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DEPARTMENT OF PHYSICS
State University of New York at Albany

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SUNY/ALBANY GLASS STUDY GROUP

1980-81 ANNUAL REPORT

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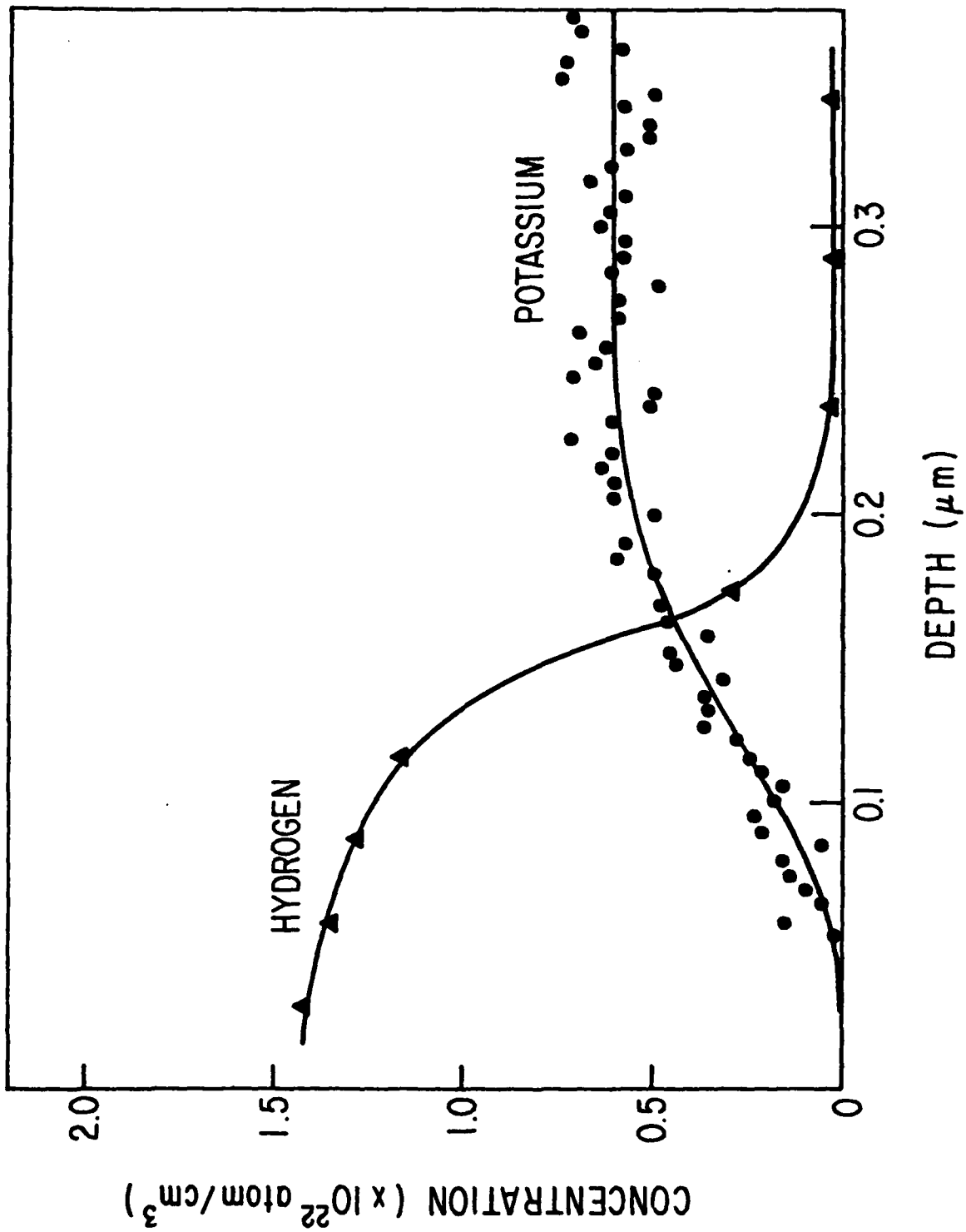
SUMMARY: During the 1980-81 year, a wide range of experiments were started to determine the mechanisms which mediate the reaction between water and glass. One of the fundamental thrusts of our research is to make full use of the ion beam analysis techniques, available at SUNY Albany to measure the changes in the concentration profiles of various elements near glass surfaces. Over the past year, a number of improvements and refinements have been made in our experimental setup for measuring hydrogen concentration profiles using nuclear reaction analysis and for measuring concentration profiles of other elements such as Na, Ca, Si, Cs and Sr using He backscattering.

The range of experiments initiated using this improved system include: (1) a detailed study of ionic interdiffusion (hydrogen ion ↔ alkali ion) which occurs when an alkali glass is exposed to water; (2) electromigration experiments where hydrogen, Na and Ca ions are selectively driven by an applied electric field with the resulting changes in elemental distributions near the electrodes being measured by ion beam techniques; (3) the development of techniques for measuring very slow dissolution rates (using ion implantation with Rutherford backscattering) and the application of these techniques to measure the effects of radiation damage and salts in solution on etch rates of glasses;

(4) a study of the permeation kinetics of H₂O in SiO₂ thin films; (4) the study of reaction between water and tektite glass; (6) a preliminary look at the reaction between water and β-alumina with emphasis on the similarity between this ionic conductor and glass; and (7) an attempt to understand why the commercial practice of treating soda-lime glass with sulfur dioxide and steam appears to improve its durability.

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Development of Techniques for Measuring Elemental Profiles
Near Glass Surfaces Using Nuclear Reaction Analysis and
Rutherford Backscattering Spectrometry.

C. Burman and W.A. Lanford

Central to our approach to the study of the mechanisms of the reaction between water and glass is the utilization of techniques which allow us to measure the concentration vs. depth of hydrogen⁽¹⁾ and other elements near the surface of glass exposed to water or aqueous solutions. These measurements often provide key information about the mechanisms which is impossible to obtain from the more traditional approach of measuring what goes into solution.

While most of the equipment necessary to make these measurements was already available at the SUNY Albany Accelerator Laboratory, a number of improvements and refinements were necessary to apply these methods to the problem at hand. These improvements include: development of a system to eliminate the effects of charging of the samples in the ion beam, improvement of the sensitivity of the hydrogen profile measurements necessary to measure hydrogen (water) diffusion into steam treated SiO_2 , improvement of the energy resolution in the silicon surface barrier detector used in Rutherford Backscattering, development of a method of freezing glass samples (to dry ice temperature) before evacuation in the analysis chamber in order to lock in loosely bound water, and study of the possible effects of prolonged

bombardment of glasses on the distribution of Na in the glass.

All of these improvements have been successfully carried out and we now have a reliable experimental setup which allows us to use the ^{15}N hydrogen profiling technique to measure hydrogen profiles or to measure Rutherford Backscattering spectra. This setup is shown schematically in figure 1. Some of the details of the use of these techniques in the study of glass surfaces are given in reference 2.

Figure 2 illustrates the use of Rutherford Backscattering in determining (confirming) the stoichiometry of one of the glasses studied. Below we will show a number of results of the application of these techniques in studying the distribution of both rather mobile and inert elements.

One of the unanticipated developments of our early measurements is the central importance of being able to accurately measure the concentration profiles of oxygen near the surface of glasses treated in water or subjected to electromigration experiments. While one gets some information from ordinary 2 MeV Rutherford Backscattering, the data are usually not sufficiently accurate for the present purposes. In order to improve the accuracy of oxygen profiles we have begun utilizing resonant He scattering (at 3.05 MeV)⁽³⁾ which is giving much more accurate and interesting data on changes in the oxygen content of altered surface layers on glasses. Some of these results will be discussed below.

References

1. W.A. Lanford, H.P. Trautvetter, J. Ziegler and J. Keller, Applied Physics Letters 28 (1976) 566.
2. W.A. Lanford "Analysis with Heavy Ions" in Heavy Ion Science. D.A. Bromley editor, Plenum Press, New York (in press).
3. G. Mezey, J. Gyulai, T. Nagy, E. Kotai and A. Manuba in Ion Beam Surface Layer Analysis. O. Megu, G. Linker and F. Kappeler editors, Plenum Press, New York (1976) 303.

Figure Captions

Figure 1: A schematic diagram of the scattering chamber used at SUNY Albany for measuring hydrogen concentration profiles and backscattering spectra of glasses treated by water.

Figure 2: A typical Rutherford Backscattering spectrum of an untreated glass. This demonstrates the use of backscattering in simple bulk analysis.

