The Use of Positrons to Survey Alteration Layers on Synthetic Nuclear Waste Glasses

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ABSTRACT In order to safeguard society and the environment, understanding radioactive waste glass alteration mechanisms in interactions with solutions and near-field materials, such as Fe, is essential to nuclear waste repository performance assessments. Alteration products are formed at the surface of glasses after reaction with solution. In this study, glass altered in the presence of Fe⁰ in aqueous solution formed two alteration layers: one embedded with Fe closer to the surface and one without Fe found deeper in the sample. Both layers were found to be thinner than the alteration layer found in glass altered in aqueous solution only. For the first time, Doppler Broadening Positron Annihilation Spectroscopy (DB-PAS) is used to non-destructively characterize the pore structures of glass altered in the presence of Fe⁰. Advantages and disadvantages of DB-PAS compared to other techniques used to analyze pore structures for altered glass samples are discussed. Ultimately, DB-PAS has shown to be an excellent choice for pore structure characterization for glasses with multiple alteration layers. Monte Carlo modeling predicted positron trajectories through the layers, and helped explain DB-PAS data, which showed that the deeper alteration layer without Fe had a similar composition and pore structure to layers on glass altered in water only.

KEYWORDS Doppler Broadening Positron Annihilation Spectroscopy, Nuclear Waste Glass, Monte Carlo Simulations, Scanning Electron Microscopy

1. Introduction

1.1 Glass Alteration

The corrosion of materials has long been a problem in several industrial and scientific fields. Glass has been studied extensively in several disciplines, including nuclear waste management.¹⁻³ The best demonstrated available technology for high level radioactive waste stabilization involves incorporation of radionuclides in the waste into borosilicate glasses.^{4,5} The successful isolation of the radionuclides from the biosphere is contingent upon glass durability, with some performance evaluations requiring calculation of performance for periods up to 10^6 years.^{1,6,7} A large body of work has been performed to test the chemical durability of glasses, to describe the chemical and dynamical mechanisms of degradation in solution, and to understand the structure observed after glass alteration in aqueous media.^{1,7-14} Under static conditions in water, alteration layers usually form at the glass surface as leachate elements' concentrations increase.^{10,15,16} The formation mechanisms of alteration layers have not yet been agreed upon and more data is needed for the community to optimize predictive models.^{10,17-28} Additionally, glass alteration is significantly modified in the presence of near-field materials.²⁹⁻³² Iron is an important near-field material as it is present in the steel containers that store vitrified nuclear waste, and in the natural environment of repositories.^{31,33} Previous work has shown glass alteration in the presence of iron leads to the production of iron silicate on the surface of the glass and embedment of iron into the alteration layer.^{31,34,35} Mechanisms suggest that metallic iron (Fe^0) reacts with H_2O to make Fe^{2+} which goes on to react with available dissolved silica to make iron silicates on the surface and permeate the alteration layer.^{31,35} However, the structural and chemical properties of altered glass – particularly alteration layers – in the presence and absence of iron must be better understood.^{9,17,36} Several techniques have been used to analyze

altered glass, but Doppler Broadening Positron Annihilation Spectroscopy (DB-PAS) with its non-destructive nature and unique sensitivity to missing-atom(s) like defects (< 100 nm) has not been used for this purpose until now.

1.2 Doppler Broadening Positron Annihilation Spectroscopy

DB-PAS is widely used to evaluate free volume in materials.^{37,38} Although other techniques can provide similar information, DB-PAS is a non-destructive technique that examines samples as a function of depth.³⁷⁻⁴⁰ In DB-PAS, probe positrons are impinged into samples at various energies, annihilating with electrons once positrons have slowed to thermal energies. Neutral or negatively charged open volume defects are attractive to positrons and trap them making positrons uniquely sensitive to such defects. Annihilation from within such traps is enhanced by about 1 million to 1 over annihilations from the un-trapped free-state. Two near opposite collinear 511 keV γ -rays are created as a result of the annihilation of the positron and electron. However, the initial momentum of the electron-positron pair before annihilation can Doppler shifts in annihilation photon energies. These deviations can be detected using a High Purity Germanium detector (HPGe) and result in Doppler broadened 511 keV γ -ray lines and.⁴⁰ Figure 1a shows a diagram of the experimental set up, an example of Doppler broadening within a sample, and a resulting energy distribution plot obtained for PAS.

