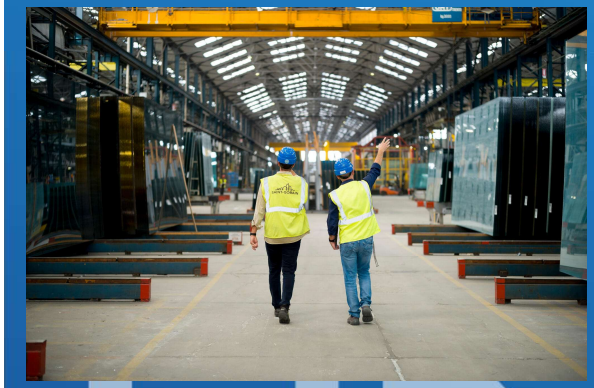


FLOAT GLASS WEATHERING IN ATMOSPHERIC CONDITIONS

Nîmes, September 28th 2023

Sophie PAPIN & Hervé MONTIGAUD
Amandine SERVE & Thierry CRETIN
Saint-Gobain Research Paris

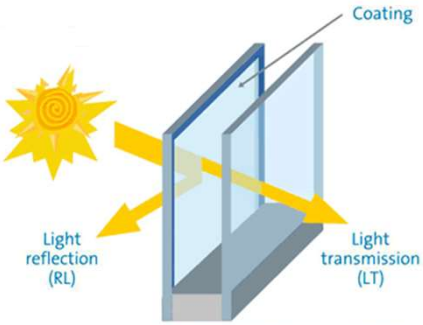
in collaboration with Odile MAJERUS & Daniel CAURANT, IRCP

sumglass 2023

SVI SURFACE DU VERRE ET INTERFACES

SAINT-GOBAIN

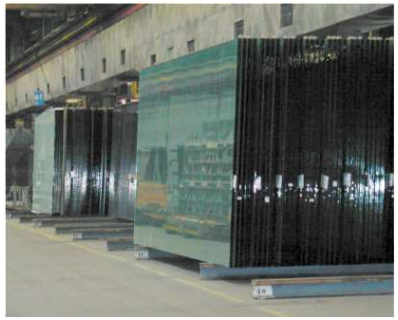
FLOAT GLASS WEATHERING IN ATMOSPHERIC CONDITIONS



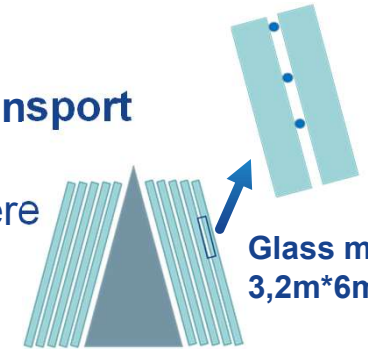
Float glass composition
is optimized to avoid **chemical durability issue** during a standard use.

But the glass surface is functionalized thanks to nm-sized coatings
➔ Requirement to preserve the float glass surface quality during the storage and/or the transportation

wt%	Flat glass
SiO_2	~72
CaO	~10
MgO	~4
Na_2O+K_2O	~14
Al_2O_3	~0.5



During **storage and/or transport**
➔ Weathering issues
due to the stuffy atmosphere
(high rate of humidity)



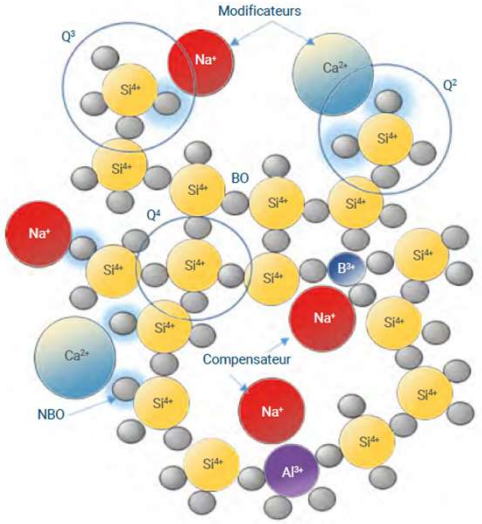
Glass maker unit
3,2m*6m

➔ **For thin coatings deposition, the first glass ageing steps need to be controlled.**

A. Serve PhD

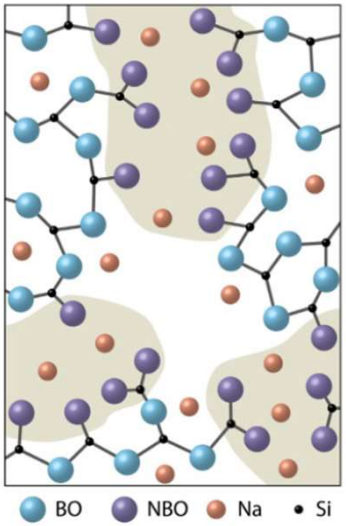
FLOAT GLASS WEATHERING IN ATMOSPHERIC CONDITIONS

Glass surface reactivity with the atmosphere ←→ Glass structure (NBO & cations type)



