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ION-BEAM DEPTH-PROFILING STUDIES OF LEACHED GLASSES

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ABSTRACT

Ion-beam depth-profiling was carried out on three different glasses leached (or hydrated) in deionized water using $^{1}H(^{19}F,\alpha\gamma)^{16}O$ nuclear reaction, secondary ion mass spectrometry (SIMS) and sputter-induced photon spectrometry (SIPS) techniques. The depth-profiles show an interdiffusion mechanism in which the sodium ions in the glass are depleted and replaced by hydrogen (H^+) or hydronium (H_3O^+) ions from the solution. The leaching behavior does not show significant difference whether the glass surface is fractured or polished. Problems of mobile ion migration caused by ion bombardment and loss of hydrogen during analysis are discussed.

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INTRODUCTION

When a silicate glass surface is in contact with water, it sets up a reaction in which hydrogen (or hydronium, H_3O^+) ions penetrate into the glass and alkali (usually sodium) ions enter the solution. This ionic interdiffusion process is known as glass leaching or glass hydration and it results in the formation of a hydrated silica-rich surface layer of a certain thickness dependent on the temperature and time of the reaction. The interdiffusion process can be written as:

$$H_2O + Na^+ \text{ (glass)} = H^+ \text{ (glass)} + NaOH \quad (1)$$

$$\text{or } 2H_2O + Na^+ \text{ (glass)} = H_3O^+ \text{ (glass)} + NaOH \quad (2)$$

Several attempts[1-3] have been made using resonant nuclear reaction techniques to determine which of the above two equations is the more appropriate mechanism by measuring the H:Na ratio in the hydrated surface layers. Experimental evidence suggests that at least for commercial soda-lime glasses, equation (2), i.e., the hydronium-sodium exchange, is the more likely operating mechanism[1,3]. Obviously, the phenomenon has important technological implication in the encapsulation of nuclear waste in glass forms since the interdiffusion mechanism may involve a radioactive alkali ion such as $^{137}Cs^+$ going into solution[4].

Ionic interdiffusion in leached glass surfaces is usually studied by measuring the concentration-versus-depth profiles of the diffusing species using ion beam techniques. $^1H(^{19}F,\alpha\gamma)^{16}O$ and $^1H(^{15}N,\alpha\gamma)^{12}C$ nuclear reactions are useful for measuring the hydrogen profile, while secondary ion mass spectrometry (SIMS) and sputter-induced photon spectrometry (SIPS) can be used to measure the profiles of several elements including hydrogen. In all depth-profiling experiments involving

bombardment of an insulator such as glass by energetic ions, the problem of beam-induced mobility of the species under study frequently arises. In this report, we compare the depth-profiles obtained by the ^{19}F nuclear reaction, SIMS and SIPS techniques in order to study the beam-induced mobility problem and we also discuss methods of overcoming such a problem. In addition, we also examine whether glass surfaces prepared by fracturing or polishing show different leaching behavior.

EXPERIMENTAL

Three glasses of known composition (shown in Table 1) were selected for this study. Both Corning 0080 and Penn Vernon Sheet are commercial glasses, while the ternary soda-lime glass was prepared in our laboratory following a procedure described in a previous report[5]. All three glasses were hydrated in a large bath (12 liters) of deionized water, with the Corning 0080 and the Penn Vernon Sheet glass for 48 hours at 88°C and the laboratory soda-lime ternary glass for several fixed periods varying from 1 hour to 13.5 hours at 90°C. The surfaces of the $20Na_2O \cdot 10CaO \cdot 70SiO_2$ laboratory glass were prepared by fracturing as well as polishing.

The ^{19}F nuclear reaction was carried out at the Oak Ridge National Laboratory Tandem Van der Graaff accelerator. The experimental set-up was similar to that described in previous reports[6,7] with one major modification: the samples in the present work could be cooled by conduction via the sample holder in contact with a copper shroud which formed part of a liquid nitrogen reservoir. A thermocouple imbedded in the holder showed a final steady temperature of -130°C after a few hours of cooling.

The ^{19}F reaction exhibits a strong resonance at 16.44 MeV in the laboratory system. Depth profiling was accomplished by raising the beam energy from

16.40 MeV to 17.50 MeV, equivalent to a depth of about 0.5 μm in the glass samples. A second strong resonance at 17.63 MeV lab energy limits the useful range to this particular depth. The total beam current was kept at 8 nA or below with a beam spot size of 2 x 2 mm^2.

The depth-profiling experiments by SIMS and SIPS were performed using a scanning ion probe described in earlier reports[8-10]. A mass-selected $^{40}Ar^+$ ion beam bombarded the sample surface at a 45° incident angle. In the SIMS experiment, the ion beam was focussed to a 100 μm diameter spot with a current of 0.25 μA. In the SIPS experiment, the beam spot was 200 μm and the beam current was 0.85 μA. In both cases the beam was rastered in a 500 x 500 μm^2 pattern and the ion signal was gated to overcome the edge-effect of the bombarded crater[11]. In the SIMS experiments, the glass target surface was also bombarded simultaneously by an electron beam to alleviate surface charging similar to the approach described by Wittmaack[11] and Magee and Harrington[12].

