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**Mechanism of alteration of the surface of lead crystal glass in contact with food:
a chemical study of the surface layer**

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Abstract:

Lead crystal glass (24 wt% PbO) is one of the tableware materials that can release lead into the environment. A deep knowledge of the release of lead (Pb) due to food contact is necessary to control and minimize the human exposure to this heavy metal. The Pb leaching was characterized by elemental analysis (ICP-AES) of the 4vol.% acetic acid solution to simulate the food contact versus leaching time. The analysis of the subsurface layer (SIMS, STEM) allows to understand the change of composition and morphology. After an initial period of rapid leaching, the diffusion of lead out of the glass slows down, due to the formation of a blocking barrier of diffusion in the subsurface layer of lead crystal glass. Experiments, carried out with a D₂¹⁸O solution, highlight the different mechanisms of hydrolysis, then condensation of the silanol groups, explaining the decrease of the diffusion coefficient of Pb by the formation of a "passive" sub-layer. This protective sub-layer can be reinforced by successive leaching processes or by the storage of lead crystal glass at high temperature after leaching.

Keywords: lead crystal glass, food contact, leaching, subsurface layer.

1. Introduction

Over the past several years, the quantity of heavy metals released into the environment has been significantly reduced to less than one tenth of the emission levels of the 1990s [1]. Concerning lead pollution, the promotion of unleaded gasoline is the main cause of this significant reduction. Simultaneously, some industrial processes such as metal refining have been improved to reduce the heavy metal release. Today, the use of lead compounds and the presence of lead in everyday objects are increasingly controlled and reduced in order to avoid lead poisoning through the contact with the skin, drinking fluid or food. Nevertheless, the lead-enriched glass, called lead crystal glass, is an important material used in the luxury tableware industry. To meet the required specifications for weight, appearance and sound, lead crystal glass must have a lead oxide (PbO) content of 24 to 40wt.% of lead oxide (PbO). Some lead-free crystal glass compositions have been developed for tableware applications, but their physical and thermal characteristics cause significant changes in glass working conditions and complicate the manufacturing processes [2].

The chemical resistance of glassware in aqueous media, also called hydrolytic resistance, is usually evaluated by measuring the release of elements after immersion in pure water of glass powder (obtained after ball milling) at 121°C for 30 minutes: this test is particularly used for pharmaceutical packaging [3]. However, the chemical stability of ceramic and glass tableware in contact with food is tested at room temperature in acetic acid solution, which is a more representative medium for food contact [4]. Actually, the foods or beverages, e.g. fruit juices, tannins in wine or vinegar in some food preparations, generally cause acidic conditions on the surface of glassware. The release limit for heavy metals such as lead or cadmium for a raw material and finished article tested in an acetic acid solution has been set to 4000 mg/L according to ISO 7086 [5], whatever the ratio of lead crystal area to solution volume. However, many parameters of the finished article, such as surface area, volume and surface

finish have to be considered. Thus, it is very difficult to understand the migration of elements from the materials and, therefore, to understand their release into the food environment.

Rahimi et al. have extensively studied the degradation of silicate glasses with high lead content ($> 40\text{wt. \% PbO}$) in aqueous media [6-8]. However, these high lead glasses undergo a particular weathering mechanism due to a connected and dense network of plumbate entities [9-11]. Palomar et al. show that the dissolution of the plumbate network leads to the formation of a layer of hydrolyzed silica glass or a layer of silica gel, which is very porous [12].

For commercial lead crystal glasses with lower Pb concentration (24 wt.% PbO), the leaching kinetics of alkali cations and lead cation from lead crystal glass have been reported in various glass preparation conditions and for several leachate solutions [13-16]; however, these are difficult to discuss and compare under food contact regulations.

Over the last 20 years, Conradt has reviewed the numerous studies carried out to improve the understanding of the mechanisms responsible for the deterioration of silica glasses by water [17]. Three main processes can be considered during glass weathering: (i) hydration related to the diffusion of water molecules within the glass lattice, (ii) hydrolysis corresponding to the reaction of metal-oxygen bonds with water to form hydroxyl groups, and (iii) an ion exchange mechanism between lattice-modifying metal cations and protons or hydronium ions in the aqueous solution [18]. These diffusion and ion exchange processes lead to the formation of a subsurface zone or layer also known as the “silica gel layer” or “residual layer”, which is depleted in alkali metals and lead in the case of lead crystal glass. In borosilicate or soda-lime glasses, a high content of alkali cations, which create non-bridging bonds in the silica lattice, appears to create channels for diffusion and hydrolysis and can disintegrate the silicate lattice in the subsurface zone [19].

Other authors focused on long leaching times (from a few hours to more than 100 days). After a few hours of immersion in aqueous solution, the subsurface layer was analysed by spectroscopic methods [15, 20, 21]. Yin could clearly detect the gel layer by metallography on

very old lead-silicate glazes on artefacts [22] or on soda-lime glass samples exposed for a very long time in an air-polluted environment [23, 24]. In the case of food contact, the formation, the thickness and the composition of the subsurface layer on lead crystal glass are crucial parameters for determining the behaviour of lead crystal glass in contact with food.

This paper proposes a comprehensive investigation of the leaching process of lead crystal glass (28 wt.%) in a 4vol.% acetic acid solution. The aim is to propose a mechanism for the formation of the subsurface layer and to investigate its protective characteristic against lead release when lead crystal glass is in contact with food or drink. For this purpose, lead crystal glass samples were prepared by mechanical polishing. After the leaching test, the composition of the acetic acid solution was determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) according to the international standard. In addition, before and after the leaching test, the chemical composition and morphology of the subsurface layer were determined in depth by Secondary Ion Mass Spectrometry (SIMS) and Scanning Transmission Electron Microscopy (STEM) under cryogenic conditions, combined with elemental analysis by Energy Dispersive X-ray Spectroscopy (EDX). The leaching mechanism was determined through the use of $D_2^{18}O$ tracer during the leaching test. Finally, the properties of the subsurface layer of leached lead crystal glass samples are discussed in the context of food contact after several successive leaches.

