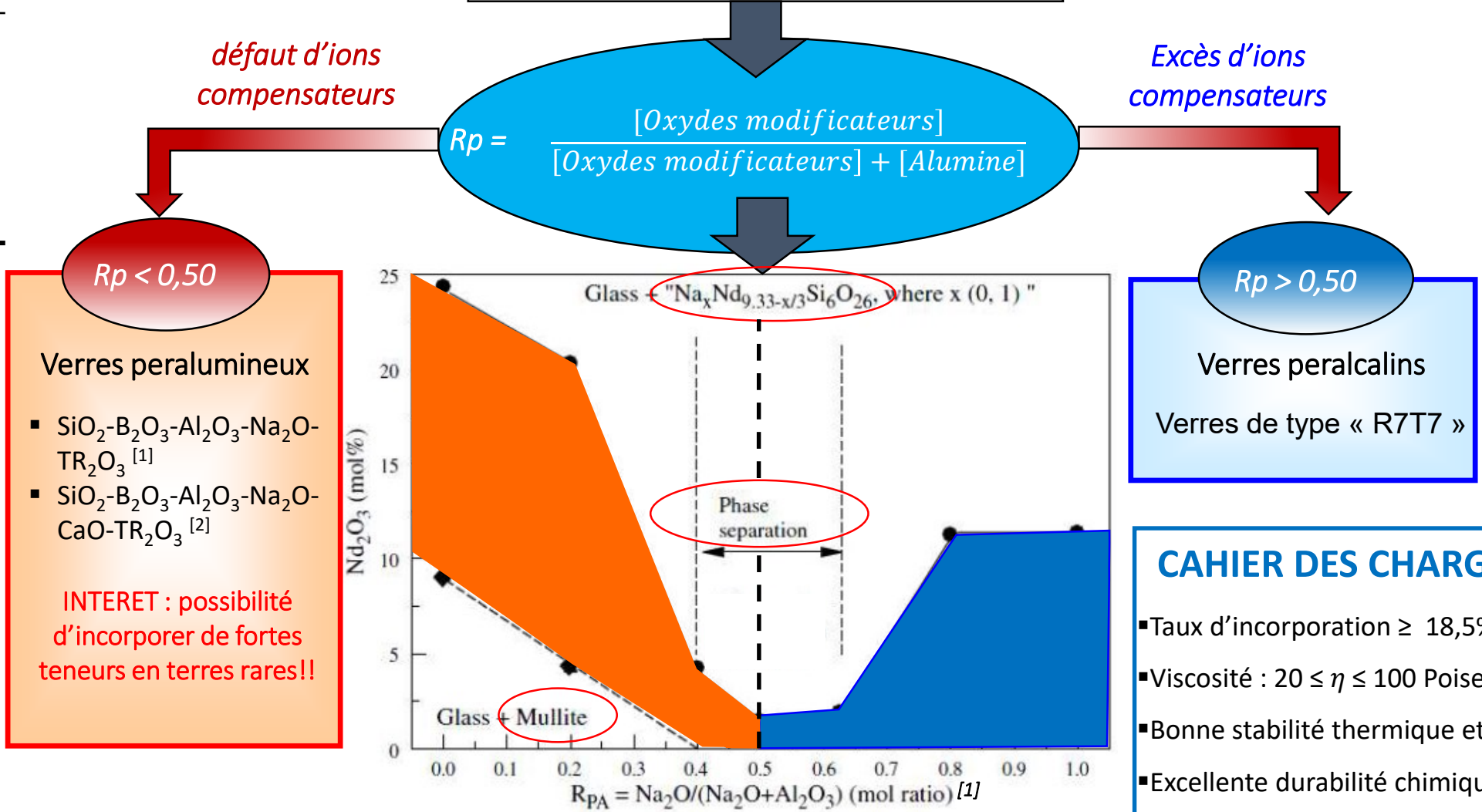
Faisabilité technologique

- Température d'élaboration
- Viscosité ...

Verres simplifiés [3]

Oxydes	% mol.
SiO ₂	[42 - 55]
B ₂ O ₃	[14 - 30]
Al ₂ O ₃	[12 - 20]
Na ₂ O	[4 - 12]
Li ₂ O	[0 - 3]
CaO	[2 - 8]
La ₂ O ₃	[0 - 8]

Verres Alumino-borosilicatés



[1] H. Li Ceram.Trans.87, Environmental Issues and Waste Management Technologies in the Ceramic and Nuclear Industries III (1998) 189

[2] Thèse E. Gasnier, 2013

[3] Thèse V. Piovesan, 2016

PLEX optimisé



Transposition

Verres simplifiés



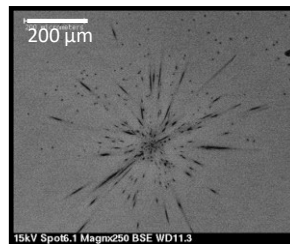
Verres complexes



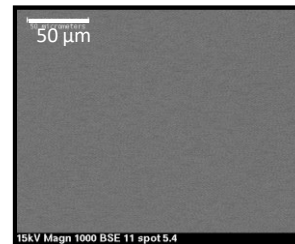
Verres simplifiés
7 oxydes

Tendance à la
dévitrification

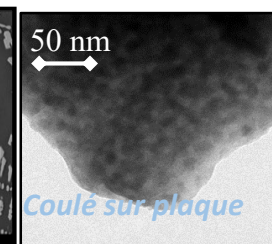
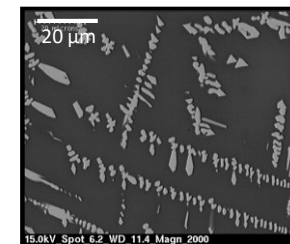
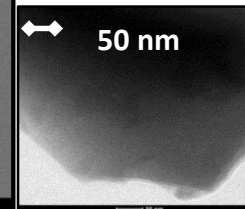
(DRX-MEB-MET)



Mullite
 $\text{Al}_6\text{Si}_2\text{O}_{13}$



Homogène



$\text{La}_3\text{Si}_2\text{BO}_{10}$ /
 LaBO_3 + SP

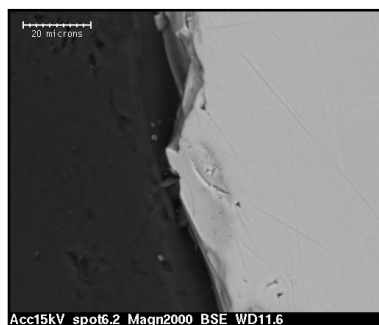
< 0

> 35

Bilan de Charges

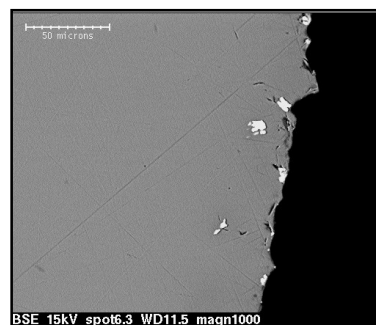
Verres complexes

Coulé sur plaque

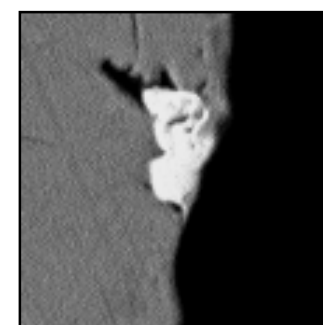


Homogène

Refroidi à 1°C/min



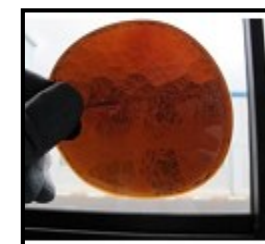
ϵ ZrO_2 Baddeleyite (Interface ~ 20 µm)



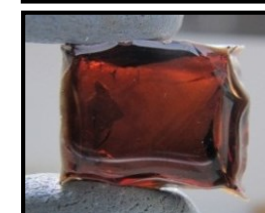
PFA = 22,5%

$[\text{Ce}_2\text{O}_3] = 1,84\%$ mass.
 $[\text{ZrO}_2] = 3,27\%$ mass.
 $[\text{MoO}_3] = 3,41\%$ mass

CP



RLT



✓ Stabilité thermique :

Homogène pour PFA $\geq 22,5\%$ massiques (CP et RLT)

✓ Viscosité :

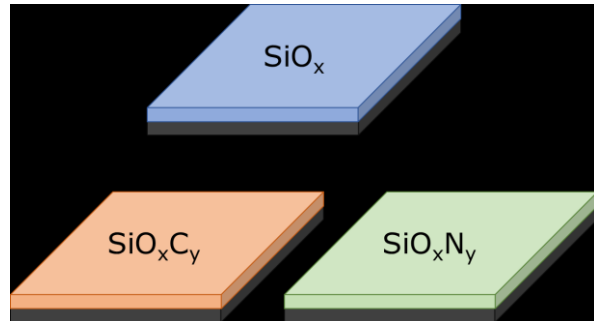
- $\eta_{(1300^\circ\text{C})} = 38$ Poises
- $\eta_{(1250^\circ\text{C})} = 67$ Poises

✓ $T_g = 657^\circ\text{C}$

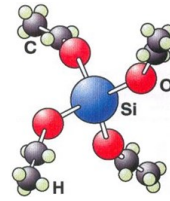
✓ Durabilité chimique :

- $V_0 = 0,5 - 1,9 \text{ g/m}^2/\text{j}$ ($\sim V_0 (R_7T_7)$)
- $V_R = 10^{-5} - 10^{-6} \text{ g/m}^2/\text{j}$ ($< V_R (R_7T_7)$) (Eau pure / Eau de Bure)
- Faible risque de reprise d'altération (précipitation de zéolithes à $\text{pH}^{(90^\circ\text{C})} > 9,5 - 9,9$)

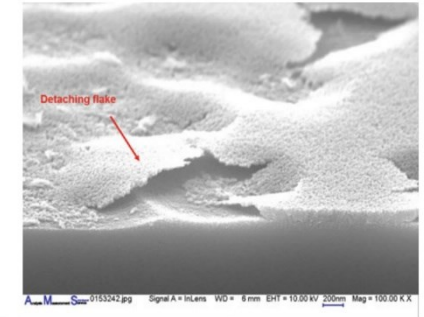
VERRE PHARMACEUTIQUE



TEOS

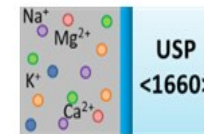


Enjeux
Durabilité chimique!
Couches minces



Couche barrière SiO_xN_y

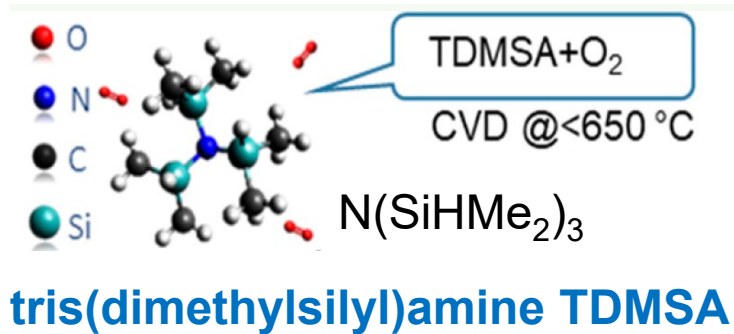
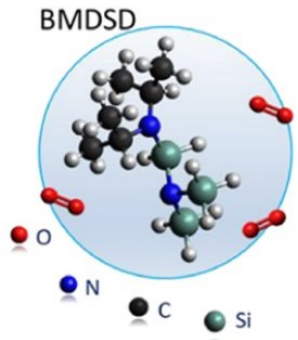
Vérification des performances



