Chemical durability of commercial silicate glasses and the impact of surface treatments

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Glasses for nuclear waste

Nuclear Waste Vitrification development TRL from 1 to 9

Lab scale		Mock up and modelling		Technologies development			Industrial support	
1	2	3	4	5	6	7	8	9

Etudes sur les matériaux vitreux (formulation, caractérisation et propriétés) et modélisation multi-échelle multi-physique

Approche expérimentale aux échelles laboratoire, maquette et pilote

Développement de procédés de vitrification et de traitement thermique des déchets

Glasses for nuclear waste

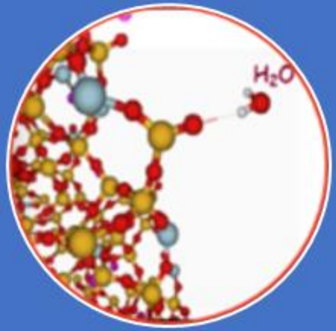
Soutien aux industriels

- Soutien aux campagnes industrielles
- Expertises

Développement et qualification de procédés

- Développement des équipements
- Robustesse procédé
- Livres de procédés

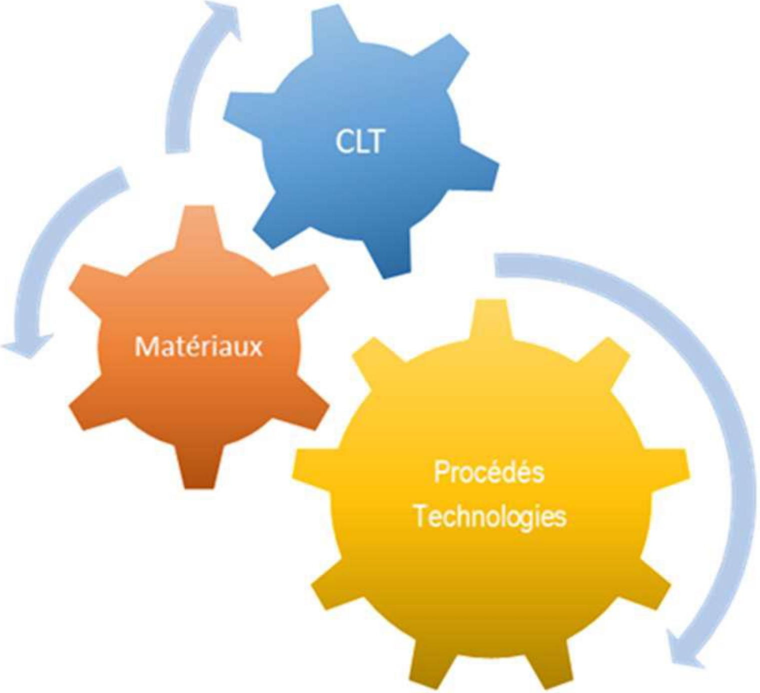
Expérimentations du laboratoire (actif/inactif) au pilote échelle 1



Modélisation et simulation multiéchelle

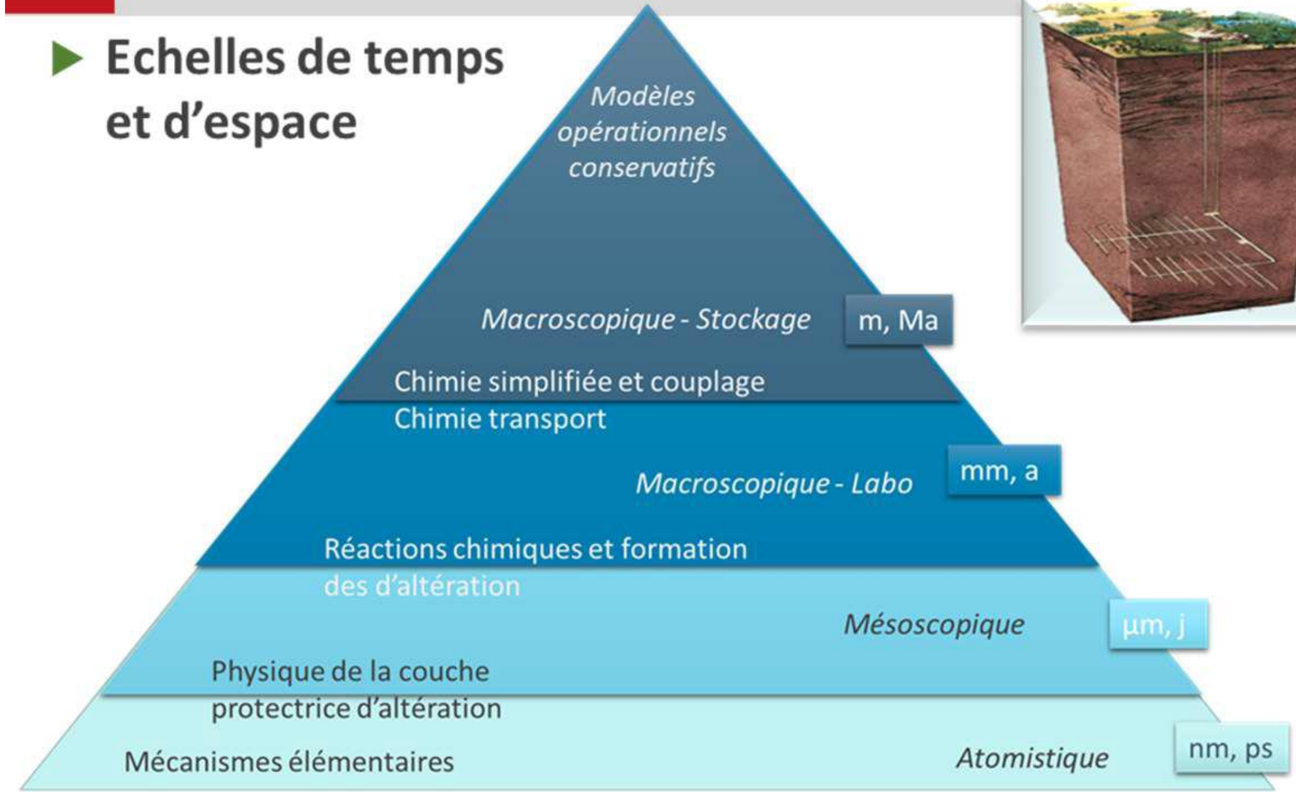
- Réactivité chimique
- Chimie-transport
- Magnéto-thermohydraulique
- Multiphysique

Procédé/Technologie – Matériaux - CLT



Modelisation tools for nuclear glass alteration

- Echelles de temps et d'espace



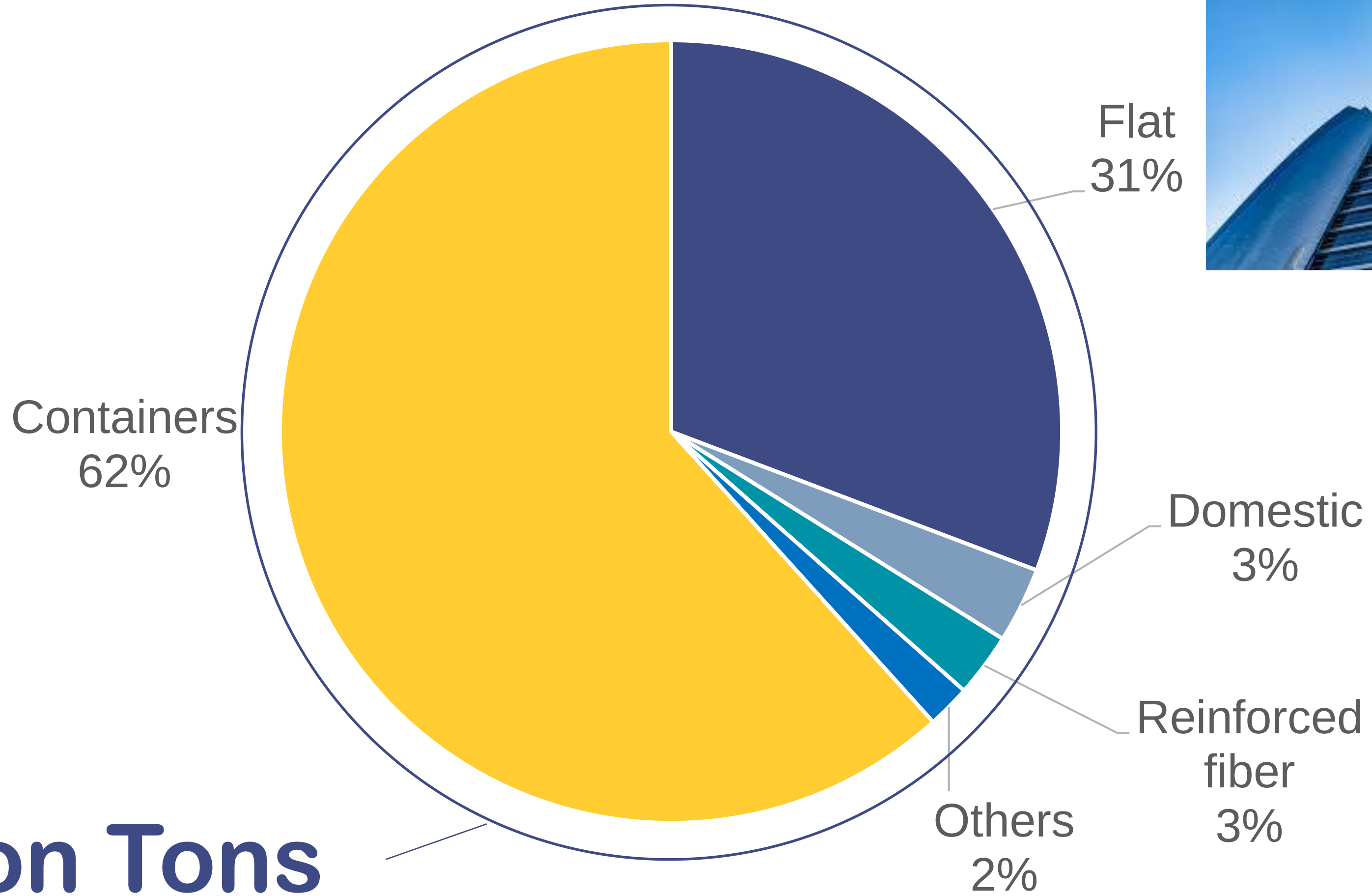
- Modèles

Outils échelle atomistiques DM, Ab Initio → Modélisation atomistique Monte CARLO → Modélisation géochimique couplée au transport → Outil simplifié MOS → Modèles opérationnels


bag
SEIGNEURS DES VENTS


bag
SEIGNEURS DES VENTS

Glass production in Europe in 2022



38 Million Tons

Definitions of glass

Glass is a hard transparent substance that is used to make things such as windows and bottles.

Glass is an amorphous material consisting of a network of atoms with no long range order which has undergone a glass transition.

Depending on its application, **glass** can be considered as a chemical and/or a finished product and is therefore regulated under the REACH regulation and submitted to the Food Contact Materials restriction.

REACH COMPLIANCE

FOOD SAFE

The challenges of glass alteration in contact with edibles

- In the 90's a series of article raised awareness about the potential dangers of lead crystal glass

Lead poisoning : legal threshold for Humans in France : **50 µg** of Pb per litre of blood

Lead exposure from lead crystal

JOSEPH H. GRAZIANO CONRAD BLUM

In a study of the elution of lead (Pb) from crystal decanters and glasses, port containing 89 µg Pb/l was placed in decanters and the Pb content of the wine rose steadily to 3518 µg/l after 4 months. Wines and spirits stored in crystal decanters for a long time contained Pb at concentrations up to 21 530 µg/l. In a short-term experiment white wine eluted small amounts of Pb from crystal glasses within minutes.

Lancet 1991; **337**: 141–42.

Historically, lead (Pb) accidentally found its way into wines in many ways, and wines to which lead salts were added as a sweetener may have contained as much as 20–30 mg/l of this toxic metal.[1,2] Lead crystal, a form of glass with high concentrations of Pb, was invented three centuries ago. The addition of Pb compounds to molten quartz yields a glass with high density and durability and a special brilliance. By the early 19th century severe occupational Pb intoxication was described in glassworkers in Paris.[3] In the United States the production of lead crystal did not develop until the late 19th century. Lead crystal vessels now contain 24–32% lead oxide (PbO), and we wondered if crystal decanters and glasses could be a source of Pb exposure for adults drinking from them.

Graziano, J. H. & Blum, C. Lead-exposure from lead crystal. *Lancet* **337**, 141–142 (1991).

The challenges of glass alteration in contact with edibles

- In the 90’s a series of article raised awareness about the potential dangers of lead crystal glass
- Currently standards of control for the release of potentially toxic elements and regulations are being discussed

FOR FOOD CONTACT

69/493/EEC
Lead crystal glass : 24 wt% PbO

84/500/EEC & DGCCRF directive
Pb, Cd (Al, As, Co, Cr^{VI})

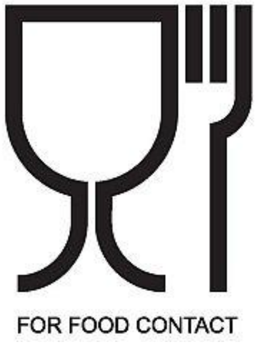
Current authorized limit: 4 mg/L of Pb

Proposed limit: 0.01 mg/L of Pb

Normalized tests (room temperature, 24h)

The challenges of glass alteration in contact with edibles

- In the 90's a series of article raised awareness about the potential dangers of lead crystal glass
- Currently standards of control for the release of potentially toxic elements and regulations are being discussed
- **European authorities are stressing on the need for manufacturers to demonstrate the innocuousness of their products upon normal use**



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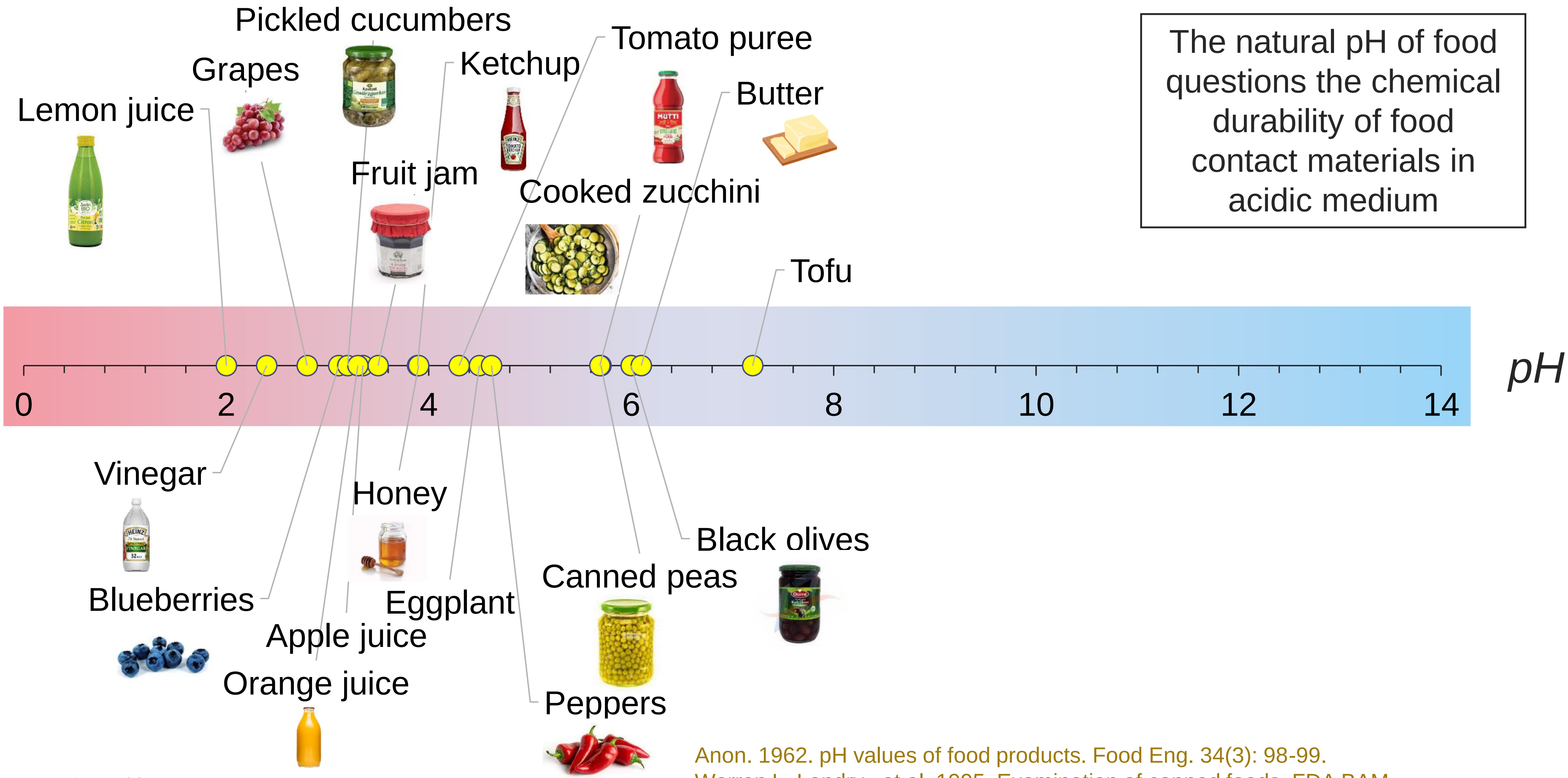
Normalized tests (room temperature, 24h)

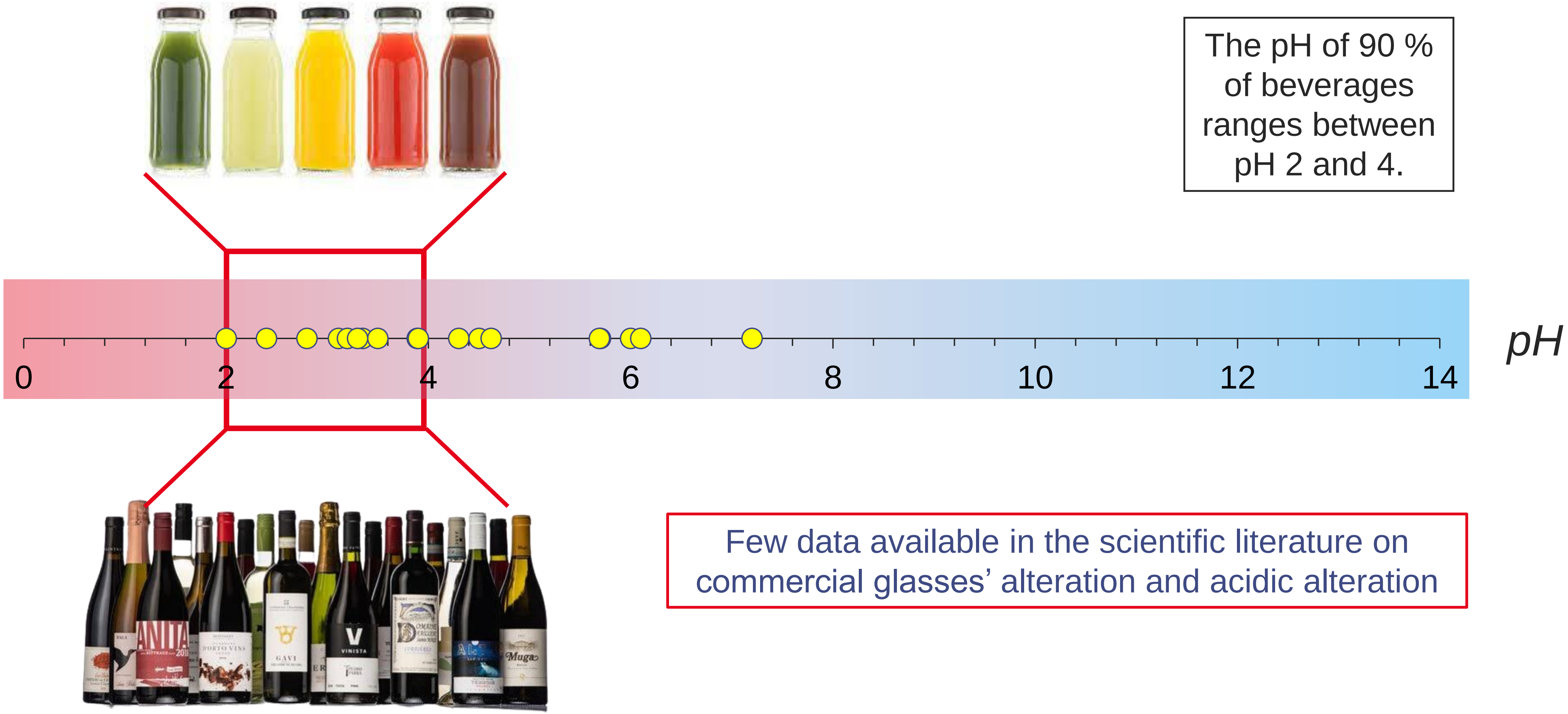
Glass containers for packaging



The natural pH of food questions the chemical durability of food contact materials in acidic medium

Anon. 1962. pH values of food products. Food Eng. 34(3): 98-99.
Warren L. Landry , et al. 1995. Examination of canned foods. FDA BAM, AOAC International.

Glass containers for packaging



The pH of 90 % of beverages ranges between pH 2 and 4.

Few data available in the scientific literature on commercial glasses' alteration and acidic alteration

Reddy, A., Norris, D. F., Momeni, S. S., Waldo, B. & Ruby, J. D. The pH of beverages available to the American consumer. *J Am Dent Assoc* **147**, 255–263 (2016).

Objectives

What is the long term durability of commercial glasses in contact with edibles or cosmetic products?

- Understand the long term alteration mechanism of commercial glasses in acidic medium

The glass industry constantly works with surface treatments, which impact on glass alteration remains unknown

- Assess the durability of glasses with industrial surface teatments

anr agence nationale de la recherche AU SERVICE DE LA SCIENCE

Industrial partners

LA MAISON FRANÇAI DU VERRE

CRISTAL & VERRE

arc

POCHET DU COURVAL

Baccarat

Behaviour of Industrial Glasses During Aqueous Dissolution (BIGDAD)

coordinator

IPGP

Université Paris Cité

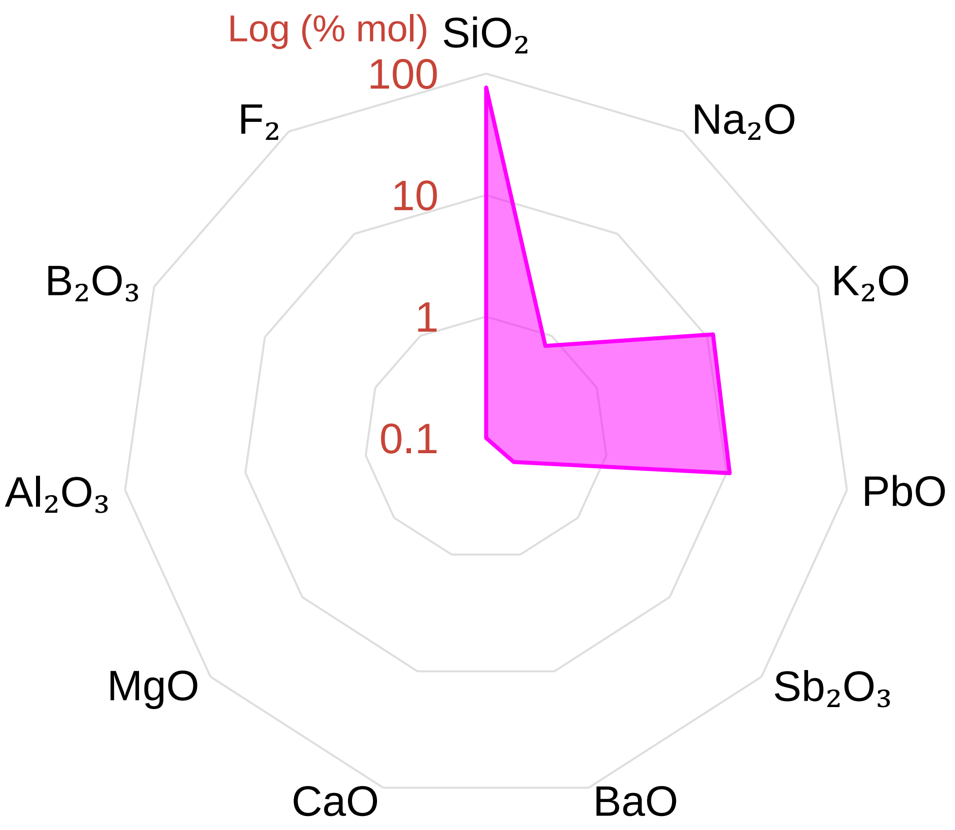
cea

Université Gustave Eiffel

Industrial glasses under study

Glass A	Lead crystal

	% mol	% wt
SiO_2	77.1	56.7
Na_2O	0.8	0.6
K_2O	11.3	13.0
PbO	10.6	29.0
Sb_2O_3	0.2	0.7



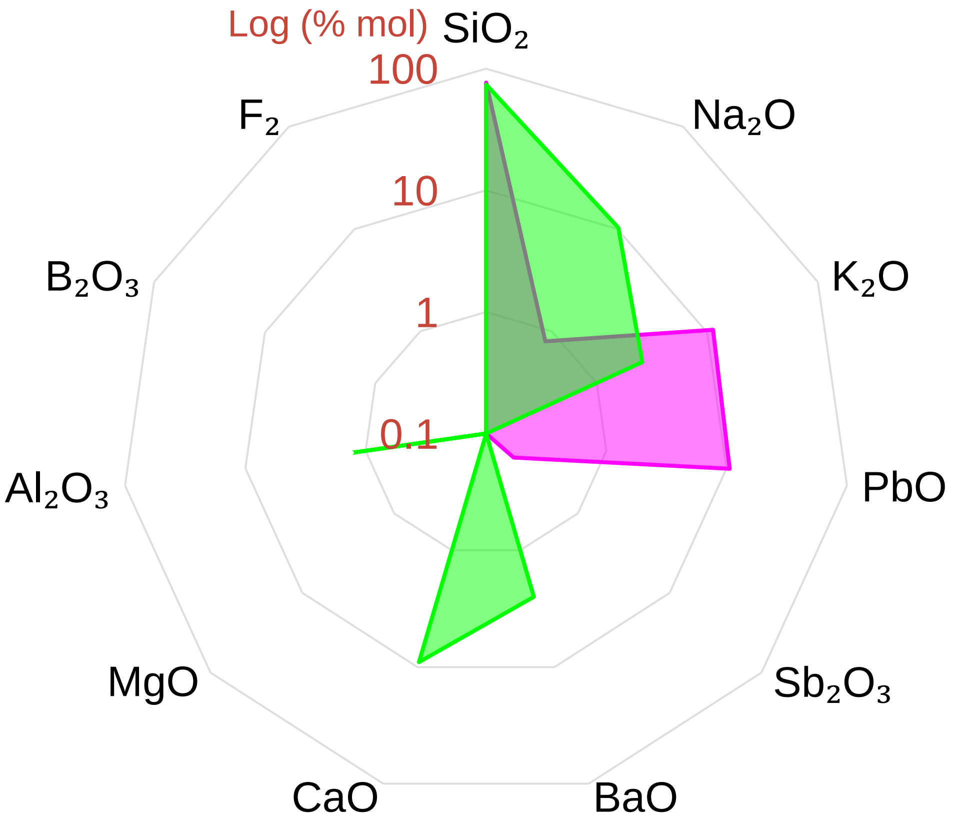
Baccarat

Industrial glasses under study

Glass A	Lead crystal

Glass B	Barium glass

	% mol	% wt
SiO_2	74.2	70.0
Na_2O	8.3-10.3	8.0-10.0
Al_2O_3	< 1.3	< 2.0
CaO	9.0-11.0	8.0-10.0
MgO		
BaO	0.5-2.5	4.0-6.0
K_2O	2.5-4.5	4.0-6.0



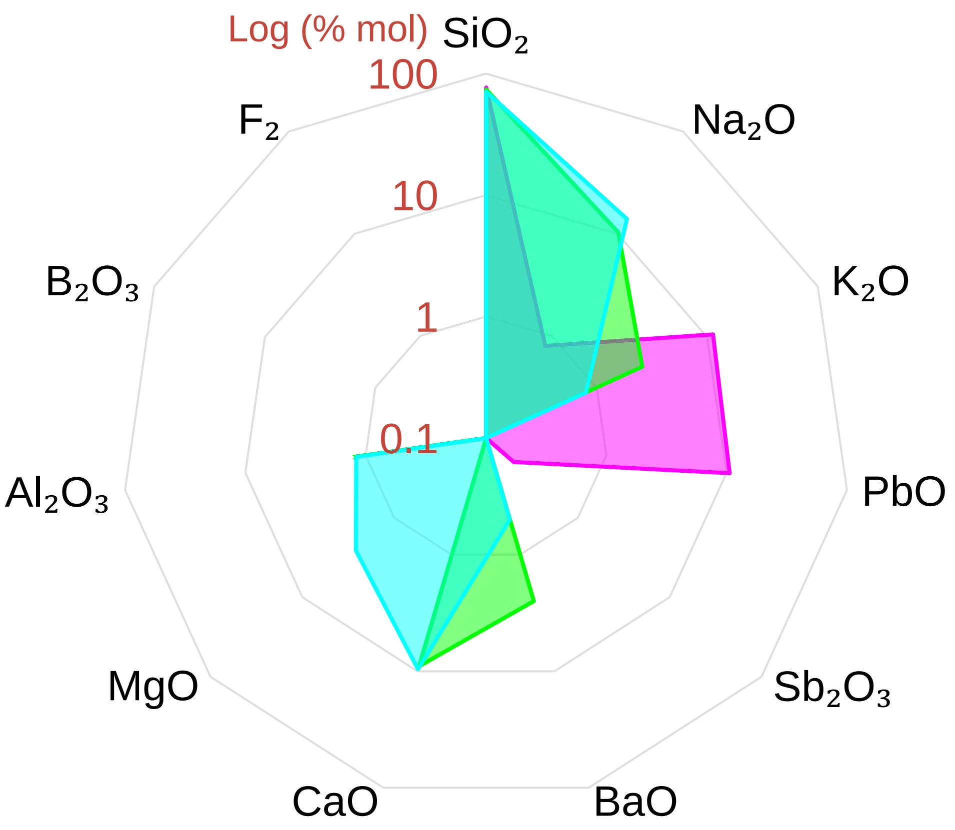
Industrial glasses under study

Glass A	Lead crystal

Glass B	Barium glass

Glass C	Soda-lime

	% mol	% wt
SiO_2	70.9	70.3
Na_2O	13.0-15.0	13.0-15.0
Al_2O_3	< 1.3	< 2.0
CaO	9.0-11.0	8.0-10.0
MgO	2.0-4.0	1.0-3.0
BaO	< 1.0	< 2.0
K_2O	< 1.0	< 2.0



