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Towards a unifying mechanistic model for silicate glass corrosion

Christoph Lenting¹, Oliver Plümper², Matt Kilburn³, Paul Guagliardo³, Martina Klinkenberg⁴ and Thorsten Geisler¹

Borosilicate glasses are currently used for the immobilization of highly radioactive waste and are materials of choice for many biomedical and research industries. They are metastable materials that corrode in aqueous solutions, reflected by the formation of silica-rich surface alteration layers (SAL). Until now, there is no consensus in the scientific community about the reaction and transport mechanism(s) and the rate-limiting steps involved in the formation of SALs. Here we report the results of multi-isotope tracer (^2H , ^{18}O , ^{10}B , ^{30}Si , ^{44}Ca) corrosion experiments that were performed with pre-corroded and pristine glass monoliths prepared from the six-component international simple glass and a quaternary aluminum borosilicate glass. Results of transmission electron microscopy and nanoscale analyses by secondary ion mass spectrometry reveal a nanometer-sharp interface between the SAL and the glass, where decoupling of isotope tracer occurs, while proton diffusion and ion exchange can be observed within the glass. We propose a unifying mechanistic model that accounts for all critical observations so far made on naturally and experimentally corroded glasses. It is based on an interface-coupled glass dissolution-silica precipitation reaction as the main SAL forming process. However, a diffusion-controlled ion exchange front may evolve in the glass ahead of the dissolution front if SAL formation at the reaction interface significantly slows down due to transport limitations.

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INTRODUCTION

When silicate glasses come into contact with stagnant water, a number of coupled processes will start to operate at the solid-water interface in order to reach a new equilibrium or steady state, such as hydration, hydrolysis, dissolution, diffusion, ion exchange, adsorption, and/or crystal nucleation, and growth. In nature and experiment, the complex interplay and succession of such reactions often produce a porous surface alteration layer (SAL) that can have a thickness of a few nanometers to several centimeters or even more.^{1–4} In the daily life, we experience such alteration layers, for instance, as whitish stains on glassware.⁵ In general, the SAL is composed of (1) a so called ‘hydrated glass’ or ‘interdiffusion layer’ that is depleted in alkaline elements and is located directly adjacent to the pristine glass, (2) an amorphous layer of porous, silica-rich material (often called ‘gel’ in case of nuclear glasses), and, in some cases, (3) by precipitates of secondary minerals such as zeolites or clays at the outer surface.⁶

In some cases, the corrosion rim detaches partly or entirely from the pristine glass,^{4,7–10} which is well known as flaking in the archeological literature.¹¹ This observation suggests that a sharp chemical and physical interface must exist between the SAL and the underlying pristine glass.¹² Indeed, an atomically sharp chemical interface between the SAL and the glass has recently been detected by atom probe tomography (APT).^{13,14} Elements with high solubility are usually not retained in the SAL and transferred to the bulk solution, but less soluble elements, including uranium,⁷ are often incorporated, at least partly, in the SAL.¹⁵ In both nature and experiment, the distribution of less

soluble elements was found to define spatial patterns within the SAL,⁸ but also structural patterns composed of sharply bound layers with different porosity and/or silica sphere packing have been reported.^{7,10,16} Until now, however, a general, coherent mechanistic model for the corrosion process that can explain the dynamic formation of the corrosion rim over a spectrum of different physicochemical conditions and glass compositions is still under debate.

Currently, two fundamentally different models for the formation of the SAL are controversially discussed.^{12–14,17–19} In the first model, the SAL is assumed to represent the product of repolymerisation reactions within a chemically modified, hydrated glass layer.^{1,20–25} This hydrated glass layer forms by solid-state, diffusion-controlled ion exchange of mobile glass network modifiers (e.g., Li, Na, or Ca) with protons from solution, forming silanol groups, while the cations are released into solution. This chemically leached layer eventually undergoes re-polymerization as the results of condensation of the (previously formed) silanol groups, releasing molecular water and producing porosity in the residual glass. In this model, it is assumed that the porosity in the gel layer directly reflects the free space created in the glass by the removal of cations from the glass structure.²⁶ Although this interdiffusion-based ion exchange or leaching model became widely accepted, particularly in the glass community, there has been a long dispute about the passivating effect of the SALs that is reflected by an experimentally observed drop in the corrosion rate with time.²⁷ It has been suggested that the SAL may be protective against further glass corrosion by pore closure or by

¹Steinmann-Institut für Geologie, Mineralogie und Paläontologie, University of Bonn, Poppelsdorfer Schloss, Meckenheimer Allee 169, 53115 Bonn, Germany; ²Department of Earth Sciences, Utrecht University, Princetonlaan 8a, 3584 CB Utrecht, The Netherlands; ³Centre for Microscopy, Characterisation and Analysis, University of Western Australia, Crawley, WA 6009, Australia and ⁴Institute of Energy and Climate Research (IEK-6) – Nuclear Waste Management and Reactor Safety, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany

Correspondence: Christoph Lenting (cl@uni-bonn.de)

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restructuring of the hydrated glass, forming a passivating reactive interphase (PRI).^{6,23,28} Whereas some researchers favor the idea that the SAL represents a diffusion barrier for reactive species,^{6,23,24,28} others attribute this drop in the reaction kinetics to solution saturation conditions (chemical affinity) and related inhibiting effects,²⁹ or to both.^{13,25}

In the second model, the SAL is assumed to form by the precipitation of amorphous silica directly from solution.^{8,12,14,18} The formation of such a silica layer is thereby spatially and temporally coupled to the congruent (stoichiometric) dissolution of the glass, i.e., both the glass dissolution and the silica precipitation reactions proceed at an inwardly moving, atomically sharp reaction interface. The driving force for such an interface-coupled dissolution-precipitation (ICDP) reaction is given by the solubility difference between the glass and amorphous silica. Such a model provides an elegant explanation for most observations made on naturally and experimentally altered glass, including the observed atomically sharp interface between the SAL and the underlying pristine glass as well as the porosity that directly results from the fact that amorphous silica forms spherical precipitates rather than from the selective removal of cations from the glass.^{8,12,19}