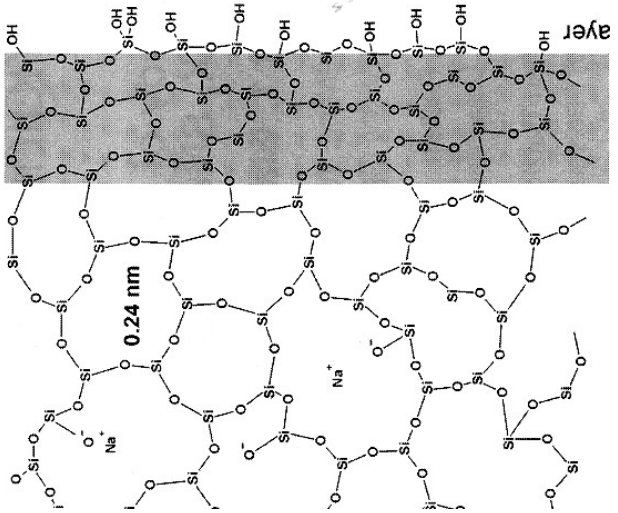
Silicate glass structure

Burov, Gouillart & Schuller Reflets de la Physique, 2021



Modified random network model

Lee & Lee *Acta Materialia*, 2022

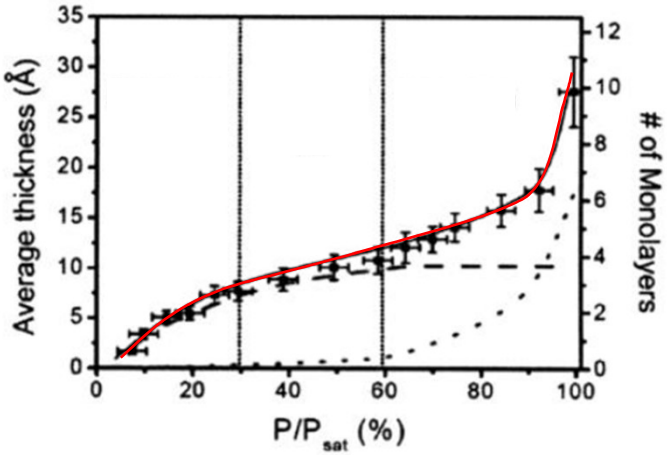


Schematic of glass structure near the surface

Wang, Hähner, Kräusch, Rädlein, Tratzky, Schramm & Martinek *Glass Sci. Technol.* 2004

FLOAT GLASS WEATHERING IN ATMOSPHERIC CONDITIONS

Glass ageing - Reminder



Thickness of the adsorbed water layer on SiO_2 surface at RT

Asay & Kim *J. Phys. Chem. B*, 2005

1. An interdiffusion between the water film and the glass surface

$$\equiv Si - O - M + H_2O \leftrightarrow \equiv Si - OH + M^+ + OH^-$$

$$\equiv Si - O - M + H_3O^+ \leftrightarrow \equiv Si - OH + M^+ + H_2O$$

} ↗ pH

2. A silicate network hydrolysis, *i.e. dissolution of the glass network*

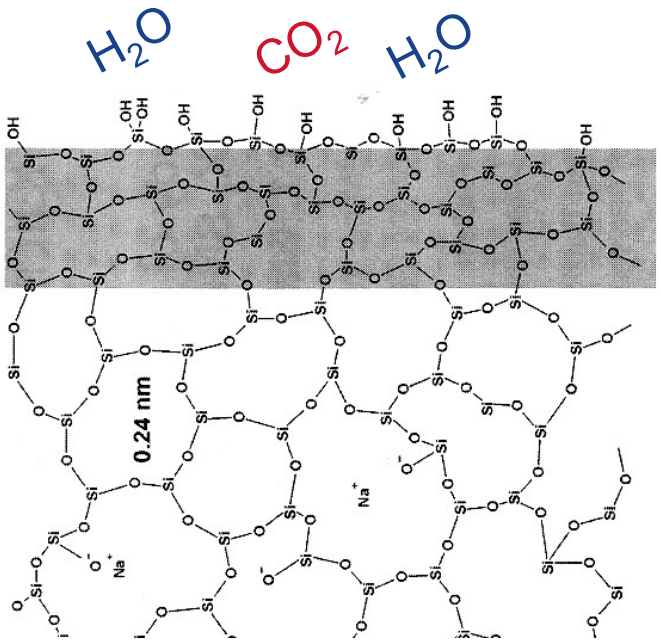
$$\equiv Si - O - Si \equiv + H_2O \leftrightarrow 2 \equiv Si - OH \text{ (hydrolysis)}$$

3. Possibly recondensation of hydrated silica

$$2 \equiv Si - OH \leftrightarrow \equiv Si - O - Si \equiv + H_2O$$

FLOAT GLASS WEATHERING IN ATMOSPHERIC CONDITIONS

Atmospheric glass ageing



1. An interdiffusion between the water film/solution and the glass surface

$$\equiv Si - O - M + H_2O \leftrightarrow \equiv Si - OH + M^+ + OH^- \quad \}\ \nearrow pH$$
$$\equiv Si - O - M + H_3O^+ \leftrightarrow \equiv Si - OH + M^+ + H_2O$$

➔ **In the case of float glass storage = no dilution in the attack medium**

Depending of the glass composition

Na^+ (glass) + $2H_2O \rightarrow H_3O^+$ (glass)+ $NaOH$

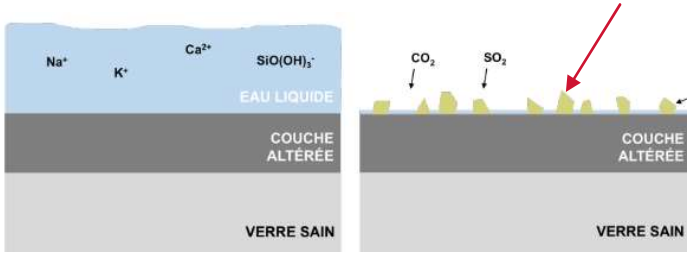
Ca^{2+} (glass) + $4H_2O \rightarrow 2H_3O^+$ (glass) + $Ca(OH)_2$

➔ **Reaction with CO_2 (air) and carbonates formation ➔ deliquescent salts**

$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$

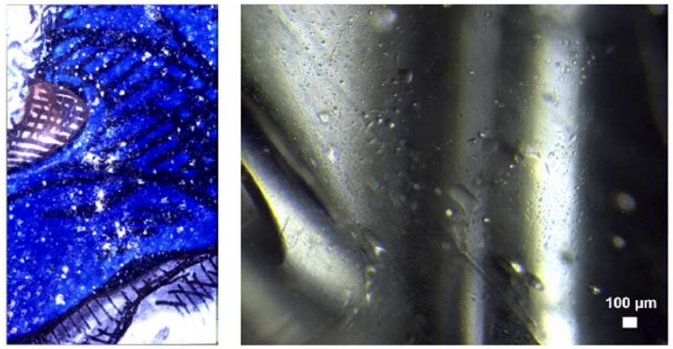
$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$

