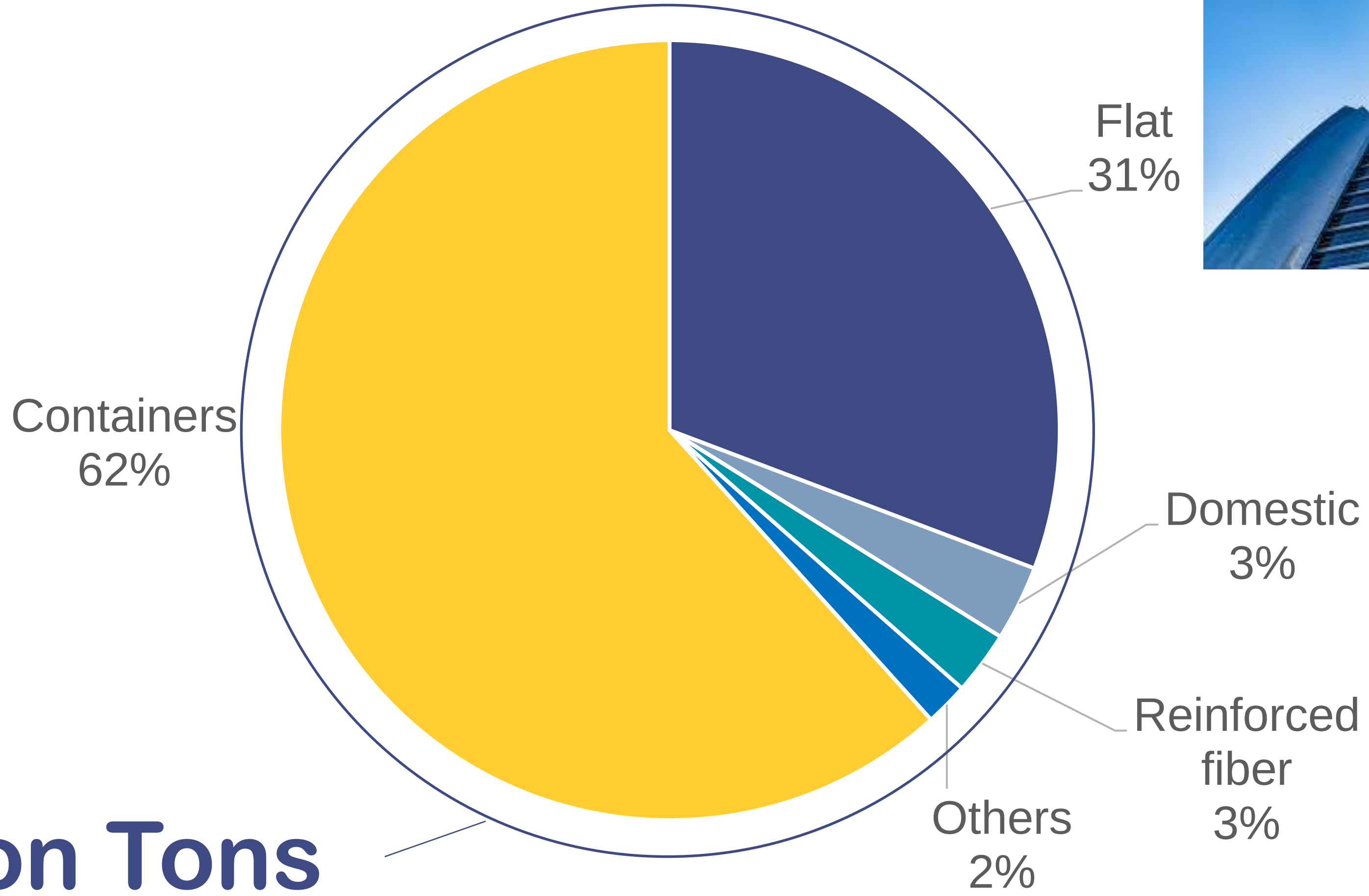
Alteration of industrial glasses

Léa Brunswic*, Frédéric Angeli, Stéphane Gin, Thibault Charpentier, Laurent Gautron, Eric van Hullebusch, Mariona Tarragó, Daniel Neuville, Xavier Capilla, Daniel Coillot, Ilyes Ben Kacem, Justine Fenech, Johann Brunie

*CEA Marcoule, DES / ISEC / DPME / SEME / LEMC – Université de Montpellier

sumglass 2023

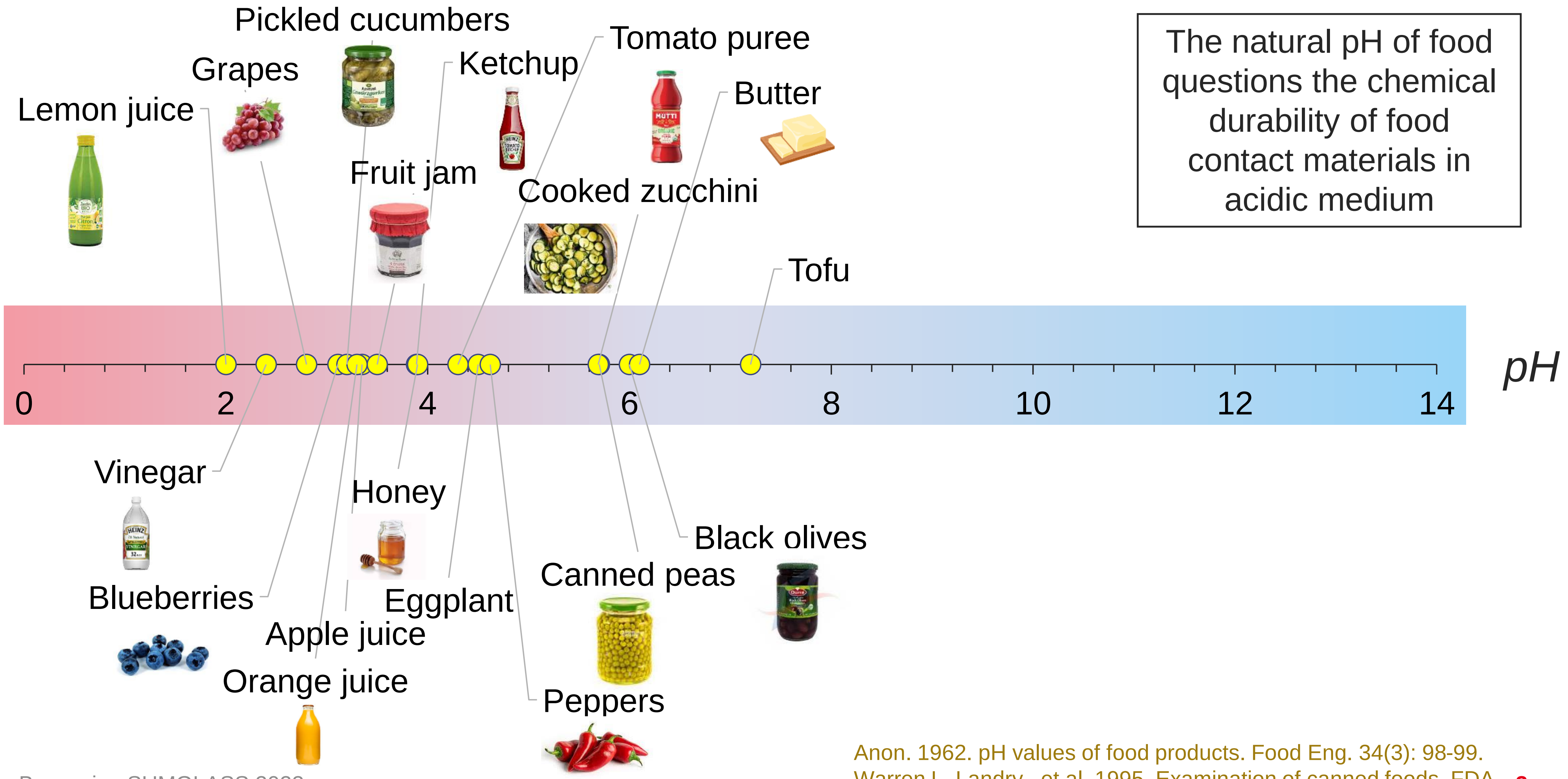
Glass production in Europe in 2022



38 Million Tons

Source : Glass Alliance Europe

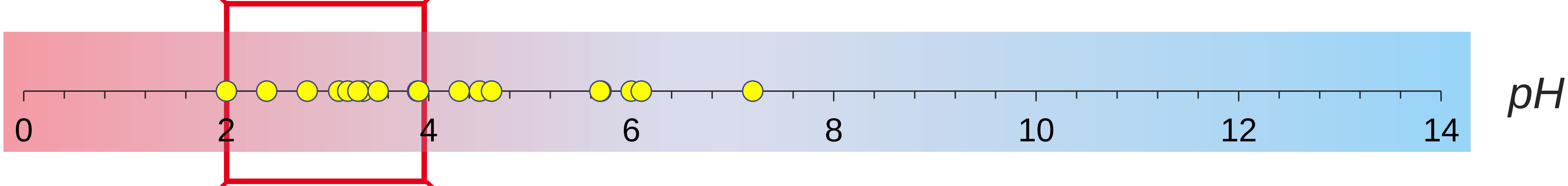
Glass containers for packaging



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

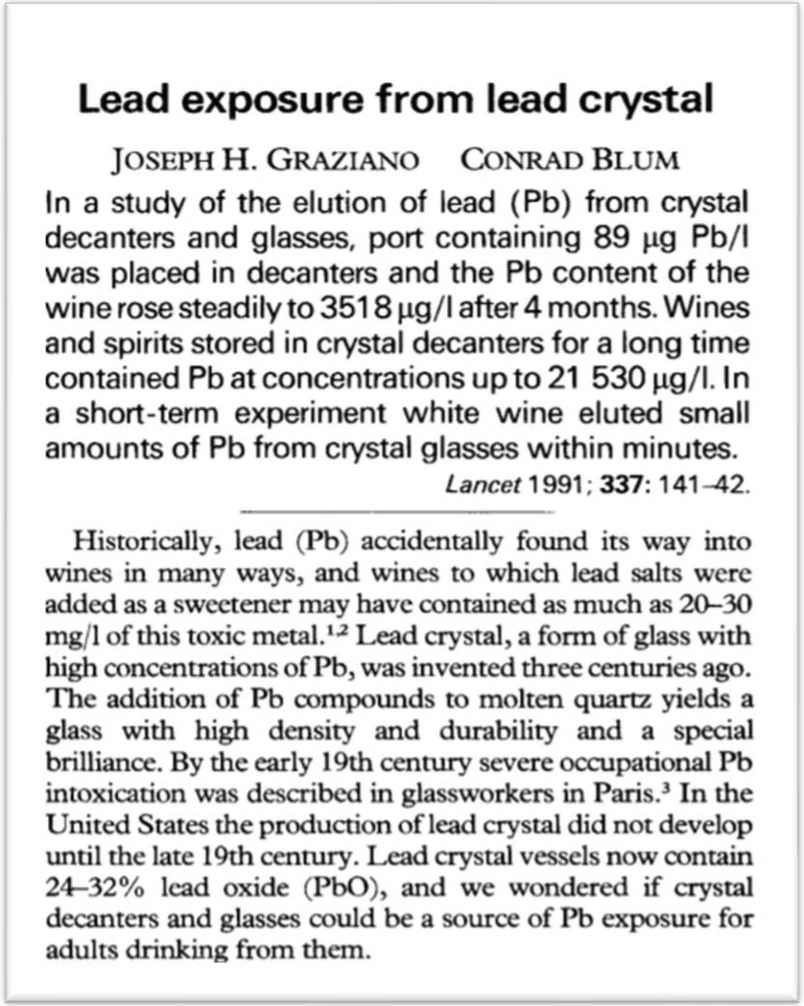


The pH of 90 % of beverages ranges between pH 2 and 4.

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).

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 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 to strength and extend for a large number of chemical elements**

Pb, Cd, Al, Co, As, Cr(VI) + Mn, Ni, Sb, Cr, Ba, Cu, Li, Zn

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 → REACH**

❑ **These regulations could have major consequences for the whole glass industry**

→ **demonstrate the ability of glass to retain potentially toxic elements** and if needed, **to propose recommendations to limit the migration** (surface treatments)

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 → REACH

❑ **These regulations could have major consequences for the whole glass industry**

→ **demonstrate the ability of glass to retain potentially toxic elements** and if needed, **to propose recommendations to limit the migration** (surface treatments)

5 widely used silicate glass from 4 major French glass manufacturers
→ most comprehensive vision of elements released in solution (with and without surface treatments)

Summary

1 Alteration of reference base glasses (Glasses A – D)

2 Alteration of glasses with surface treatments (Glasses A – D)

3 Alteration of glass-ceramic with and without surface treatments (Glass O)

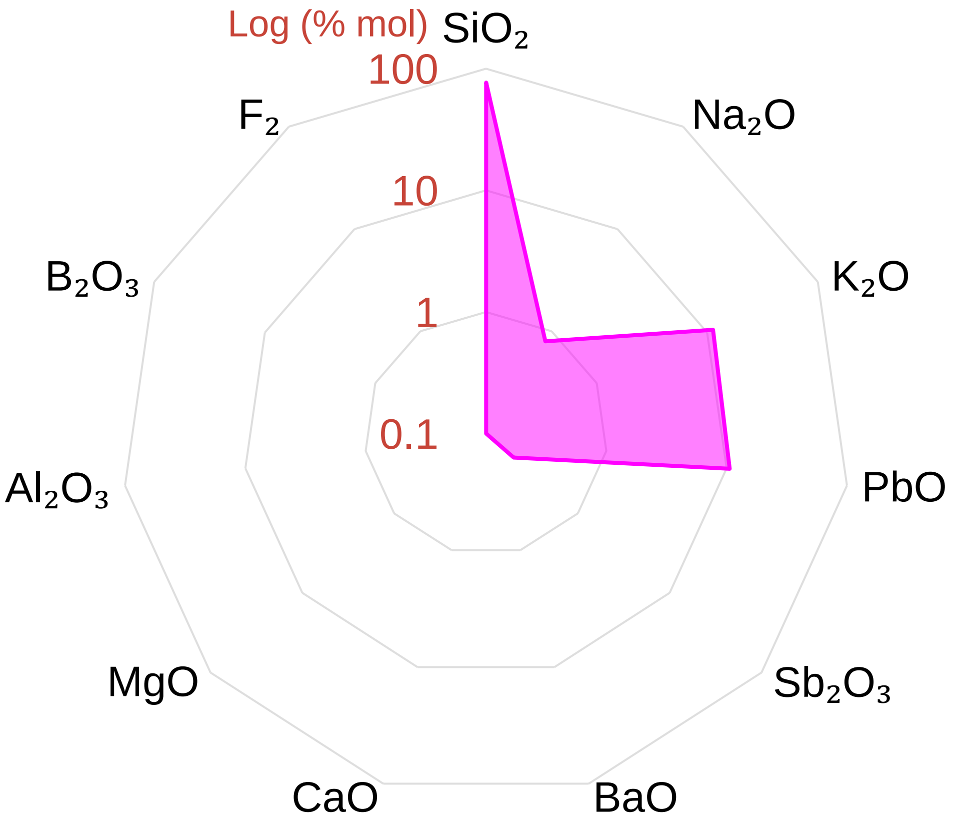
4 The impact of colorant on the durability of lead crystal glass: the case of chromium (Glass A)

