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JOURNÉES VERRE 2024
DIJON
13 – 15 Novembre 2024

USTV
UNION POUR LA SCIENCE & LA TECHNOLOGIE VERRIÈRES

DURABILITÉ CHIMIQUE DES VERRES INDUSTRIELS

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Historique

- Depuis les années 2010, par l'intermédiaire du GDR Verres et l'USTV, des collaborations ont été initiées entre des industriels verriers et la communauté du verre autour des problématiques **REACh et contact alimentaire**

- Des ateliers scientifiques et colloques ont été organisés à Avignon (USTV, GDR et CEA) en 2014, à Paris en 2013 et 2018 (IPGP)

FOR FOOD CONTACT

- Premiers travaux exploratoires puis poursuite par l'intermédiaire début 2019, d'un projet ANR de 4 ans

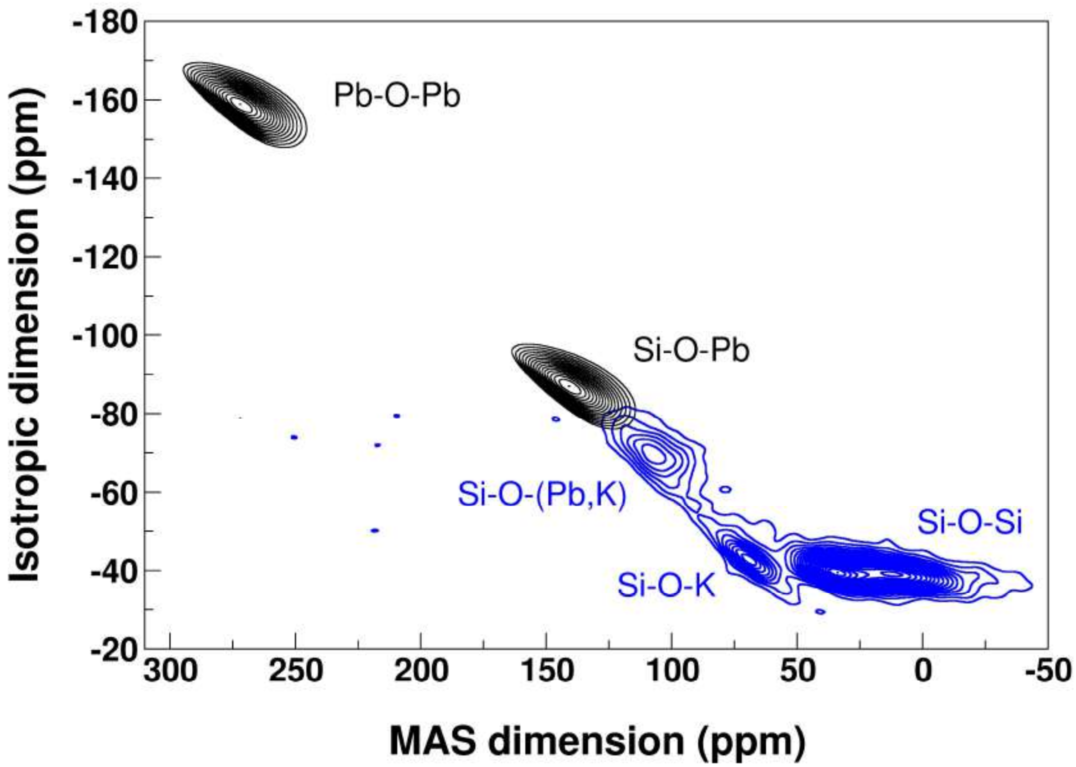
Structure and durability of lead crystal glass

Baccarat

	mol %
SiO_2	77.1
Na_2O	0.8
Sb_2O_3	0.2
K_2O	11.3
PbO	10.6

Commercial Pb crystal glass (PbO 28.3 wt%)

^{17}*O MQMAS NMR*



Pb does not form Pb−O−Pb clusters

Comparison with binary lead silicate glasses (Lee and Kim*)

$71PbO-29SiO_2$
$67PbO-33SiO_2$
$60PbO-40SiO_2$

No contribution corresponding to Si-O-Pb and Pb-O-Pb

The Si-O-(Pb,K) **line position** give information about the **proportion of Pb and K** in the mixing site

*Lee and Kim, *J. Phys. Chem. C* 119, 748 (2015)

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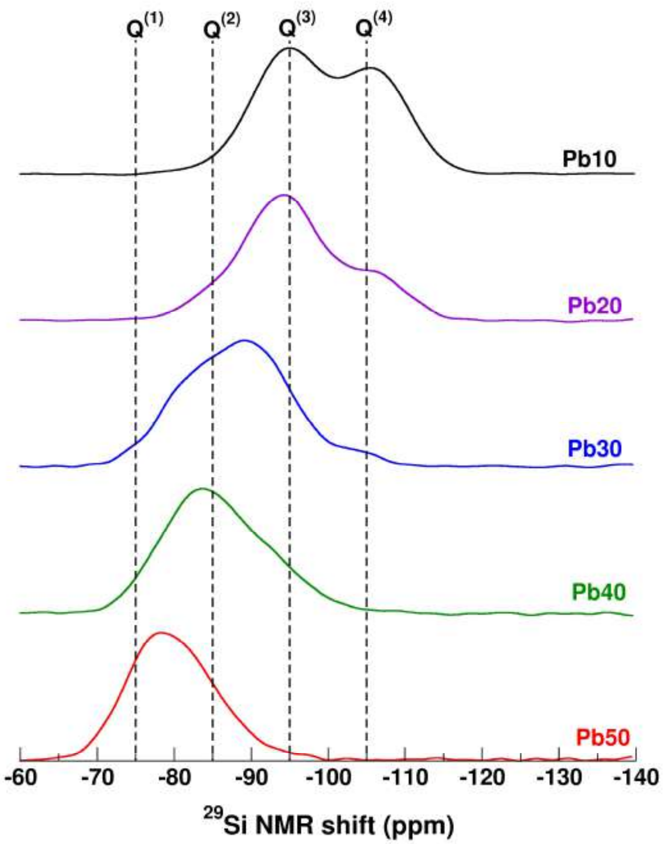
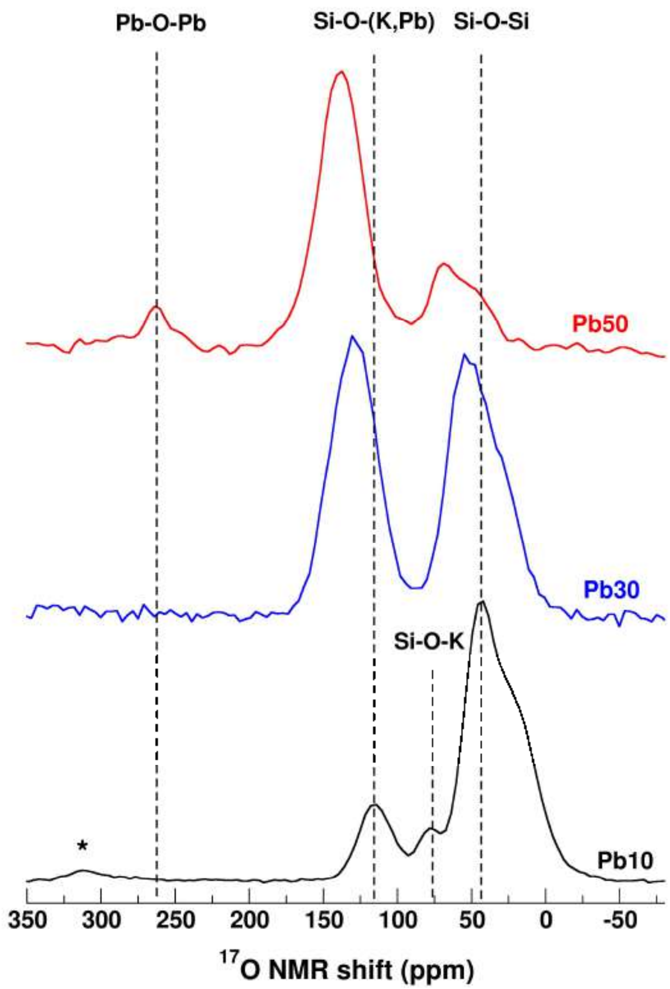
Influence of Pb content on glass structure