Optimisation du procédé CVD

SCHOTT AG, « Glass delamination »

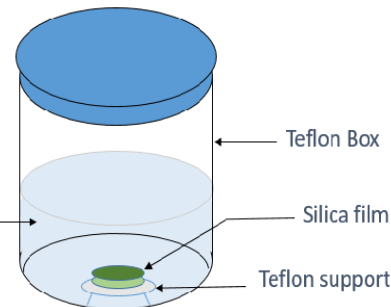
Chemical Vapor Deposition



Précurseur adapté

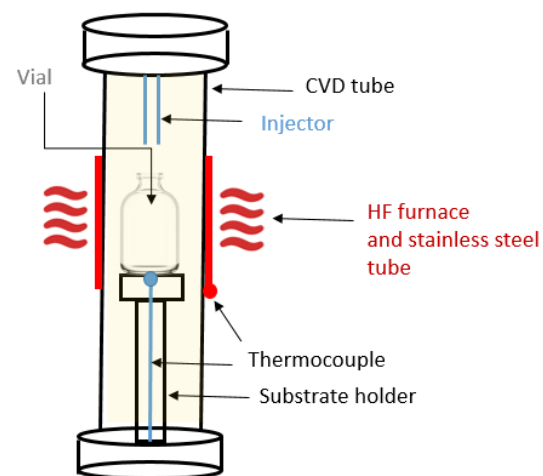
REACTEUR CVD
Dépôt chimique en phase vapeur

100 ml of aqueous
solution of citric acid
pH = 8



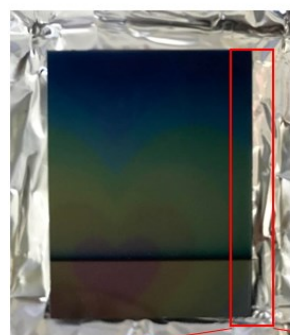
80°C
1 month

Dépôt de couches minces (50 à 150 nm) sur substrat de silicium (épaisseur 280 μm)

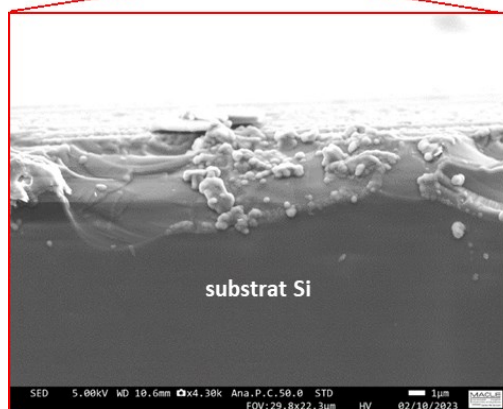
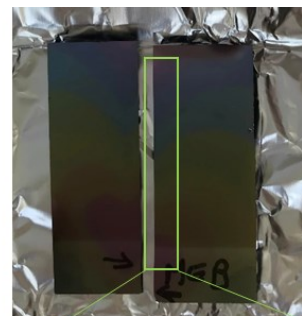


Uncoated type I glass vial

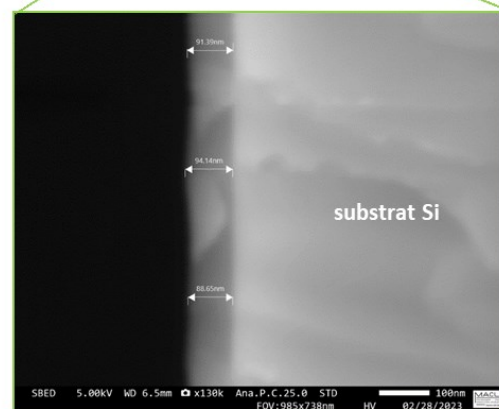
Oxide (wt %)	Clear tubing
SiO_2	72.0–75.0
B_2O_3	10.0–11.5
Al_2O_3	5.0–7.0
$\text{Na}_2\text{O} + \text{K}_2\text{O}$	7.0–8.5
$\text{CaO} + \text{BaO} + \text{MgO}$	0.5–3.0



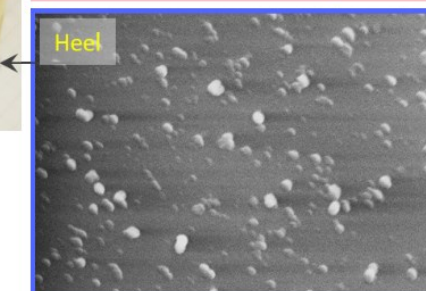
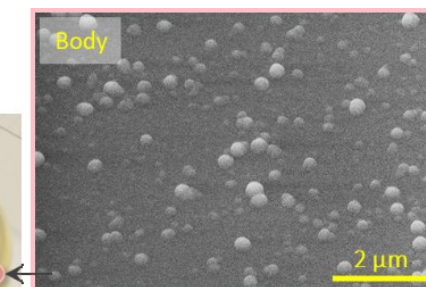
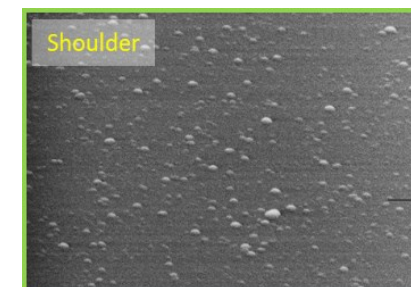
Coupe



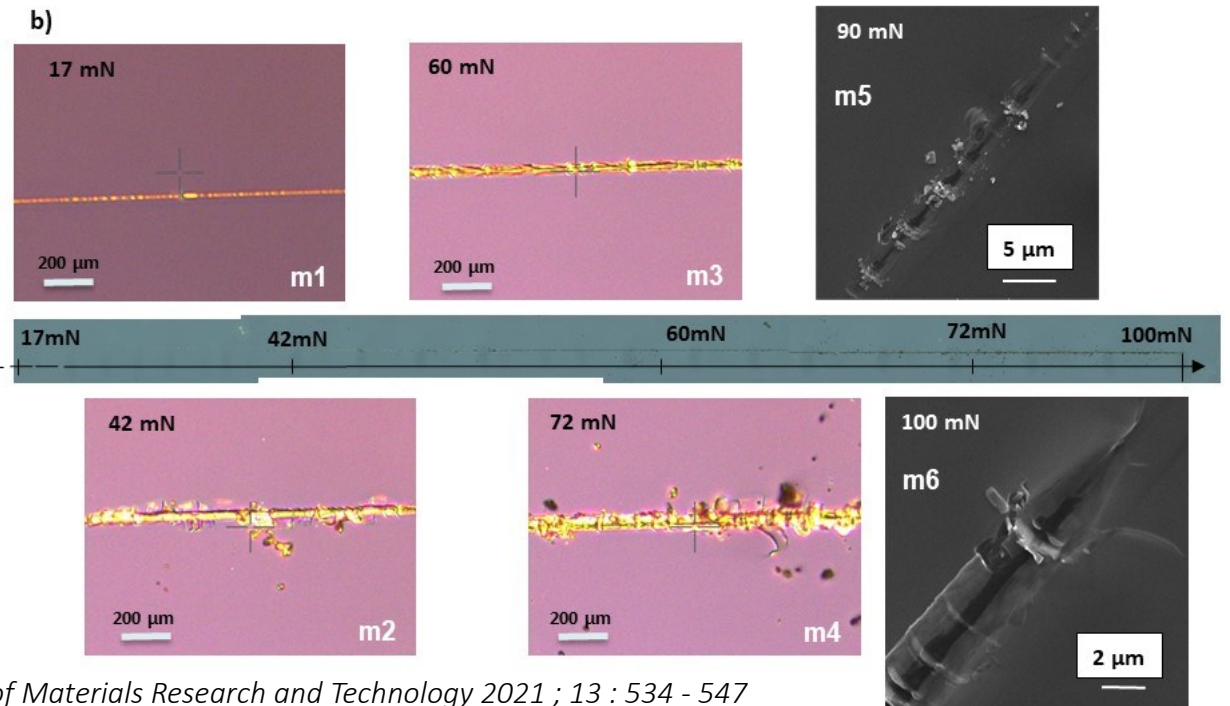
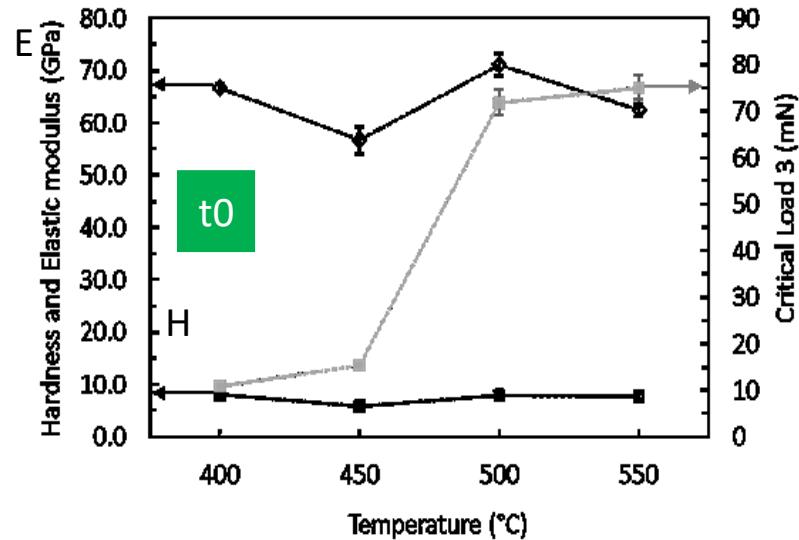
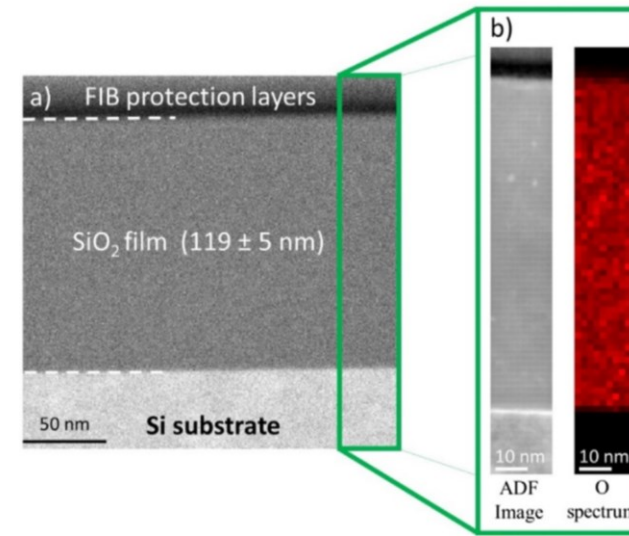
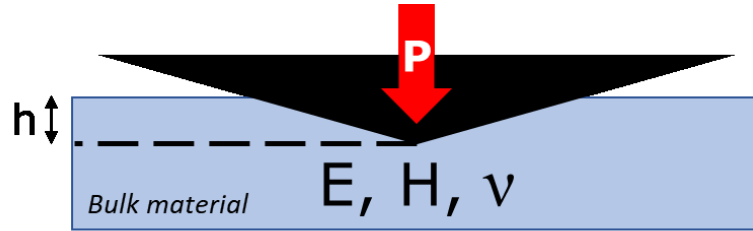
Electric voltage = 5KV under vacuum



