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NNWSI WASTE FORM TESTING AT ARGONNE NATIONAL LABORATORY SEMIANNUAL REPORT JULY-DECEMBER 1987

J. K. Bates
T. J. Gerding
W. L. Ebert
J. J. Mazer
B. M. Biwer

Work Performed at
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439-4837

July 1988

Lawrence Livermore National Laboratory

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NNWSI WASTE FORM TESTING AT ARGONNE NATIONAL LABORATORY

Semiannual Report, July-December 1987

John K. Bates, Thomas J. Gerding, William L. Ebert,
James J. Mazer, and Bruce M. Biwer

ABSTRACT

Tests are ongoing at Argonne National Laboratory to examine the reaction of glass with water under conditions that may exist in the proposed repository at Yucca Mountain, Nevada. Examination of glass reaction using the Unsaturated Test method as applied to simulated defense glass (SRL 165 black frit based) and simulated West Valley glass (ATM-10) is ongoing. The tests on SRL 165 glass have been ongoing for 104 weeks with non-stoichiometric release of Li, Na, B, and actinide elements being observed throughout the test period. The tests on ATM-10 glass have been in progress for 26 weeks and it is too early in the test cycle to assess the glass reaction.

The influence of penetrating gamma radiation on the reaction of synthetic nuclear waste glasses in tuff groundwater was also investigated. Modified MCC-1 static leaching experiments were performed under radiation exposures of 1×10^3 R/h and 0 R/h at 90°C. The groundwater was acidified by nitrous and nitric acids radiolytically produced in the air. The high bicarbonate ion concentration of the groundwater prevented the pH from dropping below 6.4, however. The glass reaction, as measured by the release of glass species and the thickness of an alteration layer formed on the glass surface, was not measurably affected by radiation. The leachate pH and Eh had a minor influence on the distribution of several released species between sorbed and dissolved phases. Conditions in the repository, namely high air/groundwater ratios, may lead to groundwaters being acidified below a pH of 6.4 if free exchange with $CO_2(g)$ does not exist. Such acidifications may affect glass reaction and eventual radionuclide release.

Finally, a preliminary matrix of experiments is in progress to determine the effect of water vapor on glass reaction. These preliminary experiments are designed to establish a method of reproducibly "aging" the glass, so that the effect of vapor reaction on eventual radionuclide release via leaching can be established. The preliminary experiments indicate the aging process continues as a function of time and that the extent of reaction in vapor, as measured by the thickness of the reacted layer on the surface of the glass, can be greater, equal, or less than that observed in liquid water at equivalent times and temperatures.

I. NNWSI WASTE FORM TESTING

The Nevada Nuclear Waste Storage Investigation (NNWSI) Project is investigating the tuff beds of Yucca Mountain, Nevada, as a potential location for a high-level radioactive waste repository. As part of the waste package development portion of this project, which is directed by Lawrence Livermore National Laboratory, experiments are being performed by the Chemical Technology Division of Argonne National Laboratory to study the behavior of the waste form under anticipated repository conditions. These experiments include (1) the development and performance of a test to measure waste form behavior in unsaturated conditions, (2) the performance of experiments designed to study the behavior of waste package components in an irradiated environment, and (3) the performance of experiments to investigate the reaction of glass with water. Previous reports [STEINDLER; BATES-1-4] document developments in these areas through June 1987. This report summarizes progress during the period July-December 1987.

Efforts this period have focused on analyzing components from the N2 Unsaturated Test series, writing a topical report describing the N2 test results, and performing the N3 Test series using ATM-10 glass. Experiments studying the effect of gamma radiation (1×10^3 and 0 rad/hr) on groundwater composition and SRL 165 type glass reaction have been completed and the results from these experiments have been compiled and the components analyzed. Experiments at 0 Rad/hr using ATM-1c and ATM-8 glasses that are being done to be compared with previous experiments done in a radiation field, have been completed through 182 days and the results have been sent to LLNL to see if they are amenable to modeling. Parametric experiments evaluating physical factors such as relative humidity on glass reaction, the composition and formation of reacted layers in natural glasses, the disposition of transuranic elements in reacted layers and the effect of sensitization on glass reaction are ongoing, and selected results are presented in this report.

A. NNWSI Unsaturated Test Method

1. NNWSI Unsaturated Test Method Development

The method is being used in the N2 and N3 test series. No new additional method development work has been done.

2. N2 Unsaturated Test

The Unsaturated Test method has been developed to study materials interactions (water/waste form/metal/air) that may occur in an unsaturated environment and to provide a measure of radionuclide release from a waste package assemblage (WPA) consisting of the waste form and metal components of the waste package. During the test, water is dripped periodically on the WPA and the extent of reaction is monitored by periodically sampling the test solution and by carefully examining the waste form and metal components upon termination of the test.

At this point the N2 continuous tests have been completed through the 104-week sampling period. All the batch tests have been completed, and three continuous tests and one blank are ongoing. A description of the test method and results through 65 weeks have been compiled into a topical report [BATES-5] and a MRS Symposium presentation [BATES-6]. Highlights and conclusions for this test series are presented below.

Glass Reaction

The extent of glass reaction is best measured by monitoring elements whose presence in solution can be associated mainly with the glass, as opposed to the EJ-13 water or the metal components of the system. Such elements include Li, U, ^{237}Np, ^{239}Pu, ^{241}Am, and B.

Blank corrected solution results demonstrate several things:

(1) All elements except Si show a net release from the glass. Silicon shows a net release in both 26-week batch tests and one 39-week batch test, but is depleted from solution in the remaining tests.

(2) An intercomparison of the batch test results indicates an apparent trend of increasing reaction for the 13- to 26-week tests. However, in the 39- and 52-week tests, the release value for Li and Na are comparable with the 26-week values, while the glass reaction as measured by B release and weight loss is actually less than for the 26-week results (Fig. 1).

(3) Normalized release values, calculated to compare the release behavior of different elements, indicate the alkali elements Li and Na are released from the glass at

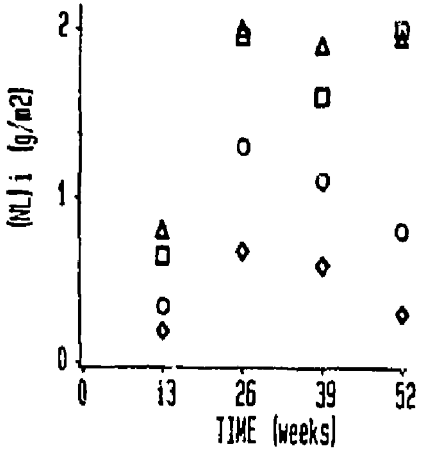

Fig. 1. Normalized Release of (△) Li, (□) Na, (○) B, and (◇) wt loss for the N2 Batch Tests

nearly equivalent rates which are larger than that calculated for B or the actinide elements (Fig. 1 and Table 1). Normalized release values are calculated based on the total surface area of the glass and on the measured amount of each element released from the waste package assembly (WPA) after rinsing. However, if the amount of Pu, Am, and U remaining with the metal components of the WPA is measured via complete stripping (Table 1) of the metal, and it is assumed that the release of these elements is associated mainly with the end sections of glass that contacts metal, then a modified $(NL)_{Pu,Am}$ can be calculated (Table 1). These modified Pu and Am release values are between 25 and 50 times larger than these released based on total surface area, and are approximately the magnitude of $(NL)_{Np}$ based on total surface area.

Table 1. Normalized Release[a] of Actinides from Unsaturated Test

Test Period (Weeks)	Solution Only				Solution + Acid Strip	
	$(NL)_{Np}$	$(NL)_{Pu}$	$(NL)_{Am}$	$(NL)_{U}$	$(NL)_{Pu}$	$(NL)_{Am}$
13	0.2	0.008	0.008	0.01		
13	0.4	0.015	0.018	0.06	0.3	0.4
26	1.3	0.024	0.022	0.21		
26	2.0	0.028	0.028	0.19	0.7	1.1
39	1.3	0.024	0.020	0.42		
39	0.4	0.008	0.008	0.04	0.5	0.7
52	0.6	0.014	0.012	0.18		
52	0.8	0.026	0.015	0.12	0.6	0.7

[a] The entire surface area of the glass was used to calculate $(NL)_i$ for the solution only results, while only the surface area of the end sections of the glass were used in the Solution + Acid Strip calculations. The units for the $(NL)_i$ values are g/m^2.

In the continuous tests, where the components have not been rinsed before the solution is analyzed, several elements, including Ca, Mg, Na, and Si, are depleted in the analyzed solution compared to the starting EJ-13 water. Normalized release values for Li in the continuous tests are plotted in Fig. 2. While these values will be slightly lower than the batch tests due to the lack of a rinse component, it is seen that there is continuous release from the glass through the 65-week time period.

Solution Composition

The composition of the solution that is in contact with the WPA can be estimated from the results of the continuous tests (Fig. 3). After 65 weeks the concentration of Li is still decreasing while the concentrations of Na, Si, Ca, and B have leveled off.

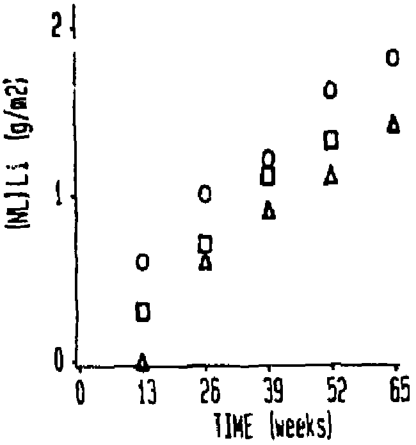

Fig. 2. Normalized Release of Li for Three Continuous Tests in the N2 Test Series. The values for each individual test are represented by the three separate symbols, (○) N2 #9, (□) N2 #10, and (△) N2 #12.

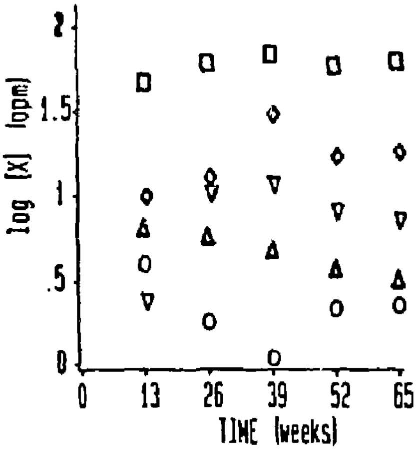

Fig. 3. Log of the Concentrations of (□) Na, (◇) Si, (▽) Ca, (△) Li, and (○) B in the Test Solutions for the Three Continuous Tests in the N2 Unsaturated Test Series

Analysis of Test Components

To characterize the interactions that have occurred during testing, the components of the batch tests have been examined using SEM/EDS and XRD. The purpose of such characterization is to (1) provide a description of the reaction progress independently of the solution results; and (2) catalog and identify alteration products that form during the course of the reaction.

Glass

The major accumulation of reaction products occurred in the regions of standing water around the circumference of the punched holes that are present in the metal retainers. These products were identified by XRD as FeOOH and ferrihydrate ($5Fe_2O_3 \cdot 9H_2O$). Silicate phases rich in either Fe, Cr, Ni, or Mn were also observed but were not as prevalent as the iron oxide phases. Other phases identified on the surface by XRD and SEM/EDS included gypsum, $CaSO_4 \cdot 2H_2O$, SiO_2 cristobalite, orthoclase ($KAlSi_3O_8$), and possibly a sodium feldspar ($NaAlSi_3O_8$). Many other accumulations of reaction products were identified often with non-uniform compositions. These groups were amorphous to XRD and consisted of Si, Ti, Ca, Mg, Cl, and S in varying amounts. Other phases had unique compositions, but were either too small to analyze with XRD or gave amorphous patterns.

Metal

The metal in contact with glass was covered with an amorphous coating rich in Al and Si. Few distinct phases were observed in the glass/metal interface region. Most of the alteration products accumulated in areas of standing water and were identified as iron oxides. Several crystalline phases were observed on the metal including a solid solution of the calcite-type structure $Ca_{.74}(Mn,Mg)_{.26}CO_3$. Other alteration products were too small to identify using XRD analyses.

After surface analyses the metal samples were acid stripped to remove actinides, cross-sectioned, epoxy mounted polished, and subjected to an oxalic acid etch to determine the extent of sensitization that had been imparted during heat treatment. The metal sections were purposefully heat treated prior to testing to simulate conditions that will occur when glass is poured into metal canisters during processing.

Two distinct levels of sensitization were imparted to the metal. In all the N series samples studied, carbide precipitation at the grain boundaries is evident in the interior of the sample. However, in the 13- and 26-week retainers the sensitization proceeds to within 10 μm of the surface of the steel, while in the 39- and 52-week tests the sensitization is to within only 40 μm of the surface. Note that the extent of B and wt loss reaction measured in the 39- and 52-week results was less than noted in the 13- and 26-week tests.

Conclusions

A complete discussion of the above results is presented in [BATES-5, -6]. The conclusions drawn from the work are that the N2 Unsaturated Test series, which are specific to the NNWSI repository site, result in the formation of several identifiable reaction phases and reasonably constant elemental concentrations in solution. The next step in interpreting the reaction process will be to use geochemical modeling codes in conjunction with the solution and phase results reported here to see if any correlation between the modeling theory and the results exists.

Other data presented suggest that when sensitized 304L ss in contact with glass is also contacted by small volumes of repository water, a reaction occurs resulting in the formation of metal (Fe, Cr, Mn, Ni) silicate phases. This reaction accelerates the breakdown of the ss and the reacted glass surface, thereby increasing elemental release up to ten times the amount observed with non-sensitized ss. However, the glass breakdown does not necessarily result in equal release to solution of all the actinide elements. Neptunium is released to solution without significant fixation in alteration phases or adsorption on metal components. However, U forms stable crystalline phases which decreases its concentration to solution. The release of Pu and Am to solution is even more greatly reduced as these elements strongly adsorb to the reaction products and the metal surfaces.

The tests reported here are still in progress and will be continued to gain additional information regarding glass/metal/water interactions under unsaturated conditions.

3. N3 Unsaturated Test

The N3 Unsaturated Test is in progress using ATM-10 glass (simulated West Valley glass containing actinides plus ^{99}Tc) that was received from the MCC.

Since the ATM-10 glass as received from the MCC had to be remelted to cast the waste form specimens, the composition and redox state may be different from the reported values [MAUPIN]. The physical properties of the glass are being remeasured, and comparative leach tests were performed to determine whether there is any difference in reactivity between the as-received and cast glass. A core was taken from bar ATM-10-2 and cut into ten glass disks and a core was taken from sample 20_2 and cored into nine glass disks. MCC-1 type leach tests have been initiated using DIW at 90°C. Tests were run in duplicate for periods of 56 and 91 days. The test matrix is given in Table 2 and the results of transuranic release and weight loss (only analyses performed) are given in Table 3.

The weight loss values and normalized releases of Np, Pu, and Am for the ATM-10 and ATM-10 (recast) glasses are identical, except for the 91-day value for $(NL)_{Am}$ which is less for the recast glass. These data indicate that the recasting process has resulted in no major change in glass performance.

The N3 test was started 7/6/87 according to the matrix shown in Table 4, and has been completed through the 26-week sampling period. While no analytical results, other than transuranic release, can be reported yet, the glass and the retainer sections are not covered with rust-colored precipitates as was observed in the N2 Test series, but looks relatively unreacted. This is despite the moderate degree of sensitization known to have been imparted to the retainer sections during the heat treatment process.

The release of Np, Pu, and Am into solution has been determined through 26 weeks. These are only partial results because the acid strip of the WPA is not included. This acid strip will be done later and thus at this time the results are not analogous to those reported for the N2 Tests. The results are presented in Table 5. The results for Np are not likely to change due to the acid strip, and therefore an $(NL)_{Np}$ has been calculated. The $(NL)_{Np}$ values increase from 13 to 26 weeks in the batch samples and mirror the normalized weight loss. While complete interpretation of the results is not possible until the test components have been examined, it appears that ATM-10 glass is reacting at about the same

Table 2. ATM-10 Comparative MCC-1 Leach Tests

Experiment Type	Expt #	Sample #	Expt Duration (days)	Date In	Date Out	Glass Thickness	Glass Diameter	Glass SA (mm^2)	$\frac{\text{Total SA}}{\text{Vessel}}$	Glass Mass In (gm)	Glass Mass Out (gm)	Δ Mass	$(NL)_{wt}$
ATM-10 Glass as received ATM-10-2	G-567	1000	56	7/29/87	9/23/87	1.41	10.93	236.1	472.05	0.35120	0.34836	284	1.16
		1001				1.43	10.91	236.0		0.35887	0.35629	258	
	G-568	1002	56	7/29/87	9/23/87	1.48	11.11	245.5	481.48	0.35968	0.35698	270	1.12
		1003				1.44	10.90	235.9		0.36464	0.36194	270	
	G-569	1004	91	7/29/87	9/30/87	1.51	10.99	241.9	477.00	0.36289	0.35963	326	1.37
		1005				1.44	10.90	235.9		0.35986	0.35657	329	
	G-570	1006	91	7/29/87	9/30/87	1.26	11.32	246.1	483.20	0.31144	0.30798	346	1.42
		1007				1.44	10.39	237.1		0.36321	0.35979	342	
	Archive	1008								0.36893			
	Archive	1009								0.41898			
ATM-10 Glass once cast #20-5	G-571	1010	56	7/29/87	9/23/87	1.44	10.94	237.6	475.94	0.35745	0.35473	272	1.16
		1011				1.40	11.00	238.5		0.34722	0.34449	273	
	G-572	1012	56	7/29/87	9/23/87	1.42	10.97	238.0	473.48	0.35147	0.34869	278	1.14
		1013				1.36	10.96	235.5		0.34045	0.33782	263	
	G-573	1014	91	7/29/87	9/30/87	1.42	11.02	239.9	477.59	0.35799	0.35446	353	1.44
		1015				1.40	10.96	237.7		0.34364	0.34031	333	
	G-574	1016	91	7/29/87	9/30/87	1.42	11.12	243.8	487.81	0.36639	0.36301	338	1.39
		1017				1.64	10.93	244.0		0.39253	0.38914	339	
	Archive	1018								0.34836			

Table 2 (Cont'd)

Leachate pH In	Leachate pH Out	Mass EJ-13 In (gm)	Total Mass In	Total Mass Out	Δ Mass	LPE Mass
5.56	10.09	47.17	155.26	154.64	0.62	48.21
5.56	10.11	48.17	156.27	155.70	0.57	47.16
5.56	10.05	47.78	156.13	155.16	0.97	48.29
5.56	10.05	48.37	156.73	155.81	0.92	48.03
5.56	10.12	47.68	155.74	155.04	0.70	48.48
5.56	10.11	47.34	155.49	154.94	0.55	46.94
5.56	10.02	47.76	156.02	155.12	0.90	48.19
5.56	9.90	48.76	156.99	156.09	0.90	47.38

Table 3. Actinide Release from ATM-10 Glasses

Glass Type	Experiment Duration (Days)	$(NL)_{Np}$ (g/m^2)	$(NL)_{Pu}$ (g/m^2)	$(NL)_{Am}$ (g/m^2)	Wt. Loss (g/m^2)
ATM-10	56	3.1	9E-4	3.0E-3	1.14
ATM-10 (recast)	56	3.0	1.1E-3	3.2E-3	1.15
ATM-10	91	3.6	7E-4	4.1E-3	1.40
ATM-10 (recast)	91	3.6	7E-4	2.0E-3	1.42

Table 4. Test Matrix and Component Weights for N3 Test Series

Description	Test #	Vessel #	Oven Position	Test Period (weeks)	Date Started	Date Stopped	Sample #	Weight Glass IN	Weight Glass OUT	Δ Mass (μg)	SA Glass	Top Canister IN (gm)
Batch	N3-1	ANL-49	3	12.5	7/06/87	10/01/87	20_2	10.42933	10.42915	180		3.16609
Batch	N3-2	ANL-50	4	12.5	7/06/87	10/01/87	20_3	10.50925	10.50862[a]	630		3.15144
Batch	N3-3	ANL-51	5	26	7/06/87	1/04/88	20_4	10.67526	10.67421	1050		3.15589
Batch	N3-4	ANL-52	6	26	7/06/87	1/04/88	20_5	10.46056	10.45984	720		3.16518
Batch	N3-5	ANL-53	7	39	7/06/87	4/04/88	20_6	10.65264				3.13878
Batch	N3-6	ANL-54	8	39	7/06/87	4/04/88	21_1	9.83140				3.14192
Batch	N3-7	ANL-55	9	52	7/06/87	7/04/88	21_2	10.72120				3.16027
Batch	N3-8	ANL-56	10	52	7/06/87	7/04/88	21_3	10.40996				3.17504
Continuous	N3-9	ANL-47 ANL- ANL- ANL- ANL- ANL- ANL- ANL-	1	7 12.5 19.5 26 32.5 39 45.5 52	7/06/87 8/24/87 10/01/87 11/19/87 1/04/88	8/24/87 10/01/87 11/19/87 1/04/88	21_4	10.35830				3.17929
Continuous	N3-10	ANL-48 ANL- ANL- ANL- ANL- ANL- ANL- ANL-	2	7 12.5 19.5 26 32.5 39 45.5 52	7/06/87 8/24/87 10/01/87 11/19/87 1/04/88	8/24/87 10/01/87 11/19/87 1/04/88	21_5	10.57790				3.14283

Cont'd

Table 4 (Cont'd)

Top Canister OUT (gm)	Δ Mass	Bottom Canister IN (gm)	Bottom Canister OUT (gm)	Δ Mass	Total Vessel IN (gm)	Total Vessel OUT (gm)	Δ Mass	Water Added During Testing
3.16823	-140	4.12108	4.12115	+70	1347.4	1348.6	+1.2	1.875
3.15159	+140	4.12082	4.08581	-40	1339.3	1340.5	+1.2	1.875
3.15800	+110	4.10002	4.10013	+110	1339.0	1341.3	+2.3	3.90
3.18519	+30	4.08635	4.08636	+10	1343.7	1346.4	+2.7	3.90
		4.10659						
		4.11724						
		4.11610						
		4.10819						
		4.10150			1338.0	1338.1	+0.1	1.05
					1342.2	1342.6	+0.4	0.0825
					1338.0	1338.2	+0.7	1.05
					1342.3	1343.0	+0.7	0.975
					1338.1			
		4.09738			1341.6	1342.2	+0.6	1.05
					1339.6	1340.0	+0.4	0.83
					1341.7	1342.4	+0.7	1.05
					1339.6	1340.2	+0.6	0.975
					1341.7			

Cont'd

Table 4 (Cont'd)

Description	Test #	Vessel #	Oven Position	Test Period (weeks)	Date Started	Date Stopped	Sample #	Weight Glass IN	Weight Glass OUT	Δ Mass (μg)	SA Glass	Top Canister IN (gm)
Blank	N3-11	ANL-57	11	7 12.5 19.5 26 32.5 39 45.5 52	7/06/87 8/24/87 10/01/87 11/19/87 1/04/88	8/24/87 10/01/87 11/19/87 1/04/88	none					
Continuous	N3-12		3	6.5 13 19.5 26 32.5 39 45.5 52	10/01/87 11/19/87 1/04/88	11/19/87 1/04/88	21_6	10.50416				

Cont'd

Table 4 (Cont'd)

Top Canister OUT (gm)	Δ Mass	Bottom Canister IN (gm)	Bottom Canister OUT (gm)	Δ Mass	Total Vessel IN (gm)	Total Vessel OUT (gm)	Δ Mass	Water Added During Testing
					1320.7	1321.3	+0.7	1.05
					1320.8	1321.0	+0.2	0.83
					1320.8	1321.4	+0.6	1.05
					1320.8	1321.4	+0.6	0.975
					1320.9			
					1345.7	1346.4	+0.7	0.975
					1347.5	1348.2	+0.7	0.975
					1346.8			

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[a] The sample was chipped during handling prior to weighing. All the observed pieces were weighed but potentially a small piece may have been missed.