Core electrons have higher momenta than valence electrons, which cause the regions that have more core electrons to produce a broader γ -ray energy distribution curve as seen in the plot in Figure 1b. The energy distribution curve of the 511 keV photoelectric effect peak region can be divided into sections to analyze the Doppler broadening effects due to core and valence electrons relative to the total signal intensity in the peak, N_T . The central part of the distribution

curve, labeled N_S in Figure 1b, is due to γ -rays with little Doppler broadening and is dominated by positron annihilation events with valence electrons. The outlier portions of the distribution curve, labeled N_{W1} and N_{W2} in Figure 1b, correspond to positron annihilation events with core electrons. Shape (S) and Wing (W) parameters are used to assess the contribution of core and valence electrons in the sample.^{38,41} The S parameter is defined as the ratio of N_S to the total intensity, N_T , of the given energy range, whereas the W parameter is defined as the sum of the N_{W1} and N_{W2} peaks divided by the total intensity. Since S parameters correspond to γ -rays that have been weakly Doppler shifted, samples with higher S parameters have a greater contribution of annihilation events from valence electrons. Similarly, since W parameters correspond to γ -rays that have been strongly Doppler shifted, samples with higher W parameters have greater contribution of annihilation events from core electrons. Figure 1c shows clusters of atoms in materials with voids (left) and without voids (right) where valence electron clouds are lightly shaded and core electron clouds are darkly shaded. When a positron is trapped in a void, valence electrons are preferentially available for annihilation, whereas when a positron reaches a perfect material, core and valence electrons are more equally available for annihilation. Therefore, S parameters for materials with vacancy-type voids or pores are higher than in dense, void-free materials.⁴² Typically, W parameters are lower in materials with voids, but annihilation events due to core electrons indicate that the sample has less open volume and/or that the elemental composition has more elements with higher atomic numbers and thus with more core electrons.^{38,41} Since the W parameter is affected by atomic mass, it is sensitive to materials' elemental composition.

The sensitivity of DB-PAS and other positron techniques to vacancies and larger open volume originates from the local electrostatic attraction to the spaces of missing atomic nuclei. Locally, the density of the positive charges of the atom nuclei is missing, resulting in a net

potential well for positrons. After thermalization, positrons may trap at these voids and annihilate from this state. If one atom in 10^6 atoms in a single crystal is missing, the positron will trap and annihilate there.^{37,39,40,43}

Monoenergetic beams of positrons can be implanted at pre-selected mean depths, similar to electron beam irradiation. The mean implantation depth (D , nm) is related to the incident kinetic energy (E , keV) by the empirical formula provided in equation (1):

$$D = \left(\frac{40}{\rho_{app}} \right) E^{1.6} \quad (1)$$

where ρ_{app} is apparent density of the sample in $\text{g}\cdot\text{cm}^{-3}$.^{40,44,45} Thus, the quantity of open space as a function of depth into the sample can be inferred by analyzing S parameter with increasing implantation energy, as higher energy positrons penetrate deeper into a solid before annihilating.

2. Experimental

2.1 Sample Configuration

International Simple Glass (ISG), developed as a reference benchmark glass for an international collaboration on waste glass alteration mechanisms, was used in this study.¹ The composition of ISG (in elemental mol. %) is found in Table 1. Each system consisted of two ISG coupons ($10 \text{ mm} \times 20 \text{ mm} \times 2 \text{ mm}$, polished to $\frac{1}{4} \mu\text{m}$) placed on top of one another, separated by 0.127 mm Teflon® spacers, and held together with Teflon® tape. Samples consisted of ISG coupons altered under static conditions in deionized water (DIW, $18.2 \text{ M}\Omega\cdot\text{cm}$) only (ISG- H_2O) as shown in Figure 2a, and in the presence of DIW and Fe^0 (Sigma Aldrich®) foil 0.1 mm thick (ISG-Fe) as shown in Figure 2b. Fe^0 foil was scratched with a knife in a grid pattern to facilitate

solution flow between ISG and the Fe^0 foil as explained in Reiser et al.⁴⁶ An additional ISG coupon was polished and left unaltered to serve as a baseline. For this study, unaltered ISG refers to the entire baseline coupon, whereas unaltered glass (UG) refers to portions of samples ISG- H_2O , ISG-Fe, and unaltered ISG that remain unaltered. Thus, unaltered ISG is composed of UG entirely except from potential surface defect as seen in DB-PAS.

Each configuration was inserted horizontally in Savillex® vials containing 20 mL of DIW to obtain a glass-surface-area-to-solution-volume ratio (S/V) of 25 m^{-1} of the entire system as calculated in Reiser et al.⁴⁶ However, the interior region (gap) of the configuration will likely have higher local S/V due to the limitation in diffusion processes as detailed in Chomat et al.⁴⁷ The glass surface area covered in Teflon® tape was subtracted from the total surface used for S/V calculation. The solutions were purged with pure argon (A-L Compressed Gases, Inc.) before sealing the closed Savillex® vials in airtight pressure vessels under argon. Experiments were carried out in an oven heated to 90°C for 3 months without disturbing the samples. The solutions were then removed. The ISG coupons were dried completely in their configurations in an oven at 50°C overnight and then were prepared for various analyses. The faces labeled with * in Figure 2 were chosen for solid analysis. For ISG-Fe, the gap face of the coupon spaced 0.127 mm from Fe^0 foil was chosen for solid analysis since it was more corroded than the face directly in contact with the Fe^0 foil. The coupon adjacent to Fe^0 foil was determined to not have access to solution even with scratches in the Fe^0 foil.