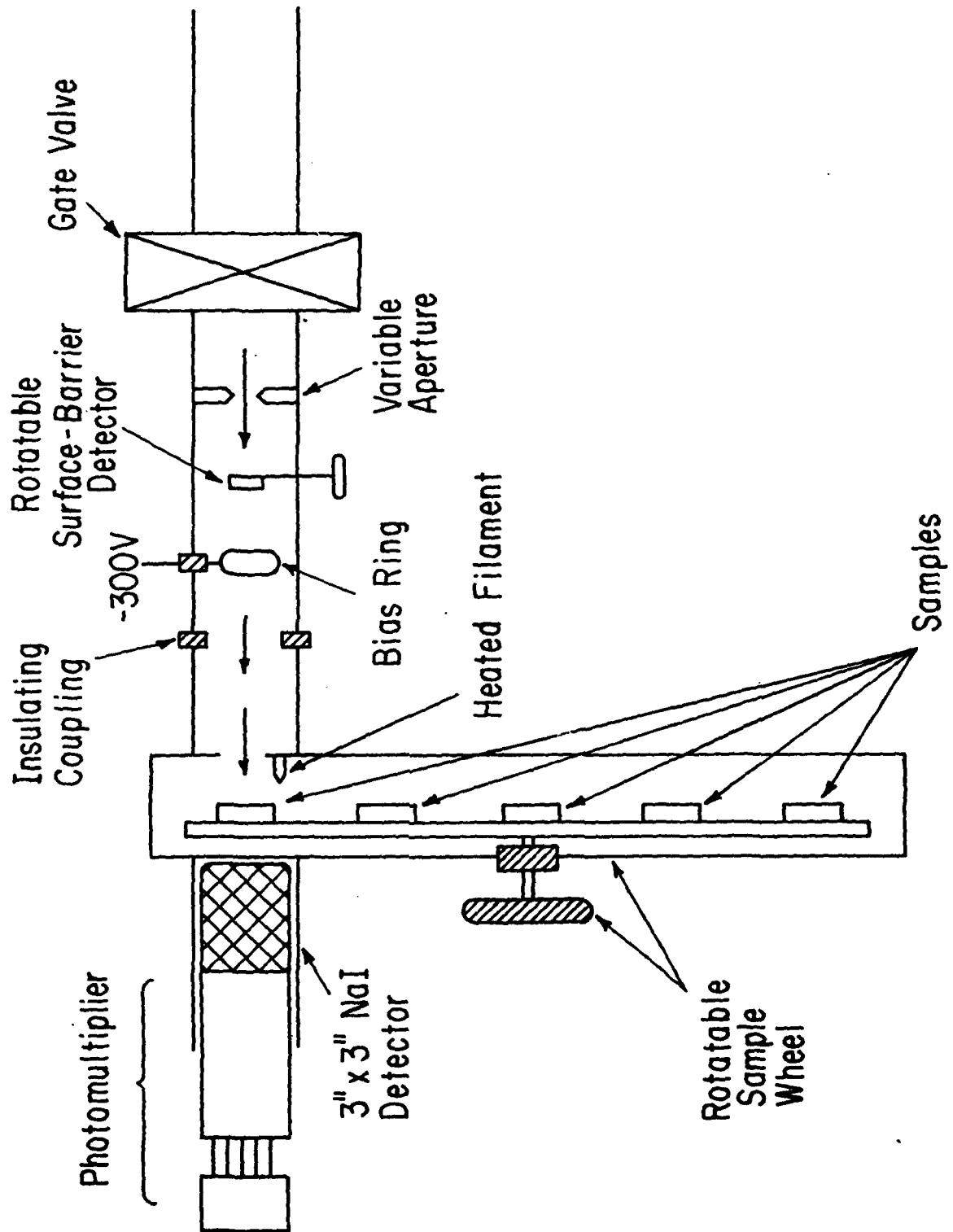


Fig. 1

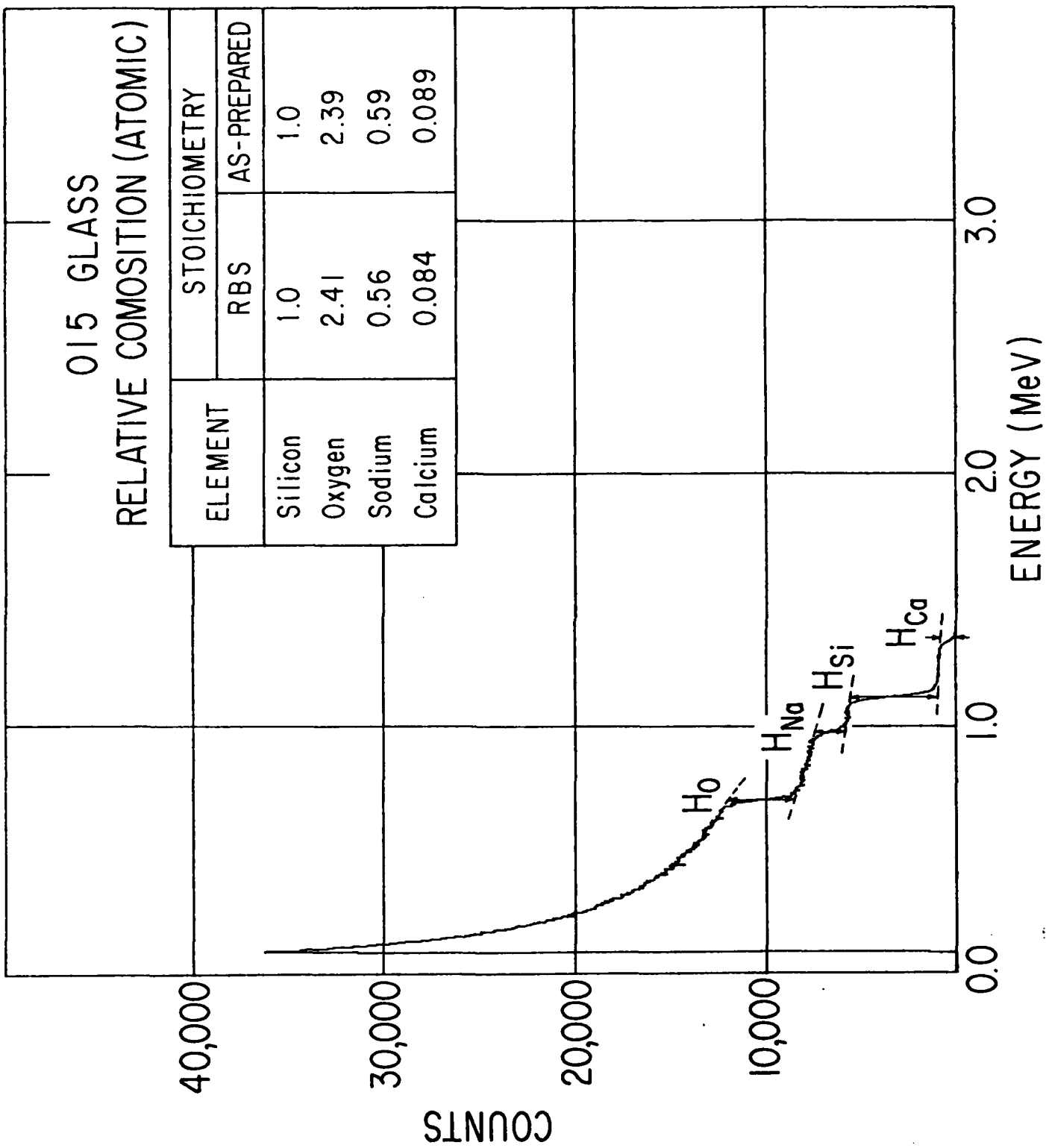


Fig. 2

Studies of Ionic Interdiffusion in Water-Glass Reactions.

Y. Mehrotra, T. Wassick, R.H. Doremus (RPI)

C. Burman and W.A. Lanford

A central part of the initial phase of our research programs was to extend our earlier studies of the reaction between water and a commercial soda-lime glass⁽¹⁾. This earlier experiment indicated that two distinct types of reactions occurred. First, an ionic exchange occurred between the Na^+ ions in the glass with hydrogen in water molecules on the surface. Second, the water slowly dissolved the glass. To study the generality of these results and to study what factors influence the rate of both these reactions, we started experiments with glasses of various but related compositions. In one series all were 72% SiO_2 , 22% monovalent ($\text{Na} + \text{Cs}$) and 6% bi-valent ($\text{Ca} + \text{Sr}$). These glasses were then exposed to distilled water or a pH-7 buffer solution at 50°C or 90°C for varying lengths of time. Following this, concentration profiles of H, Na, Ca, Cs, Sr and O were measured using either nuclear reaction analysis (for H) or Rutherford Backscattering (for other elements). Some of these data are shown in Fig. 1 - Fig. 4.

The results of these investigations can be briefly summarized as follows. For the 015 glass (72% SiO_2 , 22% Na_2O and 6% CaO), the reaction proceeds as in the commercial soda lime glass except that (1) the Na^+ -Hydrogen Ion exchange

process proceeds much faster, (2) hydrogen (water) can be lost from the hydrated glass simply by evacuation at room temperature and (3) after long times, one begins to see not only Na depletion from the surface but also Ca becomes depleted. Some of these results are indicated in Figs. 2-4.

For the 005 glass (77% SiO_2 , 17% Na_2O , 5% Cs_2O , and 6% CaO) the reaction proceeds as for the 015 glass except that only the Na is depleted, at least for the times studied. The Cs^+ does not seem to participate in the ion exchange reaction nearly as rapidly as does Na^+ .

While all the data for this series of measurements is not yet complete and electromigration measurements are also not finished, these measurements generally confirm the earlier results. Namely, the most important first stage in the reaction between water and an alkali glass is the ionic interdiffusion of Na^+ ions in the glass with H^+ or H_3O^+ ions formed by an ionic exchange reaction between the Na^+ and water on the glass surface.

The Ca depletion observed here is not completely understood. The effective diffusion coefficient for Ca depletion is about four orders of magnitude slower than that for the Na depletion, and may be the result of a similar ion exchange reaction going on independently of the Na^+ -hydrogen exchange. The fact that Ca can be forced to migrate in an applied electric field, as seen in the vacuum electrolysis experiments

reported here, may be evidence for this mechanism.

References

1. W.L. Lanford, K. David, P. LaMarche, T. Laursen, R. Groleau and R.H. Doremus, J. Non-crystalline Solids 33 (1979) 249.

Figure Captions

Figure 1: 2 MeV Rutherford Backscattering spectra from four untreated glasses used in this study.

Figure 2: An enlarged view of the Na step in the backscattering spectra of 015 glasses treated in pH-7 solution at 90°C for varying lengths of time. The shifts show the depletion of Na.

Figure 3: An enlarged view of the Ca step in the backscattering spectra of 015 glass, treated in pH-7 solution at 90°C. The shifts show the depletion of Ca.

Figure 4: Hydrogen and Na profiles of 015 treated in pH-7 buffer solution.