POCHET DU COURVAL

Industrial glasses under study

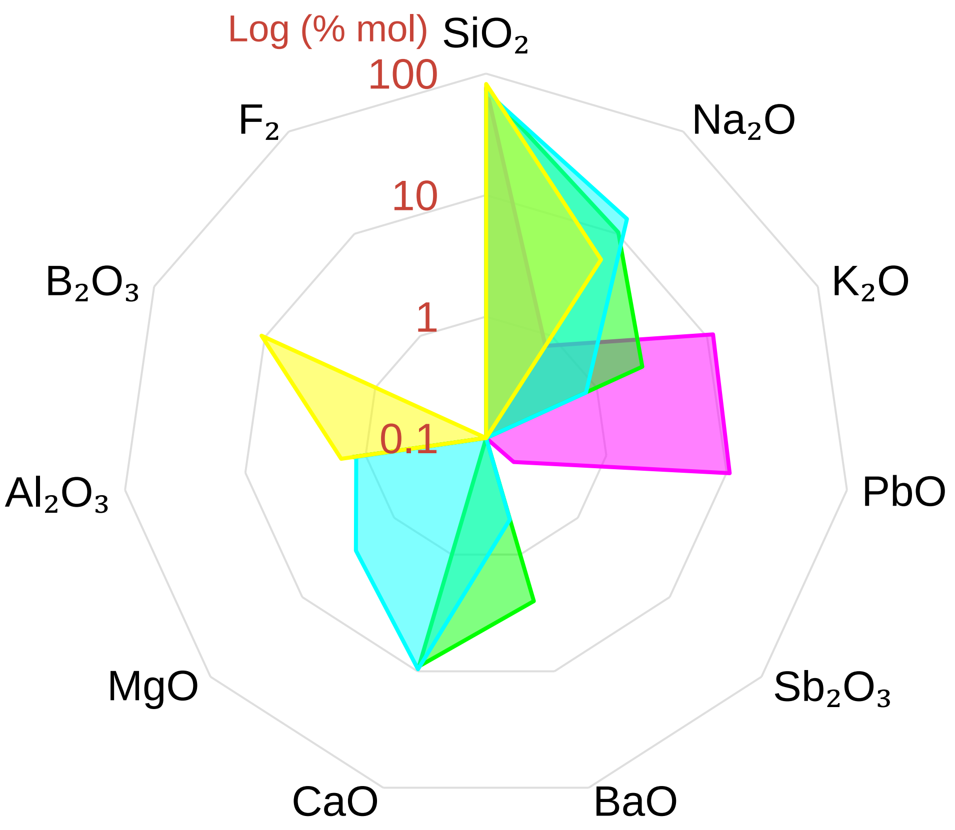
Glass A	Lead crystal

Glass B	Barium glass

Glass C	Soda-lime

Glass D	Borosilicate

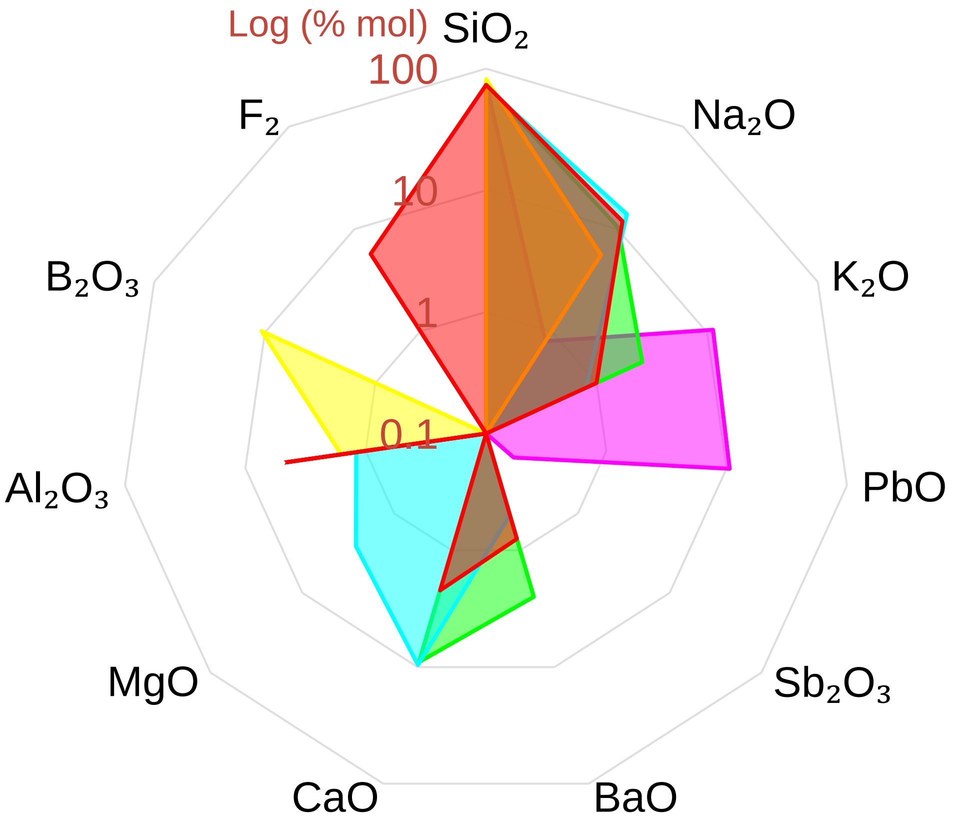
	% mol	% wt
SiO_2	82.1	79.7
Na_2O	5.6	5.6
B_2O_3	10.7	12.0
Al_2O_3	1.6	2.6



Industrial glasses under study

Glass A	Lead crystal
Glass B	Barium glass
Glass C	Soda-lime
Glass D	Borosilicate
Glass O	Opal cristal.

	%mol	%wt
SiO_2	73.6	71.3
Na_2O	11.9	11.9
Al_2O_3	4.8	7.9
CaO	2.2	2
BaO	0.8	2.0
K_2O	1	1.5
F_2	5.7	3.5



Summary

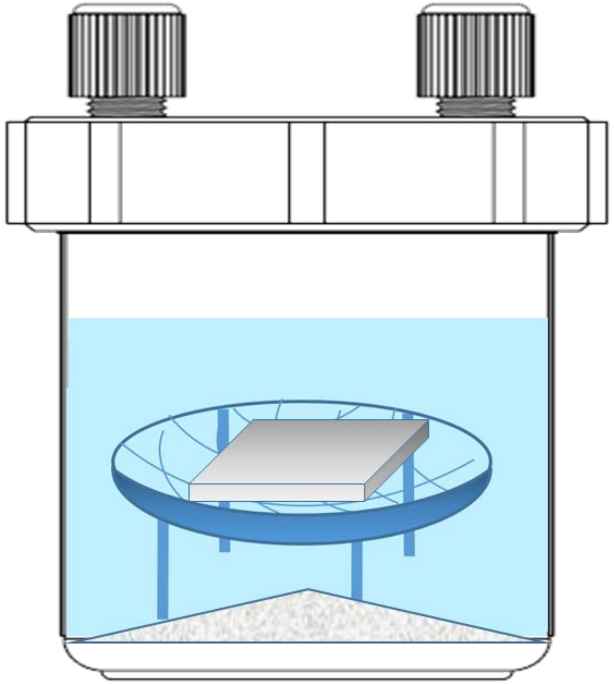
1. Alteration of reference base glasses
2. Alteration of glasses with surface treatments
3. Alteration of glass-ceramic with and without surface treatments
4. The impact of colorant on the durability of lead crystal glass: the case of chromium

1. Alteration of reference base glasses for 3 years

- ❑ Experimental approach
- ❑ Structure and alteration of the silicate network
- ❑ Leaching of the most mobile species: sodium
- ❑ Individual leaching behaviour of glasses A to D

Experimental approach

Acetic acid 4 % vol
pH = 2.4
70°C
$SA_{geo}/V \approx 50\ m^{-1}$



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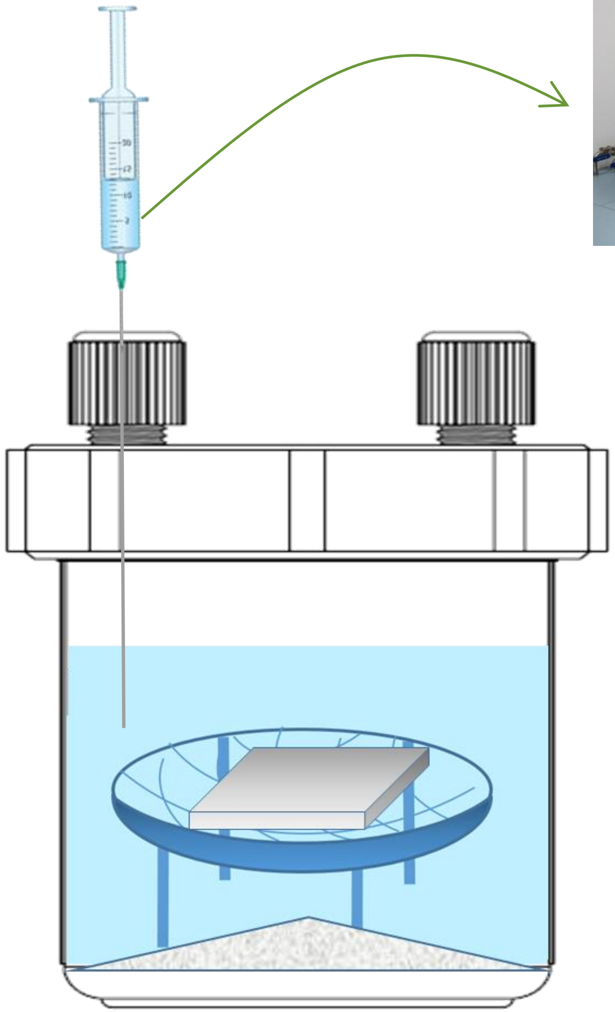

- ICP-AES

Kinetics of alteration

0 days **3 years**

alteration

Experimental approach

Acetic acid 4 % vol
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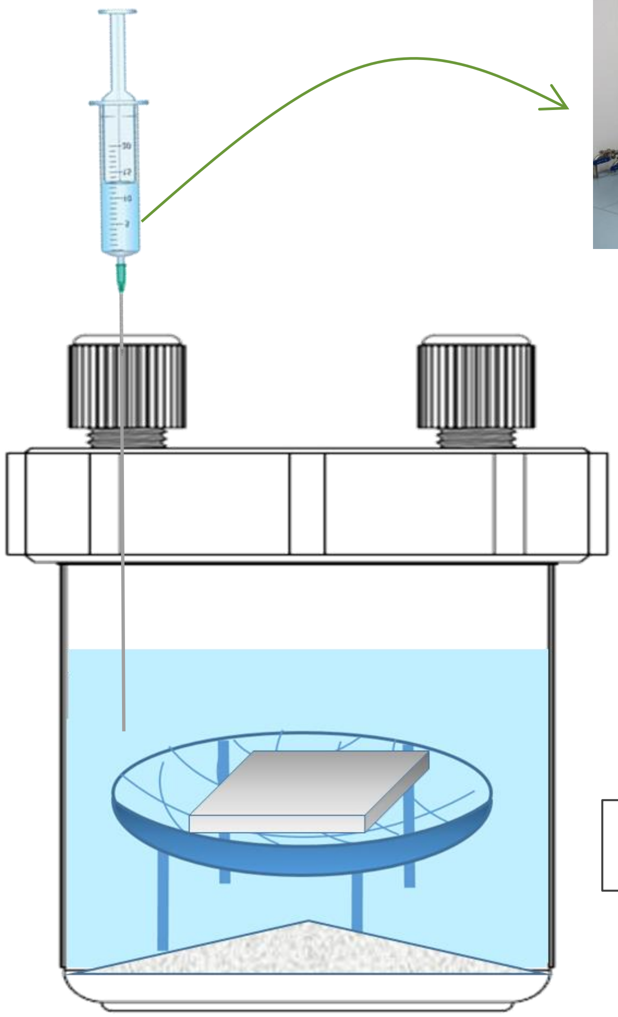
$SA_{geo}/V \approx 50\ m^{-1}$



- ICP-AES

Kinetics of alteration

- Solid state NMR
- SEM

- ToF SIMS

- Solid state NMR

- SEM

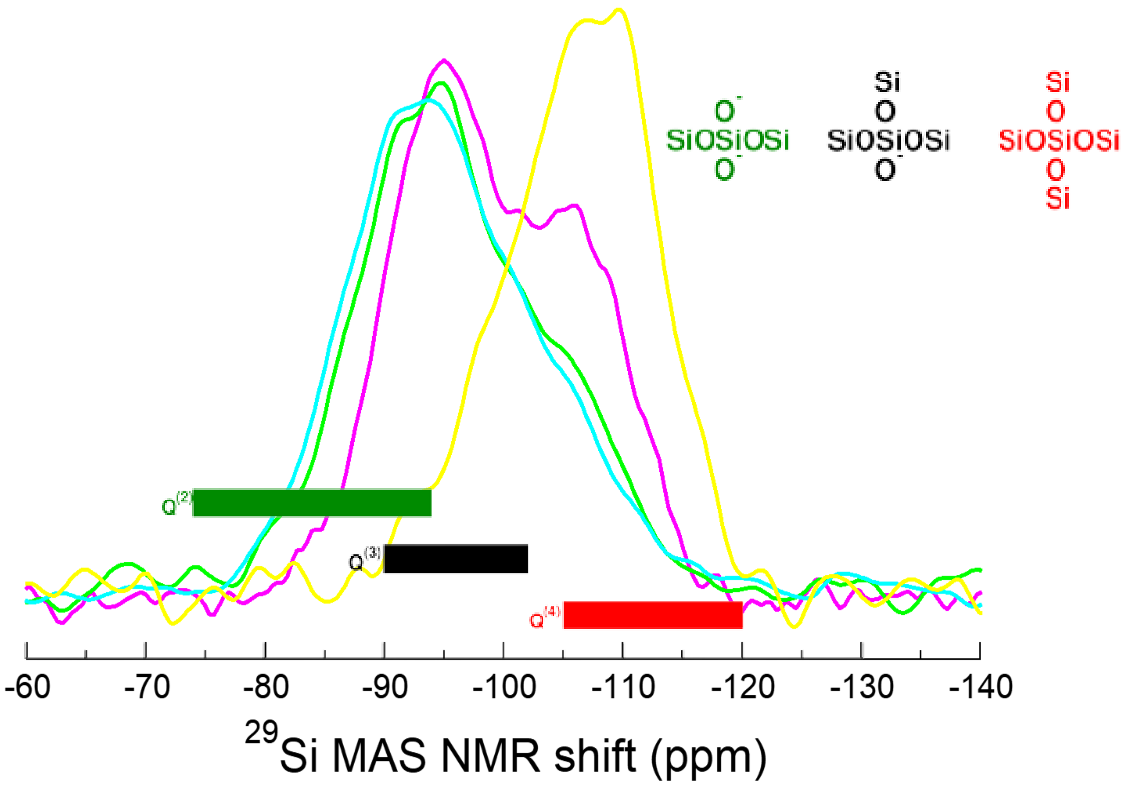
0 days **231 days** **969 days** **3 years**

alteration

Structure and leaching of the silicate network

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

^{29}Si NMR spectra of the pristine glasses



Structure and leaching of the silicate network

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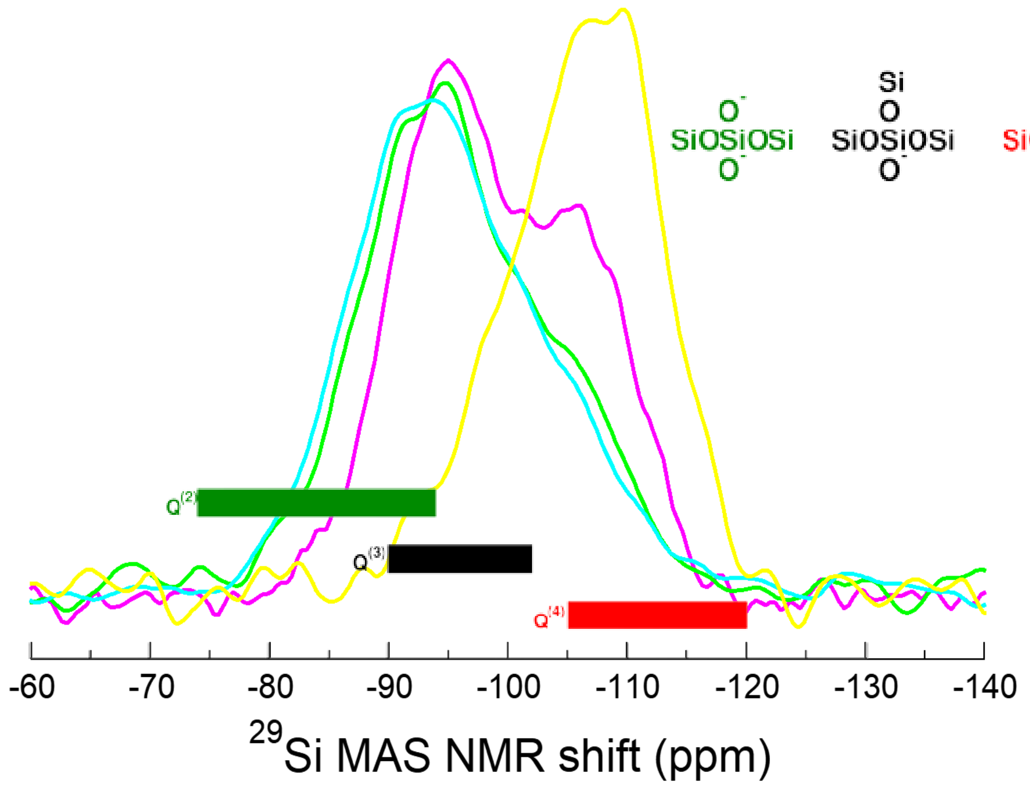
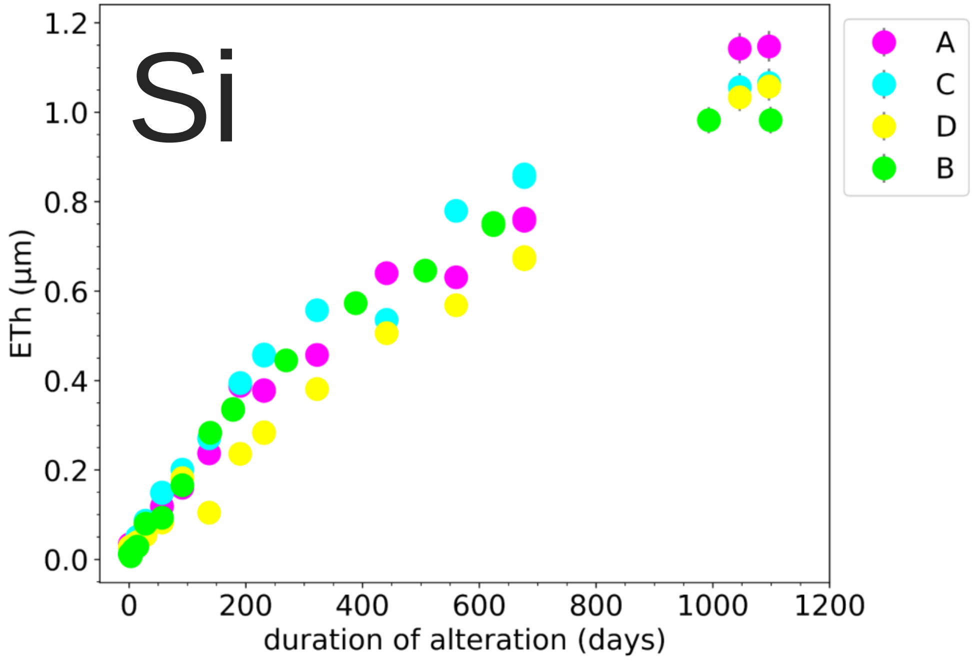
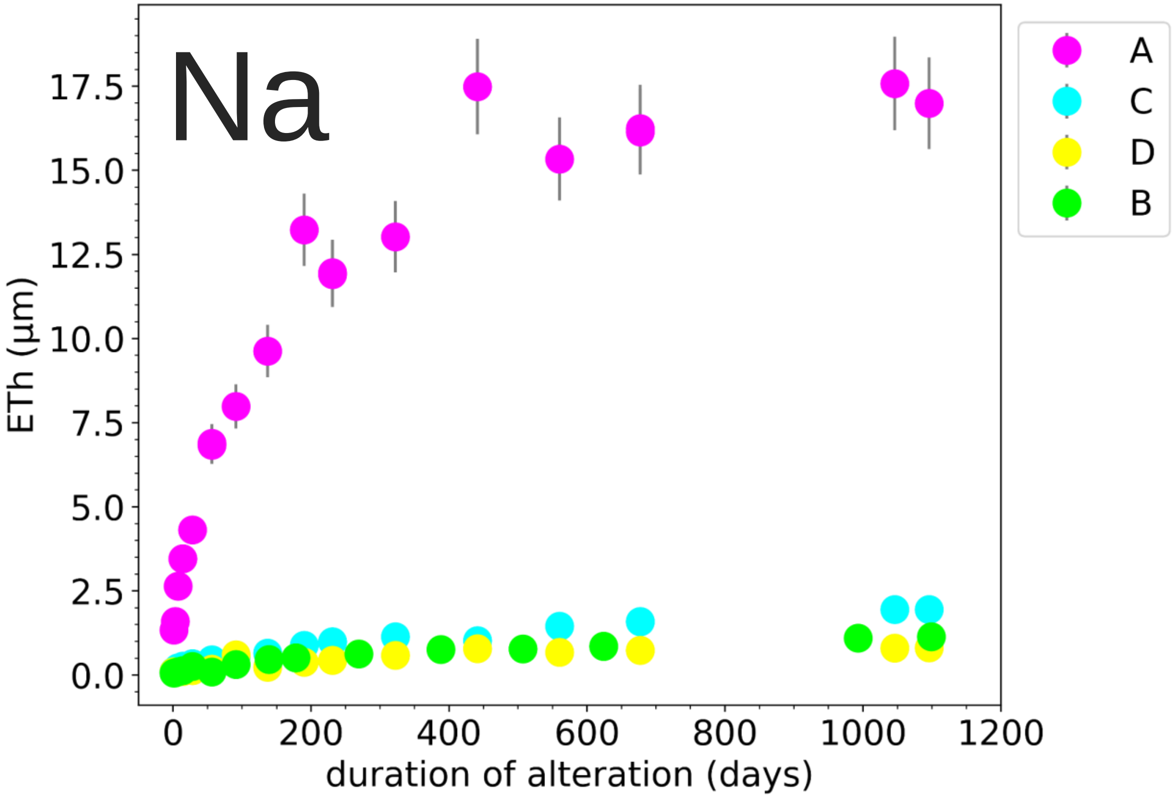




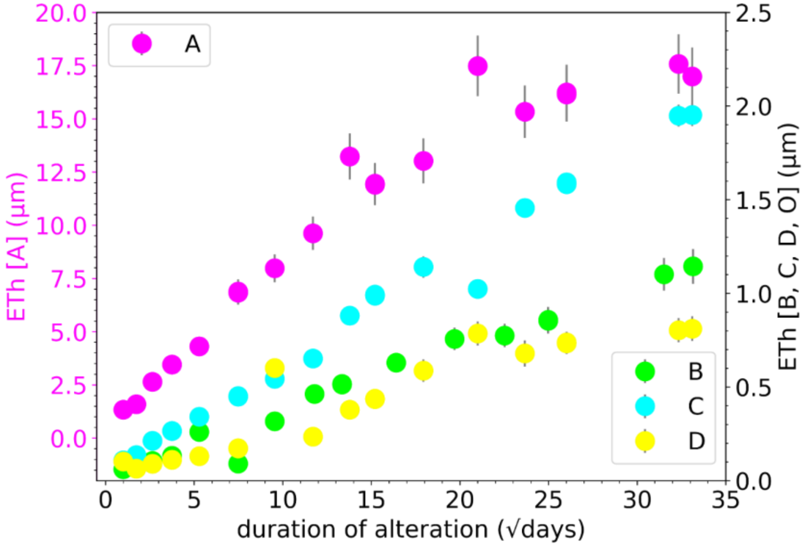
- Hydrolysis of the Si network
- All glasses release Si at very similar rates
- 1 nm of glass dissolved per day whatever the initial polymerization degree of the silicate network

Leaching of the tracing element of alteration

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

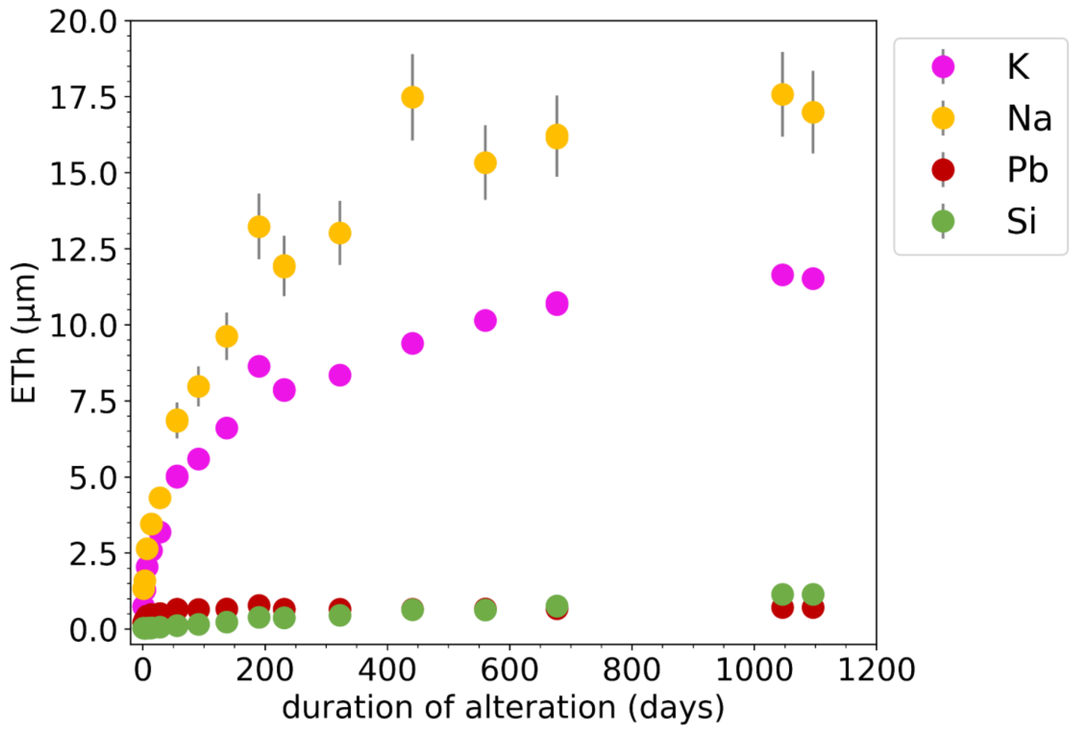


- Interdiffusion mechanism : exchange of Na from the glass and protons from the solution with different diffusion rates
- Decreasing over time
- Different orders of magnitude between various glasses

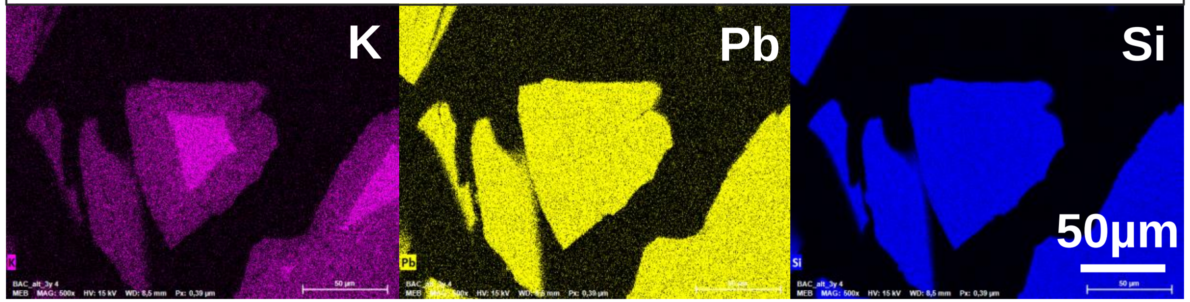


Alteration of lead crystal glass

Glass A | Lead crystal



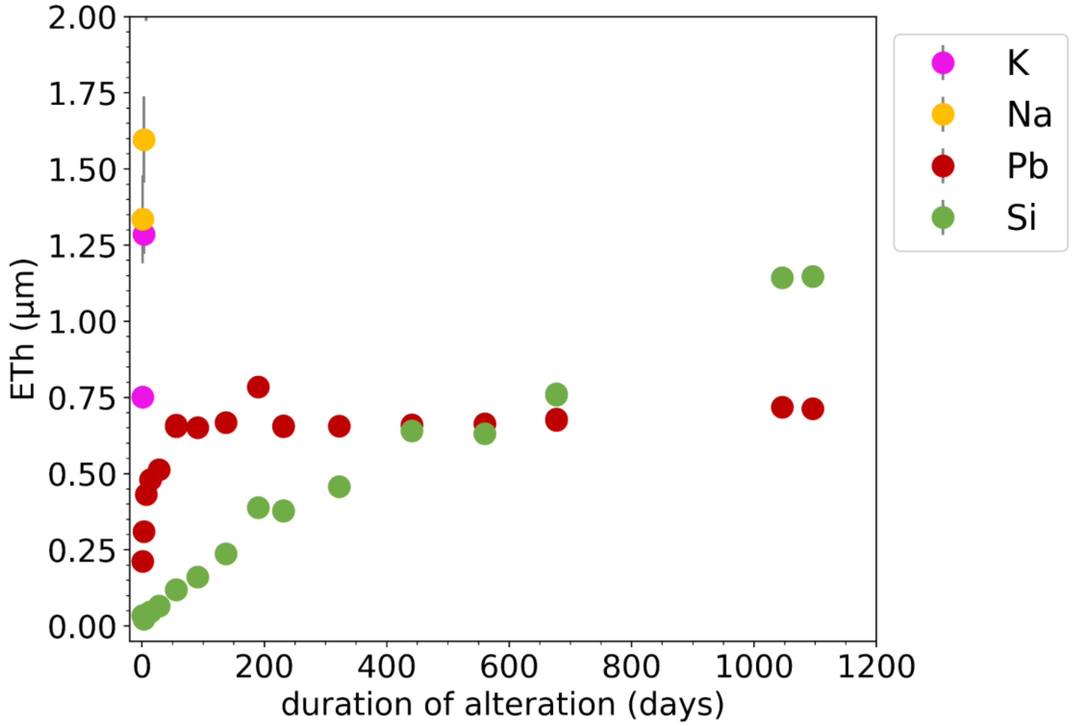
SEM-EDS after 3 years of alteration



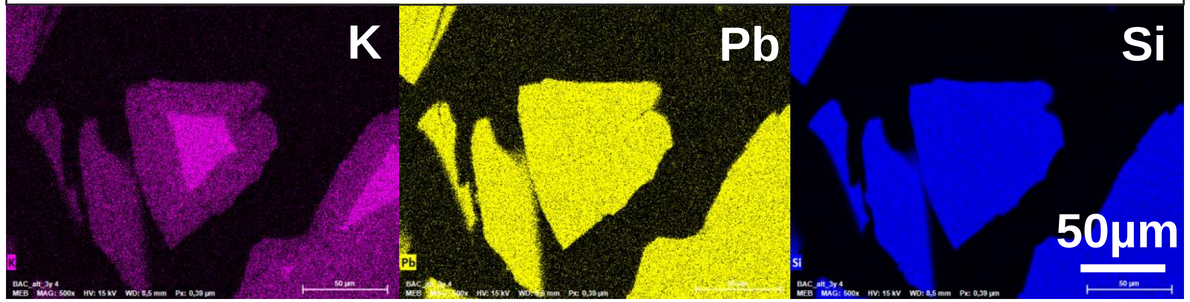
- 15 µm of glass in surface hydrated and depleted in Na and K after 3 years of alteration