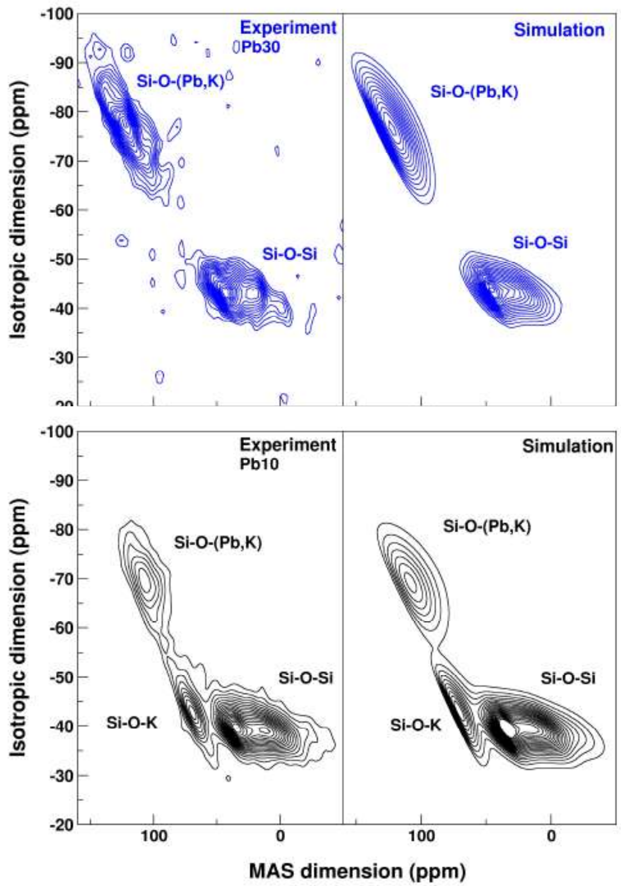


29Si MAS NMR



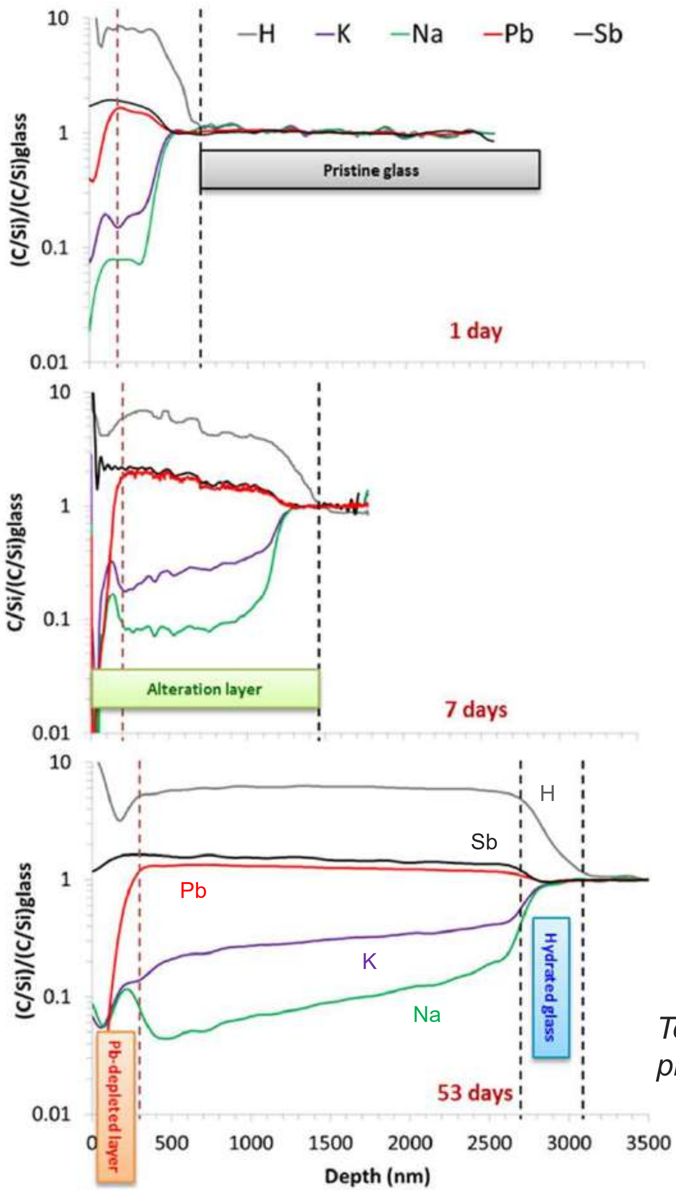
17O MAS NMR

17O MQMAS NMR

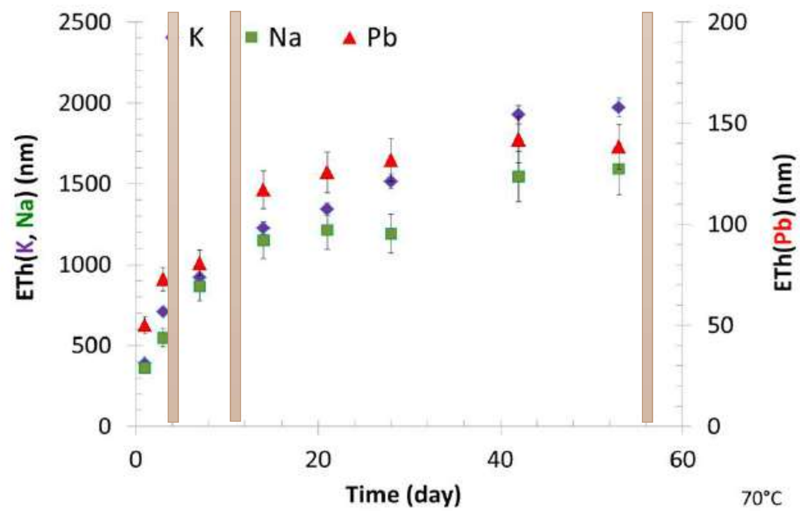


Chemical durability of lead crystal glass

Acetic acid
pH = 2.4, 70°C



ToF-SIMS elemental profiles (1-53 days, Si_{sat})



- **Alteration layer: 3 areas**
  → **hydrated glass, alkalis depletion zone, Pb-depleted external surface**

- **Progress of hydration front in the pristine glass,**
  greater H incorporation compared to Na,K depletion

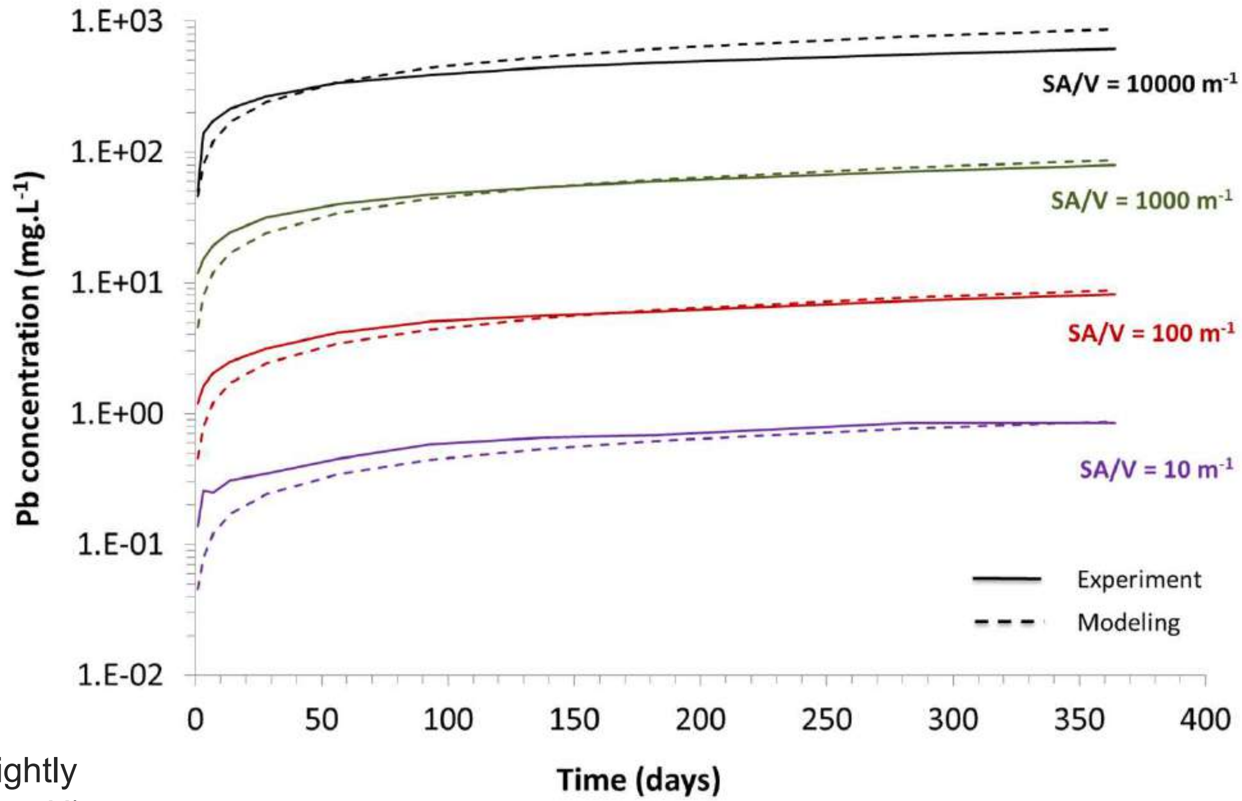
- Pb released to a lesser extent than alkalis
  (thin external surface)

Modeling of lead release in acetic acid solution

Good agreement between calculation of Pb concentrations and experimental data

$$C_{Pb} = 3.4.10^{-2} * \frac{S}{V} * \left(e^{-\frac{E_a}{RT}} * t\right)^{\frac{1}{2}}$$

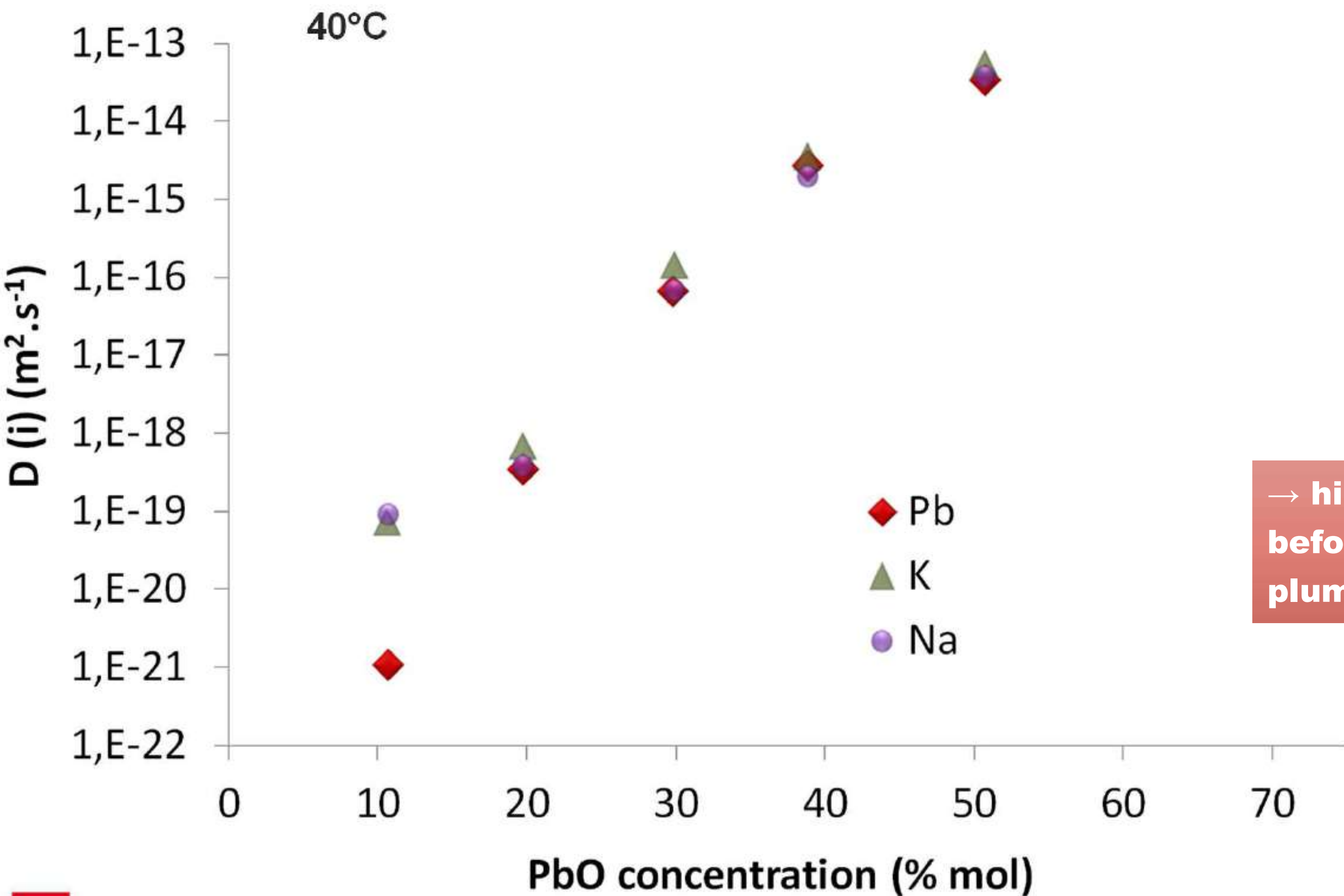
- C_{Pb}: concentration of lead in solution (**m**g.L^{-1}),
- *t*: leaching time (s),
- *T*: temperature (K),
- E_a: activation energy (37.7 K.J.mol^{-1}),
- *V*: volume of the solution (m^3),
- *S*: surface of the glass (m^2),
- *R*: gas constant (8.31 J/mol^{-1}.K^{-1}).



- Higher SA/V ratio: drift of pH
  → experimental Pb concentrations slightly lower than calculated values (lower pH)

Angeli et al., *Environ. Sci. Technol.* 50 (2016)

Influence of Pb content on glass dissolution



→ **high increase of dissolution before the formation of the plumbate subnetwork percolation**

Angeli et al., *in book: Lead in Glassy Materials in Cultural Heritage, Chapter 13 (2024)*

ANR BIGDAD – 2019 - 2023

- **Glass durability of untreated glasses**
- **Effect of surface treatments**
- Specific behavior of the **crystallized opal glass**
- Effect of a colorant on the durability of a **crystal glass with Cr**

5 widely used silicate glass from 4 major French glass manufacturers

→ **most comprehensive vision of elements released in solution (with and without surface treatments)**

Industrial glass composition

Glass A – Lead crystal

	% mol
SiO_2	77.1
Na_2O	0.8
K_2O	11.3
PbO	10.6
Sb_2O_3	0.2

Glass B – Barium glass

	% mol
SiO_2	74.2
Na_2O	8.3-10.3
Al_2O_3	< 1.3
CaO	9.0-11.0
MgO	
BaO	0.5-2.5
K_2O	2.5-4.5

Glass C – Soda-lime

	% mol
SiO_2	70.9
Na_2O	13.0-15.0
Al_2O_3	< 1.3
CaO	9.0-11.0
MgO	2.0-4.0
BaO	< 1.0
K_2O	< 1.0

Glass D – Borosilicate

	% mol
SiO_2	82.1
Na_2O	5.6
B_2O_3	10.7
Al_2O_3	1.6

Glass O – Opal cristal.