Salts at surface (nature, quantity)



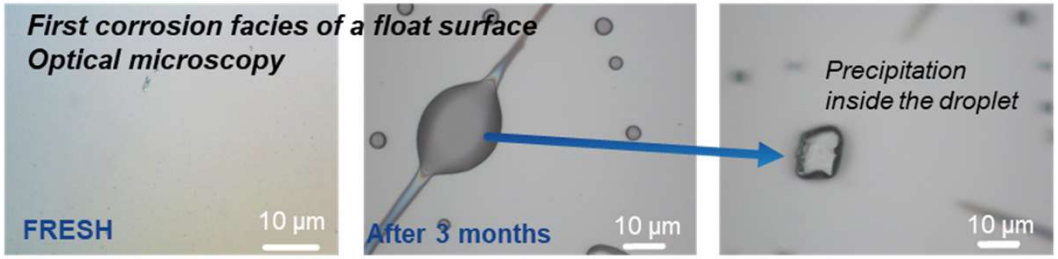
FLOAT GLASS WEATHERING IN ATMOSPHERIC CONDITIONS

Different mechanisms for corrosion in ATMOSPHERIC (vs immersed) conditions
➔ important role of the atmospheric gases.



Salts and droplets at the surface of aged stained glass and Venitian vase.

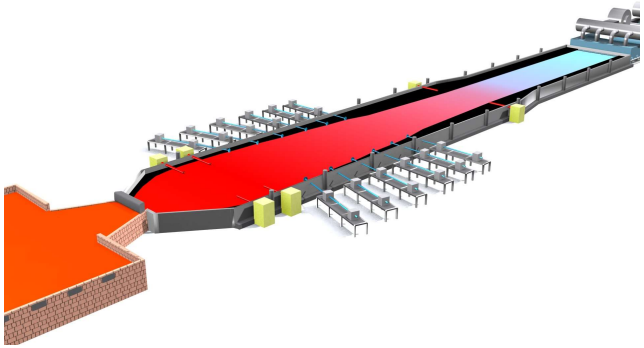
Alloteau
PhD, 2017



Apparition of droplets then salts during ageing of a float surface (RT, at lab)

FLOAT GLASS ATMOSPHERIC WEATHERING

THE SPECIFICITY OF FLOAT GLASS CASE

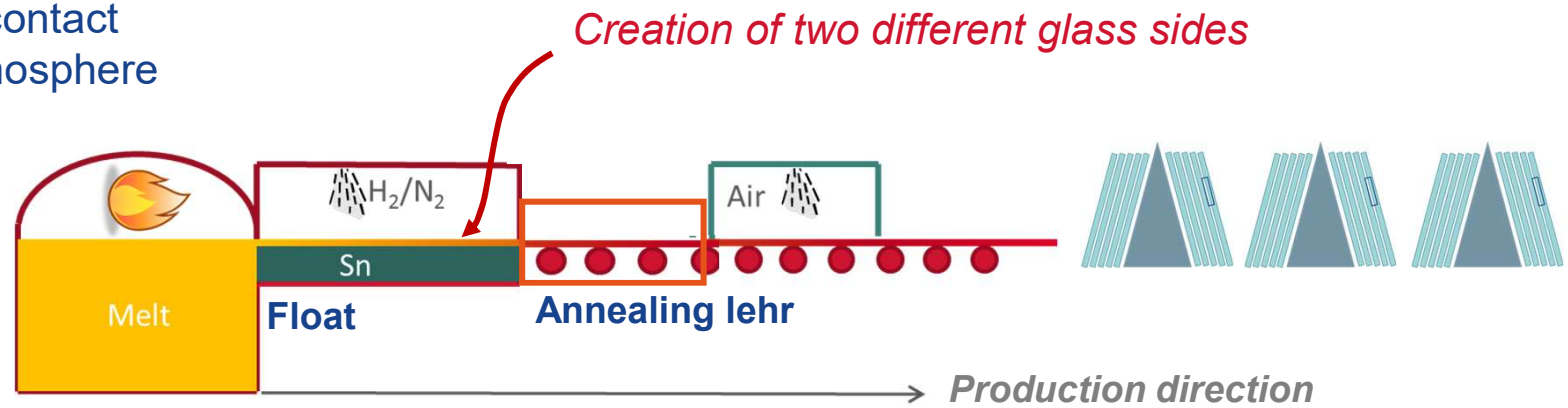


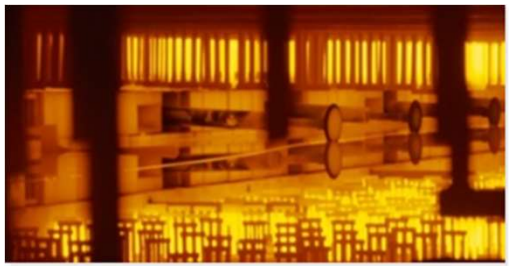
https://youtu.be/1HDWJgFLCfA?si=3_MDr4c_nqmynTUu