The SIPS technique was used to depth-profile glass surfaces prepared by fracturing and polishing. The fracturing was performed in air. The polishing was carried out using kerosene as lubricant to minimize hydration during the polishing process.

RESULTS

The depth-profiles for hydrogen in the two leached commercial glasses, Corning 0080 and Penn Vernon Sheet, determined by ^{19}F nuclear reaction, SIMS and SIPS techniques are shown in Figs. 1(a), 1(b) and 1(c) respectively. The sodium profiles were measured using SIMS and SIPS and they are shown in Figs. 2(a) and 2(b). These clearly show that sodium is depleted in the surface region where hydrogen has penetrated, indicating an interdiffusion mechanism in the leaching process.

In the laboratory ternary soda-lime glass, both fractured and polished surfaces exhibit very similar leaching behavior as far as the depth profiles are concerned. Fig. 3 shows the H and Na profiles determined by SIPS in a soda-lime glass leached for 6.6 hours at 90°C in deionized water where the surface was fractured. They show the expected interdiffusion behavior. Fig. 4 shows a Si profile and a Ca profile in the same glass. Si is unaffected by the leaching process apart from the initial transient, whereas Ca shows a slight depletion at the surface, although nowhere as depleted as the more mobile Na ion. This is in agreement with our previous observations on polished surfaces of leached simple ternary glasses[5].

The leached depths, measured from the full-width at half-maximum of the hydrogen profiles, as a function of the square-root of hydration time are shown in Fig. 5 for both the polished and fractured surfaces of the ternary glass. Both show approximately a linear dependence, indicating a diffusion mechanism is in operation.

DISCUSSION

In the nuclear reaction experiments, the samples were cooled to -130°C. This was essential for two reasons: (1) to circumvent the problem of beam-induced mobility of hydrogen in the solid, and (2) to prevent loss of hydrogen (or water) from the solid under vacuum. Both of these phenomena are frequently observed in hydrogen depth-profiling of leached glasses by nuclear reaction. The beam-induced mobility manifests itself as a decrease in γ-ray count rate as a function of exposure time of the sample to the beam. Loss of hydrogen to the vacuum can be observed in the hydrogen depth-profile showing a hydrogen-depleted region near the surface. Both of these effects are highly undesirable in that they not only

distort the hydrogen profile, but also render hydrogen quantification extremely difficult.

A high beam current will also cause migration of hydrogen in the glass. In our experiments, the total beam current was kept at 8 nA or less. Since a combination of cooling and low current appears to arrest the beam-induced mobility of hydrogen, it indicates that the migration is due to both charging and localized heating of the surface although it is uncertain which is the greater effect.

In the SIMS measurements, an electron beam was used to neutralize the surface charging. This resulted in electron-stimulated desorption (esd) of adsorbed species on the surface. Both the H and Na depth-profiles by SIMS in Figs. 1(b) and 2(a) have had the esd contribution subtracted. Without the electron beam neutralization, no SIMS signal could be obtained because surface charging drastically change the energies of the secondary ions so that they lie outside the normal band-width of the energy filter. The SIPS technique was not affected by the surface-changing problem since the excited species detected are neutral atoms. However, there are often continuum emissions due to excited clusters or molecules[13] forming a background radiation which has to be subtracted.

It is interesting to compare the hydrogen profiles by the three techniques. The depth scale in the nuclear reaction profile (Fig. 1a) was determined by the stopping power, dE/dx, of ^{19}F in the target which is 2.34 MeV/μm for Corning 0080 and 2.38 MeV/μm for Penn Vernon Sheet glass. The dE/dx values were calculated from nuclear data tables[14,15]. The depth scales in Figs. 1(b) and (c) were determined by measuring the sputtered craters with a Talysurf profilometer. The agreement between the leached depths in Figs. 1(a), (b) and (c) is remarkably good. The shape of the profiles, however, do not show such good agreement. The samples were not cooled in the SIMS and SIPS measurements and the hydrogen loss

to the vacuum can be observed in the SIMS and SIPS profiles, especially in the Corning 0080 glass, which show depletion near the surface region.

Contrary to the nuclear reaction and SIPS profiles, the secondary H^+ ions (Fig. 1b) show a higher yield for the Penn Vernon Sheet glass than the Corning 0080 glass. This probably reflects that hydrogen loss in the Corning glass was more serious in that particular SIMS experiment.

Electron bombardment was not used in the SIPS measurements and this might have caused some degree of migration of mobile species induced by the ion beam. This may be a plausible explanation why the Na profiles in Fig. 2(b) appear more depleted than the corresponding profiles by SIMS in Fig. 2(a). On the other hand, the Na leached depths by SIPS in Figs. 2(b) and 3 agree very well with the H leached depths whereas the SIMS profiles in Fig. 2(a) do not. It is uncertain whether the Na profiles by SIMS are distorted by other field effects such as over-neutralization by the electron beam. We have encountered similar difficulties with SIMS depth-profiling of Na in hydrated obsidian volcanic glasses previously[17].