Alteration of lead crystal glass

Glass A | Lead crystal



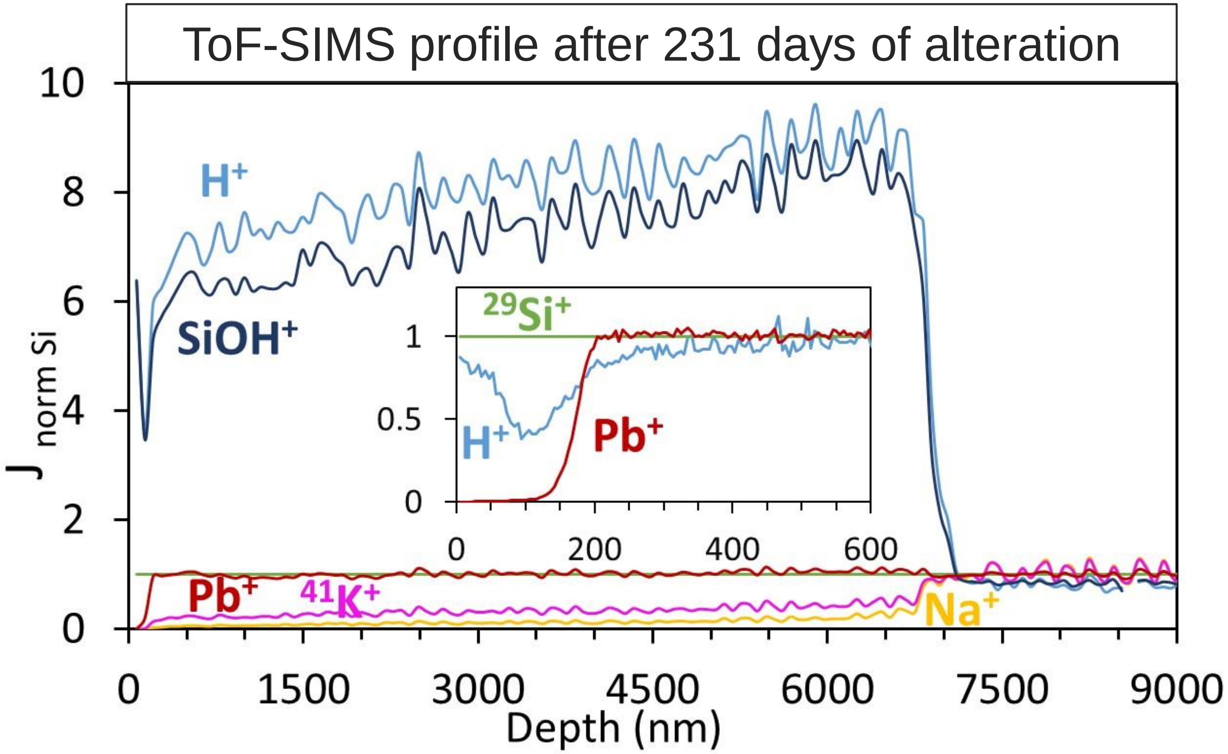
SEM-EDS after 3 years of alteration

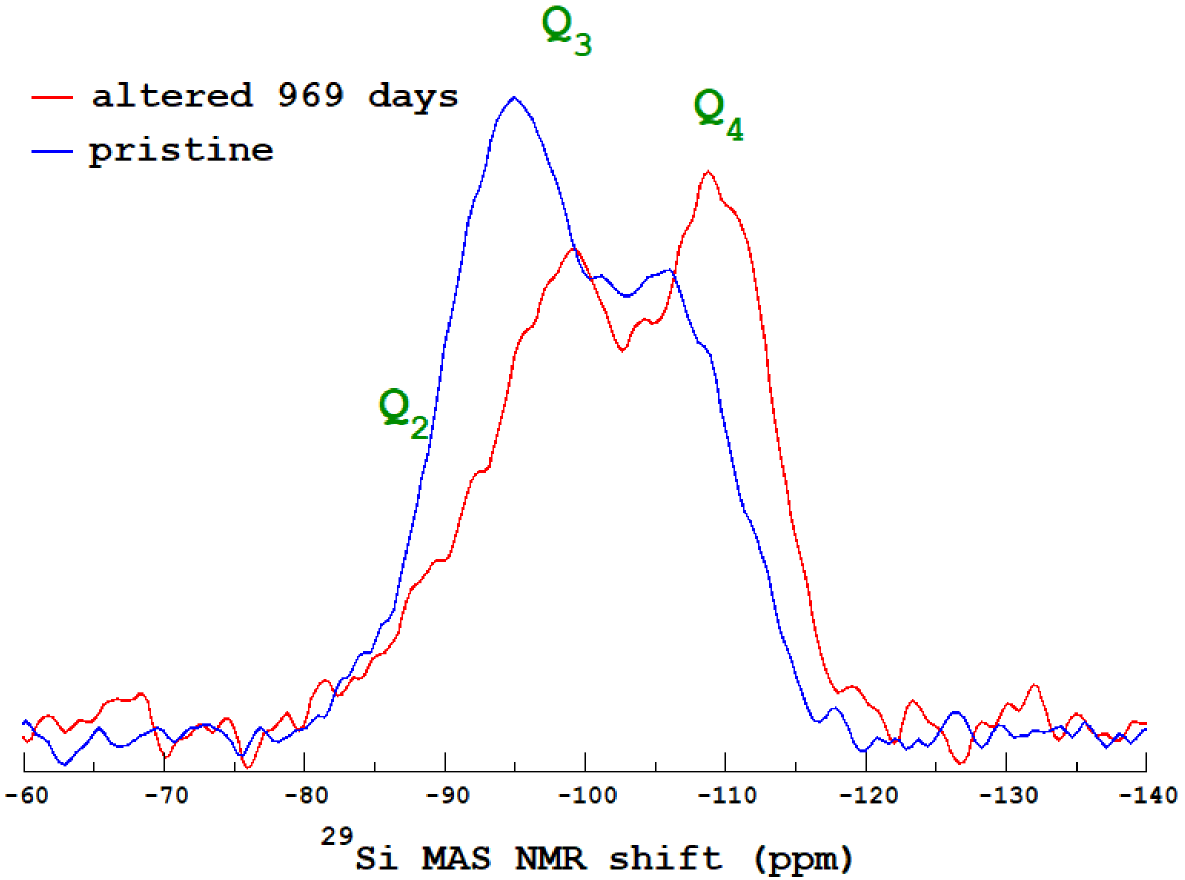


- 15 µm of glass in surface hydrated and depleted in Na and K after 3 years of alteration
- Pb retained in the altered layer with stable thanks to network repolymerization forming a diffusive barrier

Alteration of lead crystal glass

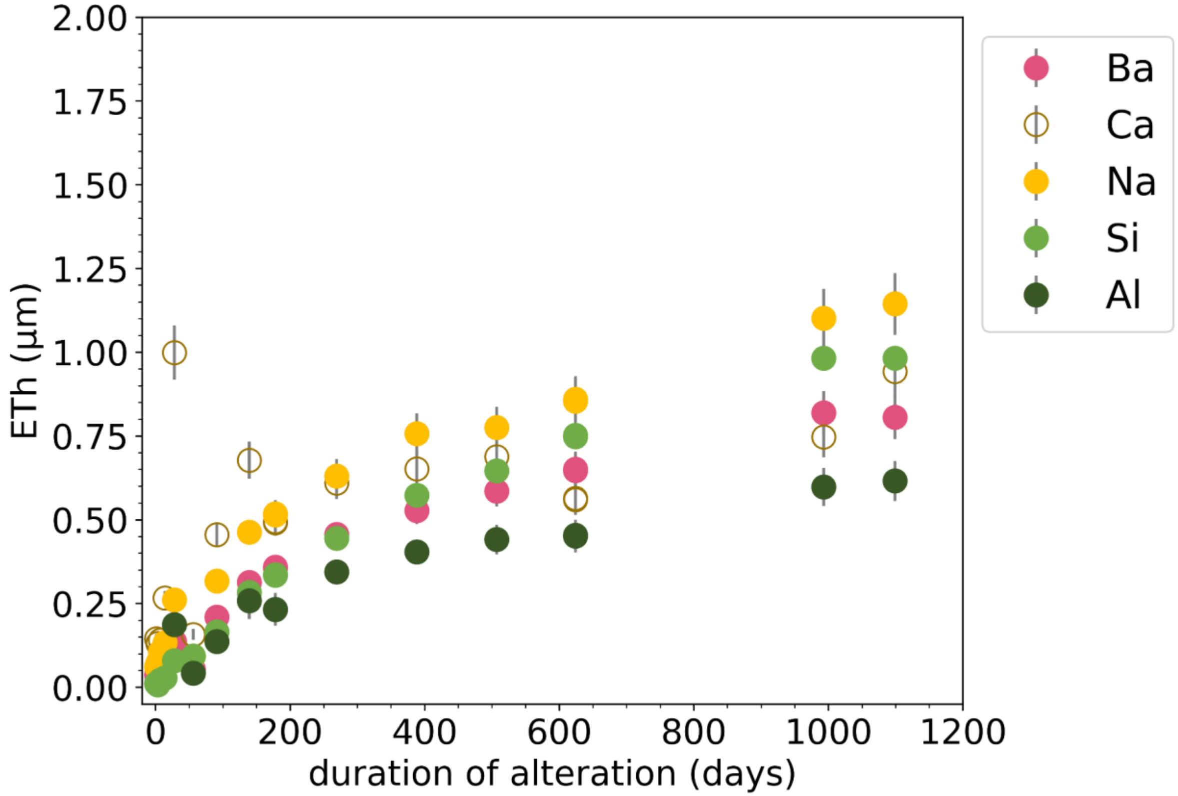
Glass A | Lead crystal



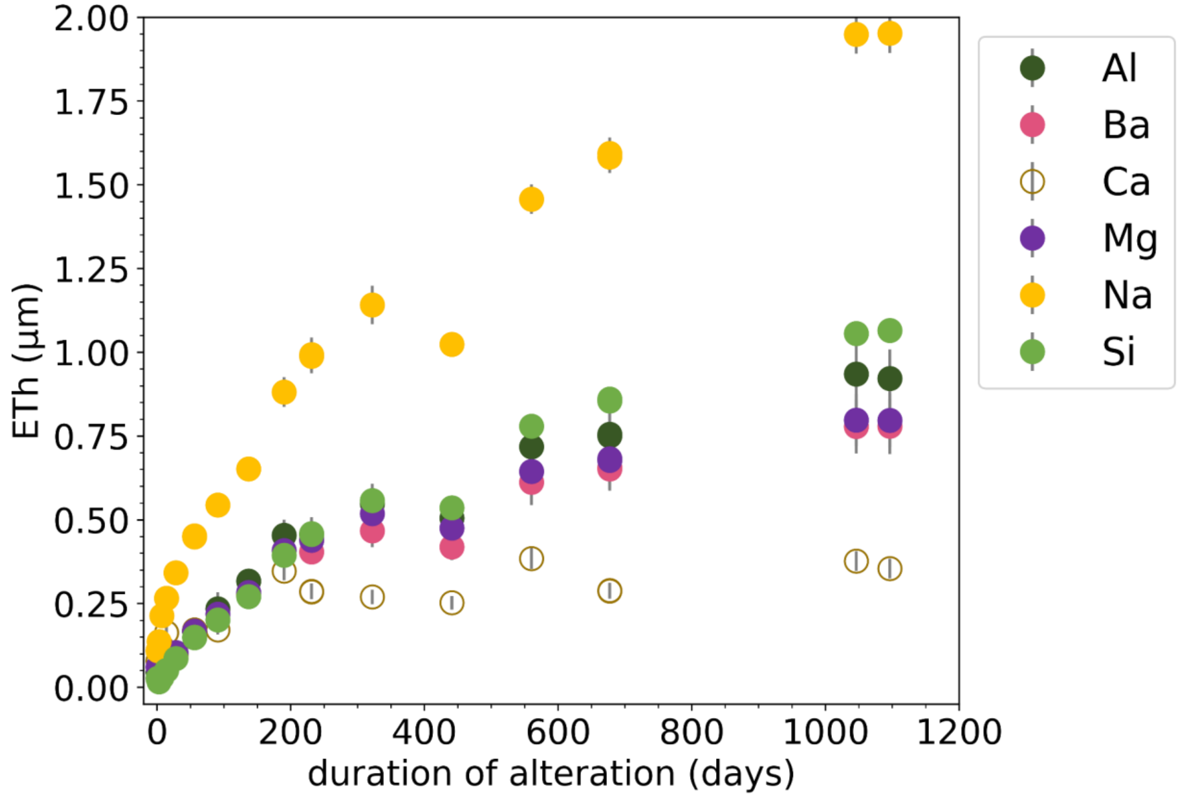


Alteration of sodalime based glasses

Glass B | Barium glass



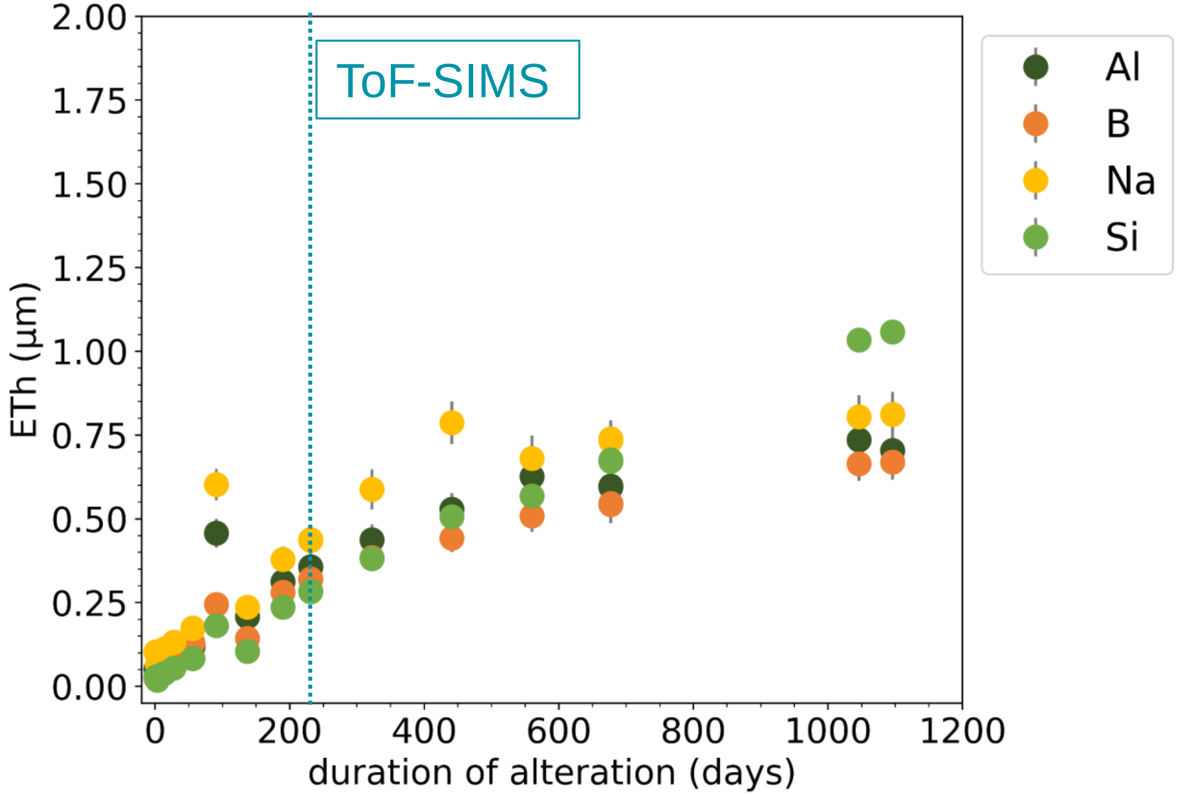
Glass C | Soda-lime



- Equivalent thicknesses obtained from leaching solutions confirmed by ToF-SIMS
- Higher leaching rate of Na in glass C because of the slightly less polymerized silicon network
- Remaining altered layer of 1 µm observed by SEM-EDS at the surface of glass C after 3 years of alteration

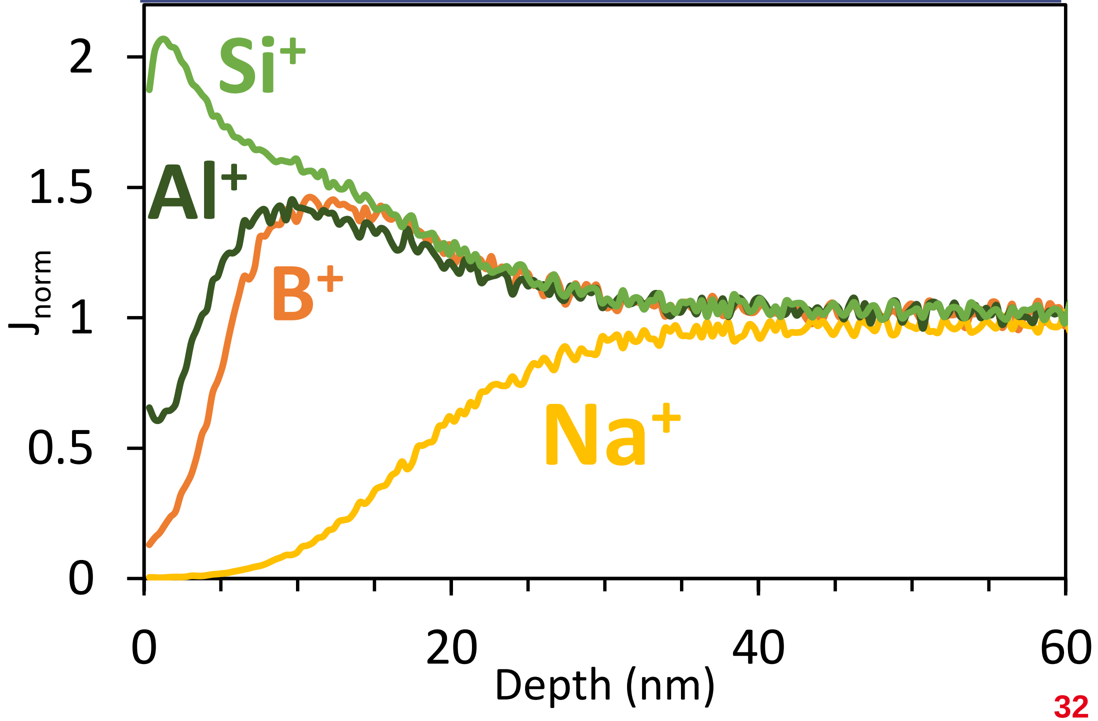
Alteration of borosilicate glass

Glass D	Borosilicate



- Congruent alteration
- Driven by the hydrolysis of the Si network
- Thin dealkalized surface layer

ToF-SIMS profile after 231 days of alteration



Alteration of commercial glasses in acid

- In acidic medium, the rate of hydrolysis is the lowest, and depends solely on the leaching parameters (T°, pH, S/V)

- The glass structure is reflected by the rate of ion-exchange and interdiffusion
  - In highly dealkalized altered layers, recondensation of the silicate units can occur, forming a diffusion barrier towards Pb
  - In glasses with varying contents of network modifiers (alkalis and alkaline earth elements), the rate of interdiffusion depends on the polymerization of the silicate network
  - In highly polymerized glasses, the rate of interdiffusion is almost equivalent to the rate of hydrolysis

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

How surface treatments affects glass alteration rates and mechanisms ?

2. Alteration of glasses with surface treatments

- Surface treatments under study
- Thin layers: the example of Sn deposit
- Impact of surface treatments on the release of Pb, Ba and B

Surface treatments under study

Chemical deposits — Si, Sn, Ti

Chemical attacks — PA, CEMa, CEMb

Surface coatings (CVD) — Si, Sn, Ti

SiO_2	Mechanical properties	~ 10 nm	450 °C
SnO_2	Grip for cold end treatments, avoid scratches	~ 10 nm	450 °C
TiO_2	Aesthetics	~ 250 nm	600 °C

Surface treatments under study

Chemical deposits: Si, Sn, Ti

Chemical attacks: PA, CEMa, CEMb

PA → Acidic etching

Before

After

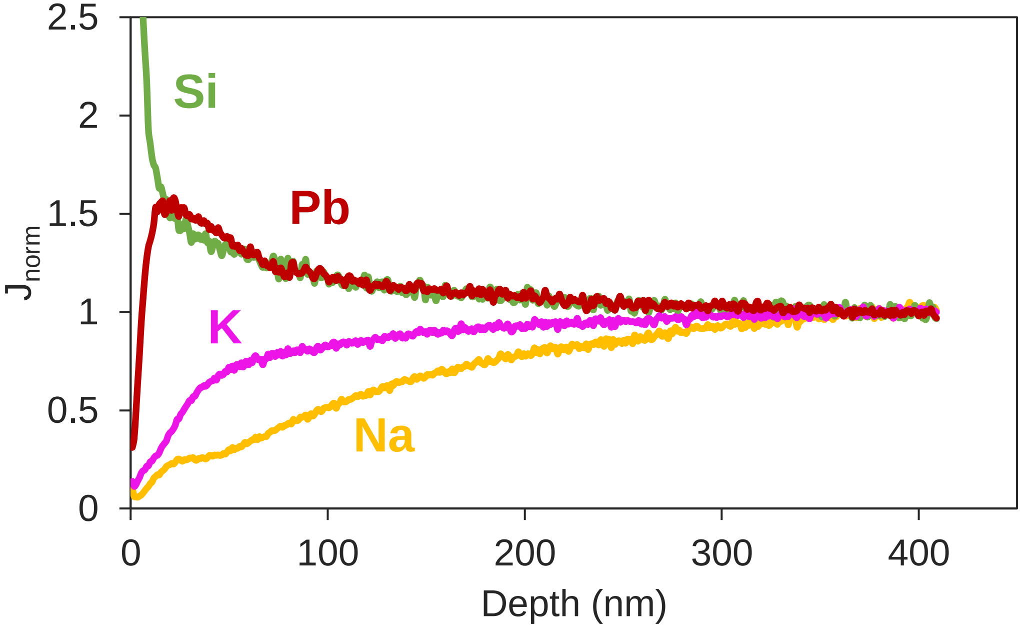
Surface treatments under study

Chemical deposits: Si, Sn, Ti

Chemical attacks: PA, CEMa, CEMb

Also known as « cementation »

Dealkalinization of the surface by SO_2 vapour treatment



Glass A | Lead crystal

ToF SIMS profile of pristine glass A treated with CEMb

Surface treatments under study

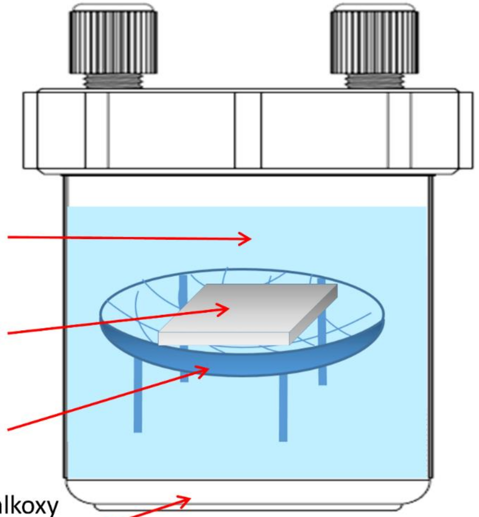
Chemical deposits: Si, Sn, Ti

Chemical attacks: PA, CEMa, CEMb

Surface treatments under study

Chemical deposits: Si, Sn, Ti

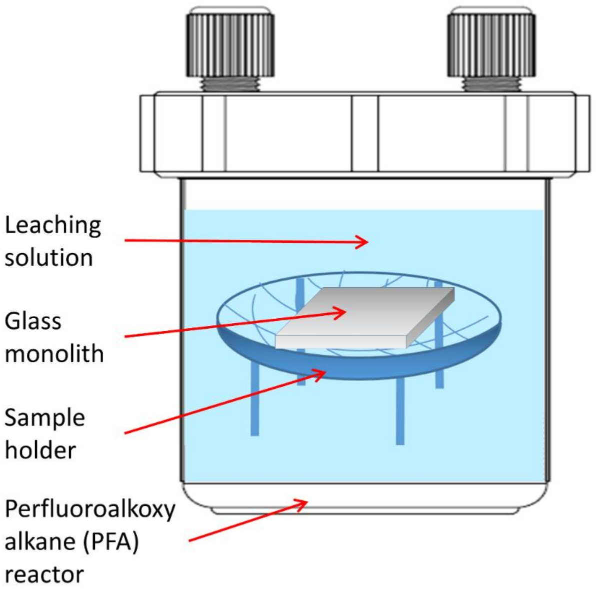
Chemical attacks: PA, CEMa, CEMb



Surface treatments under study

Chemical deposits | Chemical attacks

Ø	Si	Sn	Ti	PA	CEMa	CEMb



Acetic acid 4%vol
pH = 2.4
70°C
$S_{geo}/V = 2.5\ m^{-1}$

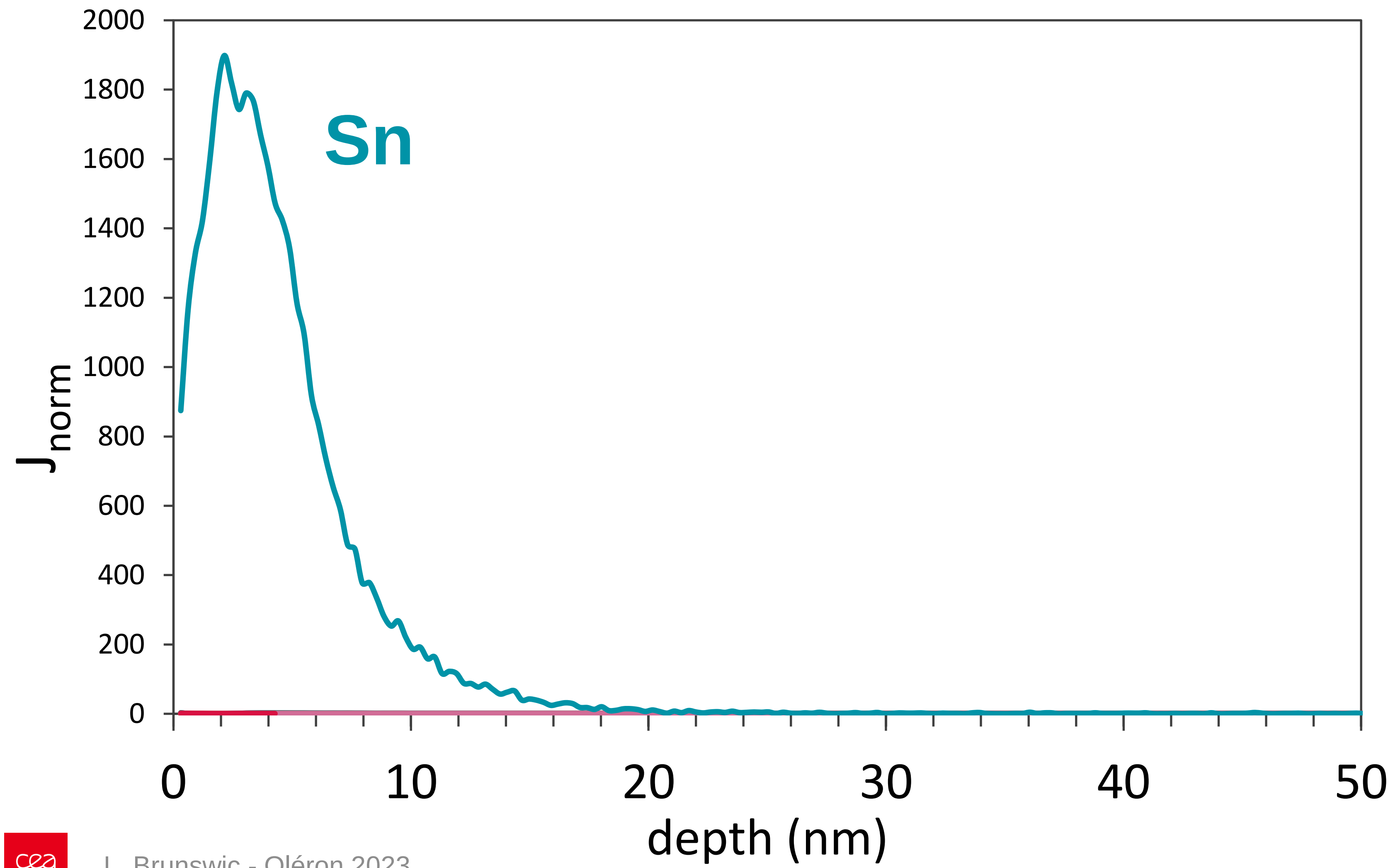
For 470 days !