Industrial glasses under study

Glass A | Lead crystal

Luxury Glassware

	% 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



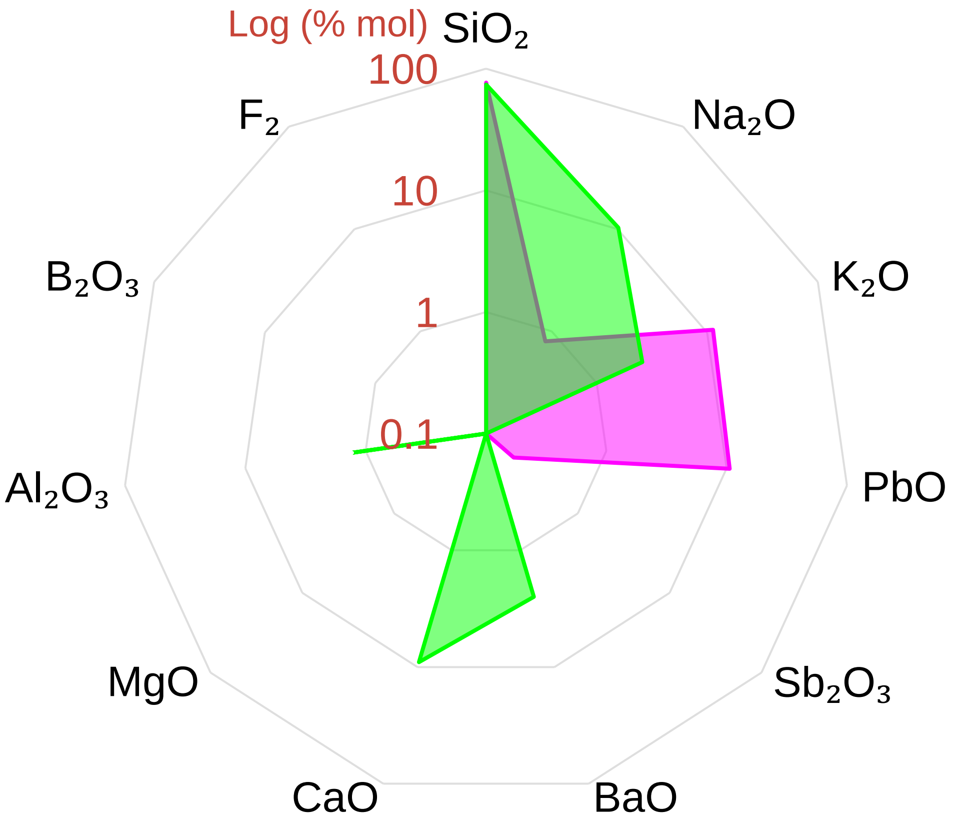
Industrial glasses under study

Glass A	Lead crystal

Glass B	Barium glass

Tableware

	% 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

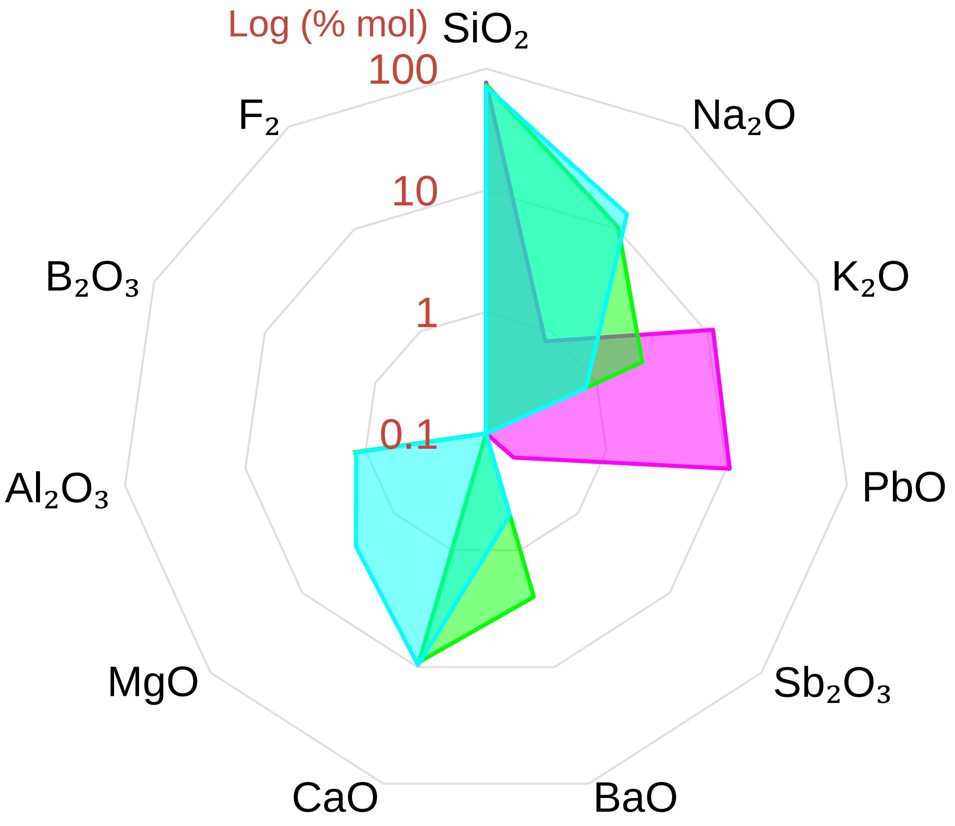
Glass A	Lead crystal

Glass B	Barium glass

Glass C	Soda-lime

Cosmetic industry (Extra-White glass)

	% 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

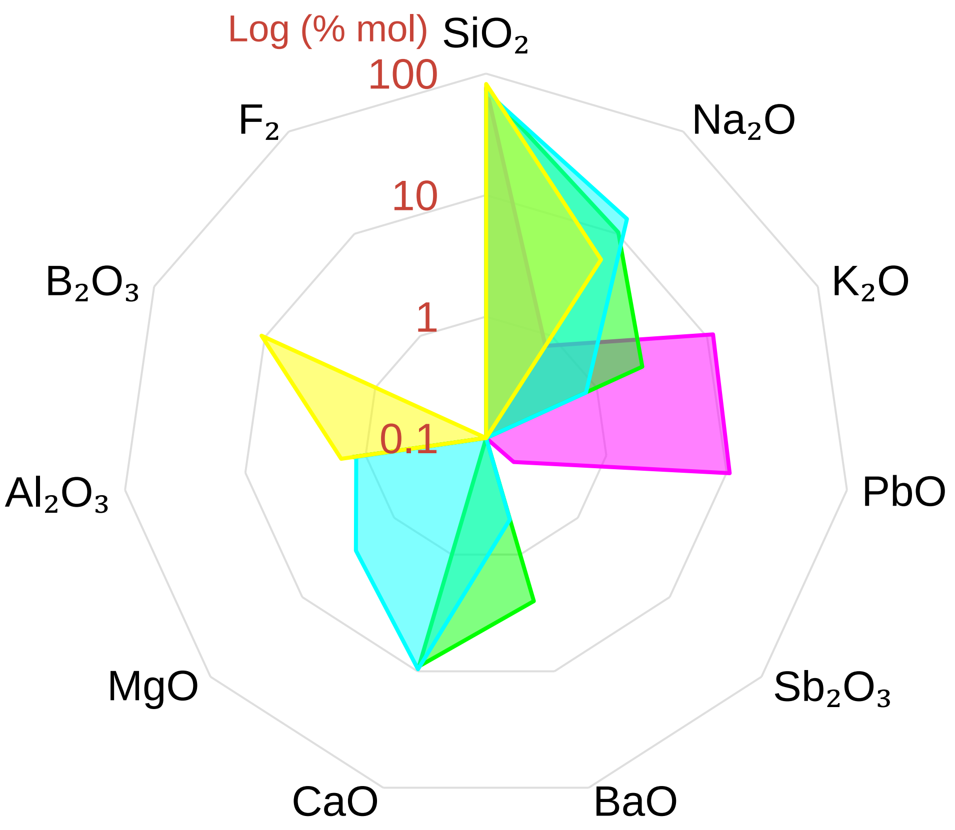
Glass B	Barium glass

Glass C	Soda-lime

Glass D	Borosilicate

Cooking dishes

	% 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



LA MAISON FRANÇAISE DU VERRE

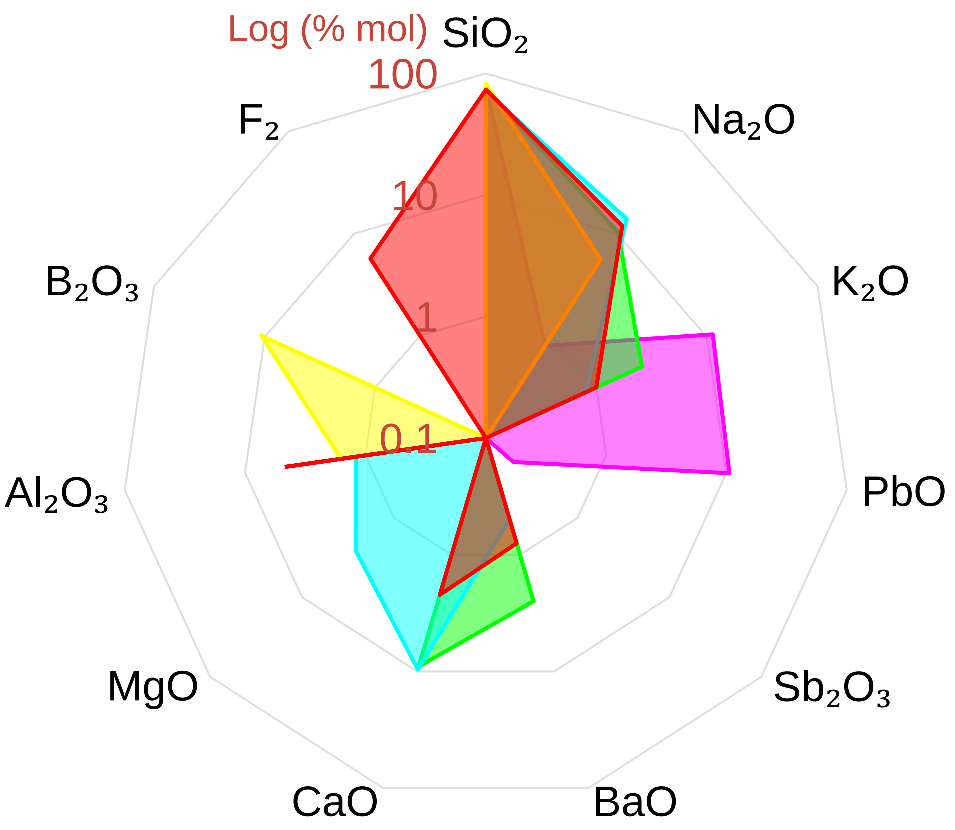
PYREX

Industrial glasses under study

Tableware

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

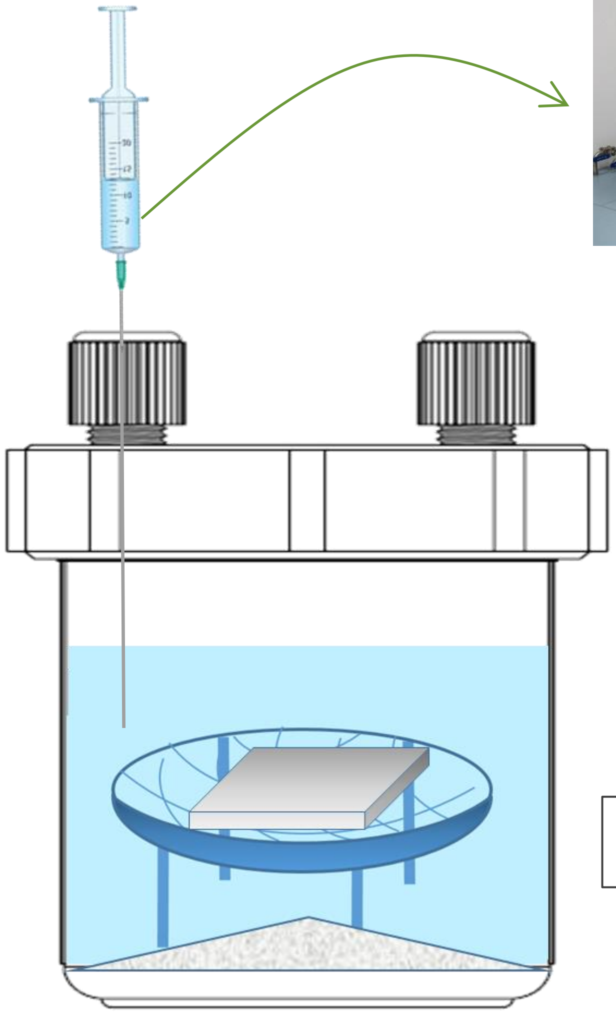


arc

1. Alteration of reference base glasses for 3 years

Experimental approach

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



- ICP-AES

Kinetics of alteration

- Solid state NMR
- SEM

- ToF SIMS

- Solid state NMR

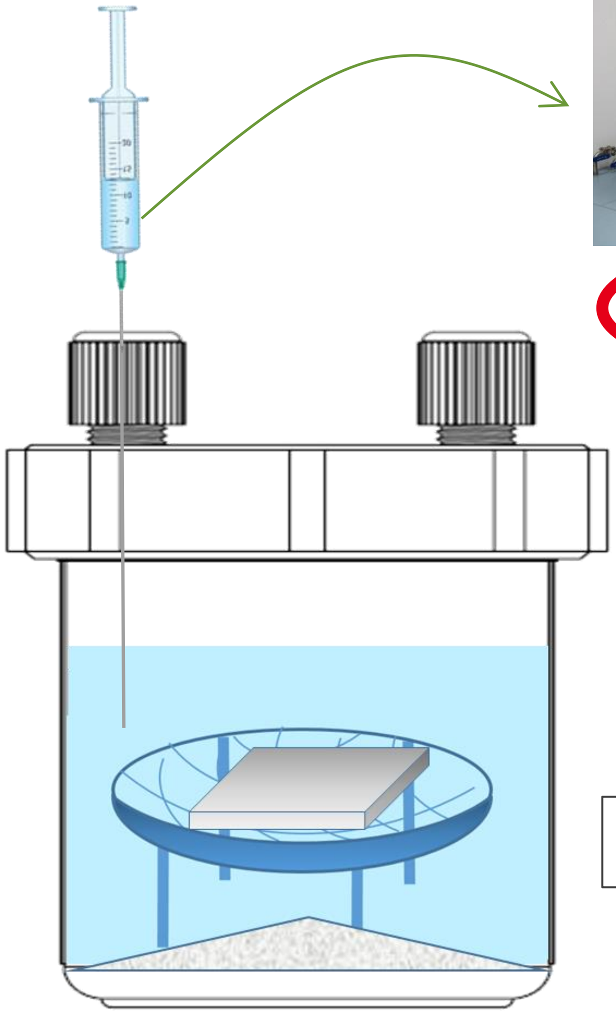
- SEM

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

alteration

Experimental approach

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



- ICP-AES

Kinetics of alteration

- Solid state NMR
- SEM

- ToF SIMS

- Solid state NMR

- SEM

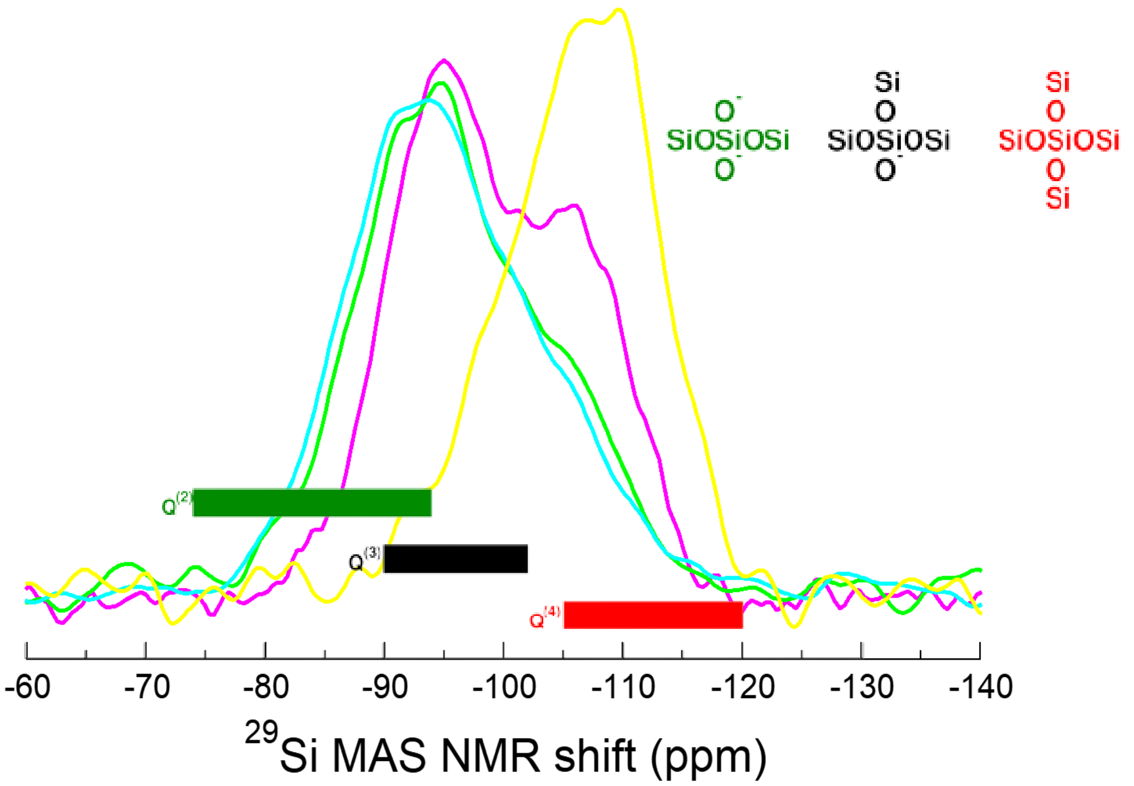
0 days | 231 days | 969 days | 3 years

alteration

Structure and leaching of the silicate network

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

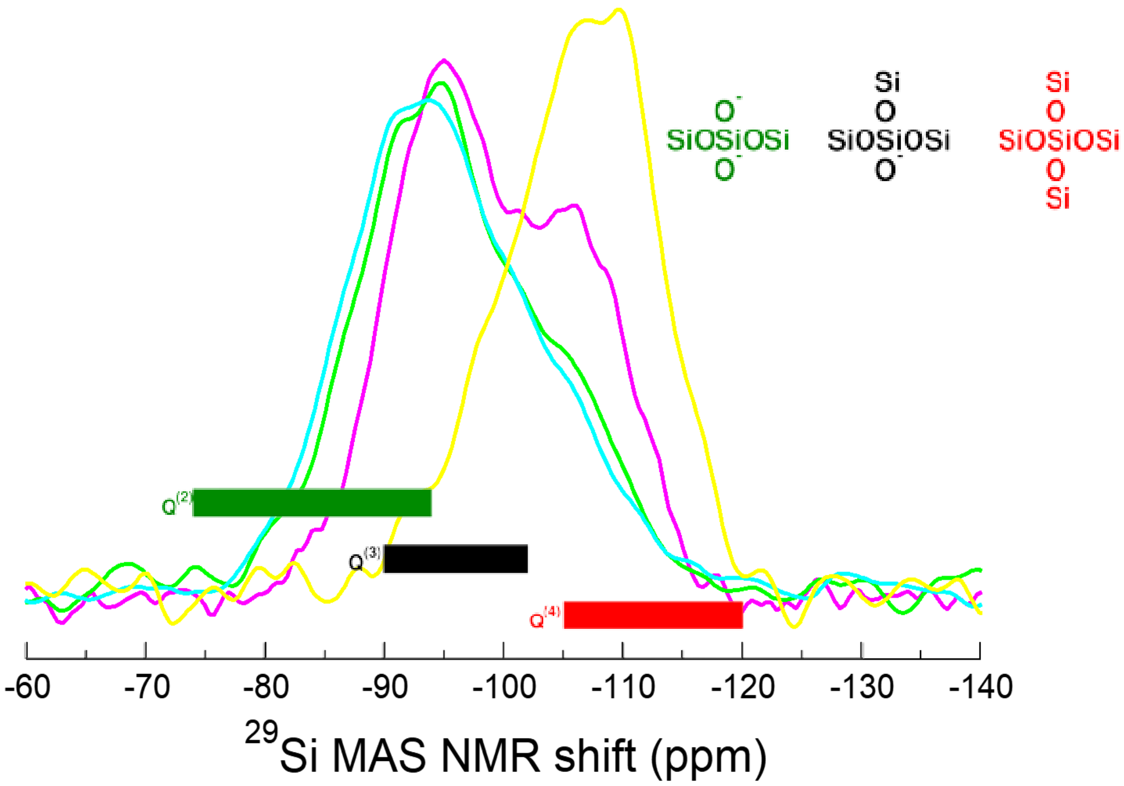
^{29}Si NMR spectra of the pristine glasses