Table 6. Release of Transuranic Elements from ATM-10 Glass during the N3 Unsaturated Test Series

Test #	Np Release (gm x 10^{-8})						Pu Release (gm x 10^{-10})				
	Solution Component						Solution Component				
	Solution	Rinsed Solution	Soak	Filtered moles Np/L	Total gm x 10^{-8}	$(NL)_{Np}$ (g/m^2)	Solution	Rinsed Solution	Soak	Filtered moles Pu/L	gm x 10^{-10}
N3 #1	2.5	2.6	0.0	2 x 10^{-8}	2.6	0.1	0.5	2.9	1.9	-	4.8
N3 #2	8.9	8.9	-	7 x 10^{-8}	8.9	0.3	0.3	1.0	-	-	1.0
N3 #3	20.4	20.4	-	2 x 10^{-7}	20.4	0.8	0.3	0.1	-	-	-
N3 #4	18.9	18.1	0.5	2 x 10^{-7}	19.4	0.8	-	-	3.0	8 x 10^{-10}	3.0
N3 #9 6.5	0.0	0.0	0.0	-	0.0		0.0	0.0	0.0	-	0.0
13.0	2.6	1.4	0.0	-	2.6		0.1	0.1	0.4	-	0.5
19.5	5.9	4.8	0.0	-	8.5		-	-	-	-	-
26.0	7.1	5.2	-	-	15.6		0.03	0.09	-	-	-
N3 #10 6.5	1.2	1.0	0.0	-	1.2		0.3	0.2	0.1	-	0.4
13.0	2.0	1.5	0.0	-	3.2		0.1	0.4	0.3	-	1.1
19.5	7.0	5.9	0.0	-	10.2		0.2	0.1	0.0	-	1.3
26.0	5.4	5.0	-	-	15.6		0.1	-	0.1	-	-
N3 #12 6.5	1.7	1.7	0.4	-	2.1		0.2	-	0.8	-	1.0
13.0	5.8	5.3	-	-	7.9		0.3	0.3	-	-	-

Cont'd

Table 6 (Cont'd)

	Am Release (gm x 10^{-11})						
	Solution Component						
Test #		Solution	Rinsed Solution	Soak	Filtered moles Am/L	Total gm x 10^{-11}	$(NL)_{wt}$ (g/m^2)
N3 #1		1.5	17.9	4.9	8×10^{-10}	22.6	0.1
N3 #2		1.1	59.6	10.1	4×10^{-9}	69.6	0.5
N3 #3		1.0	53.7	7.8	1×10^{-9}	61.5	0.8
N3 #4		1.1	11.6	18.2	2×10^{-9}	30.0	0.6
N3 #9	6.5	0.0	0.0	0.0	-	0.0	
	13.0	0.3	0.2	0.7	-	1.0	
	19.5	3.4	2.6	11.0	-	15.4	
	26.0	0.2	0.4	-	-	-	
N3 #10	6.5	0.5	0.3	1.0	-	1.5	
	13.0	0.3	1.5	0.7	-	3.7	
	19.5	0.7	0.4	1.1	-	5.5	
	25.0	1.0	2.5	-	-	-	
N3 #12	6.5	0.8	5.7	4.4	-	10.1	
	13.0	2.1	5.0	-	-	-	

rate as the SRL 165 glass when the accelerated ss/glass breakdown occurs for the SRL glass, but at a faster rate if no accelerated reaction occurs in the SRL glass [BATES-5, -6].

The release of Pu from the glass is difficult to measure due to the relatively small amount of Pu in the glass. Americium release is easily measured, but the final values are likely to depend strongly on the acid strip component and will be discussed in future reports.

II. NNWSI PARAMETRIC EXPERIMENTS

Because the NNWSI Unsaturated Test rigidly sets many of the test parameters, the effect that each parameter may have on the final radionuclide release needs to be studied. This is being done in parametric experiments. A description, purpose, and status of the parametric experiments in progress are given in Table 6. Each of the ongoing experiments has been discussed in detail previously [STEINDLER; BATES-3, -4] and are continuing as scheduled.

A. P-VI (UO_2 Experiments)

These experiments are being done with nonirradiated UO_2 pellets encased in zircaloy cladding. The Unsaturated Test protocol is being followed except for variations in drop size and interval. The total U released in the experiments to date is shown in Fig. 4. As can be seen, there was little release for about the first 39 weeks, after which the total U released increased dramatically. It appears that neither the drop interval or form of the UO_2 affects the release dramatically.

Experiment P-VI #7 was terminated after about two years so the reacted phase present on the sample surface could be examined. The sample has been studied using optical microscopy, laser Raman microprobe, and XRD.

Optical microscopy indicated the surface was covered with a thick assemblage of reaction products. These products were catalogued according to appearance and position on the sample surface (as identified in photographs). A small portion of the surface was removed for XRD analysis yielding the pattern shown in Table 7. The only identifiable phase was hydrated UO_3 (Fig. 5). This sample was also subjected to laser Raman microprobe analysis and the results are discussed in Section V.

Table 6. Description, Purpose, and Status of Parametric Experiments

Experiment #	Description	Purpose	Status
P-II	Regular-sized glass waste form, no ss holder, 0.075 mL J-13/ 3.5 days, continuous and batch expts	To study the release from glass only	Initiated 2/20/84. Batch expts completed 2/18/85. Continuous expts in progress
P-III	Half-sized glass waste form, ss holder, 0.075 mL and EJ-13/ 3.5 days, continuous and batch expts	To study the effect of waste form surface area by reducing the as-cast surface area by half	Initiated 12/6/84. Batch expts completed 12/5/85. Continuous expts in progress
P-IV	Half-sized glass waste form, ss holder, 0.0375 mL and EJ-13/ 3.5 days, continuous and batch expts	To study the effect of drop size by reducing the amount of water added and the as-cast surface area by half	Initiated 2/18/85. Batch expts completed through one year. Continuous expts in progress
P-V	Regular-sized glass waste form, ss holder, 0.075 mL and EJ-13/ 14 days, continuous and batch expts	To study the effect of lengthening the time interval between water additions	Initiated 6/10/85. Batch expts completed through one year. Continuous expts in progress
P-VI	Pressed and sintered UO_2 pellets in various forms, zircaloy holder, 0.075 mL and EJ-13/ 3.5 days and 0.0375 mL/7 days, continuous expts	To study the release of U from nonreacted fuel pellets under Unsaturated Test conditions	Initiated 4/25/85. Selected expts terminated to investigate reaction products, the remaining continuous expts in progress
P-VII	UO_2 pellets soaking in EJ-13 water at ambient temperature, batch expts	To look for reaction product formation	Three- and nine-month batch test terminated

Cont'd

Table 6 (Cont'd)

Experiment #	Description	Purpose	Status
P-VIII	Regular-sized glass waste forms in presensitized ss holders, 0.075 mL EJ-13/3.5 days, continuous and batch expts	To study the effect of presensitizing the ss waste form holder	Initiated 2/27/86. Batch expts completed through one year. Continuous expts in progress
P-IX	A variety of glasses (polished, as-cut, powdered) in a controlled atmosphere chamber	To study the effect of the the degree of water saturatio or glass reaction	Initiated 10/3/86. Selected samples terminated after ~five months and one year, remaining expts still in progress
P-X	Basaltic and SRL-165 glass vapor hydration expts	To study the use of vapor phase hydration and natural analogues in projecting long-term glass reaction	Review of existing samples and literature initiated, some preliminary expts in progress
P-XI	SRL 165 U/A glass, WV U/A glass, and ATM-1c/8 vapor hydration	To study the effect of time and temperature on the hydration of nuclear waste glasses under saturated conditions	Sample preparation completed, preliminary matrix completed, additional preliminary expts are in progress
P-XII	Regular-sized glass waste forms in variously sensitized ss holders, 0.075 mL EJ-13/3.5 days, continuous only	To verify the effect of sensitization on glass reaction	Initial 11/19/87

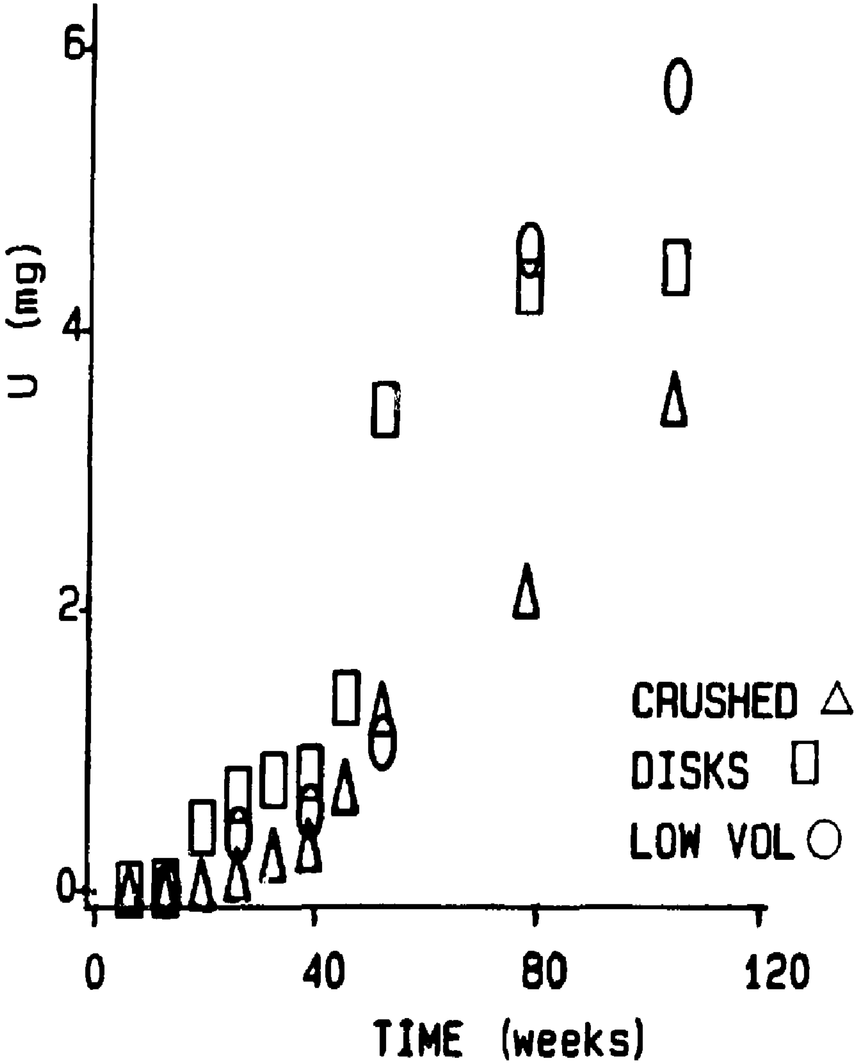


Fig. 4. Total Uranium Release from UO_2 Pellets in the P-VI Parametric Experiments

Table 7. XRD Patterns of Crystalline Phases Formed on UO_2 Surface

Observed XRD Pattern		$UO_3 \cdot (0.8H_2O)$ JCPDS 10-309	
I	d	I	d
60	5.05	100	5.11
		80	3.45
100	3.43	100	3.43
40	2.85	60	2.857
15	2.545	40	2.557
50	2.485	60	2.487
20	2.14	40	2.138
25	2.049	40	2.053
60	1.98	60	1.986
		40	1.971
15	1.82	30	1.817
50	1.78	10	1.782
40	1.74	40	1.740
		20	1.721
30	1.715	30	1.712
30	1.705	20	1.704
		30	1.641
30	1.635	30	1.632
20	1.525	20	1.528

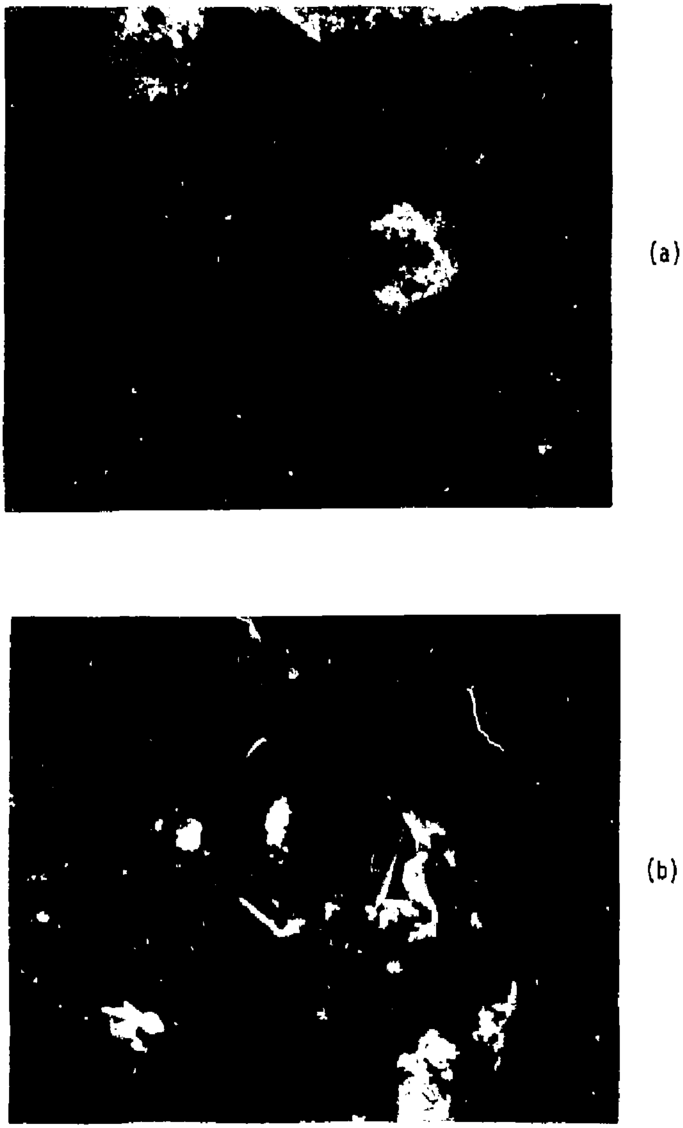


Fig. 5. General Surface of UO_2 Pellets Reacted Using the Unsaturated Protocol. (a) 200X, (b) 2,000X of the yellow precipitate covering the crystalline $UO_3 \cdot (0.8H_2O)$

B. P-XII (Sensitized Retainer Experiments)

A new parametric series has been started using SRL 165U glass with retainer sections that have been sensitized to different degrees. The retainers are made of 304L ss but of a different heat than used in the N2 Unsaturated Test. This ss proved quite difficult to sensitize, probably due to its increased nitrogen and decreased carbon content compared to the ss used in the N2 series [BATES-5], and the purpose of the experiment is to observed whether the accelerated glass/ss reaction observed in the N2 series is also observed in the present experiments. No results are yet available.

III. RELATIVE HUMIDITY AND SIMPLE GLASS EXPERIMENTS

A. Relative Humidity Experiments

The matrix for the ongoing vapor hydration experiments (P-IX parametric experiments) is given in Table 8. These experiments were designed to (1) probe the dependence of hydration rate on humidity, (2) test the effect of different glass compositions on (1), and (3) compare the hydration products formed on the various glasses [BATES-3, -4]. The glasses under study are the nuclear waste glasses SRL 131, SRL 165, and PNL 76-68 along with the natural glasses obsidian and basalt. The compositions of these glasses have been given previously [BATES-4].

All samples have been reacted at a temperature of 75°C in a relative humidity (RH) of 60%, 95%, or 100%. The samples reacted at 60% RH were contained in a Blue M humidity chamber with all samples exposed to the same atmosphere. Standard operating procedures result in some condensation on the top and sides of the bell jar, and it is possible, although unlikely, that condensed drops could fall on a sample. However, no standing water was observed on the samples at the termination of any of the experiments and none of the removed samples showed signs of being watermarked by such an occurrence.

The samples exposed to 95% RH were hydrated in a Blue M humidity chamber which does not have the above potential condensation problem, and all of these samples have been exposed to the same atmosphere. The samples reacted in a RH of 100% were suspended over water in their self-contained

Table 8. 1986 NNWSI Vapor Hydration Test

Test Type	Test #	Sample #	Duration (Days)	% RH	Date In	Date Out	Mass In (g)	Mass Out (g)	Δ Mass (× 10^{-5} g)	Remarks
165-95RH	V-104	107	INDEF	95	10/3/86		0.1950			
		108	157	95	10/3/86	3/9/87	0.1712	0.1712	0	Light ppt
	V-105	109	365	95	10/3/86	10/3/87	0.1873	0.1875	20	Medium ppt
		110	365	95	10/3/86	10/3/87	0.1678	0.1678	0	Medium ppt
	V-106	111	INDEF	95	10/3/86		0.1827			
		112	INDEF	95	10/3/86		0.2018			
131-95RH	V-108	115	157	95	10/3/86	3/9/87	0.1952	0.1953	10	Medium ppt
		116	INDEF	95	10/3/86		0.1581			
	V-109	117	365	95	10/3/86	10/3/87	0.1892	0.1897	50	Heavy ppt
		118	365	95	10/3/86	10/3/87	0.2701	0.2706	50	Heavy ppt
	V-110	119	INDEF	95	10/3/86		0.2466			
		120	INDEF	95	10/3/86		0.1860			
7668-95RH	V-112	123	INDEF	95	10/3/86		0.2051			
		124	157	95	10/3/86	3/9/87	0.2034	0.2037	30	
	V-113	125	365	95	10/3/86	10/3/87	0.2004	0.1999	-50	Light ppt
		126	365	95	10/3/86	10/3/87	0.2065	0.2064	-10	Light ppt
	V-114	127	INDEF	95	10/3/86		0.2072			
		128	INDEF	95	10/3/86		0.2048			
OBS-95RH	V-116	131	INDEF	95	10/3/86		0.2635			
		132	157	95	10/3/86	3/9/87	0.2626	0.2626	0	
	V-117	133	365	95	10/3/86	10/3/87	0.2585	0.2584	-10	Light ppt
		134	365	95	10/3/86	10/3/87	0.2611	0.2609	-20	Light ppt
	V-118	135	INDEF	95	10/3/86		0.2640			
		136	INDEF	95	10/3/86		0.2625			
BAS-95RH	V-120	139	157	95	10/3/86	3/9/87	0.1997	0.1996	-10	
		140	INDEF	95	10/3/86		0.3064			
	V-121	141	365	95	10/3/86	10/3/87	0.2313	0.2313	0	Medium ppt
		142	365	95	10/3/86	10/3/87	0.2439	0.2440	10	Medium ppt
	V-122	143	INDEF	95	10/3/86		0.2720			
		144	INDEF	95	10/3/86		0.2311			
165-60RH	V-126	151	157	60	10/3/86	3/9/87	0.1903	0.1902	-10	
		152	INDEF	60	10/3/86		0.1832			
	V-127	153	365	60	10/3/86	10/3/87	0.2003	0.2003	0	Light ppt
		154	365	60	10/3/86	10/3/87	0.1876	0.1874	-20	Light ppt
	V-128	155	INDEF	60	10/3/86		0.1845			
		156	INDEF	30	10/3/86		0.2042			

Cont'd

Table 8 (Cont'd)

Test Type	Test #	Sample #	Duration (Days)	% RH	Date In	Date Out	Mass In (g)	Mass Out (g)	Δ Mass ($\times 10^{-6}$ g)	Remarks
131-60RH	V-129	157	365	60	10/3/86	10/3/87	0.1989	0.1995	60	
		158	365	60	10/3/86	10/3/87	0.1604	0.1608	40	
7668-60RH	V-130	159	365	60	10/3/86	10/3/87	0.1735	0.1734	-10	
		160	365	60	10/3/87	10/3/87	0.1964	0.1963	-10	
OBS-60RH	V-131	161	365	60	10/3/86	10/3/87	0.2454	0.2452	-20	
		162	365	60	10/3/86	10/3/87	0.2246	0.2246	0	
BAS-60RH	V-132	163	365	60	10/3/86	10/3/87	0.2506	0.2507	10	
		164	365	60	10/3/86	10/3/87	0.2201	0.2201	0	
165-100RH	V-141	181	157	100	10/3/86	3/9/87	0.1855	0.1882	270	
		182	INDEF	100	10/3/86		0.2047			
	V-142	183	365	100	10/3/86	10/3/87	0.1798	0.1797	-10	Medium ppt
		184	365	100	10/3/86	10/3/87	0.1828	0.1828	0	Medium ppt
	V-143	185	INDEF	100	10/3/86		0.1816			
		186	INDEF	100	10/3/86		0.1975			
131-100RH	V-144	187	365	100	10/3/86	10/3/87	0.2003	0.1996	-70	Heavy ppt
		188	365	100	10/3/86	10/3/87	0.3048	0.3041	-70	Heavy ppt
7668-100RH	V-145	189	365	100	10/3/86	10/3/87	0.2045	0.2045	0	
		190	365	100	10/3/86	10/3/87	0.2208	0.2207	-10	
OBS-100RH	V-146	191	365	100	10/3/86	10/3/87	0.2416	0.2414	-20	
		192	365	100	10/3/86	10/3/87	0.2538	0.2536	0	Flipped
BAS-100RH	V-147	193	365	100	10/3/86	10/3/87	0.3852	0.3853	10	
		194	365	100	10/3/86	10/3/87	0.2107	0.2106	-10	

Teflon test vessels, additional samples were placed under the deionized water at the bottom of each test vessel for a companion leach test. Each 100% RH test (e.g., V141) therefore has a corresponding leach test (e.g., L141) associated with it. Some of the 100% vapor tests were contacted by periodic dripping as evidenced by their appearance. Improvements have been made in the experimental design to reduce the intermittent dripping.