Solution alteration analysis: ICP-MS

Characterizations by:
SEM-EDS and ToF SIMS

Impact of Sn coating on pristine soda-lime glass

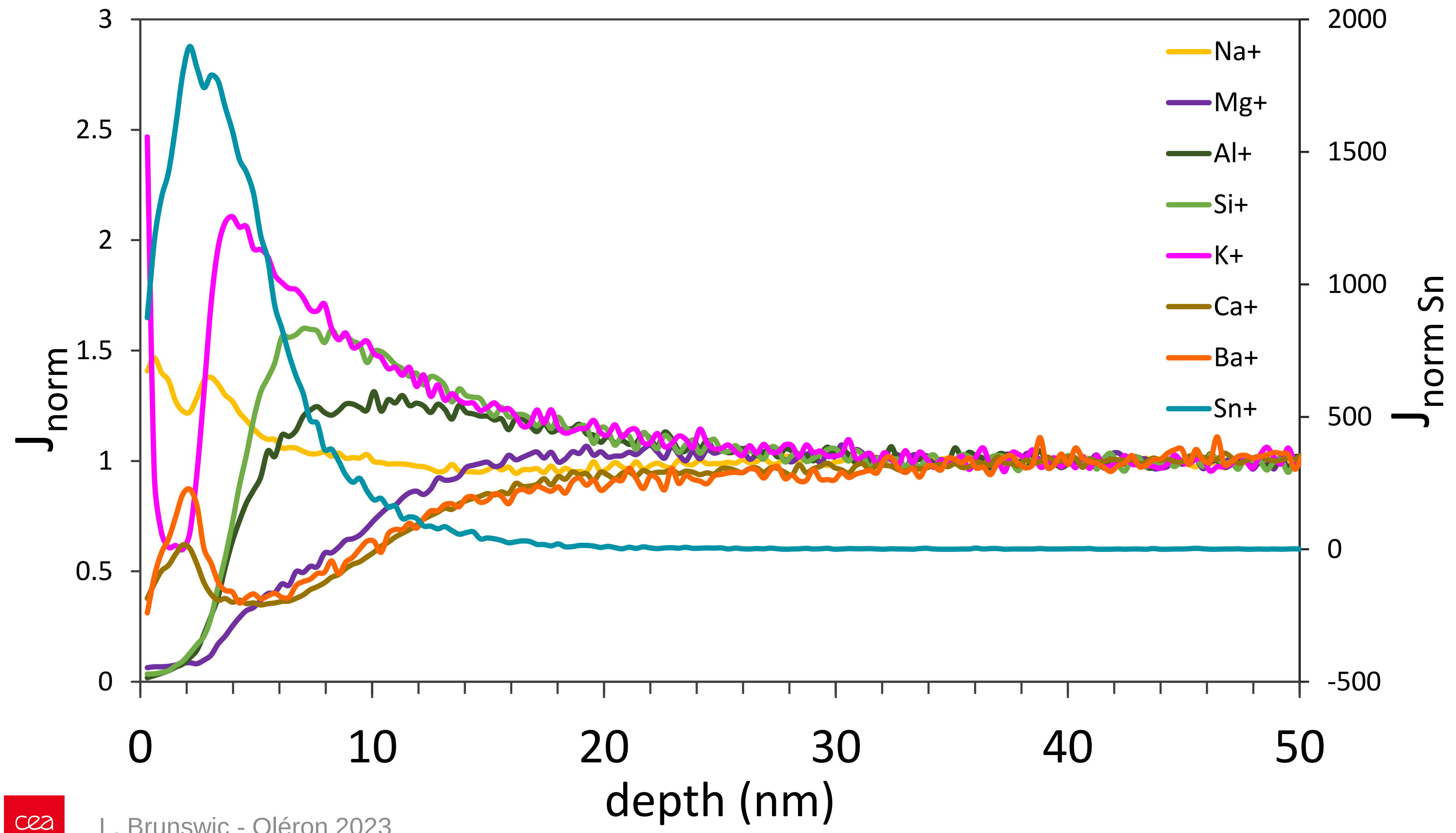
Glass C | Soda-lime + Sn



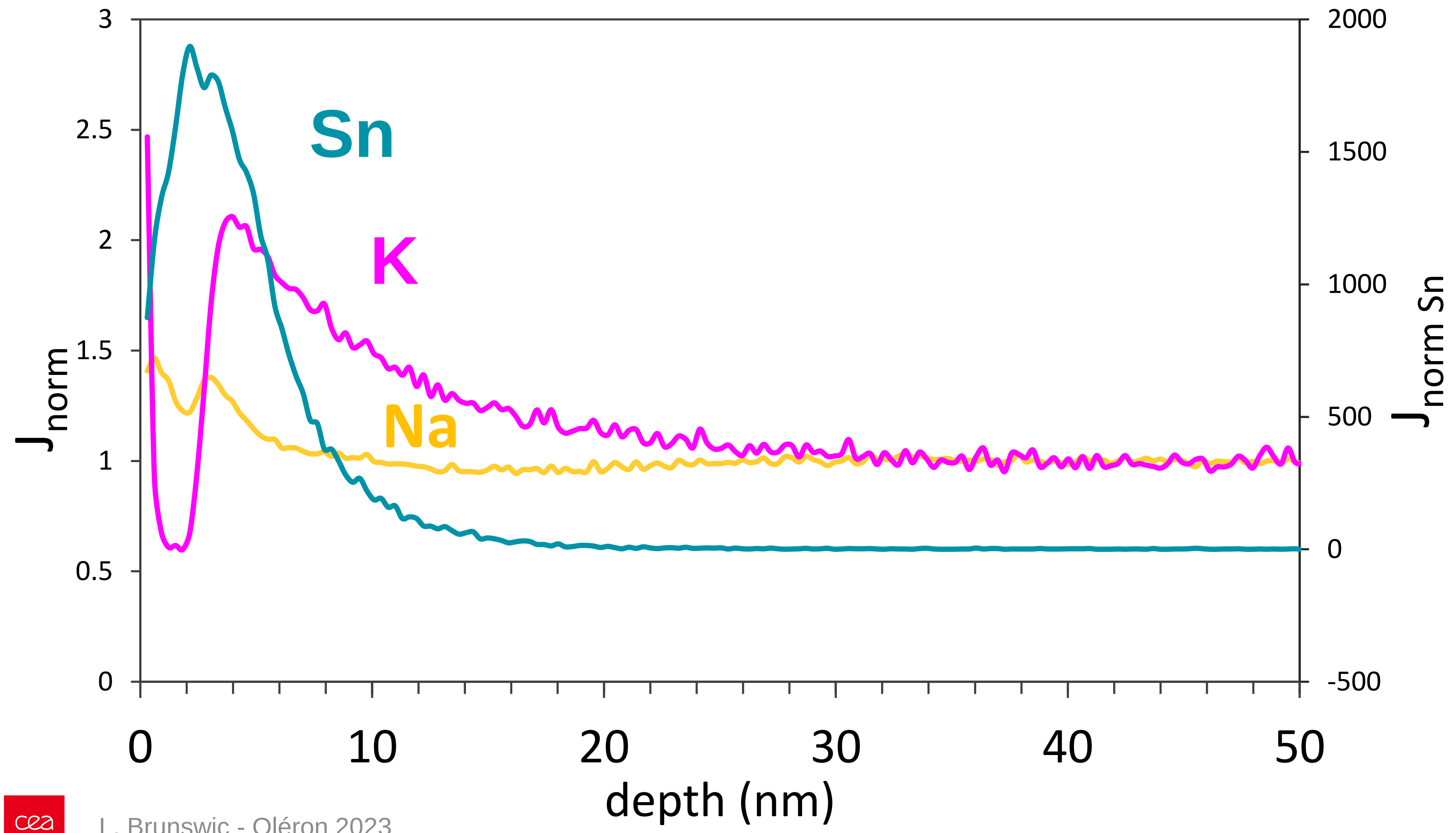
- ≈ 10 nm of SnO_2
- coating deposited at 500°C

Impact of Sn coating on pristine soda-lime glass

Glass C | Soda-lime + Sn



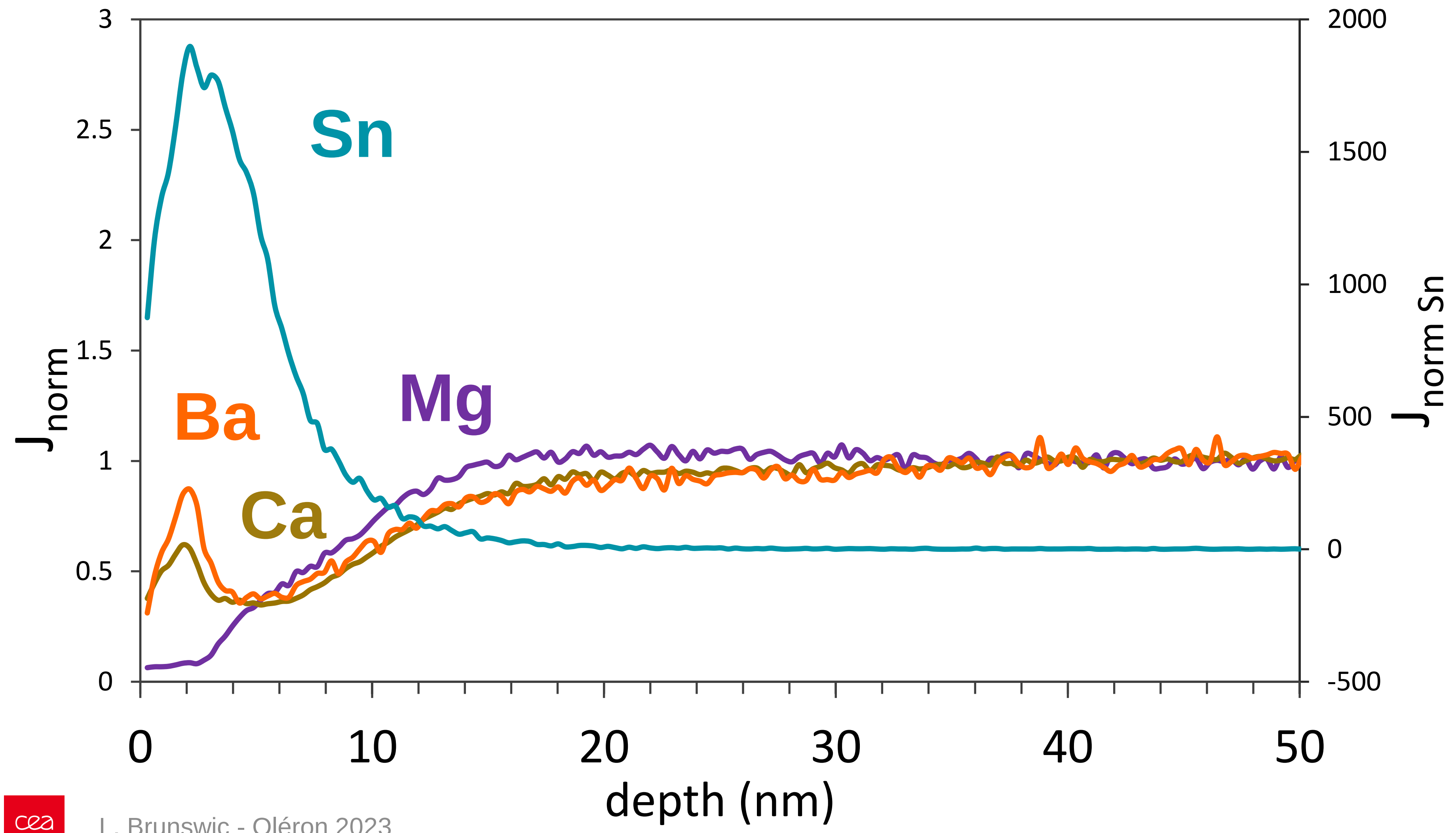
Impact of Sn coating on pristine soda-lime glass



- Alkali diffusion in the tin oxide coating
- Specific location of the alkali species at the interface with the underlying glass

Impact of Sn coating on pristine soda-lime glass

Glass C | Soda-lime + Sn

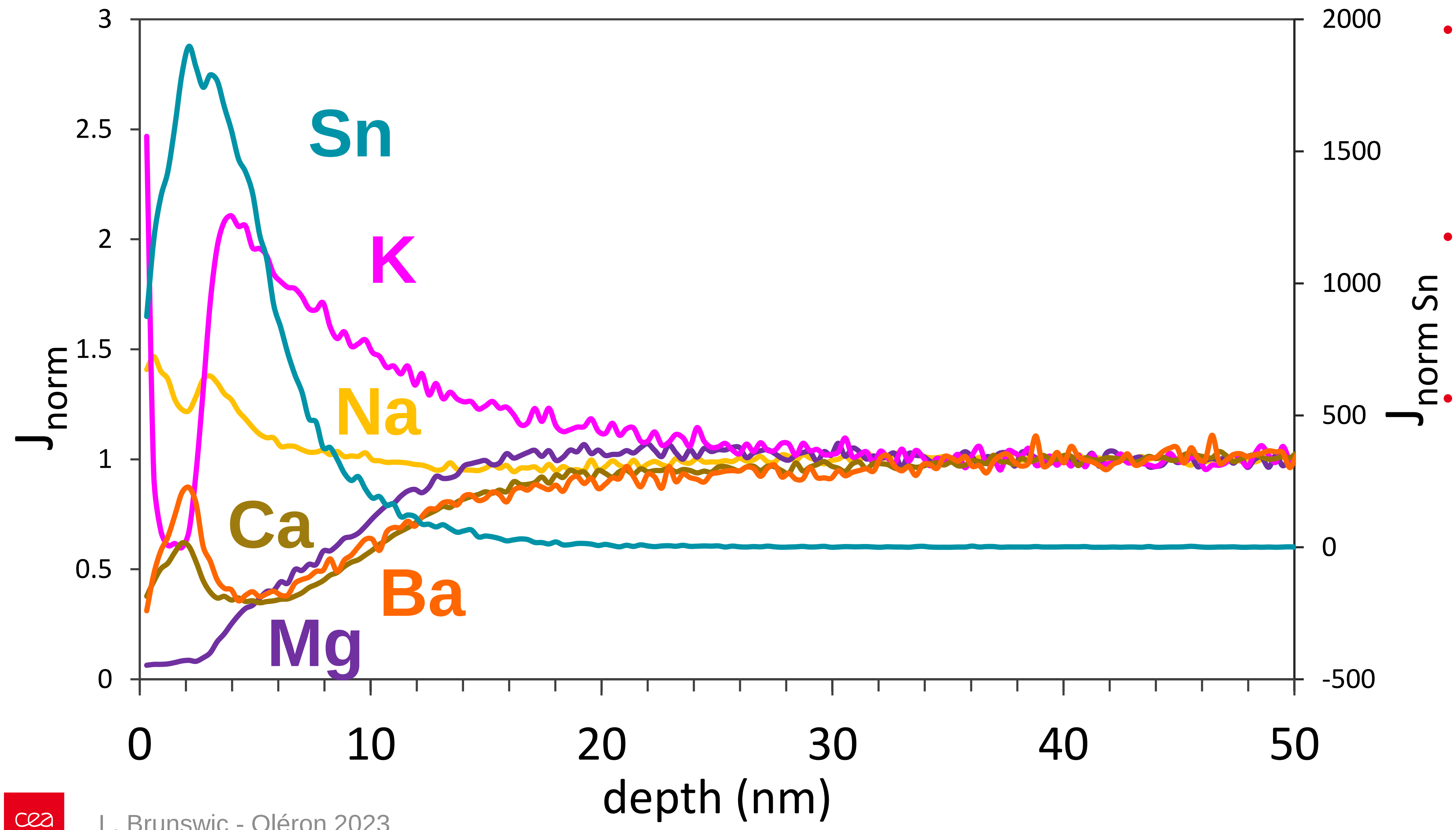


- Alkaline earth diffusion in the tin oxide coating
- Specific location of the alkaline earth species at the surface
- Mg is not diffusing in the coating

Impact of Sn coating on pristine soda-lime glass

Glass C	Soda-lime

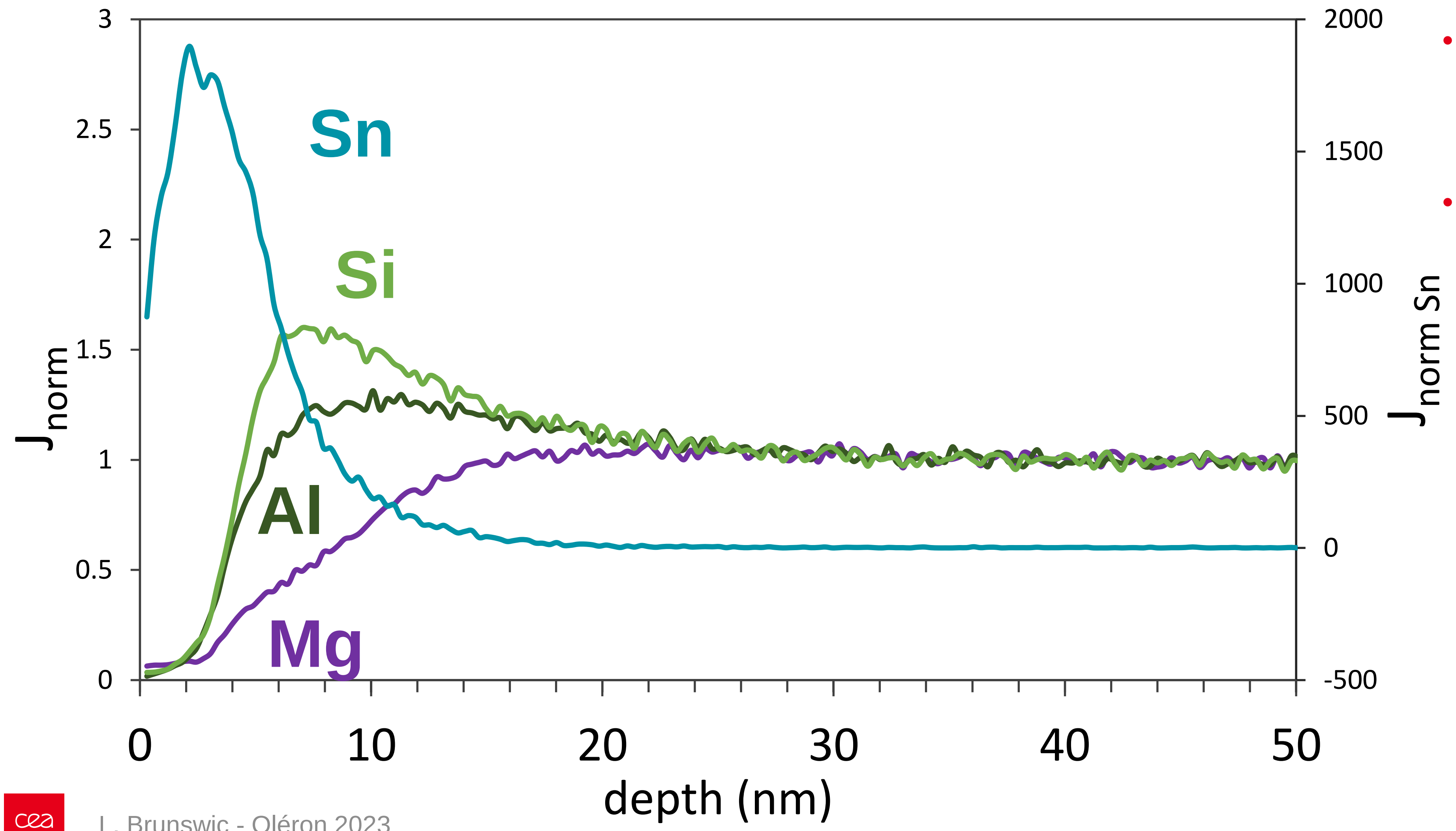
\+ Sn



- Clear distribution of alkali and alkaline earth in the subsurface region of the coated glass
- Species bearing 2 charges diffuse further from the glass
- At the exception of Mg

Impact of Sn coating on pristine soda-lime glass

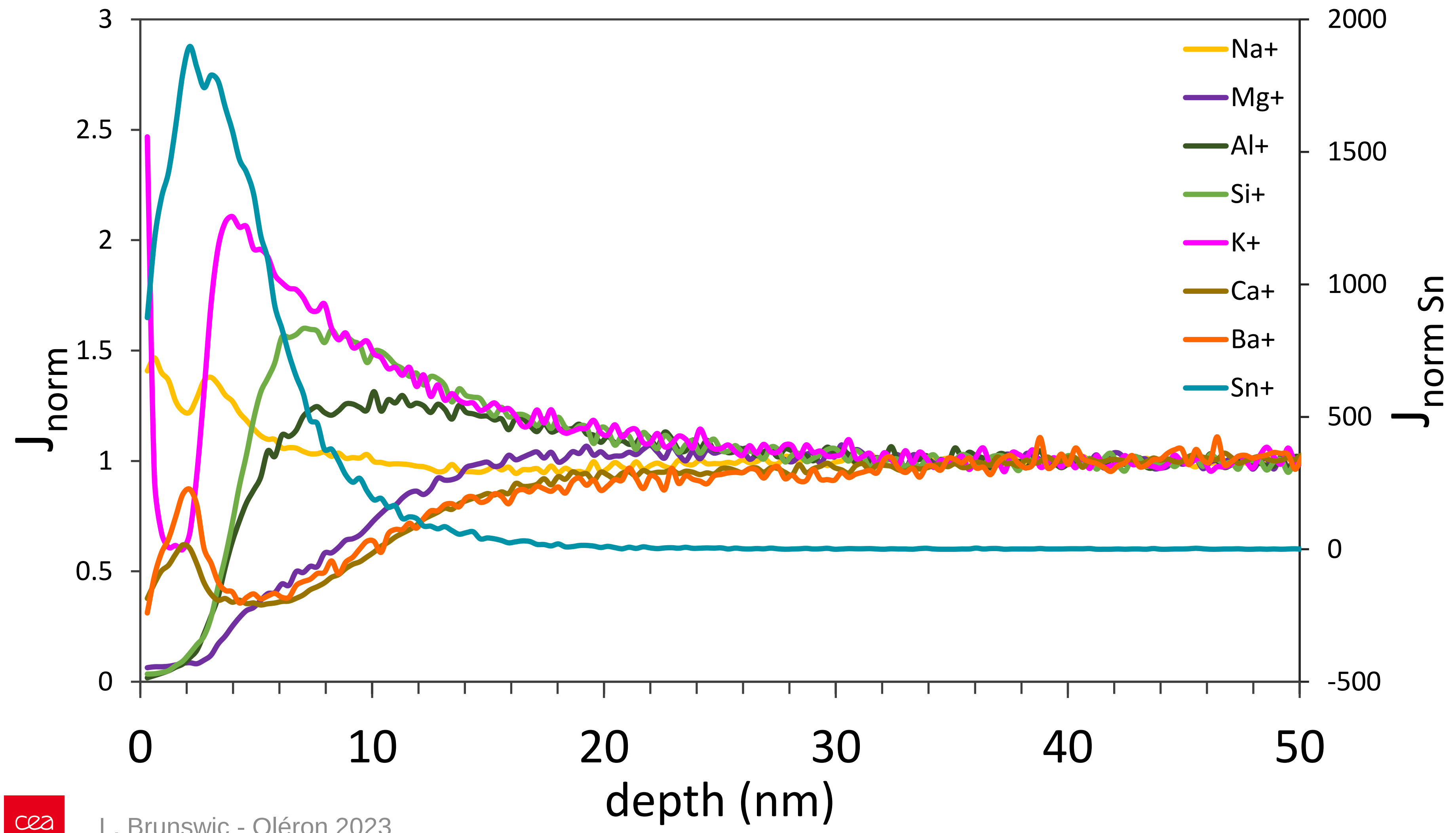
Glass C | Soda-lime + Sn



- No diffusion of network formers Al and Si into the coating
- Mg acting as a network former ?

Impact of Sn coating on pristine soda-lime glass

Glass C | Soda-lime + Sn



- Impact of thin layer depostion on glass surface: diffusion of mobile glass elements according to their charge
- For thin layers (< 20 nm) no impact on long term alteration was noticed
- Fast dissolution of the Sn coating in solution
- Same observations for Si coating

Effects of surface treatments

Physical deposits			Chemical reactions		
Si	Sn	Ti	PA	CEMa	CEMb

Surface coatings (sputtering)

Dealkalinization by SO_2 vapor treatment

Acidic etching

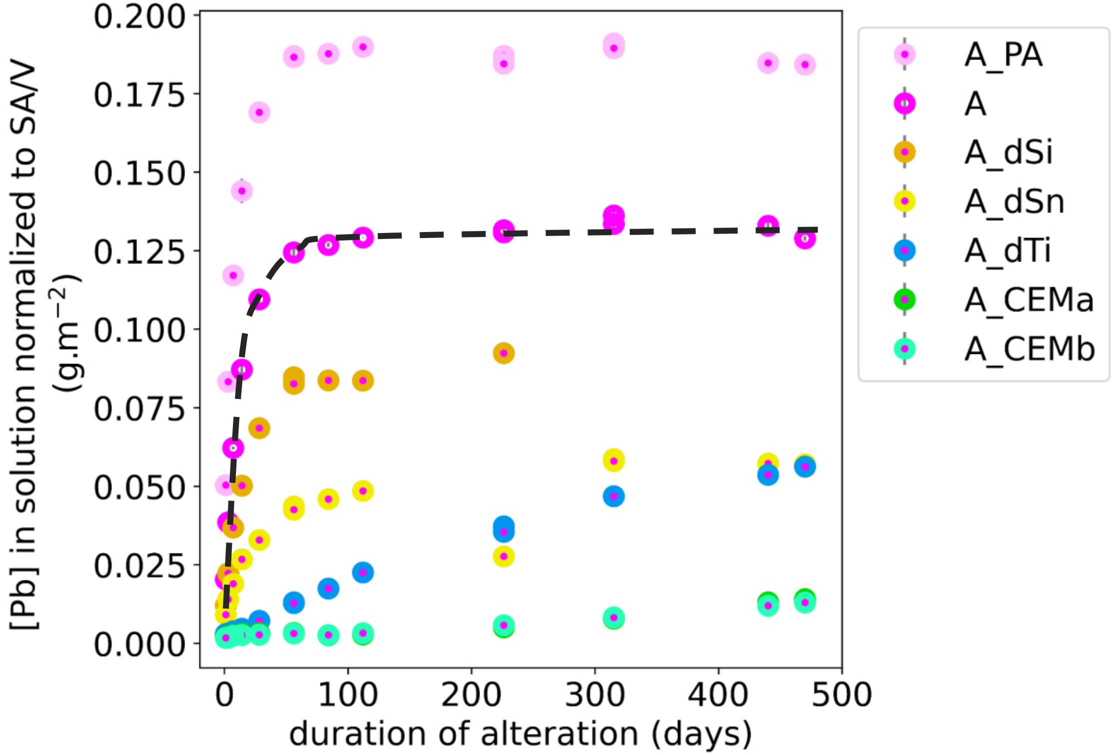
Acetic acid
pH = 2.4, 70°C
S/V = 2.5 m^{-1}
~ 500 days

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

Pb

Glass A | Lead crystal



Effects of surface treatments

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

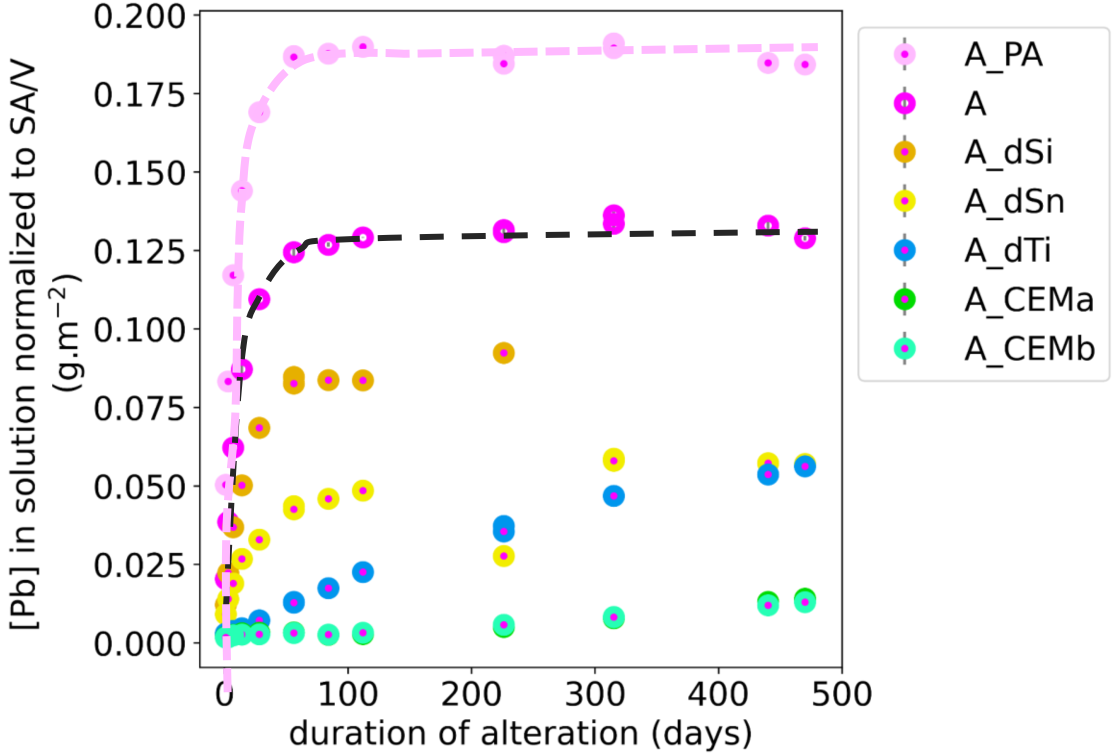
Chemical reactions: PA, CEMa, CEMb — *Dealkalinization by SO_2 vapor treatment*

Acidic etching

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_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

Effects of surface treatments

Physical deposits | Chemical reactions

Si | Sn | Ti | PA | CEMa | CEMb

Surface coatings (sputtering)