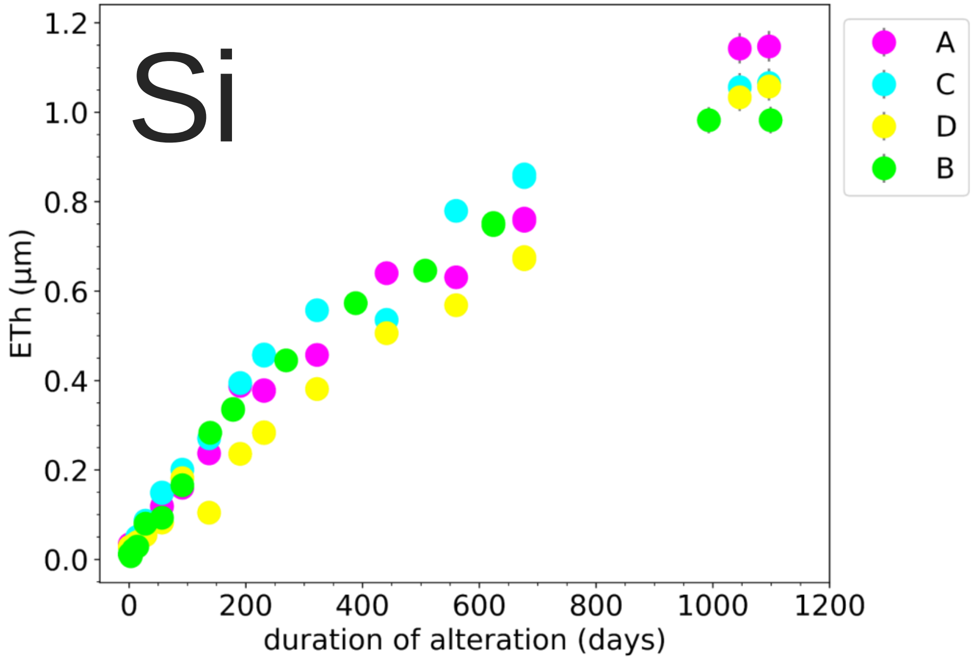


Structure and leaching of the silicate network

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

^{29}Si NMR spectra of the pristine glasses





- **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

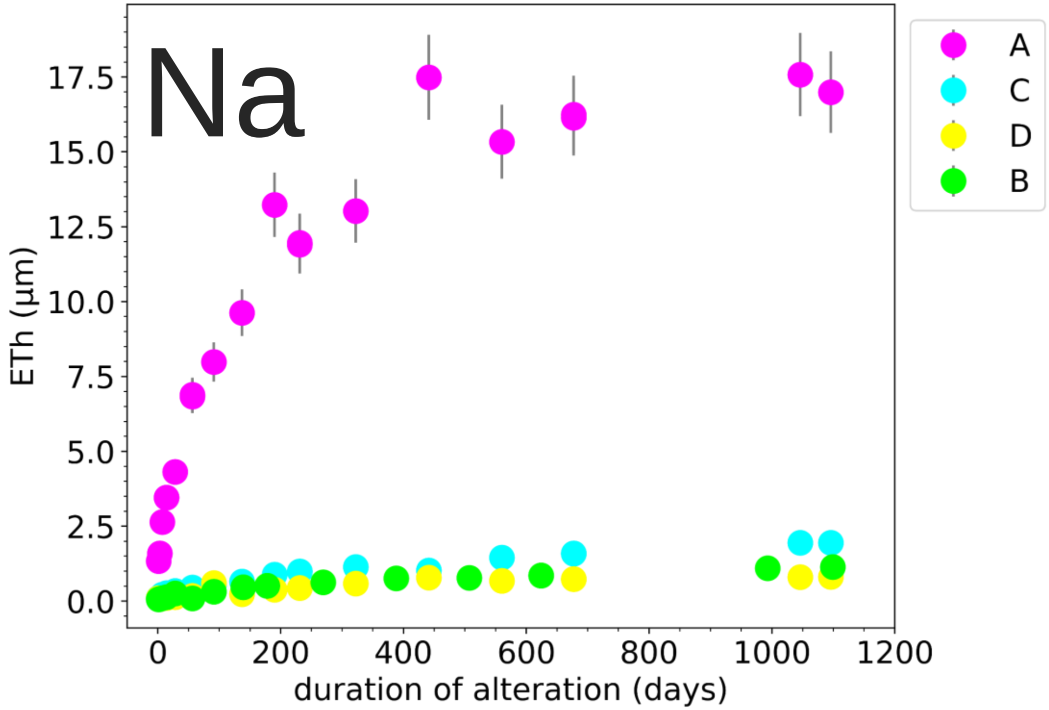
Leaching of the tracing element of alteration

Glass A	Lead crystal

Glass B	Barium glass

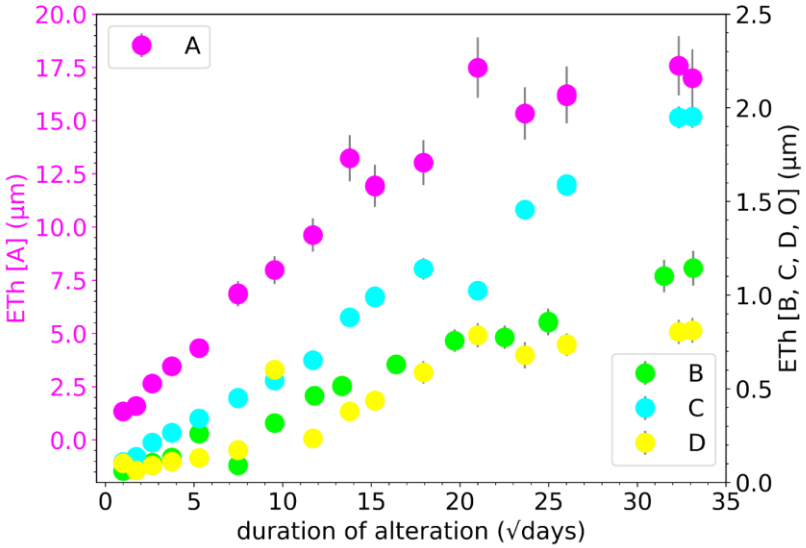
Glass C	Soda-lime

Glass D	Borosilicate



- ❑ **Na release: ions exchange mechanism**
- ❑ Interdiffusion mechanism:
  → different diffusion rates
- ❑ Na rate higher than Si

(exept for highest polymerized glass:
→ congruent dissolution) Glass D Borosilicate



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

2. Alteration of glasses with surface treatments

Surface treatments under study

Chemical deposits: Si, Sn, Ti

Chemical attacks: PA, CEMa, CEMb

Surface coatings (CVD): Si, Sn, Ti

Surface treatments under study

Chemical deposits			Chemical attacks		
Si	Sn	Ti	PA	CEMa	CEMb

PA → Acidic etching

Before

After

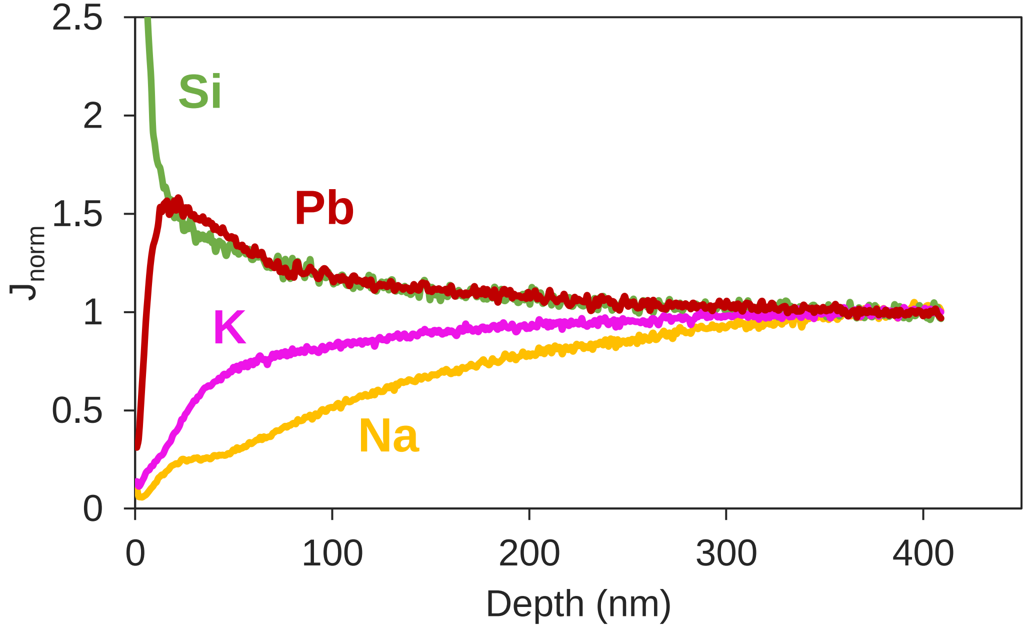
Surface treatments under study

Chemical deposits: Si | Sn | Ti

Chemical attacks: PA | CEMa | CEMb

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

Effects of surface treatments

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

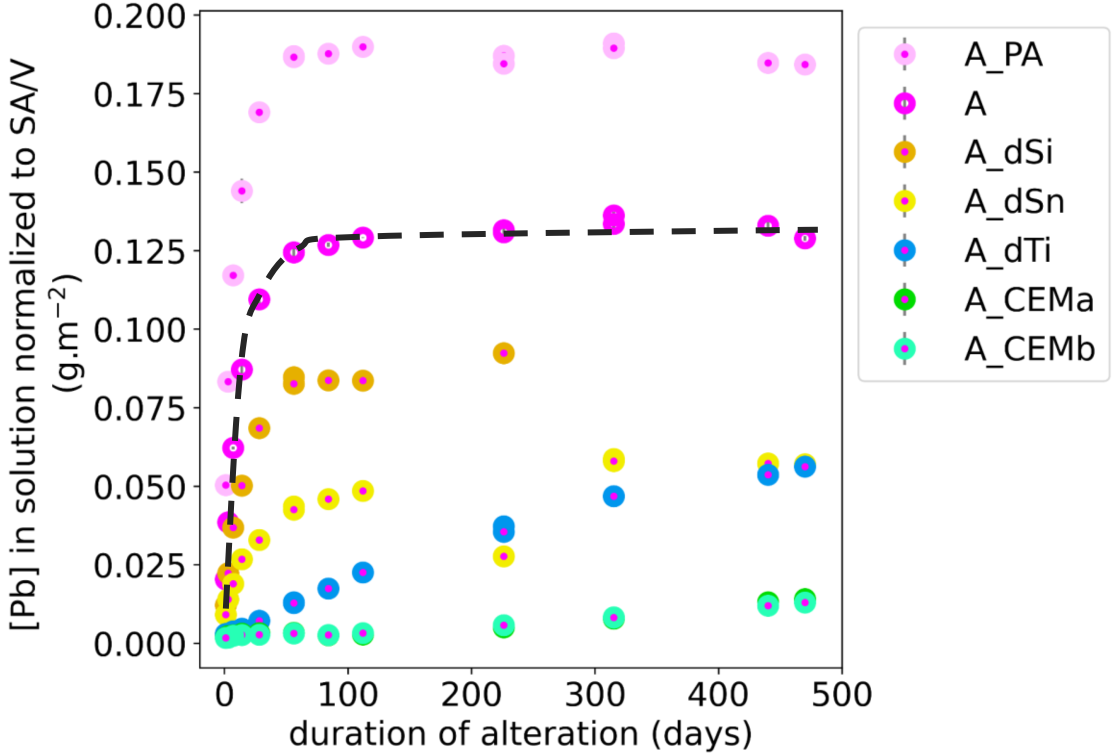
Chemical reactions: PA, CEMa, CEMb — *Dealkalinization by SO_2 vapor treatment*

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 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

Effects of surface treatments

Physical deposits | Chemical reactions

Si | Sn | Ti | PA | CEMa | CEMb

Surface coatings (sputtering)

Acidic etching

Dealkalinization by SO_2 vapor treatment

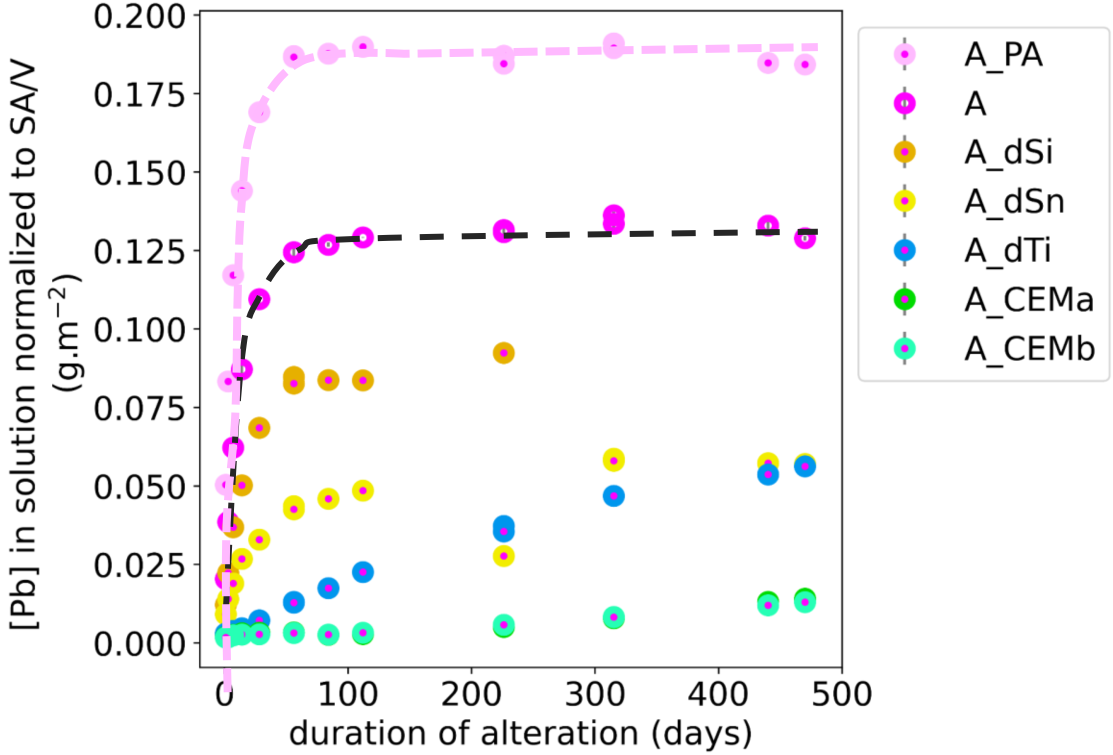
Acetic acid
pH = 2.4, 70°C
S/V = 2.5 m^{-1}
~ 500 days