The plot of leached depth versus square root of hydration time in Fig. 5 for the laboratory soda-lime glass shows very little difference in hydration rate between the fractured and polished surfaces. In fact, the best fit for the polished surfaces has a non-zero y-intercept, suggesting that there may be a very thin hydrated layer initially present. This is possible on the polished surface because of the micro-damage introduced during polishing despite the fact that we took care to minimize hydration by using kerosene rather than water as lubricant.

CONCLUSION

For hydrogen depth-profiling in leached glasses, ^{19}F or other resonant nuclear reactions appear very suitable provided samples are cooled to prevent hydrogen loss to the vacuum and a low beam current is used to minimize hydrogen migration. In SIMS and SIPS one has to overcome the background problem of esd and continuum emission signals. For sodium depth-profiling, it appears to be more satisfactory to use SIPS since one has to cope with unknown surface neutralization problems in SIMS. The leaching behavior of glasses does not seem to show any difference whether the surface is fractured or polished.

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Table 1. Chemical compositions of the three glasses studied (mol%)

Glass	SiO_2	Al_2O_3	Na_2O	MgO	CaO	K_2O	Fe_2O_3
Corning 0080	72.0	0.6	16.2	5.9	5.3	-	-
Penn Vernon sheet	72.5	0.7	12.8	5.2	8.7	0.1	0.04
Laboratory soda-lime	70.0	-	20.1	-	9.9	-	-

FIGURE CAPTIONS

Fig. 1(a) Hydrogen depth-profiles determined by $^{1}H(^{19}F,\alpha\gamma)^{16}O$ resonant nuclear reaction in two leached commercial glasses.

Fig. 1(b) SIMS depth-profiles of $^{1}H^{+}$ in two leached commercial glasses.

Fig. 1(c) SIPS depth-profiles of hydrogen determined by monitoring the H6563 Å line as a function of sputtering time.

Fig. 2(a) SIMS depth-profiles of $^{23}Na^{+}$ in two leached commercial glasses.

Fig. 2(b) SIPS depth-profiles of sodium determined by monitoring the Na5890 Å line as a function of sputtering time.

Fig. 3 Hydrogen and sodium interdiffusion profiles in a leached laboratory ternary soda-lime glass determined by SIPS.

Fig. 4 Silicon and calcium depth-profiles in a leached laboratory ternary soda-lime glass determined by SIPS.

Fig. 5 Plot of leached depths determined by the full-width at half-maximum of SIPS hydrogen profiles versus the square root of hydration time. Temperature of deionized water = 90°C.

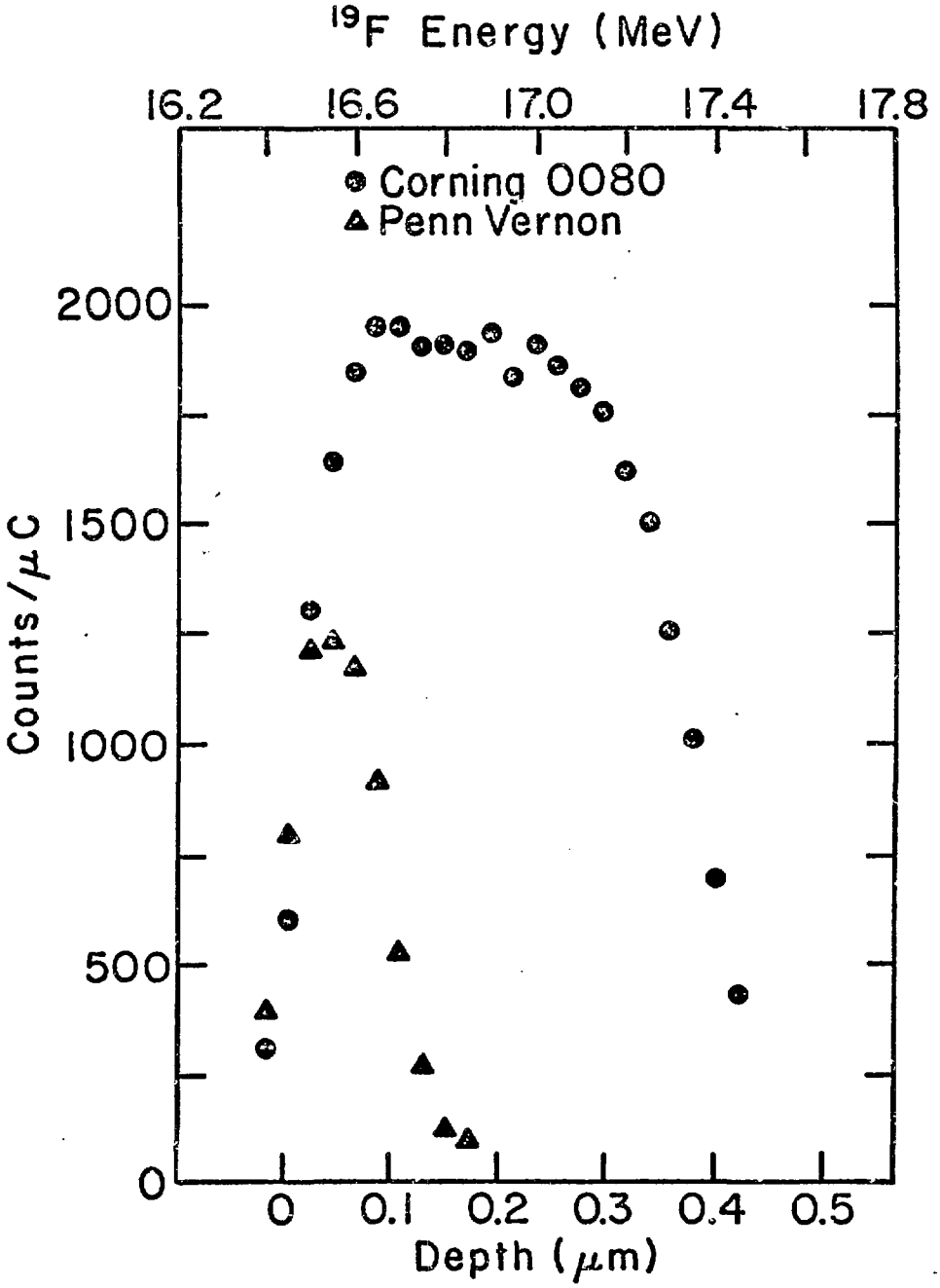
^{19}F Energy (MeV)
16.2
16.6
17.0
17.4
17.8
Corning 0080
Penn Vernon
2000
1500
1000
500
0
Counts/μC
0
0.1
0.2
0.3
0.4
0.5
Depth (μm)