The vapor hydration experiments are now in their second year with samples removed after 157 days and 365 days for study. Table 9 lists the samples removed for study.

All vapor phase samples were weighed after removal from test conditions. No significant gain or loss in mass was observed. The samples were then examined under an optical microscope and photographed. If a significant amount of reactive product is observed on the sample surface, the product is removed for XRD analysis. The 157-day 95% RH samples for SRL 165 (V104), SRL 131 (V108), obsidian (V116), and basalt (V120) were taken directly by F. Ryerson (LLNL) for H-profiling as a means of determining the depth of hydration. Unfortunately, the Li concentrations in the SRL 165 and SRL 131 interfered with the H signal which gave anomalous

Table 9. Vapor Hydration Samples Available for Study

	157 Days			365 Days		
	60% RH	95% RH	100% RH	60% RH	95% RH	100% RH
SRL 165	V126	V104	V141 L141	V127	V105	V142 L142
SRL 131		V108		V129	V109	V144 L144
PNL 76-68		V112		V130	V113	V145 L145
Obsidian		V116		V131	V117	V146 L146
Basalt		V120		V132	V121	V147 L147

results. IR reflectance measurements subsequently made on the 157-day 95% RH samples indicated that they had become covered with an organic substance which could also be seen by the naked eye. The samples were then returned to ANL for SIMS analysis. Even if degreased, each sample was seen to have a Si-rich overlayer which obscured the profiles for the underlying reacted glass. All elements appeared to be depleted with respect to Si. The SIMS data obtained for the 95% RH 157-day samples are not considered valid as a consequence.

The 365-day samples that were not covered by reaction products were analyzed using SIMS. These include all the samples listed in Table 9 except for the 365-day 95% RH samples (not including obsidian, V117) and the 100% RH nuclear waste glasses (V142, V144, V145). The SEM is currently being used to examine those samples not amenable to SIMS profiling. Since duplicate samples were reacted for 365 days, one sample for each remains to be studied using techniques to be determined. Of interest is the hydrogen profile and the form of water in the hydrated layer of a sample. Hydrogen can be profiled with the existing SIMS if modifications are made to reduce the background water pressure in the system. IR and Raman spectroscopies are also possible surface probes.

The SIMS data will be presented separately for each glass type. For reference, Table 10 presents the sputtering conditions used and the apparent hydration depth as determined by SIMS for all the glasses profiled. When possible, a Dektak profilemeter was used to determine the sputter depth after each profile. Note that spectra were collected over a two-minute period (0-75 AMU) with a delay of at least two minutes between spectra. Every fifth spectrum is indicated by a symbol in the figures, although data from each spectrum is included on the plot.

1. SRL 165

The SIMS spectra for the SRL 165 samples are given in Figs. 6 to 10. The 157-day 60% RH sample (V126) had some surface enrichment of Li and K within the first 100 Å. Possible depletion with respect to Si in the first 300 Å is noted for Al, Fe, Ca, B, and Na. Titanium, Ni, Mg, and Mn all appear to be constant through the hydration layer and into the bulk. The hydration layer itself is taken to end at the point where most elements level off to the value observed in the bulk.

Table 10. SIMS Sputter Conditions and Sample Hydration Depth

Glass Type	Sample	Hydration Depth (Å)	Sputter Conditions (ion, voltage, pressure)
SRL 165	V126	750	Ne, 2 keV, 1.2×10^{-6}
	V141	13,000	Ne, 4 keV, 2×10^{-6}
	L141	>10,000*	Ne, 4 keV, 2×10^{-6}
	V127	750	Ne, 2 keV, 1.2×10^{-6}
	L142	40,000	Ar, 4 keV, 2×10^{-6}
SRL 131	V129	750	Ne, 2 keV, 1.2×10^{-6}
	L144	>12,250*	Ne, 4 keV, 2×10^{-6}
PNL 76-68	V130	750	Ne, 2 keV, 1.2×10^{-6}
	L145	45,000	Ar, 4 keV, 2×10^{-6}
Obsidian	V131		Ar, 2 keV, 5×10^{-7}
	V117		Ar, 2 keV, 5×10^{-7}
	V146		Ar, 2 keV, 5×10^{-7}
	L146		Ar, 2 keV, 1.2×10^{-6}
Basalt	V132	250	Ne, 2 keV, 5×10^{-7}
	V147	330	Ne, 2 keV, 1×10^{-6}
	L147	4,500	Ar, 2 keV, 2×10^{-6}

*Total profile not completed.

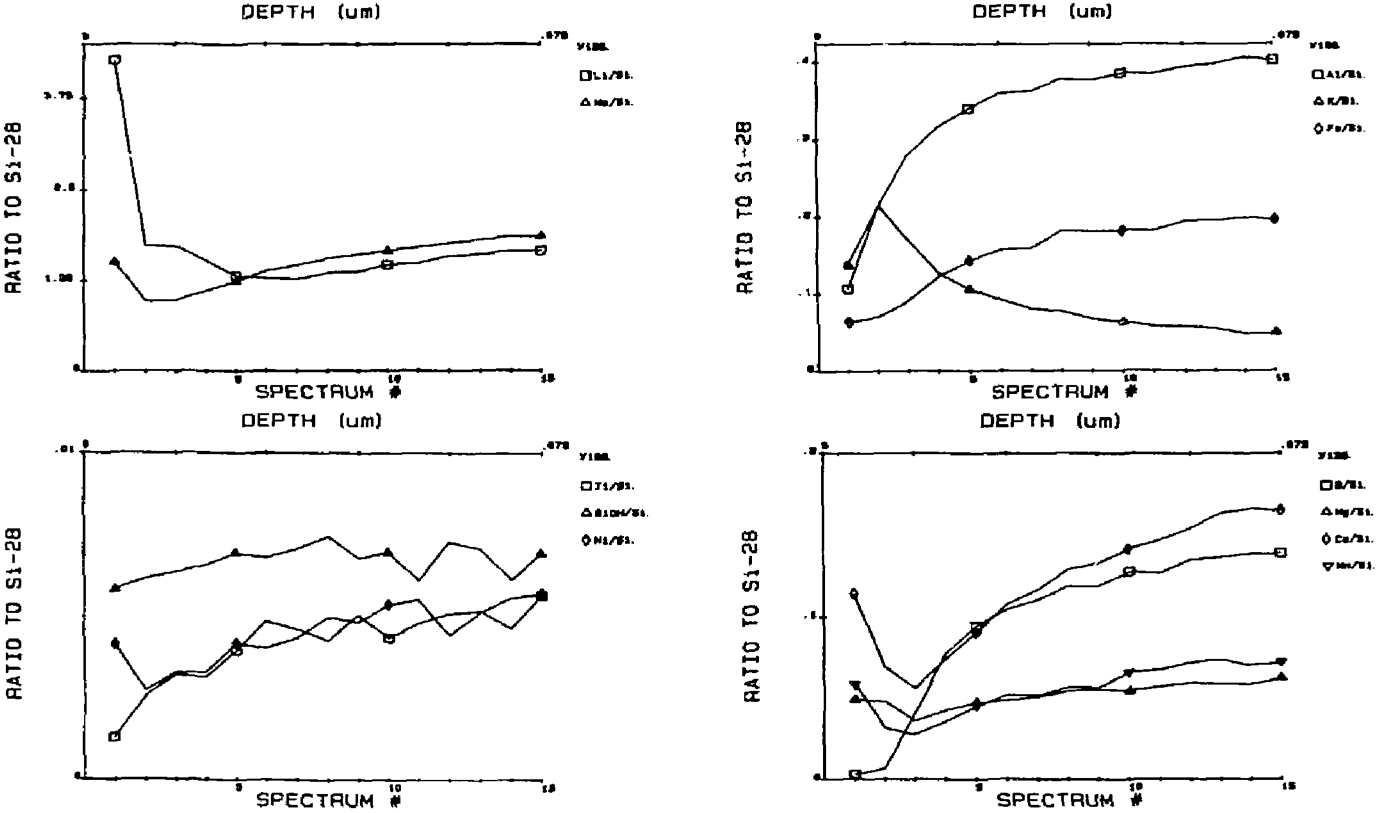


Fig. 6. SIMS Profiles of V126, SRL 165 Glass Exposed to 60% RH at 75°C for 157 Days.

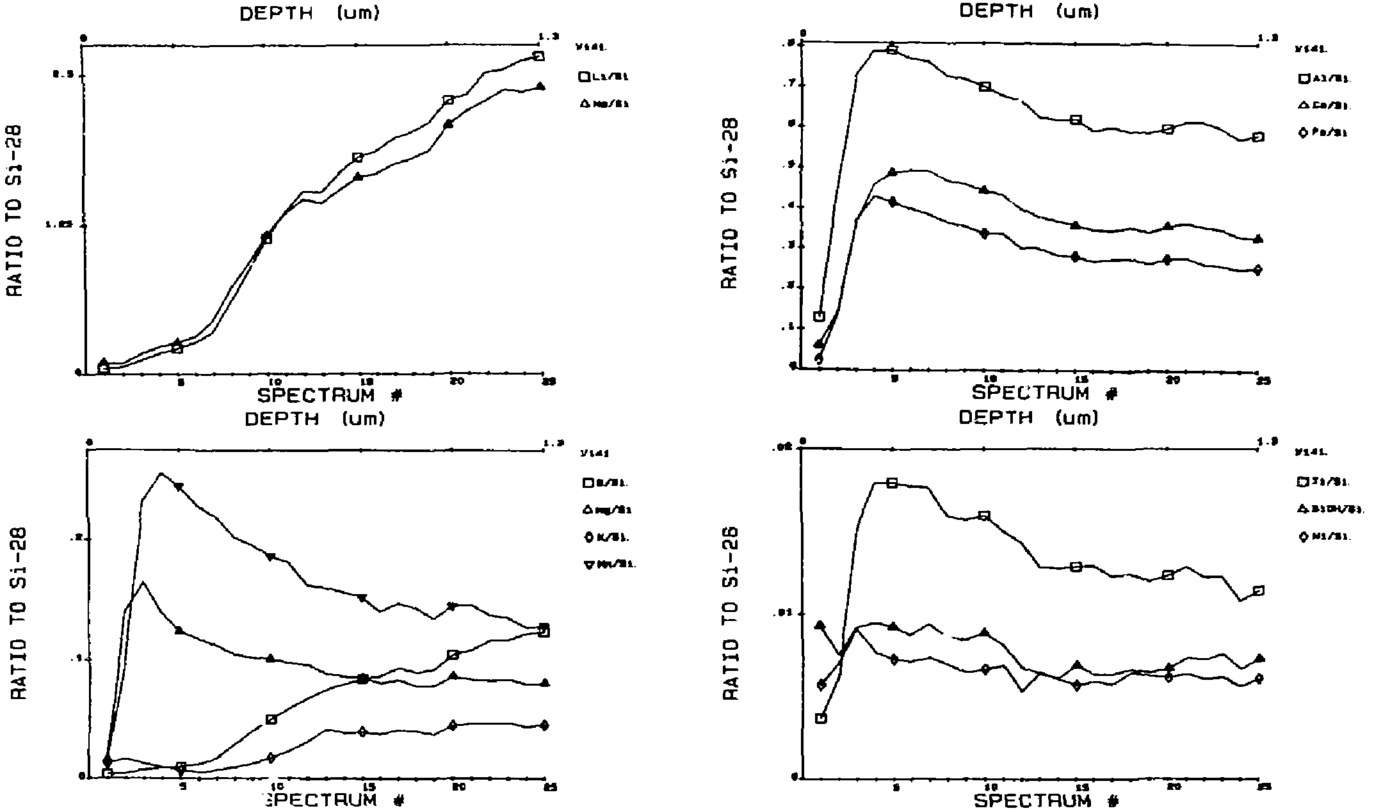


Fig. 7. SIMS Profiles of V141, SRL 165 Glass Exposed to 100% RH at 75°C for 157 Days.

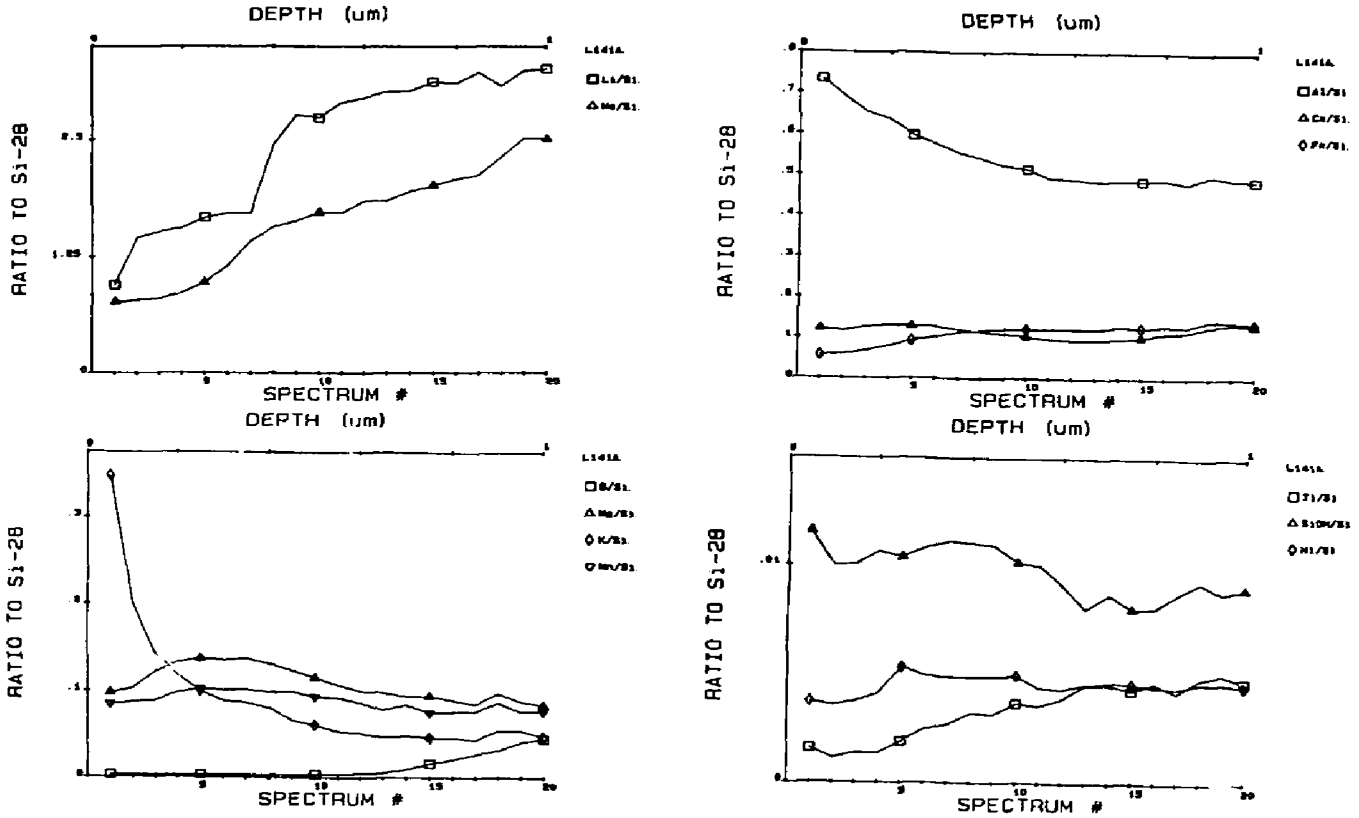


Fig. 8. SIMS Profiles of L141, SRL 165 Glass Exposed to Liquid Water at 75°C for 157 Days.

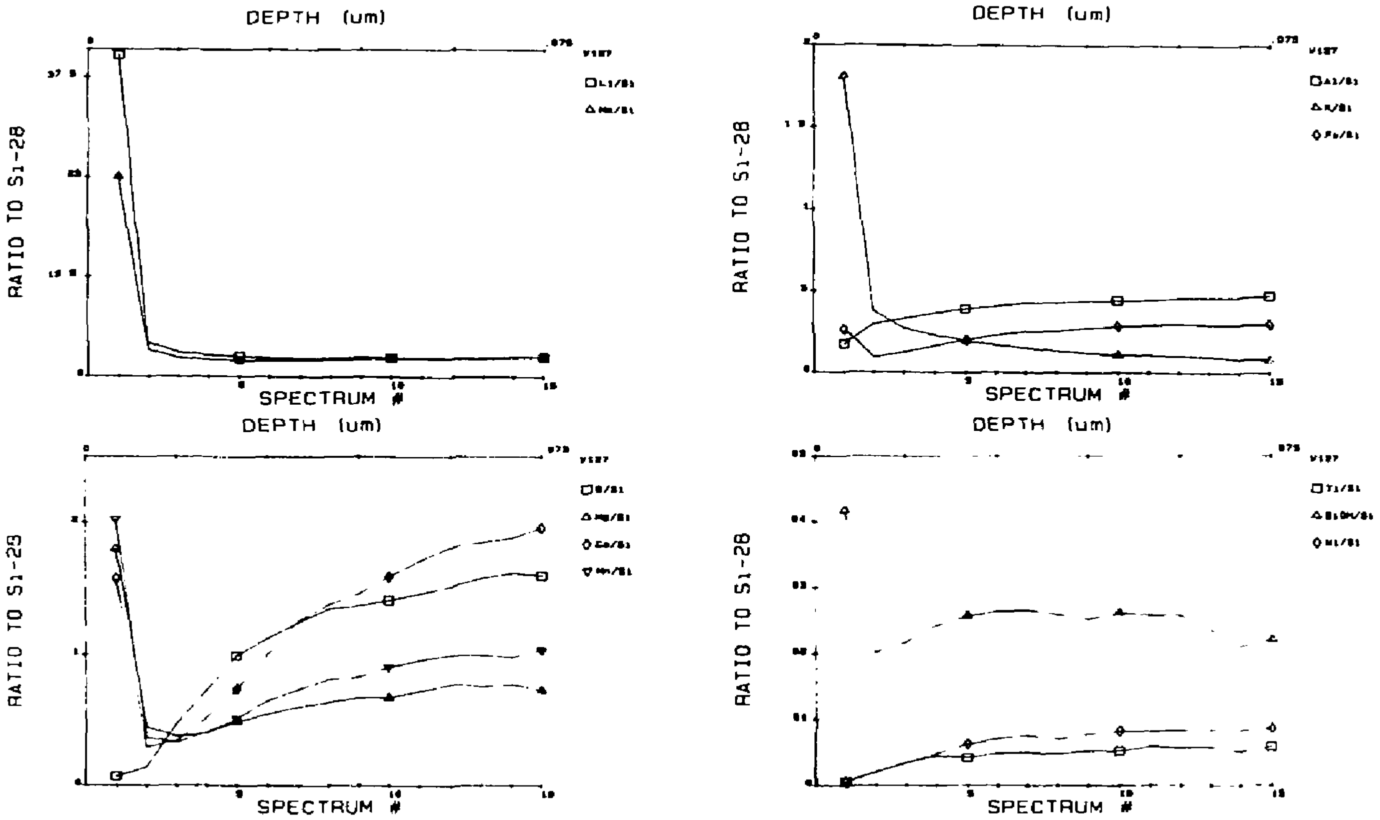


Fig. 9. SIMS Profiles of V127, SRL 165 Glass Exposed to 60% RH at 75°C for 365 Days.