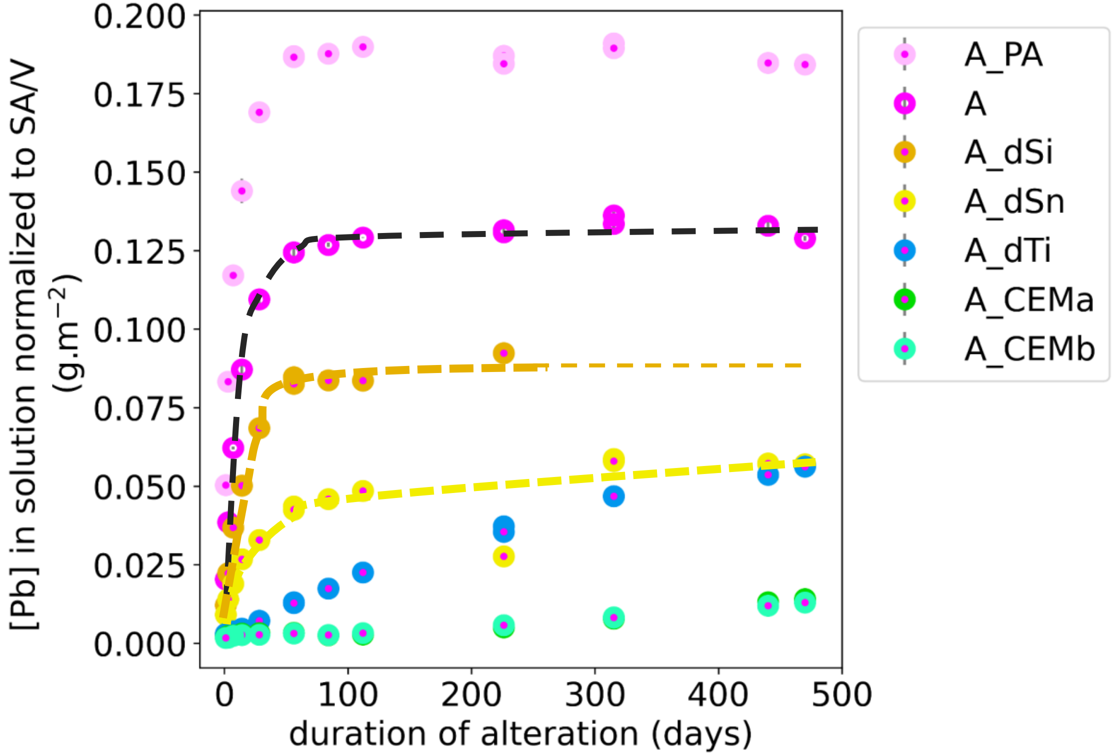
Dealkalinization by SO_2 vapor treatment

Acidic etching

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

- **Si, Sn coatings: less than 15 nm thick**

  → effect on the reduction of Pb release is moderate

Effects of surface treatments

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

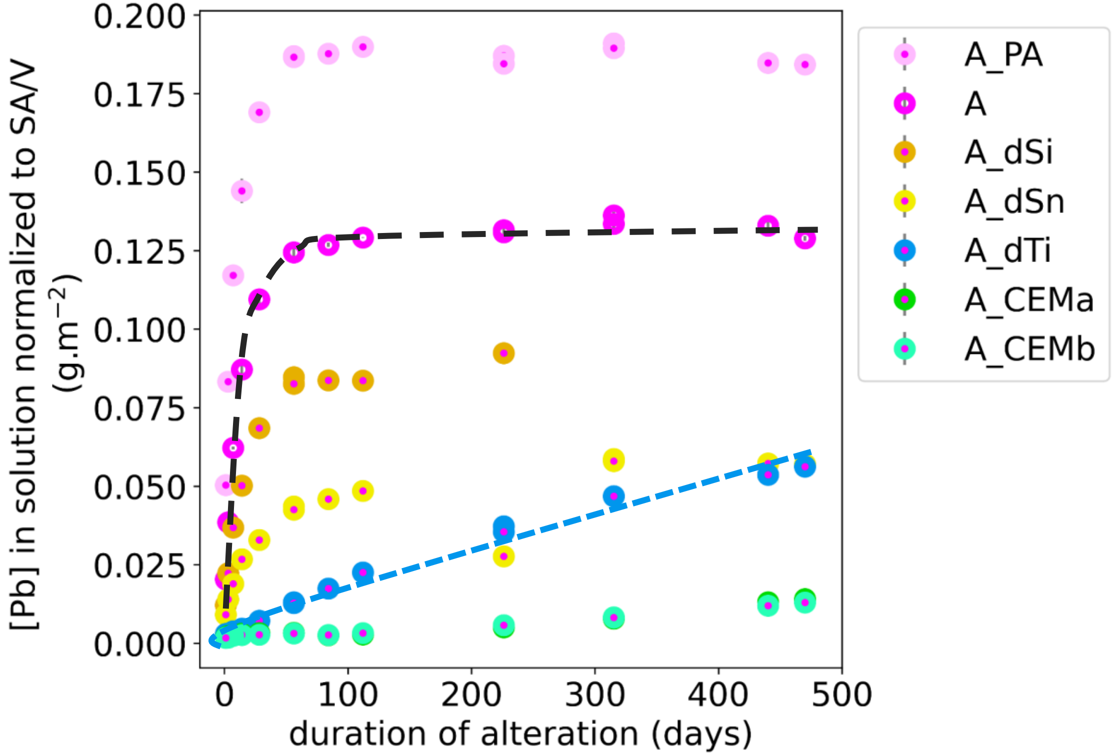
Chemical reactions: PA, CEMa, CEMb — *Dealkalinization by SO_2 vapor treatment*

Acidic etching

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

- **TiO_2 coating: less 500 nm thick**

  → 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

Physical deposits			Chemical reactions		
Si	Sn	Ti	PA	CEMa	CEMb

Surface coatings (sputtering)

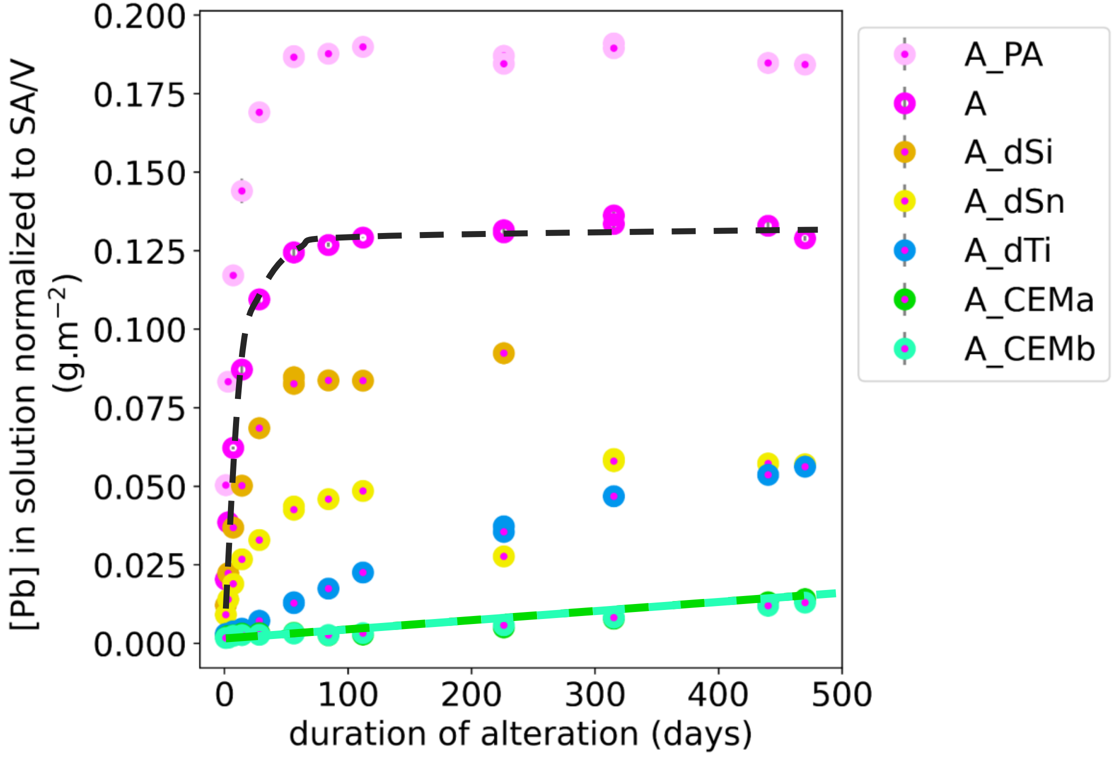
Dealkalinization by SO_2 vapor treatment

Acidic etching

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 g.m^{-2}	$[Pb]_{SA/V}/[Pb]^{ref}_{SA/V}$ 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

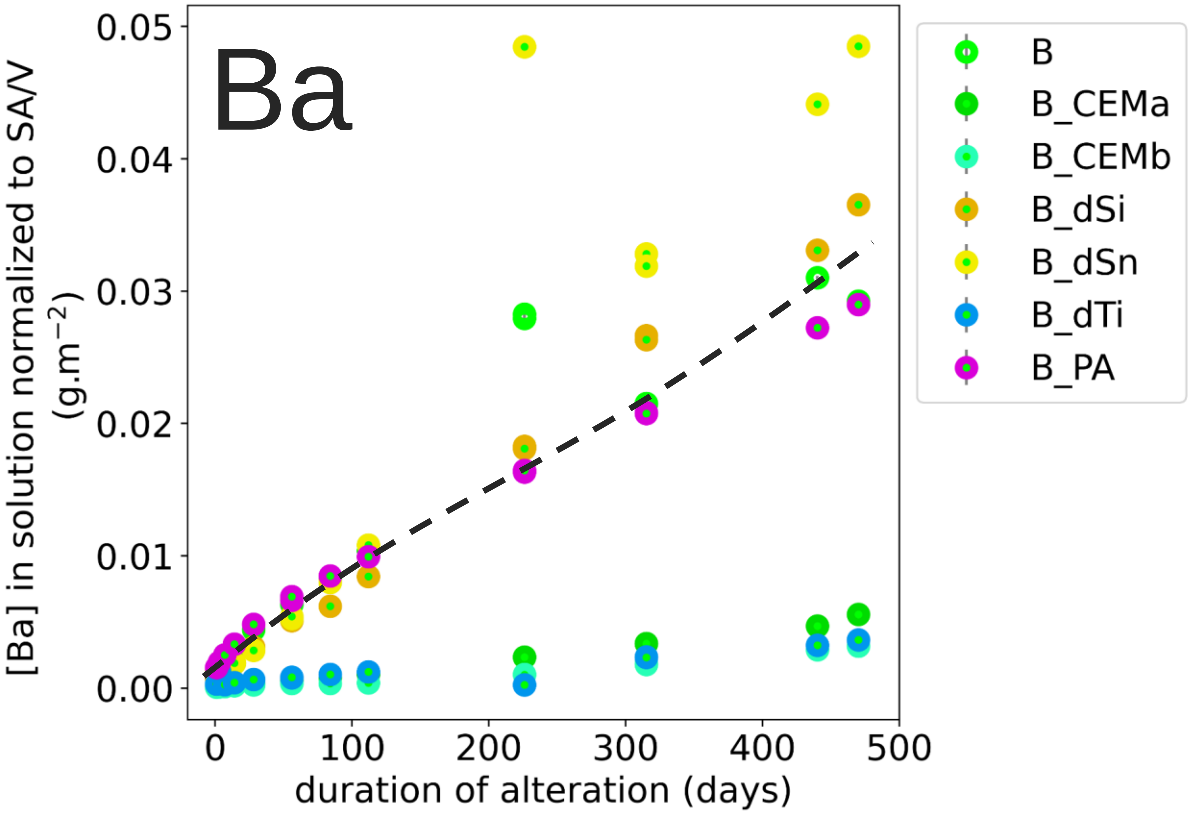
* based on $[Pb]_{SA/V}$ at 226 days

- **SO_2 dealkalization** (most efficient)

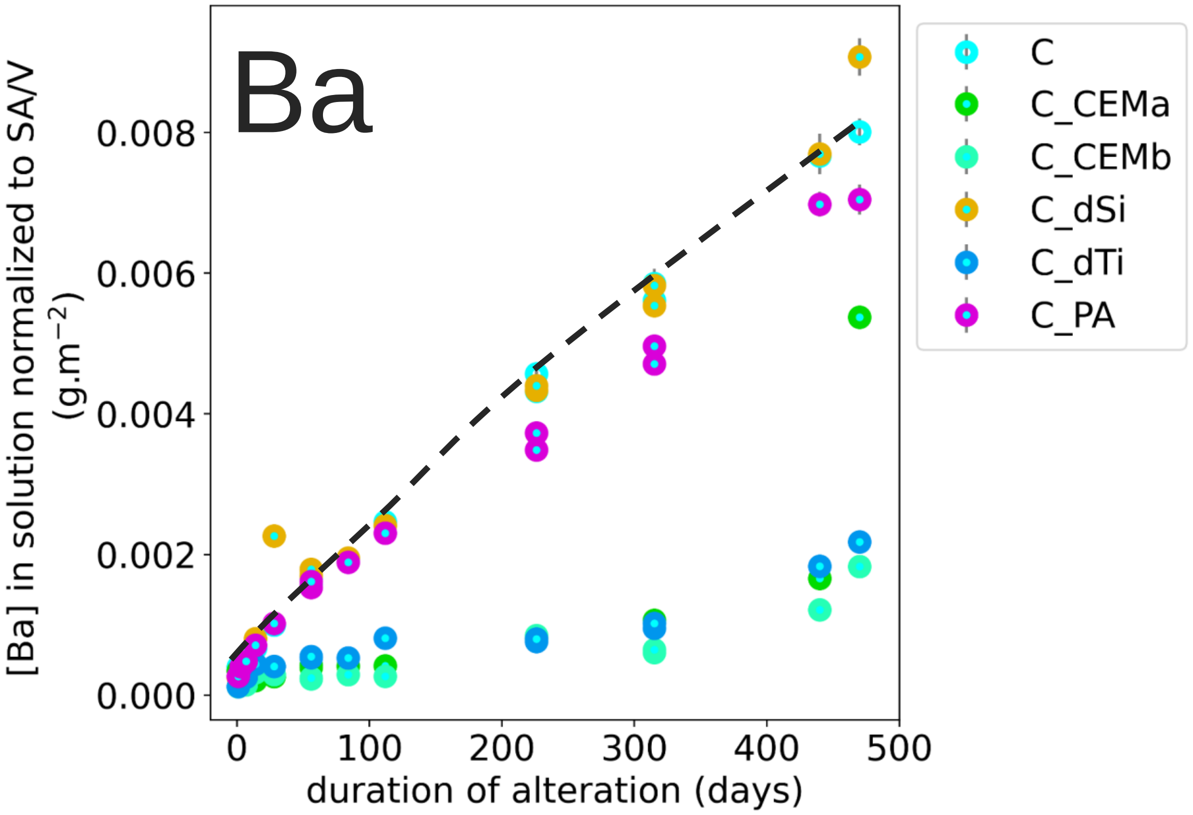
→ considerably **reduces lead release**
→ **lasts over time**
→ **reproducibility** between both industrial procedures
→ **not efficient for highly polymerized glasses** (no interdiffusion)

Effects of surface treatments on the leaching of barium

Glass B | Barium glass



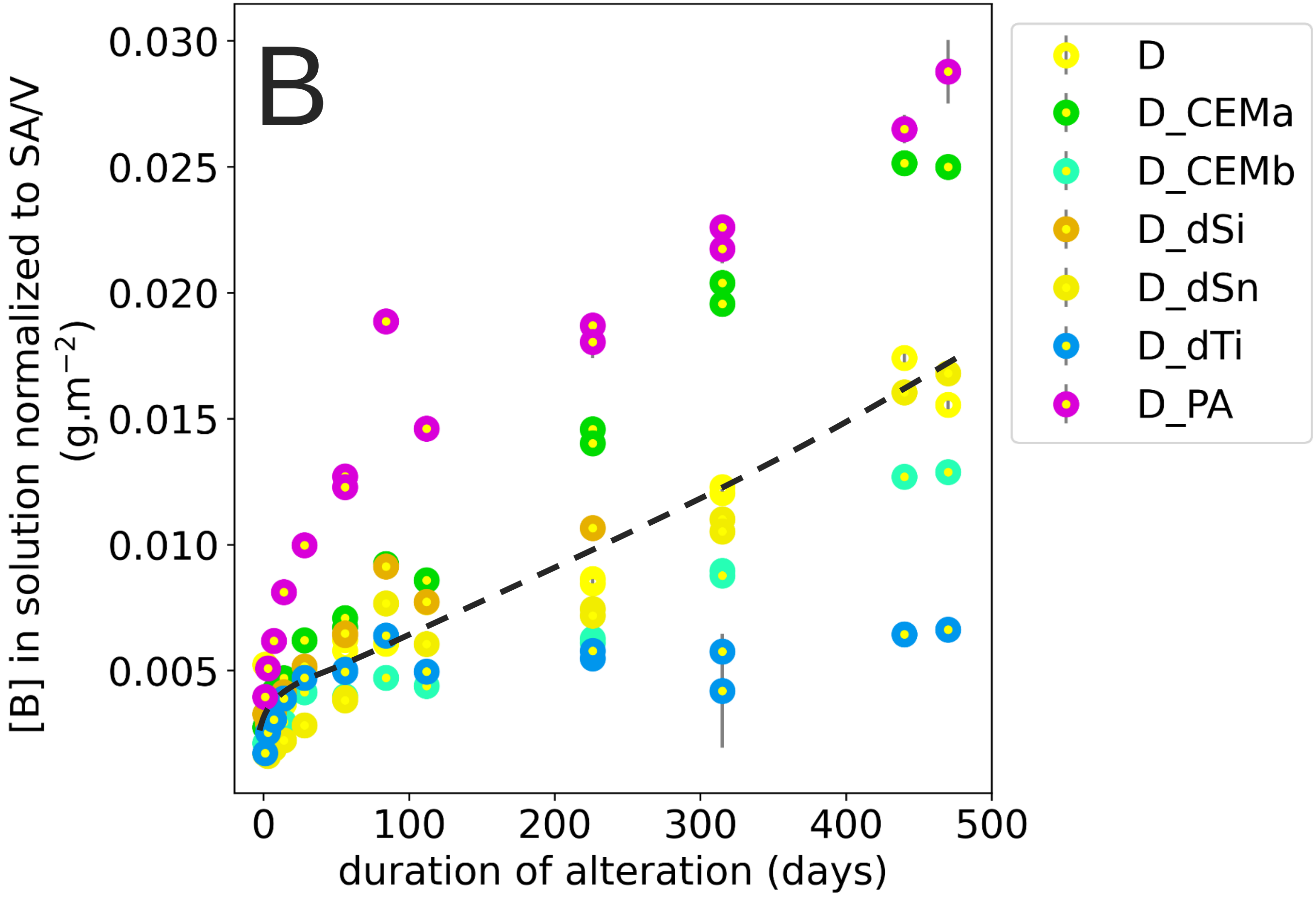
Glass C | Soda-lime



- 80 to 90% reduction of Ba leaching with SO_2 dealkalization or TiO_2 coating
- Durable effect over time of Ba leaching reduction

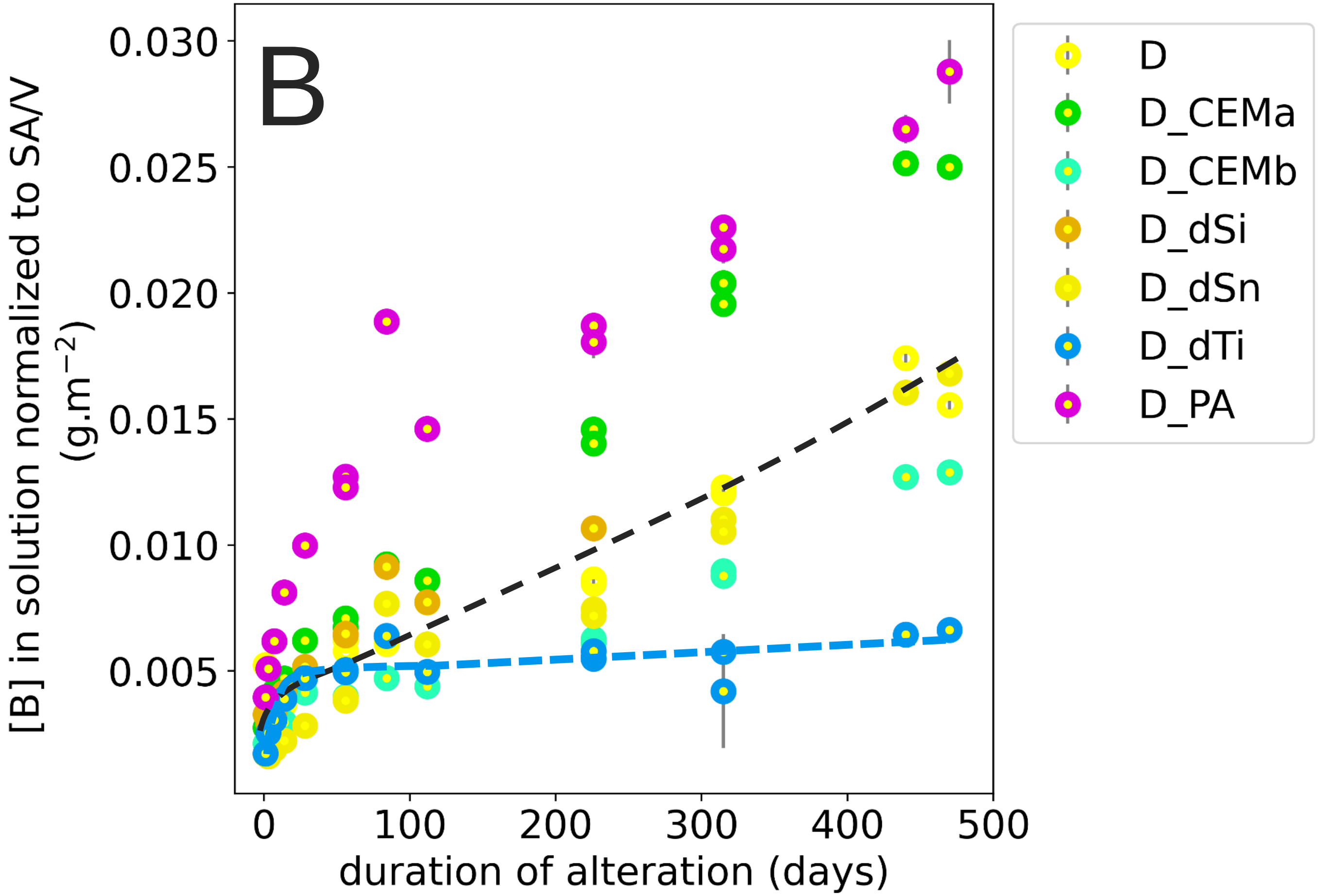
Effects of surface treatments on the leaching of boron

Glass D | Borosilicate



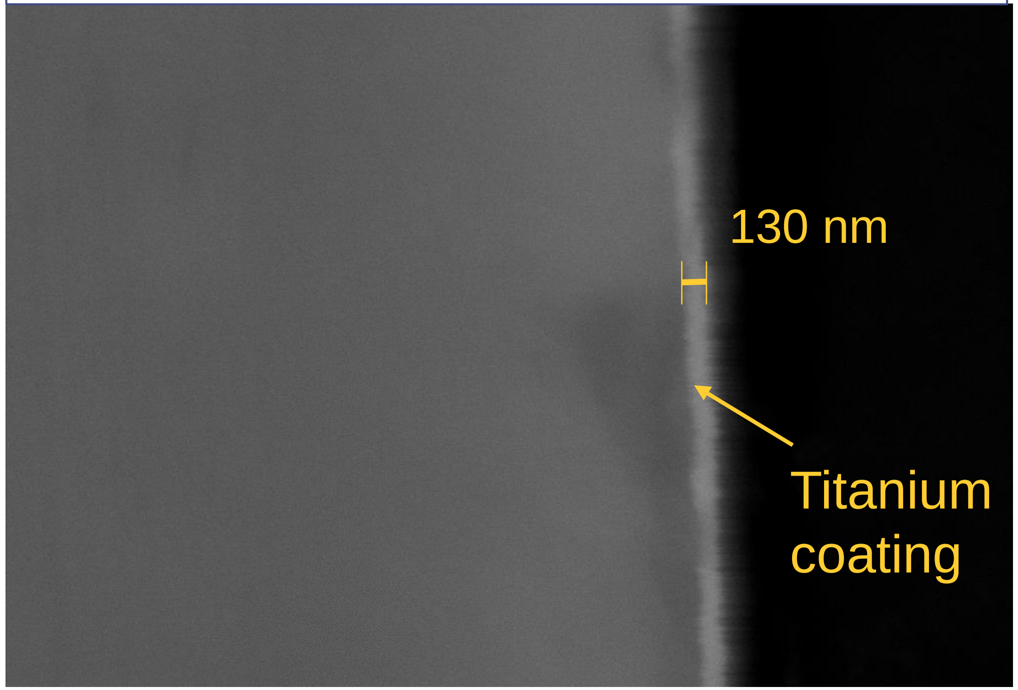
Effects of surface treatments on the leaching of boron

Glass D	Borosilicate



Maximal concentration of Ti in solution: 2.5 ± 0.4 ppb

SEM observation of glass D with titanium surface coating (D_dTi) after 470 days of alteration



- SO_2 dealkalization have no benefit for glasses altered by hydrolysis mainly
- A different mechanism of alteration is noticed for glass D with TiO_2 coating

Effect of surface treatments on glass alteration

Si Sn

- ❑ Thin surface coatings (< 15 nm) caused the migration of alkalis and alkaline earth elements towards the deposited layer without major effect on the leaching rates over long alteration periods

Ti

- ❑ Titanium oxide coating acts as a diffusion barrier, thus showing interest in the retention of potentially hazardous elements like Pb, Ba and B

CEMa CEMb

- ❑ Dealkalization by SO_2 vapour treatment showed
  - Decreases the interdiffusion rate
  - Great durability of its retention effect towards Pb and Ba over time
  - No beneficial effect on glasses altered congruently like borosilicates
  - No major difference was found between both dealkalization treatments

PA

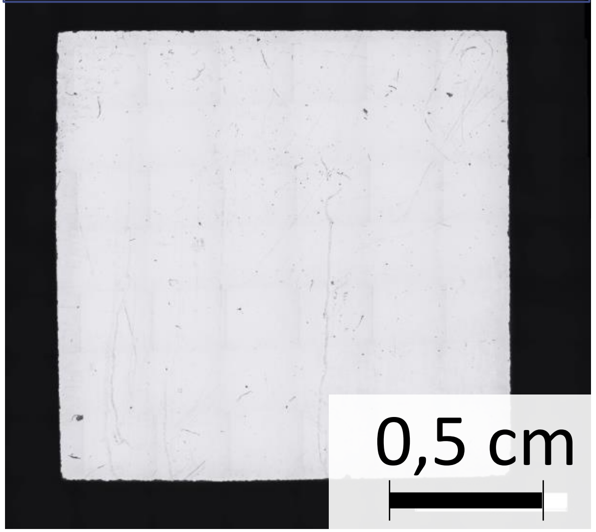
- ❑ Acid etching was found to have null to detrimental effect on glass durability

3. Alteration of glass-ceramic with and without surface treatments

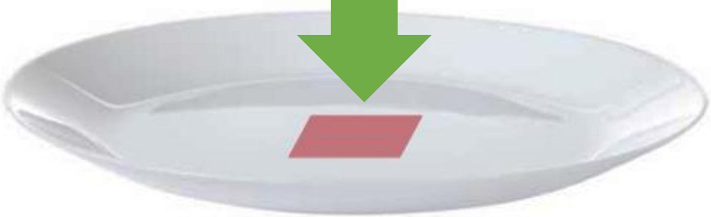
- ❑ Structure of opal crystallized glass plates
- ❑ Alteration of glass O
- ❑ Effects of surface treatment on the retention of Ba