Fig. 1(a)

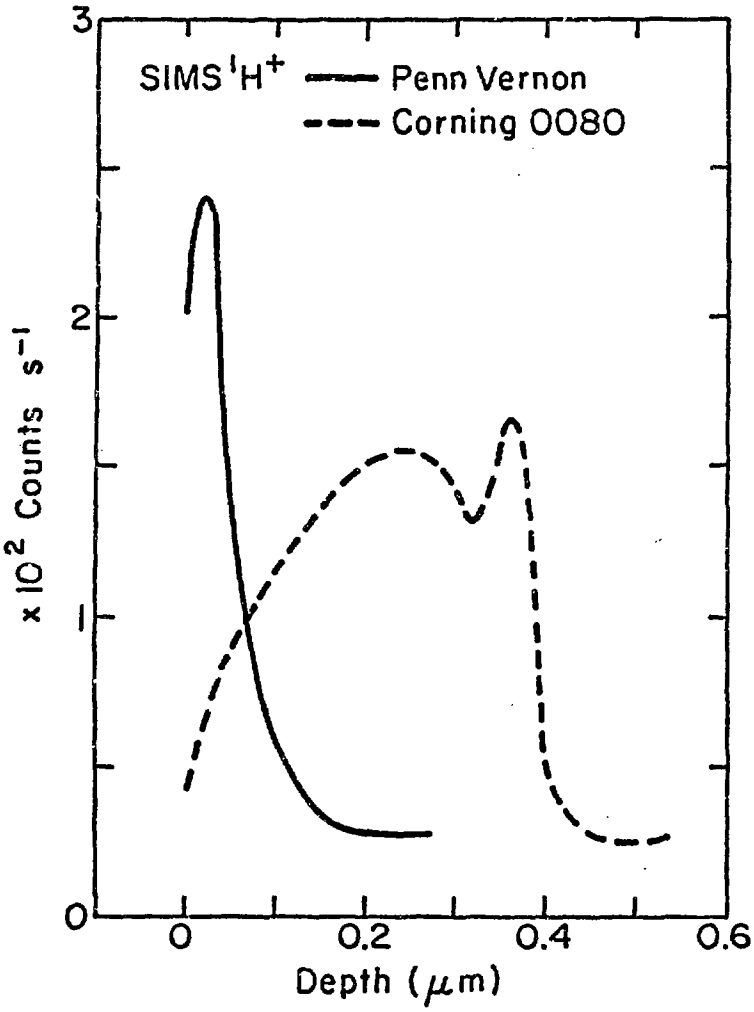
SIMS $^1H^+$
Penn Vernon
Corning 0080
x 10^2 Counts s^{-1}
3
2
1
0
0
0.2
0.4
0.6
Depth (μm)

Fig. 1(b)