2.2 Scanning Electron Microscopy/ Energy X-ray Dispersive Spectroscopy

Dried portions of the altered coupons were prepared for Scanning Electron Microscopy (SEM) analysis by embedding coupons into epoxy resin (Specifix-20®), sectioning them to expose the cross section, and then polishing this cross section to $\frac{1}{4} \mu\text{m}$. For SEM analysis, a

JEOL 5900 (JEOL, Ltd.) with a tungsten wire filament was used. This SEM was equipped with an EDAX Li-drifted silicon detector cooled with liquid nitrogen (Ametek Inc) for performing Energy X-ray Dispersive Spectroscopy (EDS) to determine the composition of the various phases. Alteration layer thicknesses were measured using backscattered electron SEM images of altered sample cross sections and ImageJ software greyscale analysis. Alteration layer thicknesses were measured at multiple points (> 100) to allow for statistically relevant results .

2.3 Inductively Coupled Plasma Optical Emission Spectrometry

Aliquots of solutions were diluted with 0.1 to 0.3 mol·L⁻¹ HNO₃ and analyzed using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) (Agilent® 5100 RV) for Al, B, Ca, Na, and Si; the instrument was calibrated using dilutions of standard solutions (Inorganic Ventures). Zr release in solution was determined to be too low to be analyzed.^{14,48}

For ISG-H₂O, the average fraction of each element i present in the alteration products R_i were calculated using Equation (2):

$$R_i = \frac{f_i \left(1 - \frac{NL_i}{NL_B}\right)}{\sum_{all\ elements\ j} \left[f_j \left(1 - \frac{NL_j}{NL_B}\right) \right]} \quad (2)$$

Where NL_i is the normalized mass loss of element i in g·m⁻² as defined in Reiser et al.⁴⁶ and f_i is the original mass fraction of element i in unaltered ISG (Table 1). Boron is used as a tracer element for glass alteration since it is not retained in alteration products.⁴⁹

Equivalent thicknesses (Eth , in μm) for altered portions of the glass of ISG-H₂O and ISG-Fe were calculated using equation (3) using boron as a tracer:

$$Eth_B = \frac{C_B}{CF \cdot \frac{S}{V} \cdot f_B \cdot \rho_0} \quad (3)$$

where C_B is the boron concentration in $\text{g}\cdot\text{m}^{-3}$, f_B is the mass fraction of boron in ISG, S/V is glass-surface-area-to-solution-volume ratio in m^{-1} , and ρ_0 is the initial density of ISG in $\text{g}\cdot\text{cm}^{-3}$. Given the experimental setup, a correction factor (CF) was applied to S/V ratios to account for the total surface covered by Teflon® spacers (4 times a $2\text{ mm} \times 8\text{ mm}$ area per experiment) for both experiments, and for the surface covered by iron for ISG-Fe (an entire $10\text{ mm} \times 20\text{ mm}$ area). The corresponding correction factors are reported in Table 2.

2.4 Doppler Broadening Positron Annihilation Spectroscopy

Glass surfaces of interest were analyzed using DB-PAS to investigate the structure of the various alteration layers and UG. The faces indicated with * in Figure 2 were chosen for analysis. Doppler broadening PAS measurements were performed using the monoenergetic positron beam at Washington State University, using a Na-22 source ($\approx 10\text{ mCi}$) and a W(100) single crystal moderator foil to create monoenergetic positrons. Positrons were accelerated from 0.1 to 70 keV for the implantation depth profiles. The beam diameter is $\approx 5\text{ mm}$. A HPGe detector cooled with liquid nitrogen was used to record the gamma rays from positron annihilation with an energy resolution of about 1.4 keV.⁵⁰ To obtain reasonable statistics, at least 10^5 counts were obtained in the 511 keV annihilation line of the spectrum for each implantation depth (energy of the gamma ray as detected which includes the Doppler shift and detector energy resolution). The spectrum is binned with 0.08 keV bin width. The S and W parameters were normalized to the corresponding S and W parameter values found in UG (normalized S with 0.4664 ± 0.0002 , and W with 0.0667 ± 0.0001).⁴⁴ An S parameter value of 1.00 represents the baseline S parameter value of unaltered ISG which is more sensitive to free volume. A W parameter value of 1.00 represents the baseline W parameter value of unaltered ISG which is more defined by the elemental makeup.

2.5 Monte Carlo Simulations of Positron Implantation

Positron annihilation occurs where positrons terminate in a sample. To establish the depth at which this occurred in each sample and the distribution of positrons annihilated in each layer, Monte Carlo simulations of positron trajectories at various energies were performed using CASINO® software.³⁵ Although CASINO® traditionally models electron implantation profiles for SEM samples, positrons behave identically to electrons except at low implantation energies (< 1 keV).^{37,38} Since the implantation energies modelled start relatively high (> 10 keV) and the alteration layers are relatively thick (> 0.5 μm), CASINO® is a valid method to model the system. Post-implantation diffusion of thermalized positrons is small in these amorphous samples and has no significant effect on the implantation profile.