Here we report new results of multi-isotope tracer experiments (^2H , ^{10}B , ^{18}O , ^{30}Si , and ^{44}Ca) with the six component international simple glass (ISG) and a quaternary borosilicate glass (QBG) (Tab. 1). The idea behind such multi-isotope tracer experiments is that—beside small fractionation effects—the different isotopes of an element behave in the same way during a particular reaction, but can be measured individually by mass spectrometric techniques. Thus, the coupling or decoupling of different isotopes in space and time can be investigated, providing insights into the mesoscopic mechanisms of distinct transport and reaction steps during aqueous glass alteration. For the multi-isotope tracer experiments we used both pristine glass cuboids (exp. series A) as well as glass cuboids that were precorroded at $90 \pm 1^\circ\text{C}$ for 7 months in an isotopically “normal” solution that was half-saturated with respect to amorphous silica at 90°C and continuously adjusted to a pH of 7 (exp. series B), following the experimental approach of Geisler and coworkers.¹² The experiments were performed for 3 months at 90 ± 1 and $150 \pm 2^\circ\text{C}$ in an unbuffered silica solution (initial pH = 7, Tab. 1). To prevent re-dissolution in any precorroded samples, this second solution was fully saturated with respect to amorphous silica at 90°C . A notable difference of the present study is that the duration of the

experiments had to be significantly extended, since both glasses are much less reactive at intermediate pH than the simple ternary borosilicate glass used by Geisler and coworkers¹² (7 + 3 months compared with 2 + 2 weeks). The structure of the SAL was characterized by Raman spectroscopy. Nanoscale secondary ion mass spectrometry (NanoSIMS) and scanning transmission electron microscopy (STEM) on electron transparent foils, cut through the SAL-glass interface by the focused ion beam (FIB) technique, were used to analyze the different isotopes and to characterize the reaction interface(s) at the nanoscale, respectively.

RESULTS

Identification of SAL phases

After quenching the experiments to room temperature, rinsing the sample in deionized water, and drying the samples at 60°C , the SALs from all eight experiments were first analyzed by confocal Raman spectroscopy. The Raman spectra reveal typical spectral features of water-rich amorphous silica that precipitated from an aqueous solution (see Supplementary Fig. S1). However, slight but distinct spectral differences between the different samples and experimental series are observable, particularly in the frequency range of Q speciation bands between 850 and 1250 cm^{-1} (see Supplementary Fig. S1), suggesting different silica structures and/or compositions. At the surface of the two samples from the QBG altered at 150°C , we additionally observe sharp bands near 717 and 1054 cm^{-1} (exp. QBG-90/150) as well as near 878 and 767 cm^{-1} (exp. QBG-150), indicating the presence of crystalline phases. The assignment of these bands to a certain crystalline phase, however, was not possible.

Element and isotope distribution in the SAL

Once the Raman surface measurements had been carried out, the samples were embedded in epoxy resin, cut in half, and finally polished for NanoSIMS measurements. Representative NanoSIMS isotope images from the SALs from the experimental series B are shown in Fig. 1. Figure 2 shows two-dimensional isotope profiles from two representative precorrosion experiments (experimental series B). Isotope profiles from all other experiments are given in the Supplement (Fig. S2–S5). The total thickness of the SALs formed after 3 months at 90°C and 150°C was estimated from the $^{18}\text{O}/^{16}\text{O}$ profiles and range between 1.6 and 1.5 and 0.7 and $1.9\text{ }\mu\text{m}$, respectively (Table 1). It is affirmative that the SAL

Fig. 1 False-colored NanoSIMS isotope images of two precorroded samples, **a** experiment ISG-90/90 and **b** experiment QBG-90/150. Each square represents the actual imaged area with the upper and lower halves (or thirds) each showing one isotope (ratio). Dotted lines represent the outer (solution-SAL) and inner (SAL-glass) interfaces derived by the inflection points of the $^{18}\text{O}/^{16}\text{O}$ profiles. Scale bars = $1\text{ }\mu\text{m}$. Plotted in colorblind- and B/W-friendly colormap ‘viridis’.³⁰

Fig. 2 NanoSIMS profiles across the SAL into the pristine glass of ISG-90/90 and QBG-90/150 samples. Colored symbols represent normalized isotope counts (or sums of them), black symbols and right ordinates represent isotope ratios. Origin of abscissa is set to the inflection point of the sigmoidal-shaped oxygen isotope ratio at the SAL-glass interface. Symbol size matches the estimated NanoSIMS probe diameter. Gray area represents the location and thickness of a dense layer observed in STEM (Fig. 3)

thickness on pristine ISG formed at 90 °C at an initial pH of 7 (Table 1) is in agreement with published values from experiment performed with this glass under similar physicochemical conditions.³⁰

Although the isotope images and profiles reveal complex features concerning the distribution of certain isotopes, some general observations can be made. First, ³⁰Si could not be detected inside the SAL of all eight experiments. A key observation, however, is that in all experiments, though with variable ²H intensities, a spatial decoupling of ²H and ¹⁸O can be observed at the boundary between SAL and the underlying glass, whereby the ²H front advanced significantly further into the glass (Figs. 1 and 2, Supplementary Fig. S2–S5). This observation is independent from spatial resolution limitations and clear evidence that a higher barrier for the transport of molecular water exists than for the transport of protons. We further note that deuterium, while it was clearly detectable at the SAL-glass interface in all experiments, it is hardly detectable in the main part of the SAL. Exchange with deionized water during sample rinsing and drying may explain the apparent loss of deuterium here.³¹ Comparing all experiments, the deuterium signal as well as the ²H/¹H ratio at the SAL-glass boundary is in most cases higher in the experiments conducted at 150 °C than at 90 °C.