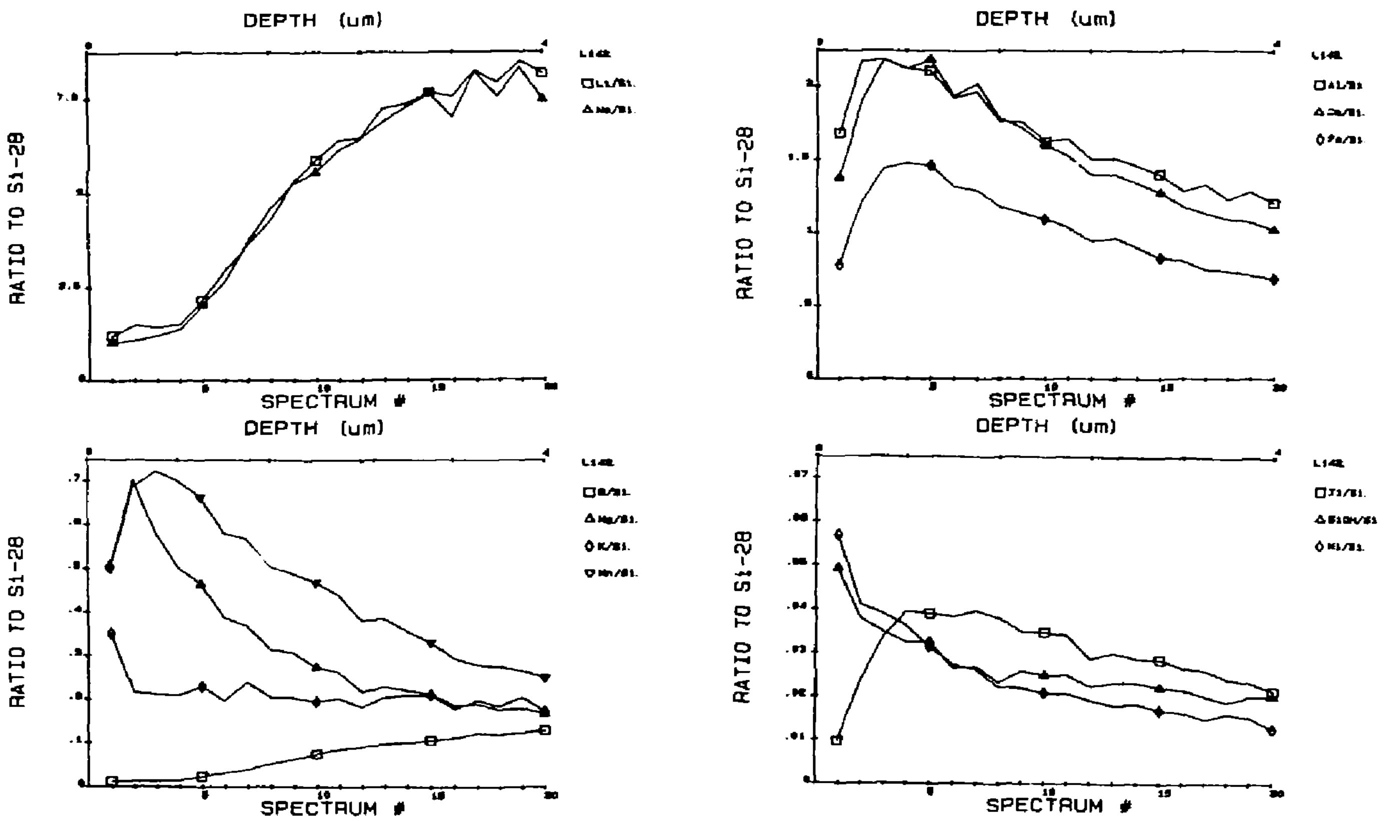


Fig. 10. SIMS Profiles of L142, SRL 165 Glass Exposed to Liquid Water at 75°C for 365 Days.

The 100% RH sample for 157 days (V141) shows a large depletion of Li, Na, and B in the first 5000 Å and an apparent enrichment of Al, Ca, Fe, and Mn near the surface. Depletion of Li and Na are characteristic of leached samples since they become dissolved in solution after migrating to the surface. In the 100% RH experiments, as the elements migrate toward the glass surface they should become enriched in the near-surface region. No such enrichment was observed which suggests that condensation in the 100% RH test vessel could have rinsed the segregated alkalis away from the surface.

The intensities for each element are plotted relative to the Si-28 signal since Si is the major bulk material. This ratioing is done to minimize effects due to slight scan-to-scan instability of absolute intensity in the system. However, if Si is either depleted or enriched (as determined by the profile of absolute Si intensity) compared to other elements, then the elemental profiles ratioed to Si may vary significantly compared to the absolute intensity profiles. To help in interpreting each set of spectra, the absolute Si profile is presented or mentioned in the text. Enrichment of the Al, Ca, Fe, and Mg is likely due to dissolution of the silicate network whereby these elements are left behind rather than having segregated to the surface. It can be seen that the higher RH sample does have a deeper hydration layer. The 157-day leached sample (L141) shows an even deeper, >10,000 Å, depletion of Li, Na, and B with a near-surface enrichment of K and Al.

After 365 days, the 60% RH sample (V127) shows an even stronger enrichment of the alkalis Li, Na, and K at the surface than was seen after 157 days (V126). Depletion of B and Ca is again seen. With the strong segregation of the alkalis to the surface, the initial Si intensity is low, thereby giving the initial values of the other elements artifically high ratios. The depletion depths of Ca and B for the two 60% RH samples (Figs. 6 and 9) are both about 750 Å. The cause of these trends, i.e., Li and Na enriched at the surface but not strongly depleted in the subsurface region, and B and Ca depleted in the subsurface region but not enriched on the surface, bears further study. It will be interesting to see whether these trends are observed for the longer term 60% RH samples.

The sample leached for 365 days (L142) exhibits the thickest hydration layer, 40,000 Å, as might be expected. Leaching of Na, Li, and B is observed along with enrichment of the other elements at the surface due to the dissolution of the silica network into the solution.

2. SRL 131

After 365 days at 60% RH, SRL 131 glass shows strong segregation of Na and Li to the surface within the first 100 Å (V129, Fig. 11). Again, the intensities for the other elements are artifically high as a result of the Si concentration being low initially. Most of the other elements would then be constant in concentration through the hydration layer of 750 Å and into the bulk. Al and B do appear to be depleted in the hydrated layer. A much thicker hydration layer is observed on the 365-day leached sample (L144). The layer was too thick for proper SIMS analysis, but reasonable EDS line profiles through the reacted layer were obtained (Fig. 12). Na and B are depleted in the reacted layer whereas Al, Ca, Fe, and Ti are enriched. The layer appears to be composed of at least two regions as suggested by the enriched species as well as by Mg, Mn, and Ni which are enriched at the surface and depleted in the subsurface region.

3. PNL 76-68

PNL 76-68 glass shows high enrichment of Na and Ca at the surface after 365 days at 60% RH and 75°C (V130), Fig. 13. Apparent enrichment of K, Fe, and Mg may be due to the low Si concentration at the surface because of Na and Ca. Strong depletion of B is observed for the first 400 Å. Al and Ti maintain constant concentrations through the hydration layer (750 Å) and into the bulk. The 365-day leach sample (L145, no spectra currently available) shows depletion in the hydrated layer of most of the elements present, B, Na, Al, Ca, Ti, and Fe. Possible enrichment of K was noted with Mg and Ti maintaining constant levels into the bulk.

4. Basalt

The natural glass basalt sample hydrated at 60% RH for 365 days (V132, Fig. 14) had a relatively low Si concentration at the surface due in part to complementary Na segregation to the surface. Mg, K, Ca, Mn, and Fe were also enriched at the surface with respect to Si. The affected region is approximately 250 Å thick and not well-defined. The hydration layer for the basalt sample in 100% RH for 365 days (V147), Fig. 15 is about the same in depth as that for V132. The major difference between the two is the amount of Na at the surface. Build-up of segregated Na on the 100% RH sample is prevented by the condensation in the test

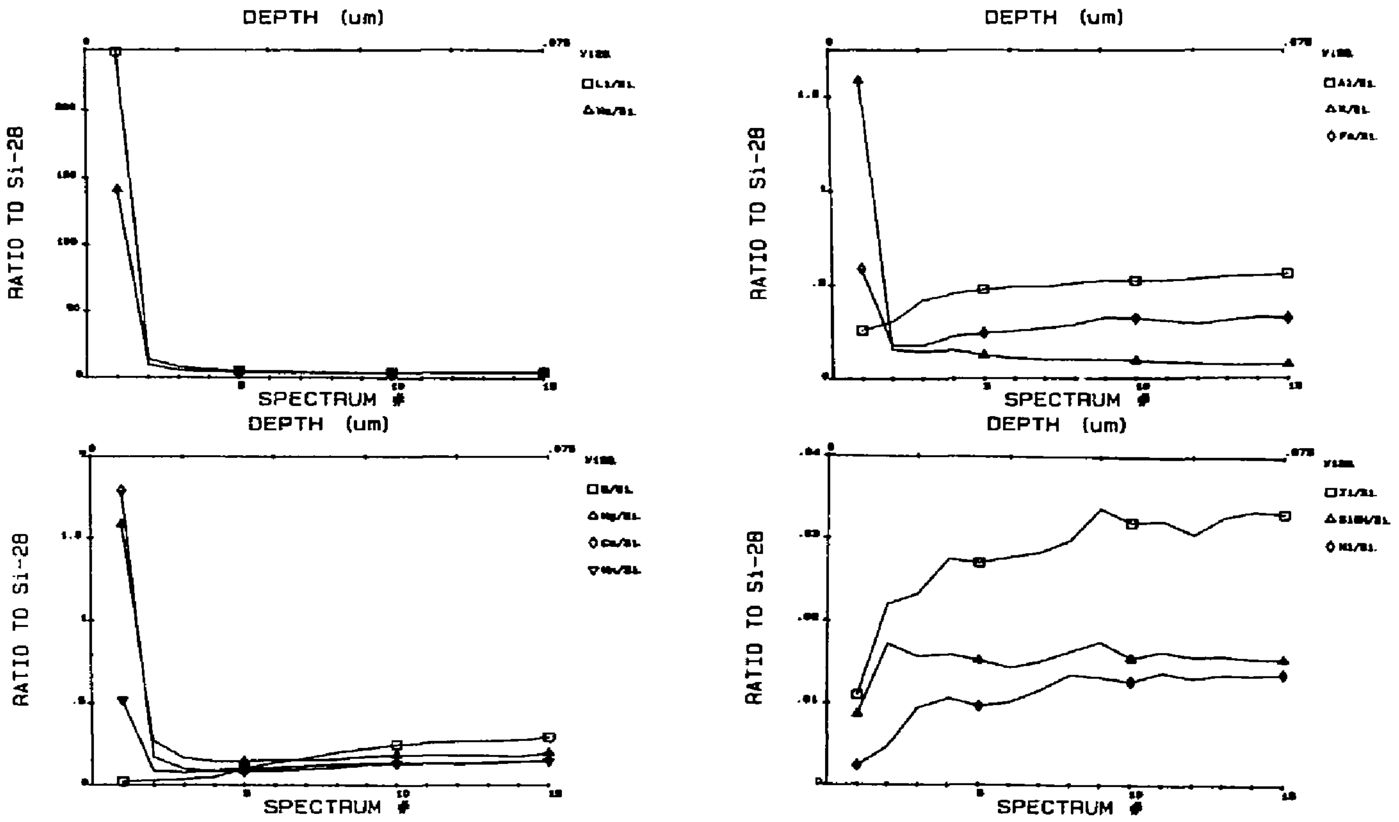


Fig. 11. SIMS Profiles of V129, SRL 131 Glass Exposed to 60% RH for 365 Days at 75°C.

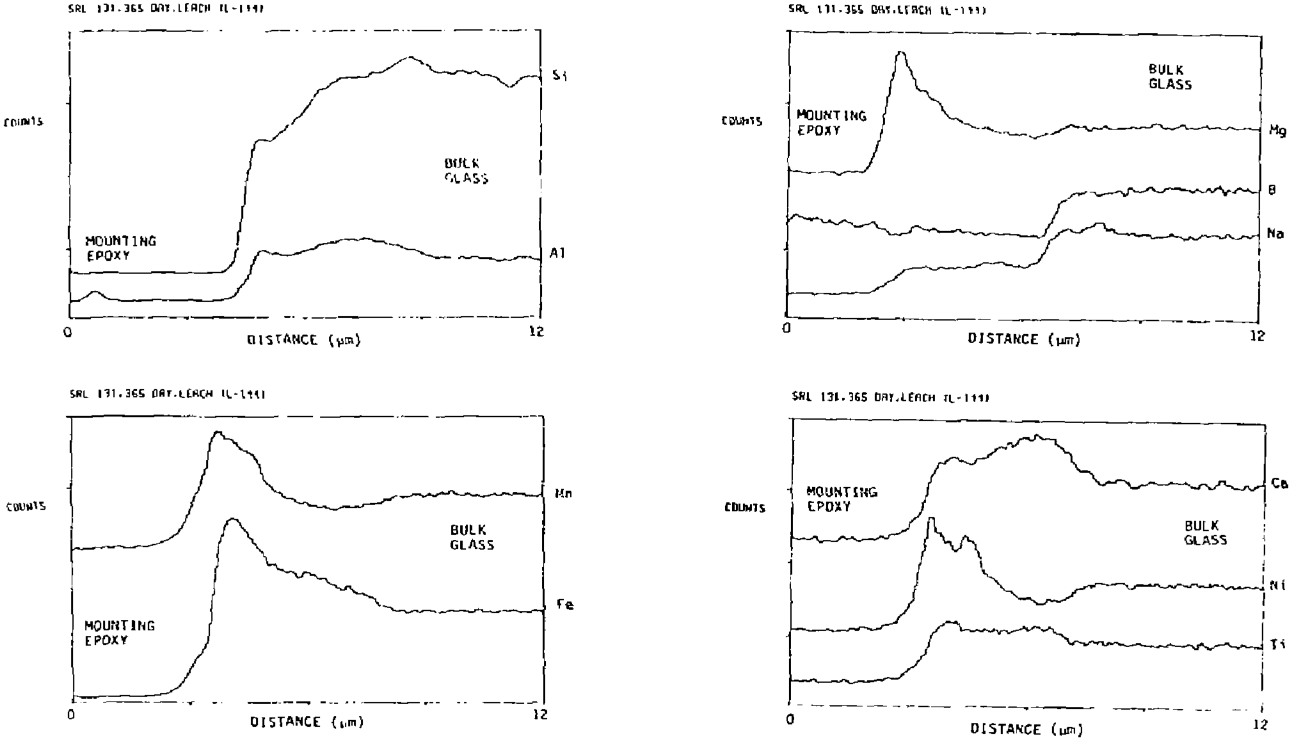


Fig. 12. EDS Line Profiles through the Reacted Layer of L144, SRL 131 Glass Exposed to Liquid Water at 75°C for 365 Days. Absolute intensities have been modified for easier comparison between elements.

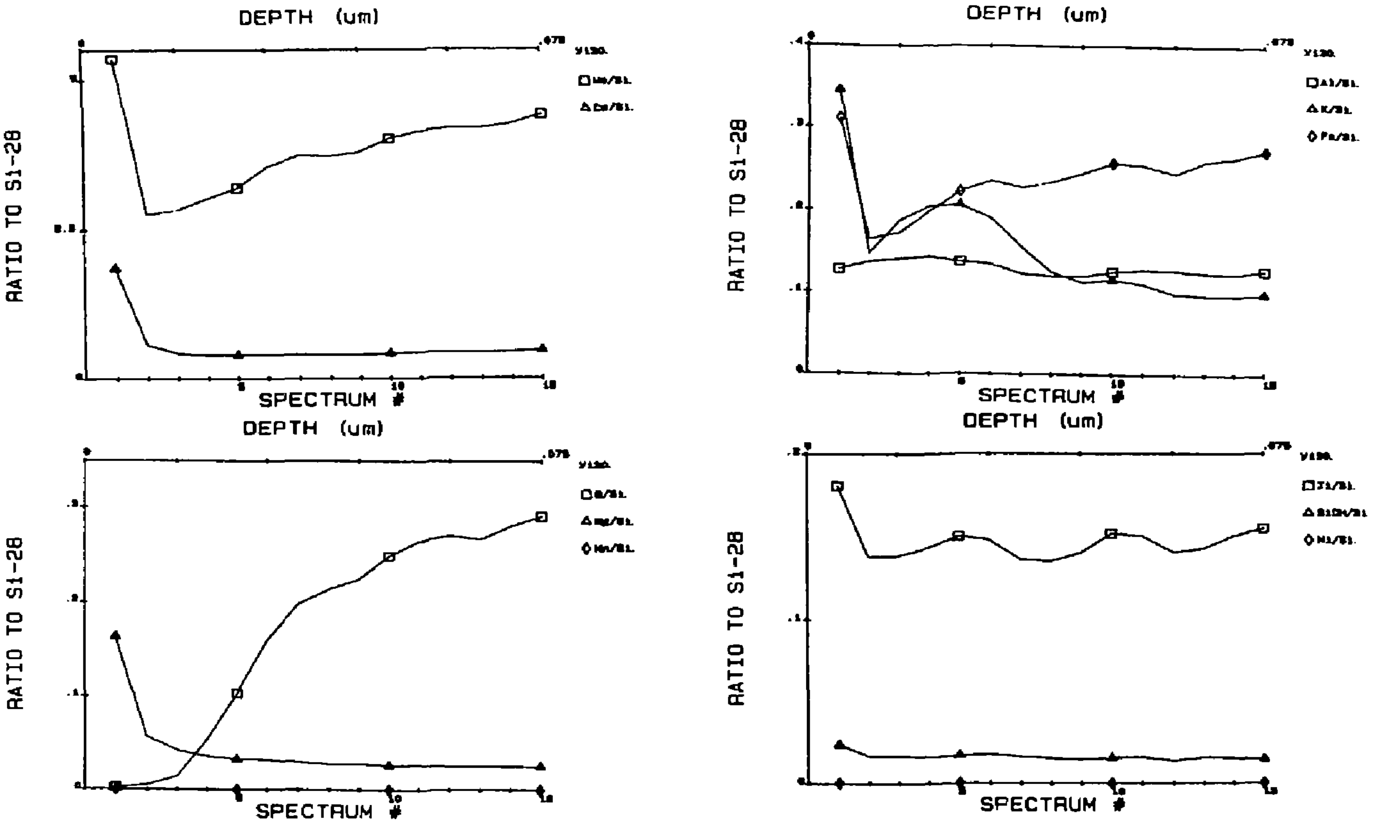


Fig. 13. SIMS Profiles of 76-68 Glass Reacted for 365 Days at 75°C with an RH of 60%.