2. Experimental

2.1 Lead crystal glass

20 kg of lead crystal glass was synthesized by mixing: 11.3 kg of silica (SiO_2), 5.9 kg of lead minium (Pb_3O_4), 207.4 g of sodium carbonate (Na_2CO_3), 5.6 kg of potassium nitrate (KNO_3), and 142.7 g of antimony trioxide (Sb_2O_3) with a batch of raw materials which was placed in an alumina crucible and melted in a gas melting furnace for 16 h at $1300^\circ C$. The lead crystal glass was cast in a graphite mold and annealed for 4 h at $450^\circ C$. The glass blocks were then

cut into small samples of 3 cm x 3 cm x 0.5 cm using a water-cooled diamond saw. The surfaces were polished on a felt wheel under water with cerium oxide powder (powder size: 0.5 - 0.6 μm) to a mirror-like surface. The samples were then cleaned with deionized water, ethanol (96wt.%) and air dried. The chemical composition of the leaded glass was checked by the Cameca SX-50 electron probe microanalyzer (analysis voltage: 15 kV, beam intensity: 20 nA). The elements Na and Si were calibrated with an albite standard ($\text{NaAlSi}_3\text{O}_8$), K with orthoclase (KAlSi_3O_8), Sb with stibnite (Sb_2S_3) and Pb with galena (PbS). The homogeneity of the lead crystal glass was verified by 10 measurements on 5 different samples (average \pm standard deviation). The composition of the synthesized lead crystal samples is detailed in Table 1.

2.2 Leaching experiments

Lead crystal glass samples were placed in closed polyethylene beakers in a 4vol.% acetic acid solution at room temperature without stirring. There are only three points of contact between the sample and the beaker, in order to keep almost all the sample surface in contact with the solution. The ratio of the glass sample surface area ($A = 24 \text{ cm}^2$) to the volume of the acid solution ($V = 50 \text{ cm}^3$) was approximately 0.5 cm^{-1} , which is approximately the A/V ratio of a whiskey glass. During the leaching time, a solution sample (1 mL) was collected after different immersion durations and diluted in 4 mL of deionized water for analysis by Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICAP 7200 Thermo) to determine the concentrations of Pb and K (Power output: 1150 kW, plasma gas flow rate: $0.50 \text{ L}\cdot\text{min}^{-1}$, integration time: 0.5 s, emission wavelengths: 220.353 nm for Pb, 766.490 nm for K). Calibrations of Pb and K were performed by the external method in a 4vol.% acetic acid matrix. After the leaching experiments, the samples were rinsed with deionized water and dried on absorbent paper. The Pb released from the lead crystal glass is expressed as Pb content per cm^2 of exposed surface area, according to the relationship (1):

$$\frac{x_i}{A/V} * 1000 = c_i \quad , (1)$$

with x_i the concentration of element i in ppm and c_i the concentration of element i in $\mu\text{g}\cdot\text{cm}^{-2}$, A the surface of the glass, V the volume of the acid solution.

The leaching experiment with D_2^{18}O water was performed in a specific microcell with a volume of acetic acid solution of 150 μL and a lead crystal glass surface area of 5.7 mm^2 to ensure the same surface area per volume ratio of 0.5 cm^{-1} . In this case, the 4vol.% acetic acid solution was prepared by mixing 1 cm^3 of D_2^{18}O (D: 99at.%, ^{18}O : 95at.%) and 40 μL of pure acetic acid (99.8wt. %).

2.3 Material characterization

Before and after the leaching experiments, the lead crystal glass samples were analysed by SIMS (Cameca IMS 7F) with a Cs^+ ion beam (4 keV and 2 nA) analysing a 60 x 60 μm^2 area. For samples enriched in deuterium and 18-oxygen, SIMS analyses were performed at high energy with a Cs^+ beam at 15 keV with a mass resolution of 4004. Crater depths were measured after analysis by confocal microscopy (GBS extended SmartWLI), and the depth calibration was calculated assuming a constant sputtering rate. Each elemental depth profile is an average of three analyses in three different areas of the samples. Prior to SIMS analysis, the samples were coated with a layer of gold by physical spraying to accurately determine the start of the sample analysis and the origin of the depth profile. The peak intensity of the atomic mass unit (a.m.u.) fragment corresponding to $^{16}\text{O}^-$, $^{28}\text{Si}^-$, $^{39}\text{K}^-$, $^{208}\text{Pb}^-$, and $^{23}\text{Na}^-$ was normalized first to the sum of the intensities of the components of the glass to avoid matrix effects and then normalized by considering the intensity in the mass of the lead crystal glass at 1 (at a depth of 160 to 200 nm), according to expression (2):

$$Jn_i^a = \frac{J_i^a / J_i^{\text{Sum}}}{\frac{1}{n} \sum_p^n J_p^a / J_p^{\text{Sum}}} \quad , (2)$$

where Jn_i^a is the normalized intensity of fragment a ($a = {}^{28}\text{Si}^-$, ${}^{39}\text{K}^-$, ${}^{208}\text{Pb}^-$ and ${}^{23}\text{Na}^-$), and J_i^a and J_p^a are the raw intensities measured at a point i of the profiles and at a point p of the unaltered lead crystal glass (or bulk glass) respectively.

For the D and ${}^{18}\text{O}$ enriched samples, the normalization of the ${}^{18}\text{O}^-$, D^- , ${}^{18}\text{OD}^-$, and H^{18}O^- fragment peaks were first normalized to the sum of the intensities and then by considering the intensity in the bulk lead crystal glass at 0.

Scanning Transmission electron microscopy (STEM) studies were performed using a JEM - ARM 200F Cold FEG TEM/STEM under cryogenic conditions (-110°C) operating at 200 kV, equipped with a spherical aberration (Cs) probe and image corrector (0.12 nm point resolution in TEM mode and 0.078 nm in STEM mode) and electron scattering X-ray spectroscopy (EDS). Surface samples were metallized with carbon and platinum, and the thin sections were prepared with a focused ion beam workstation (FEI Helios Nanolab 600i).