FLOAT GLASS WEATHERING IN ATMOSPHERIC CONDITIONS

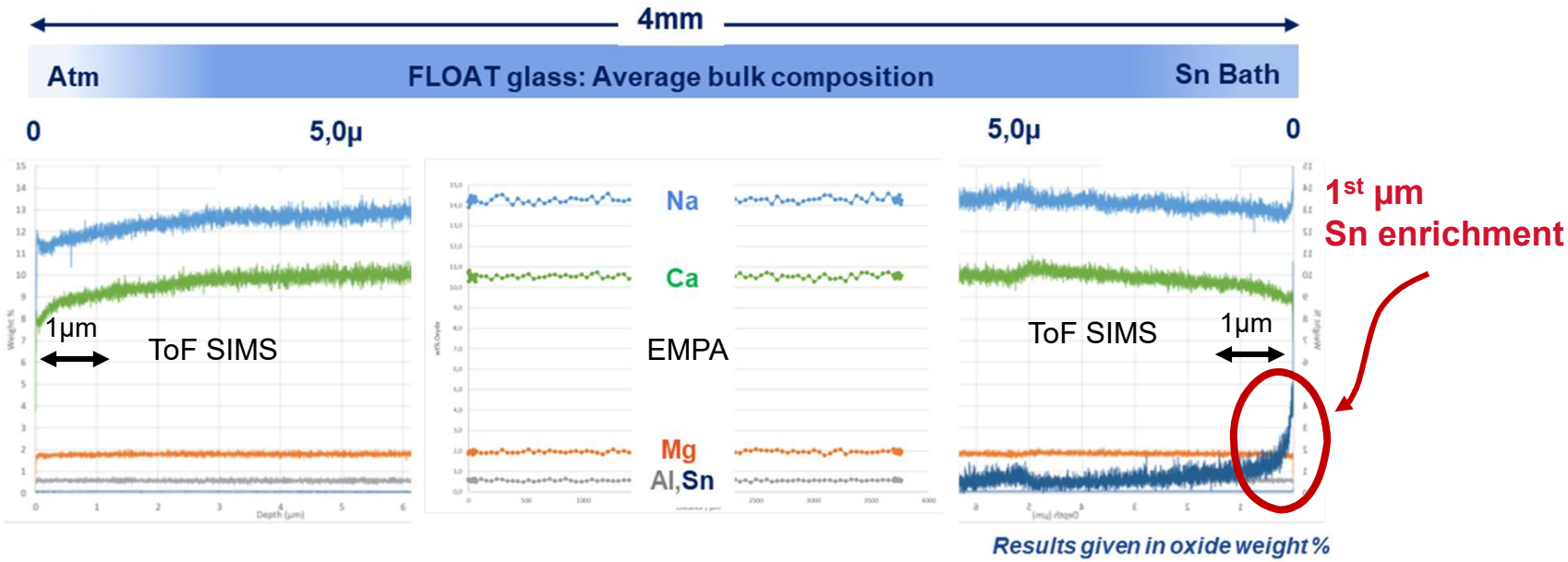
Parameters and conditions impacting glass surface

- Chemical composition
- Tin bath contact
- H_2/N_2 atmosphere





FLOAT GLASS WEATHERING IN ATMOSPHERIC CONDITIONS



FLOAT GLASS WEATHERING IN ATMOSPHERIC CONDITIONS

The Atmosphere side is less durable than the Sn bath side.

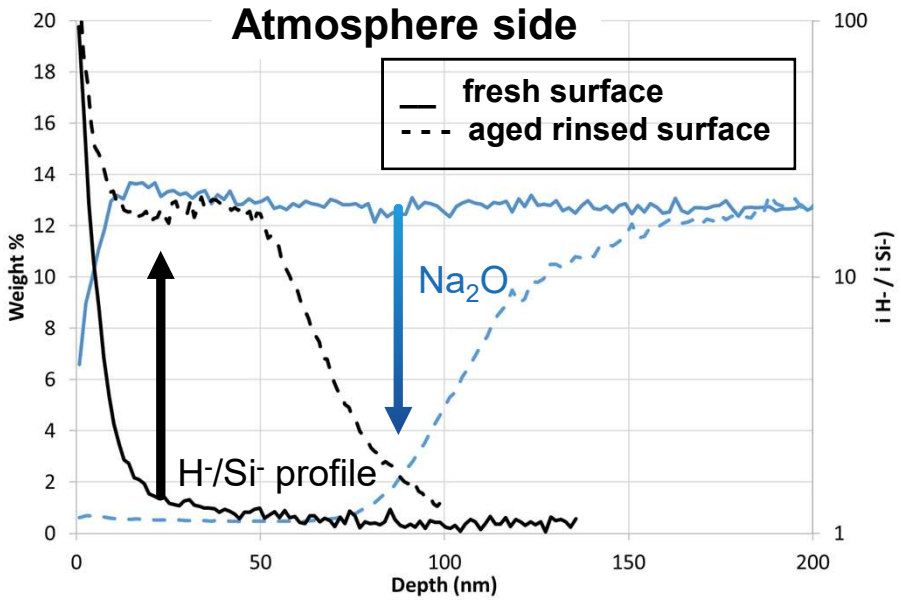


Illustration with ToF-SIMS depth profiles on rinsed surfaces after 35°C / 80%HR 28 days