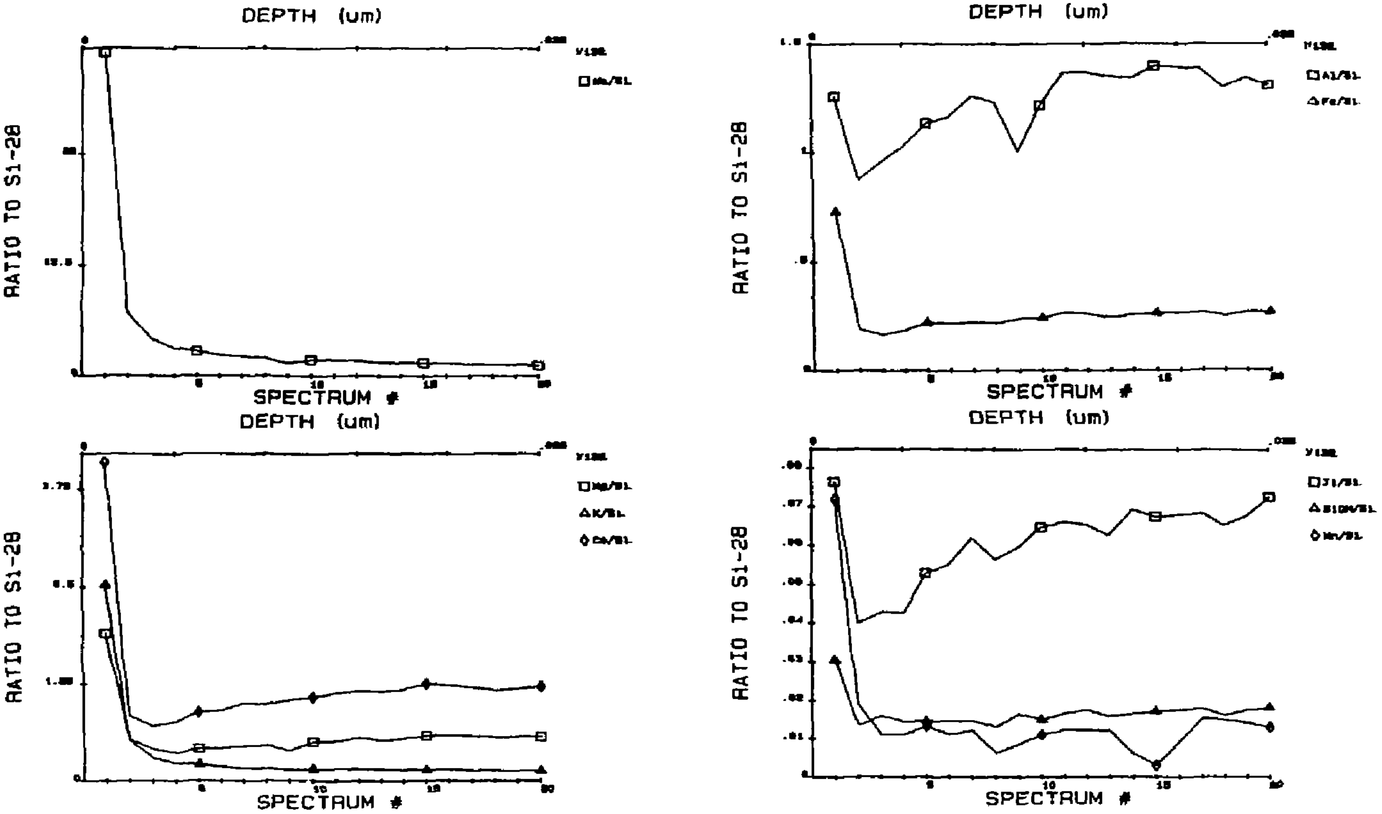


Fig. 14. SIMS Profile of Sample V132, Basalt Glass Hydrated at 60% RH for 365 Days at 75°C.

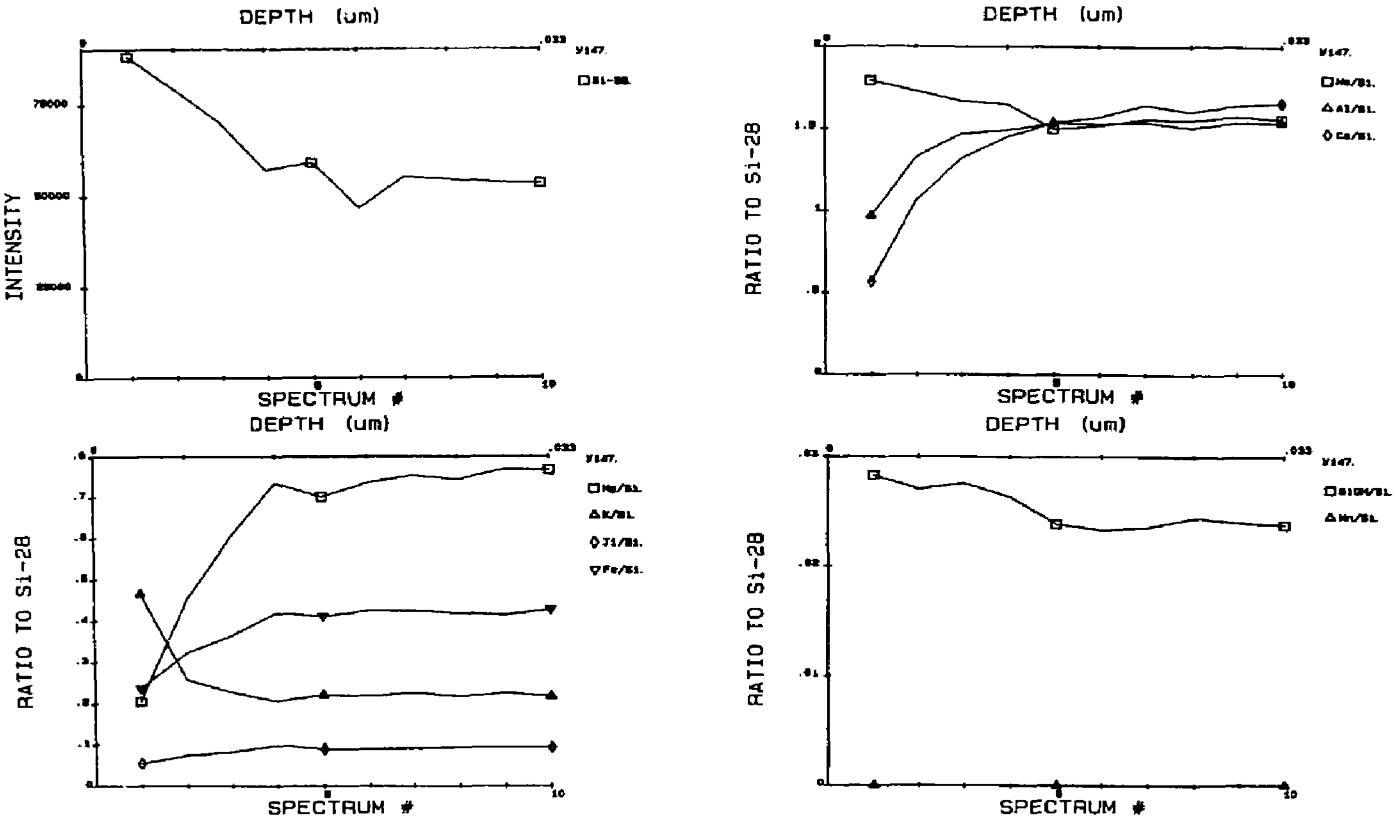


Fig. 15. SIMS Profile of Sample V147, Basalt Glass
Hydrated at 100% RH for 365 Days at 75°C.

vessel rinsing away some of the alkali from the surface. Only a slight surface enrichment of Na and K is present as compared to the 60% RH sample. As a result, the surface concentration of Si is not "depleted" and no "enrichment" of the other elements is observed for V147 as for V132. Instead, it is apparent that Al, Ca, Mg, and Fe are all depleted in the first 125 Å. Ti and Ni maintain constant concentrations through the hydrated layer and into the bulk.

Sodium, K, Ca, and Mg were found to be depleted in the first 1000 Å of L147, the 365-day leached sample (Fig. 16). The hydration depth of the leached sample is itself 4500 Å. Al, Fe, and Ti are enriched at the surface which could indicate dissolution of the silicate network, leaving undissolvable species at the surface. As observed for the other glasses studied, the hydration depth is deeper with increasing humidity, 60% $<$ 95% $<$ 100% $<$ leached.

5. Obsidian

Four obsidian samples were removed from the reaction chambers after 365 days and were observed in the optical microscope and with SIMS. All samples appeared non-reacted in reflected light. Thin sections will be prepared for examination using transmitted light at a latter date. All of the samples have been examined using SIMS.

Samples V131, V117, and V146 were exposed at relative humidities of 60, 95, and 100% respectively, while sample L146 was leached in DIW. The SIMS profiles for sample V131 (Fig. 17) shows a marked absence of Si on the sample surface. This Si poor region is about 300 Å thick, after which the Si profile is constant. In the same region where Si is depleted Ca, Na, Li, and Mg show a clear enrichment. The profiles of Li and Na level off after 300 Å while the profile for Ca and perhaps Mg show that the enrichment of these elements on the surface corresponds to a depletion in the near-surface that extends to about 1500 Å. Potassium shows perhaps a slight enrichment near the surface, while Al, Fe, and Ti show a flat profile compared to Si.

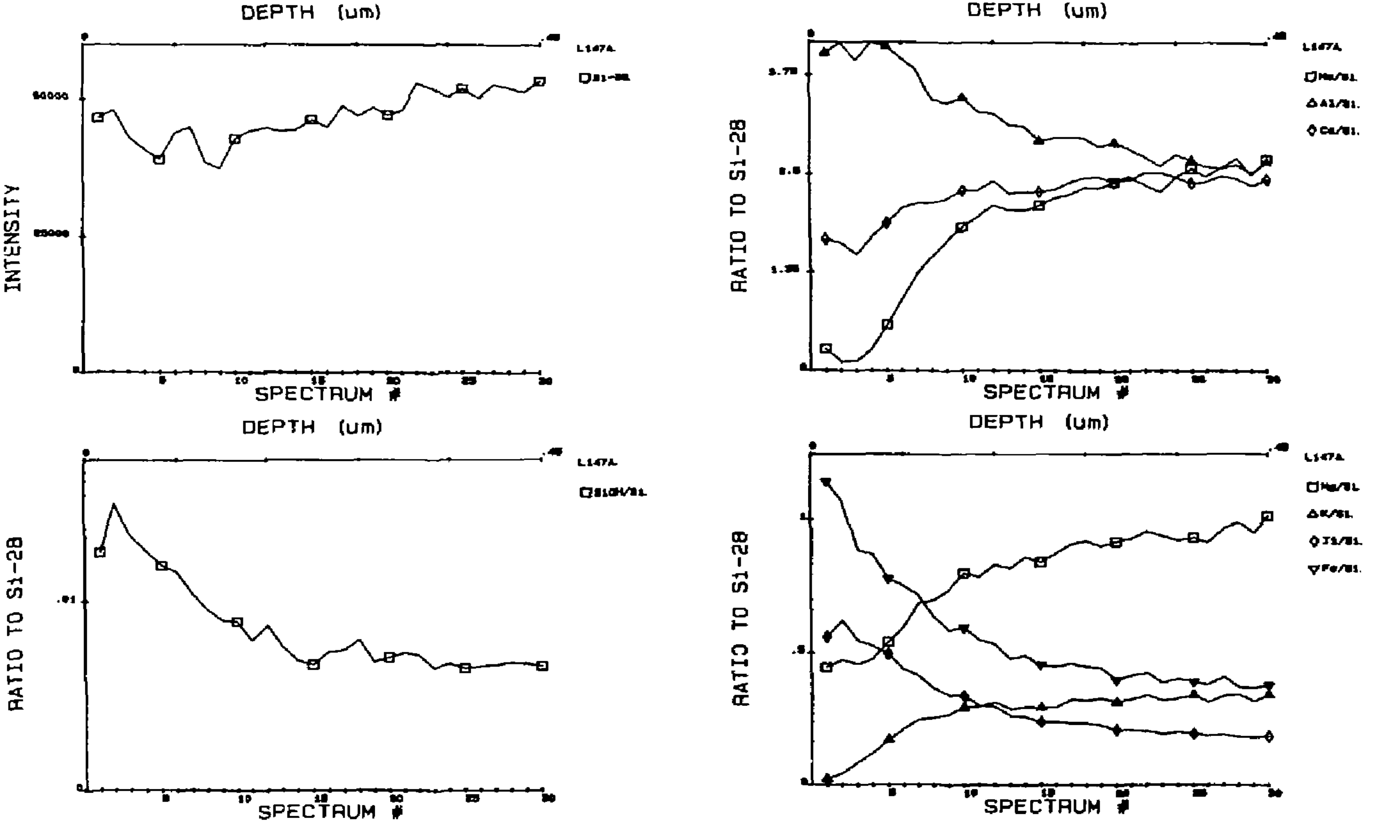


Fig. 16. SIMS Profile of Basalt Glass Leached in DIW at 75°C for 365 Days.

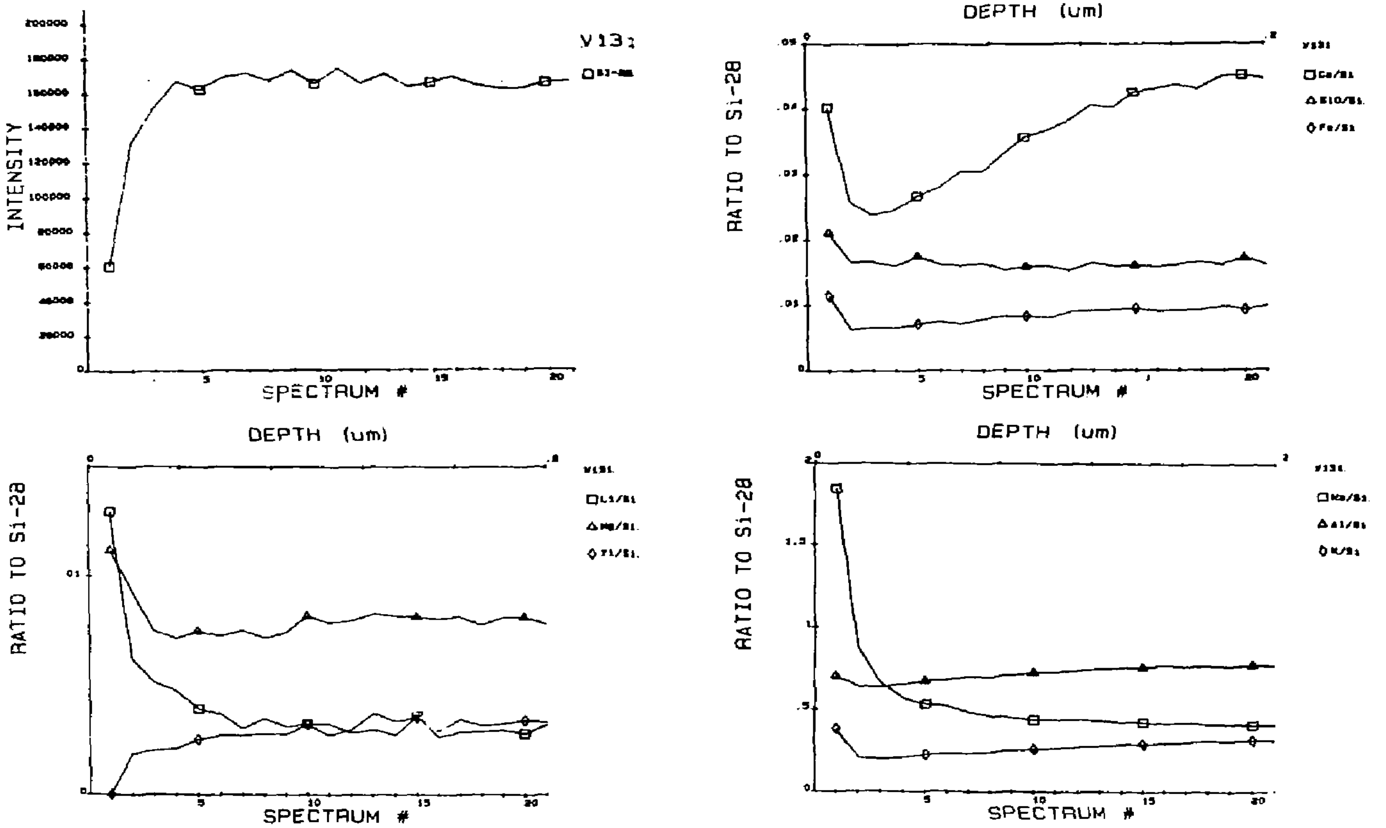


Fig. 17. SIMS Profile of Sample V131, Obsidian Exposed to Water Vapor at a RH of 60% for 365 Days and 75°C

The overall picture is one where Na, Li, Ca, and Mg form a salt layer on the glass surface about 300 Å thick. Ca and Mg are removed from the near-surface region which results in a measurable depletion of the elements from the first 1500 Å. Na and Li show no such depleted region and are presumably depleted to a lesser degree than Ca and Mg in the near-surface region. While at this time the profile of H or the penetration of water into the glass have not been measured, it is reasonable that the hydration depth (diffusion of H_2O into the glass) is greater than 1500 Å, and that the observed profiles are part of a process that is occurring separately from the more rapid diffusion of water into the glass.

For sample V117 (Fig. 18), which was reacted at 95% RH, the Si profile is quite constant but there is enrichment of Na, Li, Mg, and perhaps K on the surface. The enrichment layer is only about 200 Å thick. Sodium shows additional depletion that extends about 700 Å into the glass. Ca also shows depletion extending >1500 Å into the glass.

For sample V146 (Fig. 19) there is a slight enrichment of Na and Li on the glass surface and a corresponding slight depletion of Si. For this sample the outer salt layer is only about 50 Å thick. Na shows depletion from the near-surface region reaching the bulk level at about 300 Å. Ca also shows a near-surface depletion that extends about 1500 Å into the glass. The other elements behave similarly to Si. Thus, for all obsidian samples reacted in vapor, an enrichment of alkalis and alkaline earths is found on the glass surface. The sample reacted in 100% relative humidity, shows a more pronounced depletion of Na and Ca.

For the obsidian sample leached in water, L146 (Fig. 20), there is no enrichment of Na or Ca on the surface, but a depletion which for Na extends about 1100 Å into the glass and for Ca about 2900 Å. However, Si shows marked depletion at the surface which is compensated by an enrichment of Al, Ti, and Fe. The implication is that during the leaching process some dissolution of Si from the glass has occurred leaving behind residual Al, Fe and Ti. Li appears to be enriched at the surface due to its ratio to Si. Li is a trace element in obsidian, and the absolute value of Si increases dramatically between the first and second scans causing an artificial enhancement of the Li signal.

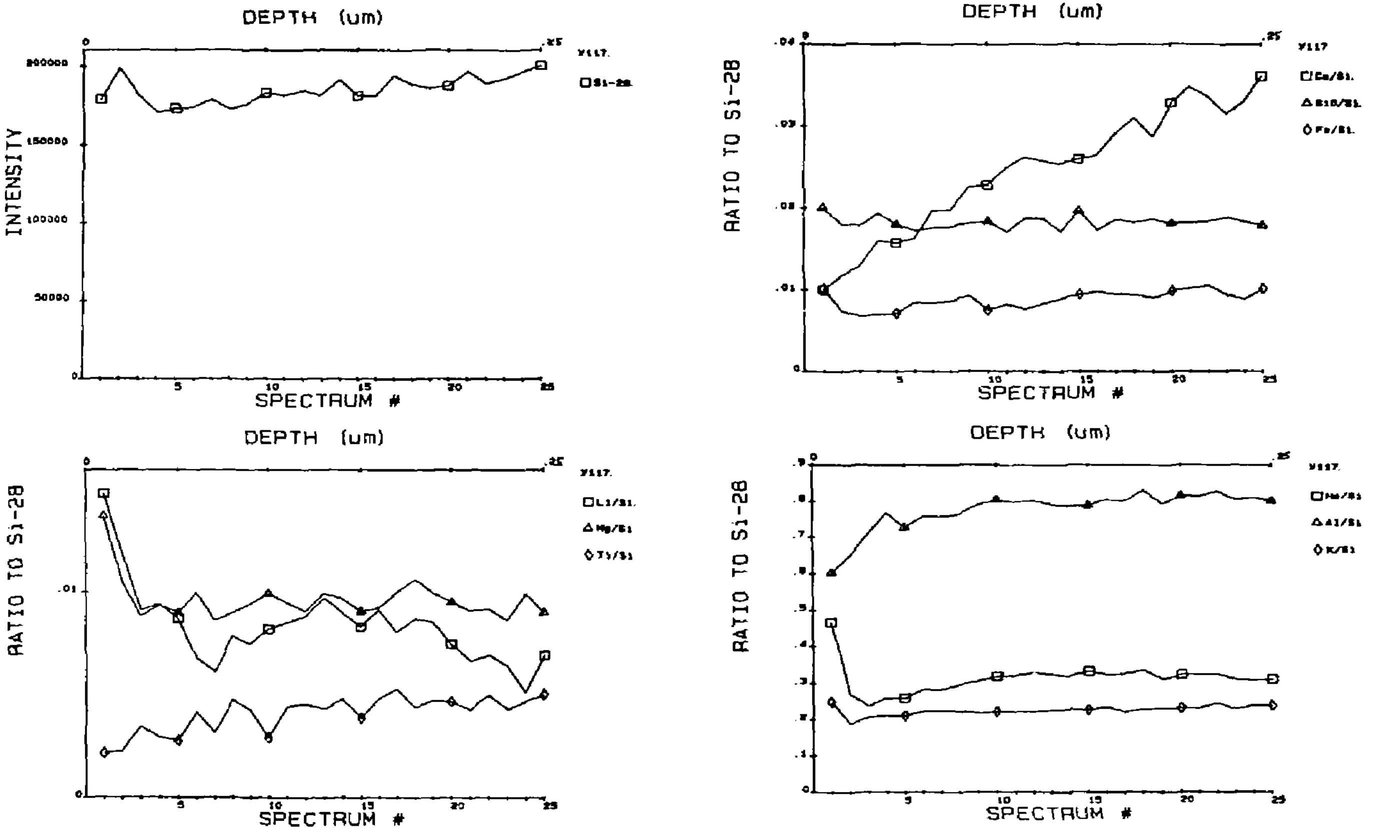


Fig. 18. SIMS Profile of Sample V117, Obsidian
Reacted at 75°C 95% RH for 365 Days