Opal crystallized glass plates

Optical microscopy



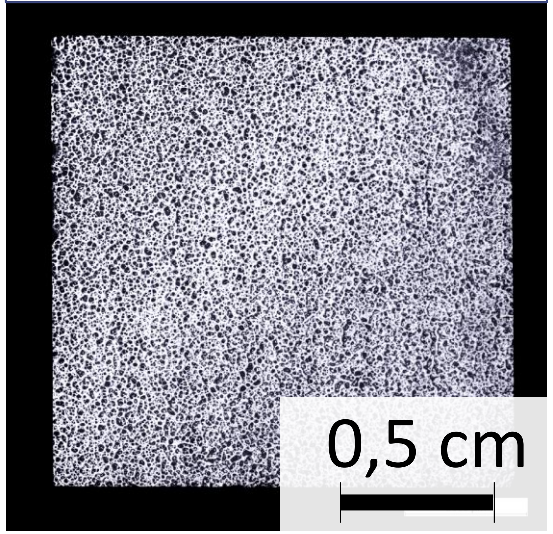
Top – Smooth
Air side



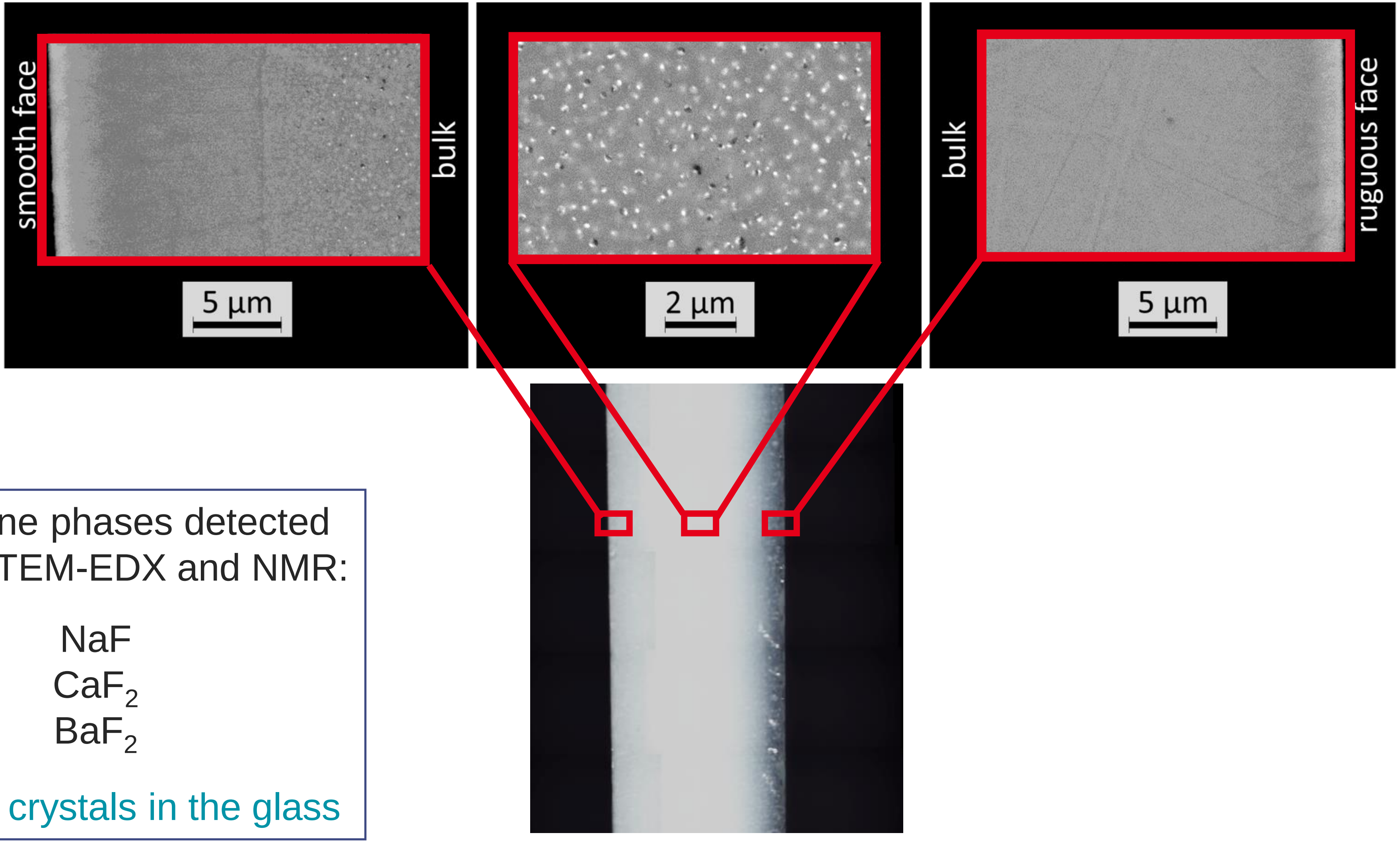
Bottom – Ruguous
Mould side

White opaque plates obtained from the addition of fluorine to a soda-lime base glass composition

Optical microscopy



Opal crystallized glass plates

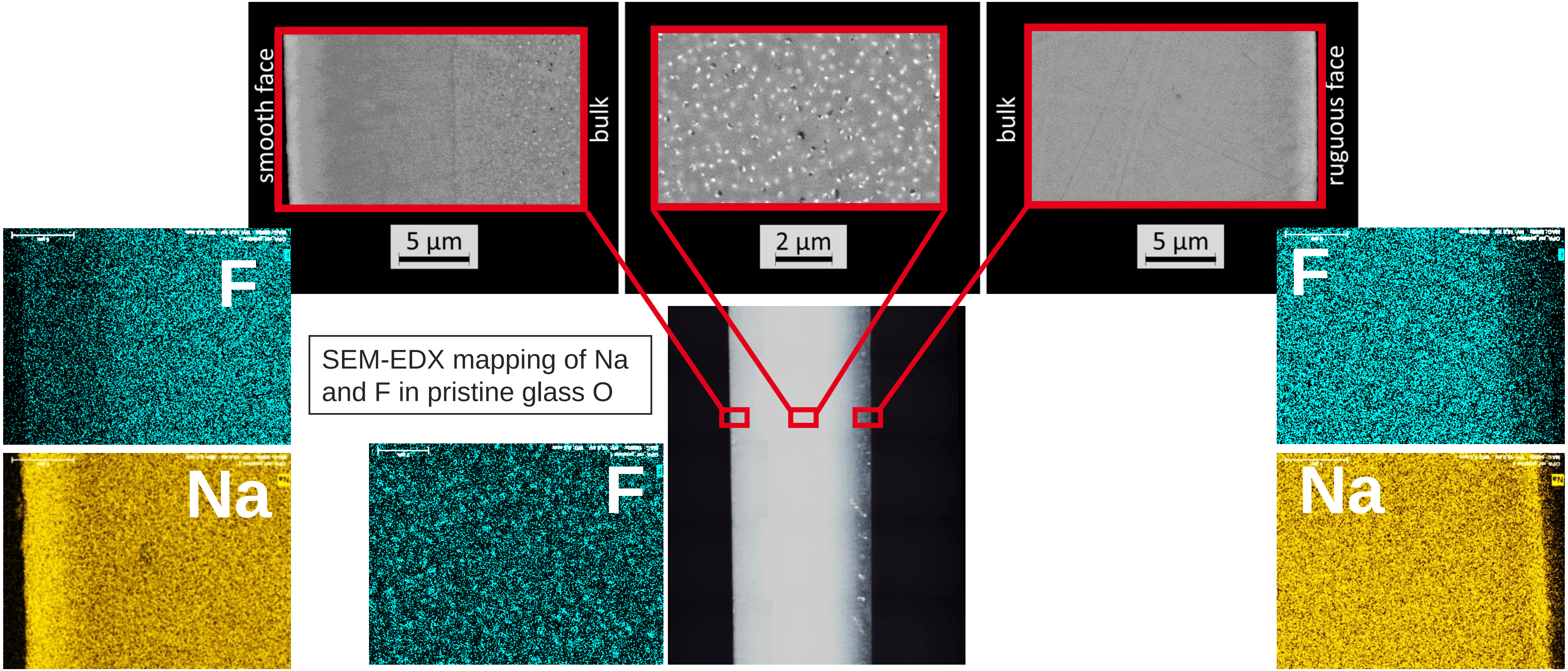


Crystalline phases detected by XRD, TEM-EDX and NMR:

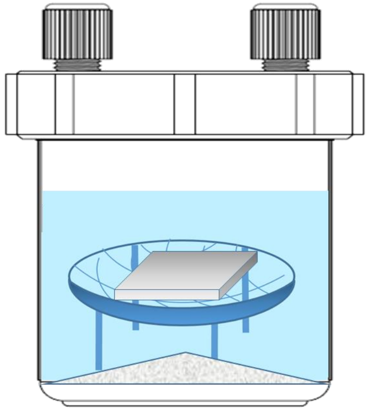
NaF
CaF_2
BaF_2

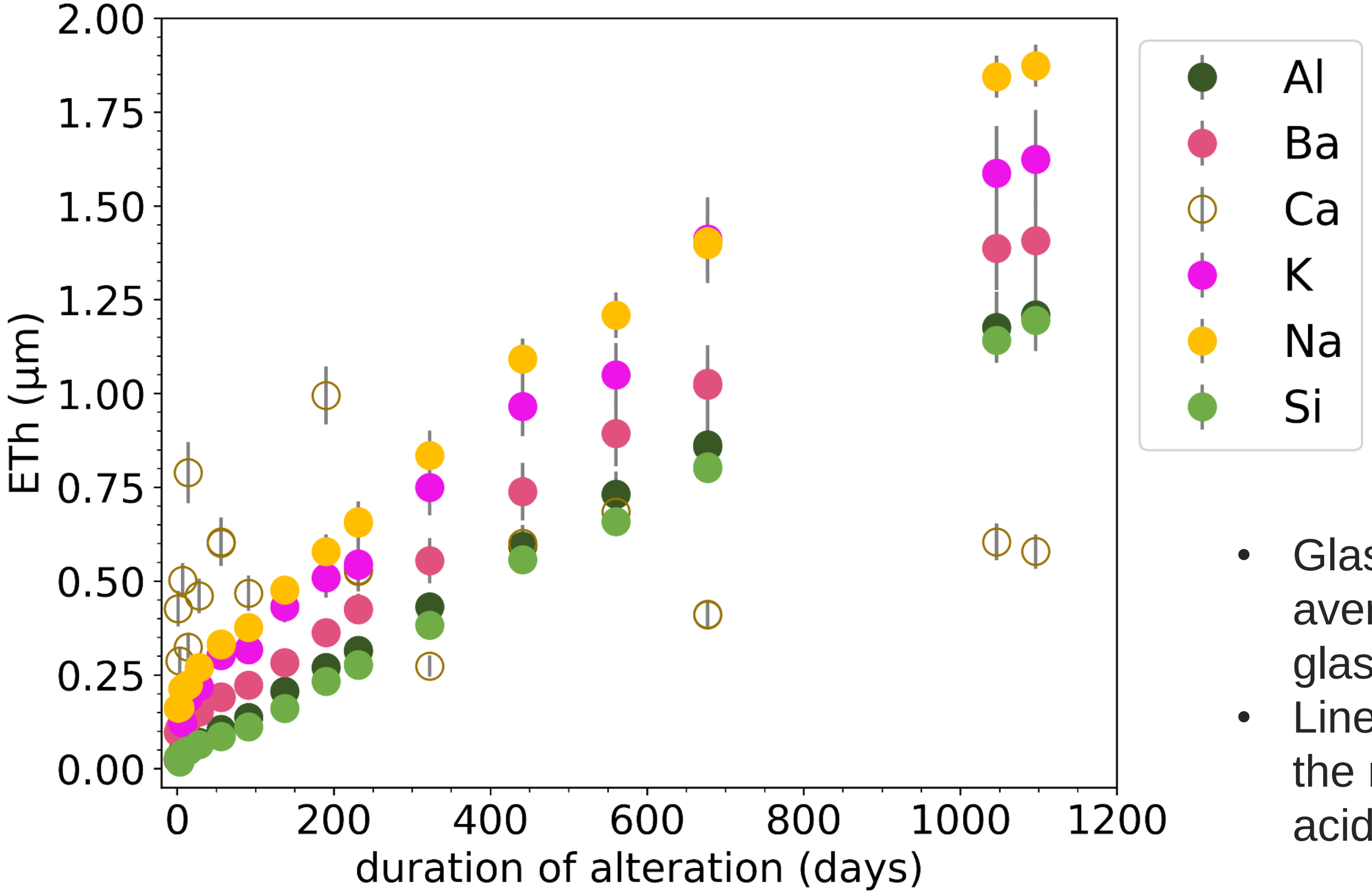
8 wt% of crystals in the glass

Opal crystallized glass plates



Leaching of opal glass powder

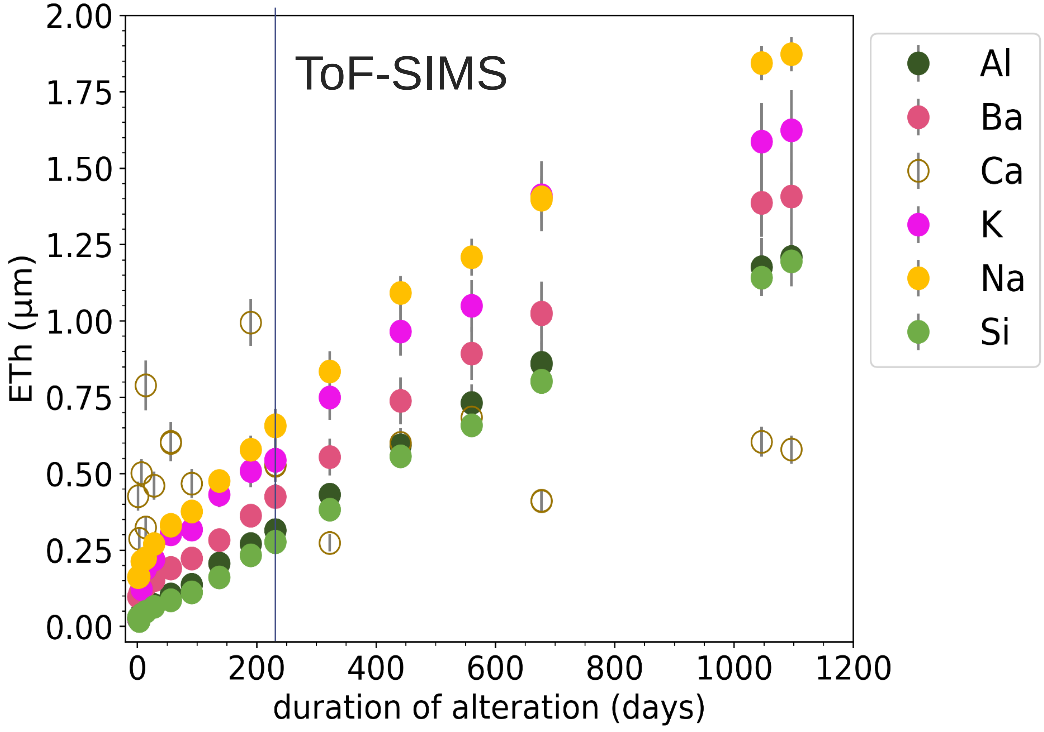




- Glass powder represents the average glass structure: glassy matrix with crystals
- Linear release: dissolution of the material in contact with acid

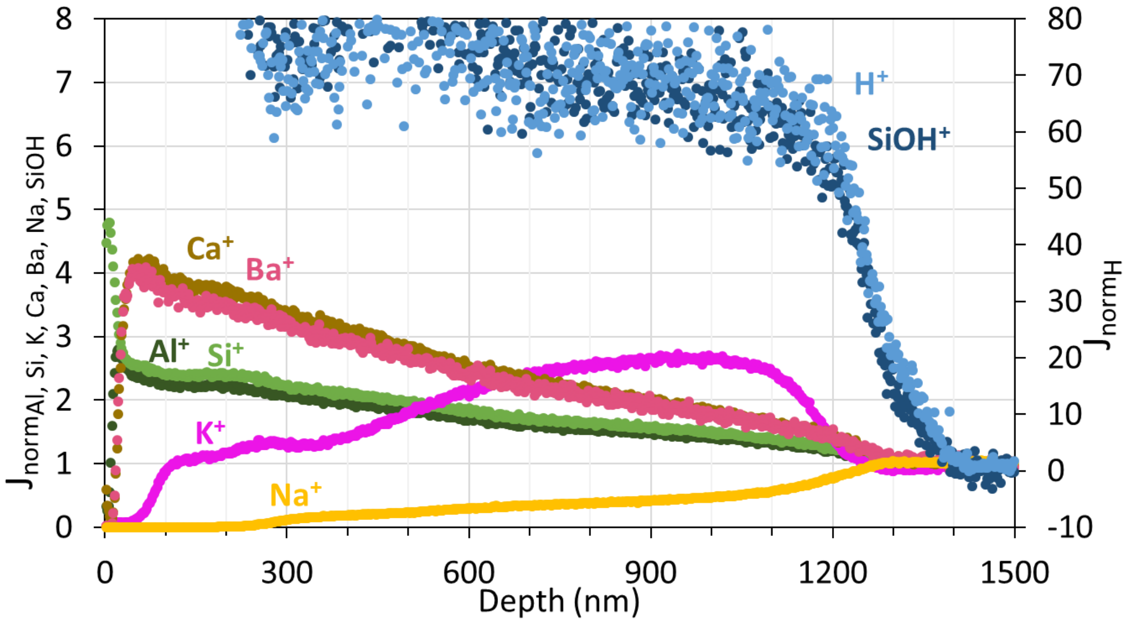
Comparison of powder vs slab alteration

Powder: average glass



450 nm of glass depleted in Na

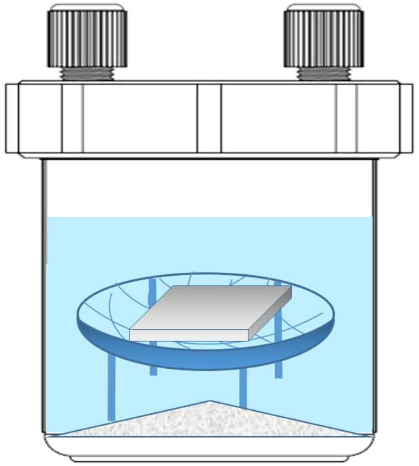
Slab: top smooth plate surface

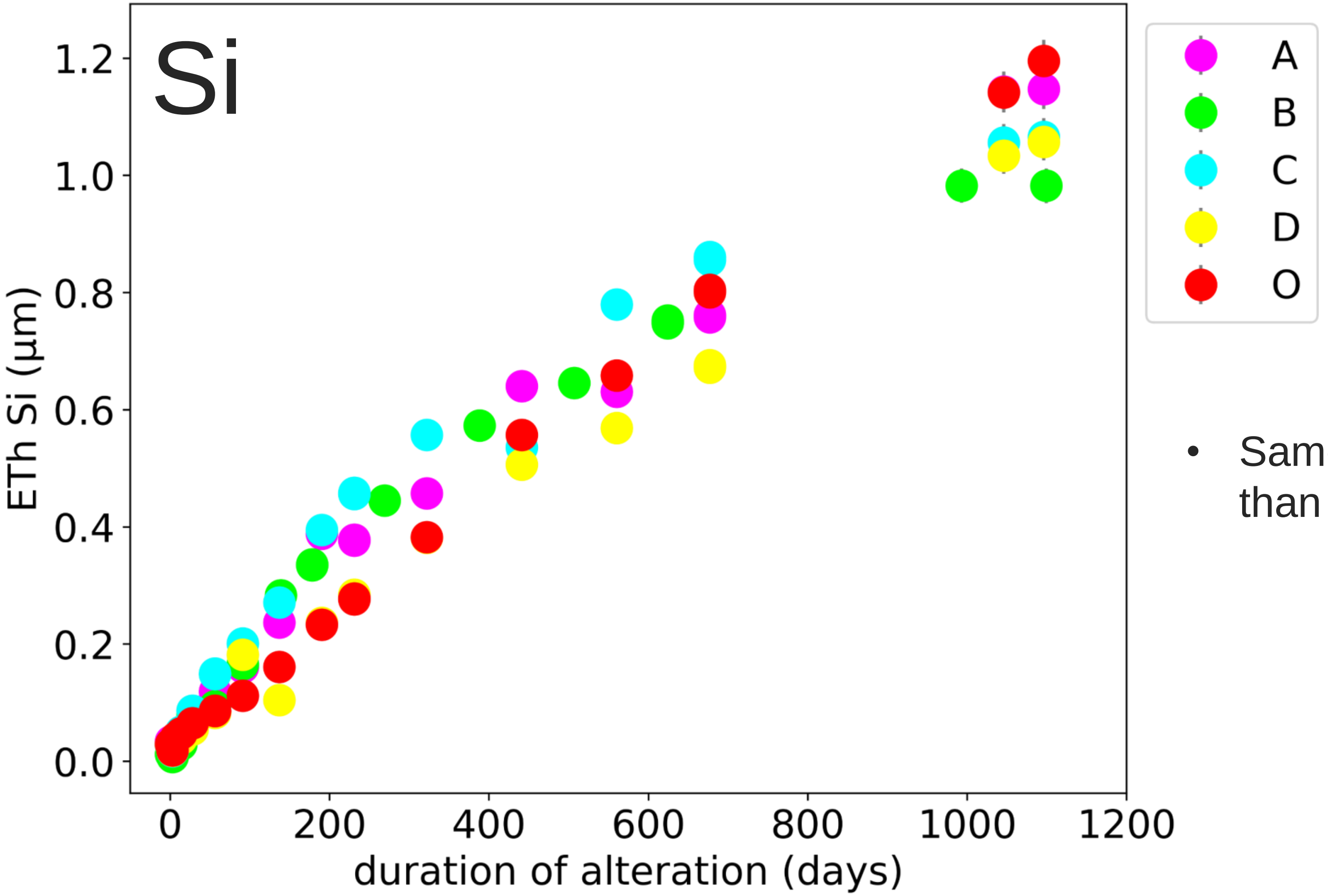


ToF-SIMS profile conducted after 231 days of alteration

1300 nm of glass depleted in Na

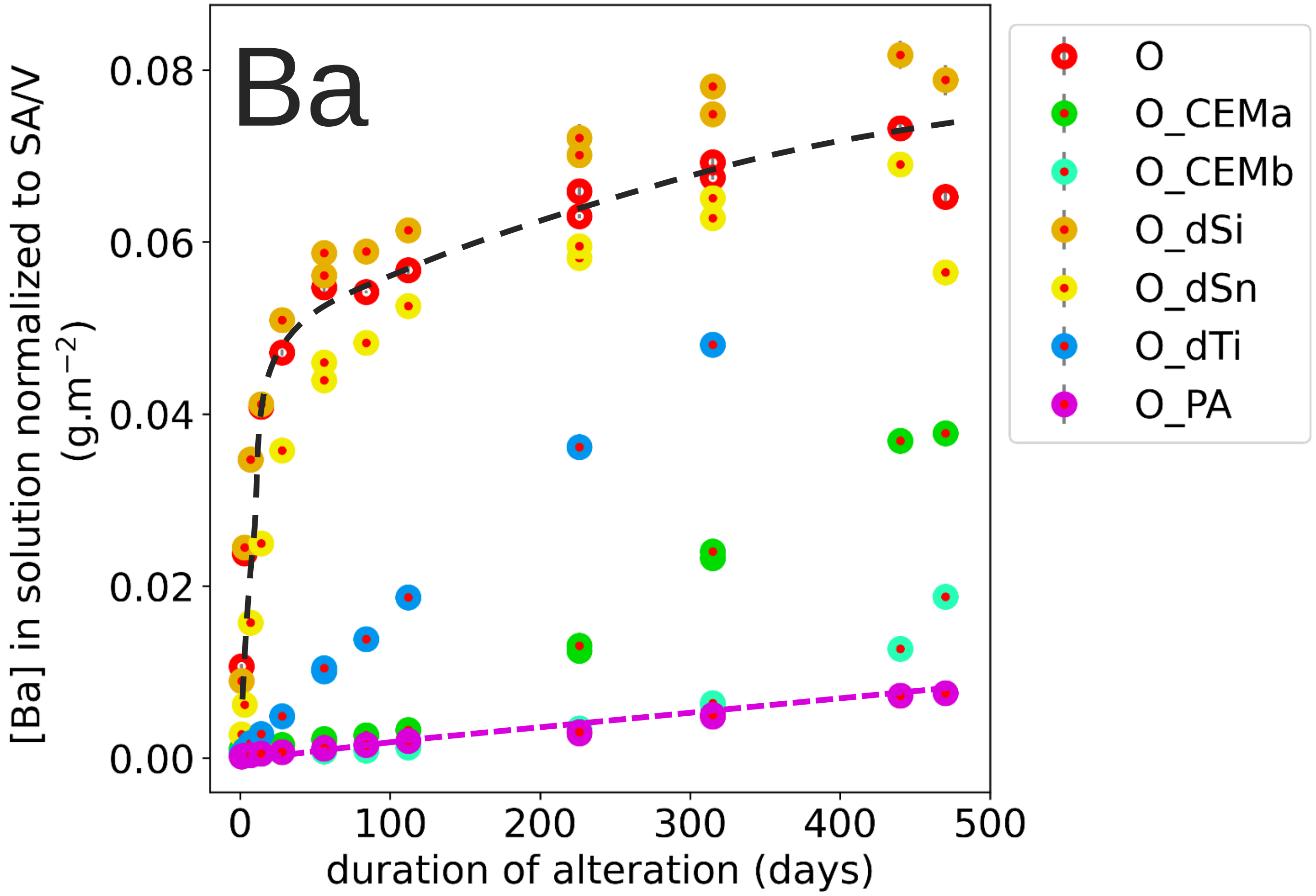
Comparison with fully vitreous glasses





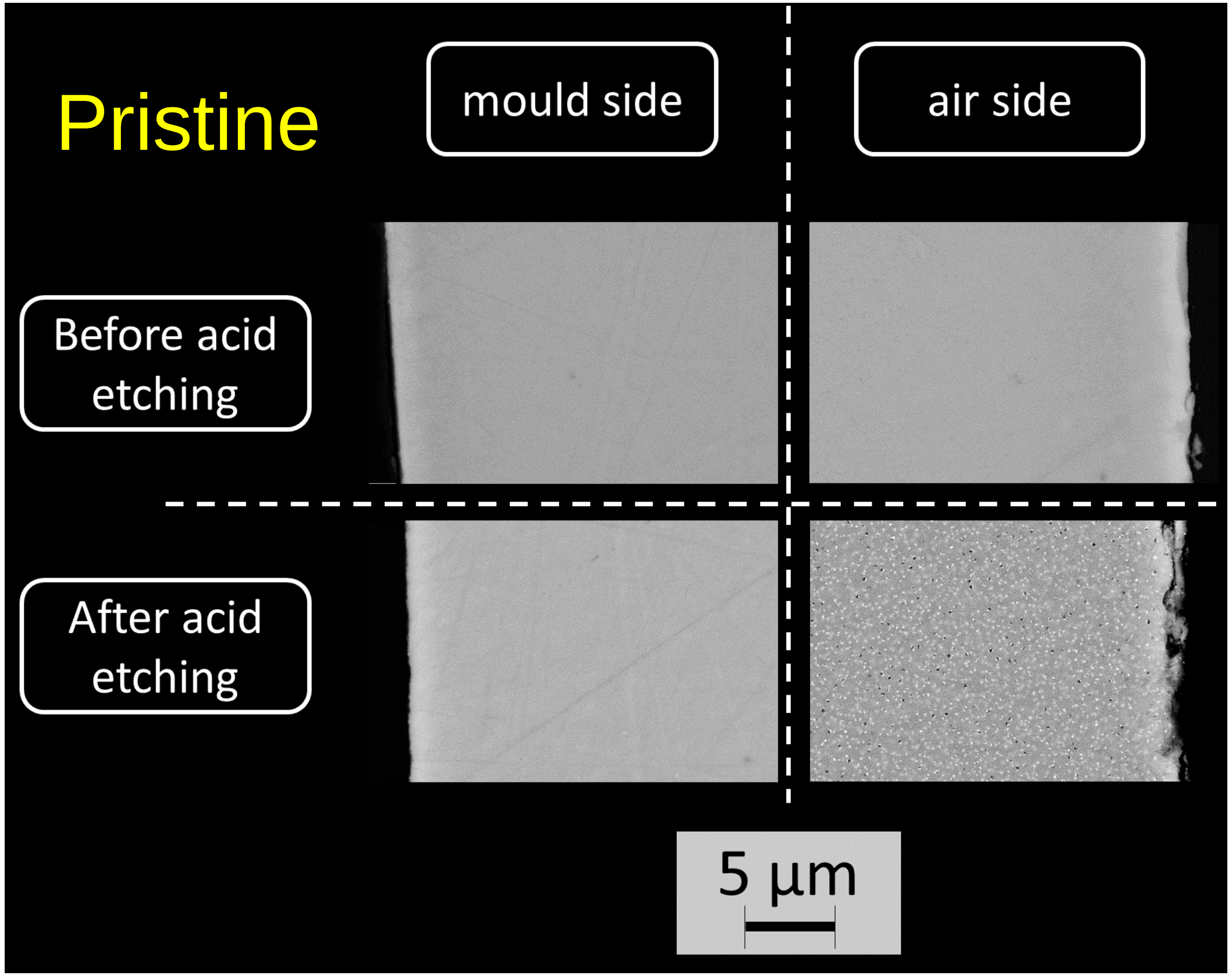
- Same rate of release of Si than fully vitreous glasses

Effect of acid etching on the release of Barium from opal crystallized glass



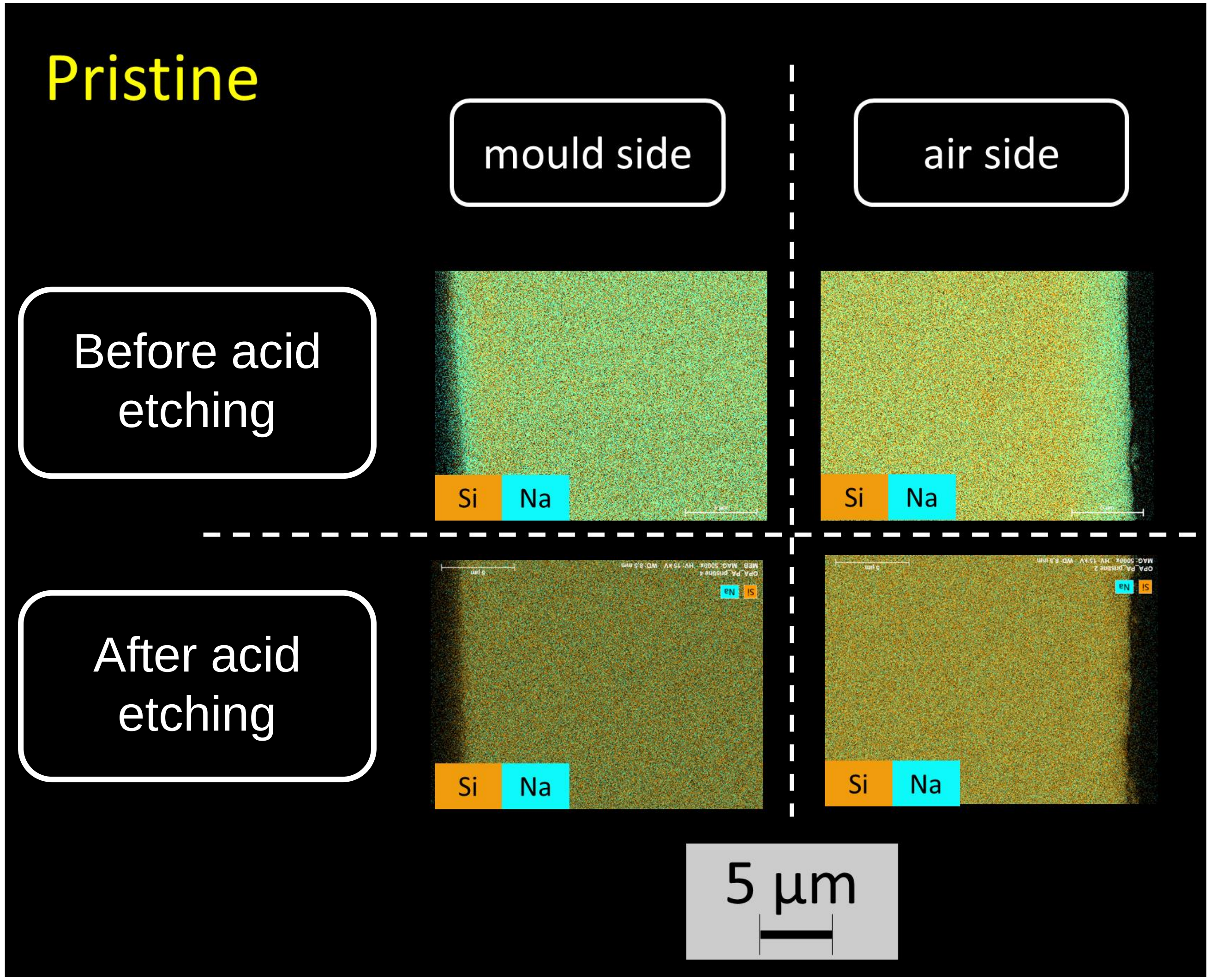
- So far acid etching did not show beneficial effect
- For opal crystal glass, acid etching (O_PA) is the best treatment for the reduction of Ba leaching after 470 days of alteration