The implantation depth was modeled for unaltered ISG, ISG-H₂O, and ISG-Fe samples as a function of DB-PAS beam conditions. Measured layer thicknesses, EDS compositions, the published ISG composition and density, and calculated alteration layer densities were used as parameters in the simulation (See Section 3.1). The compositions used as parameters for various layers, including nomenclature used to refer to them (See Section 3.1 for nomenclature explanation), are found in Table 1. The last row of Table 1 indicates which experimental method was used to determine composition. Thicknesses used for various alteration layers are found in Section 3.1. Density calculations are explained in detail in the Appendix as are the specific densities used in the simulation. CASINO® v2.48 was used to generate positron implantation profiles into unaltered ISG, ISG-H₂O, and ISG-Fe. The simulation consisted of 2 million positrons injected into samples at various energies with a probe diameter of 5 mm.

3. Results

3.1 SEM/EDS and ICP-OES Analysis

Composition of ISG-H₂O sample's alteration layer was determined using equation (2) from the concentrations in solution determined by ICP-OES after 90 days of alteration given in Table 2. Since Al and Zr were not released in solution in quantifiable amounts, NL_{Zr} and NL_{Al} are considered equal to 0 g·m⁻².^{14,48} Sodium can be accurately included in alteration layer calculations using solution data whereas many EDS systems cannot accurately detect sodium because of alkali migration. Table 2 also shows concentrations of leached species for ISG-Fe for comparison. However, since Fe was integrated into the altered region, the compositions of the individual alteration layers could not be found using ICP-OES alone as mass balance could not be achieved. Thus, altered compositions of ISG-Fe were obtained from EDS analyzed.

Figure 3 shows backscattered electron (BSE) SEM images of cross-sectioned samples of (a) ISG-H₂O and (b) ISG-Fe. The surface of ISG-H₂O features a small salt layer (SL) followed by one thick alteration layer (AL1), one thin alteration layer (AL2), and UG which can be seen in Figure 3a. The SL was likely created by evaporation of solution following the removal of the ISG-H₂O coupon from the reaction vessel. Figure 3b shows the ISG-Fe surface, which consists of a layer of Fe-silicate secondary phases (SP) followed by an alteration layer containing Fe (Fe-AL), an alteration layer without Fe (no-Fe-AL), and UG. EDS profiles of ISG-H₂O and ISG-Fe collected along areas similar to those indicated by the arrows in Figures 3a and 3b are shown in Figures 3c and 3d, respectively. Altered regions are indicated by their reduced Na concentrations compared to UG. The Na gradient between altered and unaltered glass for ISG-H₂O and ISG-Fe are comparable when considering Figures 3c and 3d are not scaled identically. Due to precision

of EDS, the existence of Na gradient cannot be confirmed: the observed gradient could originate from instrumental error.

The average thicknesses of the AL1 and AL2 for altered ISG-H₂O were 8 ± 4 μm and 0.4 ± 0.1 μm , respectively, where the error is given by two standard derivations. The large error of AL1 can be attributed to irregular alteration in various regions on the coupon. Although the Teflon® tape was expected to prevent solution contact from covered portions of the coupon, solution covered portions at some point during the experiment and altered the glass. Altered glass in the gap portion of ISG-H₂O has an average thickness of 10 ± 2 μm whereas the glass surface exposed to the bulk solution has an average thickness of 7 ± 1 μm . For the Monte Carlo simulations, 10 μm was chosen as the representative thickness because the DB-PAS analysis was performed on one of the altered glass surfaces from within the gap. The average thicknesses of SP, Fe-AL, and no-Fe-AL for ISG-Fe were 0.7 ± 0.1 μm , 1.1 ± 0.4 μm , and 1.6 ± 0.6 μm , respectively. These thicknesses were used in Monte Carlo simulations.

After analyzing altered coupons with SEM, the initial S/V ratios were determined to be incorrect due to solution contact with portions of glass under the Teflon® tape. Corrected S/V values were calculated by considering the total surface area of the glass coupons divided by the initial solution volume multiplied by correction factors. Correction factors and corrected S/V values are found in Table 2. As mentioned in Section 2.1, the correction factors account for the glass surface areas covered by the Teflon® spacers and the Fe⁰ foil. Although scratches were added to the Fe⁰ foil to allow for solution to permeate the region, the adjacent glass surface remained unaltered indicating that solution did not have access to the glass surface.

Using the corrected S/V values, equivalent thicknesses (ETh_B) were calculated and can be found in Table 2. Alternatively, the thicknesses of the altered portions of ISG-H₂O and ISG-Fe were measured with cross-sectional SEM and are included in Table 2. For ISG-H₂O, ETh_B

values agree with SEM thicknesses, indicating that the volume of altered region is the same volume as the alteration layers. For ISG-Fe, ETh_B values do not agree with SEM measured thicknesses, with the latter significantly less than the former. This suggests that some of the glass surface retreated as elements from the material were released into solution. Precipitates were observed on all surfaces of the alteration vial and the Fe^0 foil was corroded. These products were not analyzed in this study, but their existence could represent a pathway for the removal of species from solution, allowing corrosion to continue.