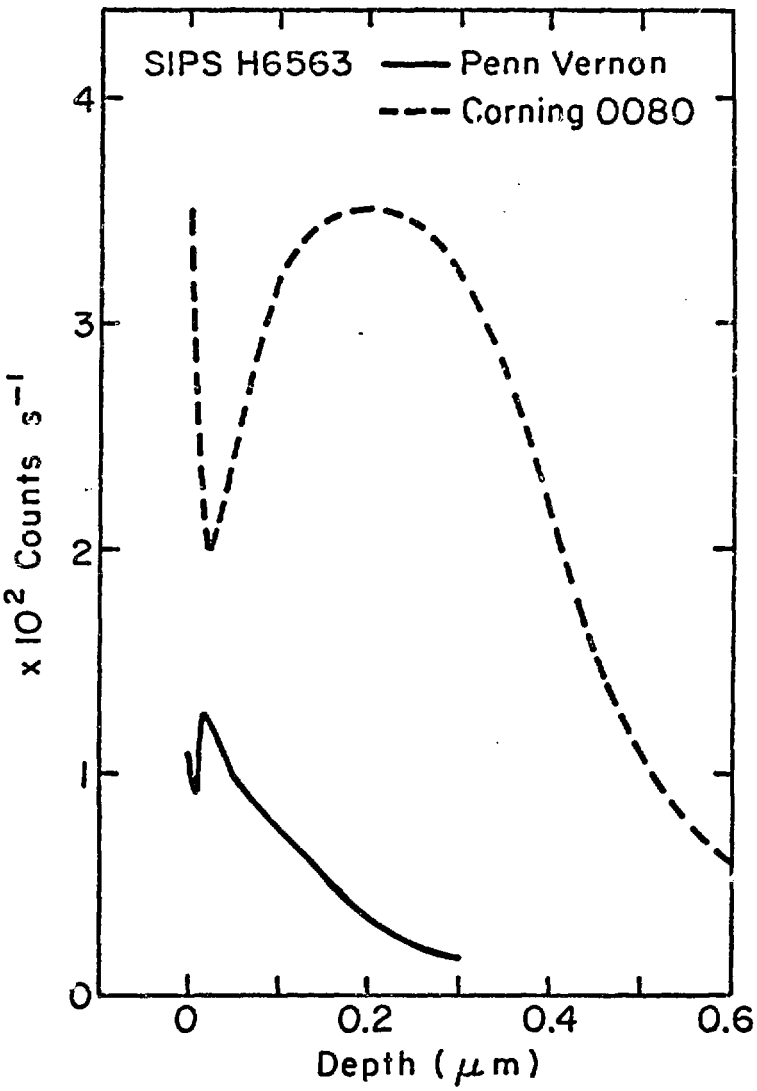
SIPS H6563
Penn Vernon
Corning 0080
x 10² Counts s⁻¹
0
1
2
3
4
0
0.2
0.4
0.6
Depth (μm)

Fig. 1(

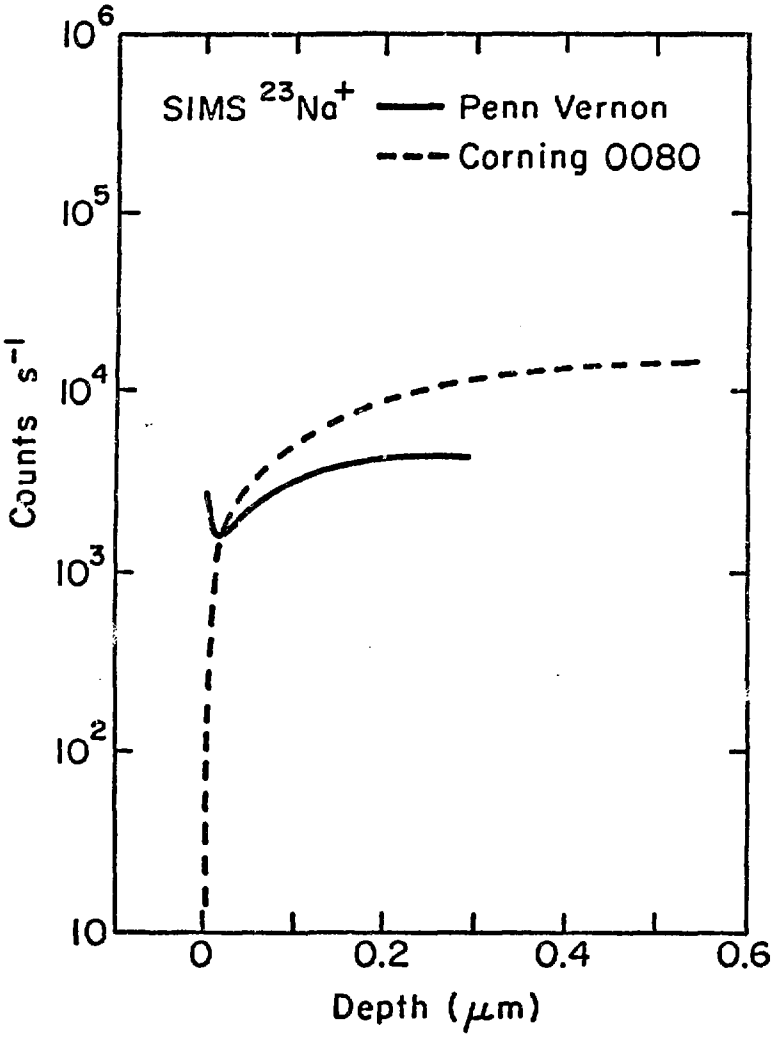
SIMS $^{23}Na^{+}$
Penn Vernon
Corning 0080
Counts s^{-1}
10^6
10^5
10^4
10^3
10^2
10
0
0.2
0.4
0.6
Depth (μm)