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



❑ **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

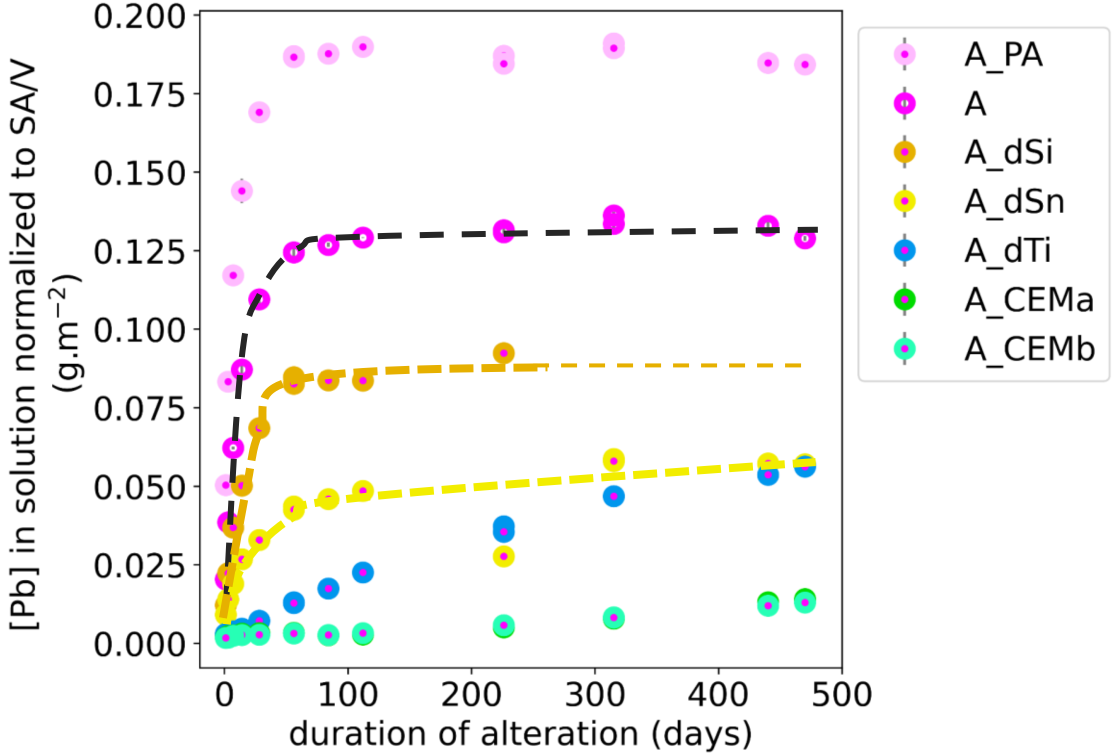
Acetic acid
pH = 2.4, 70°C
S/V = 2.5 m^{-1}
~ 500 days

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

Pb

Glass A | Lead crystal



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

→ effect on the reduction of Pb release is moderate

Effects of surface treatments

Physical deposits			Chemical reactions		
Si	Sn	Ti	PA	CEMa	CEMb

Surface coatings (sputtering)

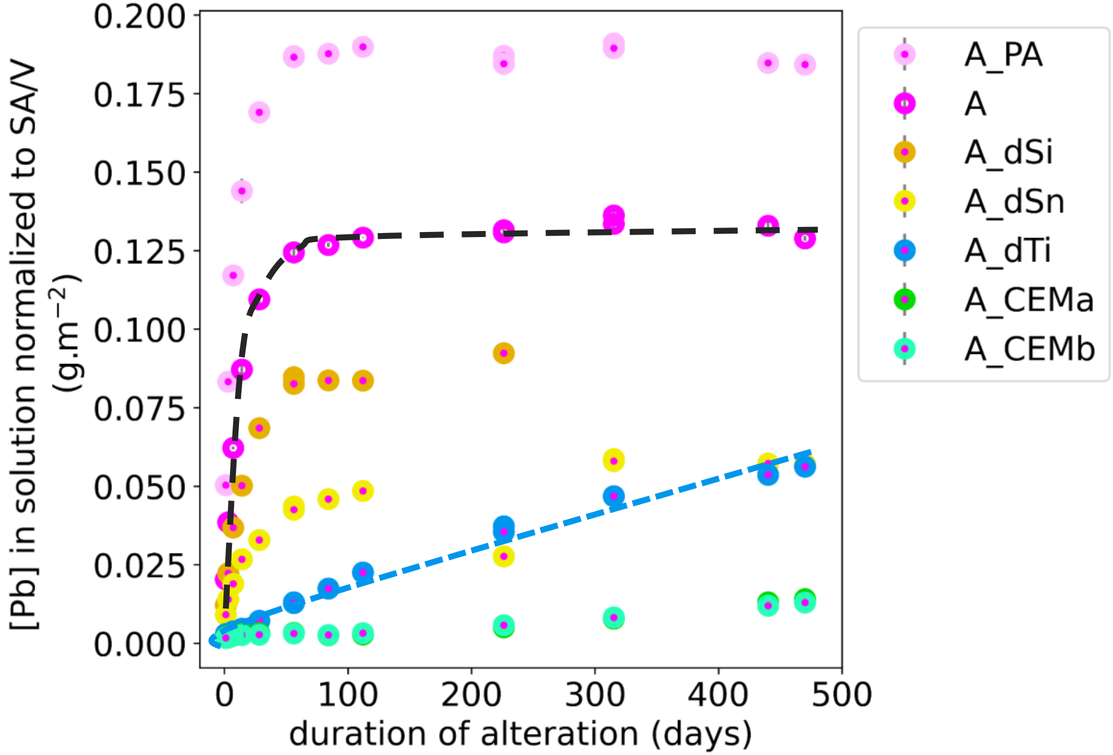
Dealkalinization by SO_2 vapor treatment

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

❑ **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**

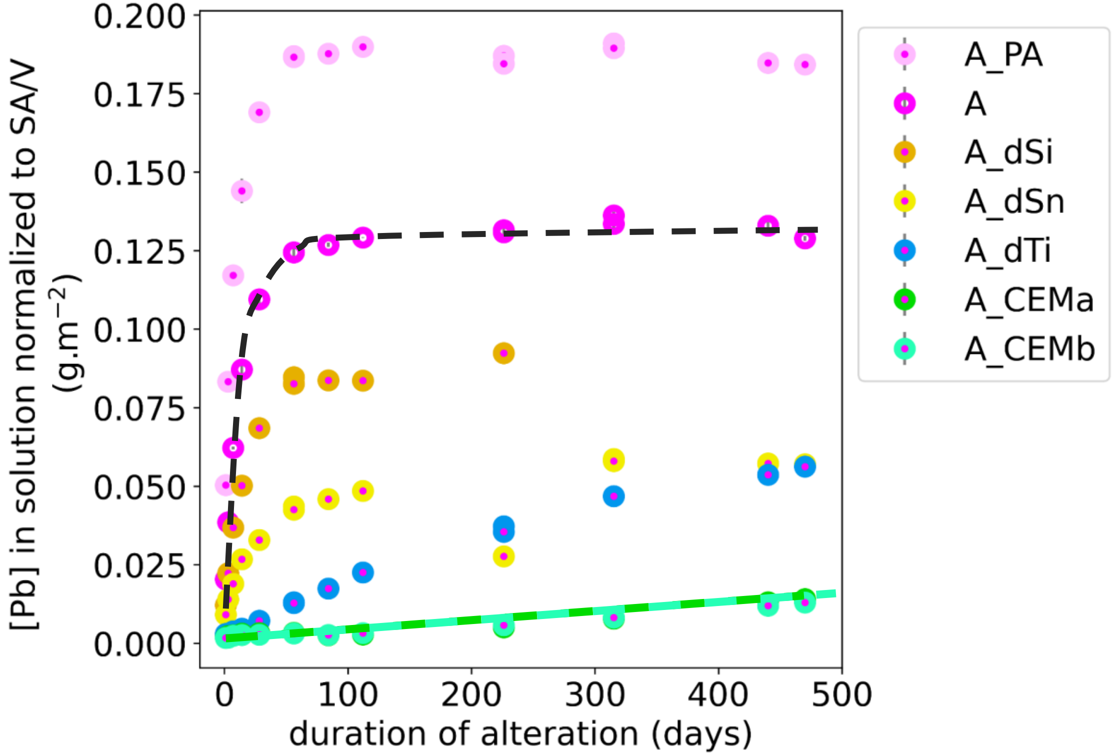
Surface coatings (sputtering) | *Dealkalinization by SO_2 vapor treatment*

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

- **SO_2 dealkalization** (most efficient)

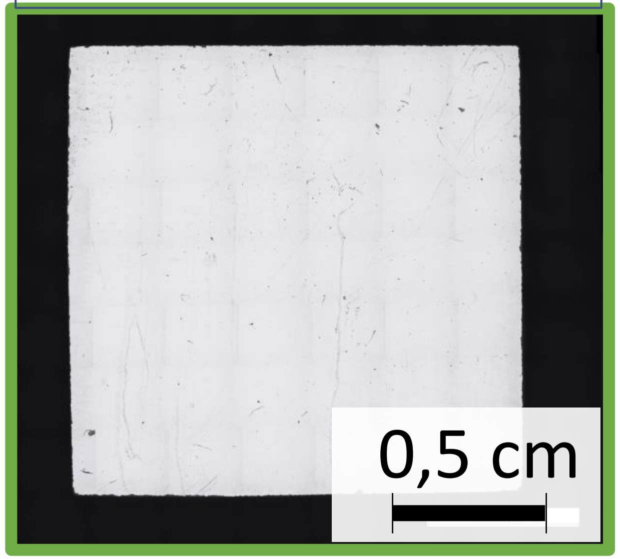
→ considerably **reduces lead release**
→ **lasts over time**
→ **reproducibility** between both industrial procedures
→ **not efficient for highly polymerized glasses** (no interdiffusion)

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

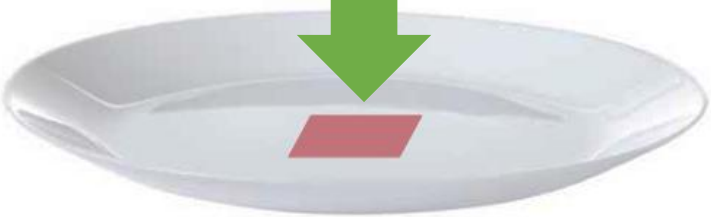
Opal crystallized glass plates

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

Optical microscopy

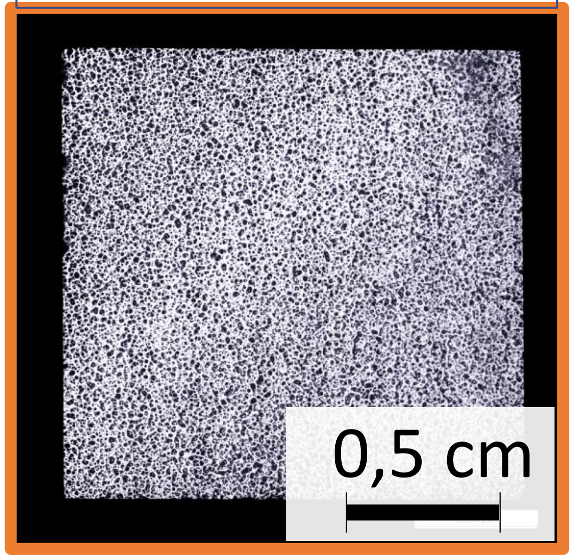


Top – Smooth
Air side

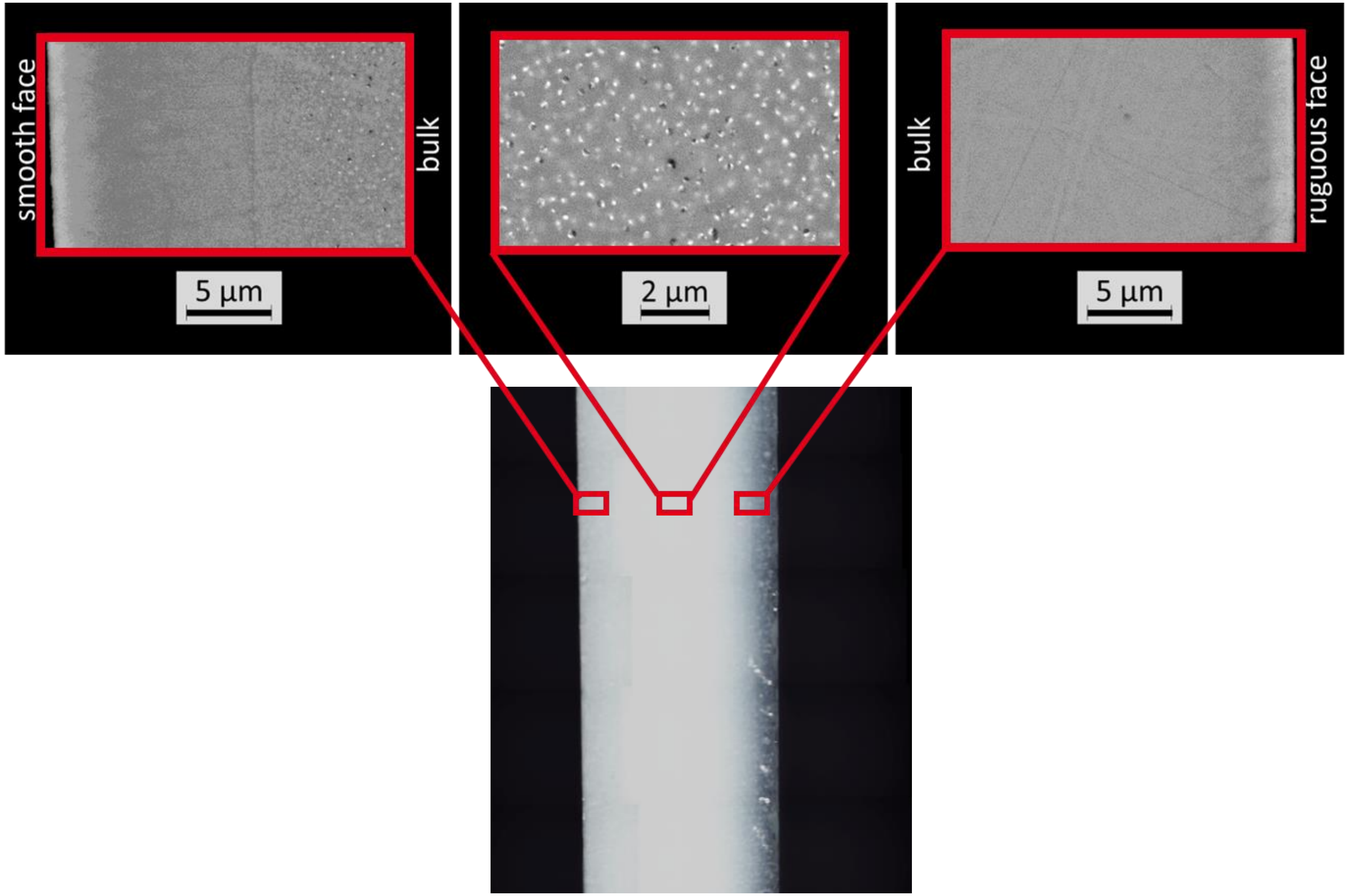


Bottom – Ruguous
Mould side

Optical microscopy



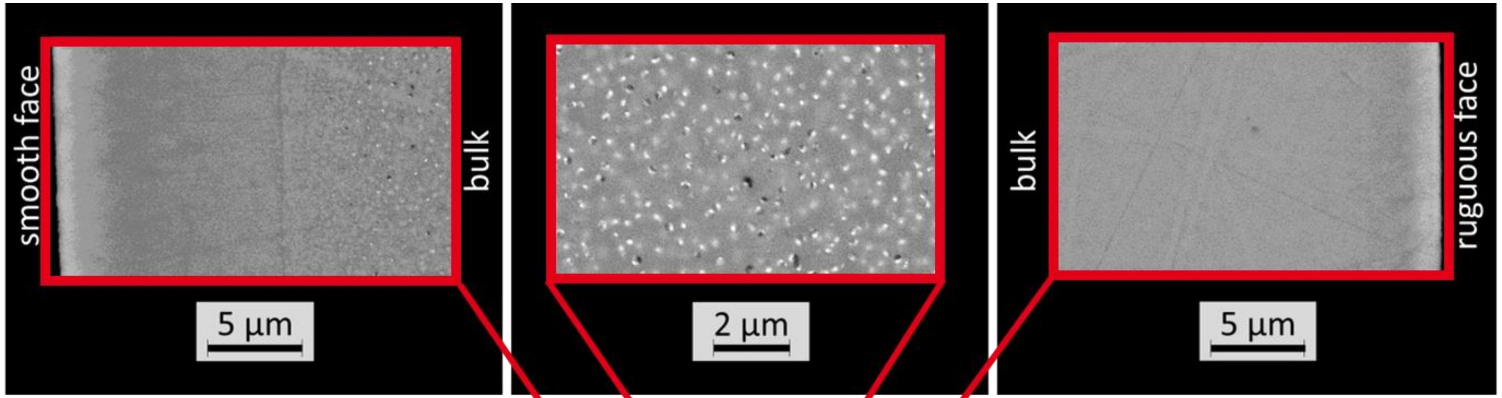
Opal crystallized glass plates

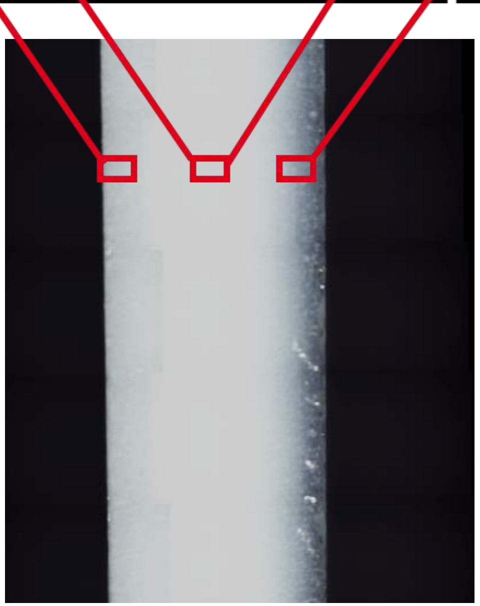


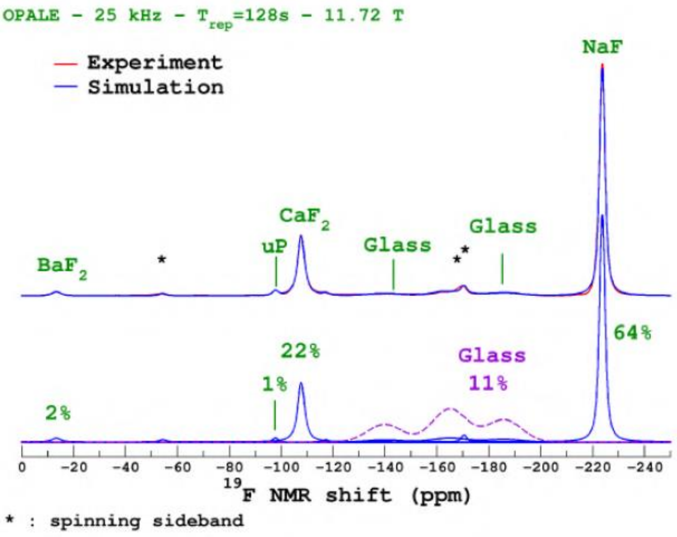
Glass surfaces (cooled faster): no crystal
(→ direct impact on the effect of surface treatments)