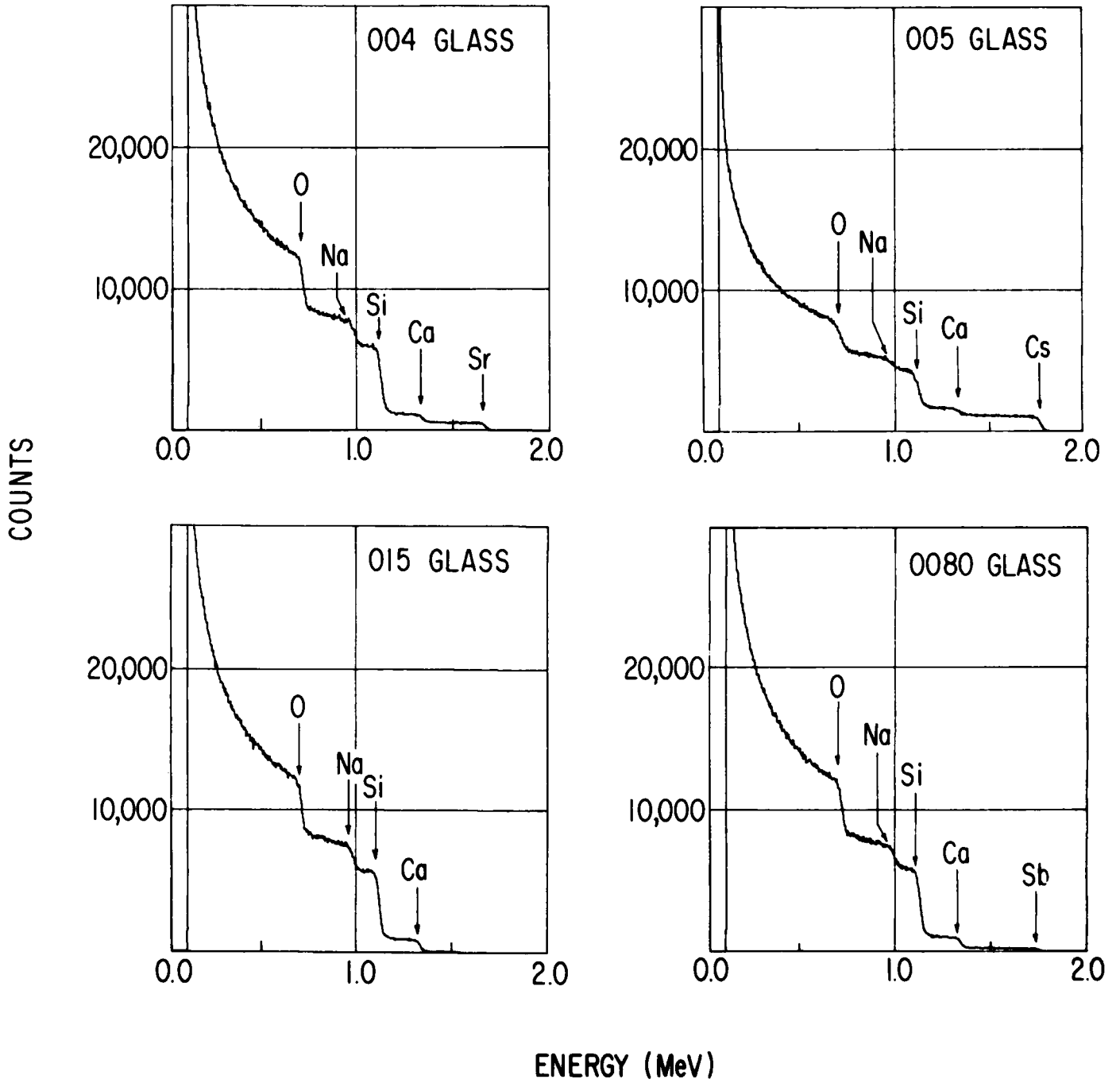


Figure 1

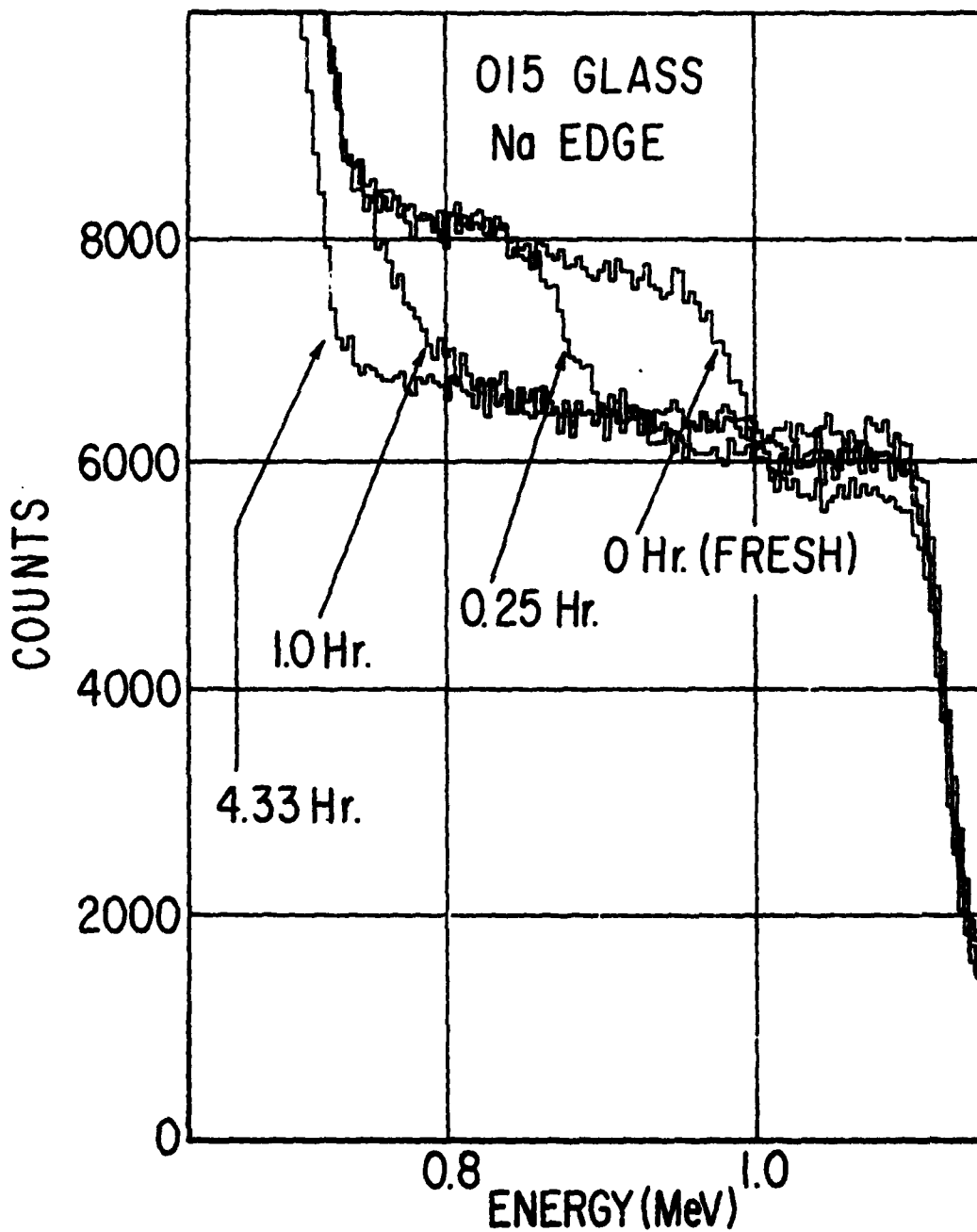


Figure 2

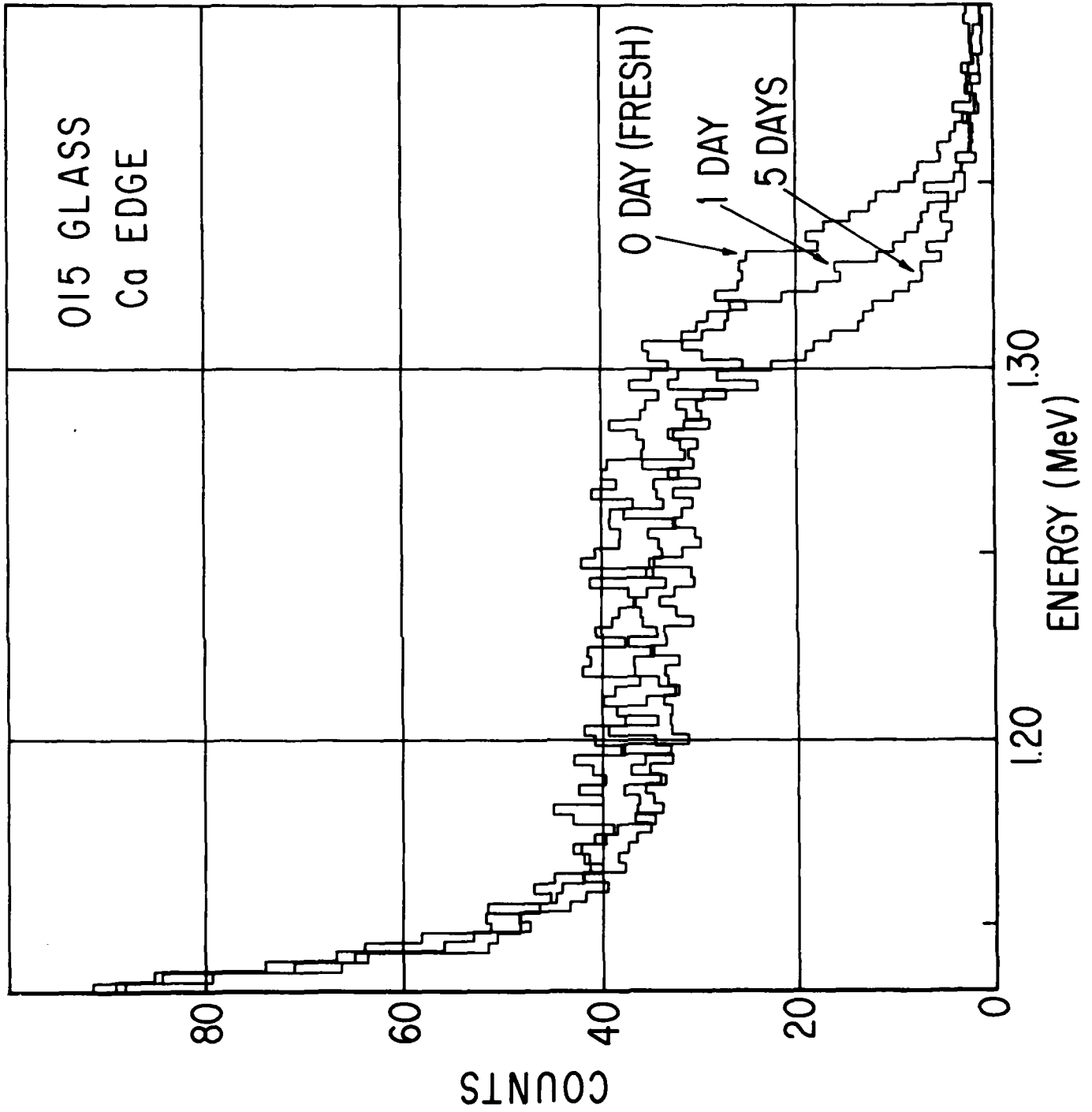


Figure 3

O15 GLASS
90°C pH 7 BUFFER
FROZEN SAMPLE
HYDROGEN PROFILE

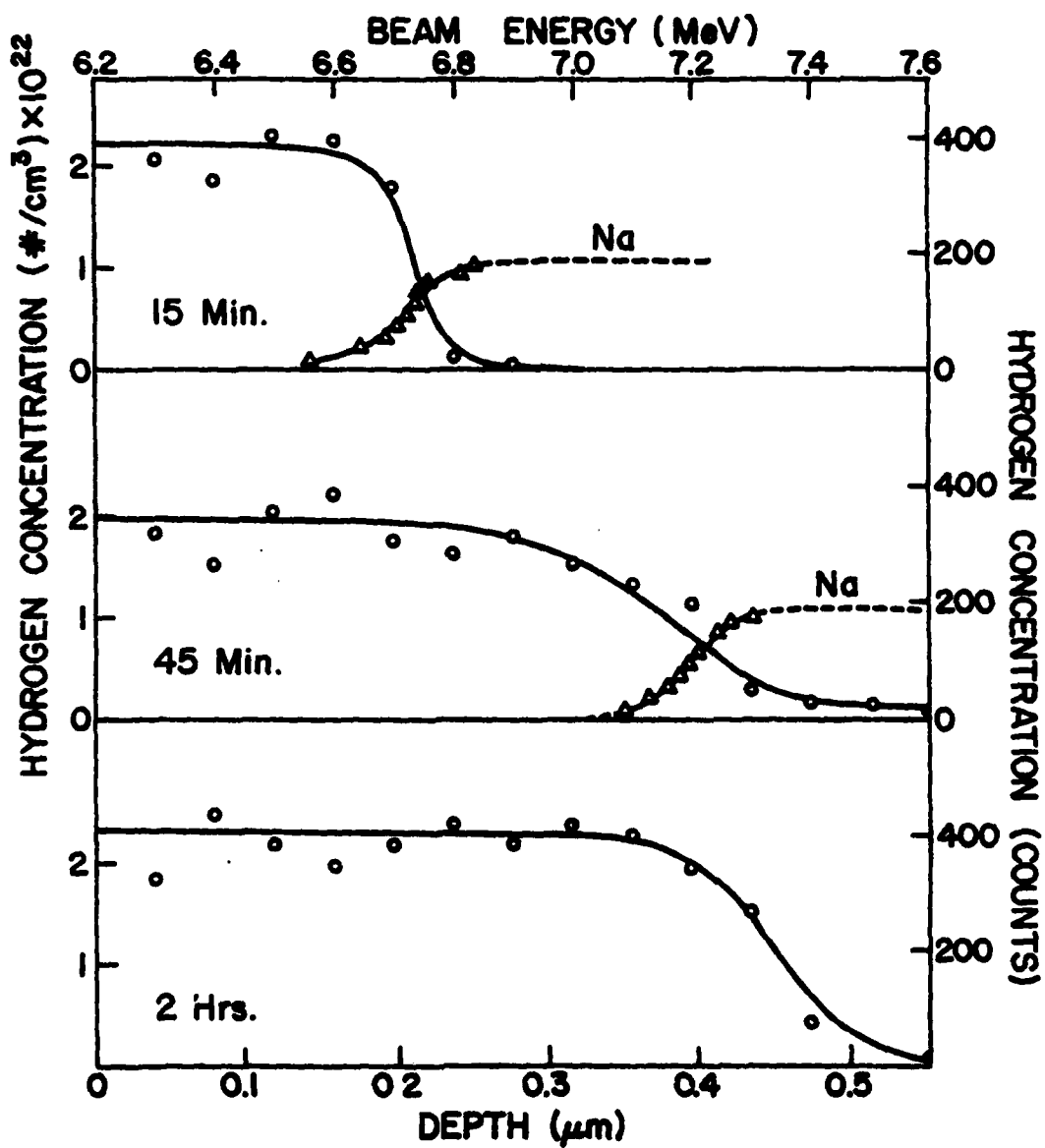


Figure 4

Electromigration Experiments: Varying Anode Conditions.