As discussed in Section 2.1 and observed in previous studies,^{35,47} the gap portions of the configurations have higher local S/V due to the limitation in diffusion to the bulk solution. As a result, ion mobility was reduced leading to local elemental accumulation (e.g. local precipitation of iron secondary phases and/or iron integration into alteration layer).

3.2 DB-PAS Analysis with Monte Carlo Simulations

Figure 4a shows S parameters for unaltered ISG, ISG-H₂O, and ISG-Fe samples as a function of implantation energy in keV. For Monte Carlo simulations, AL2 in ISG-H₂O was omitted because AL1 and unaltered glass (UG) are much thicker compared to AL2. Additionally, AL1 and AL2 are very similar in composition and solution data from ICP-OES reveal that altered ISG has the same volume as AL1+AL2. As a result, AL1 and AL2 are combined and referred as AL1+AL2 for both CASINO® calculations and DB-PAS results. Additionally, no visible distinction for S values can be seen between SP and Fe-AL for ISG-Fe sample, so they are referred to as SP+Fe-AL for DB-PAS results. Figure 4b, 4c, and 4d show the distribution of positron termination sites as a function of depth at different energies for unaltered ISG, ISG-H₂O, and ISG-Fe, with schematic descriptions of the cross-sections as a function of length. Since

Figure 4a is plotted as a function of energy, schematic descriptions of the sample cross-sections are scaled as a function of implantation energies calculated by Equation (1) using thicknesses measured on SEM images and calculated densities.

At low implantation energies (< 0.5 keV), some deviations in the S values are expected and attributed to interactions with surfaces as seen for both unaltered ISG and ISG-H₂O. Unaltered ISG shows a stable S value near 1.00 for all implantation energies greater than 1 keV (i.e. at mean depths from 0.2 to 14 μm for 1 and 70 keV, respectively), indicating unaltered ISG is homogenous throughout the whole sample.

As implantation energy increases in a homogenous sample such as unaltered ISG in Figure 4b, the positron distribution curve becomes broader. This causes the depth resolution of the system to decrease, even though the S value remains constant throughout the sample as seen in Figure 4a.³⁹ For ISG-H₂O, the S parameter reaches its maximum value while in AL1+AL2 as seen in Figure 4a, implying that AL1+AL2 has more open volume than UG. At 20 keV, Figure 4c indicates that most positrons have annihilated in AL1+AL2, correlating to S values seen in Figure 4a. At 30 keV, more positrons terminate in UG as seen in Figure 4c, causing the S value to approach the S value associated with UG. Because the resolution is poorer at higher implantation energies, a large transition zone is visible between S values of AL1+AL2 and UG in Figure 4a even though the boundaries between layers in Figure 3a are well-defined. The S values in this transition zone result from linear combinations of S values associated with AL1+AL2 and UG. Similar transition zones are apparent for ISG-Fe in Figure 4a starting around 25 keV. However, the transition zones are smaller because the resolution is improved at lower implantation energies for ISG-Fe. Even though S values for no-Fe-AL in Figure 4a are greater than UG S values, they do not approach the value of AL1+AL2, which has a similar composition. Figure 4d shows distribution curves shifted left toward SP+Fe-AL at 15 keV, split

left and right toward SP+Fe-AL and UG, respectively, at 20 keV, and shifted right toward SP+Fe-AL at 30 keV. Because SP+Fe-AL and UG have higher apparent densities than no-Fe-AL, positrons are terminating preferentially in SP+Fe-AL and UG. Consequently, the resulting S value of no-Fe-AL is always a linear combination of no-Fe-AL, Fe-AL, and UG S values. At 50 keV, the S values of both altered samples are near S values for UG since the majority of positrons are annihilating in UG. However, S values of ISG-Fe and ISG-H₂O never completely reach the S values of UG because the resolution becomes poorer as implantation energy is increased. Thus, the contribution from the alteration layers cannot be entirely eliminated.

While plots showing S parameter as a function of the implantation energy are useful tools for analyzing open volume as a function of depth, they do not provide information on the chemical environments of a sample. A plot of S values as a function of W values (S-W plot) shows distinct annihilation environments within a sample and a progression of these environments participating in positron trapping as a function of depth.^{38,55} Figure 5 shows an S-W plot for unaltered ISG, ISG-H₂O, and ISG-Fe. Important annihilation environments associated with ISG-H₂O and ISG-Fe are circled and labeled and the implantation energy progressions through the samples are shown by arrows.

The ISG-H₂O and unaltered ISG S-W values that deviate slightly above and left of the bulk UG cluster in Figure 5 were obtained from positrons with extremely small implantation energies (< 1 keV, i.e. < 20 nm in UG), indicating a near-surface environment. Similarly, the data points not in AL1+AL2, UG, or their transition regions are likely due to surface voids and/or the thin SL deposited on AL1. Typically, S and W show opposite behaviors,⁴⁴ resulting in negative slopes between different annihilation sites on S-W plots (Figure 5) as the implantation energy increases, i.e. from AL1+AL2 to UG, from SP+Fe-AL to no-Fe-AL, and from no-Fe-AL to UG. The slope between the no-Fe-AL and UG environments is similar to the slope between AL1+AL2 and UG, which could indicate that the annihilation environments are alike. Since the

three annihilation environments for ISG-Fe (SP+Fe-AL, no-Fe-AL, and UG on Figure 5) do not lie on the same slope, the W parameter is likely impacted significantly by the change in composition between the layers. Iron is likely causing this deviation in W because it is relatively abundant in SP+Fe-AL and has a high atomic number compared to Si, which is the main cation present in ISG.