3. Results

3.1 Leaching experiments

In 4vol.% acetic acid solution, the Figure 1 shows the evolution of leached lead and potassium content per centimetre square of lead crystal versus the square root of leaching time.

For lead, a first evolution is characterized by a linear increase of the leached Pb content as a function of the square root of time up to 16 h and $3 \mu\text{g}\cdot\text{cm}^{-2}$. Then, the kinetic of Pb leaching is strongly reduced and the content of released Pb in the solution reaches $3.5 \mu\text{g}\cdot\text{cm}^{-2}$ for 48 h of leaching (Figure 1a). For potassium, the kinetic of released K, displayed in Figure 1b, reveals only one linear increase, and does not show a drastic reduction with time after approximately 12 h of leaching.

According to the assumption and calculation of Helebrant et al [25] who consider that the matrix dissolution can be neglected in acidic solutions, the diffusion coefficients of an unstirred solution are equivalent to those of a stirred solution. Consequently, the diffusion

coefficient D of the elements K and Pb in lead crystal glass can be estimated by fitting each linear part of the curves $c=f(t^{1/2})$ in Figure 1 by the following equation, resulting from the solutions of Fick's law [25]:

$$c_{X\text{sol}}(t) = 2 c_{X0} \left(\frac{Dt}{\pi} \right)^{\frac{1}{2}}, \quad (3)$$

with $c_{X\text{sol}}$ the concentration of X in the solution ($\text{g}\cdot\text{m}^{-3}$), c_{X0} the concentration of X in the solid lead crystal glass ($\text{g}\cdot\text{m}^{-3}$), t the leaching time (s) and D the diffusion coefficient of X in the sample ($\text{m}^2\cdot\text{s}^{-1}$).

In Table 1, the order of magnitude of the diffusion coefficient in lead crystal glass with 24 wt.% PbO is consistent with values previously reported in the literature [15, 25]. During the first leaching regime, the diffusion coefficients of Pb and K are approximately identical around

$10^{-20} \text{ m}^2\cdot\text{s}^{-1}$ at room temperature. During the second leaching regime, the diffusion coefficient of lead is two orders of magnitude lower, while the diffusion coefficient of K is almost unchanged.

3.2 Elemental profile of lead crystal glass before and after the leaching test

Before and after the leach test, the lead crystal glass samples were analysed by SIMS as shown in Figure 2. From the raw elemental depth profile, it can be observed that the elemental composition of the lead crystal glass surface is clearly affected by the mechanical polishing process over a depth of about 100 nm (Figure 2a). The gradient of composition, highlighted by the normalized peak intensities in Figure 2c, reveals the presence of three different zones in the subsurface. The first zone 1, with a depth of about 3 to 5 nm, corresponds to both the roughness of the lead crystal glass surface and surface contamination with high carbon concentration, the latest being revealed by the intensity of the $^{12}\text{C}^-$ peak. Then, a second zone 2 with a depth of 12-15 nm is characterized by a sharp evolution of Pb, K and Na atoms and an increase in

oxygen content. Last, a larger zone 3 (about 100 nm deep) is defined by a concentration gradient of alkali atoms and contains approximately the same Pb content as in the bulk lead crystal glass but. This zone 3 also contains a slight excess of oxygen and a lack of silicon compared to the lead crystal glass, revealing that the silica lattice composition is also altered by leaching. These results demonstrate that mechanical polishing in water modifies the surface of lead crystal glass and that a leaching process is already occurring during this first preparation step.

In comparison, the composition gradient of the subsurface zones of the sample leached in acetic acid is shown in figures 2b and d. The first zone 1, corresponding to the carbon-contaminated depth, is comparable to the polished sample. However, the zone 2, depleted in Pb, has a thickness of about 35 nm. The K and Na contents are very low and this zone is almost free of alkali atoms. The low peak of Na content (at about 15 nm) can be explained by the possible retention of the Na element in this subsurface layer by the modified silica lattice, as already mentioned in some cases [25]. The silicon profile clearly shows a concentration peak at a depth of about 10 nm followed by a depletion zone at a depth of 30 to 40 nm. Then, the zone 3 is also characterized by a constant Pb content, equal to that of lead crystal glass, and a gradient of alkali atoms to about 100 nm depth.

This type of SIMS elemental profile was also analysed after 48 hours of leaching compared to the sample leached for 24 hours (Figure 3). In fact, for longer leaching time, the Pb gradient increases slightly within the lead crystal glass, which is well corroborated by the decrease in Pb leaching kinetics characterized in the solution analysis in Figure 1a. In contrast, the concentration gradient of alkali atoms shifts significantly within the lead crystal glass, which is corroborated with the sharp increase in alkali atoms in the acetic acid solution.

3.3 Morphology of the subsurface layers of leached lead crystal glass

After 24 h of leaching in 4vol.% acetic, the STEM micrograph, displayed in Figure 4, shows the general morphology of the subsurface layer. Under the carbon layer deposited during the thin section preparation steps (in white), the leached layer is relatively uniform. In the bulk lead crystal glass, some Pb and K-enriched areas can be detected, which may explain some variations in the thickness of the leached subsurface layer.

As can be seen in Figure 5a, the subsurface layer can be easily divided into two main zones, which can be correlated to the SIMS elemental profile. The first zone, named zone 2 in the SIMS profile (Figure 2d), is almost free of Pb and K atoms. Moreover, EDS analysis reveals that zone 2 is characterized by a relatively high silicon content, as observed on the SIMS analysis (Figure 5b). In-depth, the glass is not homogeneous, and the heavy atoms (Pb and K) are segregated into nanoscale nodules. This zone can be attributed to zone 3 of the SIMS profile. The thickness of zone 3 can be estimated at about 60 nm, using the EDS profile measured at the nanoscale (Figure 5b). Then, deeper than 100 nm, the lead crystal glass material is homogeneous and correspond to the bulk material.