Electric voltage = 5KV under vacuum



- STEM image : very homogeneous coating with no specific defect, texture or nanoporosity
- ADF, EELS : chemical homogeneity
- Sharp interface ~ 8 nm; amorphous nature of silica



E : Young modulus
 H : hardness
 ν: Poisson modulus
 CL3: critical load of delamination $\rightarrow 10.8 \pm 0.1$ mN at 400°C to 75.1 ± 11.5 mN at 550 °C - adhérence

B. Diallo et al, Journal of Materials Research and Technology 2021 ; 13 : 534 - 547

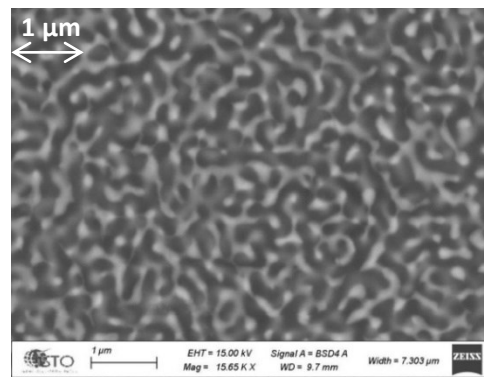
TEXTURATION DU VERRE

Irisation laser et chimique du verre

SAILOR : 'glaSs lAser chemIcaL cOLORizing'

Enjeux

- Décor sur verre: flaconnage de luxe, personnalisation
- Interaction verre séparé en phase/Laser:
 - Aspects fondamentaux:
 - Nanotexturation, structures périodiques
 - Modélisation de la réponse optique
 - Applications:
 - nouveaux décors (diffusion, irisation)
 - Nouvelles propriétés (photonique)

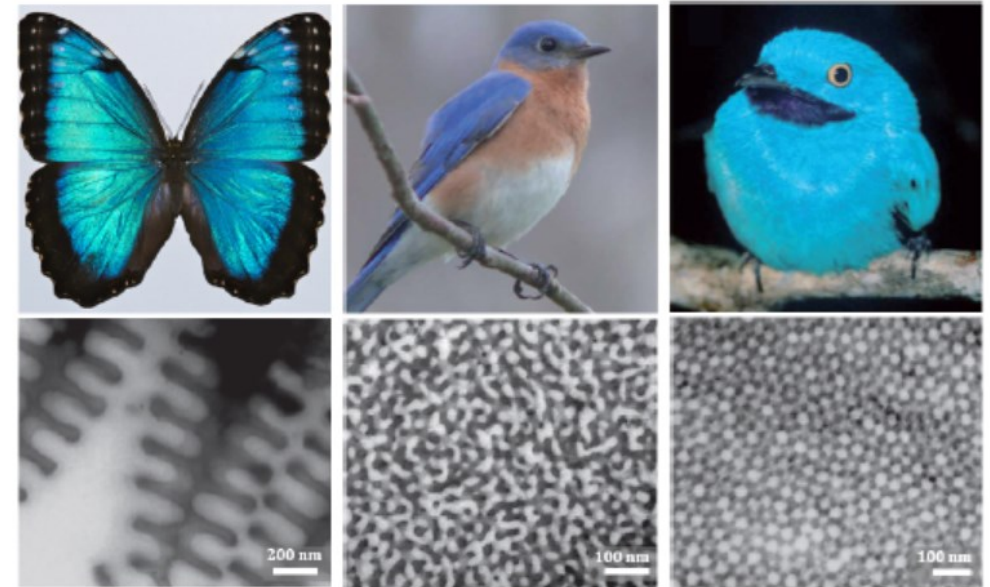


Verre séparé en phase : matrice sombre riche en silicium, matrice claire pauvre en silicium



MATEX
MULTIMATÉRIAUX EN CONDITIONS EXTRÊMES

GREMI



a . Papillon
Morpho [8].

b . Merle-
bleu [9].

c . *Cotinga*
[9].

FIGURE 1 – (a) Photographie d'un papillon *Morpho* et image TEM d'une nanostructure constituée d'une alternance de couches minces d'air et de chitine. (b) Photographie d'un Merlebleu de l'Est et image TEM d'une nanostructure interconnectée de β -kératine et d'air. (c) Photographie d'un *Cotinga* des Maynas et image TEM d'une nanostructure à base de gouttelettes d'air et de β -kératine.

Illustration d'après la thèse d'Anaïs Verron (Sorbonne Univ. – 2024)

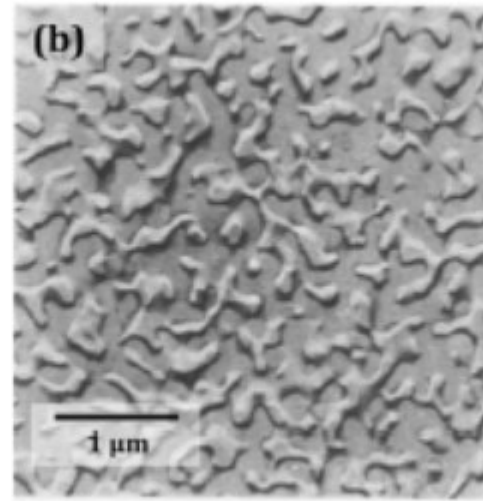
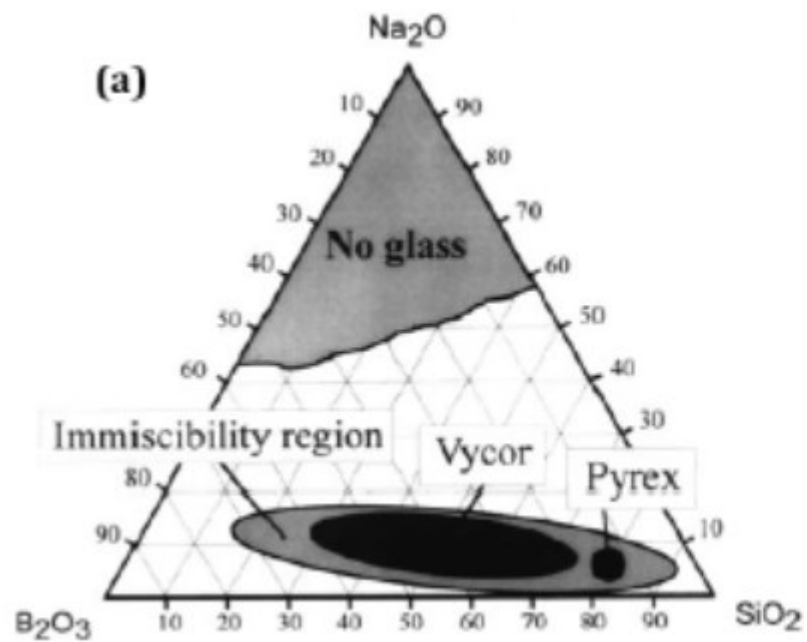