Opal crystallized glass plates

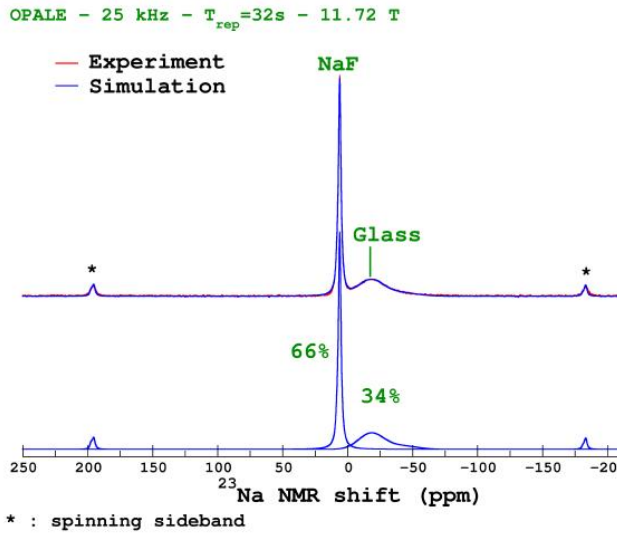
- ✓ **Bulk:** 8 wt% of crystals, mainly containing F *(NaF, CaF_2, BaF_2)*
- ✓ **Glassy matrix**: only 11 mol% of F



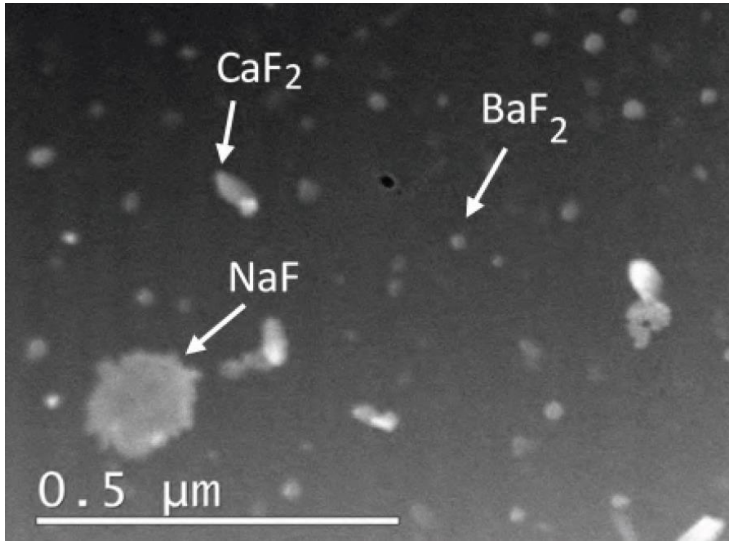




^{19}F MAS NMR

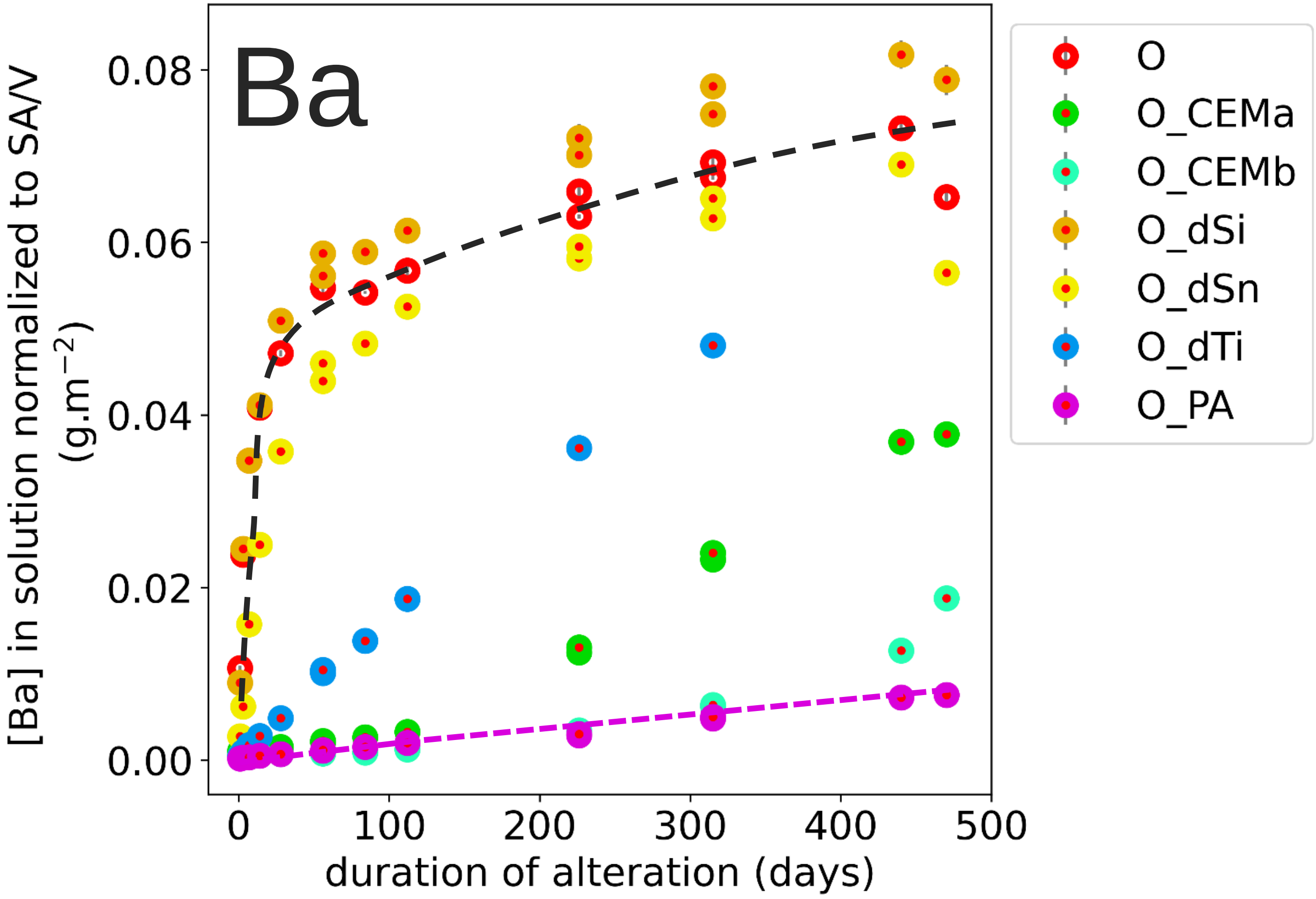


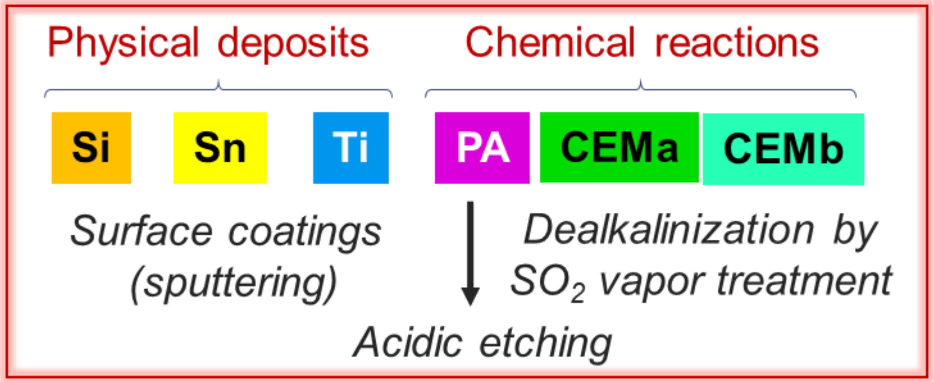
^{23}Na MAS NMR



Glass surfaces (cooled faster): no crystal
(→ direct impact on the effect of surface treatments)

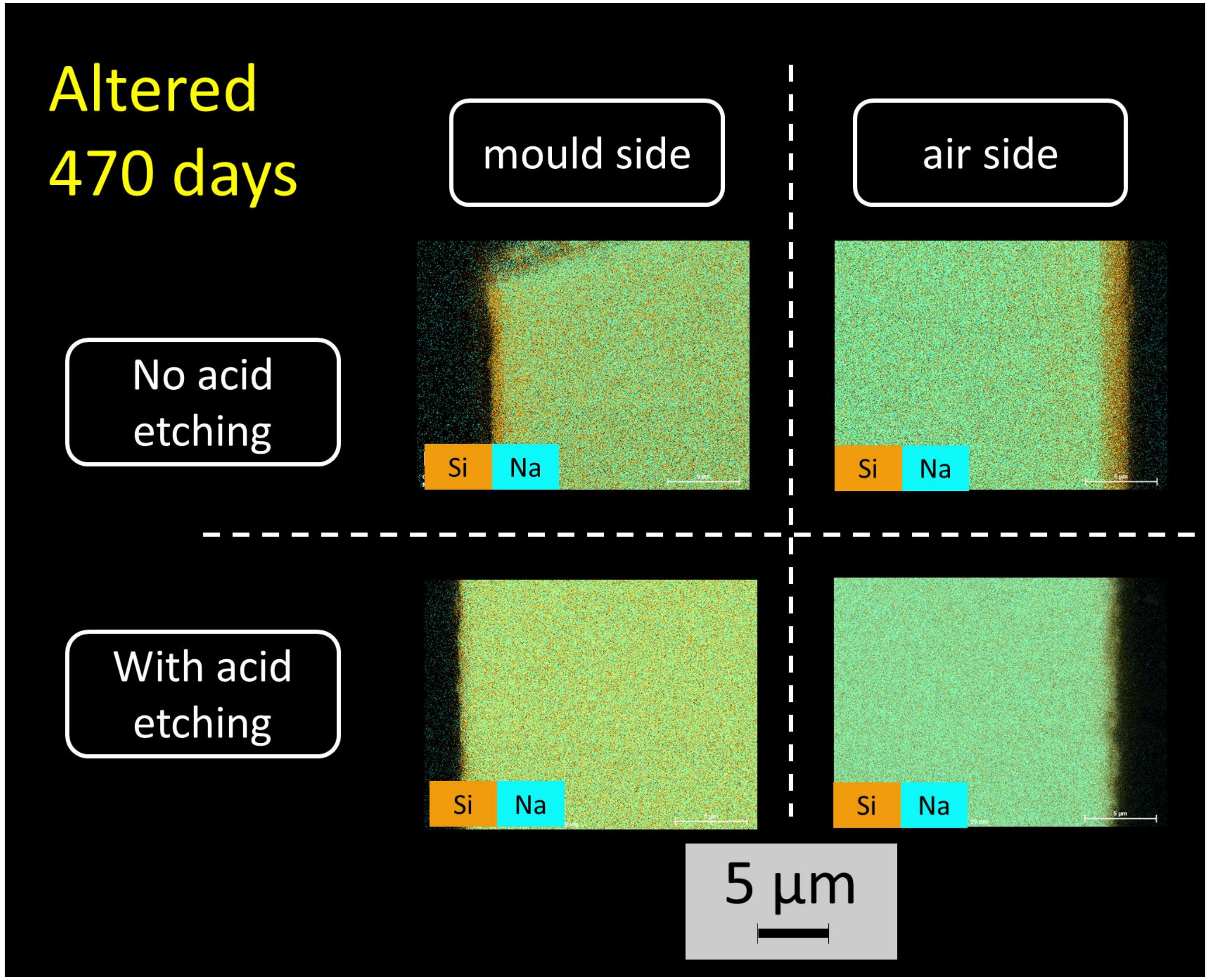
Effect of acid etching on the release of Barium from opal crystallized glass