3.4 Leaching process with the tracer D₂¹⁸O

To understand the leaching mechanism in the lead crystal glass, the leaching process was performed in D₂¹⁸O water with 4vol.% acetic acid with the same surface to volume ratio. In Figure 6a, the SIMS profile of ¹⁸O and D fragments clearly shows that deuterium and oxygen 18 penetrate down to about 100 nm depth after 24 hours of leaching. Overall, on the in-depth profile, the normalized intensity of the peaks shows that deuterium diffuses slightly deeper than oxygen 18. However, ¹⁸O is present in the first 40 nm of depth (zone 2) and the ¹⁸OD and D fragments appear mainly deeper than 30-40 nm in zone 3. A lower deuterium content can be noted in zone 2, especially in the first 20 nm of depth (Figure 6b). The ¹⁸OH fragment is also detected, as H atoms are initially present in the first hydrated layer during the polishing step and present in the acetic acid during the leaching process.

3.5 Effect of multiple leaching and aging

In practice, lead crystal glassware may undergo several successive acid leaches, due to food contact, separated by several storage times. Figure 7 shows the evolution of the Pb content released into an acetic acid solution after leaching every 2 months for 1 year, and then after 6 and 10 months. Initially, all lead crystal glass samples release about $3.1 \mu\text{g}\cdot\text{cm}^{-2}$ of lead, as already noted in Figure 1. Then, the Pb release decreases sharply to $0.4 \mu\text{g}\cdot\text{cm}^{-2}$ from the second leaching to a value below $0.01 \mu\text{g}\cdot\text{cm}^{-2}$ after 7 leachings and 12 months of storage at room temperature. If the second leaching is performed after a longer storage time at room temperature (after 6 or 10 months), lead leaching is also inhibited, as described in Figure 7. To accelerate the diffusion phenomena of the elements in the glass, the samples were stored at 100°C and 300°C . But the leaching of lead after an initial leaching process and storage at room temperature, 100°C and 300°C for 2 months reveals that storage at high temperature drastically reduces the release of lead from lead crystal glass after an initial leaching (Table 3). From a practical point of view, the successive leaching experiments demonstrate that the subsurface layer, formed during the first leaching process, can provide an efficient protective layer against successive lead leaching.

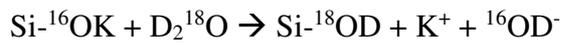
4. Discussion: towards the formation of a "passive" layer

Through the results of this study, the leaching of lead and alkali elements was clearly confirmed on the polished surface in food contact conditions, in 4vol.% acetic acid. The SIMS elemental profile and EDS analysis reveal a clear concentration gradient of Pb and alkali atoms in the lead crystal glass material after 24 hours of leaching. However, silicon and oxygen concentrations are also clearly affected by the leaching process, demonstrating a significant change in the silicate lattice. Simultaneously, the incorporation of ^{18}O to a depth of

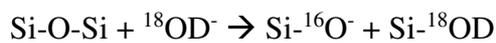
100 nm after 24 h of leaching proves that the leaching process cannot be simply described by a simple ion exchange following the reaction:



The incorporation of ^{18}O into the glass material can be explained by a nucleophilic substitution mechanism following the reaction:

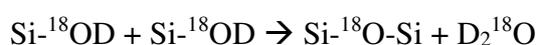


Another possible mechanism is the hydrolysis of the siloxane bonds (Si-O-Si) of the silica lattice with the help of alkaline anions generated by the ion exchange, following the reaction scheme:



The latter hydrolysis mechanism explains the rapid leaching of Pb and K in the first hours of the process due to the depolymerization of the silica lattice, as shown in the Pb leaching kinetics in Figure 1. This hydrolysis phenomenon has already been observed during the degradation of conventional alkali glasses in water or under atmospheric conditions [24].

After the first few hours of leaching, the diffusion of lead in the solution is significantly reduced and the diffusion coefficient of lead is 2 orders of magnitude lower. SIMS and EDS profiles reveal that the glass is enriched in silicon in the first 20 nm depth compared to the deeper leached zone. Furthermore, in the Pb-K-free zone, during D_2^{18}O experiments, the deuterium content in the Si-enriched zone is relatively low compared to the deeper leached zone, which can be explained by the condensation of the silanol group (Si-OH) in acidic medium into Si-O-Si to form a repolymerized silica network in the gel layer, as a result of the reaction:



Therefore, the Pb-K-free subsurface zone seems to be gradually transformed into a dense silica lattice by silanol condensation. In fact, the condensation reaction is induced by the

acidic pH of the acetic acid medium [26]. By increasing the contact time with the acetic acid solution, this zone forms a passive layer acting as a diffusion barrier for lead atoms, as shown by the lead release kinetics in Figure 1.

These mechanisms lead to the formation of a complex profile of chemical elements in the subsurface zone of lead crystal glass. Figure 8 schematize and summarize the evolution of the elemental profile in three time range: (i) the initial stage after polishing, (ii) then after several hours of leaching, (iii) then after 24 hours. The reactions scheme proposed to explain this evolution can be described in four points:

- 1) Ionic exchange: $\text{Si-OK} + \text{H}_2\text{O} \rightarrow \text{Si-OH} + \text{OH}^- + \text{K}^+$
- 2) Hydrolysis of siloxane bonds: $\text{Si-O-Si} + {}^{16}\text{OH}^- \rightarrow \text{Si-}^{16}\text{O}^- + \text{Si-}^{16}\text{OH}$
- 3) Nucleophilic substitution: $\text{Si-}^{16}\text{OK} + \text{H}_2{}^{16}\text{O} \rightarrow \text{Si-}^{16}\text{OH} + \text{K}^+ + {}^{16}\text{OH}^-$
- 4) Condensation of silanol: $\text{Si-}^{16}\text{OH} + \text{Si-}^{16}\text{OH} \rightarrow \text{Si-}^{16}\text{O-Si} + \text{H}_2{}^{16}\text{O}$