Effect of acid etching on the release of Barium from opal crystallized glass



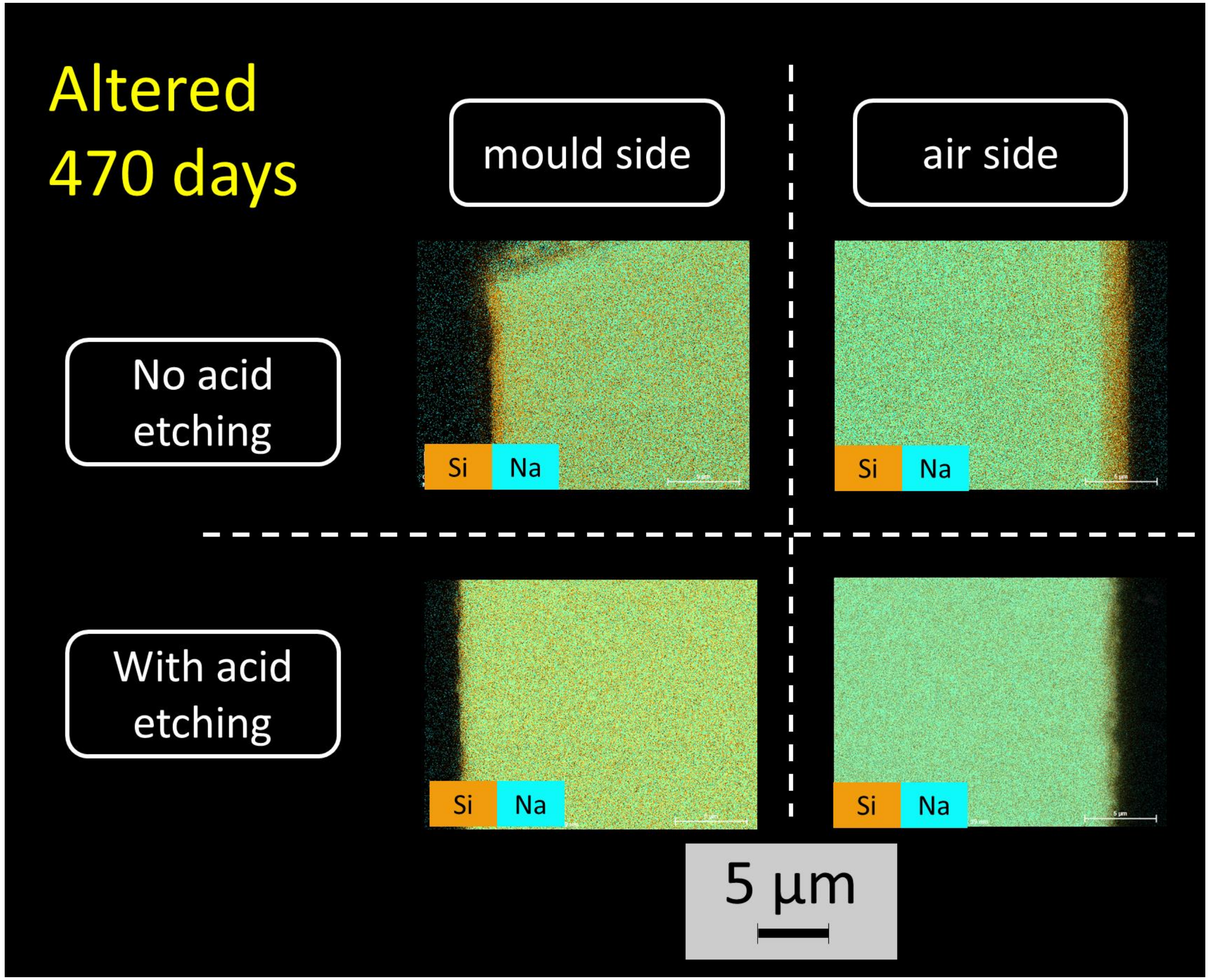
- Acid etching removes the surface less durable layer of glass enriched in Na unveiling the underlying crystals

Effect of acid etching on the release of Barium from opal crystallized glass



- Acid etching removes the surface less durable layer of glass enriched in Na unveiling the underlying crystals

Effect of acid etching on the release of Barium from opal crystallized glass



- Acid etching removes the surface less durable layer of glass enriched in Na unveiling the underlying crystals
- The underlying glass with crystals and a lower Na content is more resistant to alteration than the inital surface

4. The impact of colorant on the durability of lead crystal glass: the case of chromium

- ❑ Chromium coloured lead crystal glass
- ❑ Leaching of Pb from Cr-bearing glasses
- ❑ Structure of pristine and altered Cr-bearing glasses

The use of chromium in lead crystal glass

Cr(II) : CrO, mostly encountered as gaseous species CrO – Cr^{2+}	Cr(III) : commonly used as colorant, stable in glasses Cr_2O_3 – Cr^{3+}	Cr(IV) : brownish powder, unstable thermodynamically CrO_2 – Cr^{4+}	Cr(VI) : very mobile and toxic, classified as hazardous 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

The use of chromium in lead crystal glass

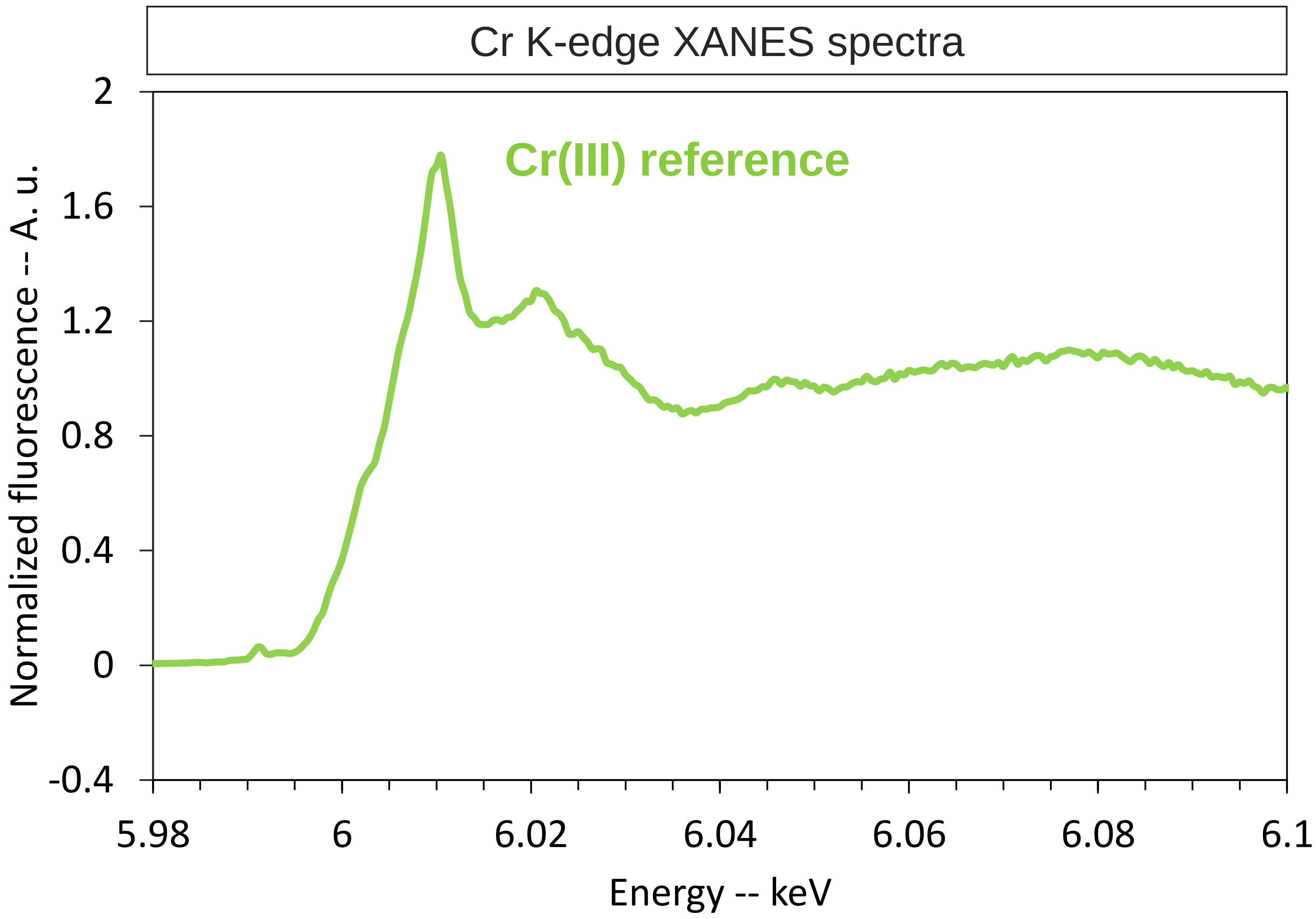
Cr(II) : CrO, mostly encountered as gaseous species	Cr(III) : commonly used as colorant, stable in glasses	Cr(IV) : brownish powder, unstable thermodynamically	Cr(VI) : very mobile and toxic, classified as hazardous
CrO – Cr^{2+}	Cr_2O_3 – Cr^{3+}	CrO_2 – Cr^{4+}	CrO_3 – Cr^{6+}

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 %

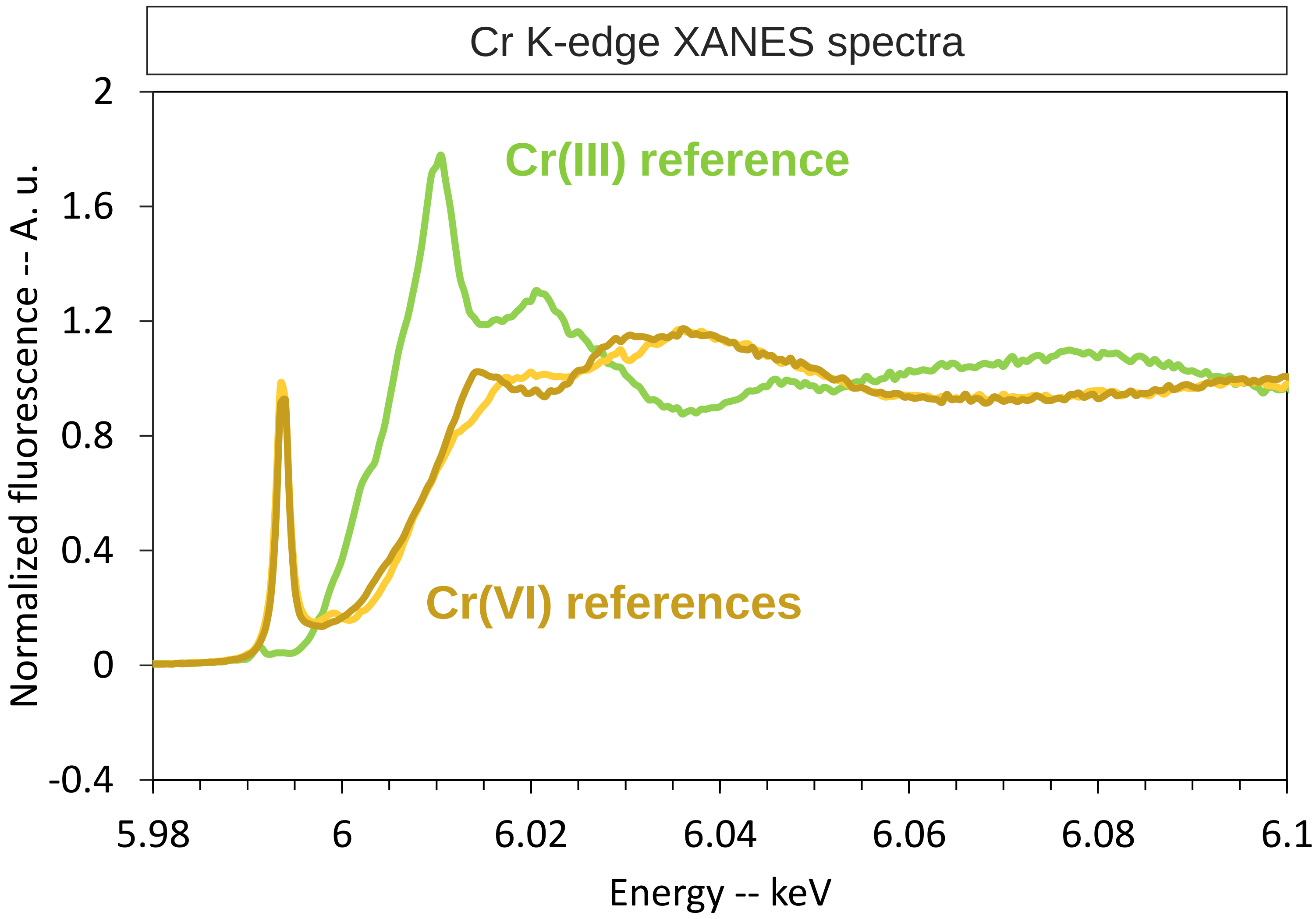
Speciation of chromium in lead crystal glasses

- ❑ **Peak position at 6.0075 eV for Cr(III) reference**



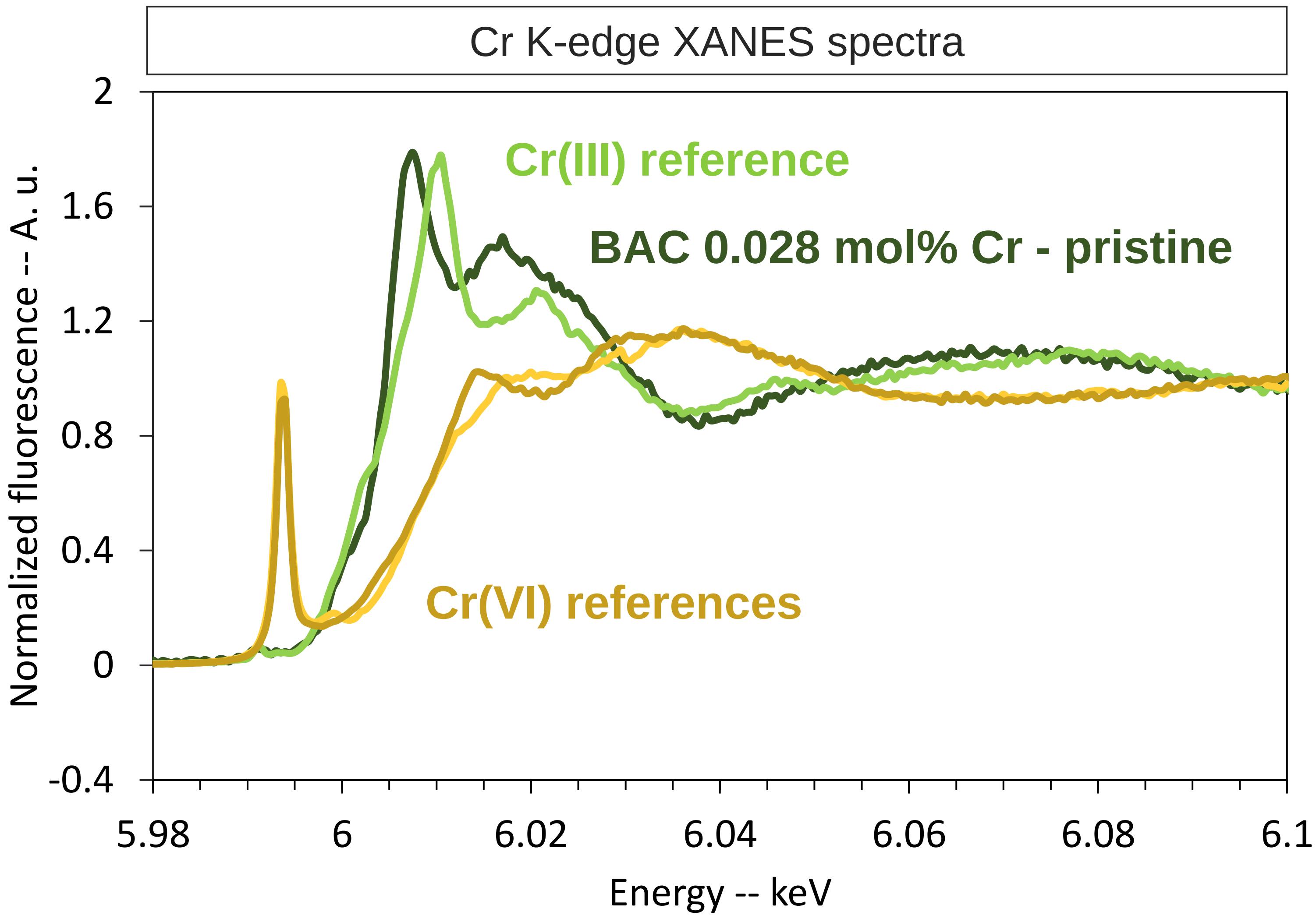
Speciation of chromium in lead crystal glasses

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



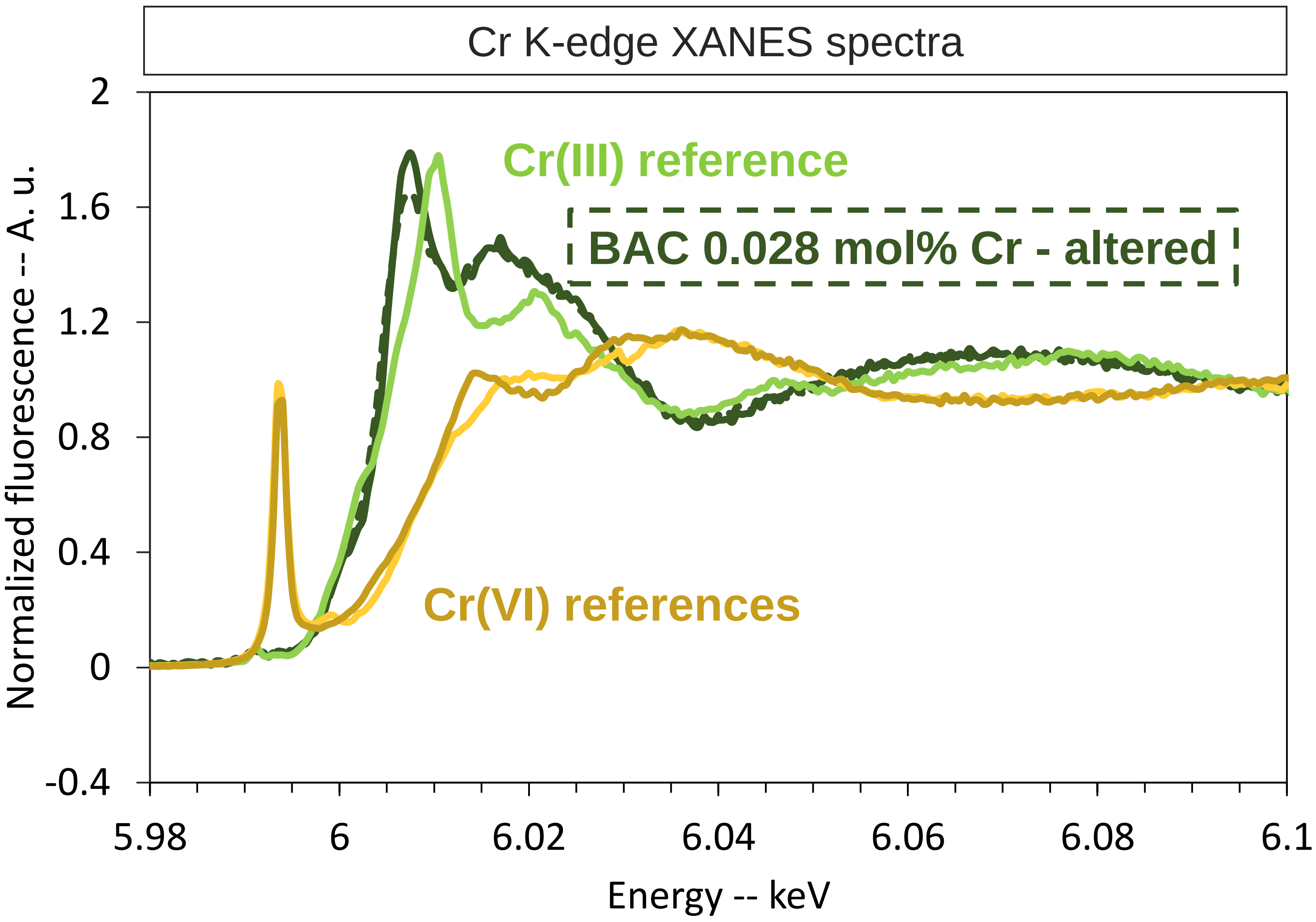
Speciation of chromium in lead crystal glasses

- ❑ 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

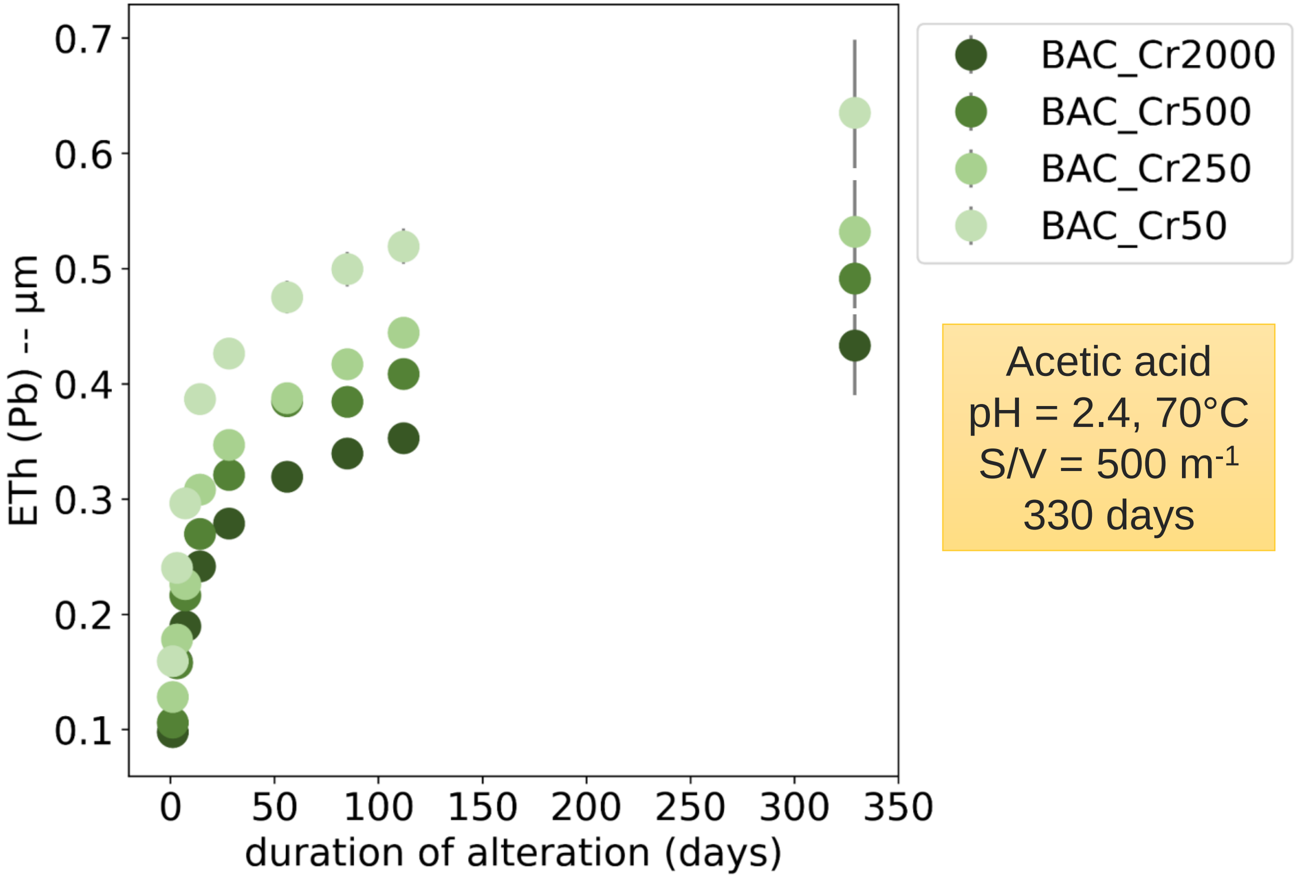


Speciation of chromium in lead crystal glasses

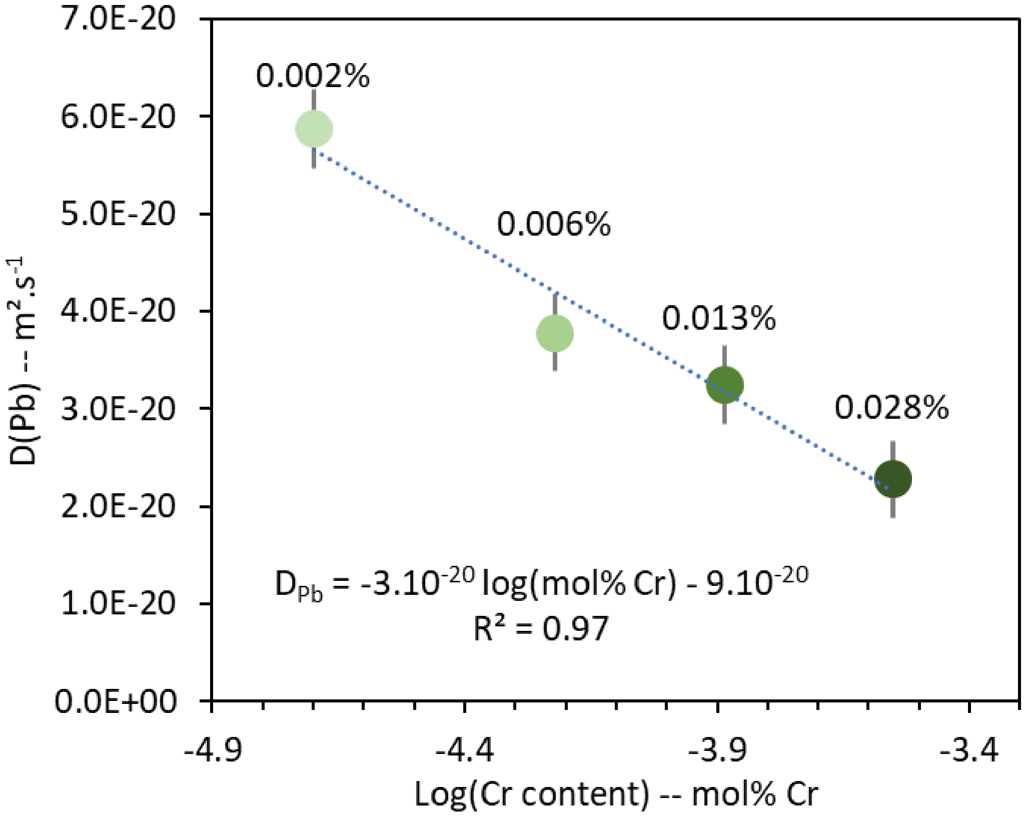
- Peak position at 6.0075 eV for Cr(III) reference
- Peak position at 5.9935 eV for Cr(VI) references
- Cr(III) only is detected in pristine Cr-bearing glasses
- **No change in the oxidation degree of Cr after alteration**



Leaching of lead crystal glass with Cr



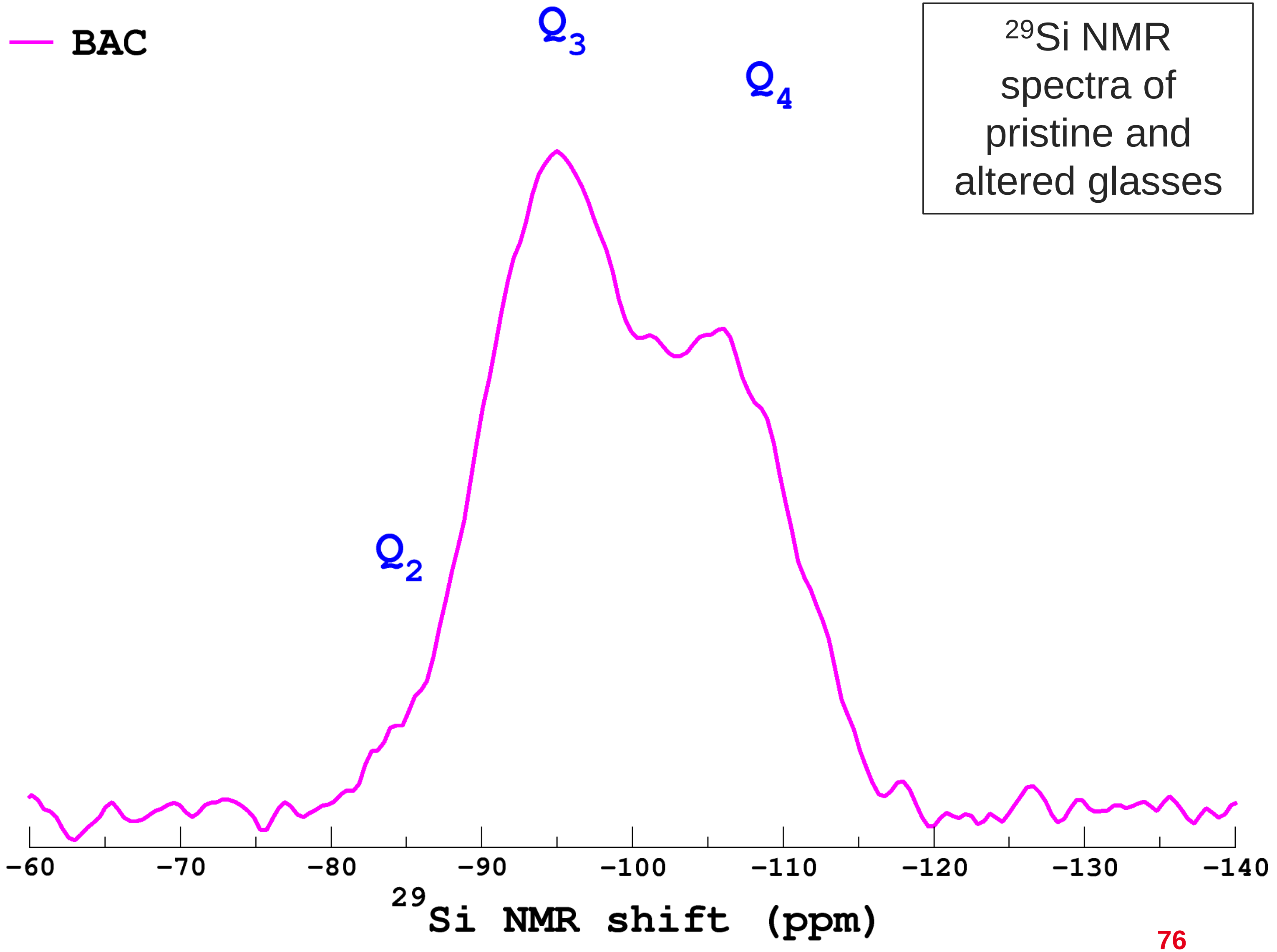
Acetic acid
pH = 2.4, 70°C
S/V = 500 m^{-1}
330 days