F.M. Ernsberger (PPG), C. Burman and W.A. Lanford

In the reaction between water and a soda-lime glass the most rapid initial reaction is the exchange of Na^+ ions in the glass with hydrogen ions from the water.

A natural extension of this ion exchange reaction is to electrically drive the hydrogen ions into the glass. By measuring the current voltage data during the electromigration and the resulting elemental profiles, one can deduce individual ionic mobilities. Further, by changing the character of the anode (e.g. by removing the presence of any hydrogen), one can force some of the less mobile ions to move.

One example of this procedure which we are presently studying is the electromigration of a commercial soda-lime glass where in one case we have electrolyzed using a hydrogen rich solution for an anode and in a second case we have electrolyzed using a nearly hydrogen free anode (graphite in vacuum). The voltage-current data are very different in these two cases with the effective resistance of the vacuum electrolyzed sample being larger.

Some of the results of the hydrogen profile and Rutherford Backscattering measurements are given in Figures 1 - 5. The hydrogen data show that when a proton rich anode is used, the electric field sweeps out the Na^+ ions which are in turn replaced by H ions, whereas when the electrolysis is done in vacuum, very little H is available and, hence, little is driven into the glass. Instead, in the vacuum case the Rutherford Backscattering data show that both Na and Ca are driven into the glass.

The question remains: for the vacuum electrolyzed glass in the surface region which has had the Na and Ca ions swept out, what is the current carrier? The results of Jorgensen and Norton⁽¹⁾ indicate that O^- ions may contribute and we are presently attempting to see changes in the oxygen distributions in this glass surface.

Reference

- (1) Jorgensen and Norton, 1965. VII ICG, paper No. 310.

Figure Captions

Figure 1: The backscattering spectrum from an untreated glass.

Figure 2: The backscattering spectrum of a glass electrolyzed with a proton rich anode.

Figure 3: The backscattering spectrum of a glass electrolyzed in vacuum.

Figure 4: The hydrogen profile of a glass electrolyzed with a proton rich anode.

Figure 5: The hydrogen profile of a glass electrolyzed in vacuum.