The protective properties of this diffusion barrier are also demonstrated by repetitive leaching every 2 months in 4vol.% acetic acid in Figure 7. During the two months of storage at room temperature, the leaching results show that lead atoms do not diffuse to the surface during the storage time, and the repetitive contact with the acidic solution tends to increase the protective character of this subsurface layer. Moreover, if the storage is carried out at high temperature between two leaches, the release of lead after successive leaches shows that the protective property of the subsurface layer is reinforced. Indeed, the heat treatment of hydrated silica glass induces dehydration of the silanol groups to produce strained Si-O-Si siloxane bonds, which seems to limit the diffusion of lead cations in the solution [27, 28]. However, even at room temperature, conversion of the silanol groups to siloxane groups is possible on silica compounds depending on the moisture conditions, as demonstrated by S. Warring et al [29], which explains the beneficial effect of room temperature storage on the protective properties of the subsurface layer against lead.

5. Conclusion

In the food contact conditions, the leaching of lead and alkali from lead crystal glass is relatively rapid during the first hours; thereafter, the leaching kinetics slow down significantly. Leaching in acetic acid medium induces the formation of a complex subsurface zone free of lead and alkali atoms. Using $D_2^{18}O$ acid leaching experiments, a two-step leaching mechanism can be proposed. After an initial rapid leaching of Pb, K by nucleophilic substitution associated to siloxane hydrolysis, the silanol group can condense to form a network of siloxane bonds again. The SiO_2 -enriched underlayer, revealed by SIMS and TEM analysis, explains the slower lead release for longer contact times in acetic acid. The protective behaviour of the underlayer can be enhanced by storage at room temperature or by annealing at high temperature.

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Oxides	Na ₂ O	SiO ₂	K ₂ O	Sb ₂ O ₃	PbO
mol. %	0.8 ± 0.05	77.3 ± 0.5	11.1 ± 0.2	0.3 ± 0.03	10.4 ± 0.5
wt. %	0.6 ± 0.04	57.3 ± 0.4	12.9 ± 0.2	0.97 ± 0.10	28.8 ± 1.5
Elements	Na	Si	K	Sb	Pb
at. %	0.57 ± 0.04	26.7 ± 0.2	7.76 ± 0.16	0.19 ± 0.02	3.60 ± 0.20

Table 1: Composition of lead crystal glass in mol.%, wt.% of oxides and at.% of elements.

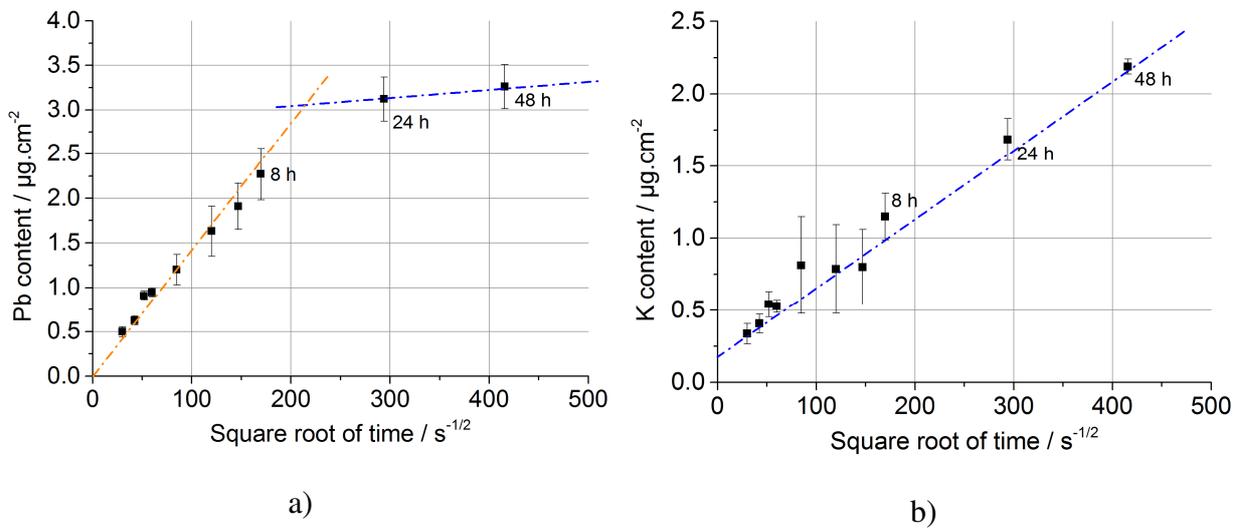


Figure 1: Evolution of leached Pb (a) and K (b) per cm² of lead crystal (µg.cm⁻²) as a function of the square root of the leaching time in a 4vol.% acetic acid solution at room temperature.

Pb		K
First regime	Second regime	$3.2 \cdot 10^{-21}$
$2.2 \cdot 10^{-20}$	$1.7 \cdot 10^{-22}$	

Table 2: Diffusion coefficients of lead and potassium in lead crystal glass in $\text{m}^2 \cdot \text{s}^{-1}$ estimated from the data in Figure 1.