All ¹⁸O/¹⁶O profiles across the SAL are very similar and are characterized by relative constant values throughout the SAL (Tab. 1) and a sigmoidal decrease towards the underlying glass (Fig. 2). The shape of the ¹⁸O/¹⁶O profiles is in full agreement with results from previous isotope tracer studies,^{12,15} implying a general involvement of ¹⁸O from solution in the formation of the SAL. Assuming a linear mixture between oxygen from the glass with that from the bulk solution (Tab. 1), the SAL contains between about 14 to 51 at.% ¹⁸O from solution. The width of the sigmoidal part of the ¹⁸O/¹⁶O fronts is about 90 nm, i.e., in the order of the NanoSIMS spot size, and the lowest observed among all isotope profiles. We therefore draw the SAL-glass interfaces in Figs. 1 and 2 at the inflection points of the sigmoidal ¹⁸O/¹⁶O curves, which facilitates the direct comparison of the different isotope profiles. In addition, higher ¹⁸O/¹⁶O values were detected in most experiments in the outer part of the SAL, likely reflecting the precipitation of secondary phases from the ¹⁸O-rich solution,¹⁵ as also indicated by the Raman measurements of the SALs from the experiments QBG-150 and QBG-90/150. Considering the results from previous isotope tracer experiments that were performed with a pre-corroded Na-borosilicate glass,¹² it was expected that the outer part of the SAL would be characterized by nearly natural ¹⁸O/¹⁶O values (~0.002), which, however, is not observed.

Table 1. Sample details, experimental conditions, and properties of the SAL

Glass composition	SiO ₂ (mol%)	ZrO ₂ (mol%)	Al ₂ O ₃ (mol%)	B ₂ O ₃ (mol%)	CaO (mol%)	Na ₂ O (mol%)	Density (g cm ⁻³)	
ISG	60.7 (7)	1.7 (1)	3.8 (1)	16.0 (8)	5.6 (1)	12.3 (15)	2.41 (14)	
QBG	65.9 (10)		4.2 (1)	11.9 (7)	0.09 (1)	17.9 (2)	2.48 (2)	
Solution composition	pH _{init,RT}	SA/V (mm ² mL ⁻¹)	SiO ₂ (mmol L ⁻¹)	KOH (mmol L ⁻¹)	BH ₃ O ₃ (mmol L ⁻¹)	CaCl ₂ (mmol L ⁻¹)	D/H	¹⁸ O/ ¹⁶ O
Precorrosion	7.0 (0)	~2.7	2.2 (3.1% ³⁰ Si)	6.0 (1)			~0.0001	0.002
Tracer	7.0 (0)	~24	5.9 (99% ³⁰ Si)	12.1(1)	4.1 (99% ¹⁰ B)	0.76 (97% ⁴⁴ Ca)	0.225	0.231
Experiments	ISG				QBG			
Temperature (°C)	90 (1)	150 (2)	90 (1)	150 (2)	90 (1)	150 (2)	90 (1)	150 (2)
Condition	Pristine	Pristine	Precorroded	Precorroded	Pristine	Pristine	Precorroded	Precorroded
Duration (months)	3	3	7 + 3	7 + 3	3	3	7 + 3	7 + 3
pH _{final,RT}	7.6 (0)	7.7 (0)	8.1 (0)	8.1 (0)	7.7 (0)	8.0 (0)	8.3 (0)	8.4 (0)
Rim thickness ^a (μm)	1.63 (11)	0.68 (21)	2.97 (25)	2.70 (21)	0.93 (22)	1.92 (21)	2.42 (7)	4.09 (26)
Avg. ¹⁸ O/ ¹⁶ O	0.05385 (69)	0.04449 (72)	0.08263 (82)	0.03602 (20)	0.07709 (38)	0.07774 (28)	0.03263 (12)	0.07587 (28)

^a The corrosion rim thickness was derived by fitting the ¹⁸O/¹⁶O NanoSIMS images with the local thickness function of the Fiji/ImageJ⁴⁸ software package

Importantly, the ²³Na concentrations clearly start to decrease inside the glass towards the glass-SAL interface in all experiments with the QBG and in two experiments with the ISG (exp. ISG-90, exp. ISG-90/90) when compared with the inflection point of the ¹⁸O/¹⁶O profiles. Thereby, the inflection points of the sigmoidal ²³Na profiles roughly coincide with those of the ²H profiles, so both profiles are anticorrelated (Fig. 2, Supplementary Fig. S2). In the two other experiments (exp. ISG-90/150, exp. ISG-150), the ²³Na intensity profiles are also anticorrelated with respect to the ¹⁸O/¹⁶O profiles, but here their inflection points coincide. The inflection points of the sigmoidal ³⁸K profiles through all SALs also coincide very well with those of the ²³Na profiles, but since ³⁸K is introduced from solution, they are anticorrelated with the ²³Na profiles.