FLOAT GLASS WEATHERING IN ATMOSPHERIC CONDITIONS

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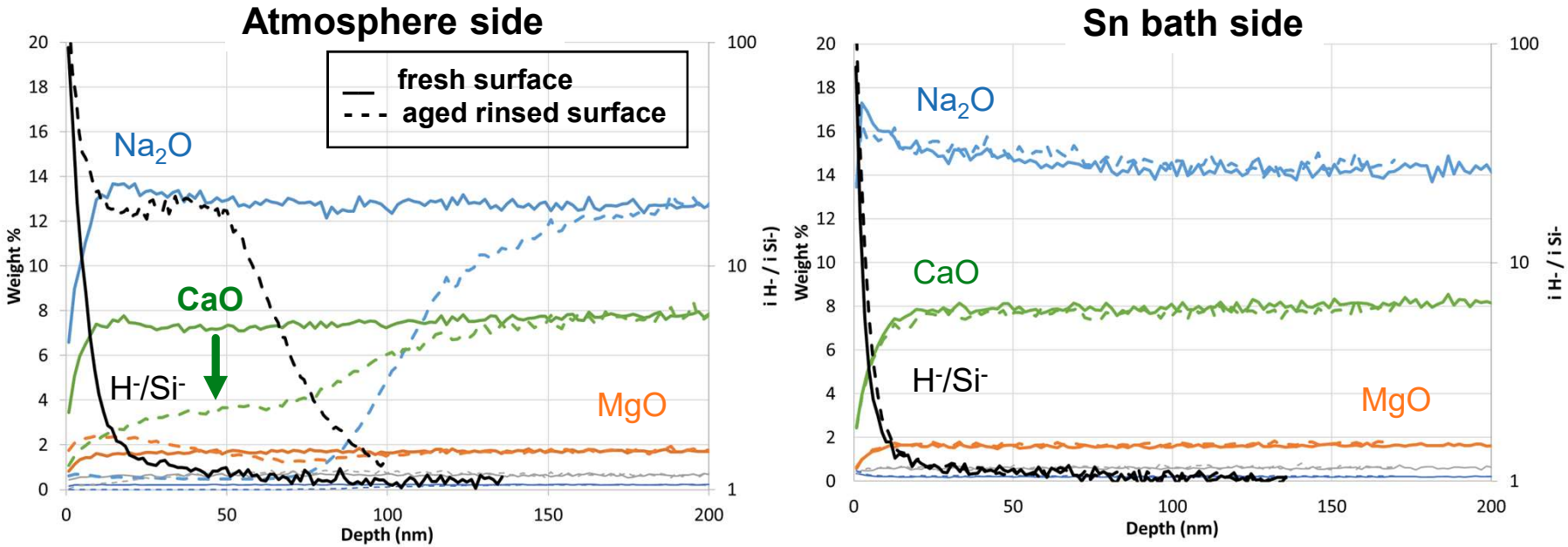
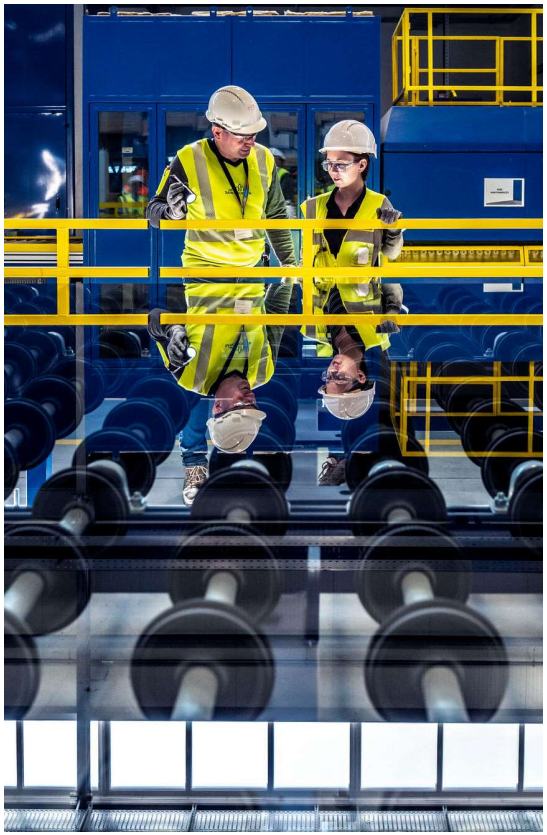


Illustration with ToF-SIMS depth profiles on rinsed surfaces after 35°C / 80%HR 28 days

FLOAT GLASS ATMOSPHERIC WEATHERING

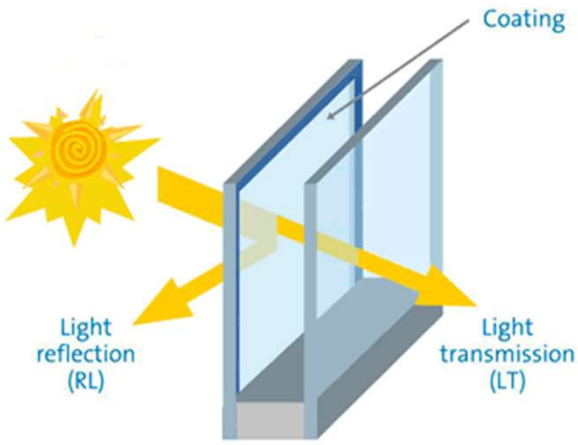
INDUSTRIAL ISSUES & SOLUTIONS

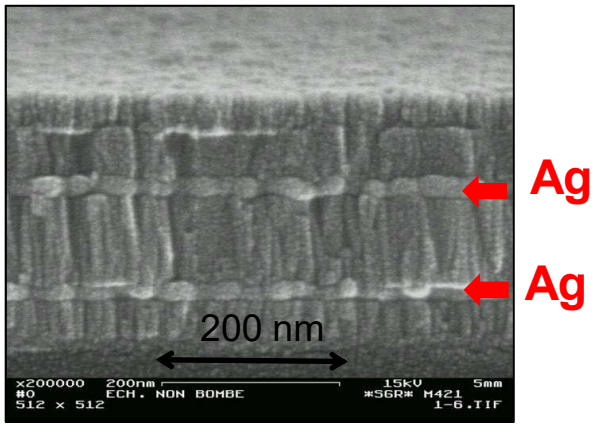


FLOAT GLASS WEATHERING IN ATMOSPHERIC CONDITIONS

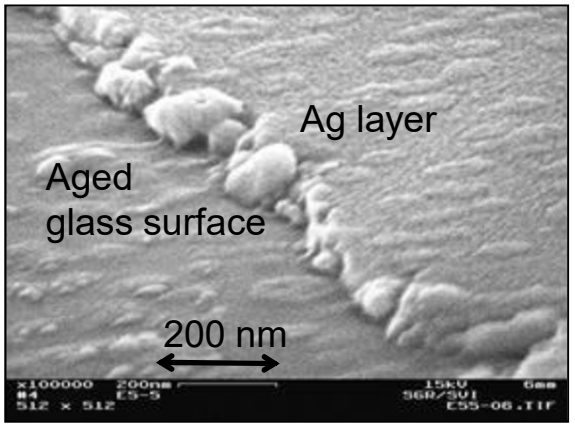
INDUSTRIAL ISSUES

Thin coatings make the weathering issues more crucial due to **their sensitivity to the glass surface quality**.