4. Discussion

The alteration layers seen in this study are similar to layers seen in several other studies that have altered glass with iron containing materials.^{31,34,35,56} Thus, this study supports mechanisms previously presented in those works but adds insight into the pore structures of alteration layers by using DB-PAS. Other studies have examined the pore structure of altered glass but each method utilized has had their own advantages and disadvantages.^{15,22,25,57,58} DB-PAS has shown to be another tool for the community to investigate the pore structure of altered glass, providing valuable insight where other techniques struggle.

Pore structures of altered glass can be difficult to characterize because alteration layers are often very thin. Thin alteration layers require that potential techniques have powerful resolutions that can differentiate altered layers and unaltered glass. Gas adsorption techniques are usually initially considered due to their low cost and wide availability. However, a large surface area is needed for gas adsorption techniques to detect changes in surface areas which requires glass samples to be in powder form as samples were in Ledieu et al.⁵⁸ Thus, gas adsorption techniques would not work well for glass coupons as used in this study. Additionally, gas adsorption techniques are limited in the size of pores they can analyze by the size of the gas molecules injected. Because gas adsorption techniques use gas molecules, only open pores are analyzed leaving closed pores unanalyzed. Meanwhile, DB-PAS uses positrons which are

approximately the size of an electron rather than gas molecules which can detect tiny pores and even individual vacancies in a structure.

Glass can often form multiple alteration layers especially when exposed to water in the presence of iron-bearing materials as in this study. Characterizing layers' distinct pore structures are very difficult for many techniques such as Small Angle Scattering (SAS) techniques. SAS techniques are very powerful tools that can characterize pore structures with exceptional ability for homogenous materials and have been used to analyze pore structures in previous studies.^{15,57} SAS techniques send X-rays or neutrons through the whole sample, requiring each layer's data to be corrected for every other layer that is present in the sample. When there is more than one alteration layer, SAS techniques are unable to distinguish between the various layers. DB-PAS provides a distinct advantage in that it analyzes pore structures as a function of depth as in this study. Figure 3a shows no-Fe-AL is more porous than SP+Fe-AL using DB-PAS, an observation which would be impossible to make with SAS techniques.

Perhaps the biggest advantage of DB-PAS is its ability to non-destructively analyze pore structures. Dyes such as methylene blue have been used to analyze pore structures on altered glass.^{22,25} While dyes can help analyze porosity as a function of depth, they leave the samples permanently colored. This can be a problem for some experiments especially for rare samples like irreplaceable archaeological glasses currently being studied in the ancient glass community. Therefore, DB-PAS would be a good choice for these samples.

Although there are several advantages to DB-PAS there are some disadvantages. In this study, DB-PAS was employed which allowed determination of relative porosity, but provided no absolute porosity measurements. To know absolute pore sizes using PAS, lifetime PAS would need to be used. Lifetime PAS has the same advantages as DB-PAS, but it requires a larger acquisition times which are dependent on the positron source intensity. In this study, the positron source was too weak to justify the long analysis time required for lifetime PAS. However, DB-

PAS provided the desired information quickly and efficiently. Another disadvantage of this particular PAS system is the large probe size (5 mm). With large probe sizes, inhomogeneities on the surface of a coupon would be averaged into the result. Thus, the technique is better in analyzing global pore structures rather than local inhomogeneities. Coupons must be wider than 5 mm in order to be properly analyzed using DB-PAS. More powerful positron beams such as at the NEPOMUC facility at the Heinz Maier-Leibnitz Center in Garching, Germany eliminate all these limitations.⁵⁹ Finally, PAS struggles to properly analyze large pores (> 100 nm). When pores become significantly large, positrons behave as if they are in a vacuum.

To understand the DB-PAS data better, Monte Carlo simulations were performed to track the positrons' trajectories through the sample using calculated densities. A better estimation of densities of the different layers would improve the precision of the simulations, especially when foreign elements get integrated into the alteration products (i.e. elements from solution or near-field materials).

5. Conclusion

The analysis of altered glass samples with DB-PAS provided structural insights on various morphologies within samples that can be difficult for other techniques to analyze. Unlike many techniques, DB-PAS showed the ability to nondestructively characterize pore structures on glass coupons with multiple alteration layers that varied in composition and porosity. In combination with SEM/EDS and Monte Carlo modeling, DB-PAS provided additional pore structure information on samples similar to previous studies.^{31,35} For alteration layers created in the presence of Fe, no-Fe-AL was shown to be more porous than SP+Fe-AL and UG. The S values for no-Fe-AL were determined to be convoluted by SP+Fe-AL and UG S values, and S-W relationships for AL1+AL2 and UG and no-Fe-AL and UG were almost identical. This evidence implies that no-Fe-AL has a similar, if not identical, structural and chemical environment as

AL1+AL2 in ISG-H₂O. Furthermore, the AL1 layer contains a large amount of open volume reflected by a 7% rise in S. AL2 is too thin and too deep to be distinguishable. Although DB-PAS provides qualitative information, it has shown that it is capable to analyze pore structures of complex altered systems, such as the ISG-Fe experiment that are difficult for other techniques to analyze. Additionally, its ability to non-destructively characterize pore structures provides the community a technique to analyze exclusive samples such as ancient glasses and glasses altered for long durations.