	%mol
SiO_2	73.6
Na_2O	11.9
Al_2O_3	4.8
CaO	2.2
BaO	0.8
K_2O	1
F_2	5.7

Baccarat

arc

POCHET DU COURVAL

MFV LA MAISON FRANÇAISE DU VERRE

PYREX

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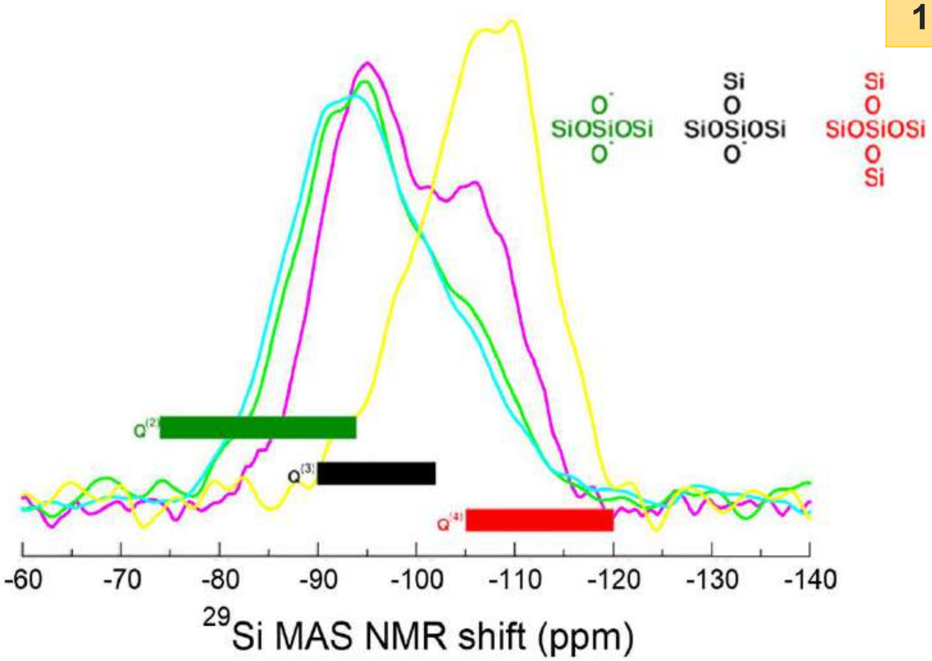
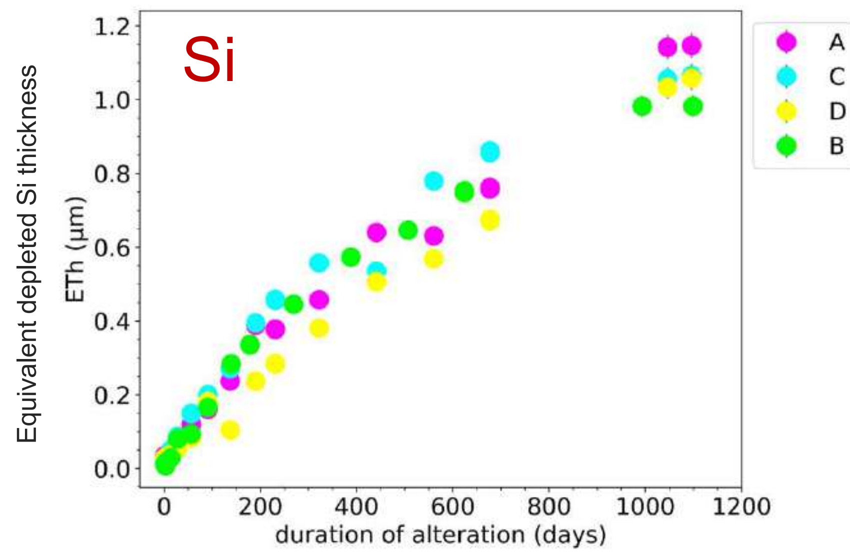
Structure and leaching of the silicate network

Glass A	Lead crystal
Glass B	Barium glass
Glass C	Soda-lime
Glass D	Borosilicate

Acetic acid
pH = 2.4, 70°C
S/V = 50 m^{-1}
1 µm ~ 3 years

^{29}Si NMR spectra of the pristine glasses



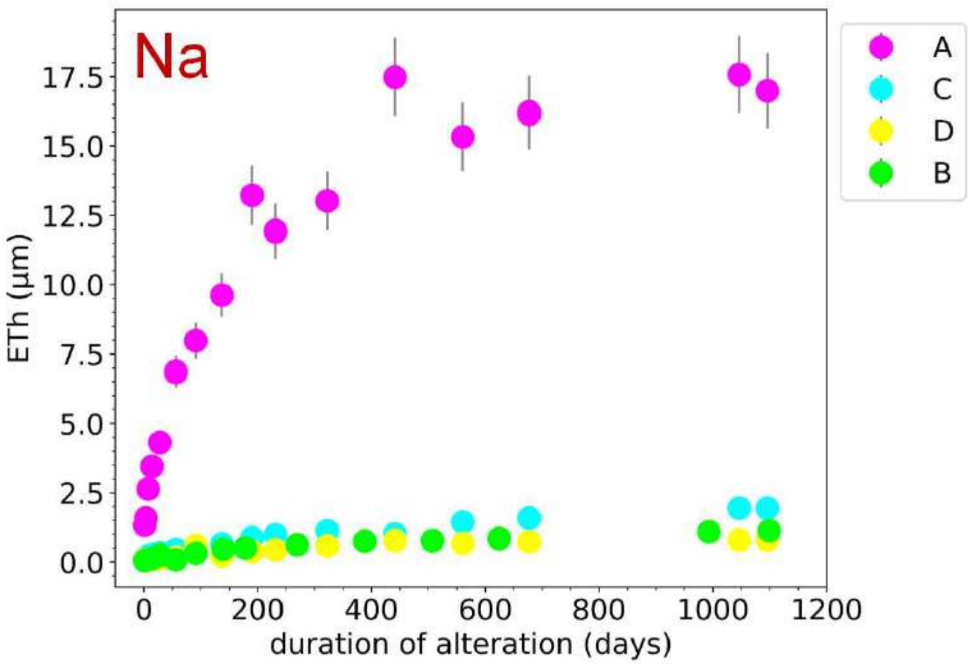


- **Si release very similar** for all glasses
- **Hydrolysis of the Si network not dependent on the polymerization** under these conditions

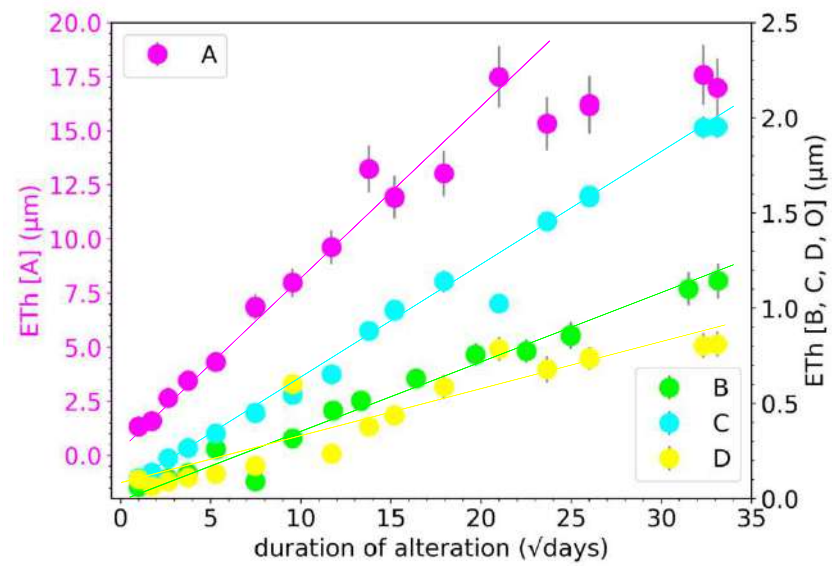
Brunswic et al., *npj-MD, 8:82 (2024)*

Leaching of the tracing element of alteration

Glass A	Lead crystal
Glass B	Barium glass
Glass C	Soda-lime
Glass D	Borosilicate



- ❑ **Na release: ions exchange mechanism** (Na-protons) → significant changes
- ❑ Na rate higher than Si



Glass leaching is controlled by the ion exchange regime (enhanced with less polymerized glasses)

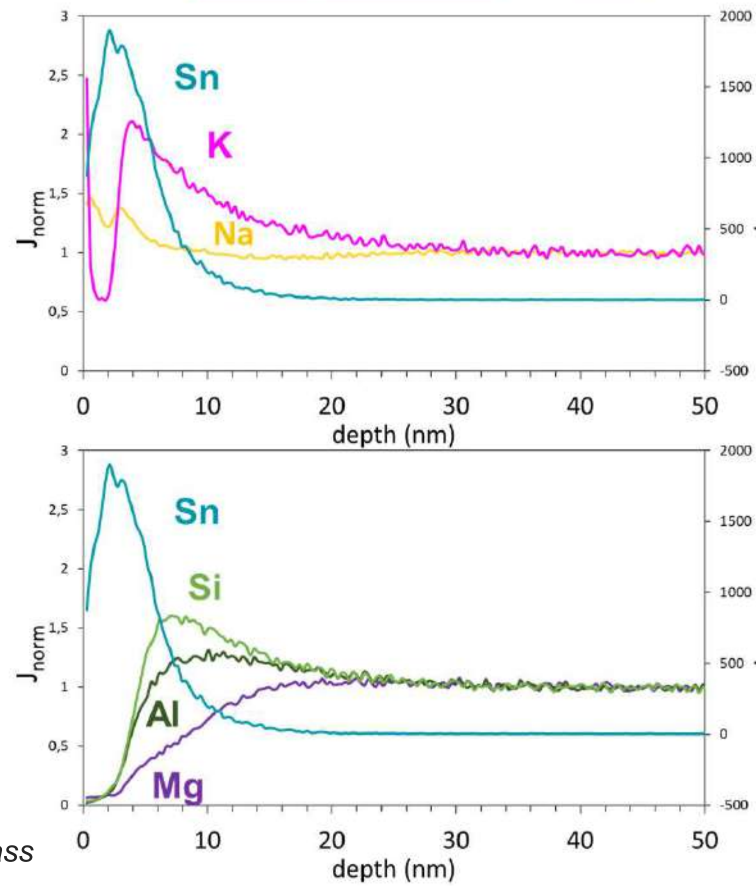
Chemical deposits

Si | Sn | Ti

Surface coatings (sputtering)

Surface effects of coating treatments

Glass C | Soda-lime + Sn



- **SnO_2 coating** : ~ 10 nm, migration of cations into the coating depending on their ionic charge (except Pb and Mg)

→ **Dissolution of Sn coating**

- **SiO_2 coating** : ~ 10 nm, no diffusion of cations in Si coating

→ **Very low dissolution of Si coating**

- **TiO_2 coating** : ~ 100-500 nm, Na diffusion in external coating surface

→ **Dissolution of Ti coating**

Brunswic et al., *npj-MD, 8:108 (2024)*

ToF-SIMS profiles of pristine glass

Surface effects of chemical treatments

Chemical deposits | Chemical reactions

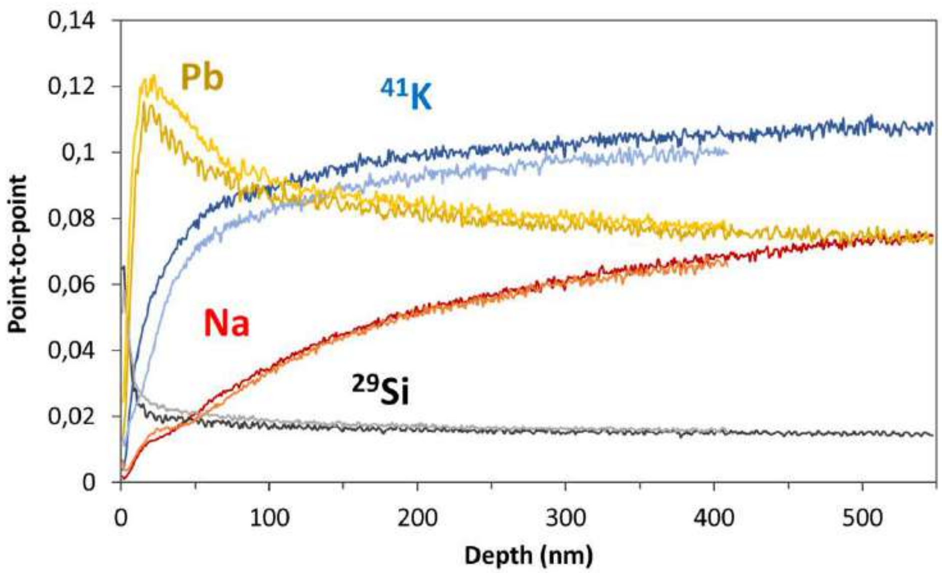
Si **Sn** **Ti** **PA** **CEMa** **CEMb**