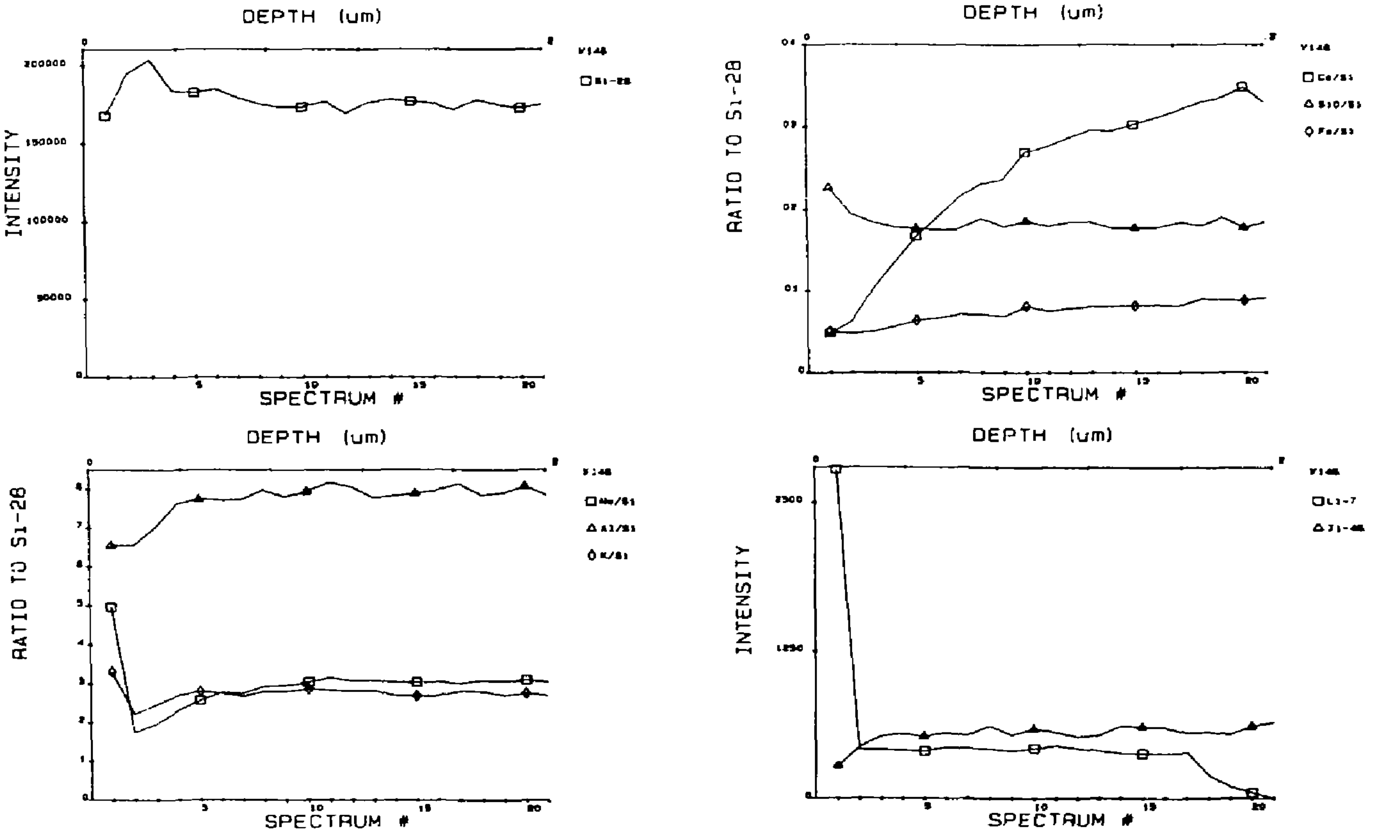


Fig. 19. SIMS Profile for Sample V146, Obsidian Reacted at 75°C 100% RH for 365 Days

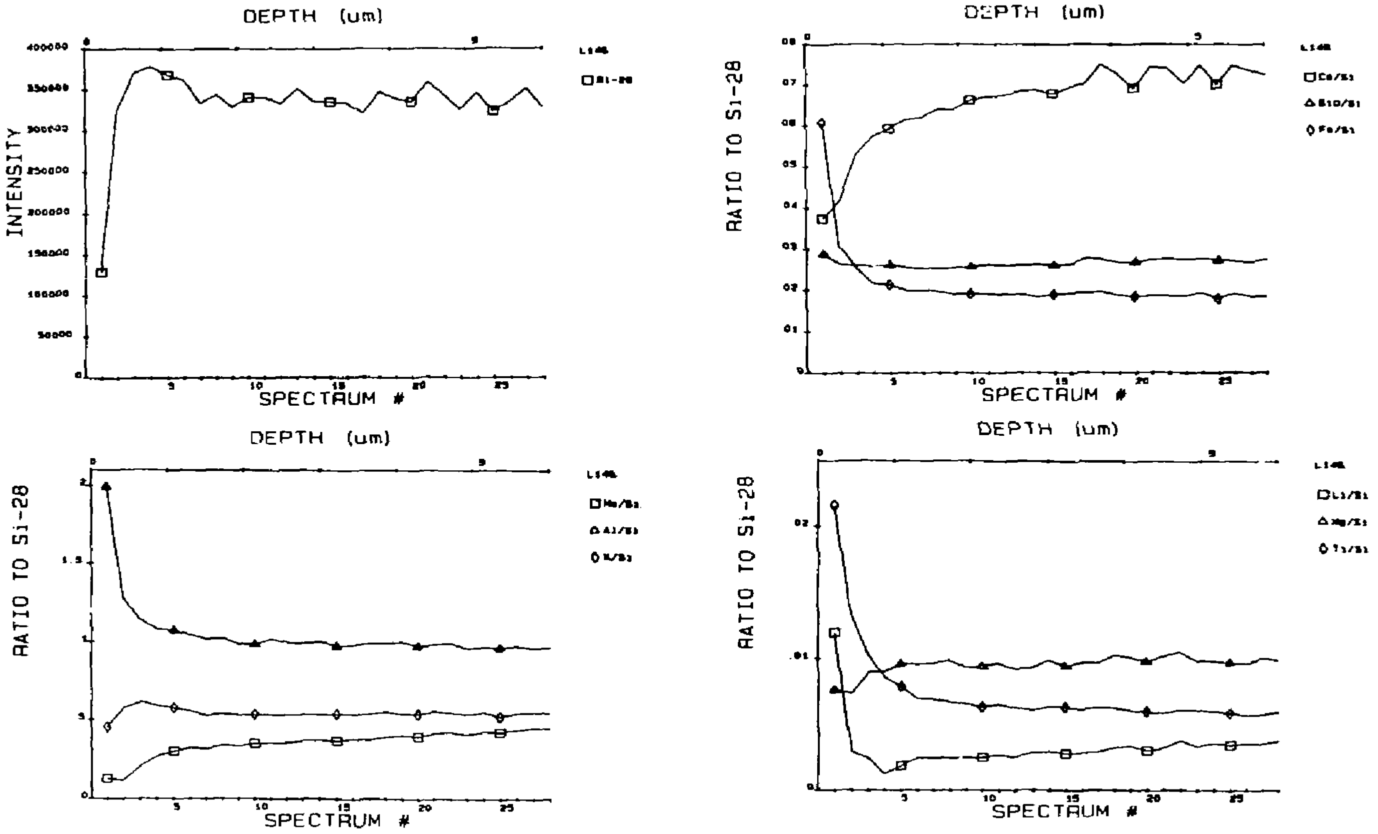


Fig. 20. SIMS Profile for Sample L146, Obsidian Reacted at 75°C, Leached in DIW for 365 Days

Also, it is likely that hydrolysis of the glass matrix is occurring which results in the release of Na and Ca from the glass. The release is greater in liquid water than in vapor and is faster for Ca than for Na.

B. Simple Glass Experiments

A 28-day leach test following MCC-1 protocol (90°C, surface-area-to-volume ratio of 0.01 mm^{-1}) was conducted from 11/3/87 to 12/1/87. It was designed to examine the effect of nonbridging oxygen ions on the process of hydration on glasses similar to those used for nuclear waste. The composition of the glasses (Table 11) was varied systematically to decrease the interconnectivity of the silica network. The concentration of the network modifier CaO was increased from its initial value in Expt. 1 to that in Expt. 11 which provides for a large number of nonbridging oxygens. By doing so, we may study a number of hydration and leaching mechanisms suggested for simpler glasses.

Charles [CHARLES] proposed that a water molecule reacts preferentially with a nonbridging oxygen

$$\equiv Si\text{-}O^-Na^+ + H_2O = \equiv SiOH + Na^+ + OH^-$$

Table 11. Glass Compositions for Simple Glass Leach Test*

		SiO_2	B_2O_3	Al_2O_3	Na_2O	CaO
Test #	1	50	18.75	6.25	20	5
	2	50	16.87	5.63	20	7.5
	3	50	15.0	5.0	20	10
	5	50	11.25	3.75	20	15
	7	50	7.5	2.5	20	20
	9	50	3.75	1.25	20	25
	11	50	-	-	20	30

*Oxide mole percent.

The resulting hydroxyl ion then attacks a Si at a bridging oxygen site

$$\equiv Si\text{-}O\text{-}Si\equiv + OH^- = \equiv SiOH + \equiv Si\text{-}O^-$$

which regenerates another nonbridging oxygen to further the network breakdown by dissociating another water molecule. If such a hydration mechanism is operative, the glass with the larger number of nonbridging oxygens should be more reactive and have a deeper hydration layer (Expt. 11).

Doremus [DOREMUS] has proposed that sodium leaching is controlled by interdiffusion of H^+ or H_3O^+ and Na^+

$$\equiv SiO^-Na^+ + H_3O^+ = \equiv SiO^-H_3O^+ + Na^+$$

With the increasing breakdown of the glass network by the addition of CaO, the hydronium ion should have faster access to the nonbridging oxygens on going from Expt. 1 to Expt. 11. Experiment 11 would then have a deeper hydration layer as is also predicted by the above mechanism by Charles. However, the nature of the hydrated glass is different for each case. Molecular water diffusion is required for hydration in the Charles mechanism followed by the production of silanol groups. H^+ or hydronium ion diffusion is required for the Doremus mechanism which leaves the hydronium ion intact. IR and/or Raman spectroscopy might be able to help differentiate between the presence of molecular water and silanol groups vs. H^+ or hydronium ions in the hydration layer [WU].

One consideration to take into account when analyzing the data is the affect of CaO on water penetration into the glass network. Addition of CaO to a simple sodium silicate glass has been shown to actually decrease the hydration rate of the glass [RANA, SMETS, MORIYA] despite the larger number of nonbridging oxygens present. The Ca ion essentially plugs holes in the glass network and sterically impedes water diffusion into the glass. On the other hand, Ca itself leaches out and water diffusion in the leached layer is much faster which then promotes faster hydration. Such an effect may manifest itself and will give us more information regarding the hydration behavior of the more complicated glasses involved in this study.

Table 12 contains the experimental data obtained. The samples in DUMMY-7 were of the same composition as those for Expt. 7; they were control samples removed once a week from the oven during the 28-day test and visually observed to monitor the integrity of the samples. The samples were allowed to dry sitting in air at room temperature after removal from their test vessels and then weighed. When dry, the samples from Expts. 7 and 9 had an outer milky white film flaking off the surface. The samples from Expt. 11 seemed to be heavily reacted and had a ceramic appearance. The MCC-1 leach samples are currently undergoing the same analysis procedure as applied to those in the NNWSI vapor hydration experiment.

IV. GAMMA IRRADIATION EXPERIMENTS

A. Review of 1 x 10^3 and 0 R/h Results

In order to characterize a repository environment many hundreds of years after waste emplacement, a thorough understanding of the materials interactions which will occur is required. Materials include the waste form, a metal canister and 304L ss container, tuff rock, J-13 groundwater, and air. Physical parameters that will likely affect the repository performance include temperature and radiation fields due to the surrounding waste. The repository is expected to increase from a pre-emplacement temperature of about 37°C to post-emplacement temperatures which will exceed 150°C then cool to about 90°C during the isolation period 1000 years after emplacement. The radiation levels in the repository will be high initially but reduce to less than 50 mR/h for most of the repository's lifetime.

Laboratory experiments designed to probe these interactions must somehow accelerate the reaction and/or magnify the interactions to produce changes that are experimentally detectable within the time constraints of laboratory experiments. Techniques such as using a high glass surface area-to-leachant volume ratio, high reaction temperatures, and flowing leachant have been used previously in an effort to accelerate the glass reaction. While perhaps they do not provide reactions which fully simulate the repository environment, these techniques do allow certain endmember or extreme cases to be identified. In the experiments described below, radiation fields that span the range anticipated in the repository have

Table 12. Simple Glass Leach Test

Test #	Sample #	Vessel #	Glass Diameter (mm)	Glass Thickness (mm)	Surface Area (mm^2)	Total Surface Area (mm^2)	Volume Water Added (mL)	SA/V (mm^{-1})	Weight Dry Vessel (g)	Total Vessel IN (g)	Total Vessel OUT (g)	Δ Mass (g)	Weight Glass IN (mg)	Weight Glass OUT (mg)	Δ Mass (mg)	pH OUT
1	G-1A-1	G-1A	9.34	0.90	163.44	323.39	32.34	0.01000	83.76	116.09	115.38	0.73	148.5	139.6	9.0	10.6
	G-1A-2		9.24	0.89	159.95								148.4	138.8	9.6	
	G-1B-1	G-1B	9.00	0.89	152.40	316.22	31.62	0.01000	85.69	117.23	116.72	0.51	144.2	133.2	11.0	10.6
	G-1B-2		9.33	0.89	162.82								153.2	143.8	9.4	
2	G-2A-1	G-2A	9.19	0.91	158.94	337.22	33.72	0.01000	85.61	119.31	118.74	0.57	150.2	144.8	5.4	10.9
	G-2A-2		9.19	1.58	176.28								246.1	237.6	8.5	
	G-2B-1	G-2B	9.17	0.90	158.01	329.64	32.96	0.01000	84.00	116.96	116.47	0.49	143.7	138.2	5.5	10.9
	G-2B-2		9.06	1.60	171.63								234.6	238.2	7.3	
3	G-3A-1	G-3A	8.60	0.89	140.22	281.07	28.12	0.01000	85.54	113.65	112.70	0.95	124.1	116.5	7.6	12.2
	G-3A-2		8.63	0.88	140.85								130.0	122.0	8.0	
	G-3B-1	G-3B	8.69	0.90	143.19	284.91	28.54	0.00990	83.59	112.14	111.58	0.56	130.0	122.0	8.0	12.3
	G-3B-2		8.65	0.89	141.72								113.8	106.3	7.5	
5	G-5A-1	G-5A	9.21	0.89	158.99	317.67	31.80	0.01000	83.84	115.63	115.06	0.57	152.6	144.8	7.8	12.3
	G-5A-2		9.20	0.89	158.66								152.1	144.2	7.9	
	G-5B-1	G-5B	9.12	0.89	156.15	314.80	31.48	0.01001	85.37	116.83	115.95	0.88	144.3	137.7	6.6	12.3
	G-5B-2		9.19	0.90	158.65								157.1	150.0	7.1	
7	G-7A-1	G-7A	9.11	0.90	156.12	311.61	31.18	0.00999	85.50	116.67	116.0	0.67	154.8	147.5	7.3	12 8
	G-7A-2		9.09	0.90	155.49								153.8	146.6	7.2	
	G-7B-1	G-7B	9.12	0.90	156.44	315.58	31.57	0.01000	83.75	115.33	114.13	1.20	151.4	143.6	7.8	12.7
	G-7B-2		9.16	0.95	159.14								154.2	146.1	8.1	
9	G-9A-1	G-9A	9.19	0.95	160.09	319.00	31.90	0.01000	83.72	115.61	115.13	0.48	162.3	157.5	4.8	13.2
	G-9A-2		9.18	0.92	158.91								150.2	146.1	4.1	
	G-9B-1	G-9B	9.16	0.90	157.70	313.82	31.37	0.01000	85.65	117.03	116.16	0.87	159.4	155.3	4.1	13.2
	G-9B-2		9.11	0.90	156.12								152.1	147.9	4.2	
11	G-11A-1	G-11A	9.08	1.53	173.16	349.79	35.02	0.00999	83.63	118.63	117.87	0.76	243.7	237.8	5.9	12.3
	G-11A-2		9.15	1.57	176.64								273.2	267.3	5.9	
DUMMY7	DUMMY7-1	DUMMY-7	9.13	0.89	156.46	313.24	31.32	0.01000	83.97	115.31	114.05	1.26	151.6	141.4	10.2	12.8
	DUMMY7-2		9.14	0.89	156.78								153.9	144.7	9.2	

been used. In some cases unrealistically high exposure rates were used to allow comparison with results obtaining using lower radiation levels. Such an approach allows an identification of the effects of radiation on reaction processes.

Previous work has shown gamma irradiation of moist air to produce nitrogen oxides which, when dissolved into an aqueous solution, form nitric and nitrous acids which acidify the solution [BATES-7]. (Nitrous acid is unstable at pH values below about 3.4.) Borosilicate glasses are known to be more unstable in acidic solutions than in near-neutral solutions. Irradiation of the repository may therefore produce small pockets of acidic groundwater in which the waste may be more reactive than in natural groundwater. To understand the repository environment after waste emplacement it is necessary to first understand how the groundwater is affected by the radiation fields.

The experiments performed were not designed to simulate any one repository scenario, rather they were designed to monitor component interactions. Experiments were performed without glass present to study the effect of radiation on the groundwater alone, and with glass present to study the effect of the irradiated solution on the glass reaction. Many of the experimental results have been presented in previous semiannual reports as the results were obtained. The series of experiments has been concluded and the results are summarized below.

The reaction between EJ-13 groundwater and synthetic nuclear waste glass formulations SRL 165, ATM-1c, and ATM-8 under the influence of penetrating gamma irradiation has been studied at 90°C. Exposure rates of about 2E5 R/h, 1E4 R/h, 1E3 R/h, and 0 R/h have been used in an effort to elucidate the effects of total gamma radiation exposure on the reaction. Experiments were performed in stainless steel vessels of approximately 22 mL volume. Synthetic waste glass, groundwater, air, and in some cases a tuff wafer were present in the reaction vessels. The amount of groundwater added to a vessel was adjusted to provide an air-to-liquid volume ratio near 0.3 and a glass surface area-to-liquid volume ratio near 0.3 cm^{-1}. The vessels were sealed and placed in an oven in the appropriate gamma radiation field and allowed to react for times up to 365 days. After the experiments were terminated, analyses of the leachates and the reacted glass surfaces were performed to characterize the reaction. The results of experiments performed under exposure rates of 2E5 R/h and 1E4 R/h have been reported previously by [BATES-7] and [ABRAJANO-1], respectively. The results of experiments performed under exposure rates of 1E3 R/h and 0 R/h have been compiled into a topical report which is currently under internal review [EBERT].

The irradiation of moist air was seen to acidify the EJ-13 groundwater from its initial pH value near 8. However, under all conditions tested the high bicarbonate content of the water (~120 ppm) acted to buffer the solution to a pH near 6.4. Actual repository conditions wherein liquid groundwater may be present in very small quantities are not well represented by these experiments. Such small volumes (relative to air) could possibly become more acidic than the leachates in these experiments because of the lower buffer capacity. The advantage of the tuff repository horizon is, of course, the scarcity of liquid groundwater and so the low probability of groundwater contacting the waste and transporting radionuclides away from the repository site. The major influence of penetrating gamma radiation appears to be through acidification of the leachate. Our results have shown the extent of glass reaction to be similar in irradiated and nonirradiated experiments, probably because the release of highly leachable components such as Li, Na, B, or Mo from the glass is not strongly dependent on pH in the range 6.5-9.5.

The behavior of some species released from the glass during reaction was influenced by radiation because of the leachate pH difference, most noticeably affected were the actinide elements. The solubilities of the actinides are known to be very pH sensitive. The distribution of the released actinides between dissolved, suspended, and adsorbed phases was seen to vary slightly at different pHs.

The concentration profiles of elements in the near-surface region of the reacted glasses were obtained using SIMS. Some species were seen to be released in a diffusional manner while others were released more congruently. The profiles of lithium and sodium showed these elements to be depleted to the greatest depths. These elements and boron had sigmoidal profiles consistent with diffusional release. Other elements were seen to be enriched on the outer surface relative to their bulk concentrations. An alteration layer could be seen in the polished cross-sections of glasses reacted 91 days or longer. Similar alteration phases form after shorter reaction times but are not observable in cross-sections. Semi-quantitative analysis of this layer showed it to have a composition very similar to an iron-rich smectite clay, nontronite. Similar clays form on reacted natural glasses. The thickness of this alteration layer increased with reaction time in a nearly parabolic manner. The appearance of the reacted region in cracks present in the glass as seen in the polished cross-sections suggests that the glass (or the alteration layer) etches to a small extent. This is inferred from the fact that the alteration layer does not completely fill the crack although the densities of the unreacted glass and the alteration layer are very similar. Such etching is consistent with the silicon concentrations measured in the leachates.

Of particular interest in the reaction of glass in the repository environment is the behavior of the actinide elements. Uranium and neptunium were shown by ion microprobe analysis to be depleted in the alteration layer (Fig. 21). The uranium was found to be both adsorbed onto the stainless steel vessel surface and fixed in precipitates (as yet unidentified) in both irradiated and nonirradiated experiments. Neptunium was not found to be contained in any surface precipitate, but was found to exist in a suspended phase in the leachate, perhaps being adsorbed onto iron-silicate colloids and adsorbed onto the stainless steel vessel surface. A significant amount of neptunium was found to exist in a nonfilterable form as well.