Fig. 2(a

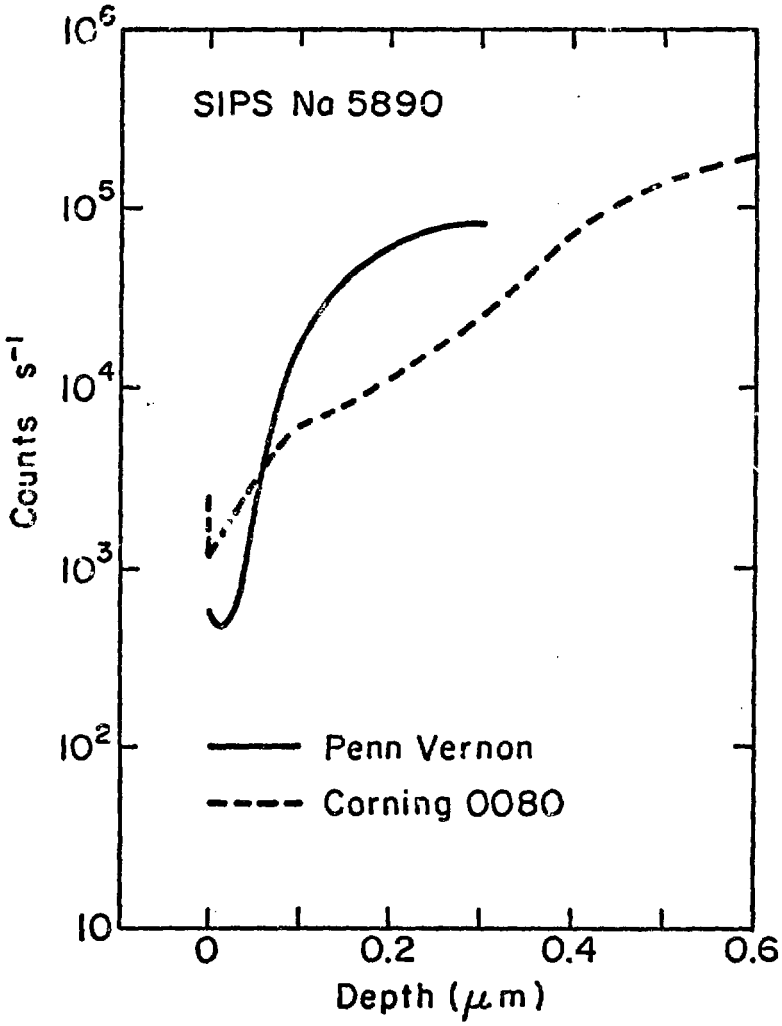
SIPS No 5890
Counts s⁻¹
10⁶
10⁵
10⁴
10³
10²
10
0
0.2
0.4
0.6
Depth (μm)
Penn Vernon
Corning 0080

Fig. 2(b)

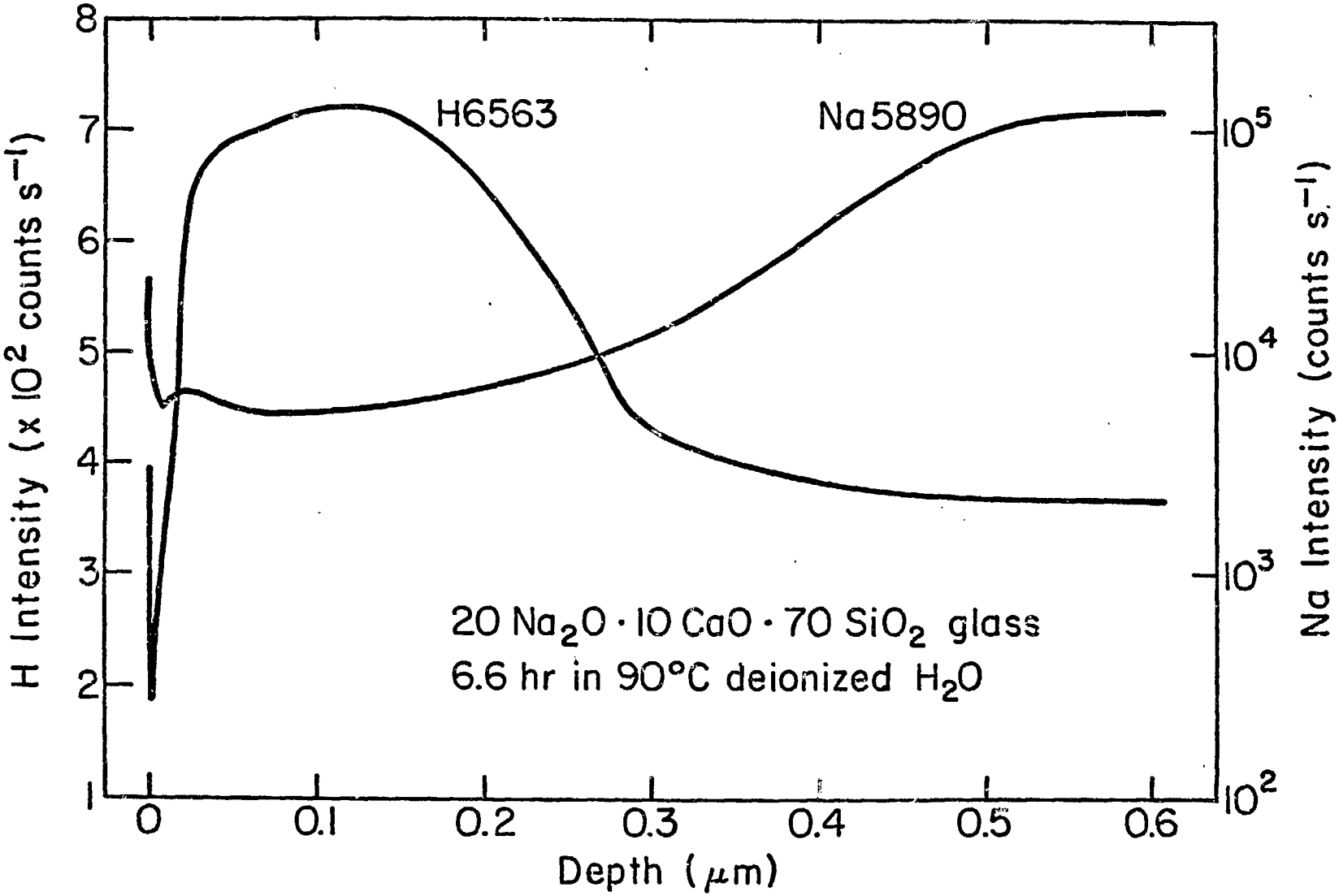
H6563
Na5890
20 Na2O · 10 CaO · 70 SiO2 glass
6.6 hr in 90°C deionized H2O
H Intensity (x 10^2 counts s^-1)
Na Intensity (counts s^-1)
Depth (μm)
0
0.1
0.2
0.3
0.4
0.5
0.6
1
2
3
4
5
6
7
8
10^2
10^3
10^4
10^5