Surface coatings (sputtering)

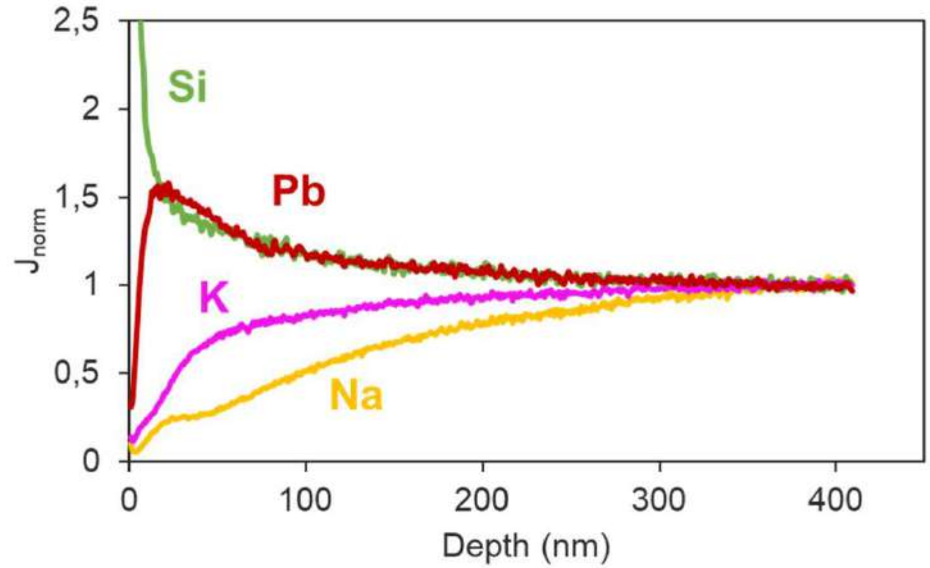
Dealkalization (sulfur-based precursors)

Acidic etching (HF, H_2SO_4)

Glass A | Lead crystal + **CEMa** **CEMb**



15 nm at the surface depleted in Pb



Brunswic et al., *npj-MD, 8:108 (2024)*

ToF-SIMS profiles of pristine glass

Effects of surface treatments

Chemical deposits			Chemical reactions		
Si	Sn	Ti	PA	CEMa	CEMb

Surface coatings (sputtering)

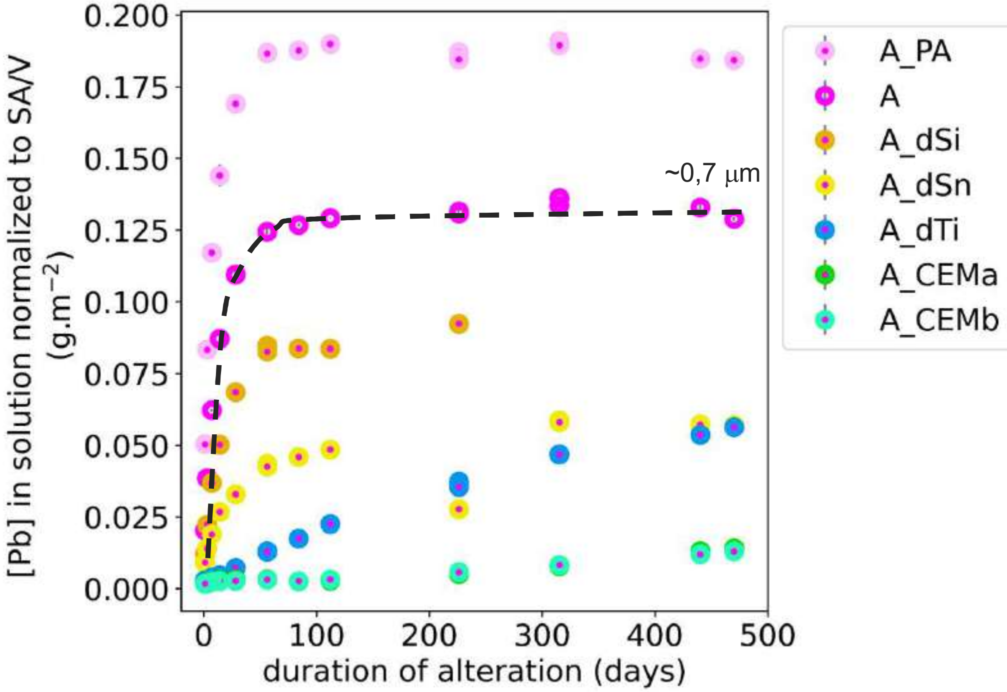
Dealkalization (sulfur-based precursors)

Acidic etching (HF, H_2SO_4)

Acetic acid
pH = 2.4, 70°C
S/V = 2.5 m^{-1}
~ 500 days

Pb

Glass A | Lead crystal



Glass sample	$[Pb]_{SA/V}$ after 1 day	$[Pb]_{SA/V}/[Pb]^{ref}_{SA/V}$	
	$g.m^{-2}$	1 day	470 days
A_PA	0.050	2.47	1.43
A (ref)	0.020	1.00	1.00
A_dSi	0.012	0.60	0.72*
A_dSn	0.009	0.45	0.44
A_dTi	0.003	0.15	0.44
A_CEMa	0.002	0.09	0.11
A_CEMb	0.002	0.09	0.10

* based on $[Pb]_{SA/V}$ at 226 days

- **Acidic etching** (acid polishing):

  → detrimental effect on glass durability (surface depolymerization in rich alkali glass)

Effects of surface treatments

Chemical deposits			Chemical reactions		
Si	Sn	Ti	PA	CEMa	CEMb

Surface coatings (sputtering)

Dealkalization (sulfur-based precursors)

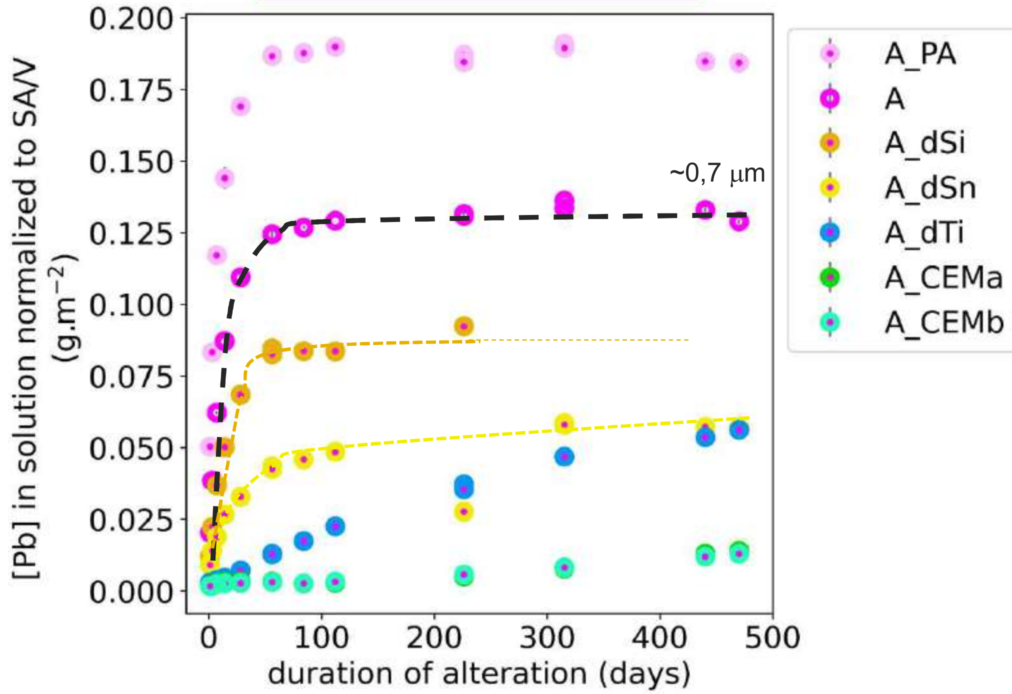
↓

Acidic etching (HF, H_2SO_4)

Acetic acid
pH = 2.4, 70°C
S/V = 2.5 m^{-1}
~ 500 days

Pb

Glass A | Lead crystal



Glass sample	$[Pb]_{SA/V}$ after 1 day	$[Pb]_{SA/V}/[Pb]^{ref}_{SA/V}$	
	g.m^{-2}	1 day	470 days
A_PA	0.050	2.47	1.43
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A_dSn	0.009	0.45	0.44
A_dTi	0.003	0.15	0.44
A_CEMa	0.002	0.09	0.11
A_CEMb	0.002	0.09	0.10

* based on $[Pb]_{SA/V}$ at 226 days

- **Si, Sn coatings**

→ effect on the reduction of Pb release is moderate

Effects of surface treatments

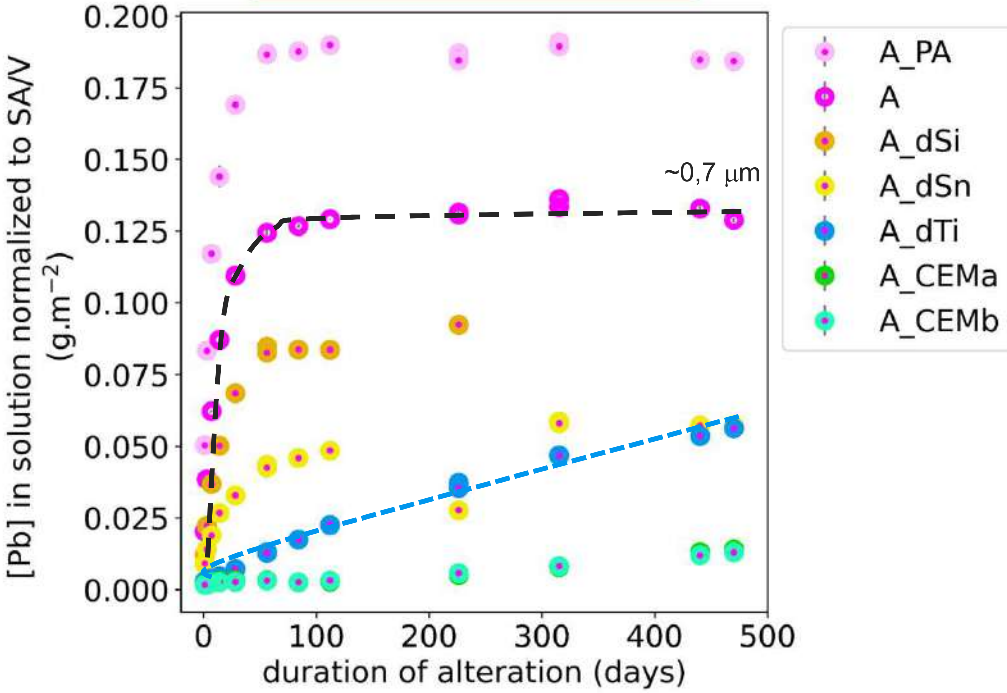
Chemical deposits — Si, Sn, Ti — *Surface coatings (sputtering)*

Chemical reactions — PA, CEMa, CEMb — *Dealkalization (sulfur-based precursors)* → *Acidic etching (HF, H_2SO_4)*

Acetic acid
pH = 2.4, 70°C
S/V = 2.5 m^{-1}
~ 500 days

Pb

Glass A | Lead crystal



Glass sample	$[Pb]_{SA/V}$ after 1 day	$[Pb]_{SA/V}/[Pb]^{ref}_{SA/V}$	
	$g.m^{-2}$	1 day	470 days
A_PA	0.050	2.47	1.43
A (ref)	0.020	1.00	1.00
A_dSi	0.012	0.60	0.72*
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A_dTi	0.003	0.15	0.44
A_CEMa	0.002	0.09	0.11
A_CEMb	0.002	0.09	0.10