Appendix

CASINO simulations require the apparent densities (ρ_{app}) of each layer for accurate simulations. The apparent density of a material is simply the mass of the material divided by the apparent volume. A porous material, for example, would have a lower apparent density than the solid phase making up the material due to the volume contributions of the pores. This appendix defines and describes the relationships between the apparent and skeletal densities of a porous material and how these relationships are applied to the porous alteration layers observed in this study.

The *porosity* (Φ , unitless) of a material is defined as the ratio of the volume of pores (V_{pores} , cm³) divided by the apparent volume of this material (V_{app} , cm³, which is the sum of the volume of solid (V_s , cm³) and the volume of pores in the material).

$$\Phi = \frac{V_{pores}}{V_{pores} + V_s} = \frac{V_{pores}}{V_{app}} \quad (4)$$

The *skeletal density* (ρ_s , g·cm⁻³) of a porous material of mass m (in g) is defined as the density of the solid component of the material only.

$$\rho_s = \frac{m}{V_s} \quad (5)$$

The skeletal densities (ρ_s) can also be estimated using linear combinations of weighted densities associated with oxides j in the calculated compositions of the porous material,

$$\rho_s = \sum_{\text{all oxides } j} \rho_j X_j \quad (6)$$

where ρ_j is the density of the oxide j from Table 3 (data from Lide et al.⁶⁰) and X_j is the mass fraction of oxide j in the specific layer. For example, the density of ISG calculated using this method is $2.54 \text{ g}\cdot\text{cm}^{-3}$ close to the literature value of $2.50 \text{ g}\cdot\text{cm}^{-3}$.¹⁴

The *apparent density* (ρ_{app} , $\text{g}\cdot\text{cm}^{-3}$) is defined based on the apparent volume of the considered material (V_{app} , cm^3), taking into account its porosity:

$$\rho_{app} = \frac{m}{V_{app}} \quad (7)$$

The skeletal and apparent densities are linked through porosity:

$$\rho_{app} = \rho_s(1 - \Phi) \quad (8)$$

These equations can be applied to calculate the alteration layers present in ISG-H₂O and ISG-Fe.

The remaining mass (m , g) of all elements i in the gel layer after ISG alteration is calculated from retention factors (R , unitless) in equation (2) and the original mass of the element i in unaltered ISG (m_o , g) :

$$m = \sum_{\text{all elements } i} R_i \cdot m_{o,i} \quad (9)$$

Equation (9) is only valid if no elements from the solution were incorporated into the alteration layer, which is true for ISG-H₂O. Additionally, ETh_B values agree with measured SEM

thicknesses for the alteration layers AL1+AL2 on ISG-H₂O. This indicates that the apparent volume of altered glass (ICP-OES) is equal to the apparent volume of the formed alteration layers, i.e the alteration is isovolumetric.

With these considerations, ρ_{app} for AL1+AL2 is calculated using Equation (7) to be 1.4 g·cm⁻³. Using this ρ_{app} value, Φ is determined with Equation (8) to be 0.48.

For alteration layers on ISG-Fe, Equation (7) is not valid since the alteration is likely not isovolumetric due to the incorporation of Fe in alteration layers and/or secondary phases. Therefore, ρ_{app} values can only be determined using ρ_s and Φ in Equation (8).

The calculated ρ_s values using Equation (6) for the alteration layers are found in Table 4. FeO was used for SP since studies have shown that Fe(II) is most prevalent in iron silicate layers, and Fe₃O₄ was used for Fe-AL since studies have shown that there is a mix of Fe(II) and Fe(III) in alteration layers enriched with iron.^{21,31,35}

Previous studies have found that glass altered in the presence of Fe can form secondary alteration products whose structure and composition is similar to nontronite.^{35,61} Nontronite is similar in composition to SP and Fe-AL,⁶² and the calculated ρ_s is identical to SP and Fe-AL as seen in Table 4. Nontronite has a published ρ_{app} of 2.3 g·cm⁻³,⁶² allowing Φ to be calculated to be 0.28 using Equation (8). Since nontronite has been observed as a secondary alteration product in studies with conditions similar to this one and nontronite has a similar composition and ρ_s relative to SP and Fe-AL, Φ of SP and Fe-AL was assigned to be 0.28 as a first estimate despite possible structural differences depending on the considered layer. Then, using Equation (8), ρ_{app} values for SP and Fe-AL were calculated and are shown in Table 4.