Fig. 3

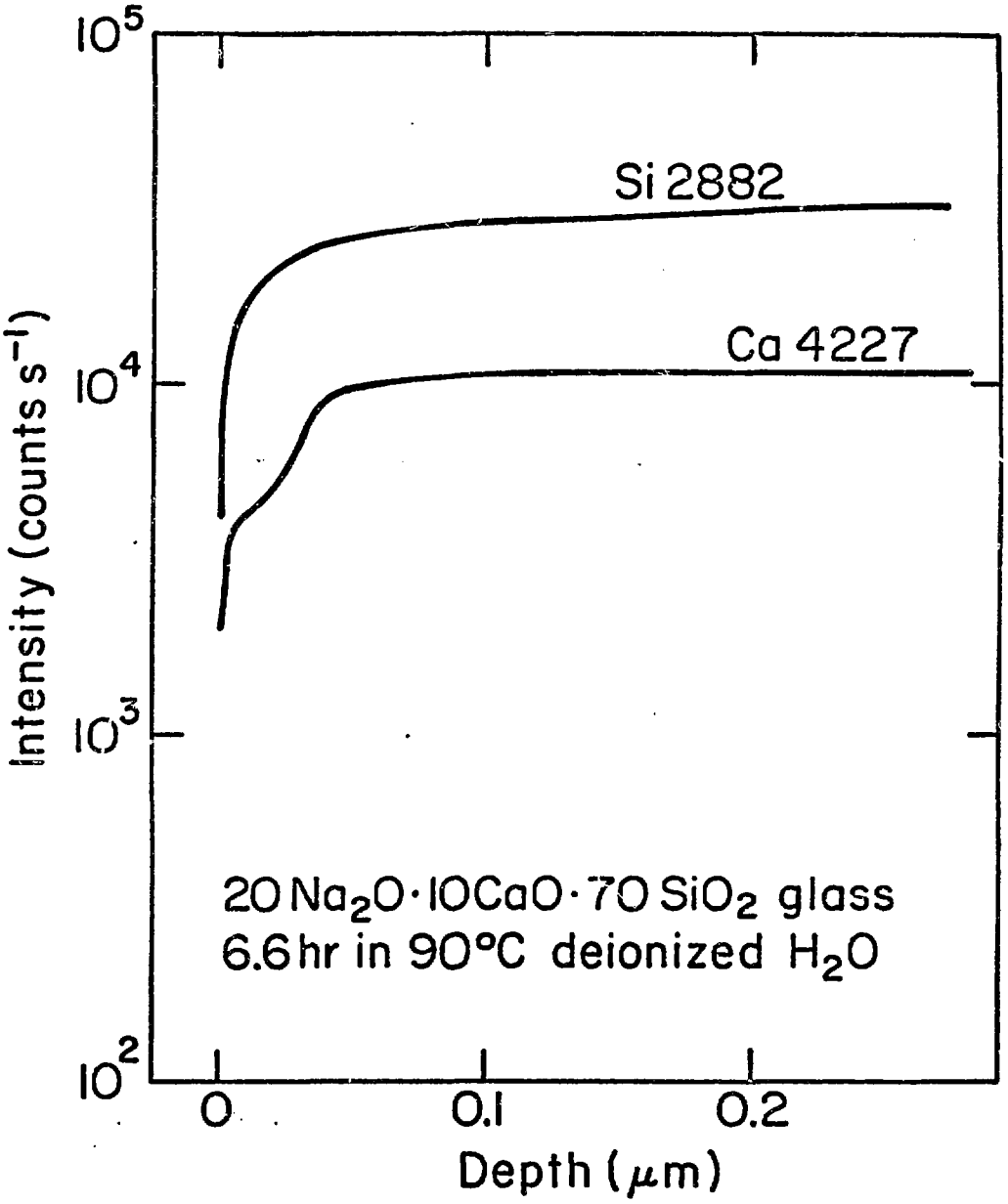
10^5
10^4
10^3
10^2
Intensity (counts s^{-1})
Si 2882
Ca 4227
20 Na_2O·10CaO·70 SiO_2 glass
6.6 hr in 90°C deionized H_2O
0
0.1
0.2
Depth (μm)