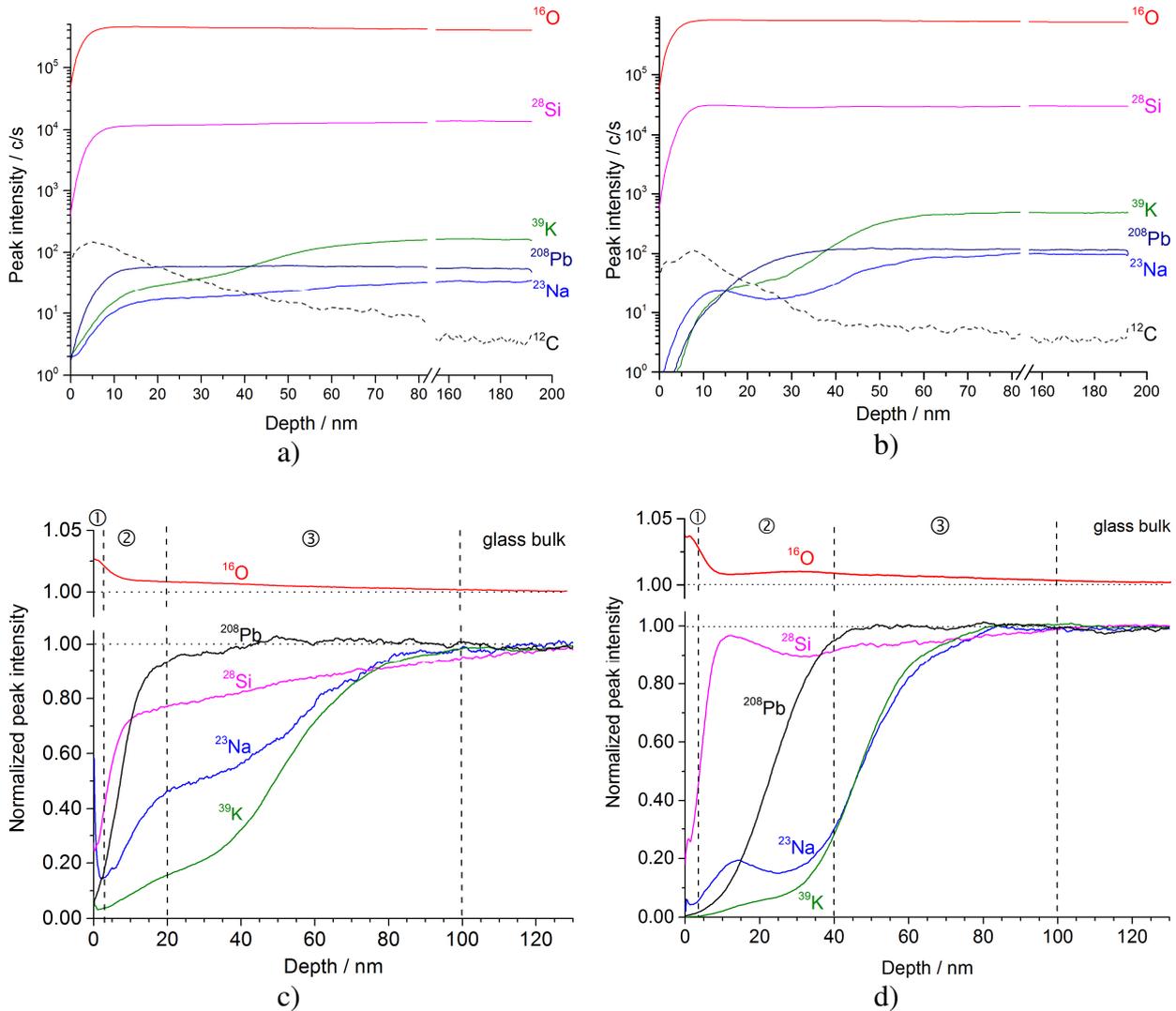


Figure 2: Depth SIMS elemental profile of as-polished lead crystal glass (a, c) and lead crystal glass leached in 4vol.% acetic acid solution for 24 h (b, d). Raw peak intensity (a, b) and normalized peak intensity (c, d) of the a.m.u. of elements as a function of depth.

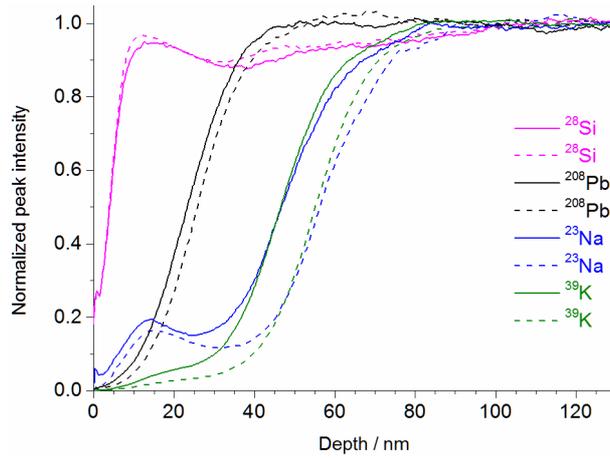


Figure 3: Comparison of the SIMS elemental depth profile of lead crystal glass leached in a 4vol.% acetic acid solution for 24 h (solid line) and 48 h (dashed line).

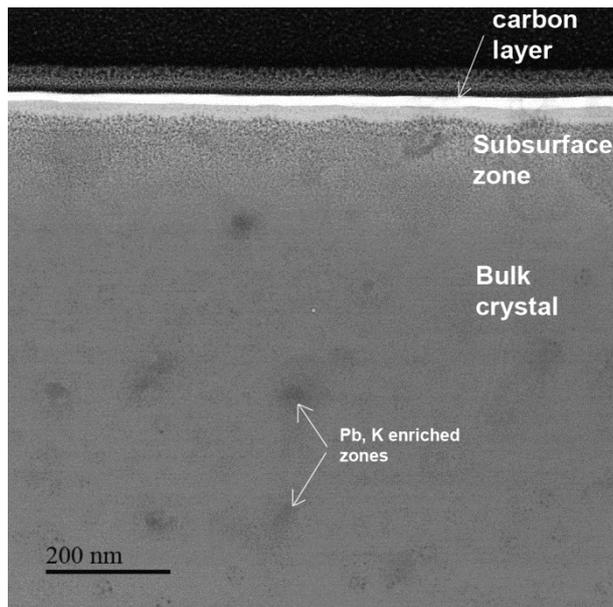


Figure 4: STEM micrograph (cryogenic conditions) of a lead crystal glass leached in 4vol.% acetic acid for 24 h at room temperature.