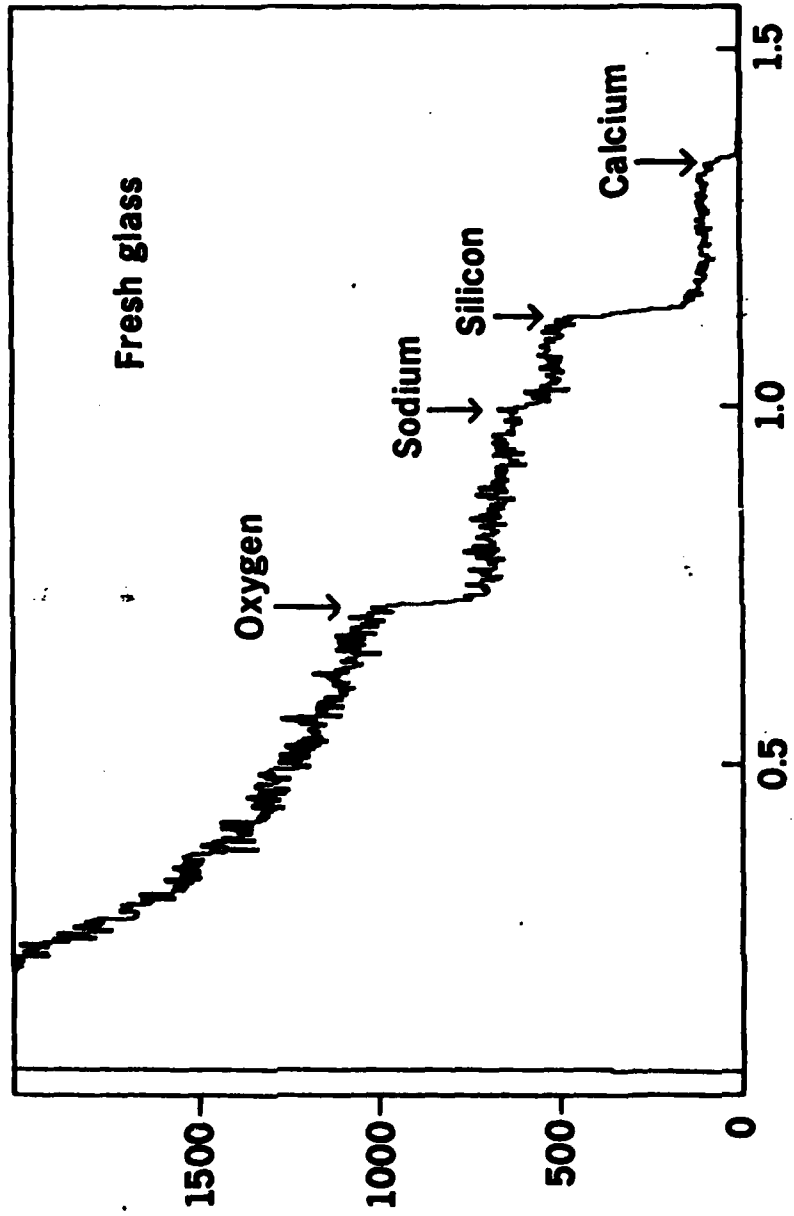


Figure 1

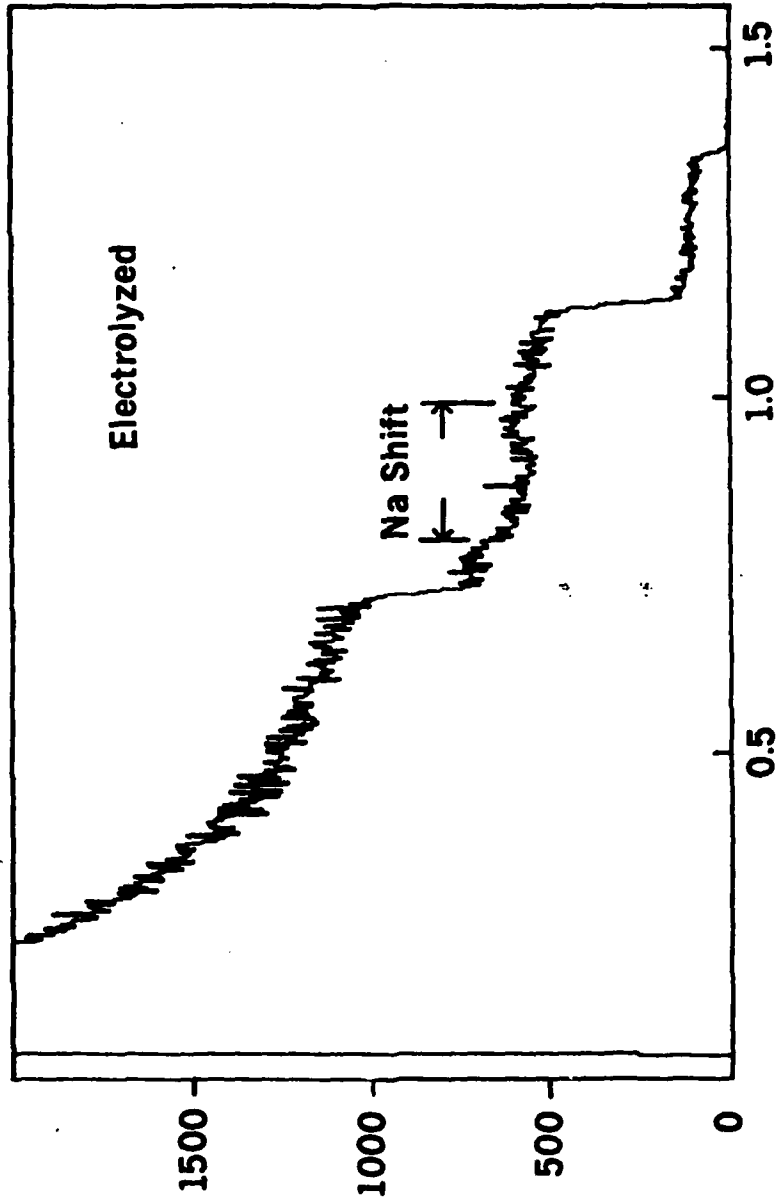


Figure 2

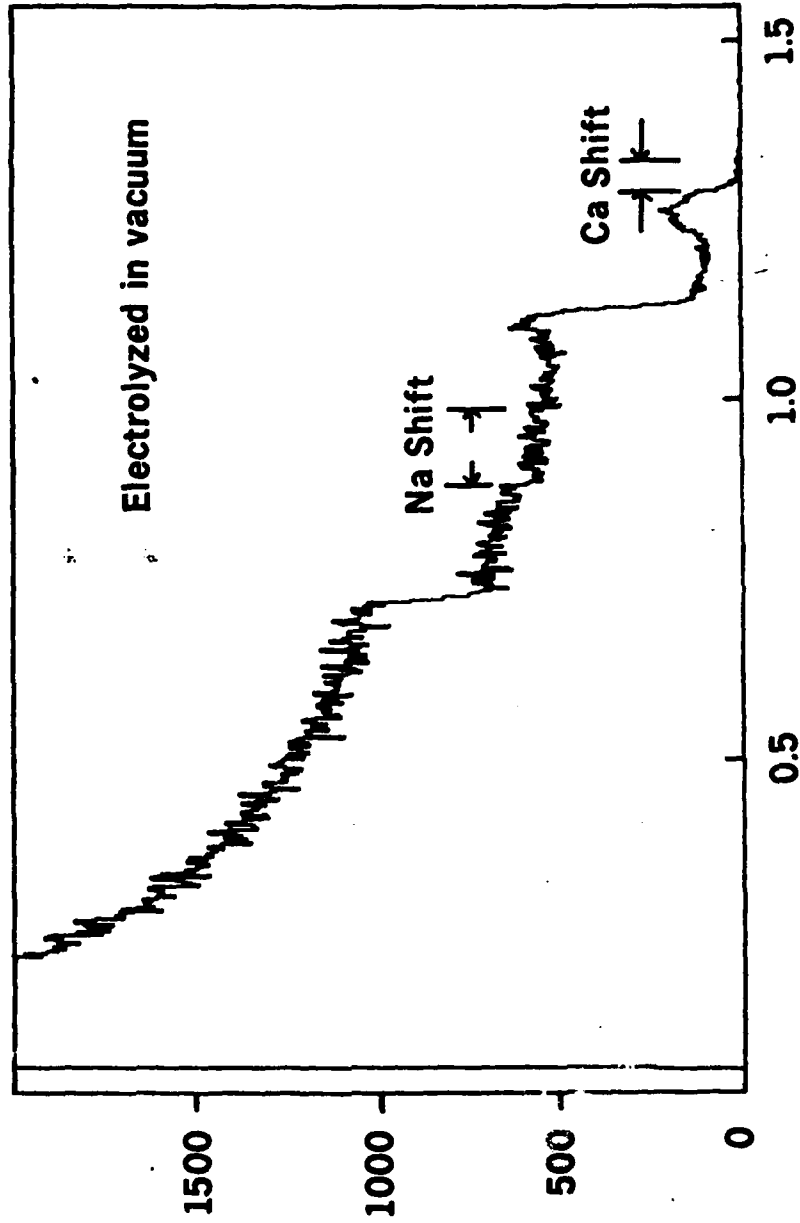


Figure 3

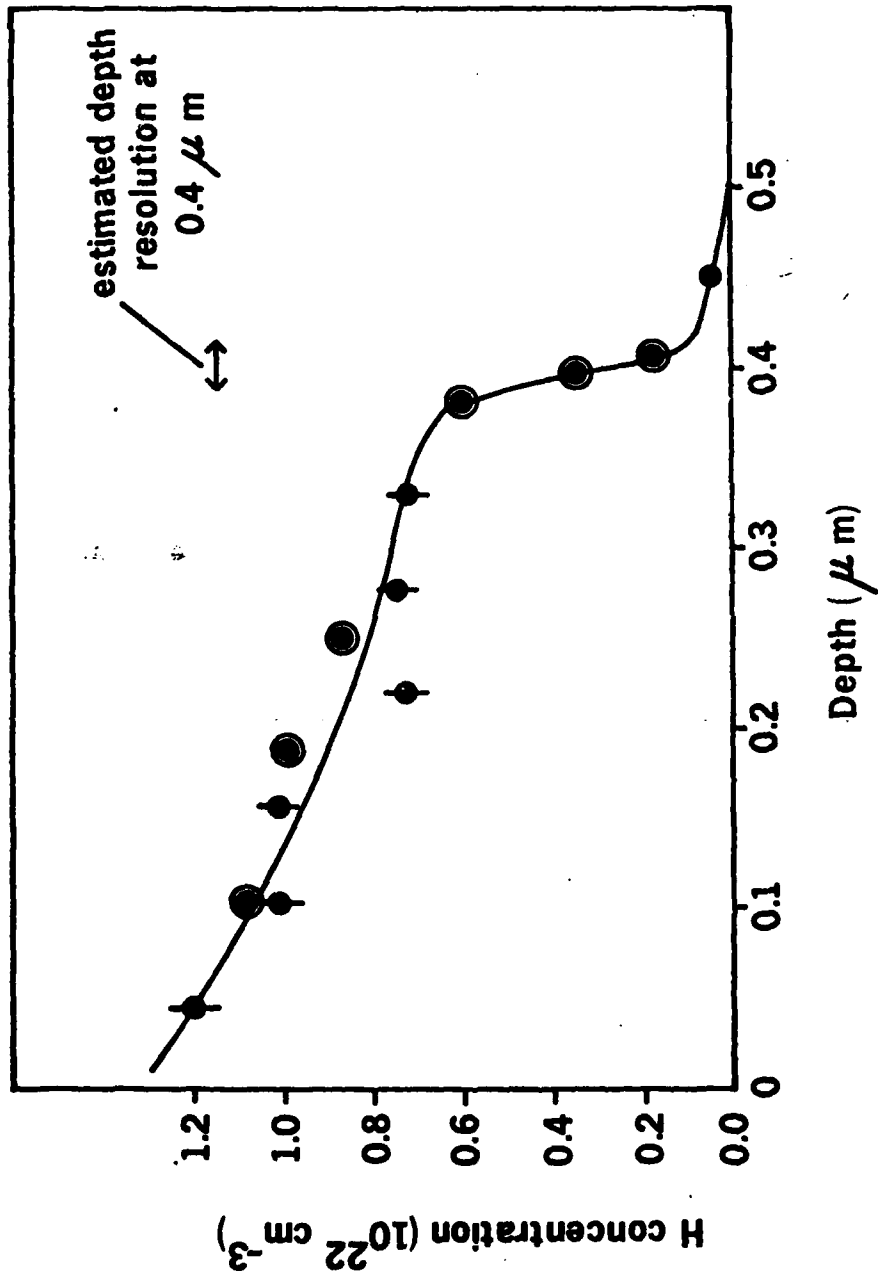


Figure 4

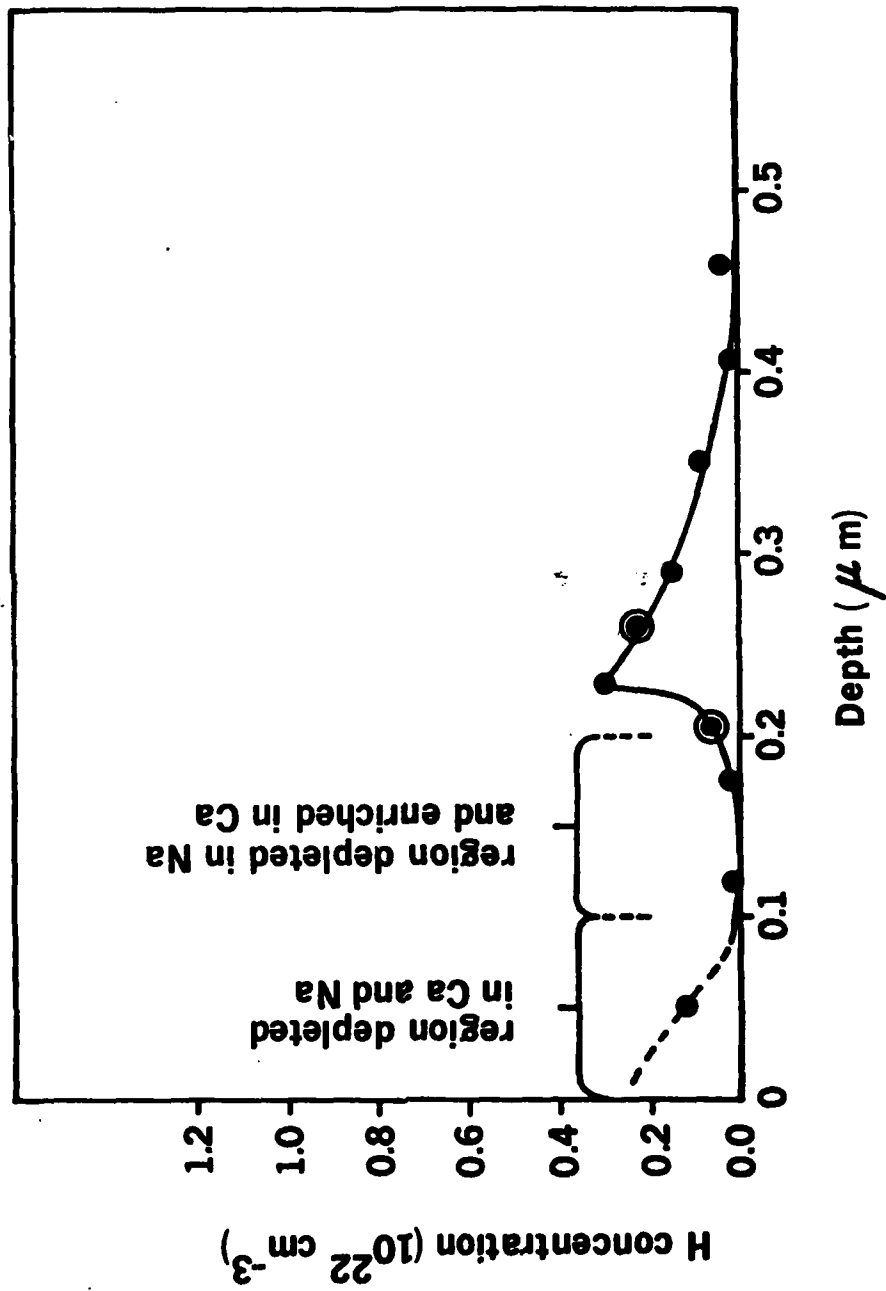


Figure 5

Dissolution of Glasses: The Effects of Salt and
Radiation Damage

C. Burman and W. A. Lanford

When alkali glasses are exposed to water, in addition to the ion exchange reaction a dissolution of the glass also occurs. This reaction is of great intrinsic interest to glass science as well as of great technological importance, especially in the field of radioactive waste disposal.

A program to study the durability of glasses in contact with various aqueous solution has been undertaken. We plan to investigate various factors affecting the dissolution of glasses including composition, radiation damage and the presence of various water soluble compounds in solution. Following is a brief summary of the techniques developed to study the attack of aqueous solutions on glass surfaces and some of the results obtained.

To study the dissolution of the surface we have developed and utilized two techniques.

a) Implantation of a "Marker" in Conjunction with
Rutherford Backscattering.

In this method, fresh glass samples are implanted with some heavy ion, for example, 1 MeV Xe ions at a dose of 2.3×10^{15} Xe/cm². For 1 MeV xenon ions, in commercial

soda-lime glass, the penetration depth is approximately 0.35 μm . This ion implantation serves two purposes. First, it creates radiation damage. Second, it provides a "marker" which in conjunction with the Rutherford backscattering can be used to quantitatively measure the dissolution of irradiated glass exposed to an aqueous solution.

b) Masking Technique.

To study the dissolution rate of unimplanted samples, glass plates are partially covered with a plastic coating. These plates are then treated in aqueous solution at 90°C. After the treatment, the plastic coating is removed. For the cases where glass dissolves during the treatment, a step is present between the coated and uncoated regions. The step height can be measured using a profilometer.

Using the above techniques durability of commercial soda-lime glass was studied. Distilled water and solutions of common salts of various concentrations at 90°C were used. Commercial common salt was selected, because of the proposal to store the waste glass in geological salt formations. Surprisingly we found that even pH neutral salt solutions have an enormous effect on the etch rate of the glass. And this dissolution rate is further enhanced by the radiation damage. Some of these results are summarized in Figure 1.

To understand the mechanism of attack of salt solutions

on glass network, experiments are also carried out using Pyrex and fused quartz glasses. In case of Pyrex we found the dissolution rate comparable to that of commercial soda-lime glass. Whereas in the case of fused quartz, for both virgin and 120 keV Kr implanted samples there is no measurable dissolution in saline for up to 24 hours.