Image MEB verre Vycor®
Attaque acide pour révéler la microstructure

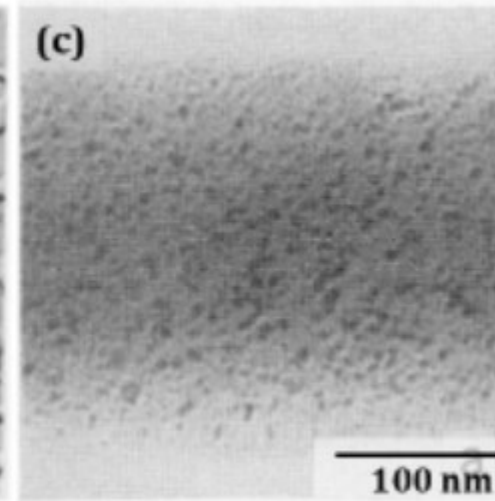


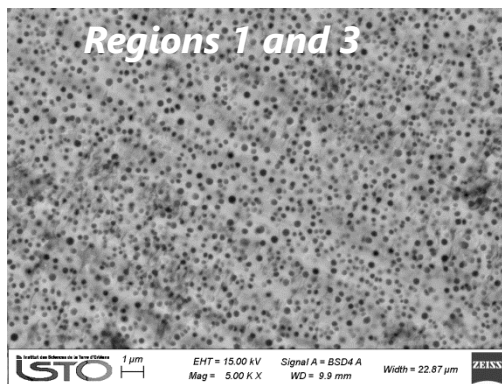
Image TEM verre Pyrex®

D'après W. Vogel, JNCS 25(1) 1977

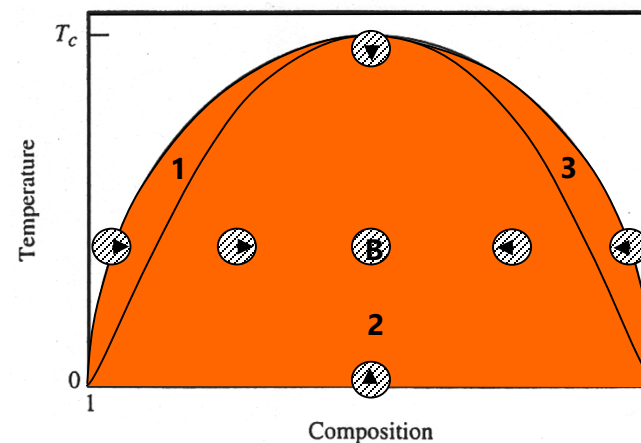
R. Doremus Science, 164 (3878) 1969

Microstructures → Linked to the glass composition and the thermal history

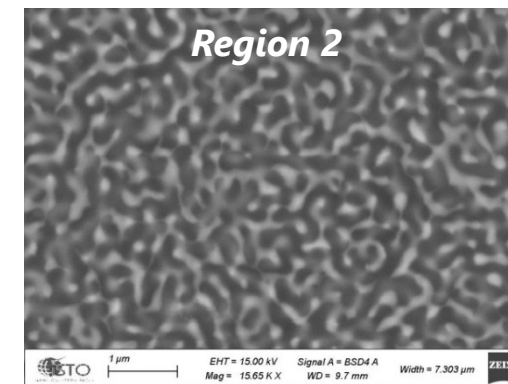
Droplets



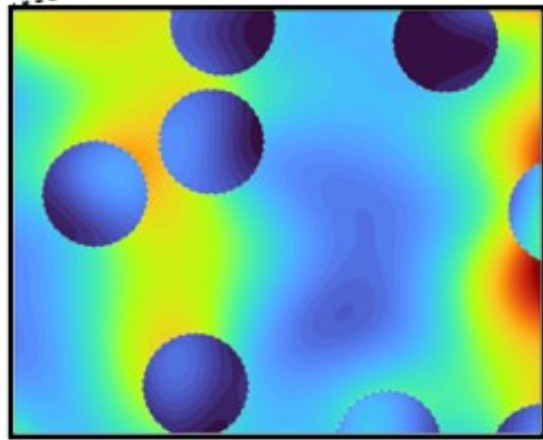
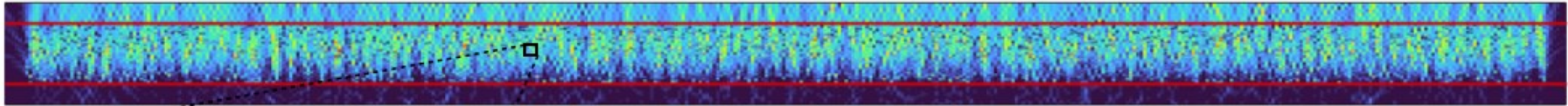
Nucleation growth



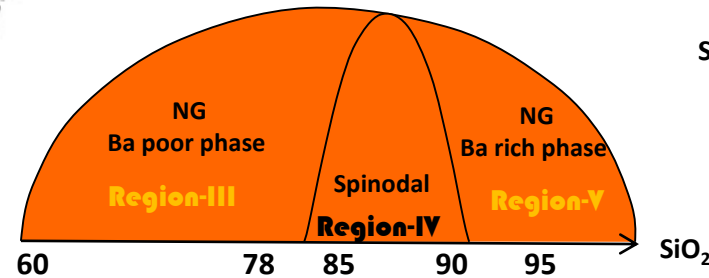
Interconnected



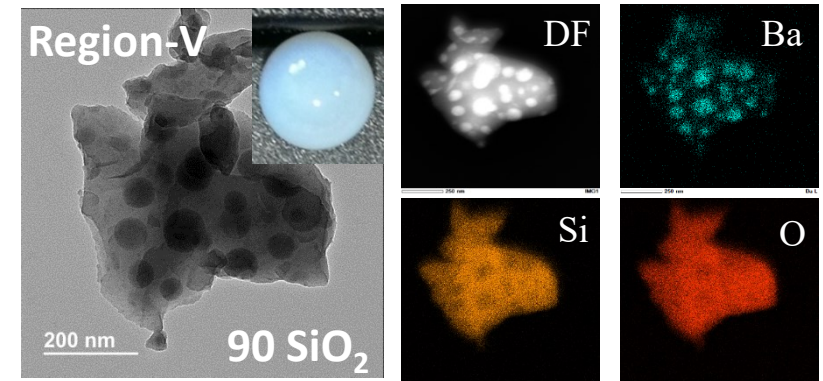
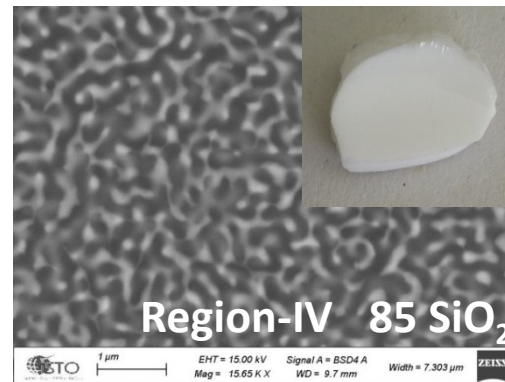
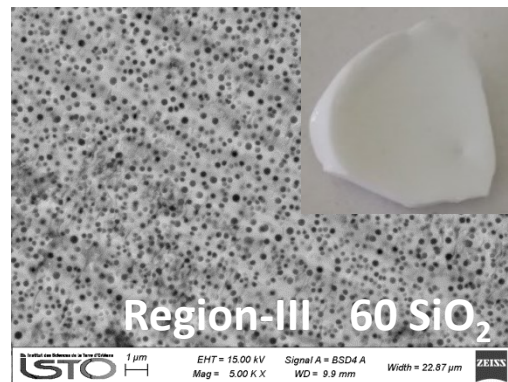
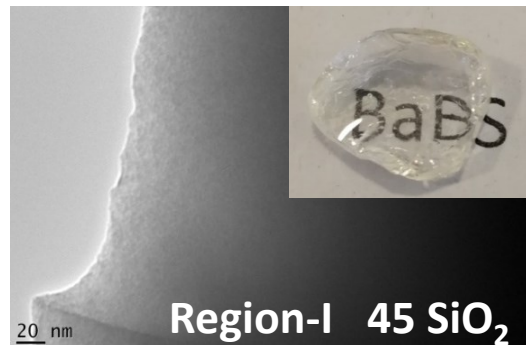
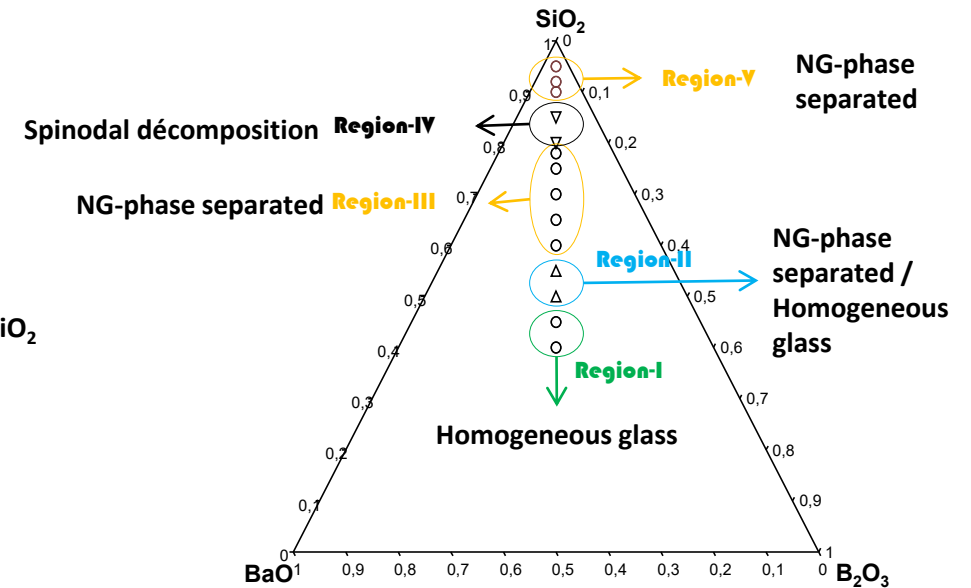
Spinodal



Modélisation : Champ électromagnétique dans un système de nanoparticules (100 nm) formant une lame bleu champ faible – rouge champ fort – indice $n=1.5$

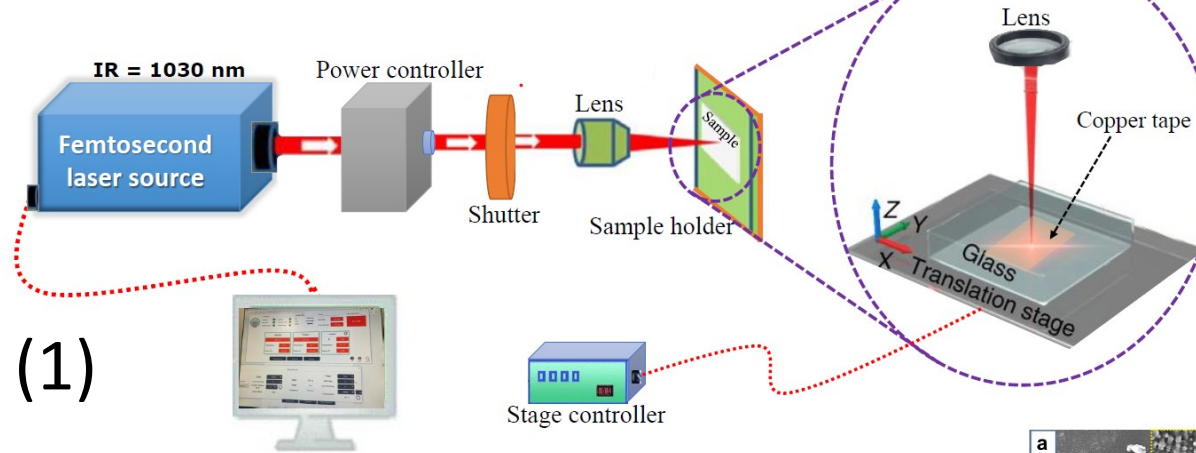
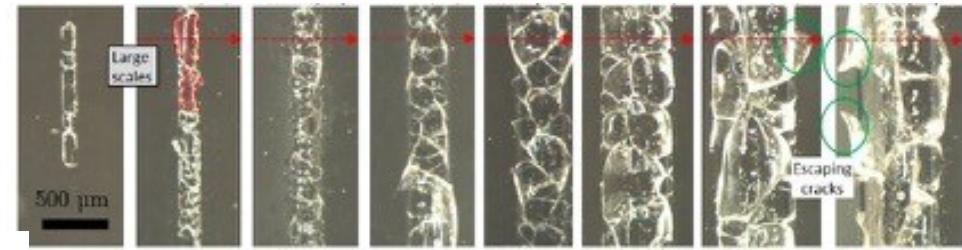
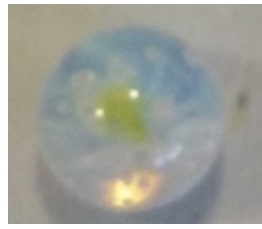
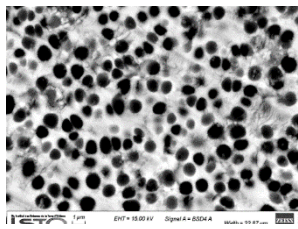


Phase separation in BaBS system :
 → Reduction of the network modifier cations (Ba) concentration
 And/Or
 → Increase the $\text{SiO}_2/\text{B}_2\text{O}_3$ molar ratio