The measured B and Ca isotope profiles through the SALs reveal a complex behavior of both elements. In two experiments (exp. QBG-90, exp. ISG-90), the total B profiles show a sharp decay at the SAL-glass interface, i.e., the inflection points of the B profiles coincide well with those of the ¹⁸O/¹⁶O profiles. In all other cases, the inflection points of the B profiles are located at variably distances away from the SAL-glass interface. In both QBG experiments performed at 150 °C (exp. QBG-150, exp. QBG-90/150) B were fully retained across those SAL sections that formed at 150 °C. Note here that the special case of almost full B retention is neither an experimental or nor an analytical error, as it was observed in two independent experiments with one pristine and one precorroded sample (exp. QBG-150, exp. QBG-90/150), but must be attributed to the specific physicochemical conditions in the SAL of this glass composition at a temperature of 150 °C. Overall, the behavior of B is surprising, because B is a highly soluble element that is usually not retained in the SAL, and thus used as proxy for the progress of corrosion.³² Nevertheless, in contrast to Na, concentration profiles of B (and Ca) can exhibit a few hundred nm long tailings into the SAL (Fig. 2),^{13,30,33} suggesting that specific SAL properties influence its retention by transport limitation and/or adsorption. Moreover, although the count rates were low due to low B concentrations, the ¹⁰B/¹¹B values in the SAL are typically on average higher than the natural B value in the glass (=0.25), showing that some B from solution is incorporated in the SAL. Similar to B, Ca also depicts complex and unexpected profiles throughout the SAL. In the ISG experiments, containing 5.7 mol.% Ca, the Ca concentration are at maximum

close to SAL-glass interface and show a smooth decrease towards the SAL surface. The ⁴⁴Ca/⁴⁰Ca values, on the other hand, decrease almost linearly towards the SAL-glass interface, whereas close to the interface they decrease sigmoidally before reaching the natural ⁴⁴Ca/⁴⁰Ca value of the glass. This is clear evidence that Ca from the glass mixed with Ca from solution, with larger Ca fractions from the glass in SAL areas that are located close to the interface. The experiments with the QBG yielded similar ⁴⁴Ca/⁴⁰Ca profiles, but here the sum of both isotopes follows the decreasing ⁴⁴Ca/⁴⁰Ca profiles (Fig. 2). Such profiles suggest that the glass is not free of Ca (of natural isotope composition) that could mix with the ⁴⁴Ca from the solution to produce the observed decreasing ⁴⁴Ca/⁴⁰Ca towards the interior of the SAL. Indeed, electron microprobe measurements revealed that the glass contains 0.055 ± 0.007 wt% Ca that must be of natural isotope composition. Thus, while mobile species such as Na, K, H, and O clearly penetrated the whole SAL, boron retention and calcium incorporation into the SAL seem to be controlled by the properties of the SAL and/or pore solution. The weakly soluble elements Zr and Al are relatively enriched throughout the SALs, but in some experiments also at the surface of the SAL, indicating precipitation of Al- and/or Zr-rich phases (Fig. 1a).

Nanostructure and nanochemistry of the SAL

Based on the NanoSIMS data, we selected two samples from the series B experiments for STEM to investigate the microstructure of the SAL and the elemental distribution across the SAL-glass interface with higher spatial resolution. We chose the sample from experiment QBG-90/150 because the isotope data show features that have not been observed in the other precorroded samples.

In this sample, the ⁴⁴Ca/⁴⁰Ca ratio and the sum of both Ca isotopes, which both come from solution, drop in the center of the SAL at about 1.73 μm from the SAL-glass interface (Fig. 2b). The opposite trend is observable for the total B content, which drops towards the outer surface from about 1.5 μm. Moreover, the Si profile shows a (decreasing) kink at this position, the ¹⁸O/¹⁶O values a small peak, and ²H is clearly detectable in the SAL between this position and the SAL-glass boundary, where ²H is strongly enriched. The second FIB foil was cut across the SAL-glass interface of the experiment with the precorroded ISG sample at 90 °C (exp. ISG-90/90). This sample was selected, because it has the

Fig. 3 Compilation of STEM(EDX) analyses of ISG-90/90 and QBG-90/150 samples. HAADF image of SAL-glass interface of ISG sample is shown in **a**, revealing a dense layer between the porous SAL and glass. Superimposed are the normalized intensities of Ca (yellow), K (green) and Na (blue) as measured by STEM-EDX. Image-based size analysis of the worm-like silica spheres of the porous SAL section (marked by orange brackets) is shown in **b**, with results being compared to QBG sample in **e**. **c** Montage of HAADF images of QBG samples revealing a second, inner dense layer and two SAL sections with differing sphere sizes, porosity, and Ca concentrations (STEM-EDX). **d**, **f** Sphere size analysis of outer (purple brackets, **d**) and inner SAL (blue brackets, **f**). Scale bars = 200 nm

largest SAL thickness of both experiments with precorroded ISG samples, was corroded at the same temperature of 90 °C during both experimental stages, and shows all key features mentioned above.

High-angle annular dark field (HAADF) STEM images of the interface between the SAL and the underlying glass from the experiment ISG-90/90 revealed the existence of an about 100 nm^{-1} thick, high-Z (mean atomic number) contrast layer that is located between a porous zone and the glass with which it has a clear phase boundary (Fig. 3a). The high Z-contrast indicates a dense material (pore size $< 1\text{ nm}$). The transition from this dense layer towards the porous part of the SAL appears to be more gradual, because at the boundary between both zones the material making up the dense layer also fills the pore space of the porous zone. The porous zone is composed of worm-like structures that themselves consist of spherical aggregates (Fig. 3a). Sphere size analyses of the HAADF images of the porous section of the SAL (Fig. 3b), using an algorithm that identifies the maximum diameter of spheres fitted into a given structure (see Methods), yielded sphere sizes in the order of 5 nm (Fig. 3e). The discrete phase boundary between the glass and the dense layer, reflected by the Z-contrast, is mirrored by the STEM-based energy-dispersive X-ray (EDX) analyses. These reveal sharp chemical gradients for Ca and K across the interface, whereas Na diffused out of the glass over a length scale of about 200 nm, which is in full agreement with the NanoSIMS data (Fig. 2a). Ca is relatively enriched inside the dense layer. The EDX profiles further reveal Ca concentrations at the interface with the glass that are significantly higher than the Ca concentrations in the glasses (Fig. 3a). On the other hand, the K concentration at the SAL-glass interface of experiment ISG-90/90 is significantly higher than the K content inside the dense zone (Fig. 3a).