Commercial soda-lime glass samples were also irradiated with 2 MeV electron beams to a dose of 2.5×10^{14} e/cm². For treatments in saline at 90°C, no measurable difference in the etch rate of irradiated samples was found.

Figure Captions

Figure 1 (left): The thickness of glass etched from the surface of a soda-lime glass as a result of various treatments.

(right): The thickness of glass etched from the surface of a soda-lime glass as a result of treatments in saline solutions of various concentrations at 90° for 24 hrs.

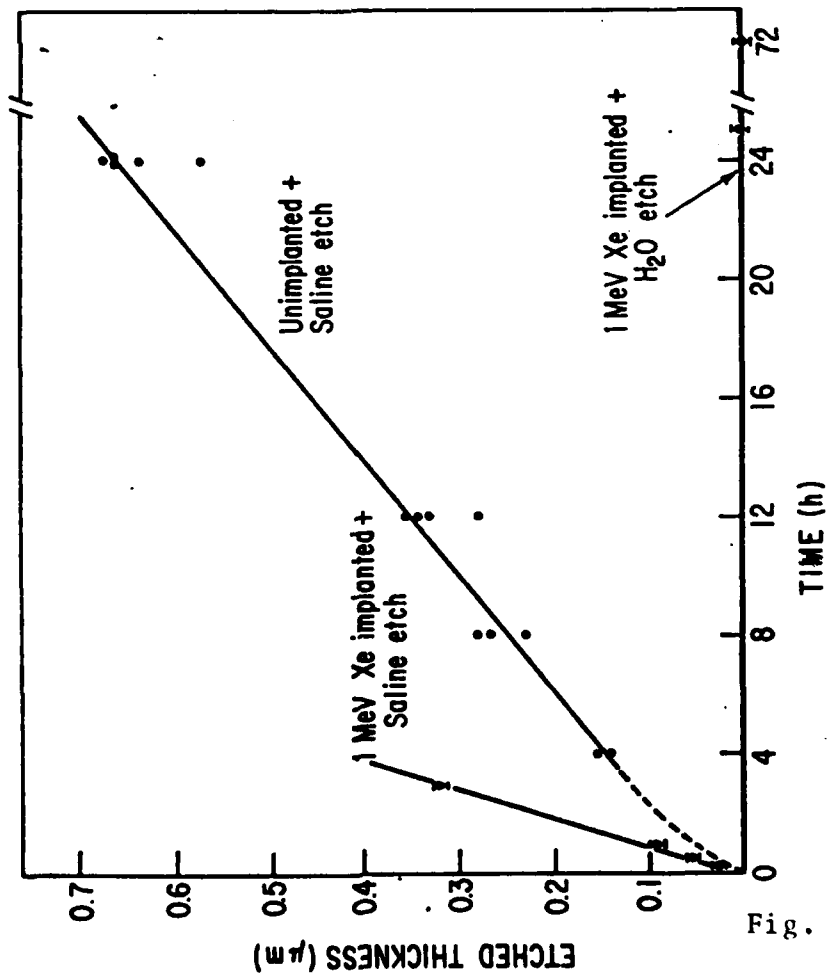
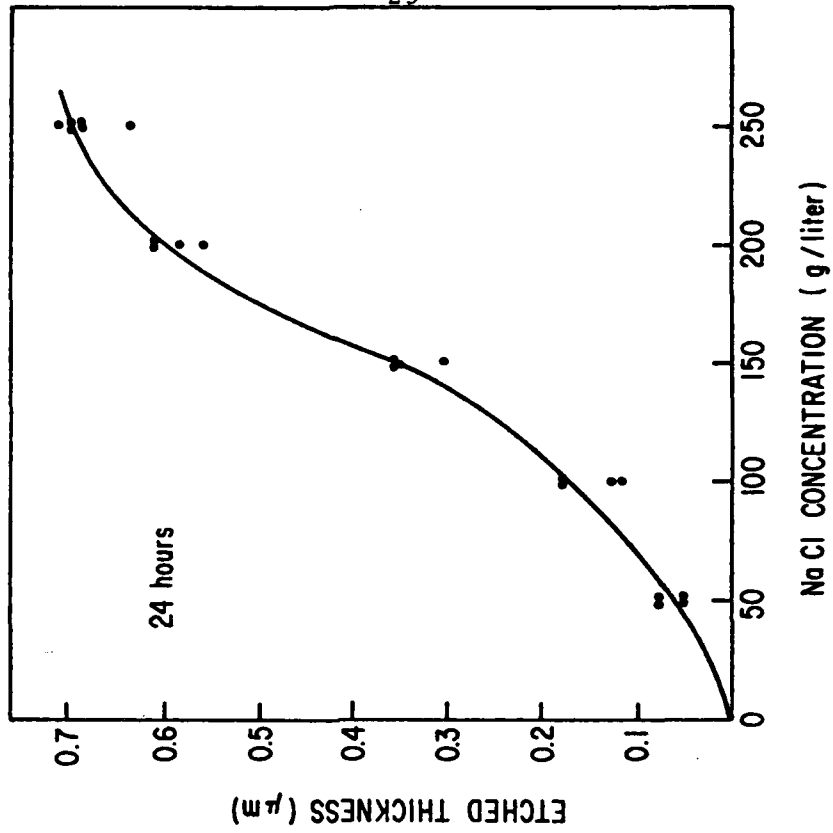


Fig. 1

Reaction Between Water and Tektites.

P. LaMarche (Yale Univ.), F. Rauch (Frankfurt, Germany)

W. A. Lanford

Tektites are naturally occurring glass fragments which are found distributed over large but well defined regions of the earth's surface⁽¹⁾. Within each of these regions (a tektite "strewn field") the tektites are remarkably uniform in chemical composition but their composition seems to bear no relationship to the composition of the local rock. For example, tektites of uniform composition are found scattered over most of Australia, part of the South Pacific and Indochina but such Australasian tektites are not found anywhere else on earth. Based on K-Ar and fission track dating, the Australasian tektites appear to be about 0.7 million years old. Perhaps the single most striking feature of tektites is that occasionally they are found with intricate aerodynamic shapes indicating that they passed through the air at very high velocity.

The origin of tektites is hotly debated. The main point of controversy is over whether they are extraterrestrial (if so, probably lunar) or result from some violent act, such as meteoric impact, on earth. O'Keefe has recently suggested that whatever their source, in addition to those falling to earth, many more may have been trapped in an earth orbit.

These orbiting tektites could form equatorial rings, the shadows of which would cause dramatic climatic changes. O'Keefe pointed out that just such a climate change (the end of the Eocene) occurred at just the same time as the formation of the North American strewn field.

The present research deals with the question of what happens to these glass objects as they lie on the earth's surface for very long times. One question is: Why don't tektites appear to hydrate as do other glasses, such as obsidian or man-made glass⁽²⁾?

A second question has to do with the rate with which ground waters dissolve tektite glass. Very little is known about the very slow dissolution processes which would be sufficient to alter grossly the appearance of glasses exposed to ground water for a million years (or longer). Some have suggested that tektite glass is remarkably durable and has not been significantly etched during its existence on earth. The existence of delicate flanges and other aerodynamic features on tektites from Australia is cited as evidence for no etching. Others have suggested that on most tektites, their sculptured shapes resulted largely from etching by ground water.

To answer some of these questions, we have carried out experiments patterned after our investigations of the reaction between water and obsidian and between water and man -

made glass. We were particularly interested in the suggestion that for some reason tektite glass was much more durable than other glasses. Confirmation of this would have important consequences in fundamental material science and in such technologically important problems as the consolidation and isolation of radioactive wastes from nuclear reactors.

Some of the results of this investigation are shown in Figure 1. Under the same conditions as we used to hydrate both obsidian and man-made glasses (distilled water at 90°C) tektites indeed do not hydrate, i.e. a surface layer of glass containing hydrogen is not formed. One of the reasons for this appears to be the rather small alkali content of this glass relative to the others we have studied. A second observation is that etch pits are observed on the surface of the obsidian and the radius of these etch pits grow linearly with the length of time the tektite are exposed to water. See Figure 1.

References

1. J. A. O'Keefe, Tektites and Their Origin, Elsevier (New York) 1976.
2. T. Laursen and W. A. Lanford, Nature 276 (1978) 153.

Figure Caption

Figure 1: The thickness of tektite glass etched from
the surface vs time.

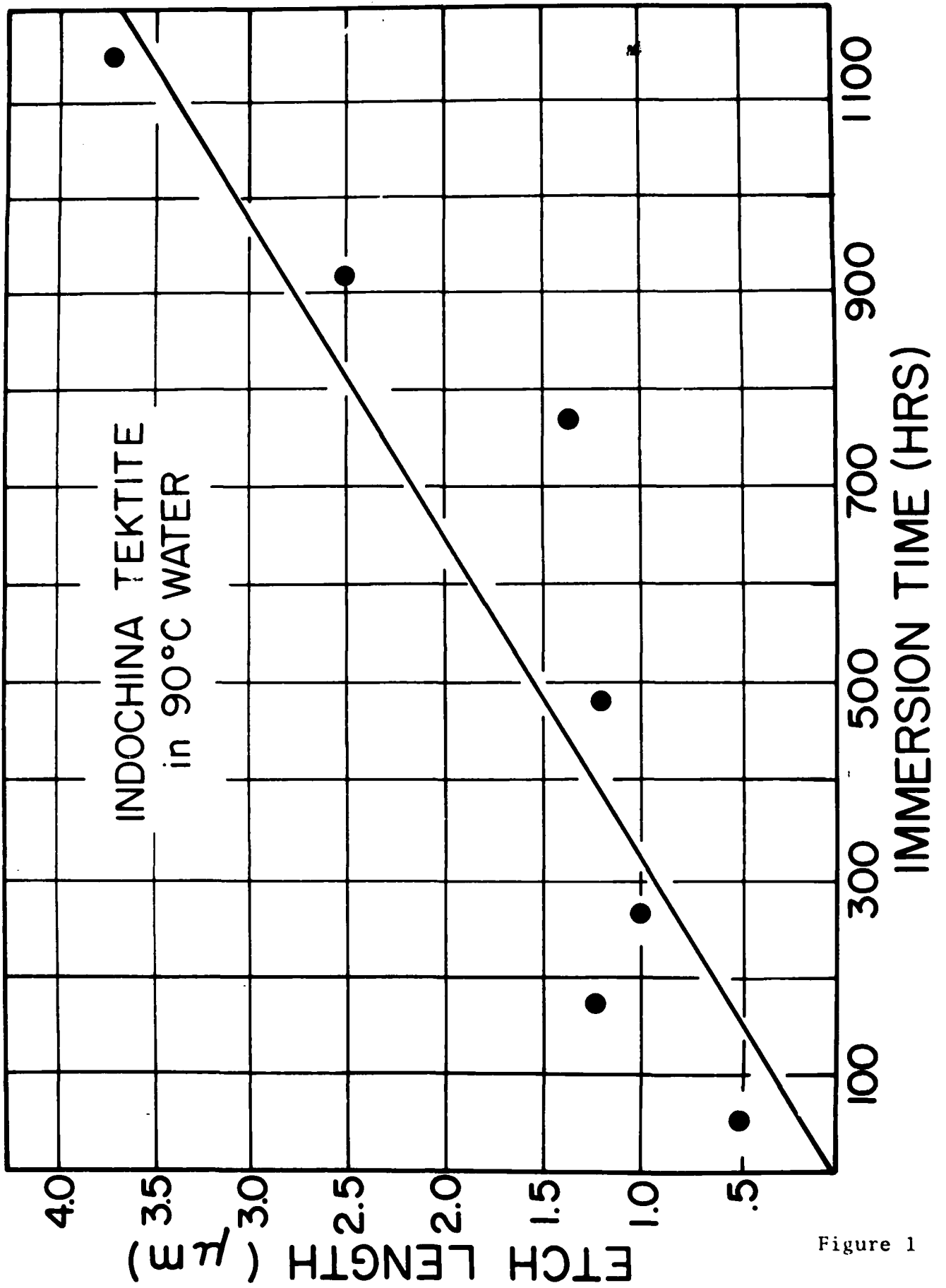


Figure 1

Permeation Kinetics of Water in SiO₂ Films.