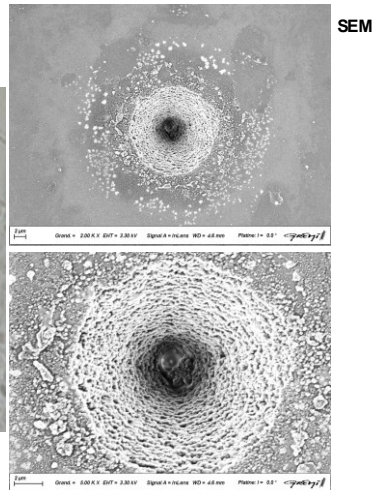
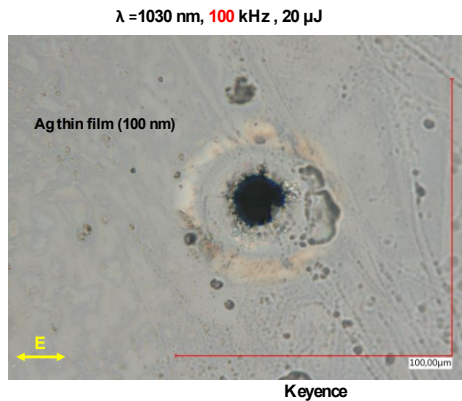
Size ≈ 250 nm, Density $\approx 24\%$

Size ≈ 18 nm

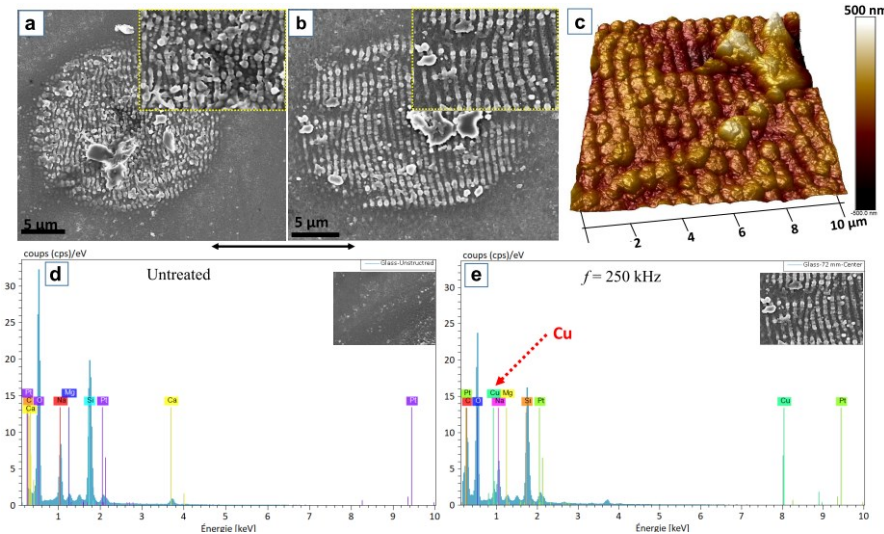


(1)

(2)

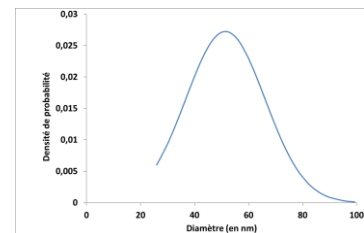
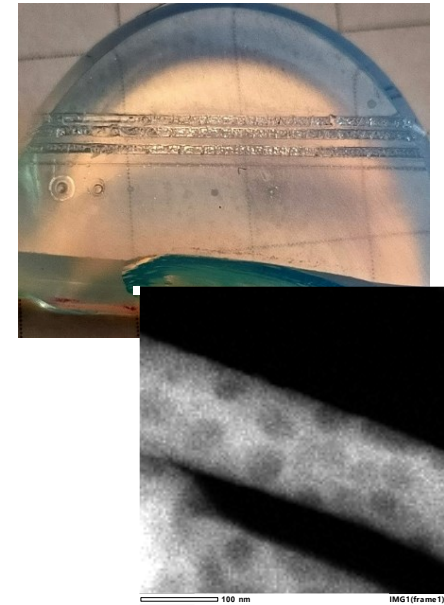


(3)



Dispositif laser (1) et résultats d'irradiation pour test de délamination (2) et test de fabrication de LIPSS* (3).

* *Laser-Induced Periodic Surface Structures*

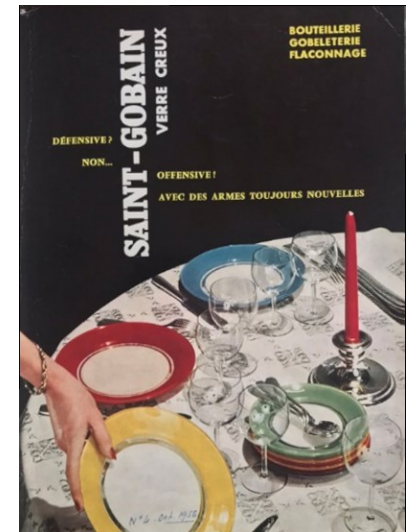
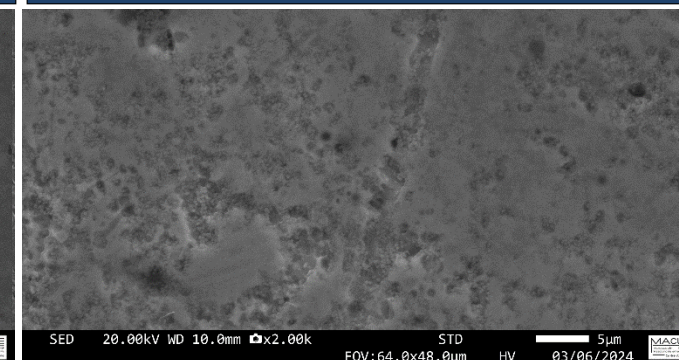
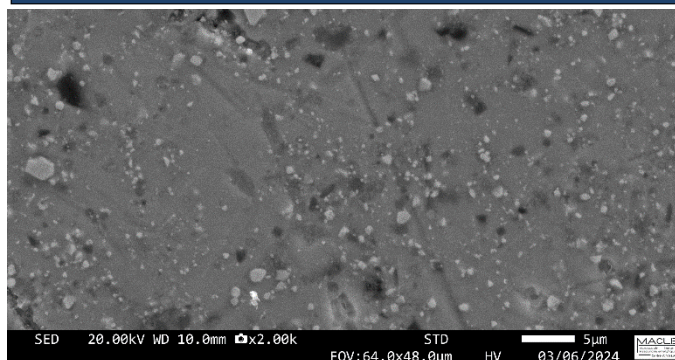
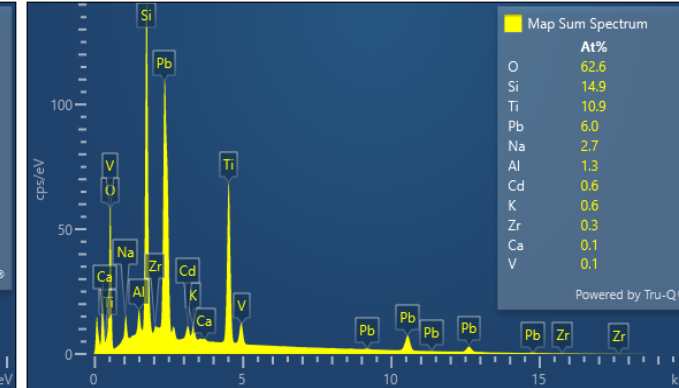
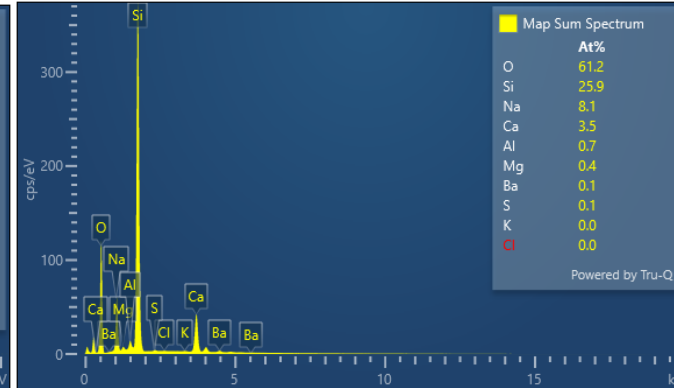
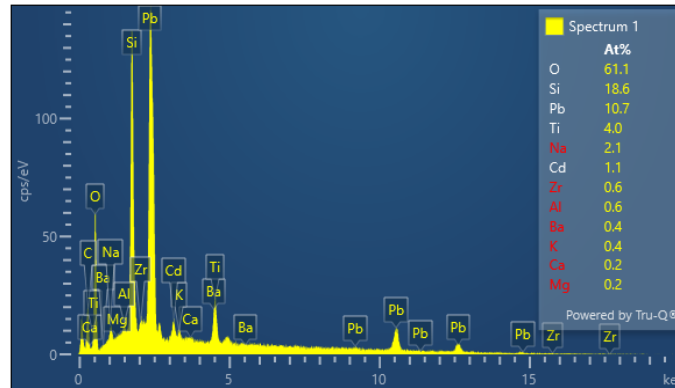
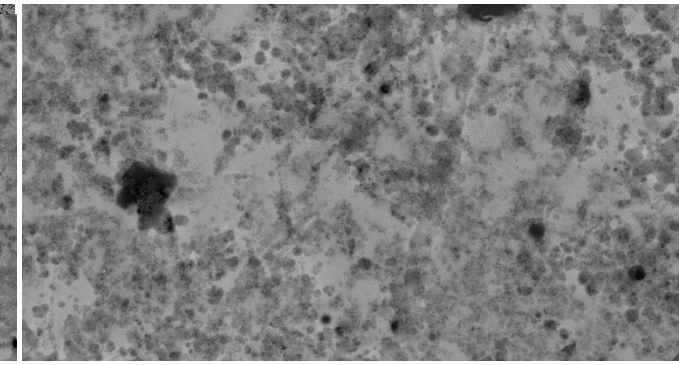
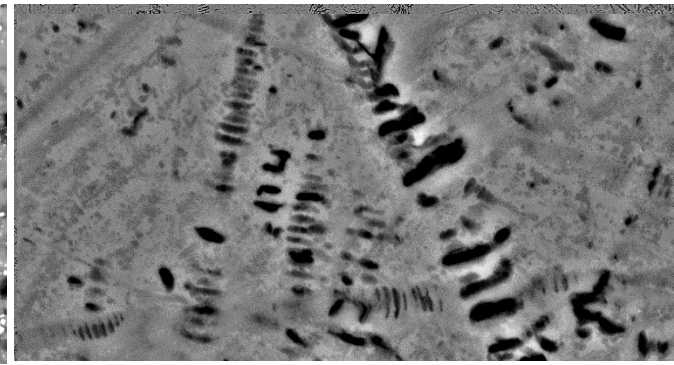
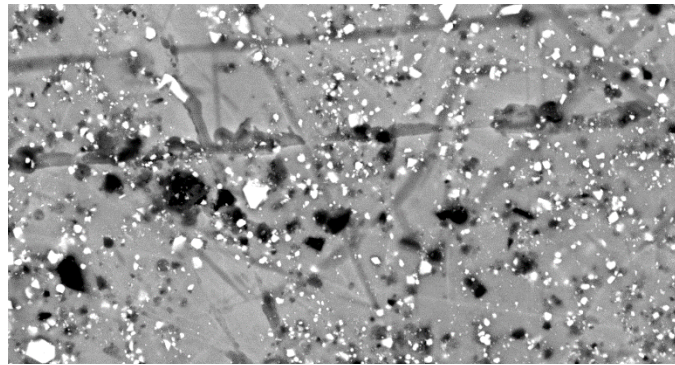