- 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

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

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

The use 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

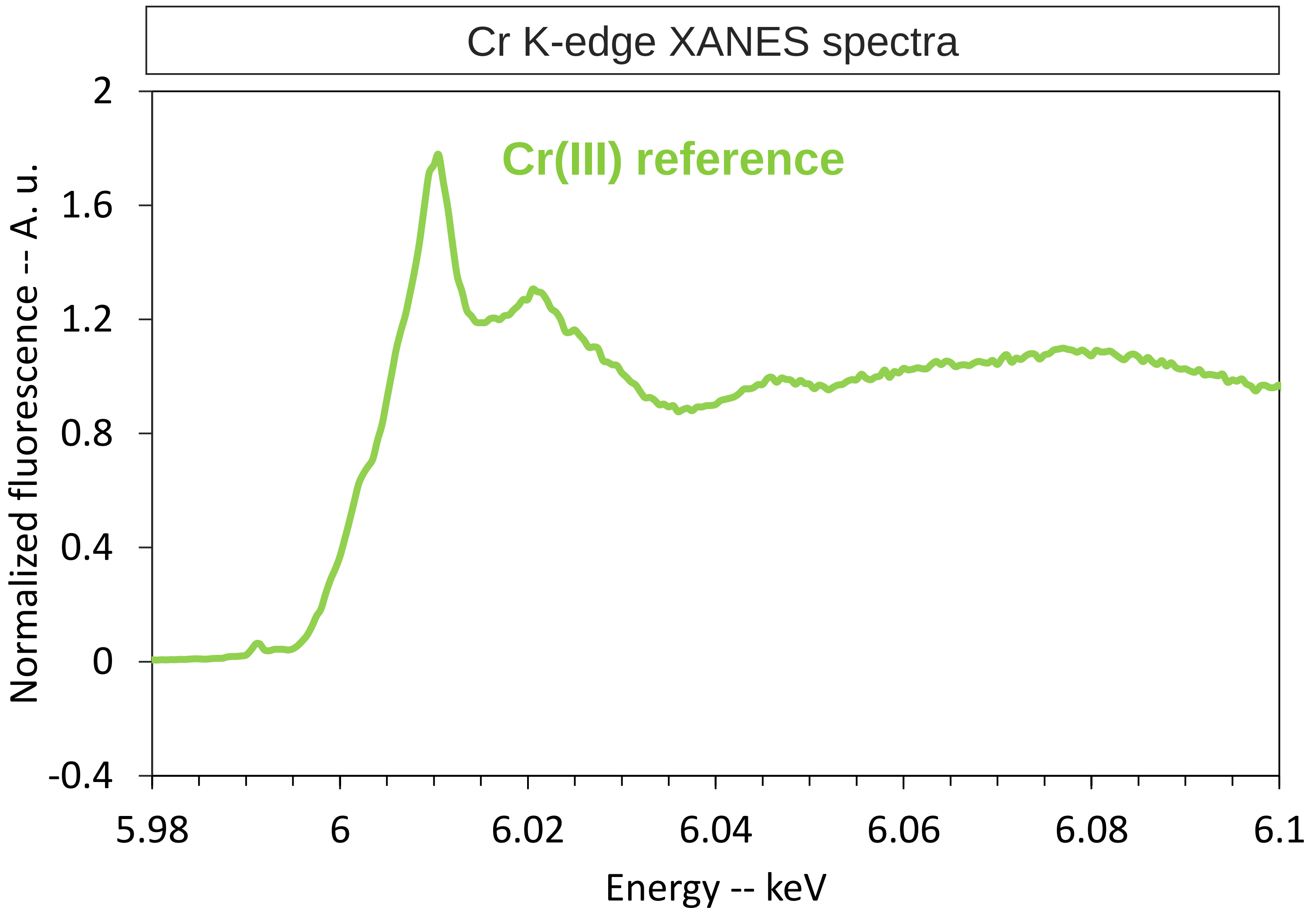
CrO_3 – Cr^{6+}

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 %

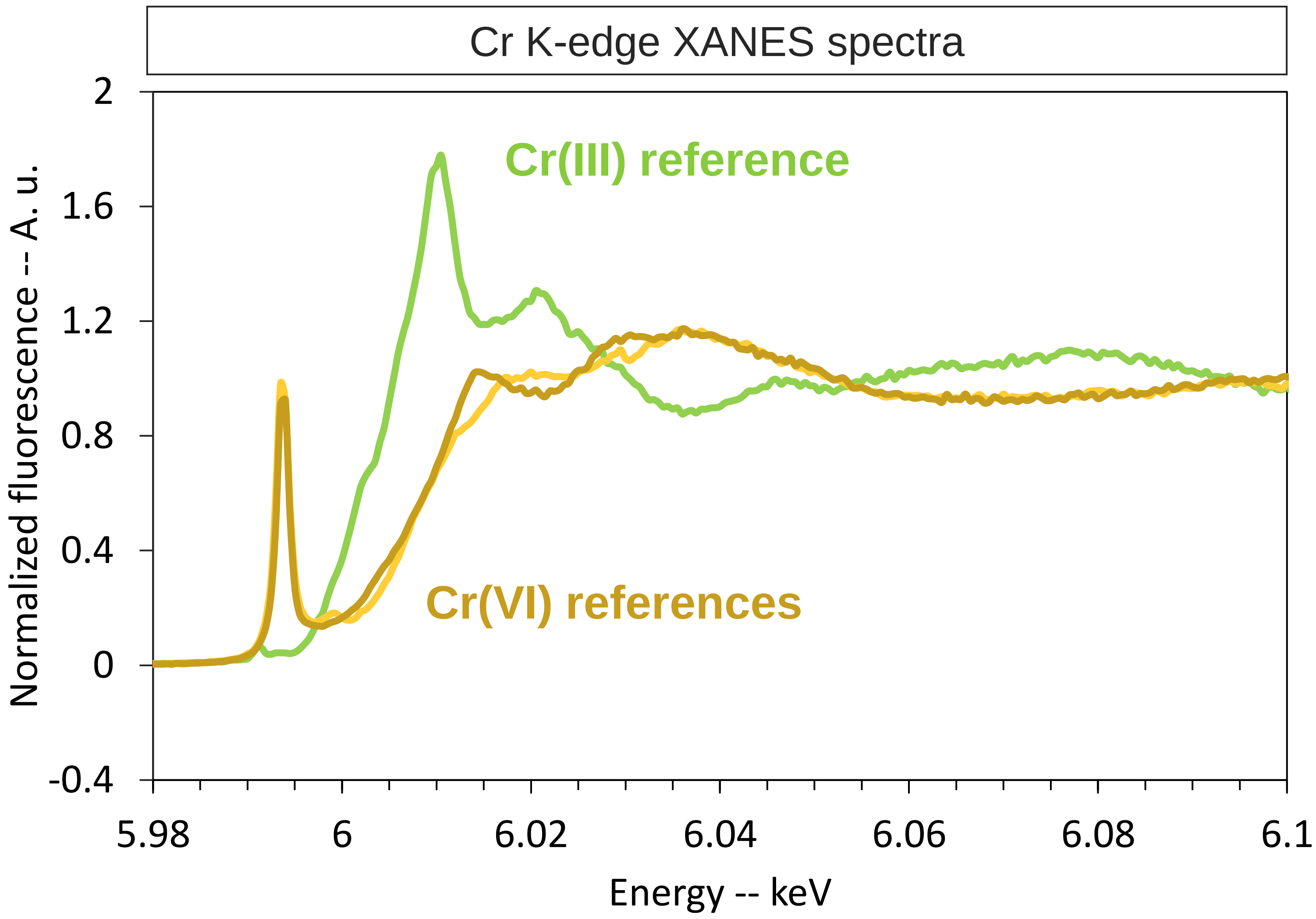
Speciation of chromium in lead crystal glasses

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



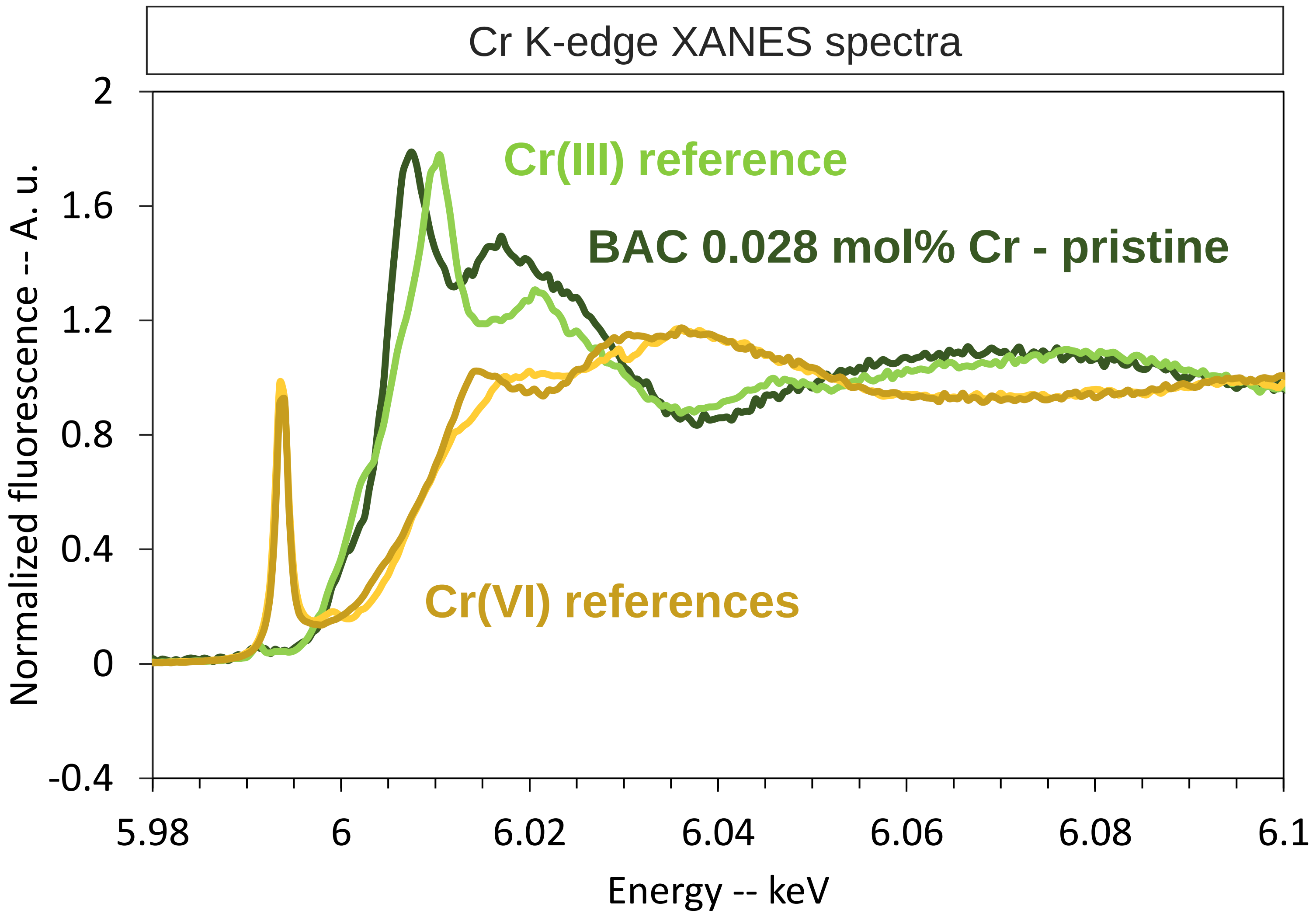
Speciation of chromium in lead crystal glasses

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



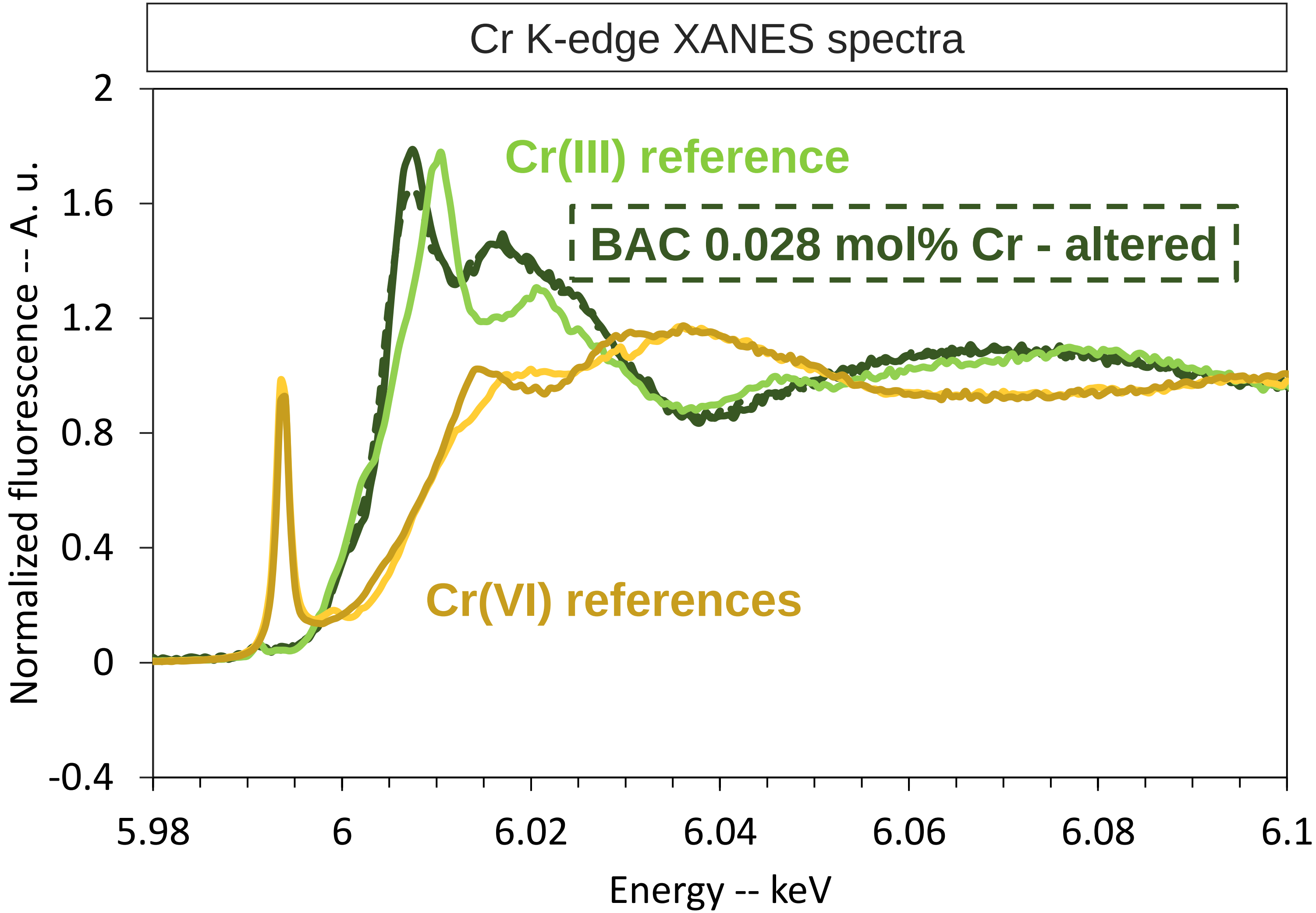
Speciation of chromium in lead crystal glasses

- ❑ **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

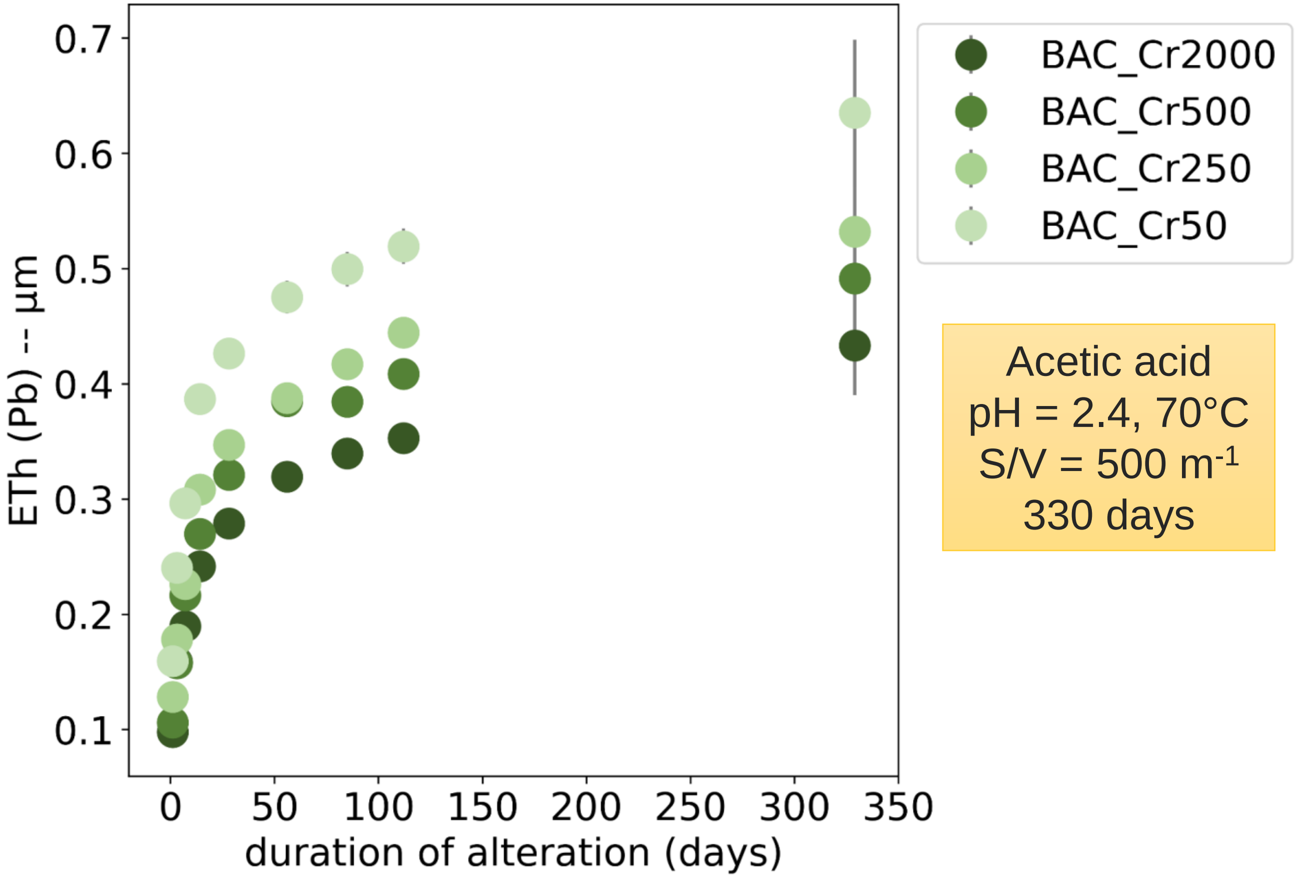


Speciation of chromium in lead crystal glasses

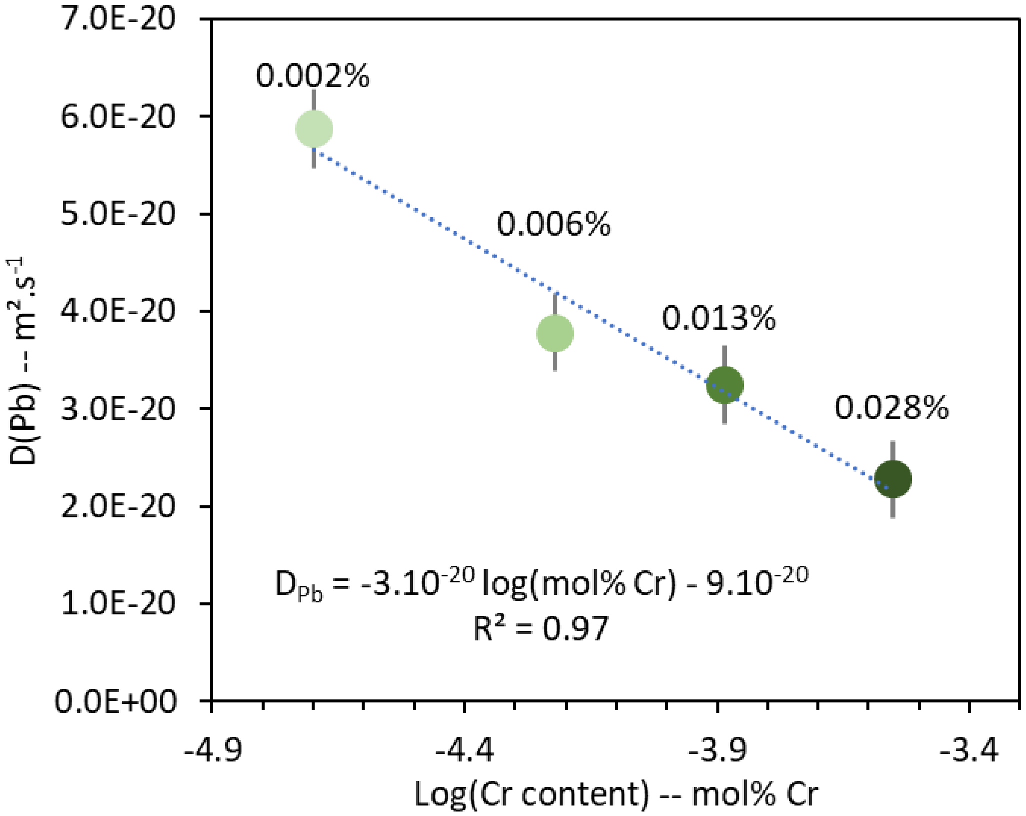
- ❑ Peak position at 6.0075 eV for Cr(III) reference
- ❑ Peak position at 5.9935 eV for Cr(VI) references
- ❑ Cr(III) only is detected in pristine Cr-bearing glasses
- ❑ **No change in the oxidation degree of Cr after alteration**