* based on $[Pb]_{SA/V}$ at 226 days

- **TiO_2 coating**

  → acts as a diffusion barrier
  (same effect for other glass cations)

  → linear increase of Pb
  (some of the coating is also leached)

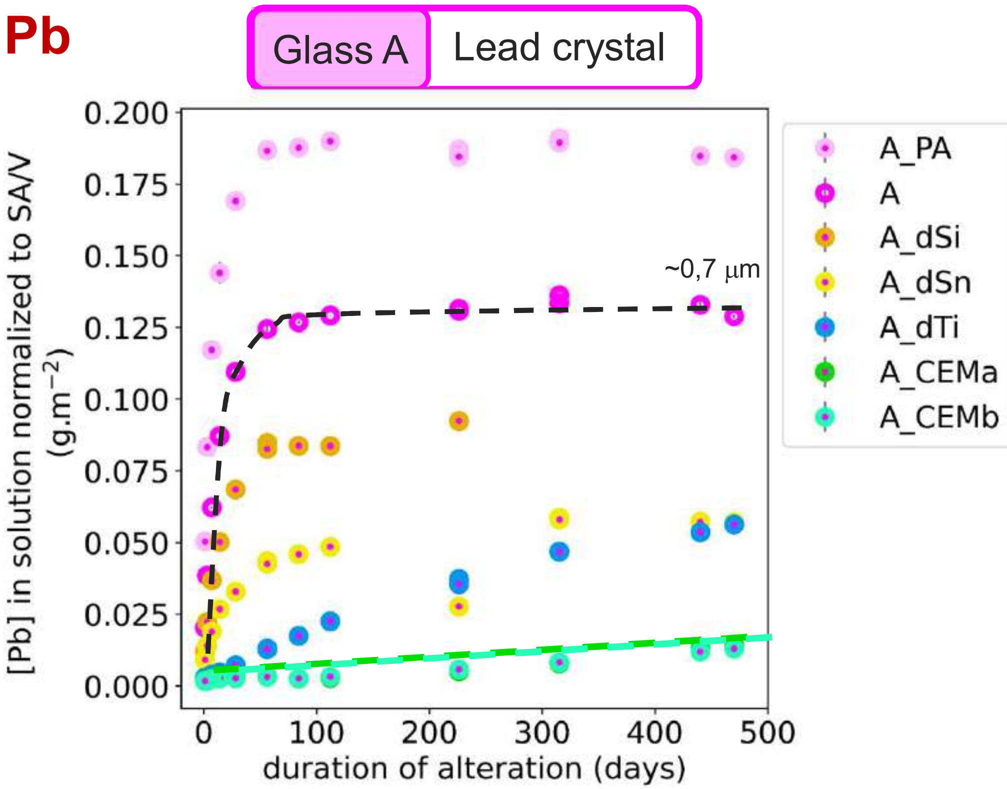
Effects of surface treatments

Chemical deposits: Si | Sn | Ti — *Surface coatings (sputtering)*

Chemical reactions: PA | CEMa | CEMb — *Dealkalization (sulfur-based precursors)* → *Acidic etching (HF, H_2SO_4)*

Acetic acid
pH = 2.4, 70°C
S/V = 2.5 m^{-1}
~ 500 days

Pb



Glass sample	$[Pb]_{SA/V}$ after 1 day (g.m^{-2})	$[Pb]_{SA/V}/[Pb]^{ref}_{SA/V}$ 1 day	$[Pb]_{SA/V}/[Pb]^{ref}_{SA/V}$ 470 days
A_PA	0.050	2.47	1.43
A (ref)	0.020	1.00	1.00
A_dSi	0.012	0.60	0.72*
A_dSn	0.009	0.45	0.44
A_dTi	0.003	0.15	0.44
A_CEMa	0.002	0.09	0.11
A_CEMb	0.002	0.09	0.10

* based on $[Pb]_{SA/V}$ at 226 days

- **SO_2 dealkalization** (most efficient)
  - → considerably **reduces lead release**
  - → **lasts over time**
  - → **reproducibility** between both industrial procedures

Effects of surface treatments

Chemical deposits | Chemical reactions

Si | Sn | Ti | PA | CEMa | CEMb

Surface coatings (sputtering)

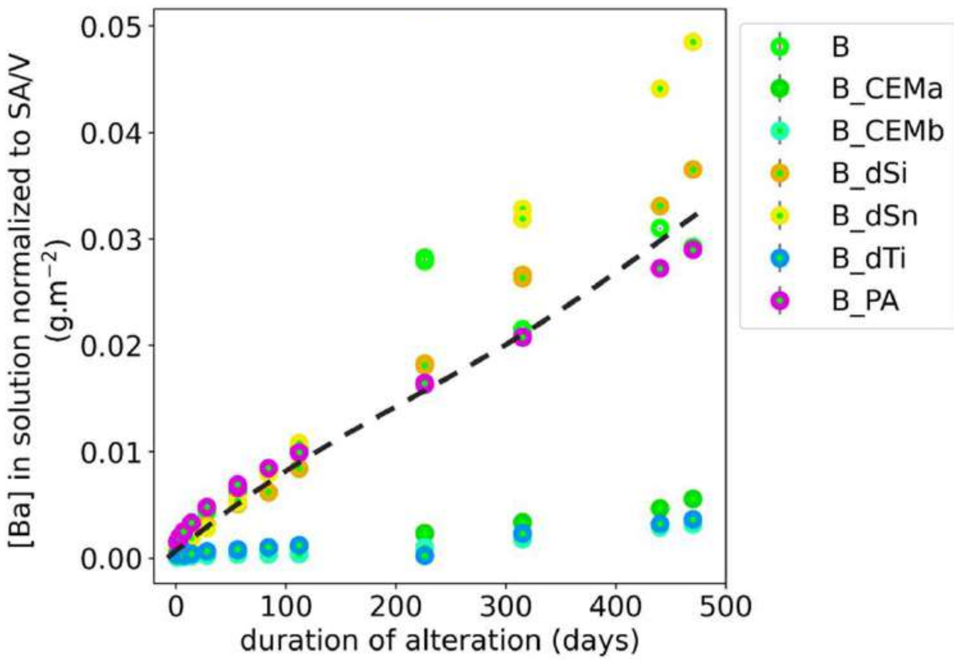
Dealkalization (sulfur-based precursors)

Acidic etching (HF, H_2SO_4)

Acetic acid
pH = 2.4, 70°C
S/V = 2.5 m^{-1}
~ 500 days

Ba

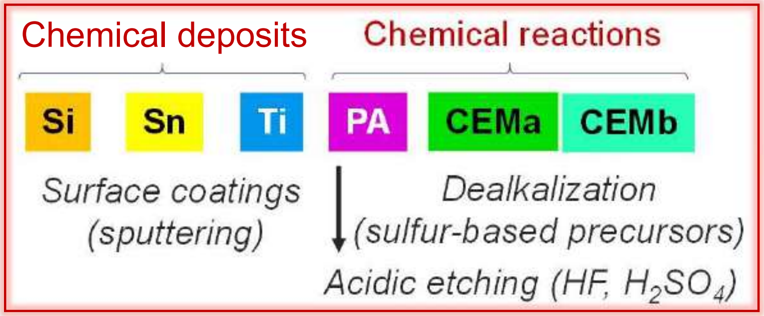
Glass B | Barium glass



❑ **SO_2 dealkalization** and **TiO_2 coating**

→ dividing 5 times the reduction of **Ba concentration**

Effects of surface treatments

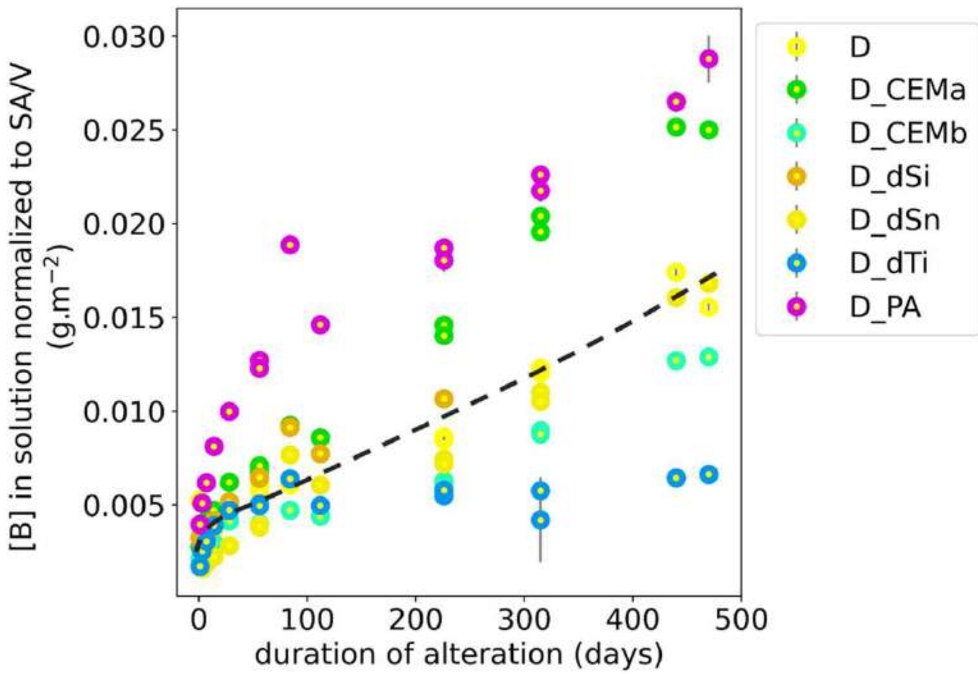


Acetic acid
pH = 2.4, 70°C
S/V = 2.5 m^{-1}
~ 500 days

	% mol
SiO_2	82.1
Na_2O	5.6
B_2O_3	10.7
Al_2O_3	1.6

B

Glass D | Borosilicate



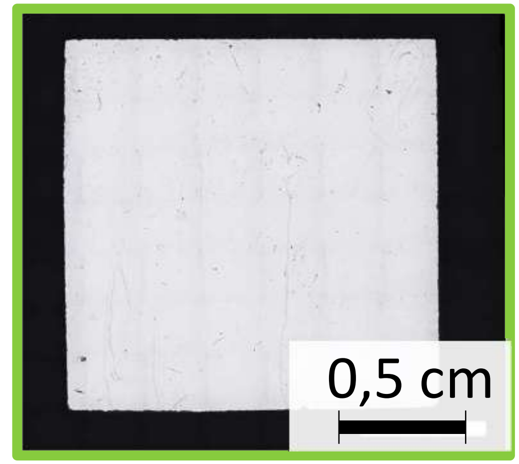
- ❑ Very low effectiveness of surface treatments for borosilicate glasses **not subjected to interdiffusion**
- ❑ Dealkalization is detrimental for maintaining the coordination of B and Al

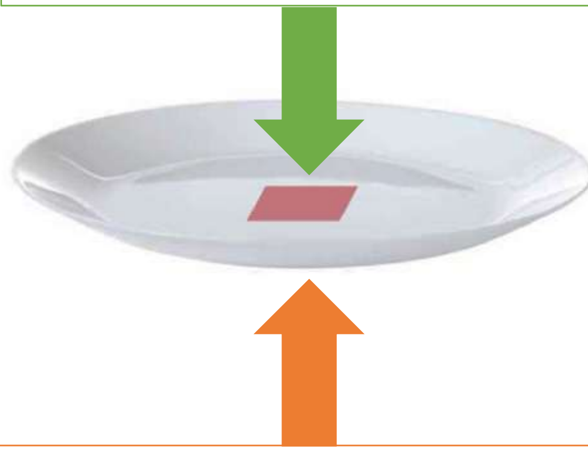
Opal crystallized glass plates

White opaque plates obtained by adding fluorine

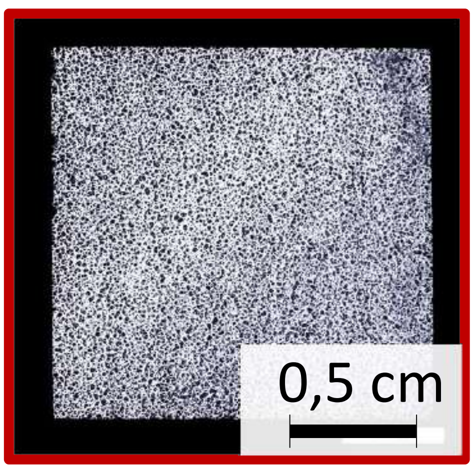
Manufacturing process: casting glass in a mold