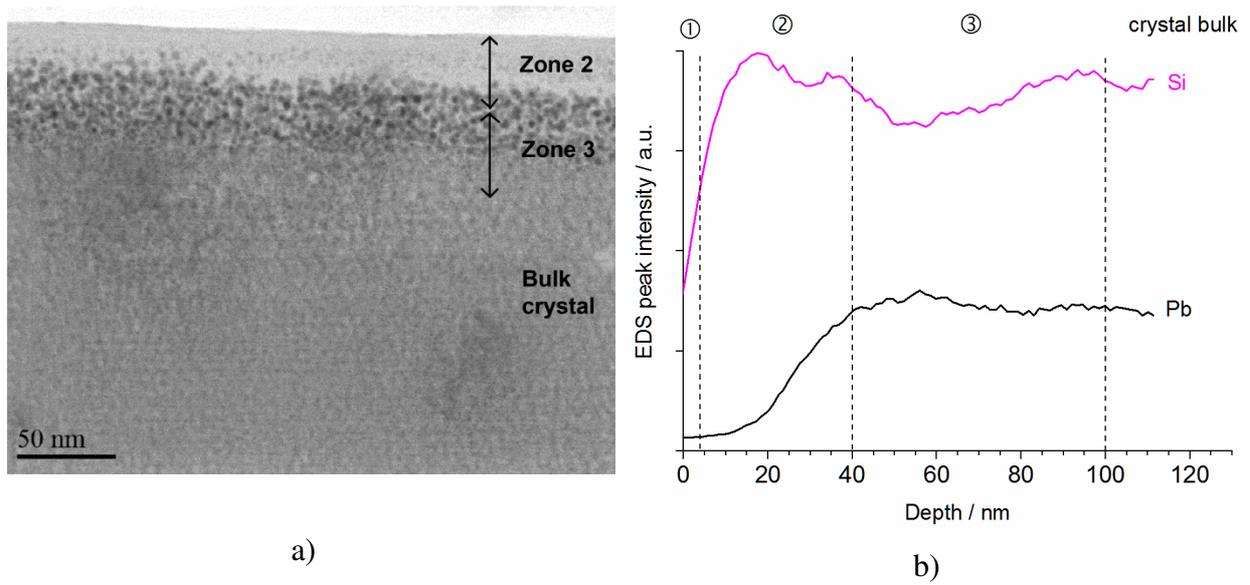


Figure 5: (a) STEM micrograph (cryogenic conditions) of the subsurface layer and (b) EDS peak intensity versus depth of lead crystal glass leached in 4vol.% acetic acid for 24 hours at room temperature.

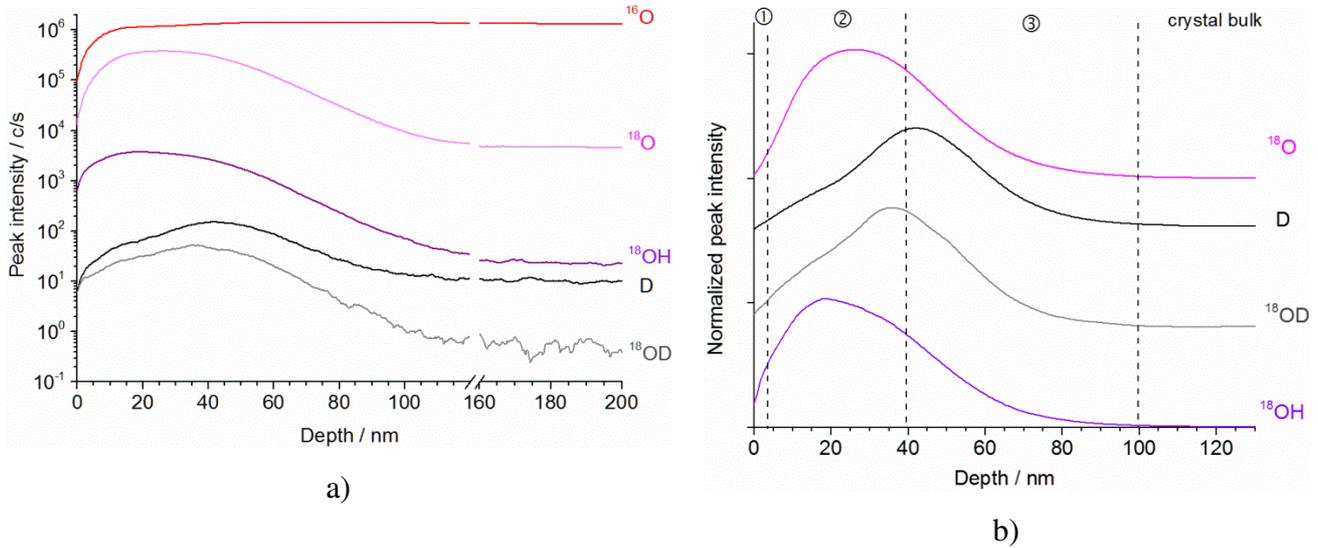


Figure 6: SIMS depth profile of lead crystal glass leached in 4vol.% acetic acid in 98wt.% D_2^{18}O solution for 24 h. (a) Raw peak intensity, (b) Normalized peak intensity.

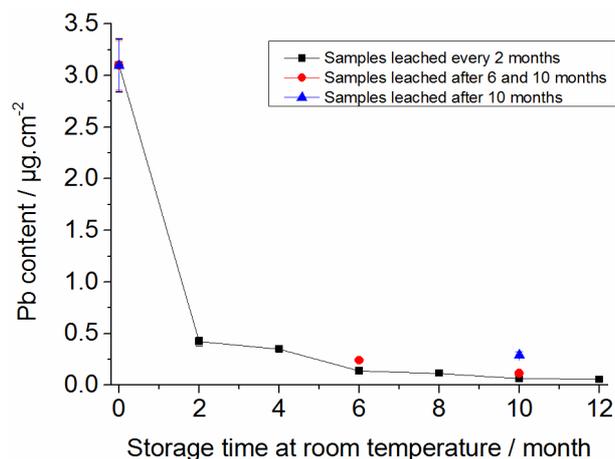


Figure 7: Evolution of Pb content released in 4vol.% acetic acid after successive leaching of lead crystal glass stored at room temperature (Leaching conditions: 24 h at room temperature).