Coating (layers stack) on a glass substrate



Transfert of glass surface defects on coating topology

FLOAT GLASS WEATHERING IN ATMOSPHERIC CONDITIONS

INDUSTRIAL SOLUTIONS

To limit the weathering problems during flat glass storage, deposits are usually made

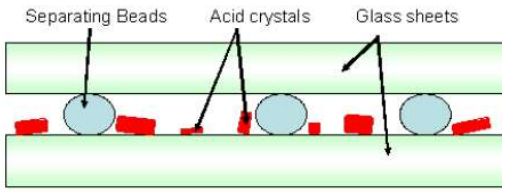
- at the end of line:

- organic acids, combined to the interleaving powder
- zinc salts, sprayed in low quantity (<mg/mm^2)

- during the production at higher temperature

De-alkalization surface treatments used with SO_3 or $(NH_4)_2SO_4$

- Efficiency demonstrated in pharmaceutical industry
- Used in **the annealing lehr in the float industry**



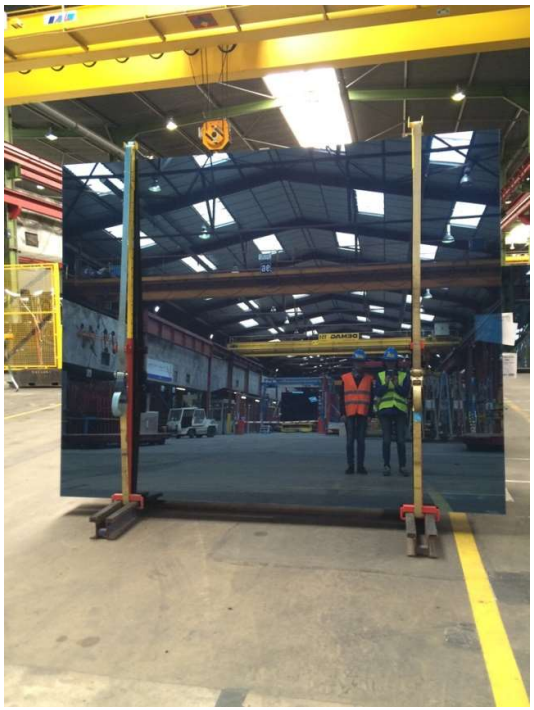
Smith & Pantano
JACS 2008

FLOAT GLASS WEATHERING IN ATMOSPHERIC CONDITIONS

To optimize our current solutions
glass ageing mechanisms must be understood.

➔ **PhD launched in 2020**

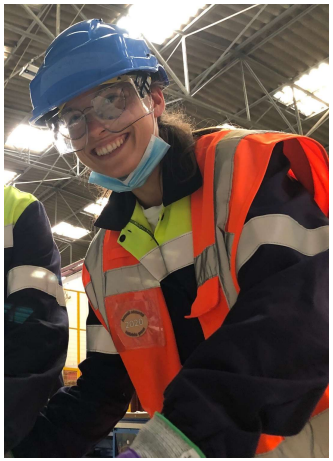
in collaboration with IRCP for their knowledge on
- atmospheric glass alteration mechanisms ➔ *short duration scale*
- soda-lime silicate glass ➔ *stable composition*

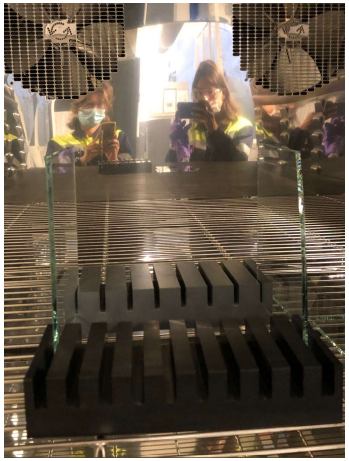


FLOAT GLASS WEATHERING IN ATMOSPHERIC CONDITIONS

PhD Amandine SERVE

R&D STUDY
on the influence
of the chemical composition





FLOAT GLASS WEATHERING IN ATMOSPHERIC CONDITIONS

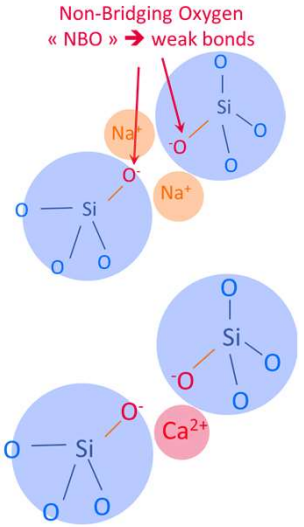
PhD Amandine SERVE

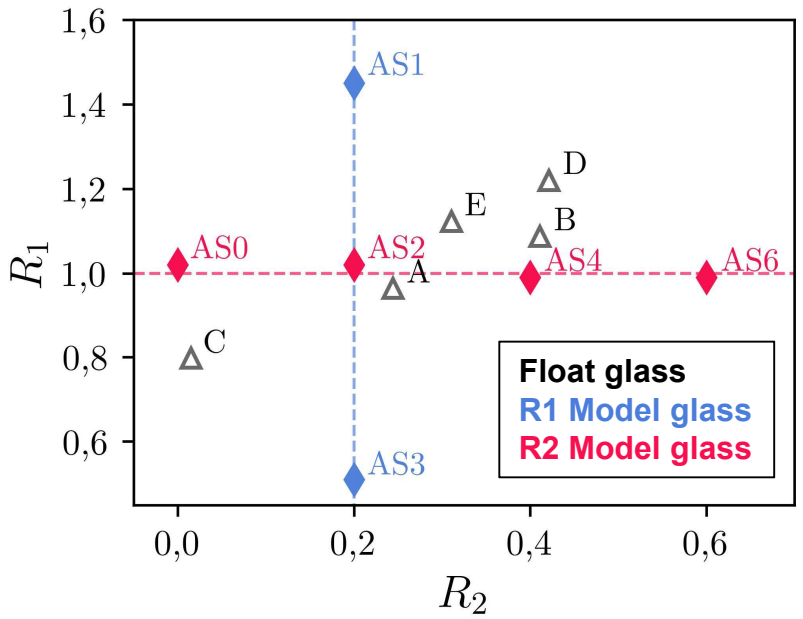
Challenges = Float samples chemistry: too much variable