Top – Smooth
Air side



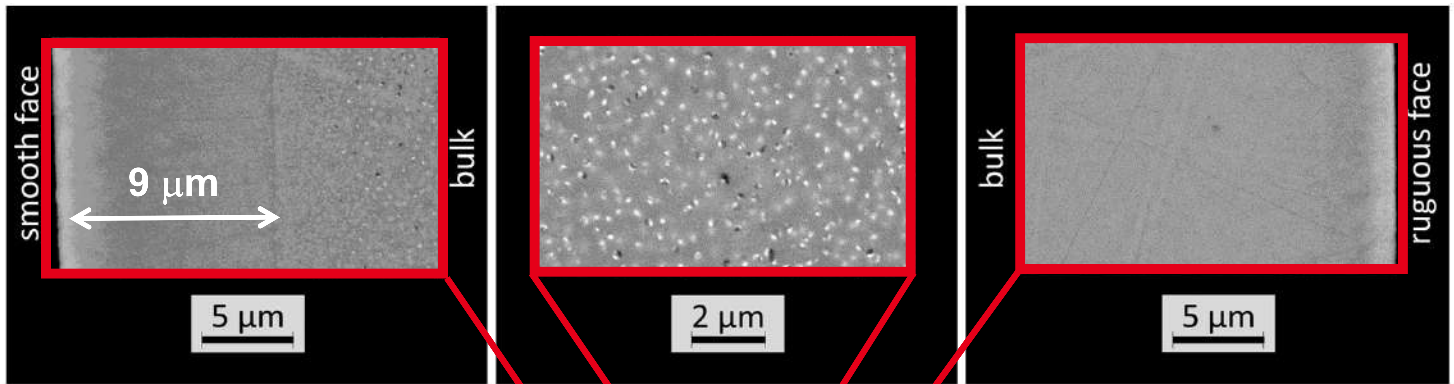


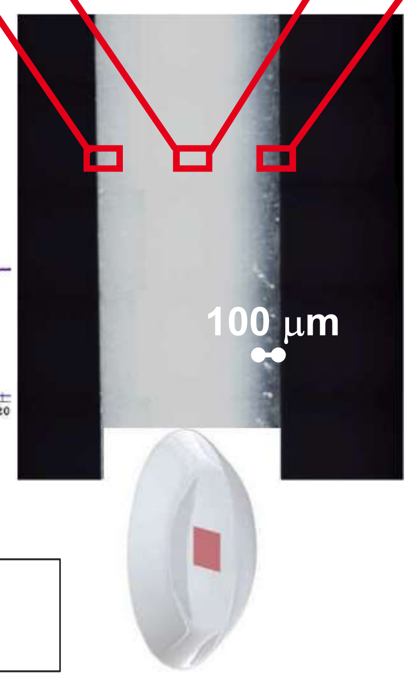
Bottom – Rough
Mold side

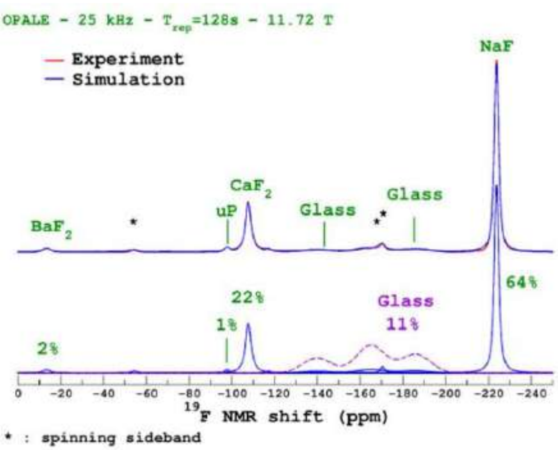


Effect on the distribution of crystals (→ cooling rate)

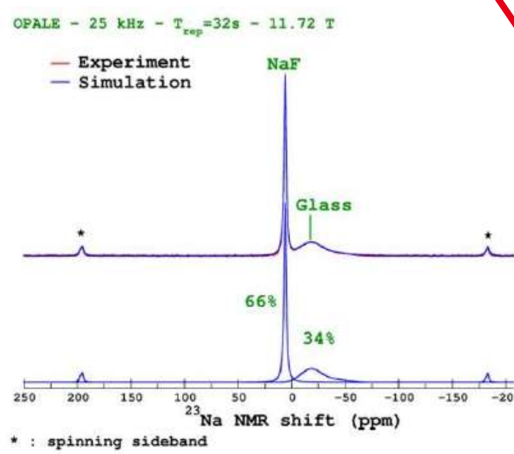
	NaF	CaF_2	BaF_2	
% crystal	64	22	2	
	Ca	Ba	F	Na
% cations in crystals	81	20	89	43



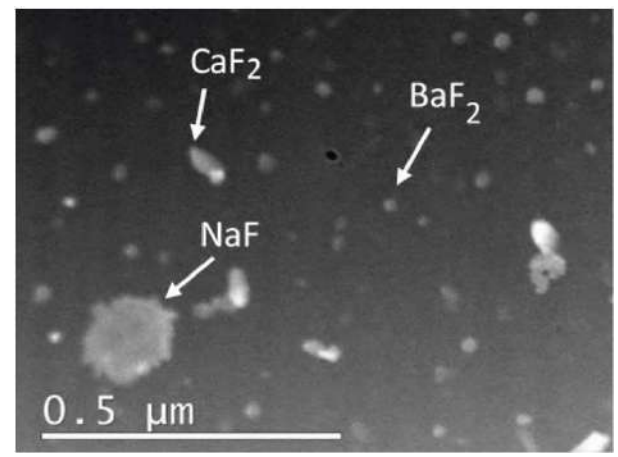




^{19}F MAS NMR

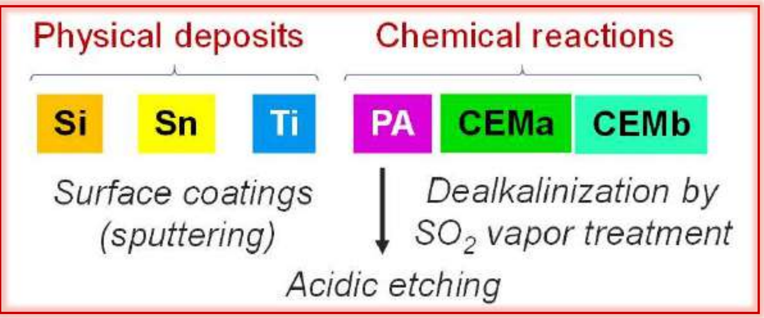


^{23}Na MAS NMR

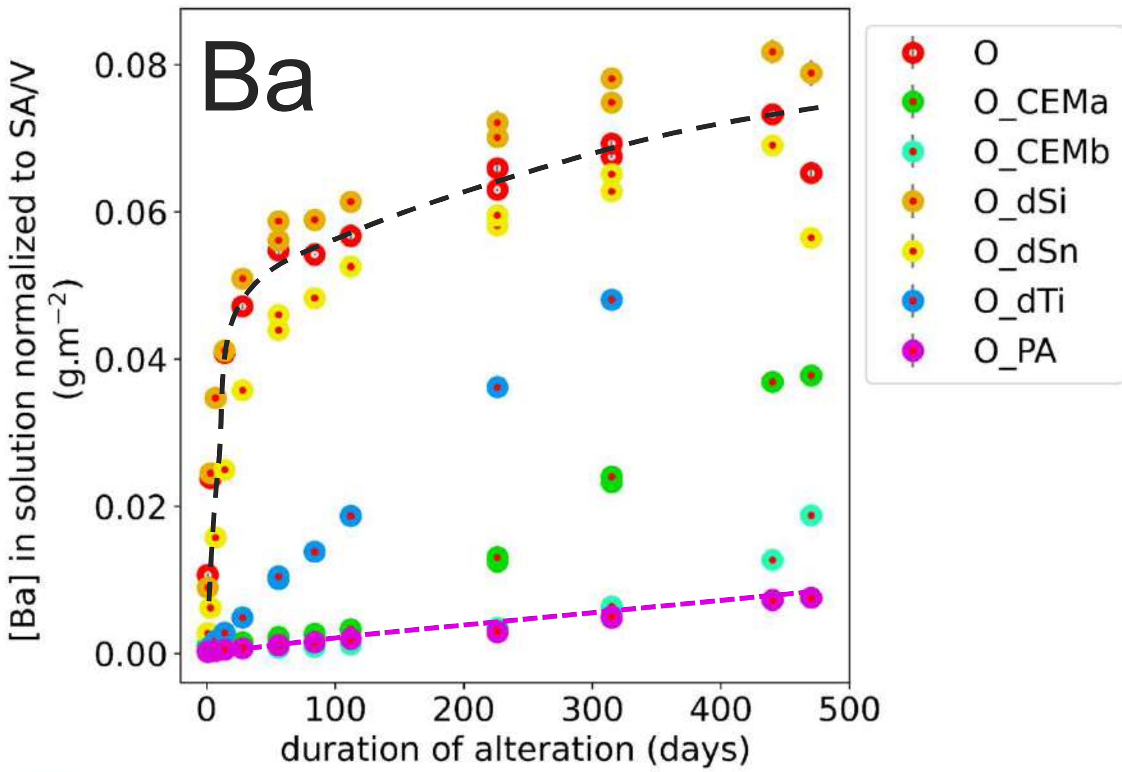


Crystals: 20 nm (surface)
to 200 nm (bulk)

Glass surfaces (cooled faster): no crystal
(→ more pronounced on the mold side)



Effect of surface treatments on the release of Ba from opal glass



- ❑ For all amorphous glasses, acidic etching did not show beneficial effect
- ❑ For opal glass, **acid etching is the best treatment** for the reduction of Ba leaching

  → removes the surface less durable layer enriched in Na revealing the underlying crystals

  → **glass with crystals and a lower Na** is **more resistant** to alteration than the initial surface