The no-Fe-AL layer is similar in composition and ρ_s to the AL1+AL2 layers (Table 4, calculated using equation (6)). Assuming the Φ for no-Fe-AL is identical to AL1+AL2, the ρ_{app} for no-Fe-AL was calculated and is found in Table 4.

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Tables

Table 1: Composition (element mol. %) of the different layers and materials observed (details provided in Figure 3). ND = Not detected. Error is given as two standard deviations.

Elements	Unaltered ISG/UG	AL1+AL2	No-Fe-AL	Fe-AL	SP
Al	2.3	4.5 ± 0.1	2.7 ± 0.1	2.8 ± 0.0	1.8 ± 0.4
B	9.6	ND	ND	ND	ND
Ca	1.7	3.2 ± 0.1	2.1 ± 0.2	1.3 ± 0.1	1.3 ± 0.2
Fe	ND	ND	0.6 ± 0.1	5.7 ± 0.3	7.4 ± 0.5
Na	7.6	1.4 ± 0.0	2.5 ± 0.4	0.9 ± 0.1	1.3 ± 0.2
Si	18.0	25.7 ± 0.6	22.9 ± 0.6	23.3 ± 0.6	25.2 ± 0.2
Zr	0.5	1.0 ± 0.0	0.6 ± 0.0	0.4 ± 0.0	0.3 ± 0.1
O	60.3	$64.(2) \pm 3$	$68.(3) \pm 1$	65.6 ± 0.7	$62.(7) \pm 1$
Method	From Inagaki et al., 2013. ⁶³	Solution analysis by ICP-OES	SEM-EDS	SEM-EDS	SEM-EDS

Table 2: Concentrations of Leached Elements for ISG-H₂O and ISG-Fe Determined by ICP-OES
 Errors are given by two standard deviations of errors propagated by multiple measurements

Samples	ICP-OES Element Concentrations (ppm)				Correction factor for S/V	Corrected S/V m ⁻¹	ETh _B μm	Measured thickness μm
	B	Ca	Na	Si				
ISG-H ₂ O	67 ± 2	3.4 ± 0.1	103 ± 2	94 ± 2	0.8 ± 0.1	43 ± 4	12 ± 2	8 ± 4
ISG-Fe	71 ± 2	2.9 ± 0.0	109 ± 3	93 ± 3	0.7 ± 0.1	34 ± 3	15 ± 3	3.4 ± 0.7

Table 3: Densities of Oxides given in Lide et al.⁶⁰

Oxides	Density (g·cm ⁻³)
Al ₂ O ₃ (α)	3.99
CaO	3.34
FeO	6.00
Fe ₃ O ₄	5.25
Na ₂ O	2.27
SiO ₂	2.196
ZrO ₂	5.68

Table 4: Calculated Skeletal Densities (ρ_s) and Apparent Densities (ρ_{app}) for Alteration Layers found in ISG-H₂O and ISG-Fe, UG, and Nontronite. Calculated ρ_{app} values were used in CASINO®. Method to determine ρ_{app} for each material is indicated.

Material	ρ_s (g·cm ⁻³)	ρ_{app} (g·cm ⁻³)	Method used to Determine ρ_{app}
AL1+AL2	2.7	1.4	Equation 7
No-Fe-AL	2.7	1.4	Equation 8
SP	3.2	2.3	Equation 8
Fe-AL	3.2	2.3	Equation 8
UG	2.54	2.50	From Gin et al., 2012. ¹⁴
Nontronite	3.2	2.3	From Wilson, 2013. ⁶²

Figures

Figure 1: (a) Diagram of experimental set up of DB-PAS, Doppler broadening effect within a sample and resulting energy distribution plot; (b) Energy distribution schematic for γ -rays detected from samples with voids (left) and with no voids (right). Central (N_s), outlier portions (N_{w1} , and N_{w2}), and total counts (N_T) are indicated; (c) Schematic atom clusters for materials with (pink) and without (blue) voids where valence electron clouds are lightly shaded and core electron clouds are darkly shaded.

Figure 2: Schematic Representation of the Experimental Configurations ISG-DIW (a, without Fe^0 foil) and ISG-Fe (b, with Fe^0 foil). Scratches made into Fe^0 foil allow solution to pass between the bottom glass coupon and Fe^0 foil.

Figure 3: Cross-sectional BSE-SEM images of (a) ISG-H₂O and (b) ISG-Fe; EDS profiles were analyzed over areas similar to areas indicated by arrows for (c) ISG-H₂O and (d) ISG-Fe. Layer designations are detailed in the text.

Figure 4: Normalized S parameter as function of implantation energy for unaltered ISG, ISG-H₂O, and ISG-Fe (a), and the distributions of positron termination sites as a function of depth at different energies for (b) unaltered ISG, (c) ISG-H₂O, (d) ISG-Fe. Error bars in Figure 2a are calculated from error propagations from instrumental variations.

Figure 5: S parameter versus W parameter plot for unaltered ISG, ISG-H₂O, and ISG-Fe. Arrows show implantation energy progression through ISG-H₂O and ISG-Fe. Important annihilation environments are circled and labeled.