VARIABLES CHOICE

$$R_1 = \frac{CaO + MgO}{Na_2O + K_2O}$$

$$R_2 = \frac{MgO}{CaO + MgO}$$



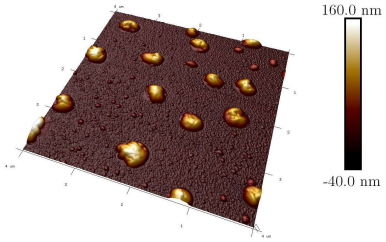


➔ Necessity to get representative **Lab** samples

FLOAT GLASS WEATHERING IN ATMOSPHERIC CONDITIONS

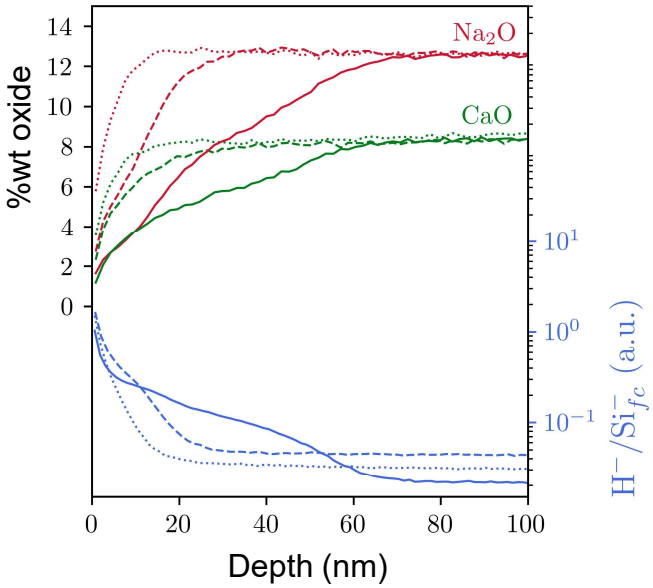
PhD Amandine SERVE

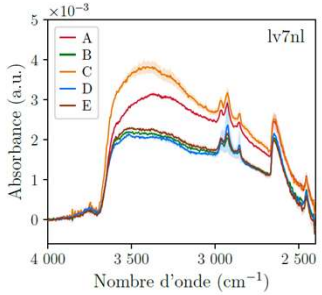
THE METHODOLOGY



Corrosion salts quantity AFM
(+ identification by Raman, SIMS mapping)

ToF-SIMS Glass depth profile composition
with an optimized source to limit ion migration





Carbonated/Hydrated corrosion layer ATR-IR

FLOAT GLASS WEATHERING IN ATMOSPHERIC CONDITIONS

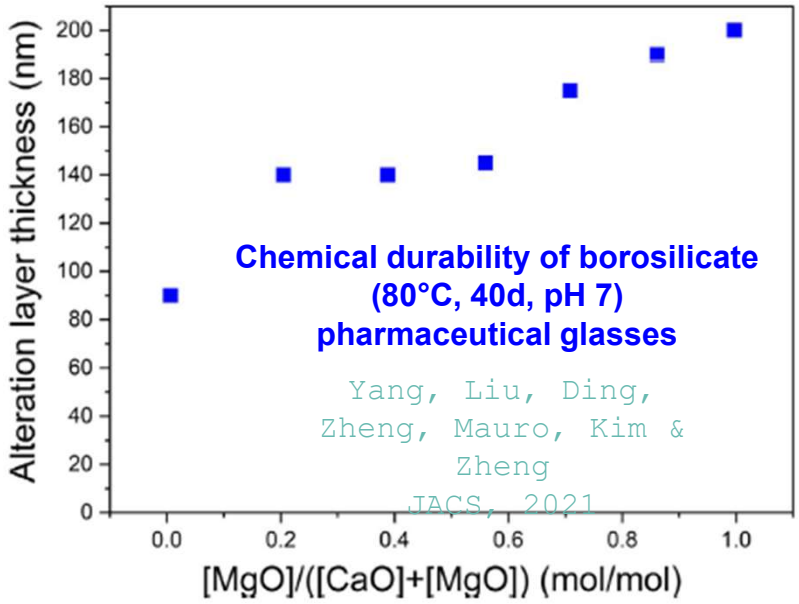
PhD Amandine SERVE

KNOW HOW | FLOAT GLASS | ISSUES & SOLUTIONS | COMPOSITION STUDY

LEARNINGS:

- **Fruitful role of magnesium in the study conditions**

A non-intuitive result:



Chemical durability of borosilicate pharmaceutical glasses: Mixed alkaline earth effect with varying [MgO]/[CaO] ratio

Rui Yang[1] | Hongshen Liu[2] | Zhijie Ding[1] | Jinfeng Zheng[1] | John C. Mauro[3,4] | Seong H. Kim[2,3,4] | Qiuju Zheng[1]

FLOAT GLASS WEATHERING IN ATMOSPHERIC CONDITIONS

PhD Amandine SERVE

LEARNINGS:

- **Fruitful role of magnesium in the study conditions**
  decrypted through the characterization of unwashed samples

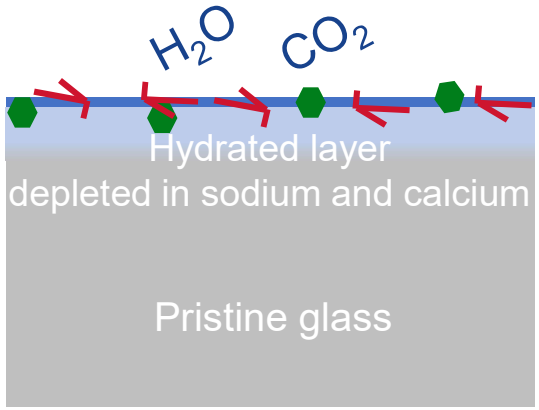
FLOAT GLASS WEATHERING IN ATMOSPHERIC CONDITIONS

PhD Amandine SERVE

LEARNINGS:

- **Fruitful role of magnesium in the study conditions**
  decrypted through the characterization of unwashed samples

AT THE EARLIER STAGES
An « intermediate » role of magnesium due to its high field strength
slows down the hydration
➔ and the global sodium/calcium migration



FLOAT GLASS WEATHERING IN ATMOSPHERIC CONDITIONS

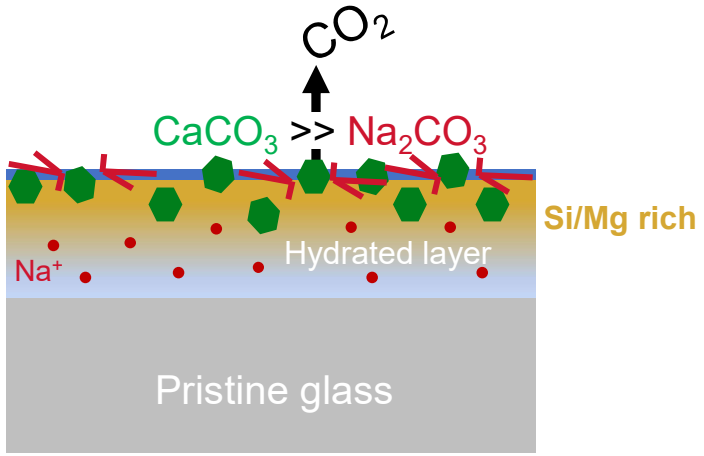
PhD Amandine SERVE

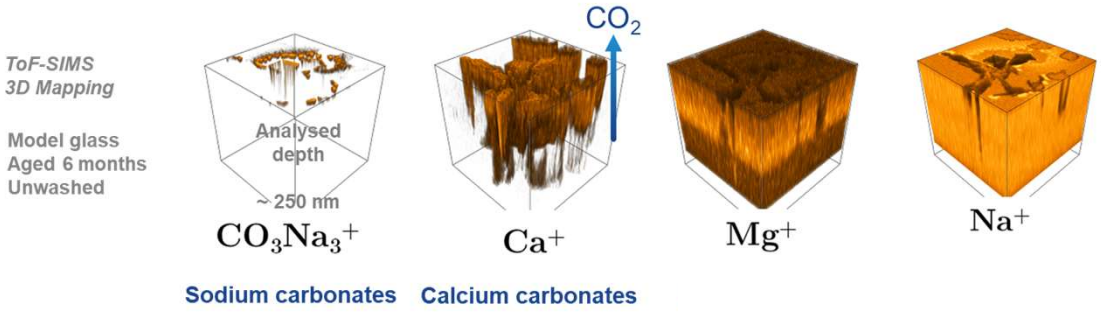
LEARNINGS:

- **Fruitful role of magnesium in the study conditions**
  decrypted through the characterization of unwashed samples

FOR LONGER DURATION

Mg → Glass surface structuration
with a hydrated magnesium silicate layer
Sodium ions • are trapped inside
On the contrary: important calcium migration
and calcium carbonates ⬢ precipitation





FLOAT GLASS WEATHERING IN ATMOSPHERIC CONDITIONS

SUMMARY

Glass surface ageing in atmospheric conditions
can be a real issue
for the magnetron deposition of **sensitive coatings**
… even ***the earlier weathering stages*** (first ten nms)

Amandine Serve's PhD

- Optimization of the methodology
- Development of the analytical tools

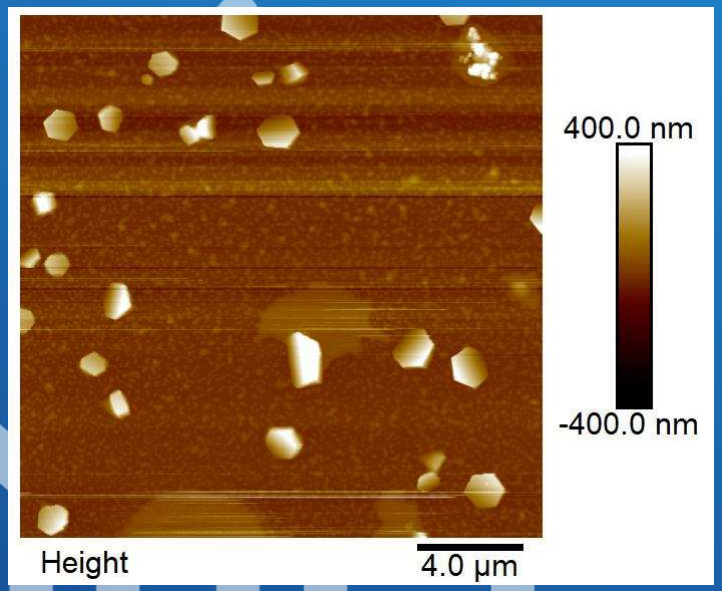
➔ Important learnings
on the **composition influence** in the ageing mechanisms

Structure--property relationship and chemical durability of magnesium-containing borosilicate glasses with insight from topological constraints

N. Bisbrouck[1], M. Micoulaut[2], J. M. Delaye[1], S. Gin[1] and F. Angeli[1]✉

Borosilicate glass alteration in vapor phase and aqueous medium

Sathya Narayanasamy[1]✉, Patrick Jollivet[1], Christophe Jégou[1], Mélanie Moskura[2], Abdesselam Abdelouas[3], Thibault Charpentier[2]✉ and Frédéric Angeli[1]✉



MANY THANKS FOR YOUR KIND ATTENTION

Sophie PAPIN & Hervé MONTIGAUD
Amandine SERVE & Thierry CRETIN
Saint-Gobain Research Paris

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TRANSVERSAL R&D CENTERS BY SAINT-GOBAIN

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SVI SURFACE DU VERRE ET INTERFACES

SAINT-GOBAIN