Plutonium was seen to have a rather flat profile in the near-surface area of the reacted glass although plutonium was found to be adsorbed onto the stainless steel vessel surface. Very little plutonium was found in the leachate. Americium was found to be enriched on the outer surface of the alteration phase on the glass. A small amount of americium was also present on the stainless steel vessel surface.

Uranium and neptunium are interpreted as being released from the glass in a different manner than are plutonium and americium. Uranium and neptunium are thought to be released by a mechanism similar to boron. As water infiltrates the glass and an ion-exchange reaction occurs to free

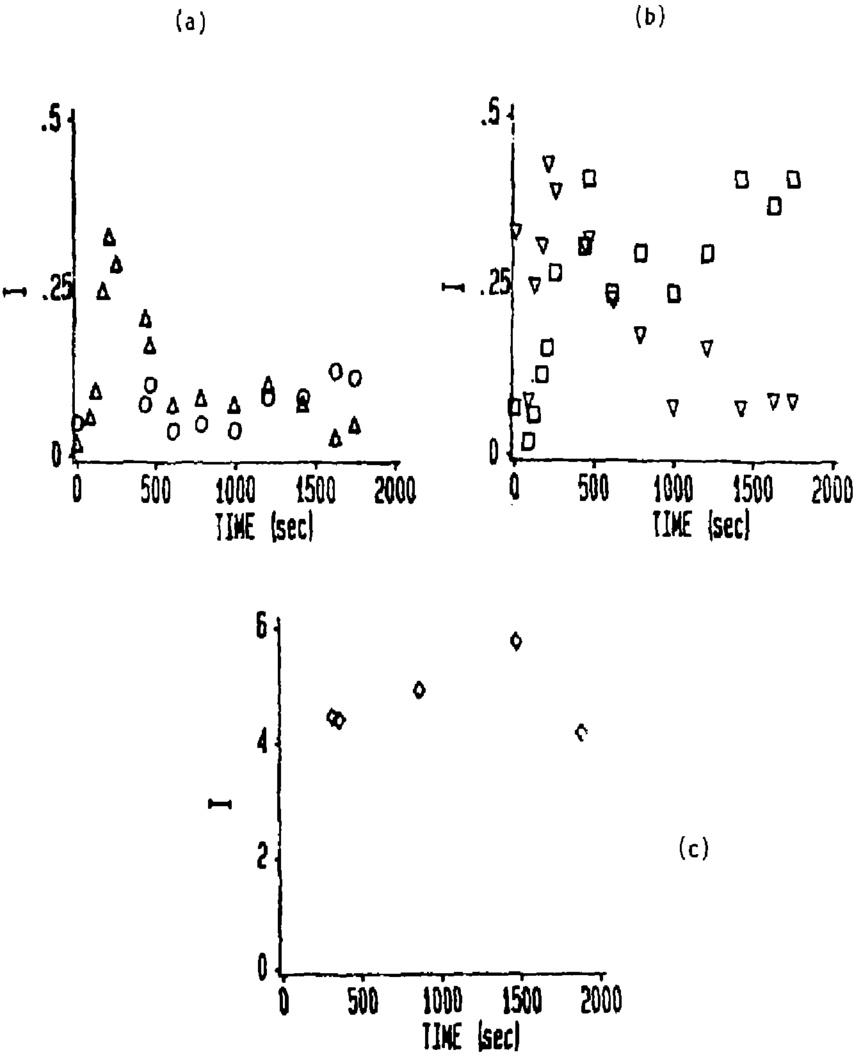


Fig. 21. Ion Microprobe Profiles of (a) (Δ) Am and (O) Pu; (b) (∇) Np and (□) U; and (c) (◇) Si for Sample #253 that was Reacted for 91 Days at 1 x 10^4 R/hr. Note the enrichment of Np at the surface is due to an interference at mass 237 due to a Au + Ca combination formed during gold coating. The Np profile as verified by the profile of NpO_2 is actually constant throughout the depth sputtering.

sodium and lithium, a reaction between boron (or uranium or neptunium) in the glass and water species frees a boron- (or uranium- or neptunium-) containing species from the glass network which can migrate out of the glass surface and into solution.

As water continues to infiltrate the glass, glass components are released at various rates to form a layer having a composition that varies with depth, the so-called alteration layer. Species at the surface of the alteration layer, at the leachate interface, may become totally dislodged from the residual glass network in the layer and become solvated. In this way the alteration layer etches. Insoluble species such as aluminum, americium, and iron remain in the alteration layer bound to the residual glass network. These species may become enriched at the surface of the alteration layer as the surface etches and they are left behind. Such enrichment of aluminum is seen on surfaces reacted for short times and enrichment of americium on the outermost surface is seen at all reaction times. The presence of these insoluble species on and in the alteration layer may, under certain conditions [WICKS], slow the flow of water into the glass and thereby slow the reaction. Also, the solution concentrations of glass components may effect the reactions which release them from the glass network and so slow the overall glass reaction. By buffering the concentrations of glass components in solution, precipitates may influence the glass reaction.

Gamma irradiation influences the reaction between groundwater and nuclear waste glass through acidification of the groundwater. Experiments were performed at air-to-groundwater ratios that were too small to overcome the buffering capacity of the EJ-13 groundwater, and the most acidic pH obtainable was about 6.4. This was not sufficiently acidic to accelerate the glass reaction, although it did affect the distribution of released actinides somewhat. The low solubilities of the actinide species at these pHs confined them to being adsorbed on the stainless steel vessel surfaces, existing as suspended material, or as residue on the glass surfaces.

Conditions that are more repository relevant may result in an increase in the dissolved fraction of the actinides if the pH is able to become more acidic than 6.4. The reduced volume of water necessary to produce such acid solutions will at the same time decrease the likelihood of released radionuclides being transported away from the waste package.

V. ANALYTICAL SUPPORT

Development of analytical capabilities this year was limited, as analysis of samples generated during the FY 1986 Gamma Irradiation Experiments consumed much of time originally allotted for these projects.

Three new analytical instruments were obtained, including a PEAK FOCUS wavelength dispersive spectrometer (WDS) for X-ray emission analysis in the SEM. This crystal spectrometer allows for the X-ray analysis of light elements. The crystals in the spectrometer used to disperse the X-rays and focus them onto the detector are configured so that only a very small range of X-ray energies, and therefore a limited number of elements, can be analyzed using each crystal. With the crystals currently in place, we are able to analyze for boron using a manufactured layered crystal; oxygen and fluorine using an OV60 crystal; aluminum, silicon, and strontium using a TAP crystal; and phosphorus, zirconium, and lanthanum using a PET crystal. Other elements producing high order X-rays with energies similar to those of these listed elements may also be detected. This instrument is controlled by the System IV software which also controls the energy dispersive spectrometer (EDS) on the SEM. We are currently familiarizing ourselves with this instrument so to be able to analyze for light elements in the vapor hydrated glasses.

A Dektac IIA profilimeter was also obtained. This instrument measures contours via a stylus/piezoelectric crystal transducer. For our purposes, this instrument is useful in determining the sputter rate for SIMS analyses by measuring the crater depth produced during analysis. A similar instrument was used . . LLNL to determine the sputter rate for analysis of FY 1986 Gamma Irradiated Experiment samples, as was discussed previously [BATES-4]. Access to this instrument will allow us to more confidently determine the sputter rate for analyses as the SIMS configuration is varied.

An optical microscope is now available for viewing and photographing reacted surfaces on a larger scale than is possible in the SEM. This is essential in performing a complete analysis of reacted surfaces. This light microscope is also a convenient way to analyze other system components such as SEM filaments for detecting unusual wear or misalignments.

A. Development of a Laser Raman Microprobe System

A laser Raman microprobe (LRM) system is being developed to analyze microcrystalline precipitates which form during the hydration of nuclear waste glass. By using standard microscope objectives, an argon ion laser can be focused to a beam diameter less than 2 µm. This allows spectra to be collected from very small samples. X-RAY emission spectroscopy, available on the SEM, can be used to compositionally analyze the sample. The Raman spectra of compounds having compositions consistent with the unknown can then be consulted and compared to the spectrum of the unknown for comparative identification. The LRM should be particularly useful in analyzing samples that are too small to be isolated and studied using X-ray diffraction techniques.

Development of the laser Raman microprobe continued during this reporting period. Problems with the photon counter and laser tube have been identified and corrected. Difficulties in optimizing the signals collected were encountered due to what is thought to be extreme sensitivity of the collection optics to the positioning of the exciting beam on the sample. Work has concentrated on analyzing uranium-containing samples.

A variety of samples generated from the reaction of glass or UO_2 with water have been examined using LRM. While the difficulties in obtaining good spectra have led to the optimization studies using other samples that have been reported earlier, the spectra of relevant samples collected to date demonstrate the potential of the technique for this application and the current ability to collect spectra of isolated phases.

One type of precipitate that is often seen in glass leaching and hydration studies or UO_2 reaction is one that is rich in uranium. In many samples the U-rich precipitates are found at only one or two locations on the sample surface, and they are often too small to isolate for analysis using XRD. However, because of their importance as an actinide-containing phase their identity is of paramount importance. Example of such phases are shown in the topical reports describing the N2 Unsaturated Tests and the FY 1986 gamma experiments. Other examples include the phases that formed on the unsaturated experiments performed with UO_2, and weeksite that forms during the vapor hydration of SRL 165 type glass.

In the present development, the LRM is used to obtain a reference set of spectra of uranium-containing phases. These spectra are then used for comparative identification of unknown samples. Spectra of other unique U phases will be collected as more samples become available.

The LRM was used to obtain the spectra of several uranium-containing phases. Uranium trioxide (UO_3) and triuranium octoxide (U_3O_8) were obtained as reagent-grade powders. Other uranium-containing phases were available on the surface of a reacted sample of UO_2 (see section 2). XRD analysis of phases scraped from the surface of the latter sample showed the presence of a schoepite phase $UO_3 \cdot (0.8H_2O)$. Optical microscopy of the sample surface showed the presence of small transparent crystals and a yellow coating on a gray substrate. Both the crystals and the yellow coating were analyzed. Figure 22 shows preliminary spectra of these uranium-containing samples. Additional effort in refining the spectrum-collecting procedure will be required to provide definitive spectra.

The crystallites seen in the reacted UO_2 sample are dehydrated schoepite, $UO_3 \cdot (0.8H_2O)$. The molecule UO_2 belongs to the point group $D_{\infty h}$. The antisymmetric stretch and bend modes are IR active and occur at about 776.1 and 765 cm^{-1} [GABELNICK]. The Raman peak near 560 cm^{-1} is presumably the symmetric stretch mode, which is Raman active and IR inactive. The UC molecule has a single stretch which occurs at 820 cm^{-1}. It is surprising that the UO_2 antisymmetric stretch occurs so far removed from the UO stretch frequency. The peak also is seen to have an odd shape, which was obtained consistently. Hopefully, the question as to the peak's origin will be clarified when a reference schoepite spectrum is obtained.

These early analyses show the LRM technique to have the potential of discriminating between compounds of similar composition, although more experience is required to optimize the collection optics and sample positioning in order to acquire the best possible spectra. As familiarity with the equipment increases and the computer programs are debugged, the quality of the spectra is expected to improve significantly. Analysis of the crystalline samples may benefit by the addition of a goniometer sample holder. This would allow for the precise positioning of the sample under the beam to maximize the signal. Such a sample stage is commercially available.

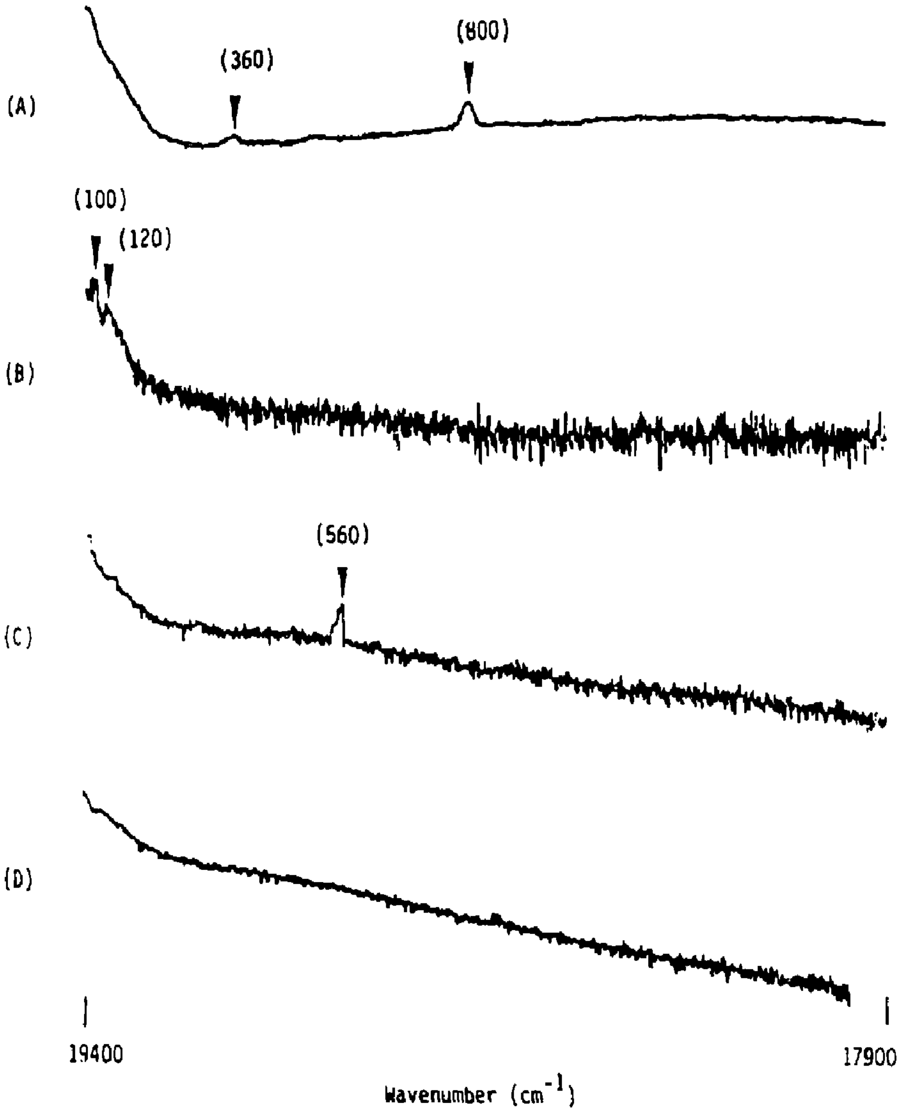


Fig. 22. Raman Spectra of (A) UO_3, (B) U_3O_8, (C) Crystal on Surface of Sample Shown in Fig. 5, and (D) General Surface of Sample Shown in Fig. 5, Acquired using the Laser Raman Microprobe. The Raman shifts of peaks are labeled in parentheses.

B. Development of a Gas Analysis System

A gas analysis system is being developed around a quadrupole mass analyzer (UTI model 100C). Gas samples may be leaked in directly from a sample ballast, evolved from solution, or desorbed from a solid. The latter experiment is referred to as temperature programmable desorption (TPD) wherein the solid sample is heated at a constant rate while the evolved gases are continuously monitored. Current emphasis is on this technique, although analyses of gaseous samples will be performed as a part of the calibration procedure.

The laboratory space where the system is being relocated has now been cleared of old equipment. The mass analyzer system has been moved to its new location and reassembly of the instrument is under way. Direct-drive roughing pumps have replaced the belt-driven pumps, and preliminary measurements indicate that the base pressure of the system may be reduced by an order of magnitude using these better pumps. Reactivation of this system is a priority of the upcoming quarter.

VI. BASALT ANALOG

A. Reanalysis of Hydrothermal Solution and Vapor Experiments

A series of hydrothermal leaching and vapor phase hydration experiments have been performed using two synthetic basalt and one SRL glass composition (see Table 13) and deionized water. A discussion of these experiments has been presented in [BYERS]. While these experiments were completed under a different sponsor, they provide a wealth of samples and data that still require analysis and interpretation, where the synthesized information will be of use to the NNWSI program. For this reason work is continuing with these samples.

Two test matrices were completed by [BYERS]; in one matrix the glasses were leached at temperatures ranging from 90°C to 187°C for times up to 546 days, and in the second the glasses were vapor hydrated at temperatures ranging from 122°C to 240°C for up to 150 days (Tables 14 and 15). The solutions were analyzed for the cation concentrations, and the surfaces of the reacted glasses were characterized to identify mineral phases that had formed. The reacted glasses are presently being quantitatively analyzed with respect to the layer composition and growth kinetics of the layer.

Table 13. Compositions[a] of the Three Glasses Used in C. Byers' Experiments in Weight Percent and Stoichiometry, Normalized to Eight Silicon Atoms

	SRL 165 wt %	Hawaiian Basalt wt %	New Basalt wt %
Li	1.99	-[b]	-
B	2.15	-	-
Na	8.30	3.37	3.33
Mg	0.43	3.64	4.03
Al	2.23	7.12	6.20
Si	25.48	23.53	23.68
K	-	0.52	0.53
Ca	1.19	7.42	7.57
Ti	-	1.04	1.15
Mn	1.80	0.14	0.14
Fe	8.45	8.85	9.13
Ni	0.69	-	-
Zr	0.49	-	-
O	46.80	44.37	44.24
TOTAL	100.00	100.00	100.00
	Stoichiometry		
Li	2.53	-	-
B	1.75	-	-
Na	3.18	1.40	1.37
Mg	0.16	1.43	1.57
Al	0.73	2.52	2.18
Si	8.00	8.00	8.00
K	-	0.13	0.13
Ca	0.26	1.77	1.79
Ti	-	0.21	0.23
Mn	0.29	0.02	0.02
Fe	1.33	1.51	1.55
Ni	0.10	-	-
Zr	0.05	-	-
O	25.77	26.48	26.24

[a] Compositions are based on total dissolution and subsequent ICP analysis of each glass. These analyses were then normalized to 100%, discarding trace elements (<0.10 wt %). Stoichiometries were normalized to eight silicon atoms to easily compare the layer stoichiometries with that of smectite clay.

[b] - = not present.

Table 14. Test Matrix of Hydrothermally Leached Synthetic Basalt and SRL 165 Glasses, Glass Surface Area-to-Solution Volume Ratio (SA/V) = 1 cm^{-1}. Each number represents the sample number of the glass reacted. These experiments were performed by [BYERS].

Days	Hawaiian Basalt Glass (except where noted)				SRL 165 Glass
	90°C	122°C	150°C	187°C	187°C
14	820, 821				
15			550, 551		150, 151
28	822, 823	252, 253	552, 553	852, 853	152, 153
56	824, 825	254, 255	554, 555		154, 155, 169, 469,* 470*
65				854, 855	
91	826, 827			889,** 890**	156, 157, 171, 172, 471,* 472*
93		256, 267	556, 557	856, 857	
183	828, 829	258, 259	558, 559	858, 859	158, 159
364	813** 814**	260, 261	560, 561	860, 861, 809,** 810**	160, 161
546	811,** 812**				

*SA/V = 4 cm^{-1}.

**New basalt glass.

Table 15. Test Matrix of Vapor Phase Reacted Synthetic Hawaiian Basalt and SRL 165 Glasses. Each number represents the sample number of the glass reacted. These experiments were performed by [BYERS].

	Hawaiian Basalt Glass				SRL 165 Glass
Days	122°C	150°C	240°C	187°C	187°C
10			33	44	45
14			24	46	47
20		63	25	48	49
28		67	36	50	51
32		65			
40		68	37	52	53
56	89	69	38	59	55
75			39		
76		64			
80	90	70			
84				56	57
91	91	71	40		
92					59
95				58	
120		72			
146				60	
150		73			

Results of quantitative layer composition measurements are presented for basalt samples hydrothermally leached at 90, 150, and 187°C for varying lengths of time, for a basalt sample, vapor phase hydrated at 240°C for 91 days, and for an SRL 165 type glass sample, leached at 187°C for 183 days. Quantitative analyses were made using an SEM/EDS system with Princeton Gamma Tech (PGT) System IV software. Spectra were collected from many points on each cross-sectioned sample. Five spectra were collected from the unreacted center of each sample, and these bulk glass spectra were averaged to create a "standard" for the analyses of each sample.

These "standards" were analyzed, using sample #860 as the standard, in order to determine the reproducibility of the technique (Table 16). In general, the analyses are reproducible to within the error of the instrument, ±10%. The largest variations are in the Fe and Mn contents. The detection limit of the instrument is ~0.10 wt %, and consequently elements with concentrations approaching this level show the greatest variations.

Analysis of reacted layers produces several additional considerations. These types of experiments result in hydrated layers forming on the glass surface and since the SEM/EDS system is not sensitive to H_2O, it is assumed that the difference of 100% and the total wt % is due to water in the glass. Analysis of thinner layers (<3 µm) may also include x-rays from bulk glass and the mounting resin. The probed area is approximately 1 μm^3, depending on the probe current, accelerating voltage, and the density of the material. Consequently, the analyses of the thinner layers may vary in total weight percent, but the stoichiometric ratios should be similar if the layers are similar. For this reason, results of quantitative analyses are presented in terms of total wt % and the stoichiometric ratios normalized to eight Si atoms (Table 17). Boron and lithium cannot be measured using the present SEM/EDS system. Therefore, the analysis of the SRL 165 glass layer assumes that B and Li are not present.