HAADF images of the interface between the SAL and the underlying glass from the experiment QBG-90/150 also show a dense zone at the border with the underlying glass (Fig. 3c). Furthermore, the STEM-EDX elemental line profiles across the interface resemble those seen in experiment ISG-90/90 (Fig. 3a) with the difference that (i) Ca diffused about 100 nm into the (Ca-poor) QBG and (ii) K shows a maximum at both sides of the phase boundary. The most important observation, however, is that a second dense zone is visible in the HAADF images about $1.73\text{ }\mu\text{m}$ away from the SAL-glass interface, i.e., exactly at the position where the NanoSIMS measurements indicate a distinct transport barrier for aqueous Ca^{2+} . It is further notable that the void structure of the SAL on both sides of the central dense layer is clearly different (Fig. 3c, d, f). The void structure and the sphere size distribution of the outer SAL is similar to those of the SAL formed in the precorrosion experiment with the ISG, i.e., both having its maximum near 5 nm (Fig. 3e). The inner SAL, however, has a much higher porosity, directly reflecting a significantly larger average size of the spheres ($\varnothing \sim 15\text{ nm}$) that also here form worm-like aggregates.

DISCUSSION

The new isotope tracer experiments revealed several observations that are not consistent with the classical SAL formation concept.^{1,20–25} In particular, the formation of several individual layers with largely different porosity inside a single SAL (exp. QBG-90/150) is difficult to explain by a leaching model that considers (i) the SAL as a residual and restructured glass and (ii) its porosity as a reflection of the free space created by the selective removal of certain network formers and modifiers from the glass,²⁶ and (iii) a transitional zone presented as hydrated glass² or PRI²³ running

ahead of the SAL. On the other hand, the structural, textural, and isotopic features are fully consistent with the ICDP model that considers the SAL as being an amorphous silica precipitate. The decoupling of ^{18}O and ^2H at the boundary between the SAL and the glass indicates a drastic difference in the transport of molecular water and protons as would be expected for a silica-silicate glass phase boundary. An unexpected observation, at first glance, is that we did not observe an outer part of the SAL that has a natural oxygen isotope composition as observed in our previous study with a ternary borosilicate glass.¹² This suggests that the ten times longer duration of the tracer experiments in this study (40 vs. 4 weeks) and for some experiments the higher temperature (150 °C vs. 90 °C) enabled the complete re-equilibration of the oxygen isotope composition of the SAL. Moreover, we anticipated to observe ^{30}Si enrichment in the SAL. Comparing recent isotope tracer studies, it seems that the amount of silicon from solution being incorporated into the SAL may be anti-correlated to the silica saturation of the bulk solution, i.e., at low to medium silica saturation abundant silicon tracer could be detected in the SAL,^{15,34} while at high silica concentration only slight enrichment could be detected.³⁰ The silicon isotope exchange rate must be coupled to the residence time of the ion in solution. This would mean that at high silica saturation silicon, released from the glass during congruent dissolution, quickly polymerizes and reprecipitates at the glass surface to form the SAL before the Si of the tracer solution and the dissolved Si from the glass can mix and equilibrate.

The dense layer at the SAL-glass interface found in this study resembles in many respects the dense interfacial zones that were observed in many other studies and were called PRI.²³ The PRI was found to have pore sizes smaller than 1 nm, and was interpreted to represent either a passivating hydrated glass or a reorganized residual glass (gel). The observation that the dense silica phase fills larger pores in the border region with the porous part of the SAL, however, is not consistent with such an explanation. We suggest that the dense layers most likely formed during quenching from a silica-rich and silica-supersaturated interfacial solution that was located between the porous part of the SAL and the glass. Such an interfacial solution is an immanent feature of the ICDP model and its verification has been rated most critical for the credibility of the ICDP model.¹³ Chemically, an effect of quenching is noticeable by the higher K^+ concentration on the glass than in the dense layer itself, which indicates that K^+ was higher at the interface during the experiment and has been transported away from the interface at a later stage. This can only have taken place during quenching, rinsing, and drying of the sample at the end of the tracer experiment (Fig. 3a). In fact, the measured element distributions across the SAL do not necessarily mirror to the actual concentrations that prevailed during the experiments when solution still filled the voids of the SAL. This is evident when considering ^2H that was only detected in the inner dense layers, in the inner porous layer of experiment QBG-90/150, and in the glass, but not in the outer porous layer (Fig. 2b). During the experiment, $^2\text{H}^+$ must have been loosely bound to surface Si-O^- groups throughout the SAL, but quickly exchanged with $^1\text{H}_2\text{O}$ during rinsing the sample with water and drying it at the end of the experiment. Only in the dense layers and inside the glass the ^2H - ^1H exchange was slow enough, so some ^2H remained.

It is self-evident that the inner dense layer of experiment QBG-90/150 formed during the precorrosion treatment, where it marked the reaction interface between the SAL and the glass at the end of the experiment. It is thus a stable structure that did not significantly re-structure during the second corrosion step. The formation of individual layers in this experiment is thus not related to a self-organization process as observed in other experiments,^{7,8} but instead reflects the effect of (i) two corrosion steps with repeated quenching of the sample to room temperature and (ii) additional rinsing and drying of the sample at the end of the

isotope tracer experiment. It follows that the occurrence of detectable ^2H in the inner porous part of the SAL of experiment QBG-90/150 must reflect incomplete ^2H - ^1H exchange. Note that also the ^{44}Ca tracer is only observed in the outer, less porous layer of this experiment (Fig. 2b), both suggesting that the inner dense layer acted as a distinct transport barrier during and at the end of the isotope tracer experiment. Hence, this barrier must have also caused a different local chemical environment (such as different pH) during the second corrosion step, producing a more porous silica product. This can be understood when considering that, depending on the local conditions, silica nanoparticles (1–2 nm) either directly agglomerate or first grow to larger colloidal particles of up to 200 nm before crosslinking.³⁵ As such, gels of almost all possible combinations of specific surface area pore volume, and pore diameter can potentially form throughout the process. We argue that it is not possible to form such a complexly and sharply layered SAL structure via a diffusion-controlled “leaching” process nor from a leached residual glass. Nevertheless, it is evident that a diffusion-controlled ion exchange front, involving the inward diffusion of H^+ (and K^+ , Ca^{2+}) that is coupled to an outward diffusion of Na^+ (and Ca^{2+}) and B, had been developed inside the glass (Figs. 2 and 3), which has not been taken into account in previous ICDP model.^{12,14}