R. Pfeffer, R. Lux, H. Berkowitz (U.S. Army, Fort Monmouth),

C. Burman, Wang Ke-Ming and W. A. Lanford

Because of their commercial importance and because of the richness of different phenomena available to experimentation, most of our work is centered on the study of the reaction between water and alkali glasses. However, it is clearly important for both fundamental reasons and for important applications (e.g. electronics) to understand the reaction between water and pure SiO₂. To do this we have been measuring hydrogen profiles in thin (2600 Å) films of SiO₂ grown (presumably dry) on silicon. These SiO₂ films have been exposed to steam at temperatures from 250°C - 600°C for various times.

The quantitative measurement of H profiles for these samples turned out to be more difficult than anticipated. Because of the relatively small amount of H incorporated in SiO₂ by this treatment (10^{20} H/cm²) and because of the desire for quantitative profiles to be fit with theoretical models, we had to increase the sensitivity of the ¹⁵N hydrogen profiling technique beyond that normally utilized. We spent a great deal of time tracing down sources of background and increasing the ¹⁵N beam intensity; both of these required modification of our accelerator.

Shown in Figure 1 are some typical hydrogen profiles for these films. Included here are the hydrogen profiles of an unoxidized silicon wafer, an SiO_2 film on silicon which had not been exposed to steam and a steamed SiO_2 film. We have measured H profiles on a large number of such films and are in the process of trying to understand these profiles with various models.

Figure Captions

Figure 1: Hydrogen profiles of an untreated Si wafer,
a dry SiO₂ film and a steam treated SiO₂ film.

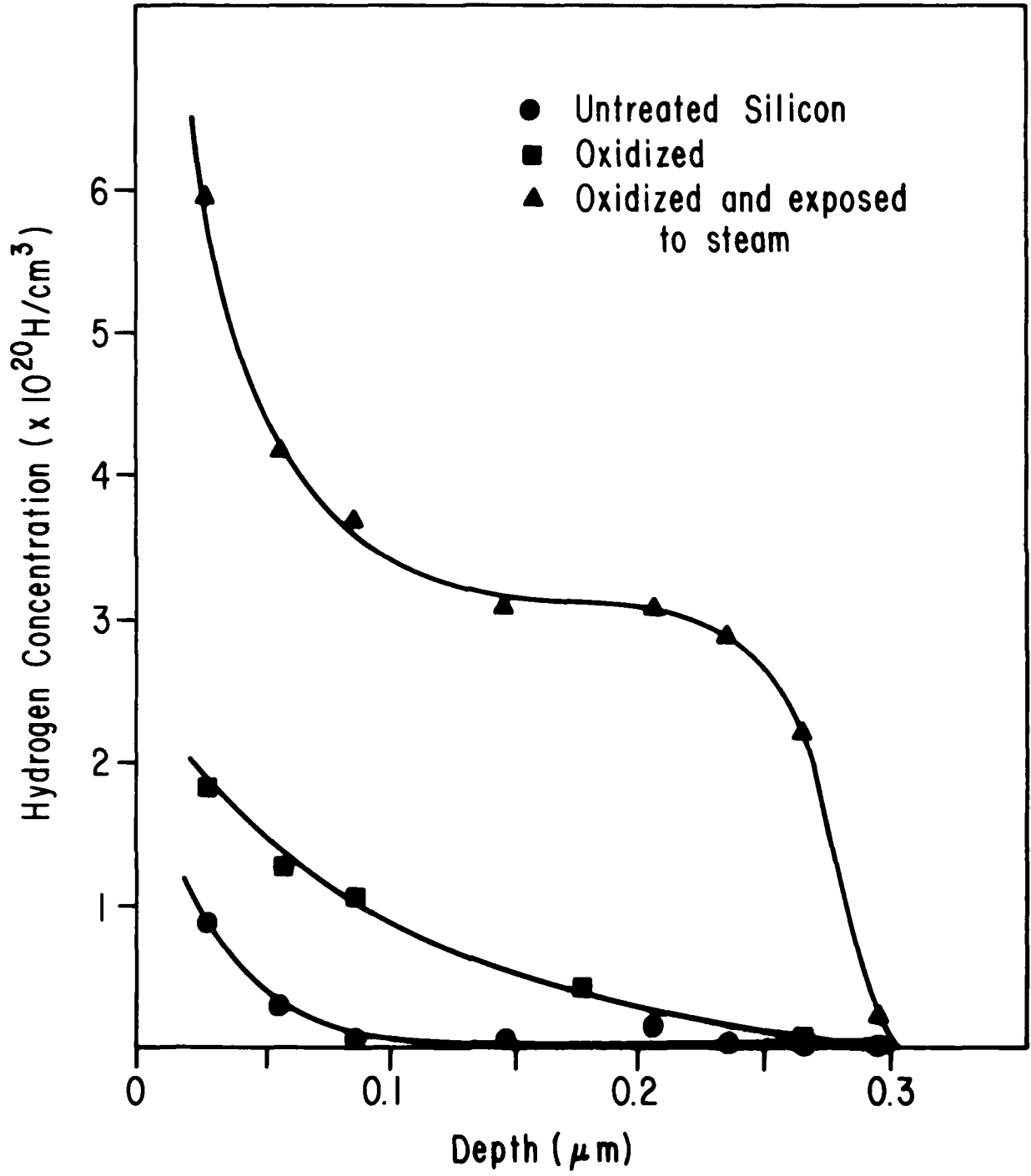


Figure 1

Hydrogen Isotope Experiments

C. Burman and W. A. Lanford

Attack of water on silicate glasses containing alkali ions involves three steps. First, hydrogen ions from the solution exchange with alkali ions present in the glass. Second, there is a partial hydration of the silicon oxygen network of the glass. Third, the solution can dissolve the glass. As a result of exposure to water a layer of hydrated glass is formed on the surface of the glass, which is characterized by the absence of alkali ions and the presence of hydrogen.

In an attempt to understand further the transport patterns of hydrogen into the glass, we have started measurements exposing glasses to H_2O followed by D_2O and vice versa.

As compared to ^{15}N resonance for hydrogen, which has a sharp resonance at 6.4 MeV giving 4.43 MeV gamma-rays, the interaction between ^{15}N and deuterium gives rise to gamma-rays greater than 4.43 MeV and there are no sharp resonances. Hence, the number of gamma-rays greater than 4.43 MeV gives a measure of the total amount of deuterium in the sample.

To evaluate the feasibility of the method, the following measurements were carried out.

One set of soda-lime glass samples was hydrated for 23

hours at 90°C in water and another set was hydrated in heavy water (D₂O). A sample from the first set was subsequently hydrated in heavy water, and a sample from the second set was hydrated in H₂O.

These samples were analyzed with ¹⁵N beam monitoring gamma rays for energies greater than 4.43 MeV along with the 4.43 MeV gamma-rays. Some of the results are shown in Figure 1. The presence of gamma rays greater than 4.43 MeV indicates presence of deuterium in the layer. For the sample treated with D₂O we see >4.43 MeV gamma-rays. Whereas for the sample which was further treated in H₂O we find the absence of deuterium in the hydrated layer, indicating a rapid exchange of deuterium with the hydrogen.

Figure Caption

Figure 1(a,b): Yields for 4.43 MeV and >4.43 MeV gamma-rays
as a function of ^{15}N beam energy.

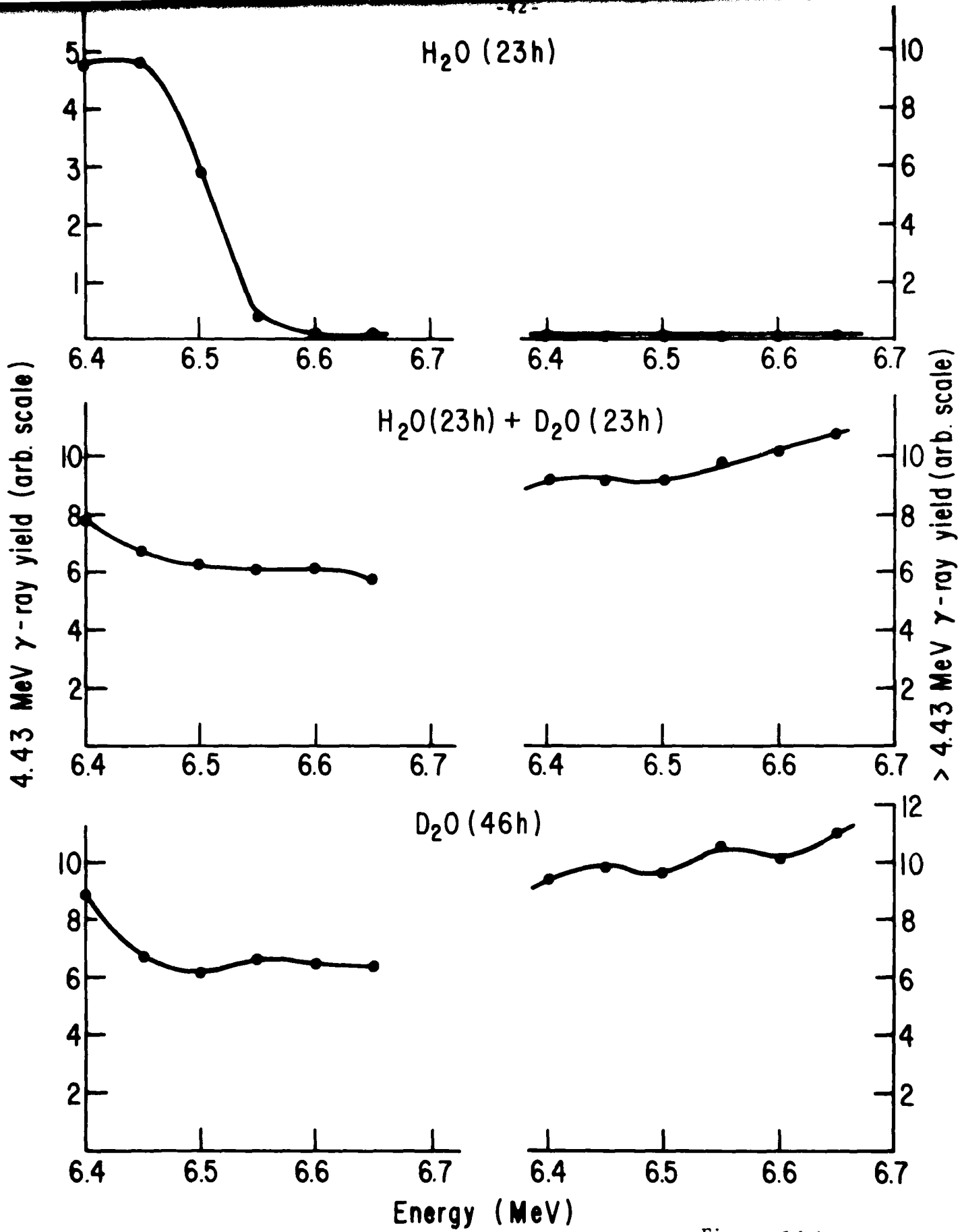


Figure 1(a)