Leaching of lead crystal glass with Cr

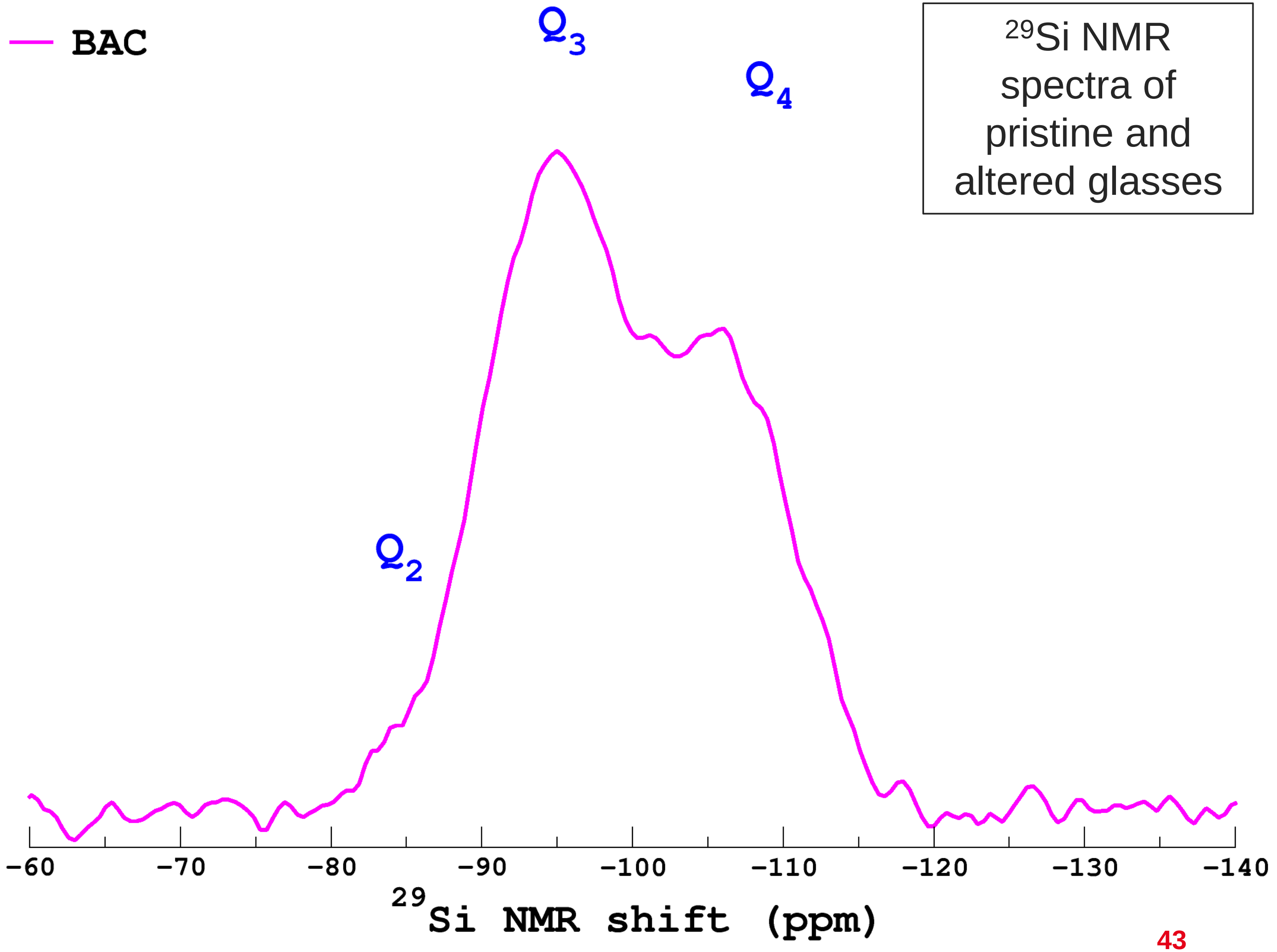


Acetic acid
pH = 2.4, 70°C
S/V = 500 m^{-1}
330 days



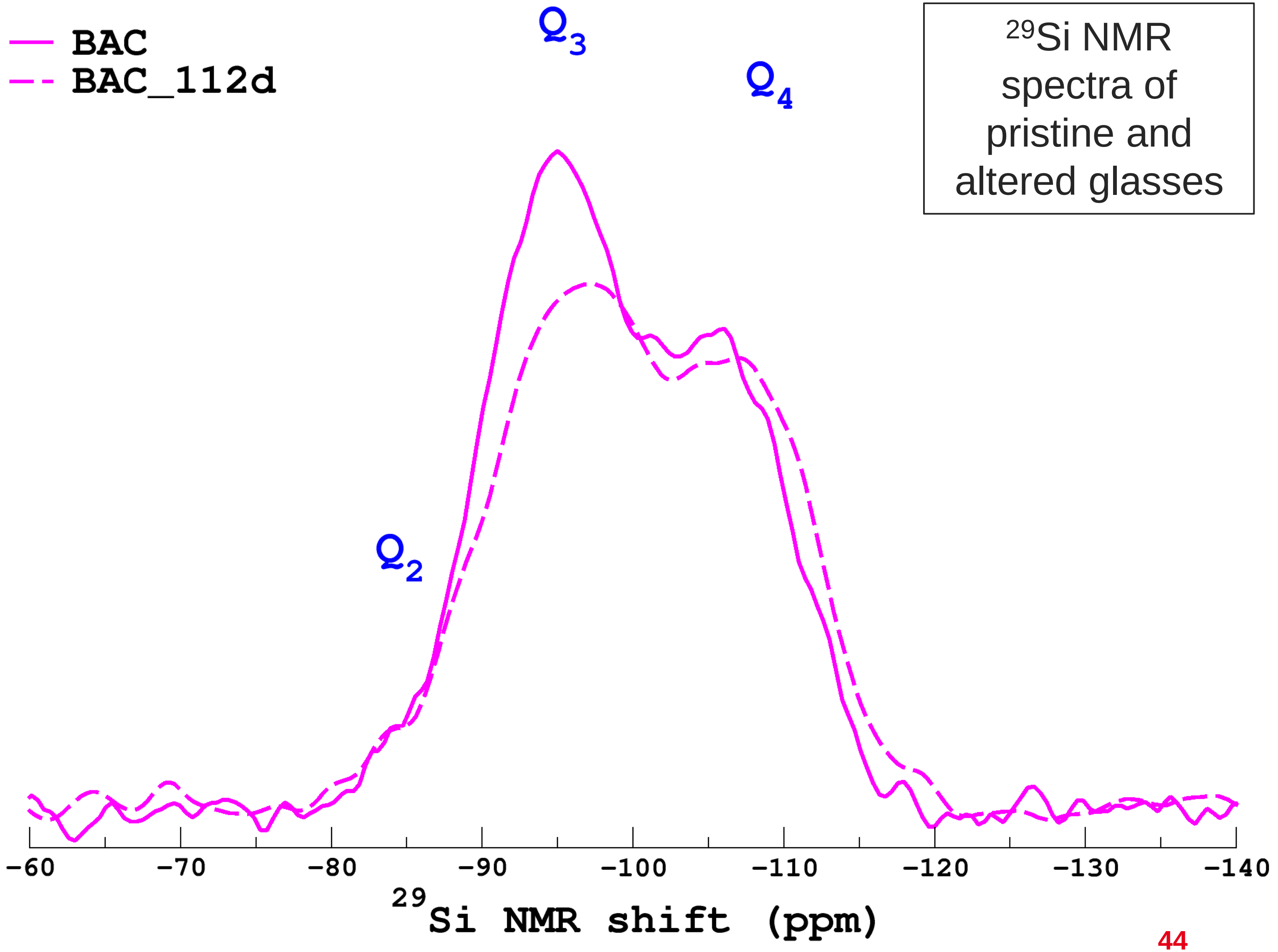
- ❑ The addition of **Cr strongly impacts Pb release** by decreasing its leaching rate
- ❑ **Linear decrease in of D(Pb) as a function of the Cr content**

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



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

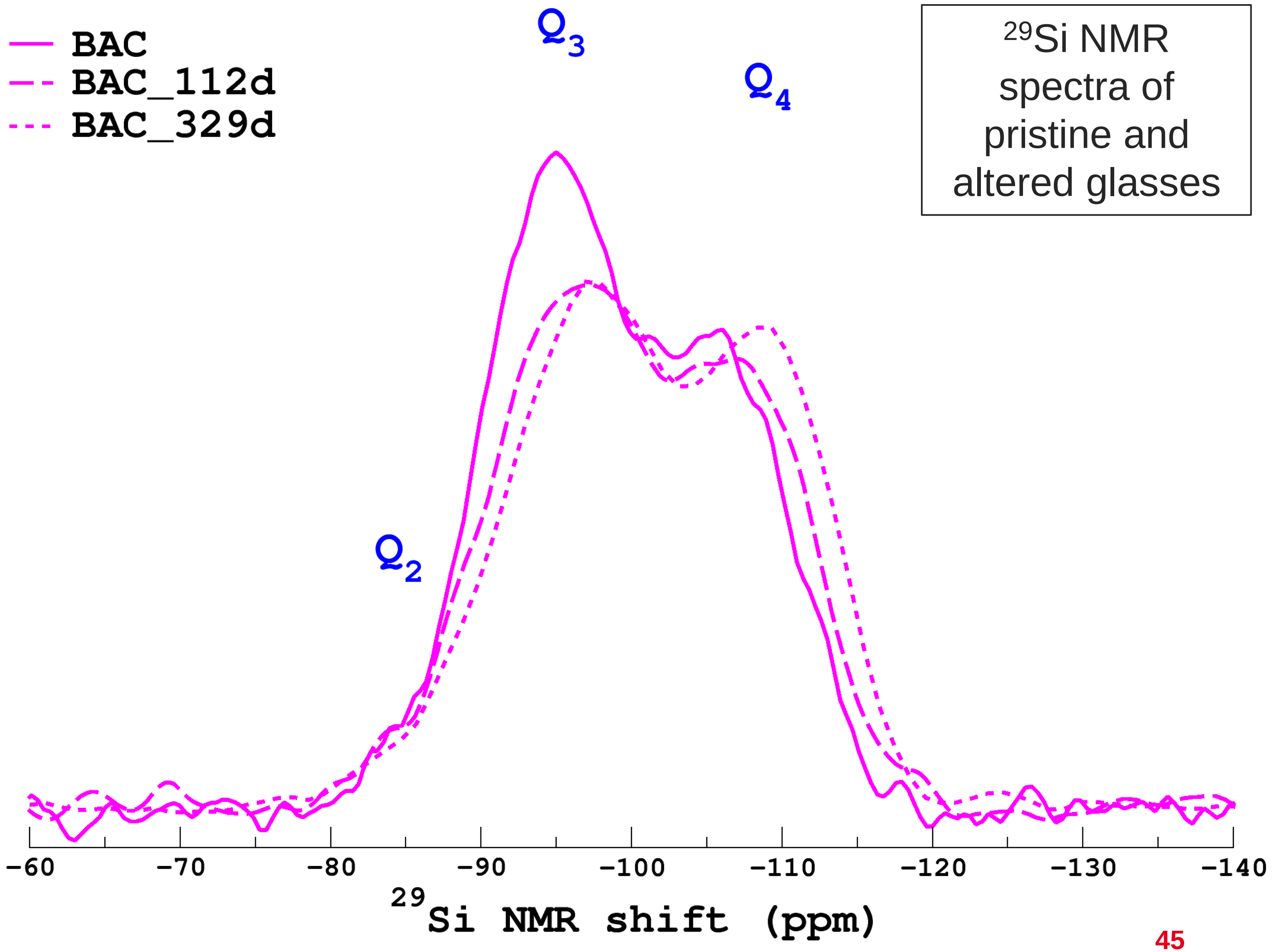
Impact of Cr on the structure of lead crystal glass during alteration



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

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

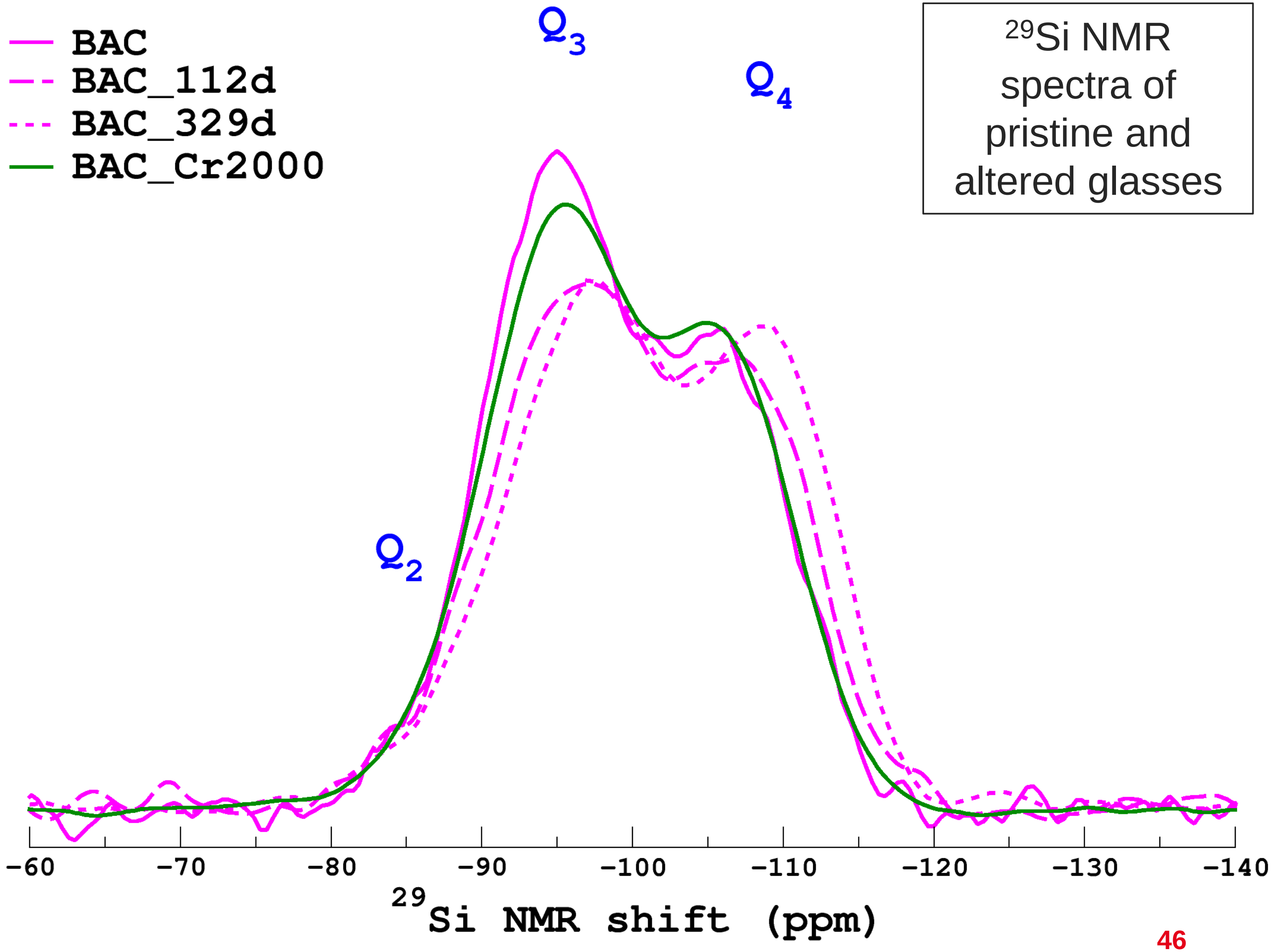
❑ Network repolymerization is observed from lead crystal glass over time