Based on the new experimental results, we propose a unifying refined mechanistic glass corrosion model that in many aspects unifies all critical observations made on experimentally and naturally altered glass samples, such as an atomically sharp reaction interface,^{13,14} interdiffusion profiles in the glass,^{13,30} the formation of porosity,^{7,12,30,36,37} as well as chemical and structural patterns in the SAL.^{7,8,10,12} A schematic outline of the proposed mechanistic model is given in Fig. 4. In a silica-undersaturated solution, glass–water interaction starts with the congruent dissolution of the glass until (super)saturation of amorphous silica is reached in a solution boundary layer at the glass surface (Fig. 4a). At this stage, the glass dissolution reactions are coupled in space and time to the precipitation of amorphous silica so that a dissolution-precipitation interface moves into the glass, leaving behind a SAL composed of amorphous silica. The local physico-chemical conditions in the SAL determine, on the one hand, the size of the precipitating silica spheres and their arrangements,³⁵ and on the other hand, the amount of chemical impurities in the newly formed silica (e.g., B and Al incorporation)³⁸ and/or redistribution of glass constituents and solution components across the SAL (e.g., Ca, Zr).³³

As in our and numerous other experiments, the SAL may be overgrown by secondary minerals (Fig. 4e). The model now extends the ICDP model with an interdiffusion (ID) process between proton and glass network species inside the glass,^{39,40} (Fig. 4e). However, this ID process can only precede an ICDP front if the front velocity is slower than the ID process itself. Since diffusion of H^+ into the glass is extremely slow at temperatures around 90 °C ($1.3 \times 10^{-23} \text{ m}^2 \text{ s}^{-1}$), the ID process will only operate once the ICDP replacement process has almost fully stopped. At this stage, the release of elements from glass into the bulk solution is controlled by solid-state diffusion inside the glass, as also suggested by other studies,^{13,41,42} but also by contemporaneous outward transport of these elements through the SAL. The elemental release to the bulk solution, thus strongly depends on the transport properties of both the glass and the SAL.

The temporal development of such an interdiffusion zone is demonstrated by time-of-flight secondary ion mass spectrometric chemical profiles from a systematic set of glass corrosion experiments performed by Gin and coworkers.¹³ These revealed an increasing mean diffusion distance for H^+ inside the glass with reaction time after the growth of the SAL had almost stopped. The authors, however, consider the SAL as a residual and restructured glass rather than as a precipitate. This, however, is in contrast to results of the APT study by Hellman and coworkers¹⁴ that revealed

Fig. 4 Refined phenomenological model of aqueous glass corrosion. **a** In silica-undersaturated solution the corrosion starts with congruent dissolution of glass, resulting in the formation of etch pits with an initial or forward rate r_0 . **b** Depending on the ratio of transport of dissolved silica into the bulk solution and silica release from glass dissolution, a concentration gradient will develop,⁴⁷ enabling localized saturation of aqueous silica triggering condensation and nucleation reactions.³⁵ **c** After silica-supersaturation has been reached in the solution boundary layer, amorphous silica spheres precipitate onto the dissolving glass surface, mimicking the initial glass surface. **d** Congruent glass dissolution continues, while dissolved species are transported through the developing SAL. Transport limitations (of water and dissolved species) lower the rate of congruent dissolution at the reaction interface ($r_0 \rightarrow r_r$), which eventually is slow enough for solid state diffusion of protons and ion exchange with glass constituents to occur **e**.¹³ The occurrence of the inner dense layer in exp. QBG-90/150 is schematically outlined in **f** and **g**. **f** Quenching the sample before solution exchange causes the precipitation of silica from the interfacial (pore) solution. **g** During the following (isotope tracer) reaction step, this quenched layer potentially acts as transport barrier, influencing the composition of the inner (pore) solution

atomically sharp concentration gradients for all elements at the interface between the glass and a silica-based SAL, demonstrating the development of an ICDP front without the formation of an interdiffusion zone. This led the authors suggest that the ICDP model is universal and that the sigmoidal elemental profiles across the ICDP front observed in numerous previous studies^{15,30,33,43,44} are an analytical artifact related to the restriction of the respective spatial resolution of the applied analytical techniques to several tenth of nanometers or even larger¹³ (see also Supplementary Fig. S6). However, as the decoupling of the $^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/^1\text{H}$ profiles and the sigmoidal decrease of Na inside the glass observed in this study (Figs. 2 and 3) clearly exceed the limits of the respective spatial resolution of the measurements, we argue that the isotope and elemental profiles inside the glass indeed reflect a solid-state interdiffusion process that operated ahead of an ICDP front. Note that such a zone will not be observed if the experiment will be terminated before this stage has been reached. This could explain why Hellmann and coworkers¹⁴ did not observe an ID zone in their high-resolution APT study on a glass altered for 1 month in pure water.