Thèse A. Capelle 2025

Email vert: surface extérieure

Verre nu: Surface intérieure

Email blanc: surface extérieure

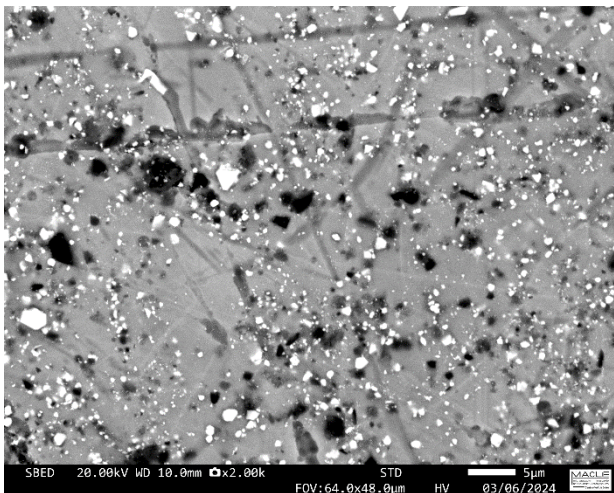


Duralex® plates 'double enamel'
(1953 – 1970) : SEM images and EDX for green enamel (links) and white enamel (right)

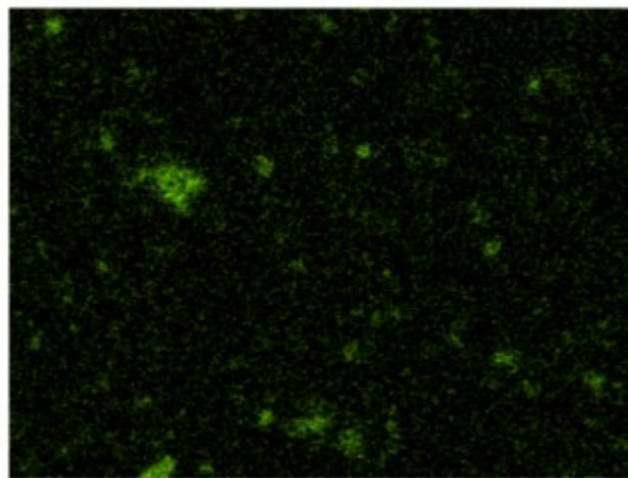
Matrice: O, Si, Pb, Na, Zr
Grains 'blanc': O, Pb, Sb, Ti, Al
Grains sombre: O, Al, Cr, Co, Zn, (Cd, Sb) / Ti / Si

Verre: O, Si, Na, Ca, Al

Verre: O, Si, Ti, Pb, Na, Al, Cd, K

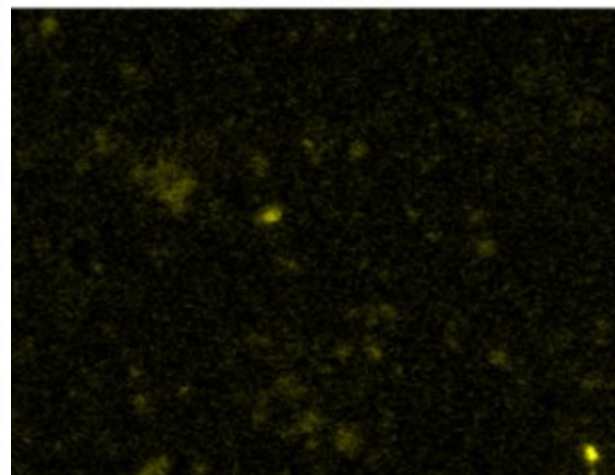


Co K series



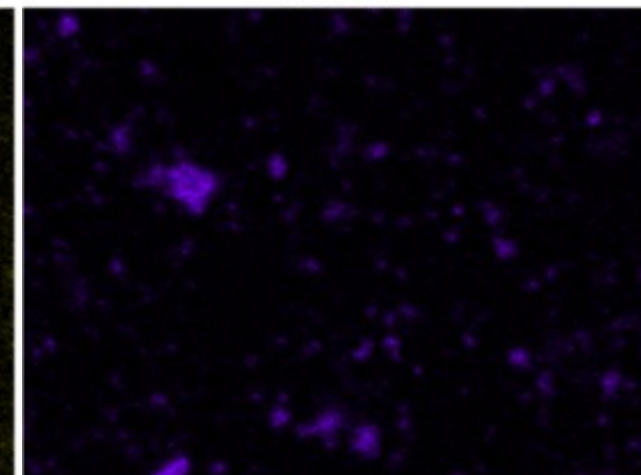
25µm

Al K series



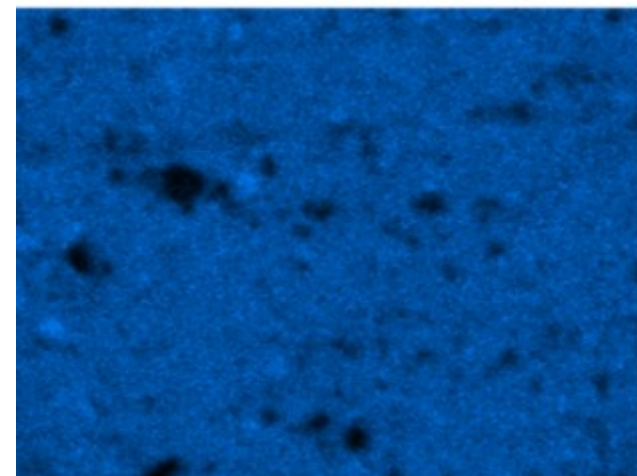
25µm

Cr K series



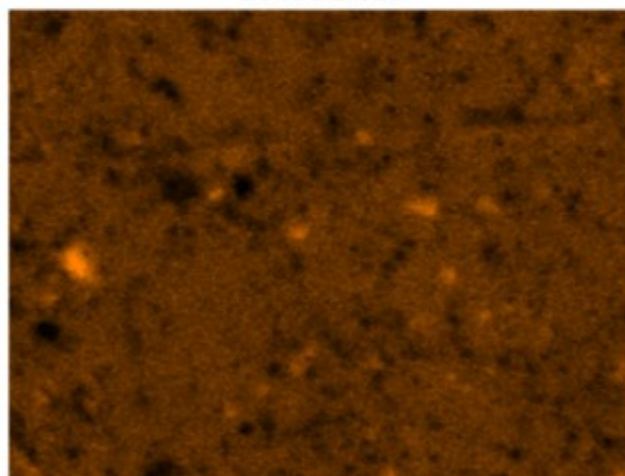
25µm

Pb M series



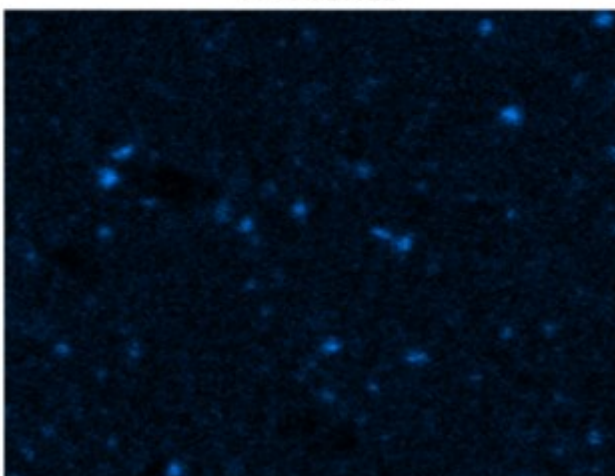
25µm

Si K series



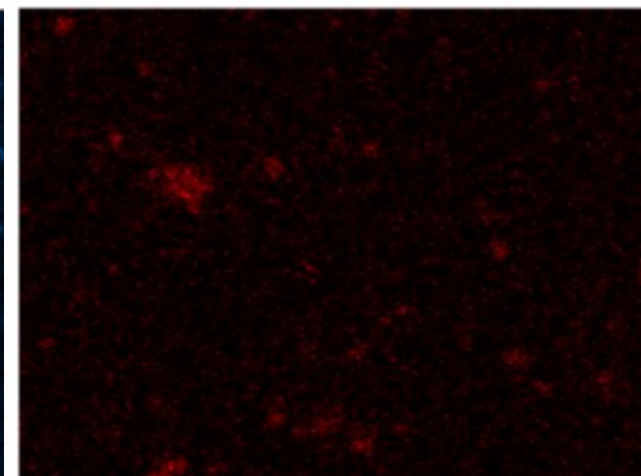
25µm

Ti K series



25µm

Zn K series

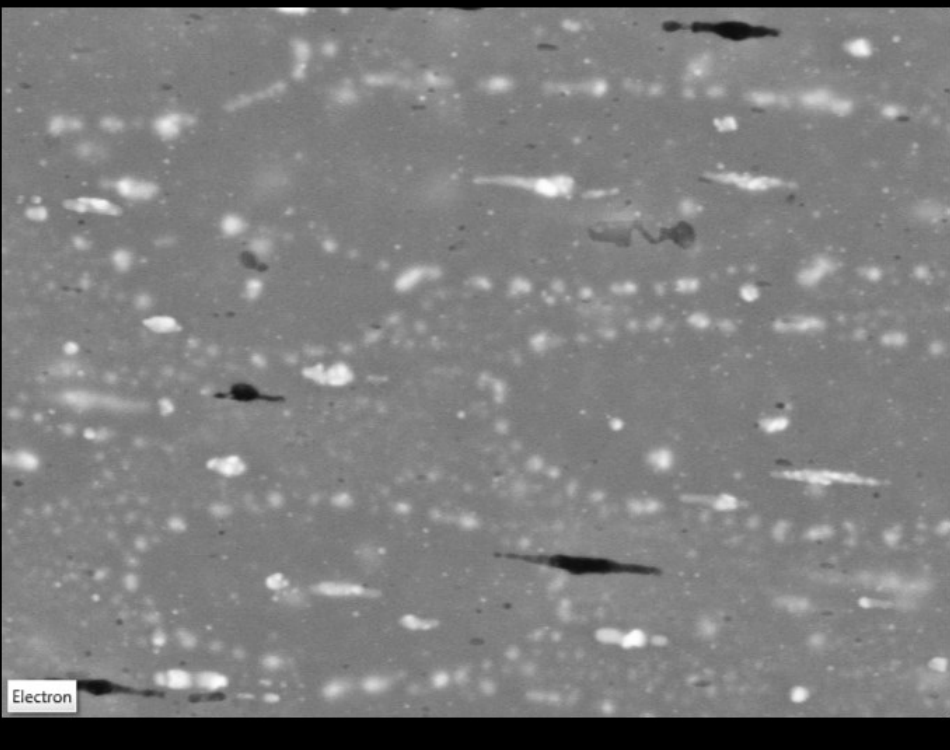


25µm

Grains contraste blanc: nettement associés au Pb

Grains de contraste sombre:
O,Si (quartz)
O,Ti,Ba (titanate de barium)
Aluminates de Co, Cr, Zn (pigments spinelle ?? $\text{CoAl}_2\text{O}_4 - \text{CoCr}_2\text{O}_4$)