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

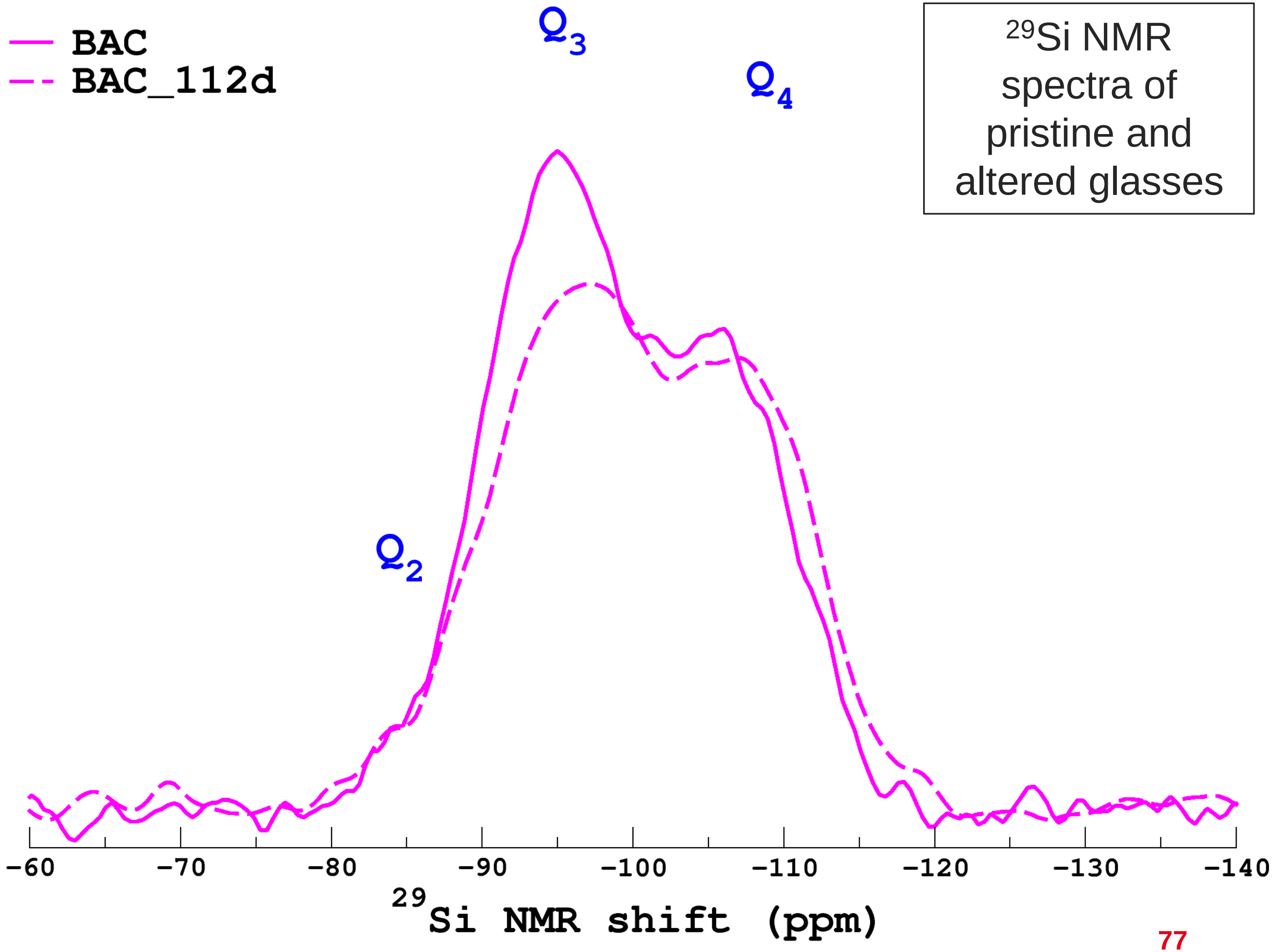
- **Linear decrease in of D(Pb) as a function of the Cr content**

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



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

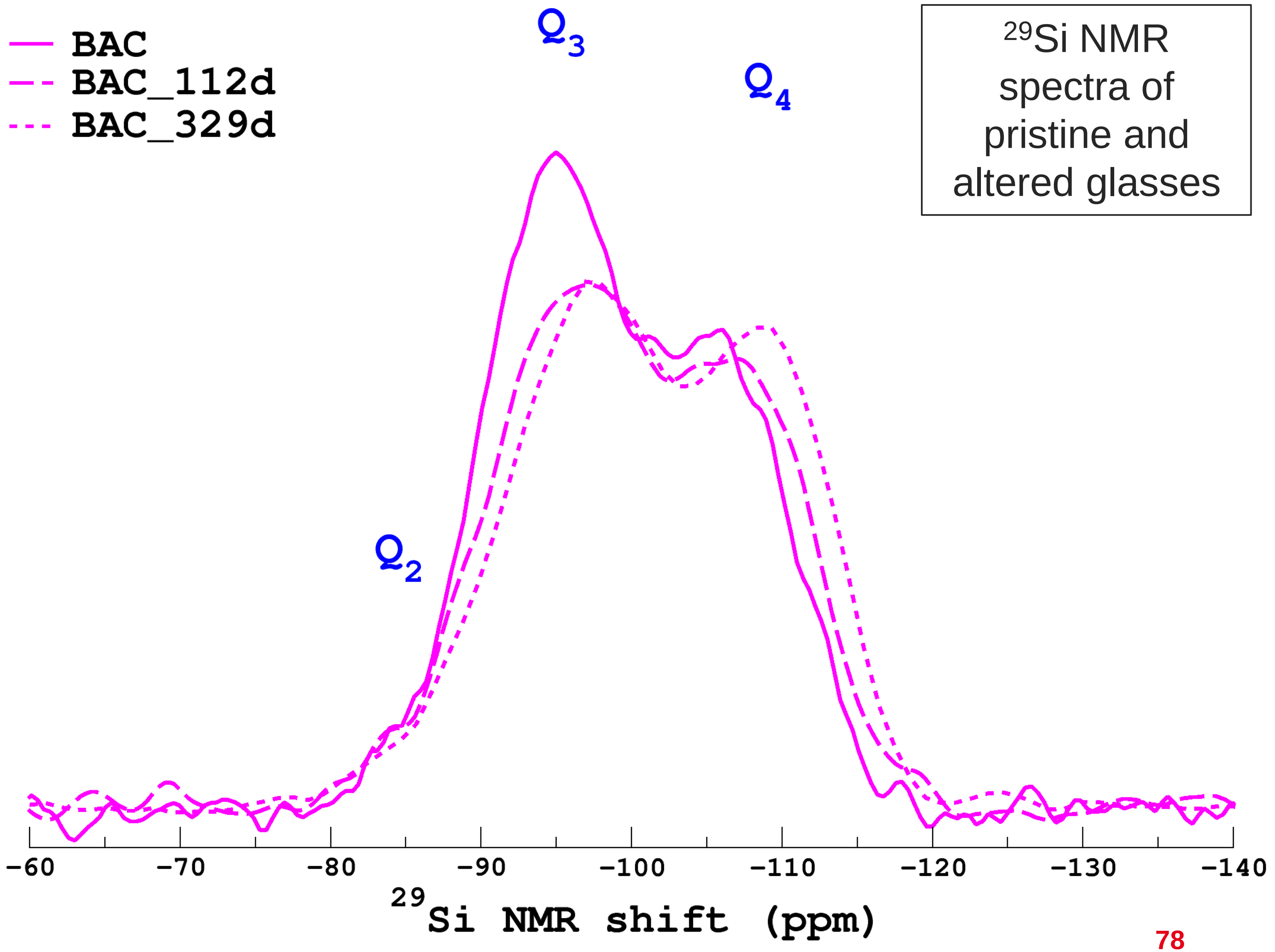
Impact of Cr on the structure of lead crystal glass during alteration



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

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

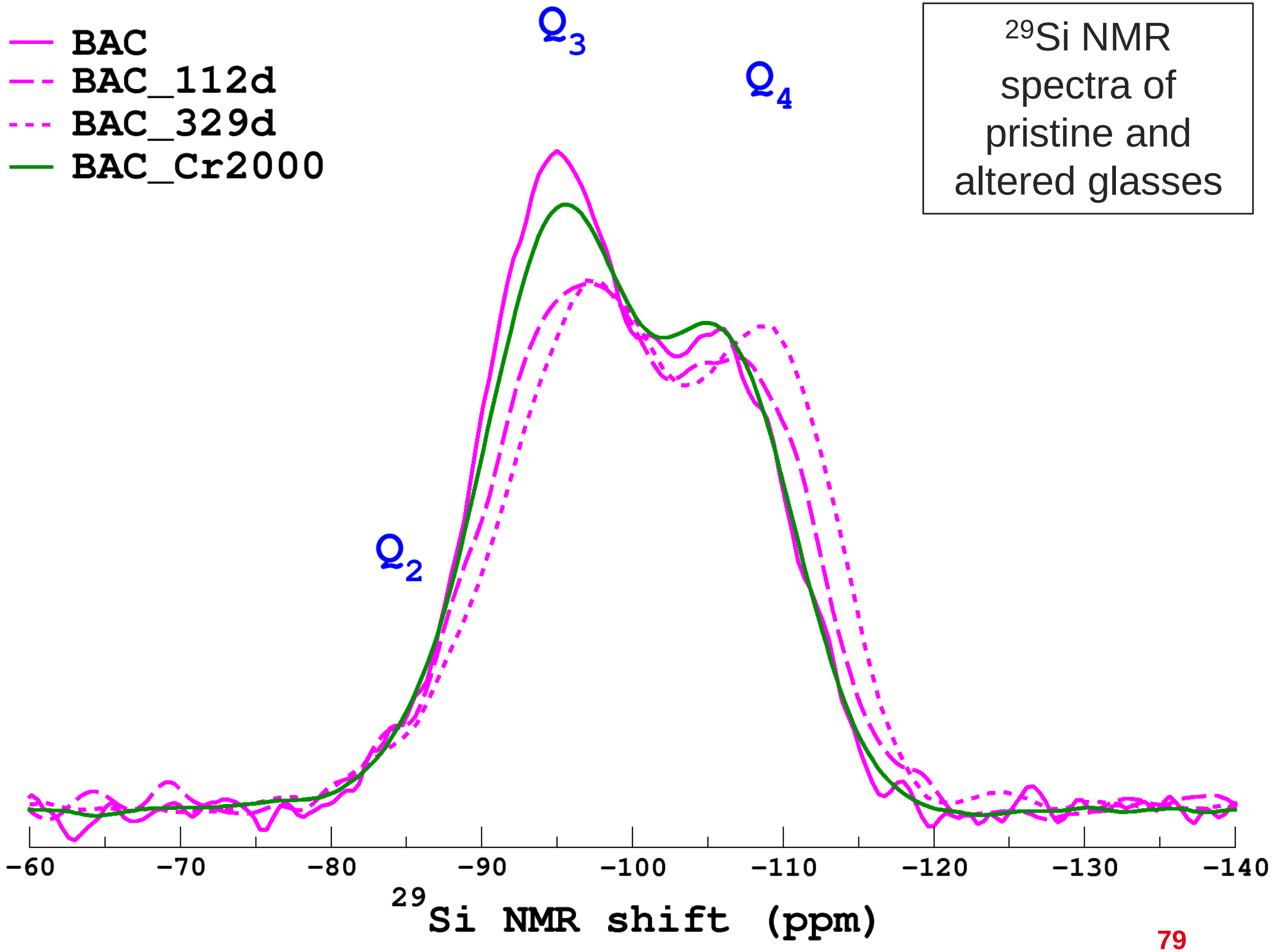
- The addition of Cr enhances the polymerization of the Si network before alteration.



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

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

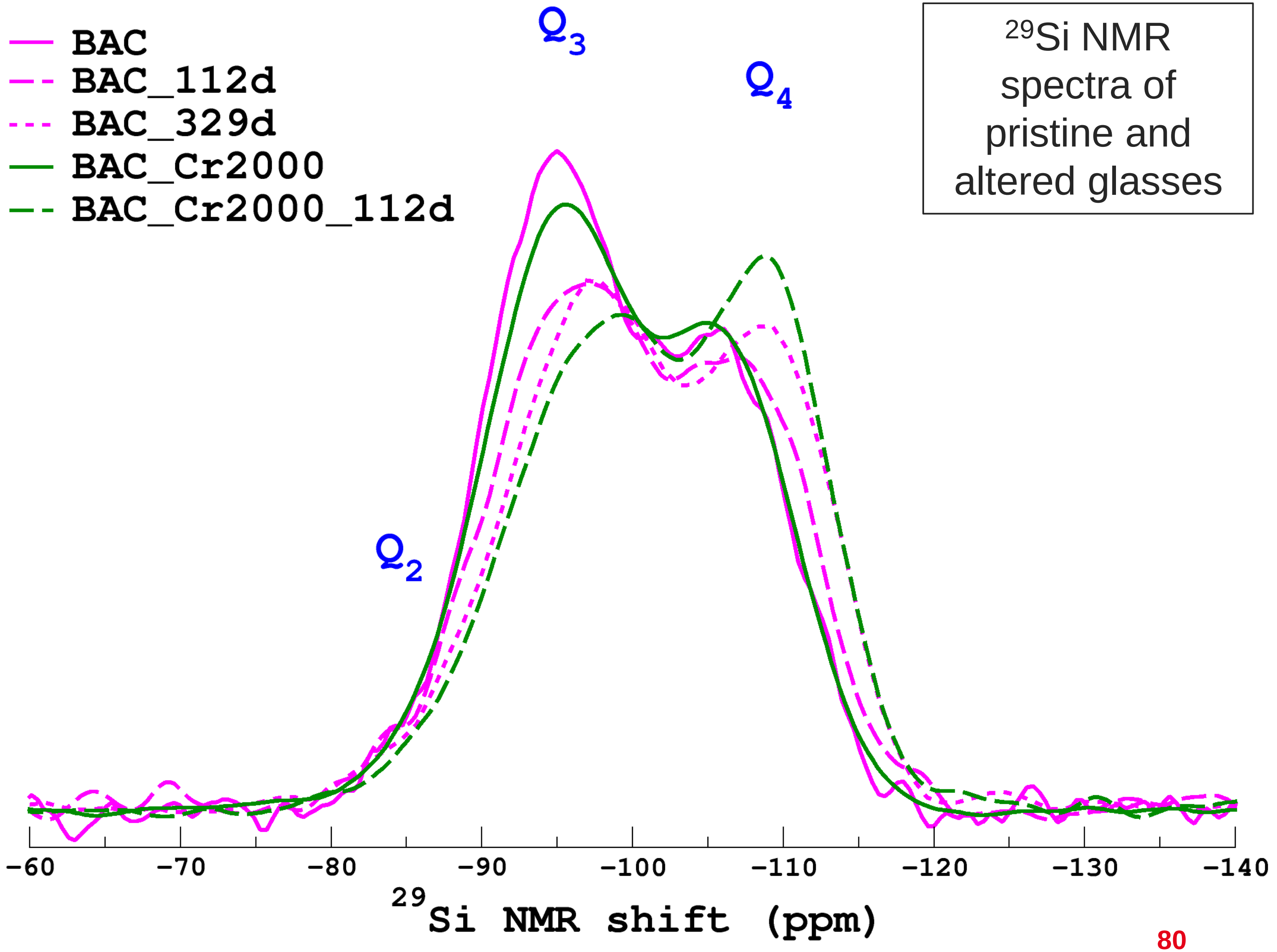
- The addition of Cr enhances the polymerization of the Si network before alteration.



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

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

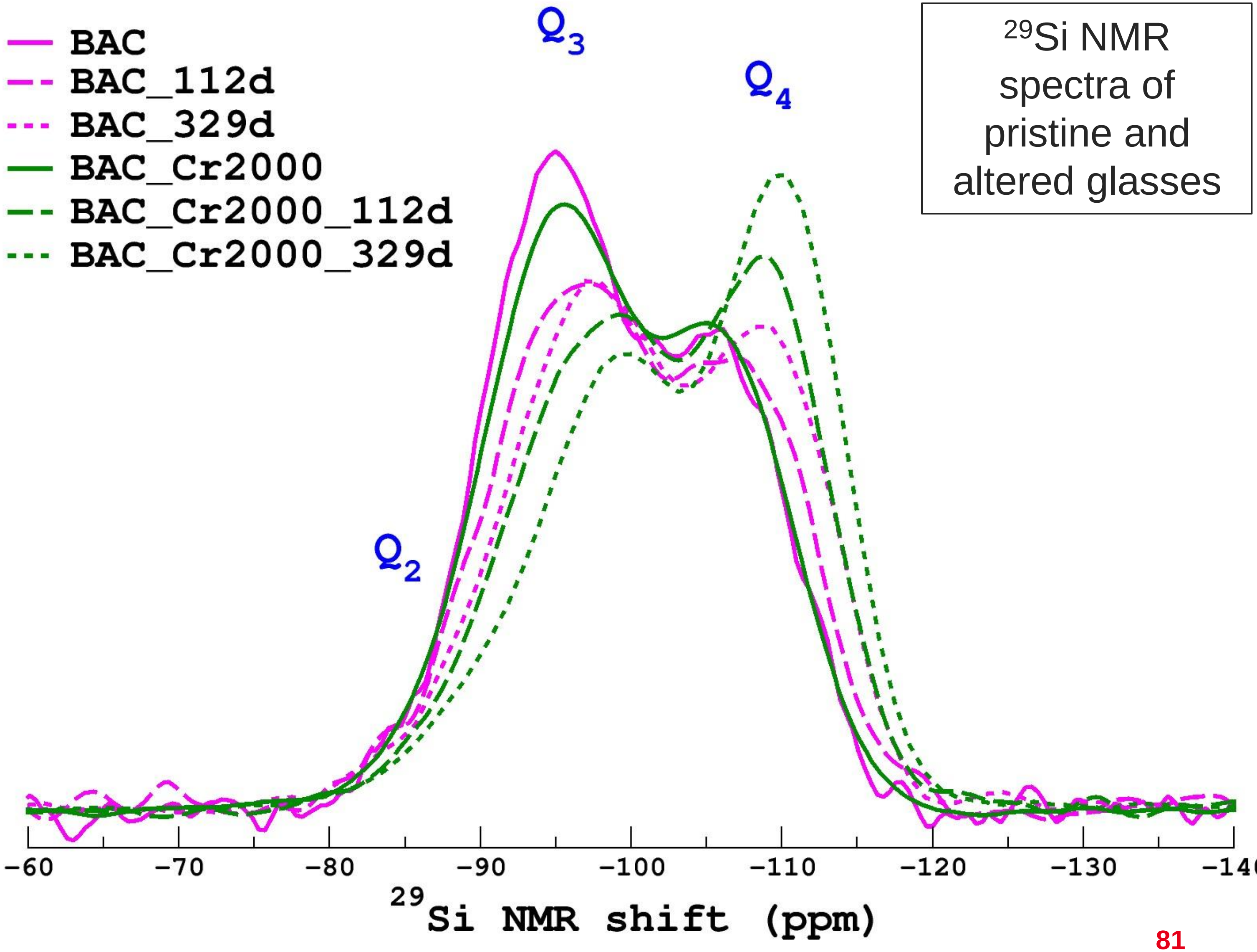
- The addition of Cr enhances the polymerization of the Si network before alteration and **after alteration**



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

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

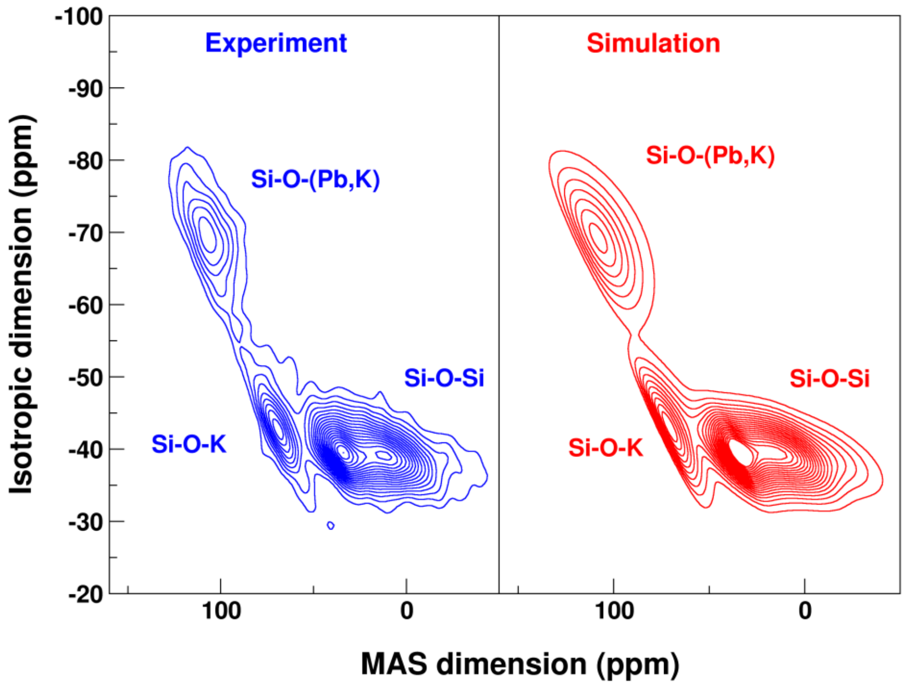
- The addition of Cr enhances the polymerization of the Si network before alteration and **after alteration**



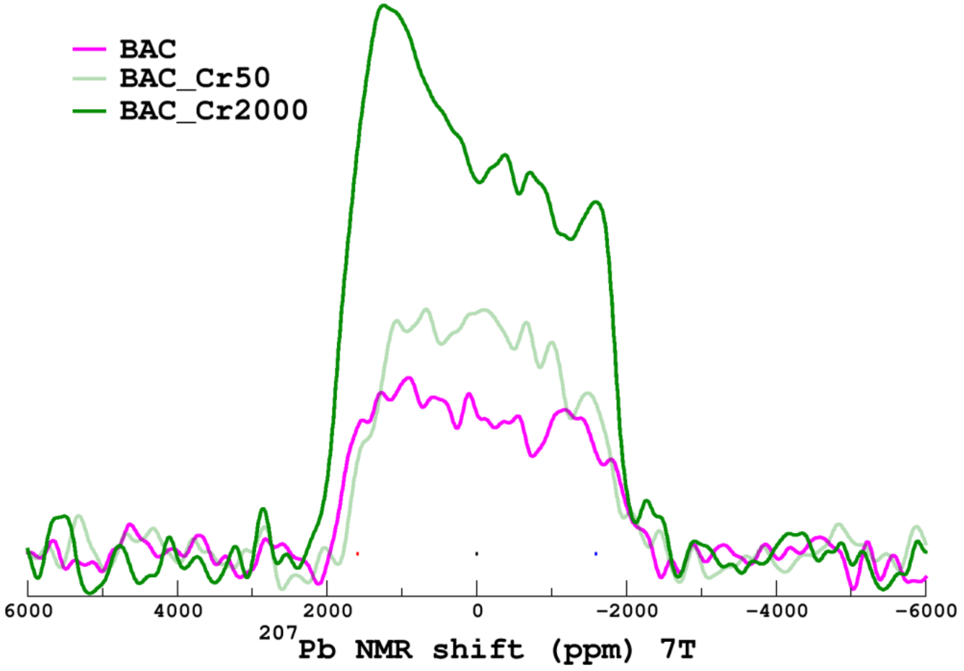
^{29}Si NMR spectra of pristine and altered glasses

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

^{17}O MQMAS NMR
Enriched oxygen-17 crystal glass (without Cr)



^{207}Pb MAS NMR
Spectra are normalized to the same sample mass



❑ A part of K is located near Pb, forming **mixed Si−O−(Pb,K) near NBOs**

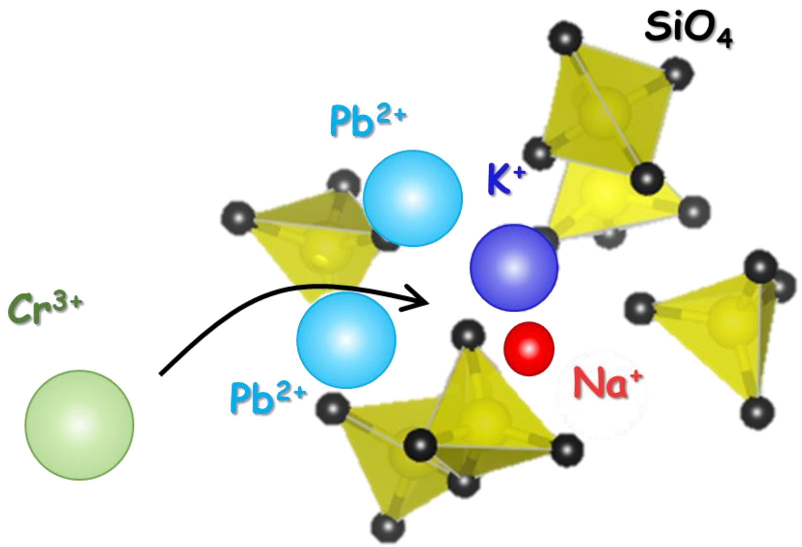
**Angeli, F. et al. (2016), Environmental Science & Technology, 50(21)*

❑ Pb NMR intensity signal increases with Cr content

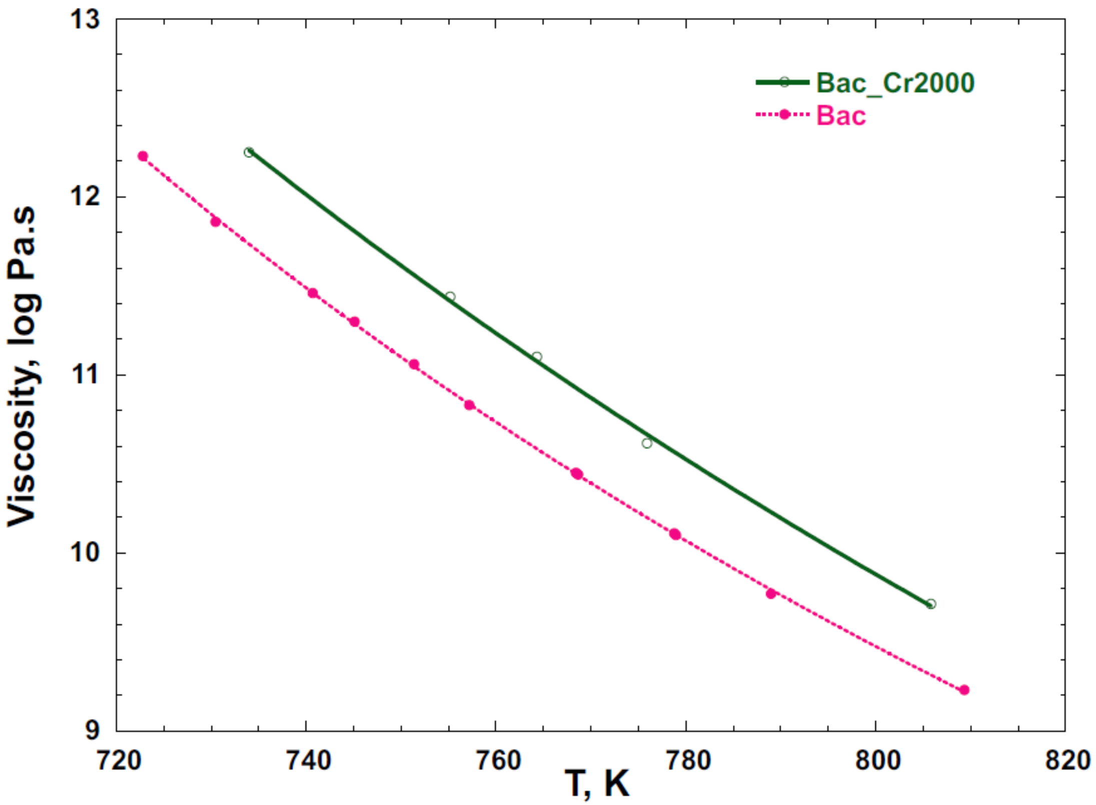
Cr (paramagnetic): increases Pb relaxation time, and then the spectra intensity

→ **Proximity between Pb and Cr**

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



- The mixing sites with (Pb,K) **contain Cr**
- **Cr** acts as a **hardener for the glassy network**
- **Cr is retained** in the glass structure during alteration, also **improving Pb retention**
- **Cr^{3+} only, stable during alteration**



- ↑ Cr = ↑ viscosity

Conclusions & Perspectives

Conclusions

- Unique database on the **leaching behavior of industrial glass**
  - Commercial glass products: **resistant and durable materials** towards alteration
- Unique database on the **most suitable surface treatments to limit cation release**
  - Potentially toxic elements from glasses: can be limited by **surface treatments that last over time (aggressive leaching conditions)**
- Cation **local structural configuration**
  - **highly favorable to cation retention in glass** (ex. Cr and Pb in lead glass)

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