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

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

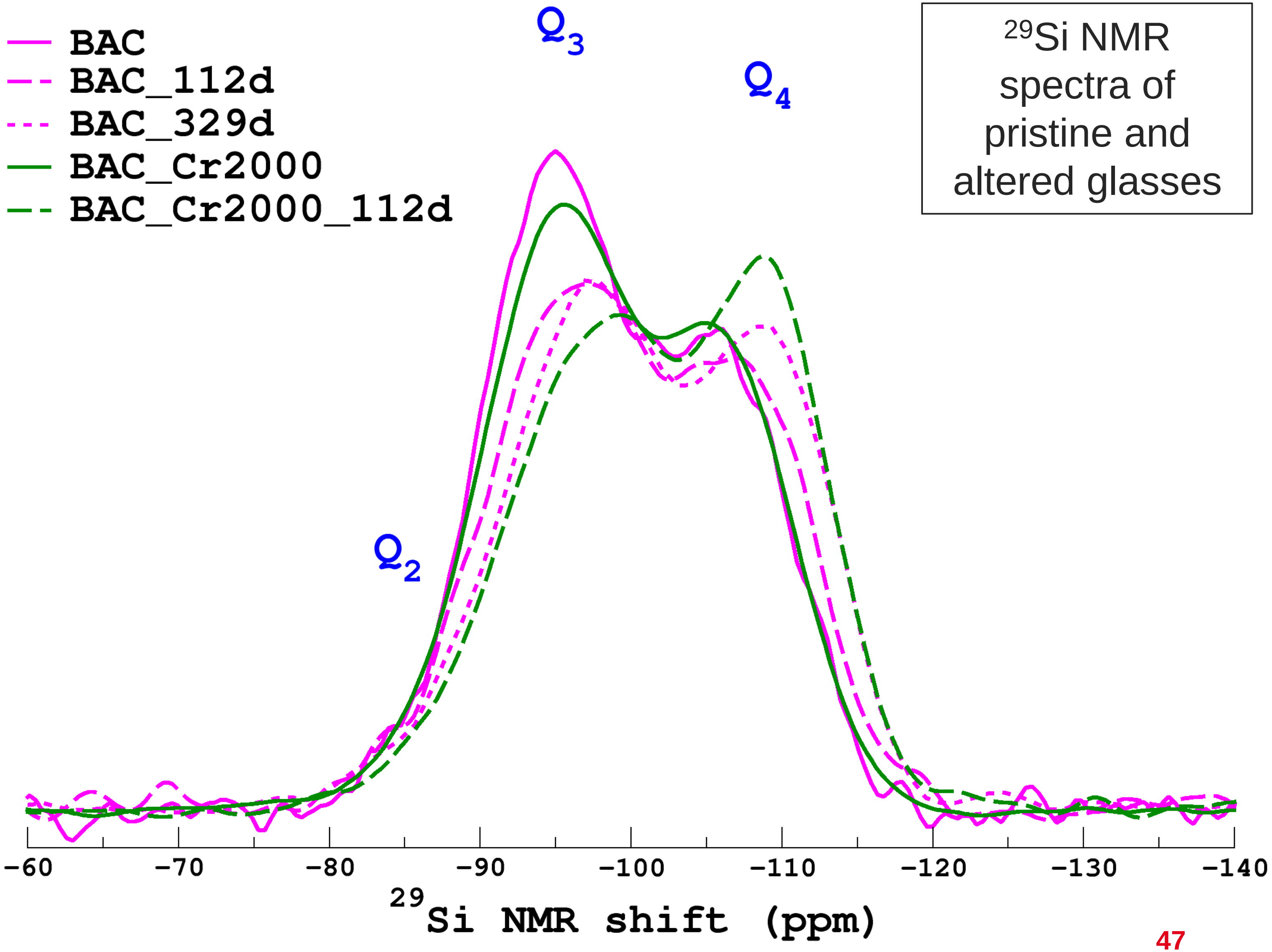
- The addition of Cr enhances the polymerization of the Si network before alteration.



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

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

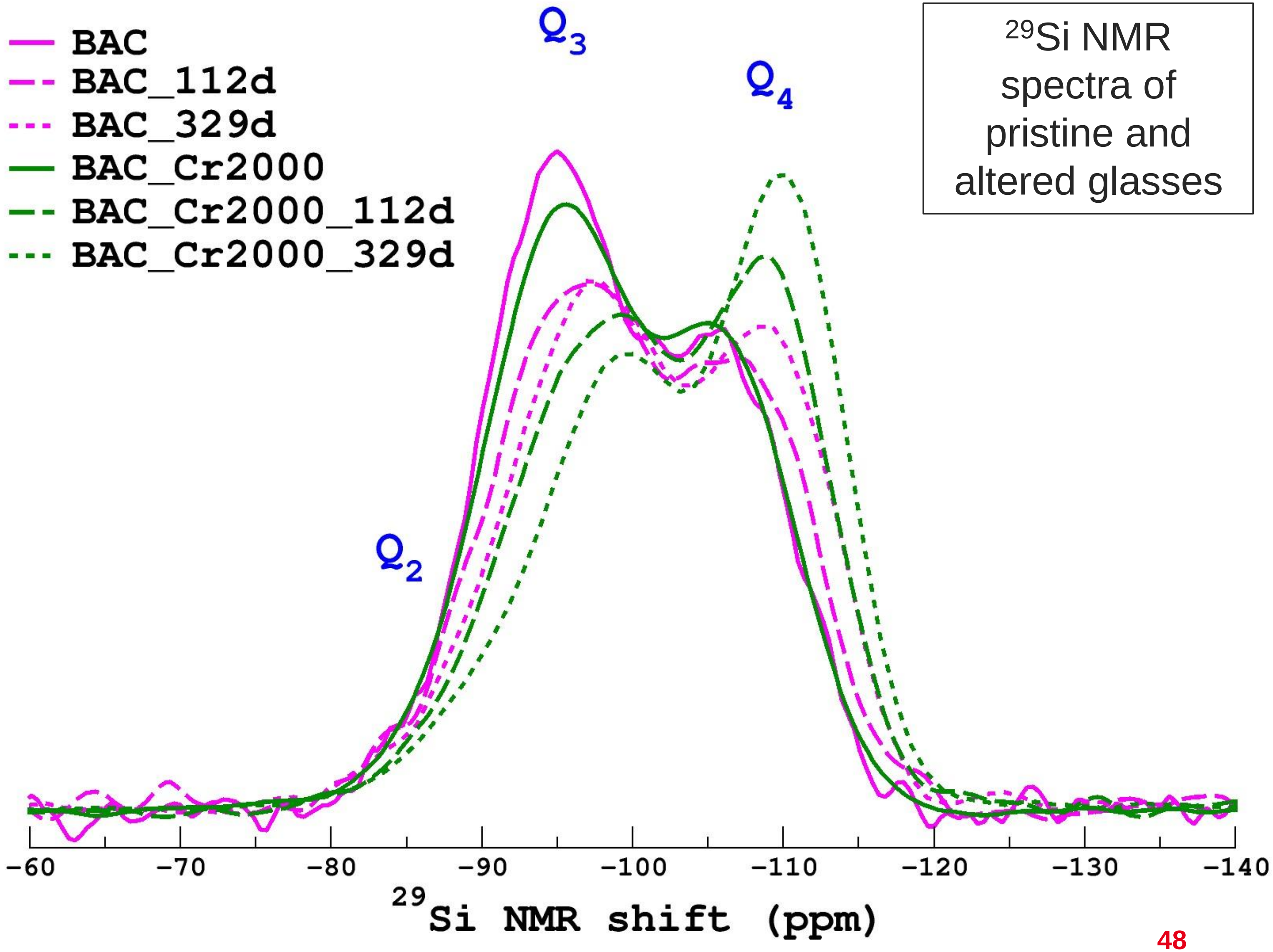
❑ The addition of Cr enhances the polymerization of the Si network before alteration and **after alteration**



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

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

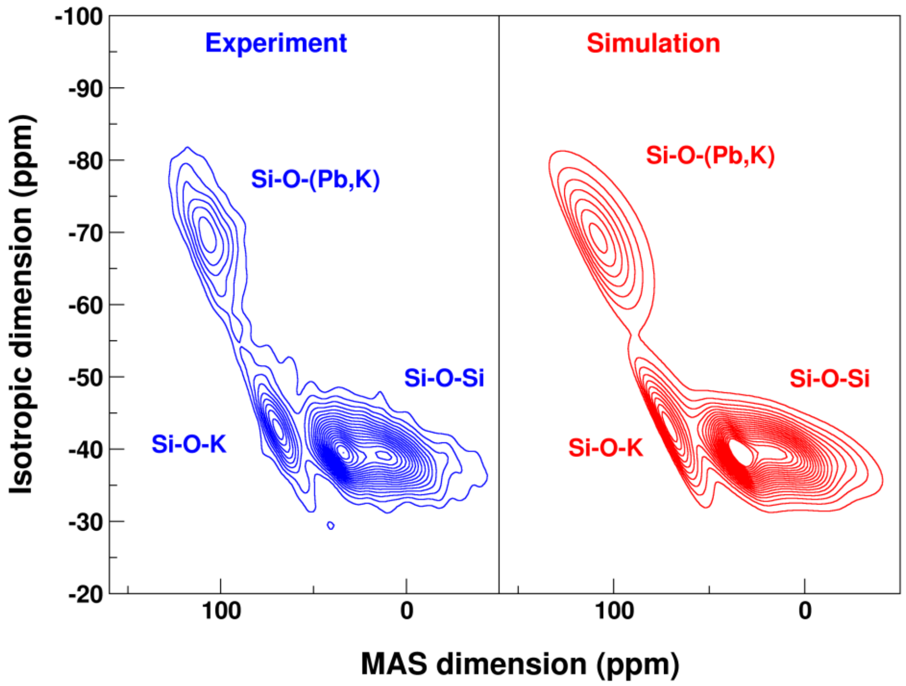
- The addition of Cr enhances the polymerization of the Si network before alteration and **after alteration**



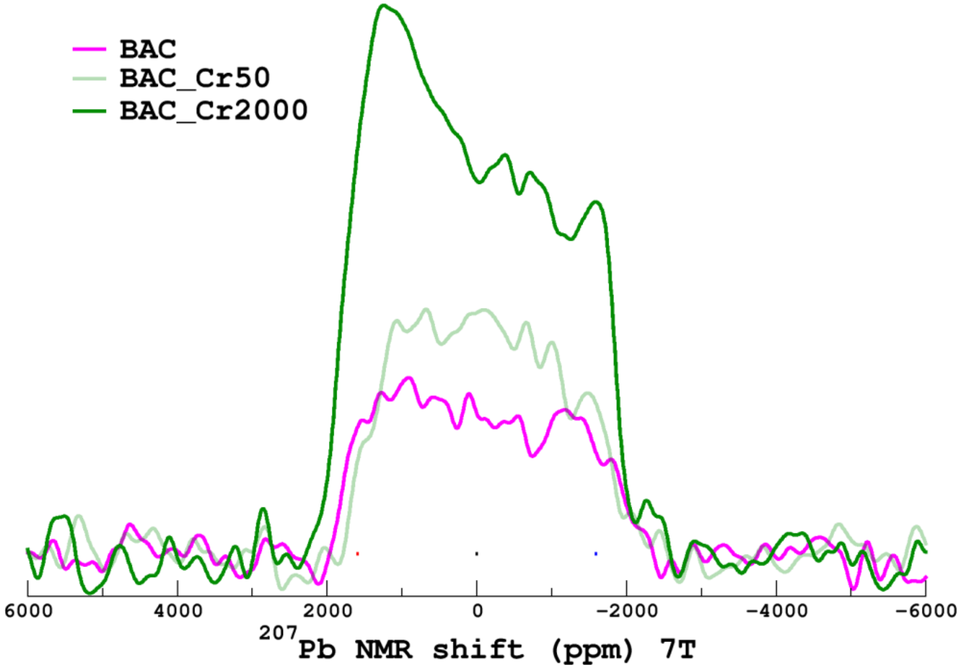
^{29}Si NMR spectra of pristine and altered glasses

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**

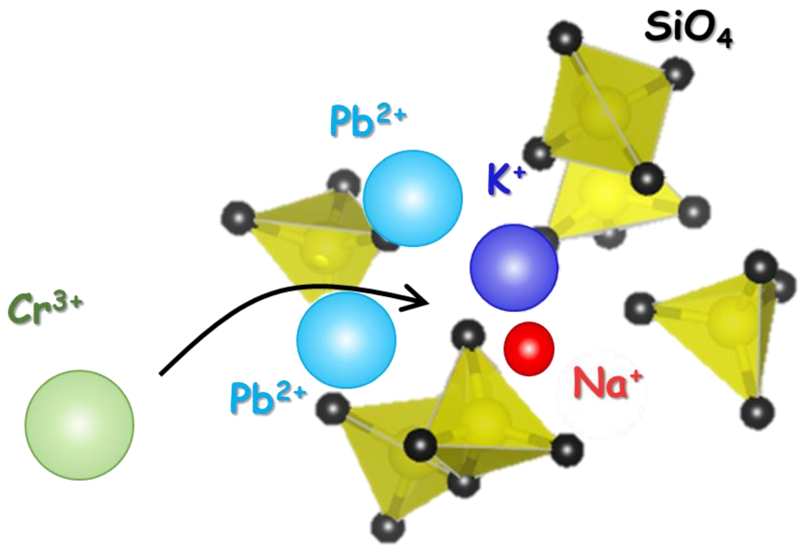
**Angeli, F. et al. (2016), Environmental Science & Technology, 50(21)*

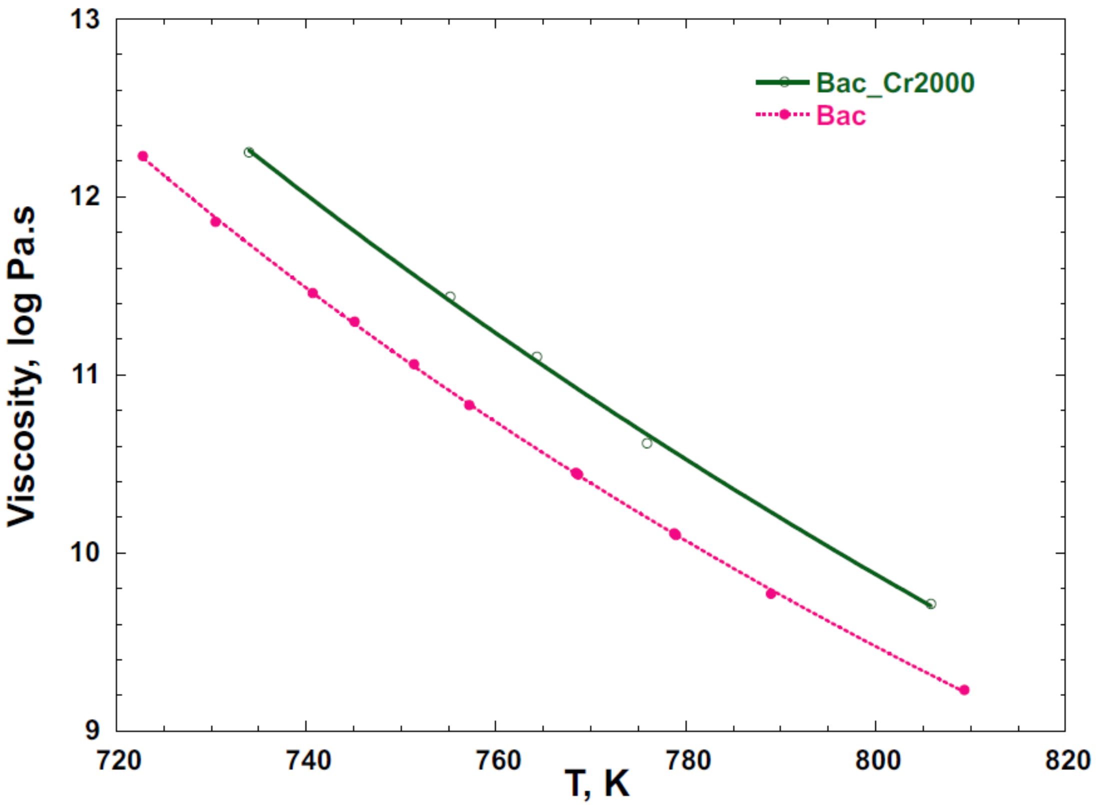
- ❑ Pb NMR intensity signal increases with Cr content

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)

Acknowledgements

anr agence nationale de la recherche
AU SERVICE DE LA SCIENCE

Industrial partners

LA MAISON FRANÇAISE DU VERRE

CRISTAL & VERRE

arc

POCHET DU COURVAL

Baccarat

Behaviour of Industrial Glasses During Aqueous Dissolution (BIGDAD)

coordinator

cea

IPGP

Université Paris Cité

Université Gustave Eiffel

Pyrex (2019)

Pochet (2020)

Baccarat (2021)

ARC (2022)

Part of this work supported by the IPGP multidisciplinary program PARI, and by Paris–IdF region SESAME Grant no. 12015908