Email vert: surface extérieure



DURALEX® (1964 – 1966)



Opaline bleue
(Cu, Fe)

Matrice:

O, Si, P, Na, Al, Ca, Mg

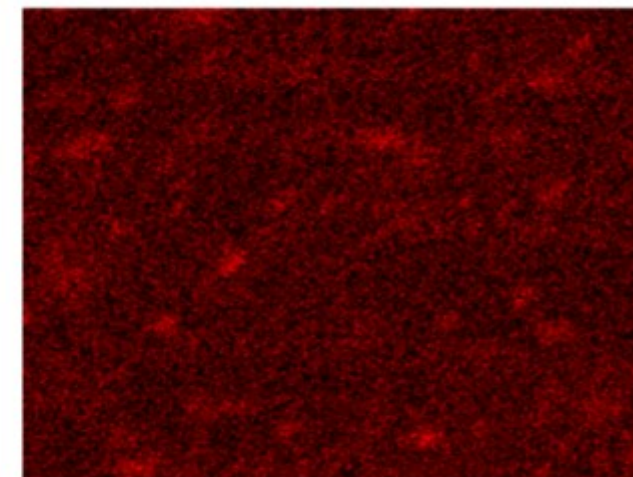
Grains de contraste très blanc:
nettement associés à O, P, Ca, Ba

Si K series



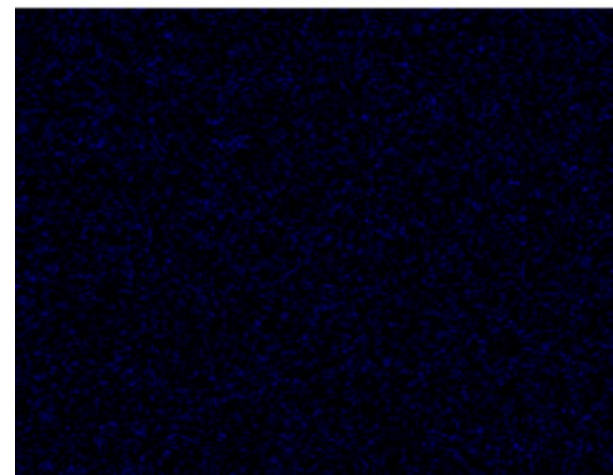
10µm

P K series



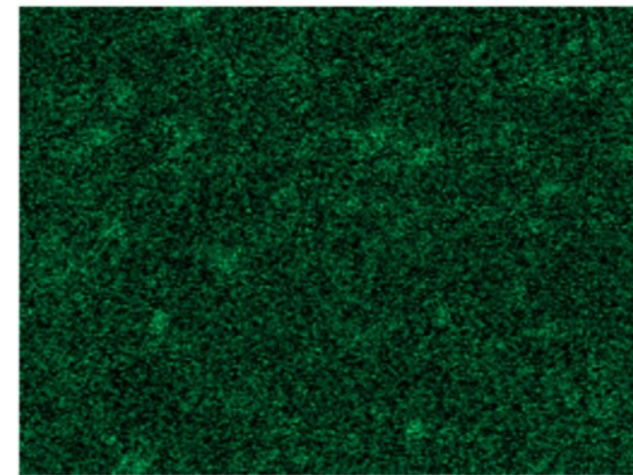
10µm

Fe K series

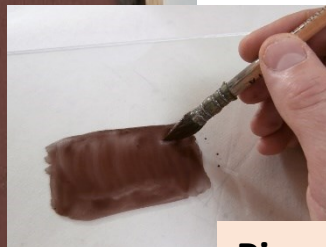


10µm

Ca K series



10µm



Paramètres de l'étude:

- Verre support
- Véhicule
- Traitement thermique

Pigment : oxydes métalliques (Fe, Zn)

Fondant: verre au Pb et Si

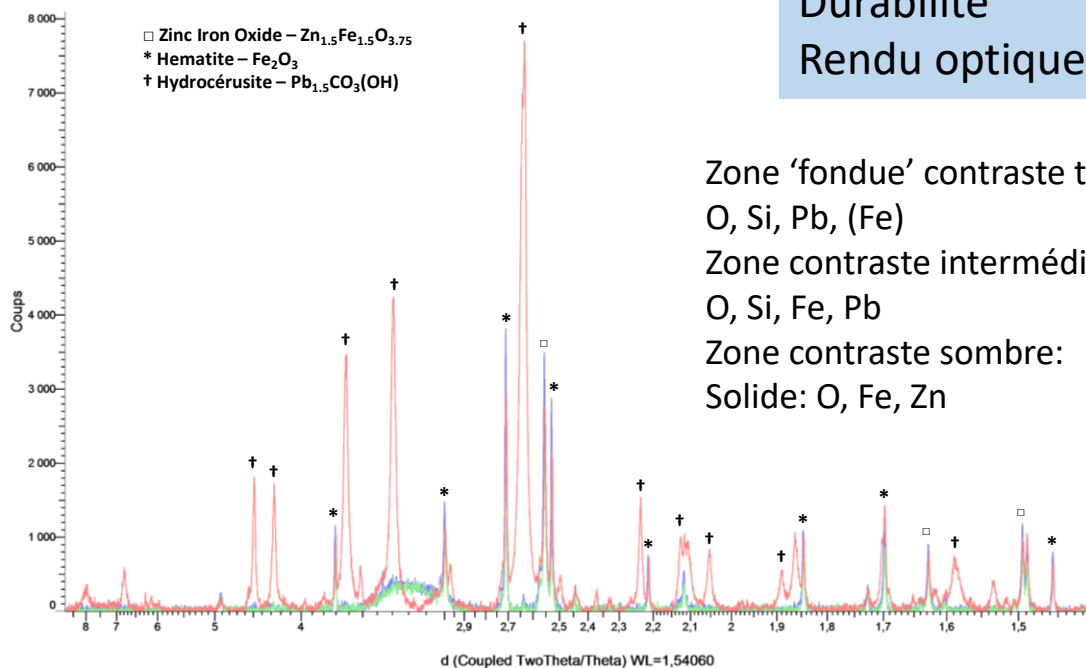
Grisaille Brun XIII^e Debitus
Restauration / contours

Enjeux:

Adhérence

Durabilité

Rendu optique satiné



Zone 'fondue' contraste très clair:

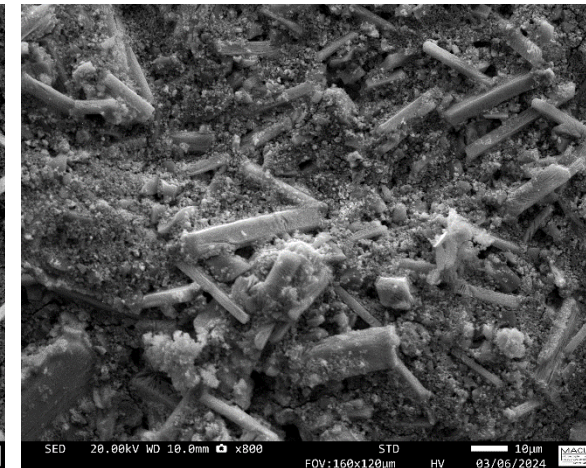
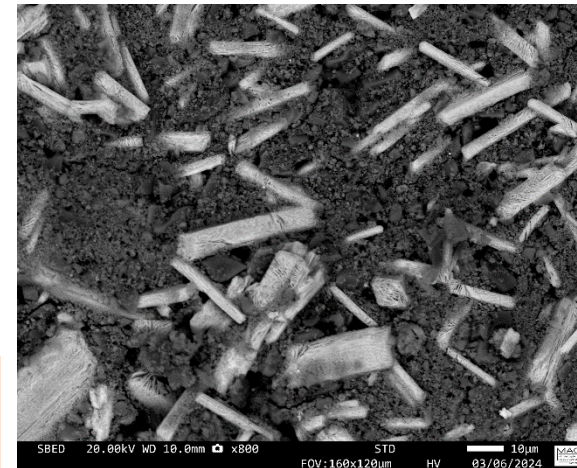
O, Si, Pb, (Fe)

Zone contraste intermédiaire :

O, Si, Fe, Pb

Zone contraste sombre:

Solide: O, Fe, Zn

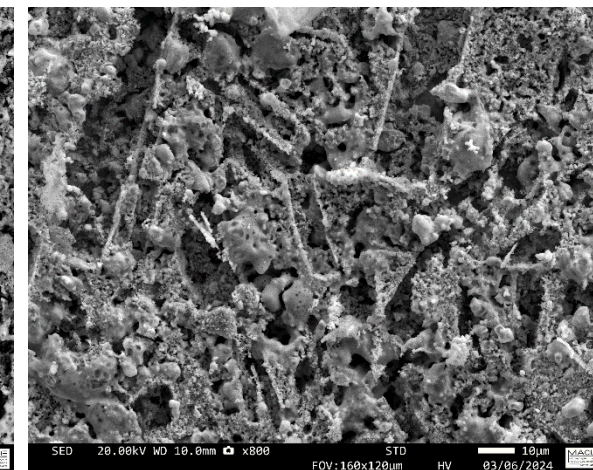
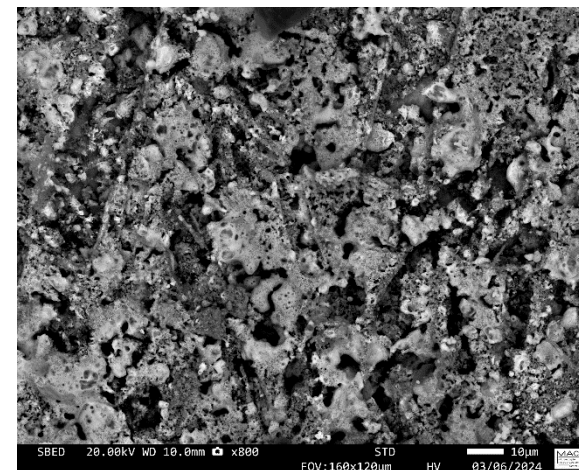