The reason for the commonly observed drop of the corrosion rate with time, which in our refined ICDP model is a prerequisite for the development of an ID zone, is still controversially discussed in the literature. In the notion of the ICDP model, the drop cannot directly be linked to the affinity effect of silicic acid on the glass dissolution rate as assumed, for instance, in Grambow's first-order rate law,²⁴ because glass dissolution (and contemporaneous silica precipitation) proceeds even though the solution is saturated with amorphous silica. Thermodynamically, the irreversible reaction is

merely driven by the solubility difference between the glass and amorphous silica. The transport of water through the SAL cannot be rate-limiting either, as the ^{18}O profiles in this and other studies^{12,15} indicate that water in these experiments reached the ICDP interface at all times. We further propose that the slowdown of the replacement reaction is related to a pile up of alkali elements and, in particular, aqueous silica in this interfacial solution due to an increasing thickness of the SAL, and thus an increasing transport distance between the interfacial and the bulk solution with increasing time. This could have led to a high supersaturation of silica in a highly saline solution. Such solution is more basic and can thus dissolve much more silica than the corresponding bulk (and pore) solution. Under such conditions, silica in solution polymerizes with the initial formation of low polymers such as the cyclic tetramer, which may further condense to form small three-dimensional polymer particles. This solution increasingly confines water in its pore space, which slows down its mobility.³⁵ If the silica concentration further increases in solution by ongoing dissolution of the glass, the solution may eventually rapidly convert into a silica gel by aggregation and gelling, which may already happen during the experiment, but at the latest during quenching. At this point, a viscous, polymeric silica gel with non-Newtonian fluid properties forms. At the same time, the kinetic barrier of hydrolysis, detachment, and transport of silica from the glass surface into the interfacial suspension or gel also increases. This will inevitably slow down glass dissolution reactions, so that eventually the solid state ID process can start to operate. It follows that the properties of the interfacial zone were likely different during the experiment. Although an ICDP

process does not inherently produce a pattern, it involves complexly coupled reactions at the interface along with chemical transport limitations due to the growing SAL, which increasingly drives the interfacial solution away from thermodynamic equilibrium with the bulk solution. This provides an important prerequisite, whereby the system is able to chemically and/or structurally self-organize to complexly layered and patterned structures.^{7,8}

In summary, several observations made in this study as well as in other recent studies challenge the available corrosion models that consider the SAL as a residual and restructured glass. First, the finding of a clear phase boundary between a dense silica-based layer and a chemically leached glass, which agrees with the nanometer-sharp reaction interfaces observed by APT,^{13,14} question the intensively propagated concept of a continuous ion exchange-based transition from a pristine glass to a residual, chemically leached and re-structured glass. However, our new isotope tracer data from two experimentally corroded borosilicate glasses, containing variable amounts of Al, Ca, and/or Zr, unambiguously reveal the formation of an interdiffusion zone ahead of an ICDP interface. This implies that both processes are not mutually exclusive as suggested by Hellmann and co-workers^{14,19} and supports previous assumptions that solid-state interdiffusion and related structural relaxation of the glass may be an important process during long-term glass corrosion.^{13,41,42} However, since the interdiffusion of hydrogen and network modifiers in silicate glasses is usually slow at temperatures that are relevant in most natural or technical systems ($D_i < 10^{-23} \text{ m}^2/\text{s}$), the ICDP process must slow down significantly from typical forward glass dissolution rates in the order of 10^{-12} – $10^{-15} \text{ m s}^{-1}$ ⁴⁵ before an ID zone can form. Based on textural evidence from HAADF-STEM images, we suggest that a dense silica layer, observed at the boundary to the glass, reflects the product of quenching and drying of an interfacial solution that was rich in dissolved silica. This solution forms since with increasing thickness of the SAL aqueous silica cannot effectively be transported away anymore from the dissolution-reprecipitation interface towards the bulk solution. Silicic acid and other glass constituents therefore pile up at the ICDP interface, which may lead to aggregation and gelation. It follows that less and less silicic acid can be detached from the glass, transported, and dissolved into the interfacial suspension or gel, slowing down the surface-controlled dissolution process so that the interdiffusion process becomes the faster process.

We conclude that an ICDP and an interdiffusion (ID) process are not mutual exclusive. The ID process may replace the ICDP process but only if the ICDP process significantly slows down. In such a case, the long-term release of elements from the glass becomes dependent on the diffusion properties of the glass and the growing SAL. Following reactions have so far been identified in this and other studies:

1. Congruent dissolution of the glass (including several individual microscopic reaction steps such as hydrolysis, detachment, transport).
2. Silica precipitation/deposition from an interfacial solution (including several individual microscopic reaction steps such as, e.g., condensation, coagulation, aggregation, ripening).
3. Solid-state ion exchange/interdiffusion inside the glass (e.g., Doremus model^{39,40}).
4. Silica aging (e.g., polymerization, ripening).²⁹
5. Chemical transport through the silica-based SAL (porosity-controlled).^{8,12}
6. Precipitation of secondary minerals within and at the silica surface (e.g., zeolites, clays etc.⁴⁶).
7. Aqueous diffusion within a solution boundary layer that allows for silica-saturation at the glass surface before the bulk solution is silica-saturated.^{8,12,47}

A sound description of the reaction mechanisms and the identification of the rate-limiting steps is essential to predict reliably the long-term corrosion of silicate glasses, particularly when time scales must reach several thousand to millions of years as necessary for safety regulations for a nuclear repository. We thus argue that all above given processes and their interdependencies as well as the dependence of transport properties of the SAL on the morphology of precipitated silica should be considered in future kinetic models.

METHODS

Raman spectroscopy

Raman spectra of the corroded sample surfaces were collected with a confocal Horiba HR800 Raman spectrometer equipped with an Olympus BX41 microscope at the Steinmann Institute of the University of Bonn, Germany. A solid state Nd:YAG laser (532.09 nm) with about 0.1 W laser output power, a 100x objective with a numerical aperture of 0.9, a 600 grooves mm^{-1} grating, a confocal hole of 500 μm , and a spectrometer entrance slit widths of 100 μm , yielding a spectral resolution of about 3.5 cm^{-1} , were used for the measurements. Samples were analyzed over the range of 100–4000 cm^{-1} in three spectral windows, each measured for 60 s.