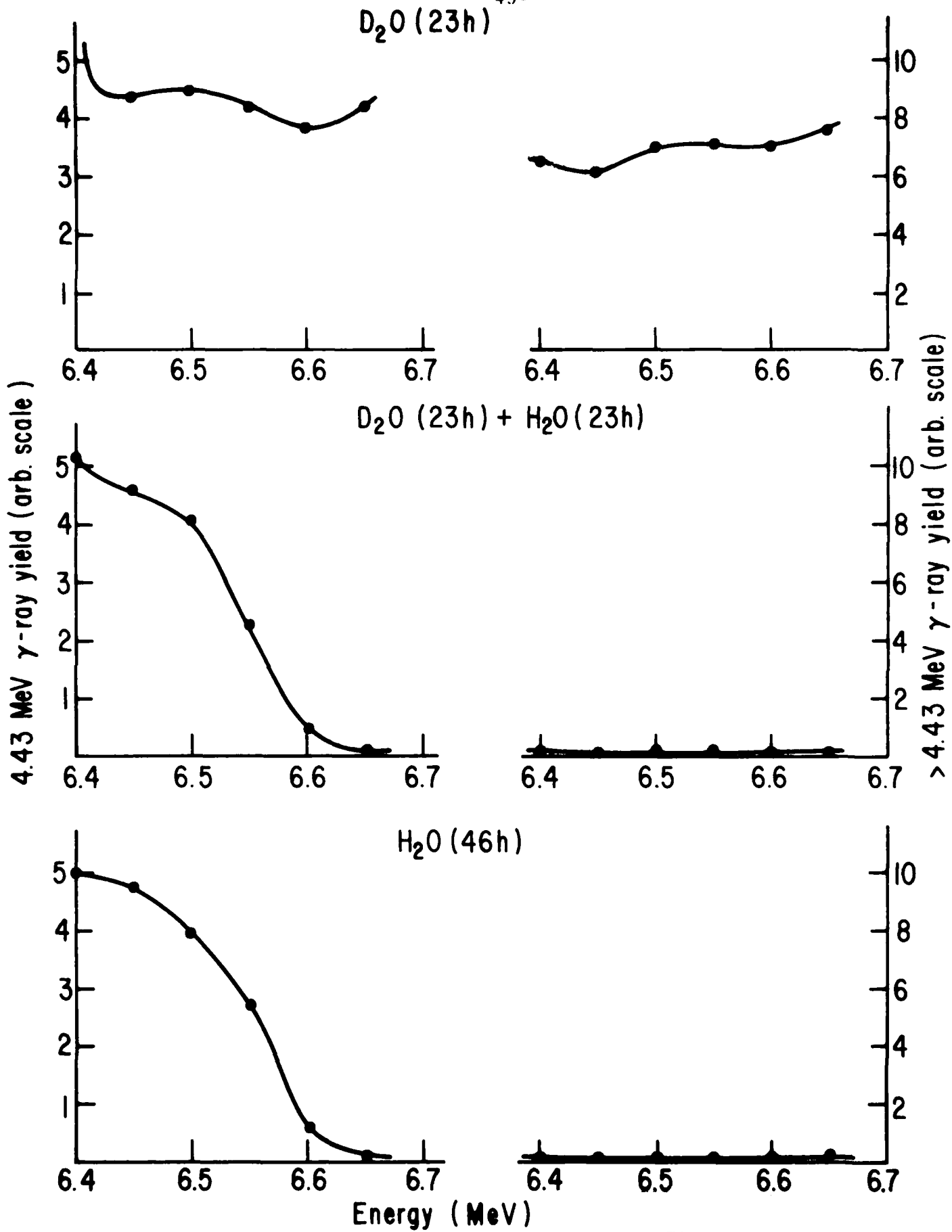


Figure 1(b)

Reaction Between Water and β -Alumina

W. Roth, C. Burman, Wang Ke-Ming and W. A. Lanford

β and β'' alumina ceramics are of intense interest because of their extremely high Na ionic conductivities which suggest their use as a solid electrolyte for high energy density batteries. While they might appear to be very different from typical alkali glasses in that β -alumina is polycrystalline and not amorphous, in fact, β -alumina shares a great deal in common with glasses. Most importantly, both are good ionic conductors with virtually no electronic conduction. As such, one would expect the Na^+ hydrogen ion exchange mechanism which is so important in water glass reactions to be important in the reaction between β -alumina and water. Hence we have just begun measurements on β -alumina similar to those carried out on alkali glasses.

One of the exciting prospects of this work is that because β -alumina is crystalline, diffraction studies of its detailed structure can and have been carried out. By comparing our nuclear reaction profiling results with the results of the great assortment of complementary measurements already available in β -alumina, we hope to learn more about hydrogen ion and water transport in both β -alumina and in glass.

Shown in Figure 1 are some of our first hydrogen measurements which show that even heating this material to 400°C for 24 hours is not sufficient to remove all the water (hydrogen) from the material.

Figure Captions

Figure 1: Hydrogen profiles of a variety of β -alumina samples treated in various ways.

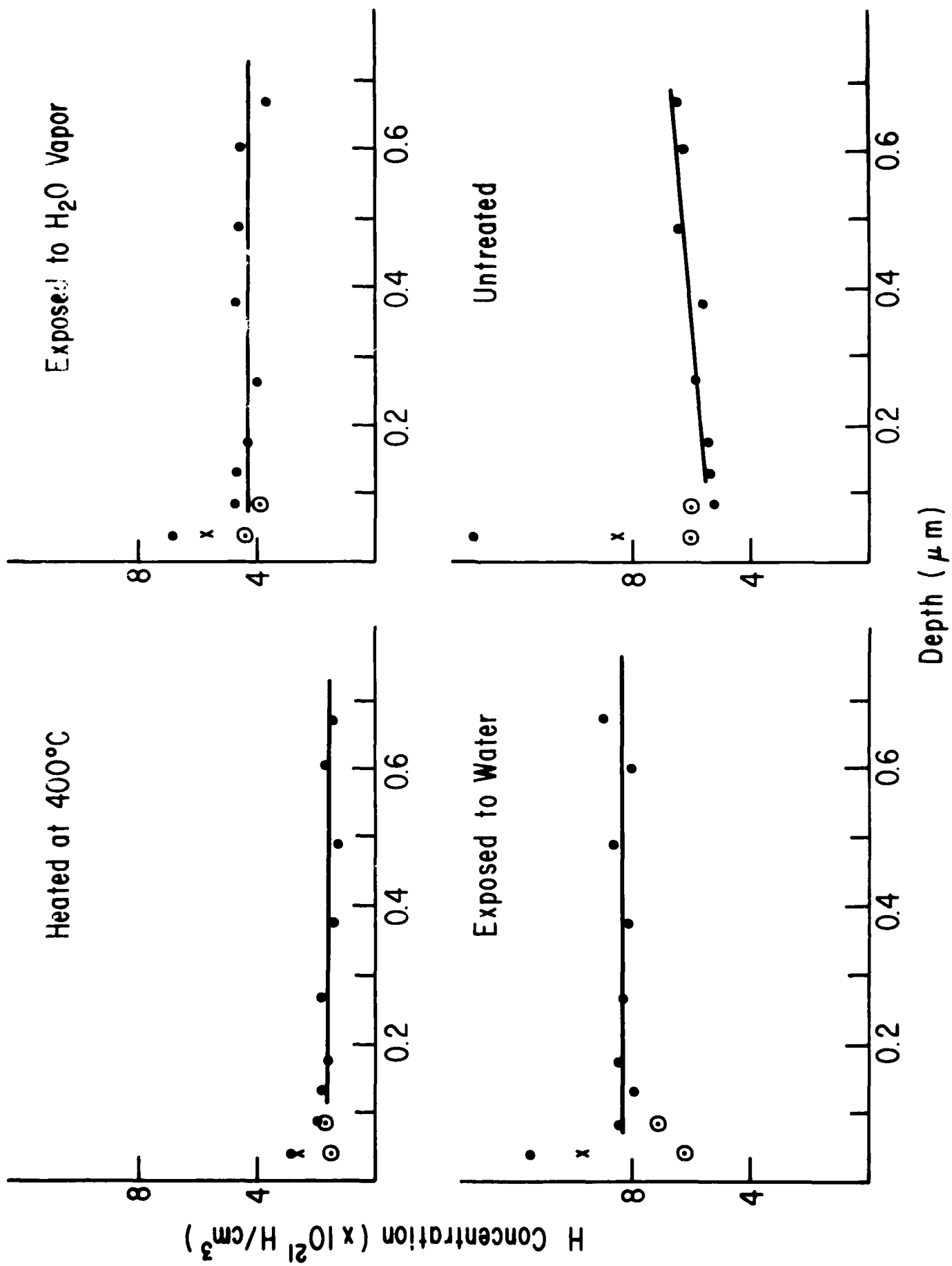


Figure 1

Study of SO₃ Treatment of Soda-Lime Glass

R.H. Doremus(RPI)

P. Anderson and R. Downs (KMS)

C. Burman and W.A. Lanford

It has been known for a long time that the chemical durability of soda-lime glasses can be significantly improved by treatment of the hot glass by SO₂ or SO₃ in the presence of steam. We have been studying the process in an attempt to understand the detailed mechanisms responsible for these beneficial changes.

We have carried out measurements of the hydrogen concentration vs depth in treated and untreated glass and Rutherford backscattering measurements to determine changes in the concentration profiles of other elements as a result of SO₃ treatment. These measurements show that little hydrogen is incorporated into the glass but the Na is completely removed from the surface. One might have anticipated that the de-alkalization was accompanied by incorporation of hydrogen in order to maintain charge neutrality in the surface layer. To understand the lack of large amounts of hydrogen, we have started hydrogen profile measurements of glasses which were first treated in water to induced Na-ion \leftrightarrow hydrogen ion exchange then, subsequently, annealed at various temperatures. These preliminary data indicate that the hydrogen incorporated in glass by low temperature water treatments is removed by heating with some of this hydrogen diffusing deeper into the bulk glass

and some of it leaving the glass, presumably in the form of water.

Therefore it is possible that in the SO_3 -treated glass hydronium-sodium ion exchange takes place just as at lower temperatures in water, but after exchange the hydronium ion and the SiOH group decompose to form water, which diffuses out of the glass.

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