The case of chromium in lead crystal glass

Cr(III) : green, commonly used as colorant

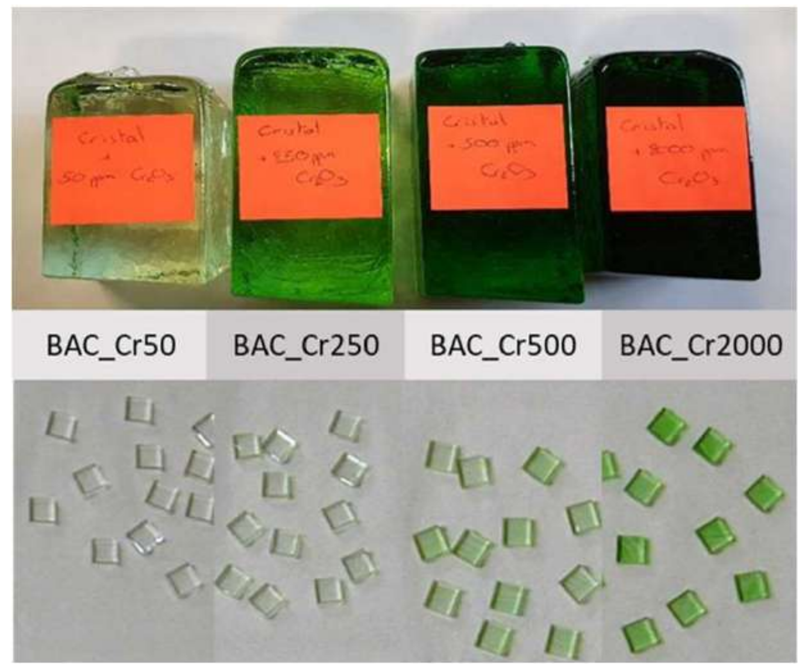
$Cr_2O_3 – Cr^{3+}$

Cr(VI) : yellow, very mobile and toxic

$CrO_3 – Cr^{6+}$

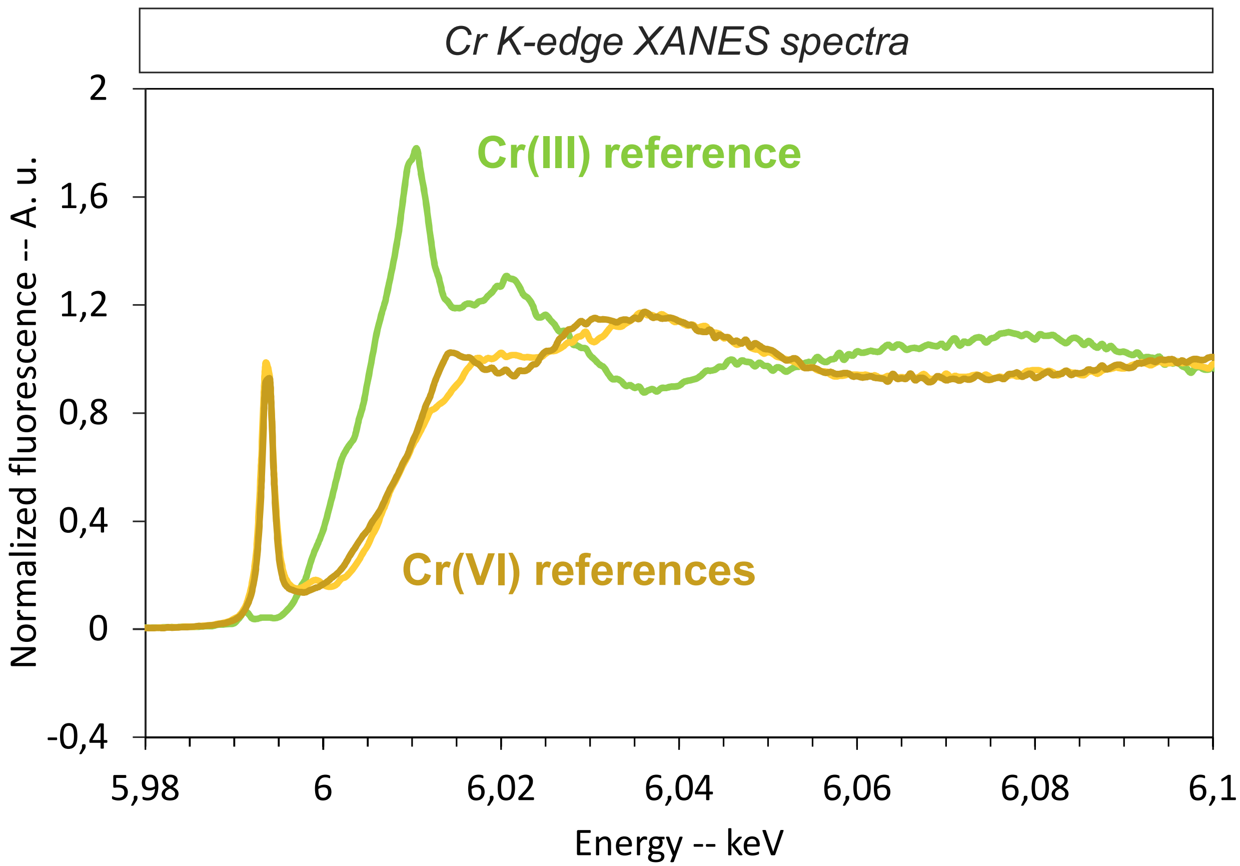
wt%	Si	Pb	K	Na	Cr
BAC	26.76	26.87	10.21	0.47	0.000
BAC_Cr50	26.85	26.53	10.08	0.48	0.003
BAC_Cr250	26.84	26.66	10.04	0.47	0.011
BAC_Cr500	26.89	25.86	10.21	0.47	0.024
BAC_Cr2000	26.81	26.60	10.14	0.46	0.052

= 0.028 mol %



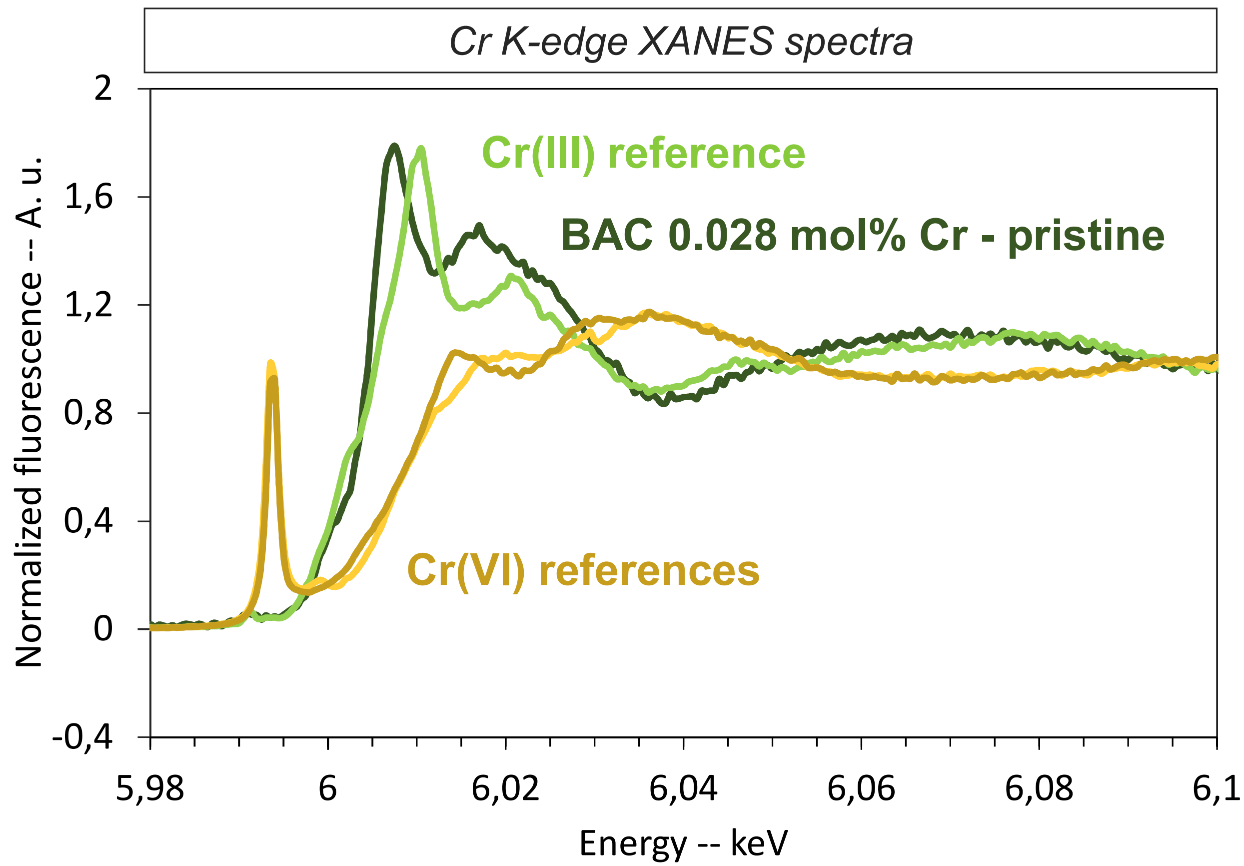
Speciation of chromium in lead crystal glasses

- Peak position at 6.0075 eV for Cr(III) reference
- Peak position at 5.9935 eV for Cr(VI) references



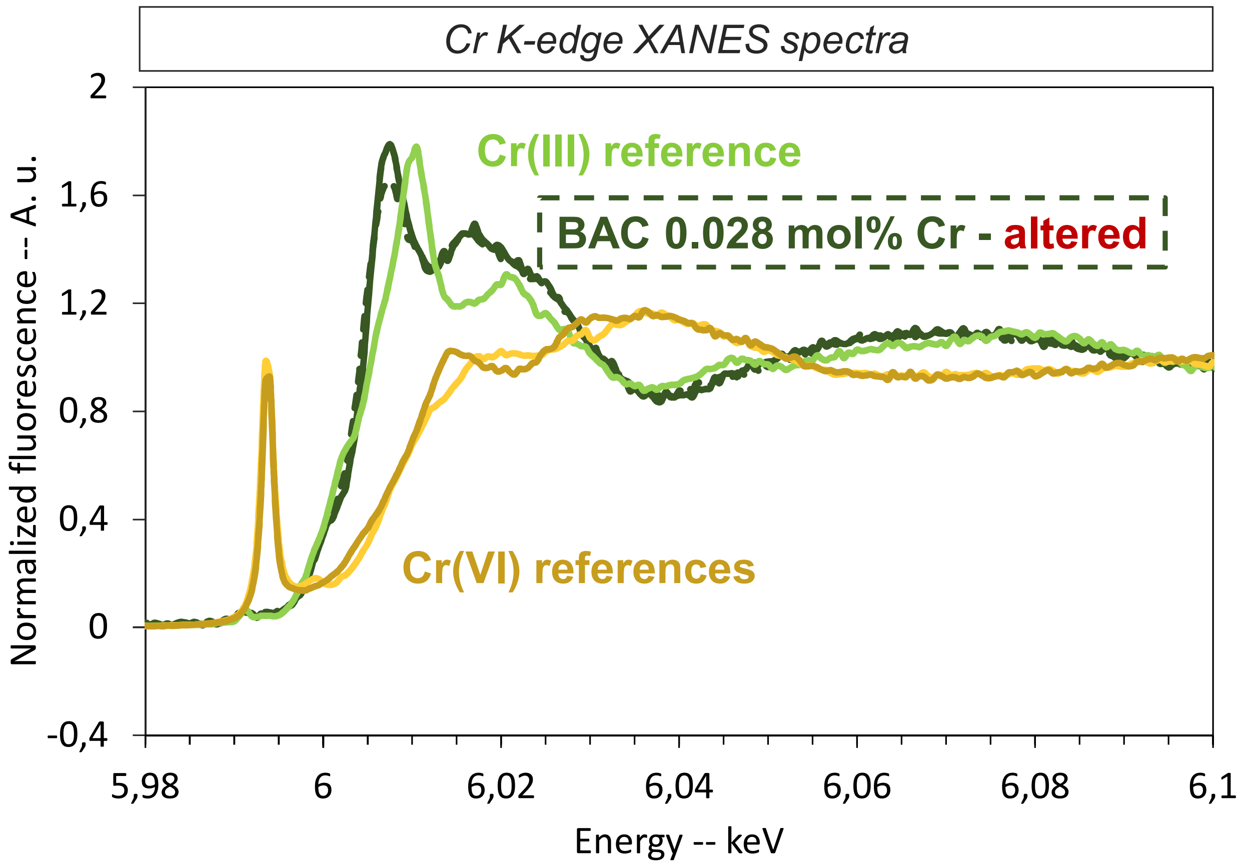
Speciation of chromium in lead crystal glasses

- ❑ Peak position at 6.0075 eV for Cr(III) reference
- ❑ Peak position at 5.9935 eV for Cr(VI) references
- ❑ **Cr(III) only is detected in pristine Cr-bearing glasses** (confirmed by optical absorption spectroscopy)