Storage temperature	Ambient temperature	100 °C	300 °C
After 2 months of storage	0.42 ± 0.04	0.065 ± 0.006	0.010 ± 0.001

Table 3: Comparison of released Pb content (µg.cm⁻²) in 4vol.% acetic acid after 2 months storage at different temperatures (Leaching conditions: 24 h at room temperature).

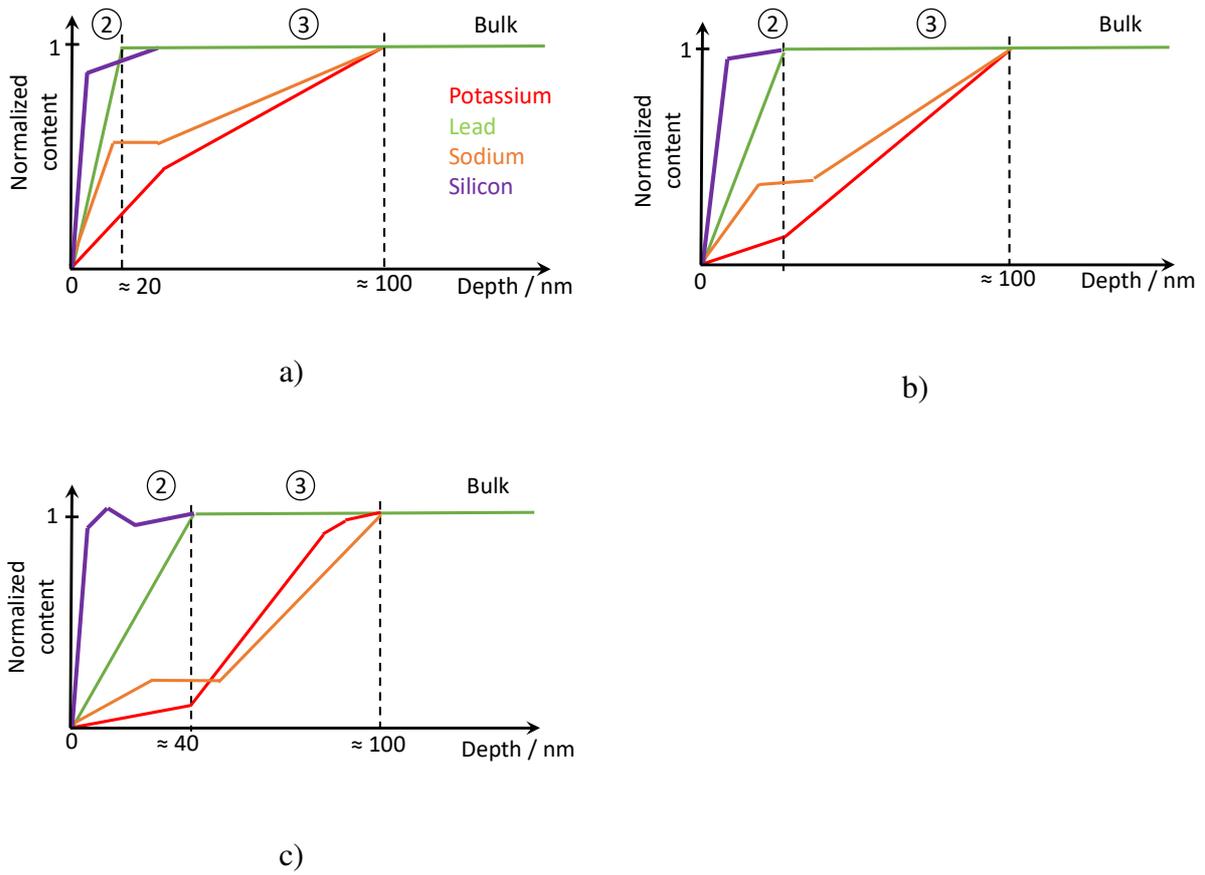
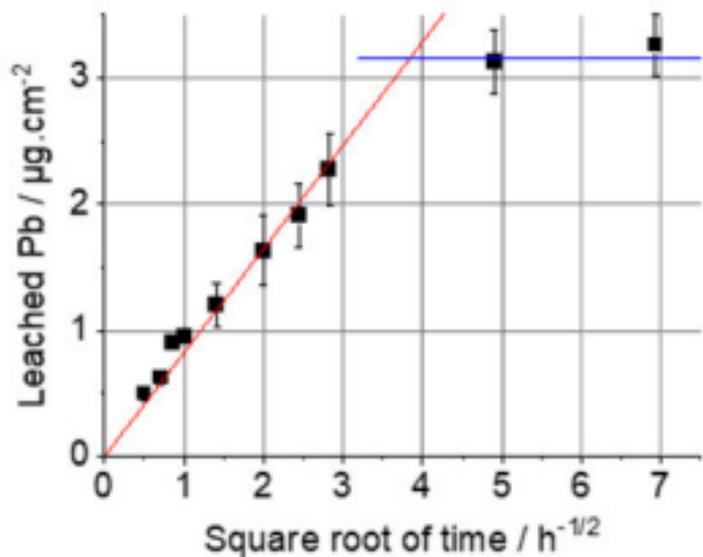


Figure 8: Scheme of the evolution of the composition of the subsurface zone of lead crystal glass at the initial state (after polishing) (a), after several hours of leaching (b), and after 24 h of leaching (c) in 4vol.% acetic acid. (The typical normalized contents are displayed in function of depth for potassium in red, lead in green, sodium in yellow and silicon in violet)

Leached Pb during food contact (4 vol.% acetic acid)



Pb-K free layer
→ «passive» layer