Nanoscale secondary ion mass spectrometry (NanoSIMS)

NanoSIMS analyses were performed on resin-mounted and cross-sectioned samples with a CAMECA NanoSIMS 50 L at the Centre for Microscopy, Characterization and Analysis at the University of Western Australia. The polished sample mounts were coated with gold to provide conductivity. Prior to each analysis, every area was presputtered with the primary beam to a dose of more than $2 \times 10^{17} \text{ cm}^{-2}$.

Isotope mapping was performed in three runs per location, two for positively charged ions with the oxygen scesium one for negatively charged ions:

- (1) O^- : ¹⁰B, ¹¹B, ²⁷Na, ²⁸Si, ³⁰Si, ⁴⁰Ca, ⁴⁴Ca
- (2) O^- : ¹⁰B, ²³Na, ²⁷Al, ³⁰Si, ³⁸K, ⁴⁴Ca, ⁹⁰Zr
- (3) Cs^+ : ¹H, ²H, ¹⁰B, ¹¹B, ¹⁶O, ¹⁸O

The beam diameter was approximately 150 and 75 nm for the oxygen and cesium source (see Supplementary Fig. S6), respectively, and the impact energy was 16 keV. The high-resolution O^- beam was obtained with a Hyperion (H200) RF plasma oxygen ion source. The beam current was approximately 3 pA for Cs^+ and 14 pA for O^- . Images were carried out with a raster size of 10–50 μm^2 , with a resolution of 256 × 256 px and a dwell time of 25–60 ms per pixel.

Multiple two-dimensional isotope mappings for each set of isotopes were performed on all glass samples by manual or preprogrammed automated runs (overnight). In a few cases mappings of the latter had to be discarded/repeated due to an incorrect focus (the focus cannot be adjusted in automated runs). Note that all measurement sets have some isotopes (marked bold) in common to allow for direct data correlation. The second set with then three unmeasured isotopes were located directly adjacent to the first one to minimize beam damage for the third run in the original position again (reposition error: <2 μm). Data handling was performed with ImageJ/Fiji⁴⁸ and the OpenMIMS plugin,⁴⁹ in which profiles were extracted from the isotope maps perpendicular to the reaction front, accumulating a width of 50 pixels per step. Then the sigmoidal-shaped ¹⁸O profiles at the rim-glass interface were fitted with a double Boltzmann function. For coherence, double Boltzmann functions were in general chosen over a single one to account for tailings some isotopes like boron reveal in the reaction rim. The inflection point of ¹⁸O fit close to the interface was then chosen as point of origin for data visualization. Consequently, coordinates of the two data sets measured by oxygen source were shifted by aligning the inflection points of the double Boltzmann fitted boron profiles, while also cross-checking the sodium profiles of the first two data sets for congruence. Hence, the data alignment around the interface can be taken as accurate, while the matching of the outer rim boundary might underlie minor discrepancies due to small variation in rim thickness and focus issues during automated analysis. Moreover, as evidenced by a small gap between samples and embedding resin, the extended drying of the epoxy resin caused shrinkage by which less consolidated material was ripped-off the sample surface.

Scanning transmission electron microscopy (STEM)

An electron-transparent thin foil was prepared from a corroded ISG-90/90 sample by utilizing a Zeiss NVision 40 cross beam station. The sample was coated with C to enhance the electrical conductivity. The lamella was extracted perpendicular to the surface including a layer of resin, corroded glass, and pristine glass. To avoid beam damage by the Ga^+ beam, a protective layer of approximately $2\text{ }\mu\text{m}$ C was deposited on the glass surface. A thick slice of $1\text{ }\mu\text{m}$ was cut out of the sample (beam current $30\text{ kV}/300\text{ pA}$) and attached to an Omniprobe TEM-grid. The lamella was stepwise thinned $>100\text{ nm}$ using decreasing beam current for each step ($30\text{ kV}/150\text{ pA}$, $30\text{ kV}/80\text{ pA}$, $30\text{ kV}/40\text{ pA}$). Another thin foil of the QBG-90/150 experiment was prepared by using a FEI Helios Nanolab G3 UC focused ion beam-scanning electron microscope (FIB-SEM).

The FIB foils were investigated in a FEI Talos F200X (scanning) transmission electron microscopy ((S)TEM) equipped with four energy-dispersive X-ray detectors (Super-X EDX). The FEI Talos F200X TEM information limit is 0.12 nm . All FIB-SEM and TEM analyses were carried out at the Microscopy Square, Utrecht University.

Sphere size analyses was performed on HAADF-STEM images of the porous sections of the ASLs (Fig. 3) with the Fiji/ImageJ⁴⁸ software package by first applying a FFT band pass filter to minimize illumination effects followed by an estimation of the sphere size diameter with a brightness threshold and the included local thickness plugin. The latter is a routine that finds the maximum diameter of spheres fitting into a given structure.

DATA AVAILABILITY

All data that support the findings of this study are available from the corresponding author upon reasonable request.

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AUTHOR CONTRIBUTIONS

C.L. and T.G. planned, designed, and performed the experiments, analyzed and evaluated all data, and wrote the first draft of the manuscript. M.K. and P.G. performed and processed the NanoSIMS data. O.P. and C.L. carried out the STEM work and FIB section preparation of most samples, M.K. prepared the FIB section of experiment ISG-90/90. All authors contributed to the final manuscript.

ADDITIONAL INFORMATION

Supplementary information accompanies the paper on the *npj Materials Degradation* website (<https://doi.org/10.1038/s41529-018-0048-z>).

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