Fig. 4

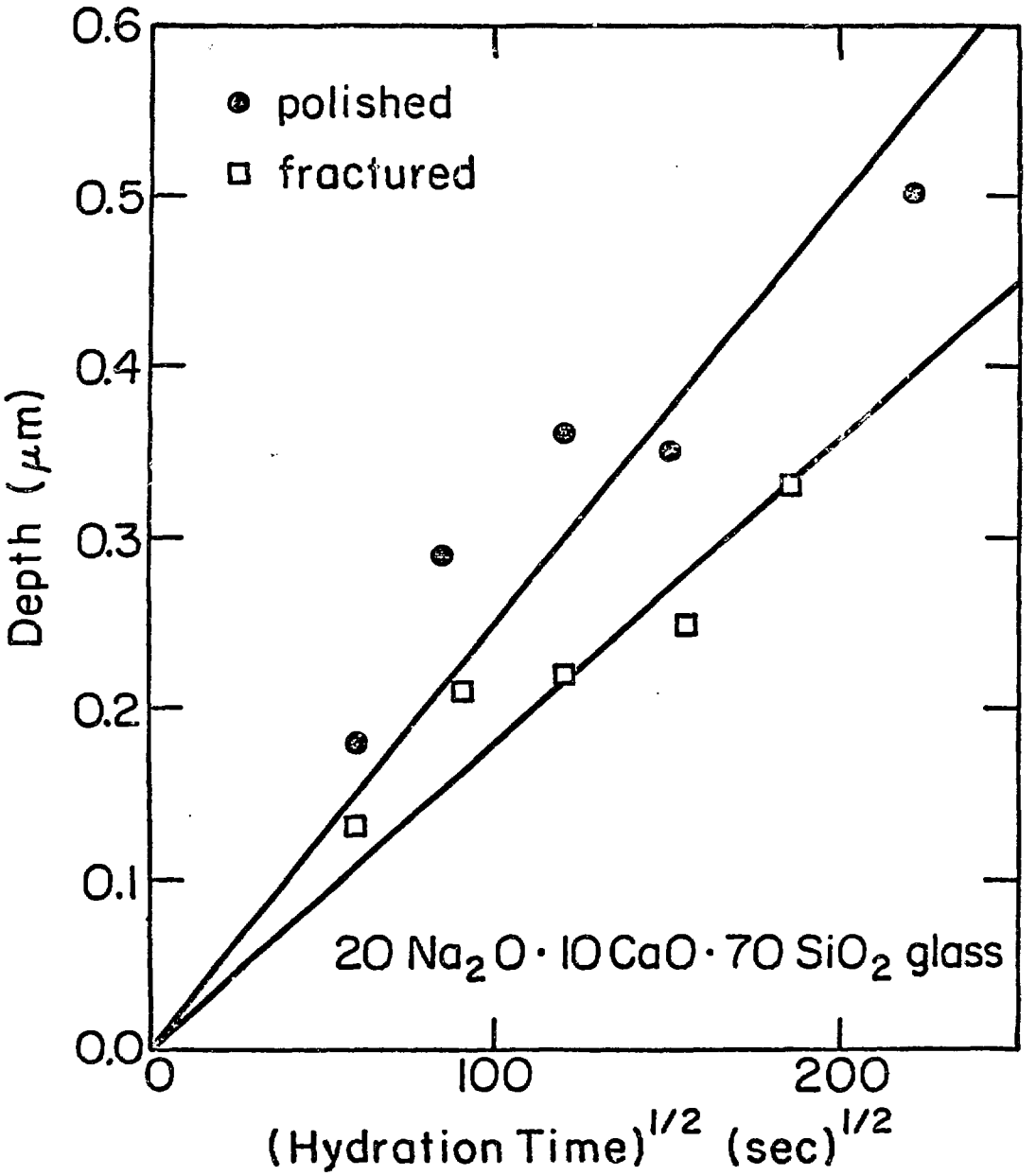
0.6
0.5
0.4
0.3
0.2
0.1
0.0
Depth (μm)
polished
fractured
20 Na2O · 10CaO · 70 SiO2 glass
0
100
200
(Hydration Time)1/2 (sec)1/2

Fig. 5