↗ **Avant recuit**: dépôt sur verre float, véhicule VIN = Vinaigre d'alcool blanc

Cristaux: hydrocerusite $\text{Pb}_{1.5}\text{CO}_3(\text{OH})$

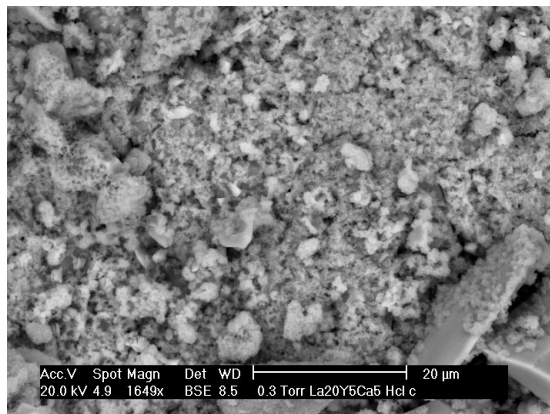
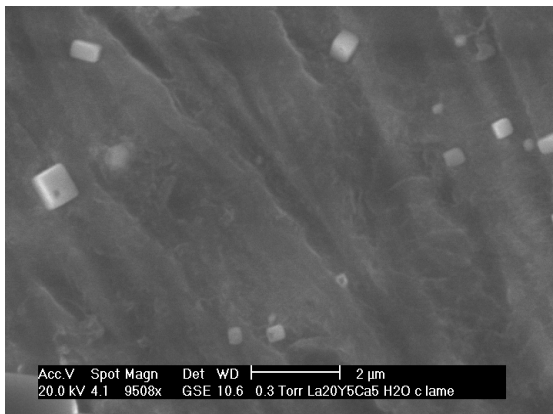
Gangue: cristaux O, Fe, Zn et grains O, Si, Na, Mg, Ca, Fe, Pb, Mn.

↘ **Après recuit 670°C – 7 min** : dépôt sur verre float, véhicule: VIN

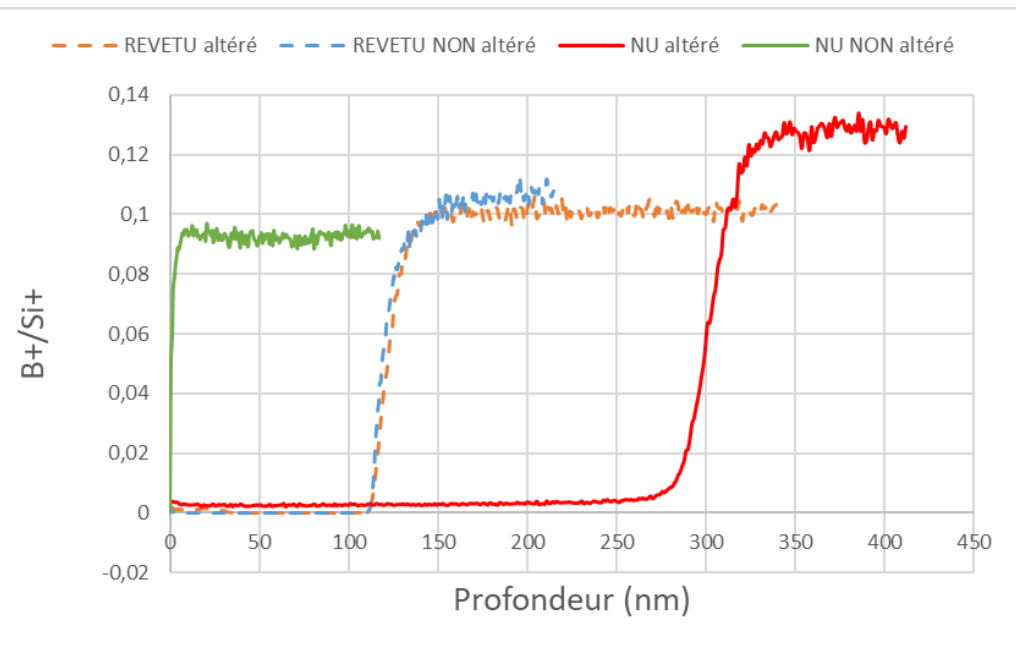


Eau ultra pure (pH 5)

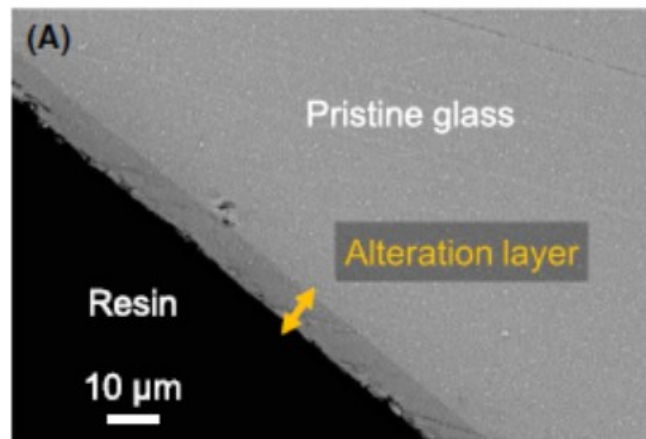
Milieu acide (pH 2)



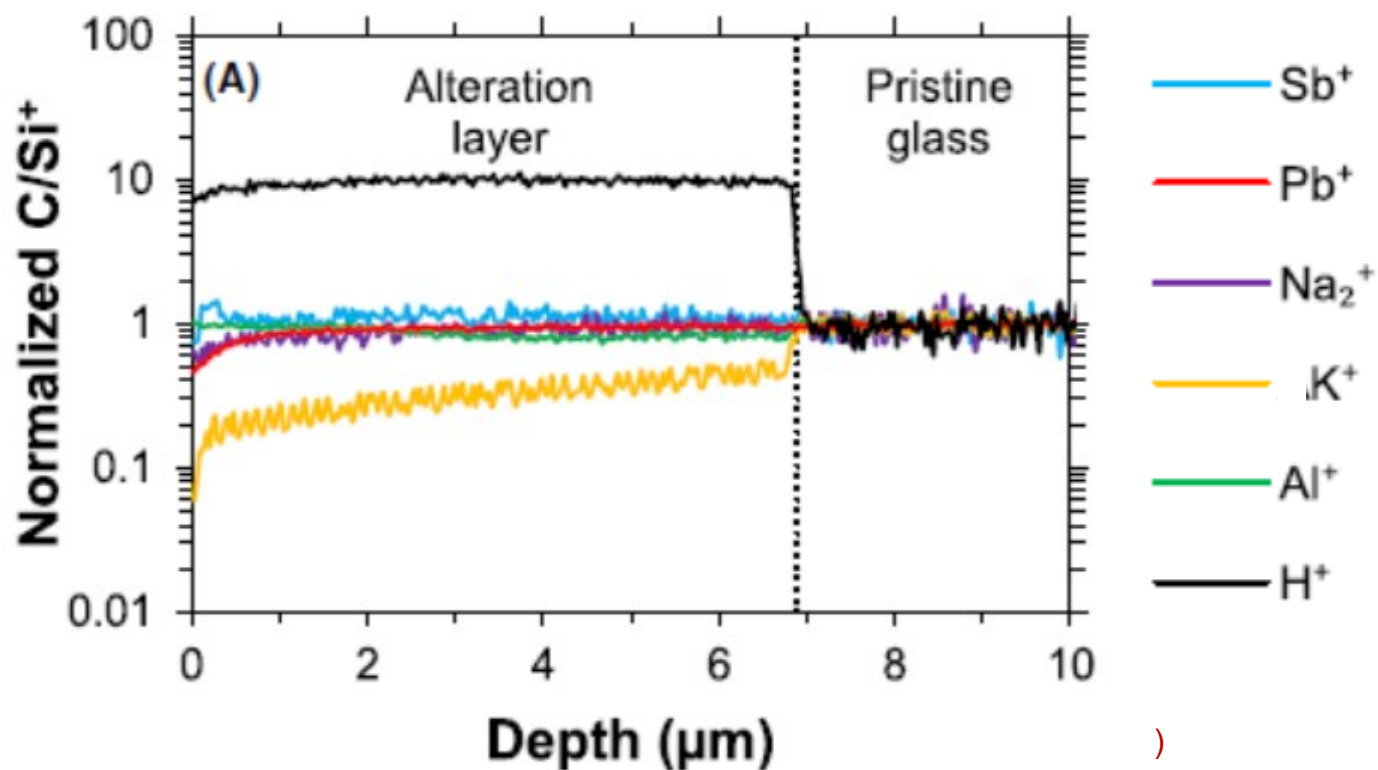
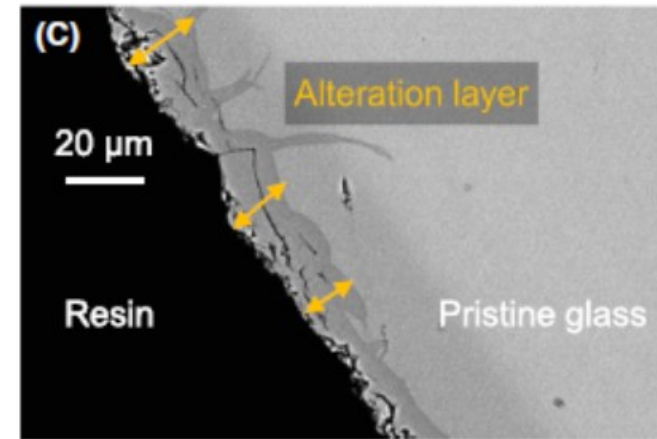
Surface d'un verre aluminosilicate de Ca et La : altéré 6 mois, à 60°C – à gauche : cristaux riches en La. A droite: format d'un gel d'altération



Non-surface-treated sample altered 20 days in aqueous conditions



Ground sample altered 20 days in aqueous conditions





MERCI POUR VOTRE ATTENTION!

Farah Inoubli, Babacar Diallo, Emmie Beauvoit, Marie Colin, Thierry Sauvage, Cécile Genevois, Valérie Montouillout, Mathieu Allix, Pierre Florian, Vincent Sarou-Kanian
Alex Capelle, Barthélemy Aspe, Anne-Lise Thomann, Nadjib Semmar
Olga Shavdina, Martin Depardieu
Konstantina C. Topka, Hugues Vergnes, François Senocq, Diane Samelor, Marie-Joëlle Menu, Viviane Turq, Raphael Laloo, Brigitte Caussat, Constantin Vahlas
Pierre-Luc Etchepare
Christian Dussarrat
Victor Piovesan, Estelle Gasnier, Isabelle Giboire
Emmanuel Véron et Guillaume Wille pour les magnifiques clichés et les échanges scientifiques !!