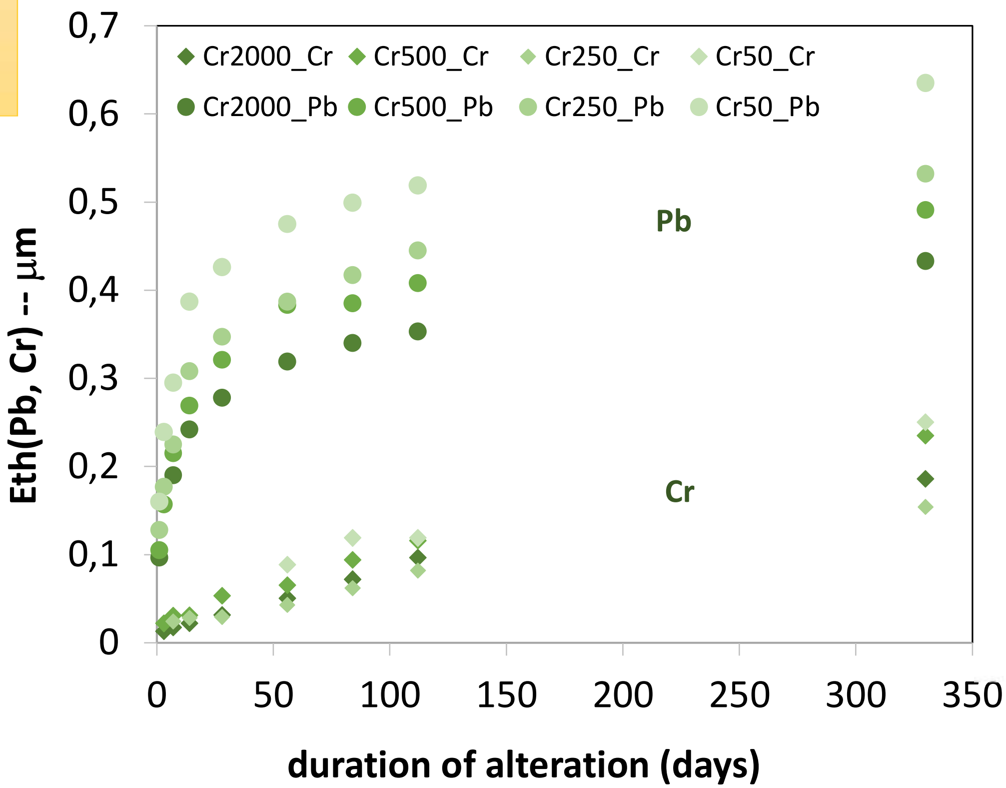
Speciation of chromium in lead crystal glasses

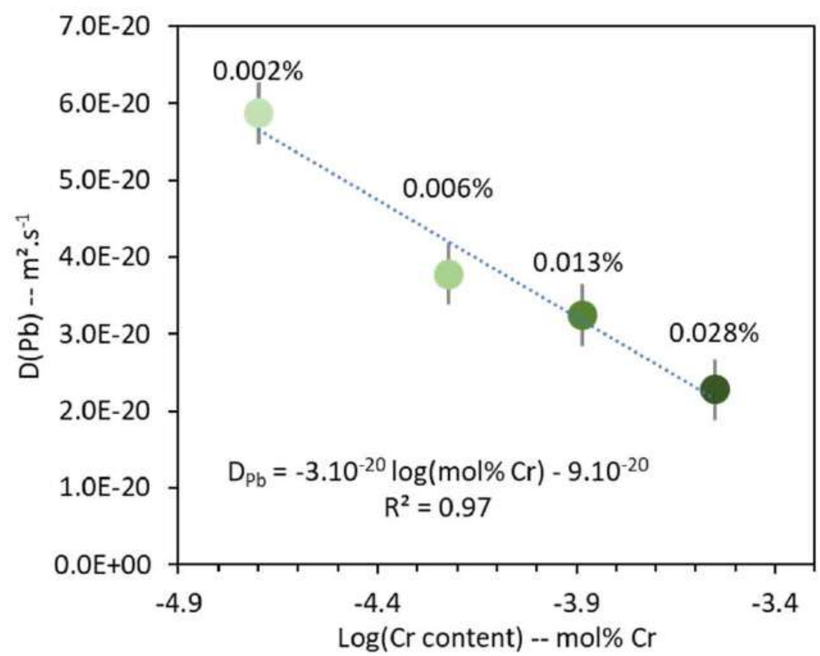
- Peak position at 6.0075 eV for Cr(III) reference
- Peak position at 5.9935 eV for Cr(VI) references
- **Cr(III) only is detected in pristine Cr-bearing glasses** (confirmed by optical absorption spectroscopy)
- **Cr^{3+} only, stable during alteration**



Leaching of lead crystal glass with Cr

Acetic acid
pH = 2.4, 70°C
S/V = 500 m^{-1}
330 days



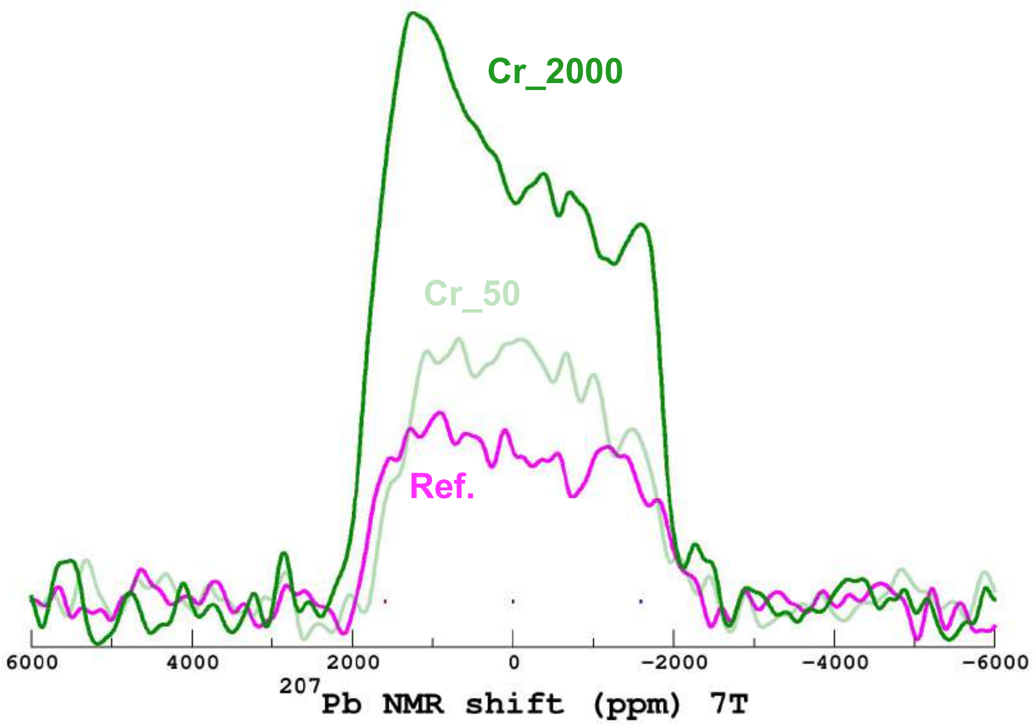


330 days
Cr leached: ~ 200 nm
Pb leached: ~ 500 nm

The addition of **Cr strongly impacts Pb release** by decreasing its leaching rate

Relationships between structure and durability of Cr-bearing lead crystal glass

^{207}Pb static NMR



Spectra are normalized to the same sample mass

- ❑ Pb NMR intensity signal increases with Cr content

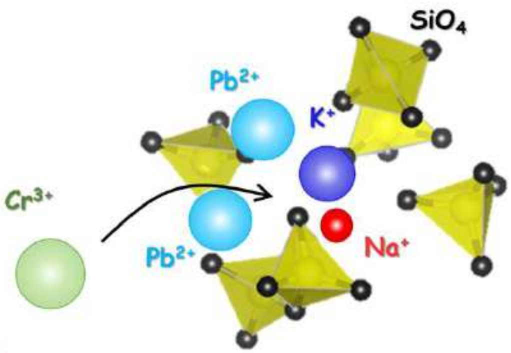
  Cr (paramagnetic): increases Pb relaxation time, and then the spectra intensity

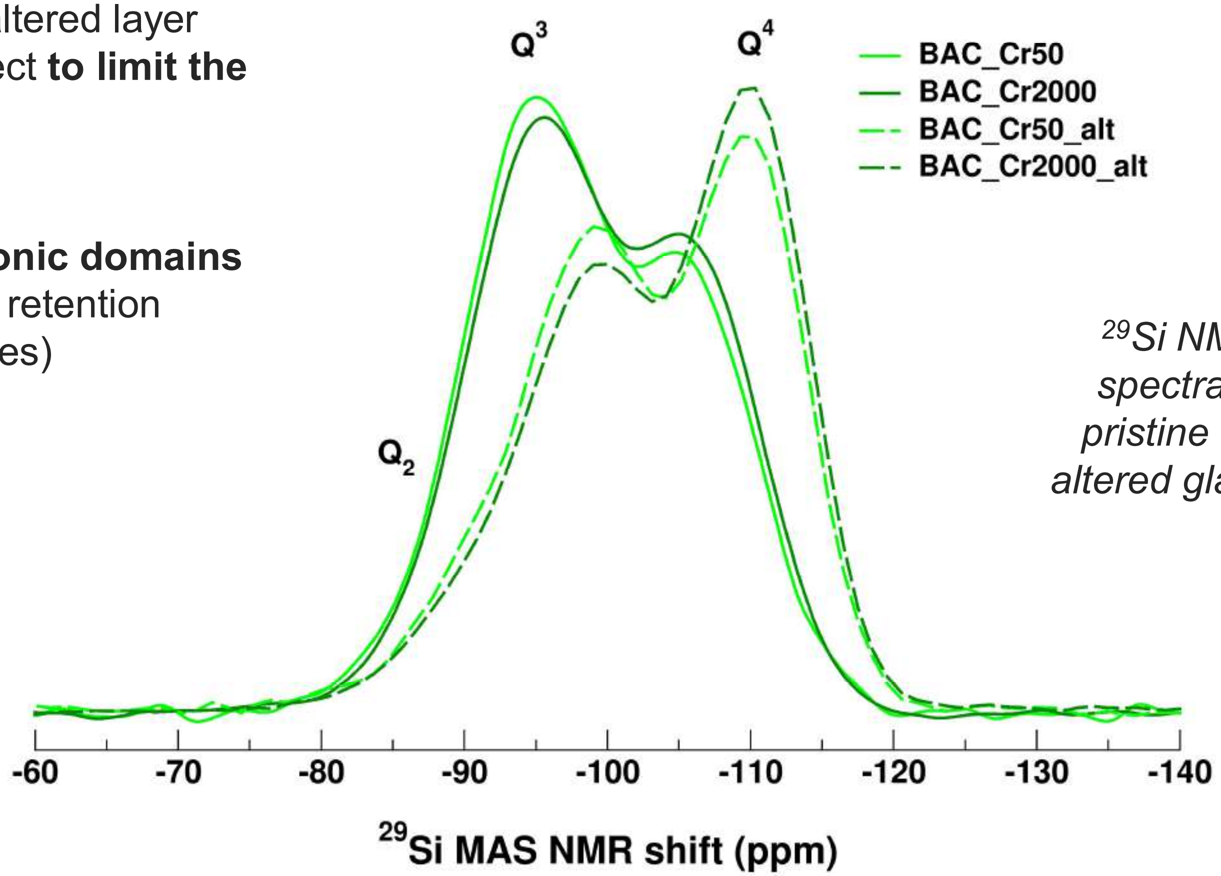
→ **proximity between Pb and Cr**

Impact of Cr on the structure of lead crystal glass during alteration

- Increase of **polymerization** in the altered layer that adds to the diffusive barrier effect **to limit the Pb release**

- **Cr is partially retained in the cationic domains** during alteration, also improving Pb retention (less accessible to protonated species)
  Cr(III) acts as a network hardener





^{29}Si NMR spectra of pristine and altered glasses

Conclusions

- Unique database on the **leaching behavior of industrial glass**
  - Commercial glass products: **resistant and durable materials** towards aggressive leaching alteration (> 1000 days)
- Overview of the **most suitable surface treatments to limit cation release**
  - **Dealkalization surface treatments last over time:** maintained while the thickness of the altered glass (700 nm) is greater than that of the treated layer (300 nm)
- Local structural configuration of potentially problematic cations
  - Correlations with **cation retention in glass**

Thank you

fédération des industries du verre

MFV LA MAISON FRANÇAISE DU VERRE

POCHET DU COURVAL

Pyrex 2019

Pochet 2020

Baccarat

Baccarat 2021

cea

arc

ARC 2022