The results in Table 17 are the averages of many (usually ≥ 10) spectra collected from reacted layers on a sample. In general, the compositions of the layers did not vary significantly. When individual elements did vary, it did not appear to be systematic.

Table 16. Bulk Glass Analyses Made Using 860STD as the Standard Spectra. The actual composition of the Hawaiian Basalt glass is presented as "Haw. Basalt." The lower half of the table presents the stoichiometric ratios of each analysis, normalized to eight Si atoms.

	Haw. Basalt	Element Wt %					
		860STD	859STD	559STD	827STD	46STD	40STD
Na	3.37	3.37	3.38	3.36	3.62	3.57	3.65
Mg	3.64	3.64	3.67	3.70	3.74	3.64	3.74
Al	7.12	7.12	7.18	7.28	7.20	6.88	7.27
Si	23.53	23.53	24.33	24.61	23.95	23.08	23.85
K	0.52	0.52	0.49	0.52	0.48	0.43	0.45
Ca	7.42	7.42	7.82	7.91	7.40	7.05	7.57
Ti	1.04	1.04	1.05	1.15	0.98	0.96	1.03
Mn	0.14	0.14	0.00	0.04	0.02	0.04	0.05
Fe	8.85	8.85	9.59	9.88	8.95	8.02	9.37
O	44.37	44.36	45.74	46.41	44.98	43.06	45.22
TOTAL	100.00	99.99	103.25	104.85	101.32	96.73	102.20

	Stoichiometric Ratio (Normalized to Eight Si Atoms)						
Na	1.40	1.40	1.40	1.33	1.48	1.51	1.49
Mg	1.43	1.43	1.43	1.39	1.44	1.46	1.45
Al	2.52	2.52	2.52	2.46	2.51	2.48	2.54
Si	8.00	8.00	8.00	8.00	8.00	8.00	8.00
K	0.13	0.13	0.13	0.12	0.11	0.11	0.11
Ca	1.77	1.77	1.77	1.80	1.73	1.71	1.78
Ti	0.21	0.21	0.21	0.22	0.19	0.20	0.20
Mn	0.22	0.02	0.02	0.01	0.00	0.01	0.01
Fe	1.51	1.51	1.52	1.62	1.50	1.40	1.58
O	26.48	26.48	26.48	26.49	26.38	26.21	26.64

Table 16 (Cont'd)

	50STD	56STD	561STD	857STD	
Na	3.47	3.77	3.66	3.38	
Mg	3.64	3.86	3.83	3.59	
Al	6.96	7.31	7.31	7.10	
Si	22.81	24.07	24.08	23.28	
K	0.43	0.47	0.47	0.50	
Ca	7.04	7.58	7.60	7.42	
Ti	0.96	1.06	1.17	1.03	
Mn	0.08	0.07	0.05	0.00	
Fe	7.99	9.18	9.20	8.52	
O	42.79	45.58	45.61	43.85	
TOTAL	96.16	102.95	102.97	98.75	
					Average
Na	1.49	1.53	1.48	1.42	1.46 ± 0.06
Mg	1.47	1.48	1.47	1.43	1.45 ± 0.03
Al	2.54	2.53	2.53	2.57	2.52 ± 0.03
Si	8.00	8.00	8.00	8.00	8.00 ± 0.00
K	0.11	0.11	0.11	0.12	0.11 ± 0.01
Ca	1.73	1.77	1.77	1.79	1.76 ± 0.03
Ti	0.20	0.21	0.23	0.21	0.21 ± 0.01
Mn	0.01	0.01	0.01	0.00	0.01 ± 0.01
Fe	1.41	1.53	1.54	1.47	1.51 ± 0.07
O	26.35	26.60	26.61	26.46	26.47 ± 0.13

Table 17. Quantitative Analyses of the Reaction Layer Formed on SRL 165 Glass and Basalt Glasses. Results are presented as stoichiometries normalized to eight silicon atoms. Also presented are the total weight percent of the analyses; these values allow the water content of the layer to be estimated. These compositions are the average of many analyses.

	Hawaiian Basalt Leached at					
	187°C			90°C	150°C	
Element	#857 (93 days)	#859 (183 days)	#860 (364 days)	#827 (91 days)	#559 (183 days)	#561 (364 days)
Na	0.29 ± 0.10	0.30 ± 0.12	0.40 ± 0.08	0.33 ± 0.33	0.31 ± 0.10	0.51 ± 0.06
Mg	3.64 ± 0.61	4.05 ± 0.53	3.68 ± 0.85	2.32 ± 0.87	3.17 ± 0.97	3.46 ± 0.55
Al	4.42 ± 0.30	4.58 ± 0.17	3.96 ± 0.30	4.13 ± 0.50	4.16 ± 0.29	4.05 ± 0.20
Si	8.00 ± 0.00	8.00 ± 0.00	8.00 ± 0.00	8.00 ± 0.00	8.00 ± 0.00	8.00 ± 0.00
K	0.02 ± 0.01	0.01 ± 0.01	0.03 ± 0.03	0.12 ± 0.04	0.03 ± 0.02	0.09 ± 0.03
Ca	2.07 ± 0.14	2.12 ± 0.12	1.94 ± 0.23	1.36 ± 0.24	1.82 ± 0.49	1.51 ± 0.20
Ti	0.61 ± 0.05	0.63 ± 0.07	0.62 ± 0.11	0.97 ± 0.10	0.75 ± 0.13	0.51 ± 0.04
Mn	0.04 ± 0.03	0.04 ± 0.03	0.05 ± 0.02	0.16 ± 0.11	0.02 ± 0.01	0.12 ± 0.09
Fe	4.37 ± 0.31	4.69 ± 0.48	4.82 ± 0.88	5.95 ± 0.90	4.97 ± 1.10	3.90 ± 0.43
O	36.34 ± 1.00	37.56 ± 1.34	36.33 ± 0.57	37.29 ± 1.76	36.43 ± 2.52	34.48 ± 1.40
TOTAL wt %	85.23 ± 2.89	89.85 ± 1.58	86.41 ± 2.67	72.30 ± 0.91	92.92 ± 3.14	86.17 ± 2.34

Cont'd

Table 17 (Cont'd)

	New Basalt Leached					
	at 90°C	at 187°C		Hawaiian Basalt Vapor Hydrated at 240°C		SRL 165 Leached at 187°C
	#811 (546 days)	#889 (Inner) (91 days)	#889 (Outer) (91 days)	#40 (91 days)		#159 (183 days)
Na	0.48 ± 0.06	0.79 ± 0.20	0.35 ± 0.06	0.51 ± 0.12	Na	0.87 ± 0.19
Mg	1.78 ± 0.67	1.05 ± 0.76	3.49 ± 0.08	2.58 ± 0.54	Mg	0.32 ± 0.06
Al	3.85 ± 0.29	3.47 ± 0.39	1.99 ± 0.09	2.38 ± 0.54	Al	1.24 ± 0.14
Si	8.00 ± 0.00	8.00 ± 0.00	8.00 ± 0.00	8.00 ± 0.00	Si	8.00 ± 0.00
K	0.08 ± 0.03	0.25 ± 0.08	0.00 ± 0.00	0.14 ± 0.10	Ca	0.43 ± 0.07
Ca	2.63 ± 0.19	3.31 ± 0.38	0.25 ± 0.15	2.05 ± 0.26	Mn	0.66 ± 0.38
Ti	0.64 ± 0.07	0.67 ± 0.15	0.00 ± 0.00	0.48 ± 0.10	Fe	2.69 ± 0.35
Mn	0.14 ± 0.10	0.00 ± 0.00	0.03 ± 0.03	0.08 ± 0.05	N	0.11 ± 0.02
Fe	4.82 ± 0.26	5.26 ± 1.08	0.17 ± 0.05	2.21 ± 0.30	Zr	0.07 ± 0.02
O	34.94 ± 1.00	35.32 ± 1.61	23.21 ± 0.22	28.96 ± 0.66	O	24.77 ± 1.39
TOTAL wt %	88.06 ± 2.86	90.65 ± 4.95	65.34 ± 3.38	79.10 ± 11.61	TOTAL wt %	85.05 ± 3.67

The composition of the reacted layer seems to be similar between points or a particular sample and between different samples. The stoichiometries of the analyses are consistent with a smectite clay, ideally $(1/2Ca,Na)_{0.7}(Al,Mg,Fe)_4[(Si,Al)_8O_{26}](OH)_4 \cdot nH_2O$. While not an ideal end member, the composition is probably some sort of clay intermediate between nontronite (Fe-rich) and saponite (Mg-rich). Variations in analyses are more likely due to composition variety rather than analytical error, and may have resulted from more than one mineral phase being present. Before any more definitive discussion is made regarding these layers, further analyses will be made.

In the experimental procedure used, the test vessel was allowed to cool for periods up to an hour. It is probable that, with these changing conditions, additional secondary phases may have precipitated from solution. Indeed, several phases have been observed on the surface of some samples which are distinct from the majority of the layer, both in appearance and composition.

It is of prime importance to know whether these precipitates formed during the reaction or during the quenching of the leachate. Access to the geochemical code EQ3/EQ6 is being obtained to attempt to resolve some of these problems. Becoming more familiar with this code will also help to understand how modeling work being performed at LLNL is applicable to this study.

In addition to quantitative analyses, the reacted layer thicknesses are being measured in order to deduce the reaction kinetics of the experiments. The only experiment for which complete data are available is the leach test of Hawaiian basalt at 187°C. The layer was not of constant thickness. The thicknesses measured are presented in Fig. 23. The thicknesses are presented as a function of time$^{1/2}$.

To provide some insight as to the kinetics of vapor phase hydration of SRL 165 glass and to compare hydration rates in hydrothermal leach experiments with vapor phase conditions, the samples of SRL 165 black frit reacted previously by [BYERS] at 187°C were also examined. Measurements were made on existing mounts, on newly mounted samples, and on previously prepared samples that were recut and polished. The problem in measuring an

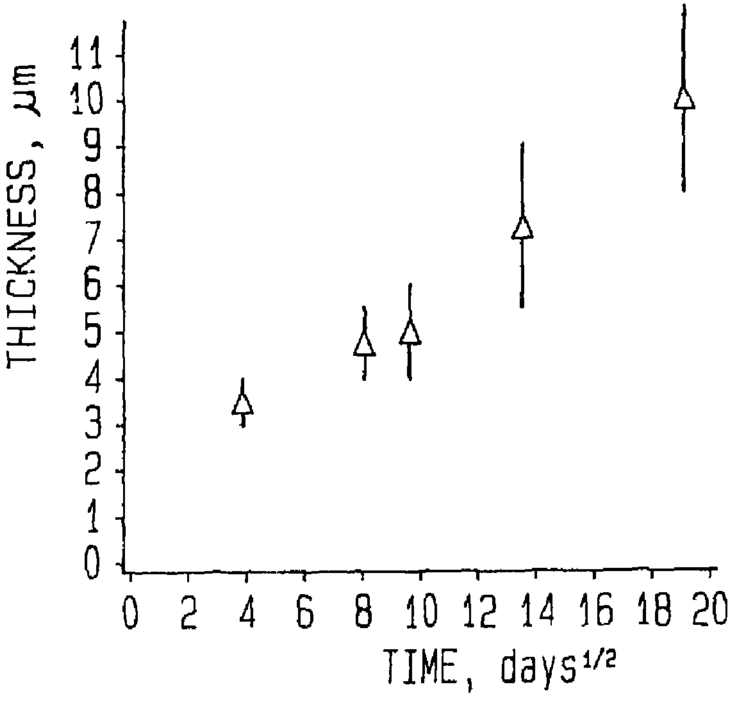


Fig. 23. Reaction Layer Thicknesses of Hawaiian Basalt Leached at 187°C as a Function of Time$^{1/2}$. Error bars depict the range of values measured.

accurate layer thickness is to be able to identify whether the entire layer remains and to what extent cracking and peeling of the layer affects the thickness measurement.

A typical layer is shown in Fig. 24. As is apparent the layer consists of many separate layers, some or all of which may be detached from the glass or each other. An intact layer provides the best measure of the thickness, and measurements are made from the surface on which the alteration products form to the bulk glass. At least 20 thickness measurements are made per sample, if enough intact layer exists, thereby generating a range of thicknesses and a median thickness.

The samples investigated are listed in Table 15 and the results are plotted in Fig. 25. The bars represent the range of layer thickness per sample. The large variation in layer thickness probably results from the

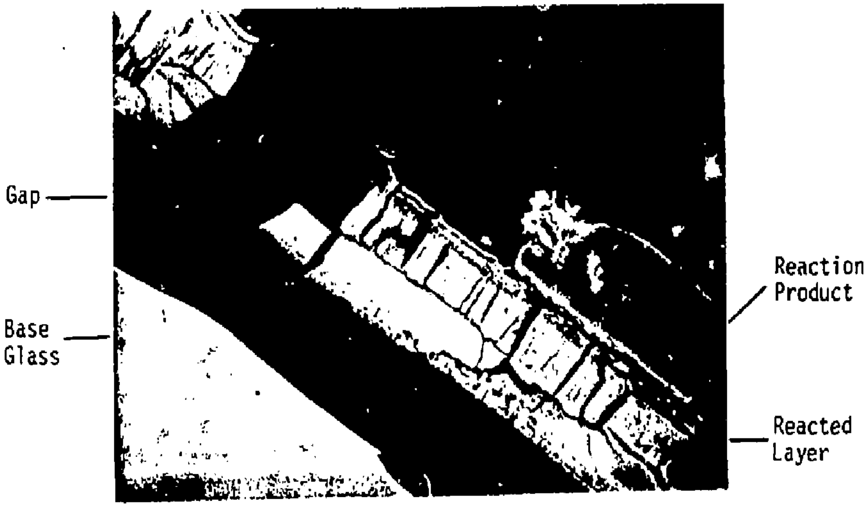


Fig. 24. Surface Layer and Associated Reaction Products from SRL Black Frit Reacted at 187°C in Water Vapor. Magnification = 500X.

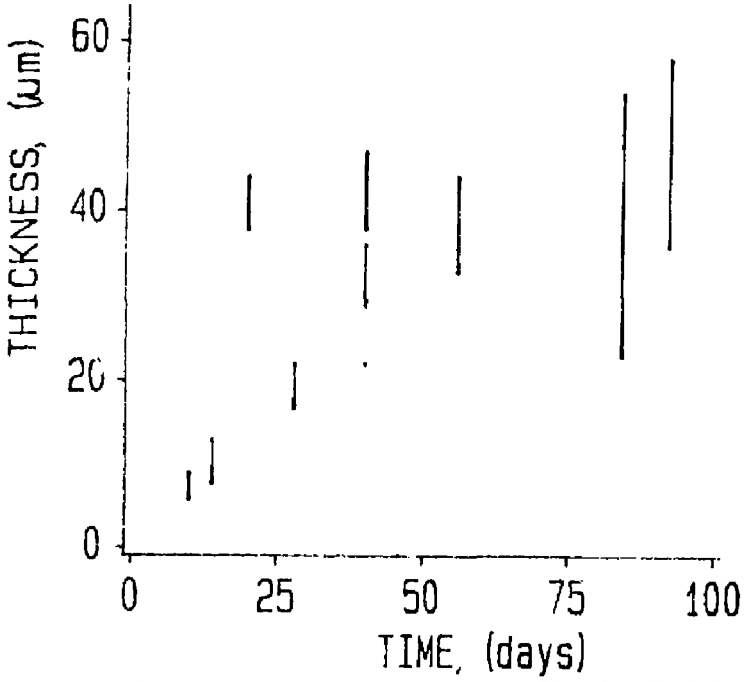


Fig. 25. Plot of Reaction Layer Thickness vs. Time for the Hydration of SRL Black Frit in Saturated Water Vapor at 187°C. Lines represent ranges found for a particular sample. More than one line per time period indicates results from separate x-sections of the same sample.

excess water that was added to the reaction vessel to ensure that 100% RH was always maintained. This excess water likely resulted in regions of liquid water accumulating on the glass surface which reacted faster than regions where only a thin film of water was present due to the vapor conditions. While the general trend of the reaction progress is for the reaction layer to increase with time, no clear functionality is apparent. These results stress the importance of performing replicate experiments and of carefully controlling the environmental conditions such that only a thin film of water contacts the glass.

In addition to measuring the thickness and composition of the reacted layers for the above samples, it was of interest to study the glass remaining with the bulk sample. Since the layers had completely detached from the glass without physically disturbing the sample, the remaining surface could be examined using optical microscopy and SIMS. Samples CB-150, 152, and 155 were chosen for examination because in each case only base glass was exposed. The samples were examined first with the optical microscope and surface features were recorded in photographs. Samples 150 and 155 were covered with a white haze. The coverage in sample 150 was continuous while for 155 there was a cross-linked pattern. Sample 152 had no haze. All the samples had a pock-marked appearance indicating that the penetration of the reaction layer into the glass did not result in a straight front moving into the glass.

Each sample was examined with SIMS, using the same sputtering conditions (Ar^+, 1.2 x 10^{-6} torr, 2 keV, 2 min delay between collections). Plots of the intensity ratios of Li, Na, B, Al, Ca, and Fe vs. Si for each glass are shown in Figs. 26a-c. Lithium and sodium are depleted near the surface of each sample, and the depth to which each element is depleted increases with reaction time. The other elements are also depleted compared to Si, but the apparent depletion depth is not as great as for Li or Na and is fairly constant between samples.

The absolute intensity of Si for each sample increases to a constant level that is reached somewhere between five and ten spectra. The absolute intensities of B, Al, Ca, and Fe also increase but at a faster rate than Si, thus the profiles ratioed to Si appear as though B, Al, Ca, and Fe are depleted at the outer surface. The absolute intensities of Li and Na also

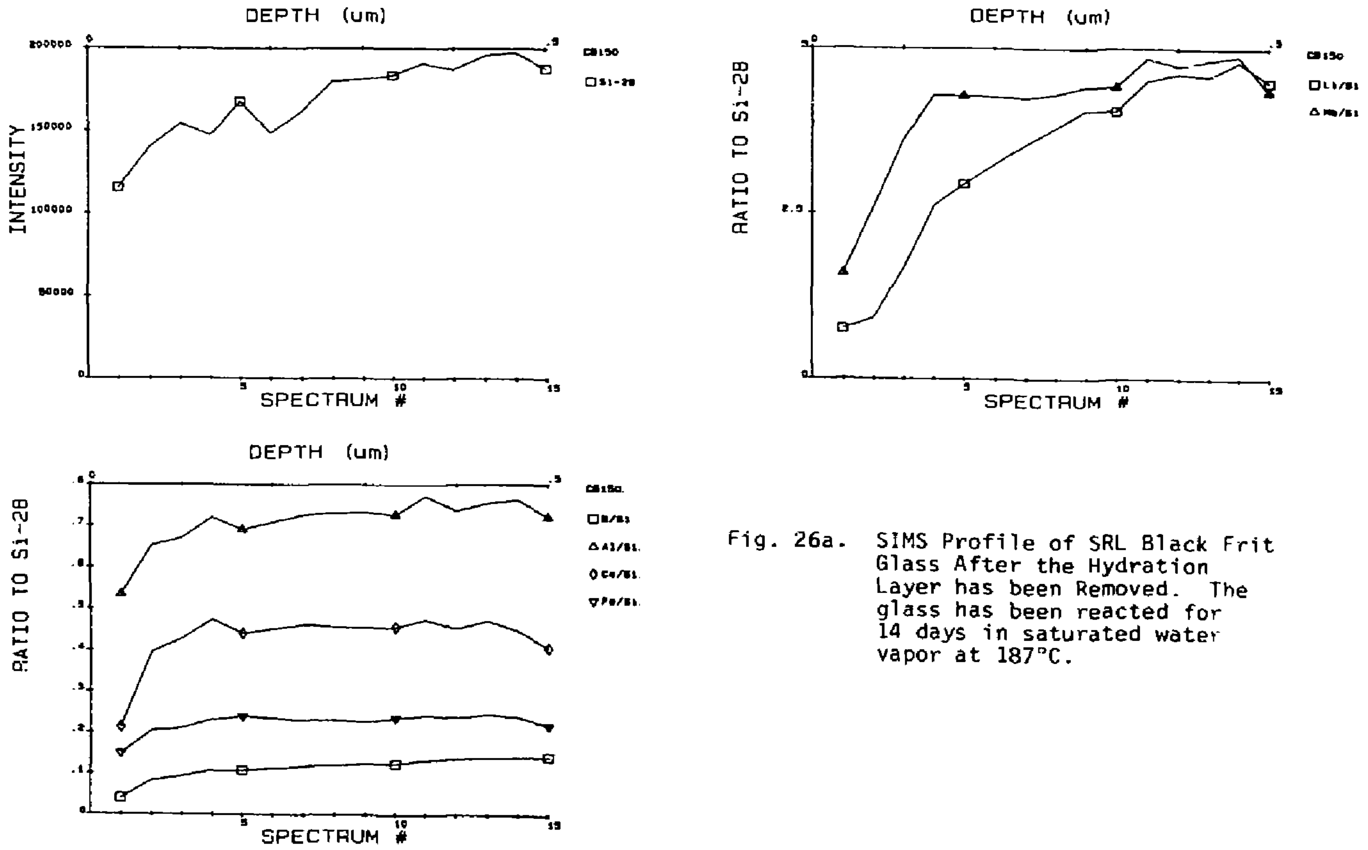
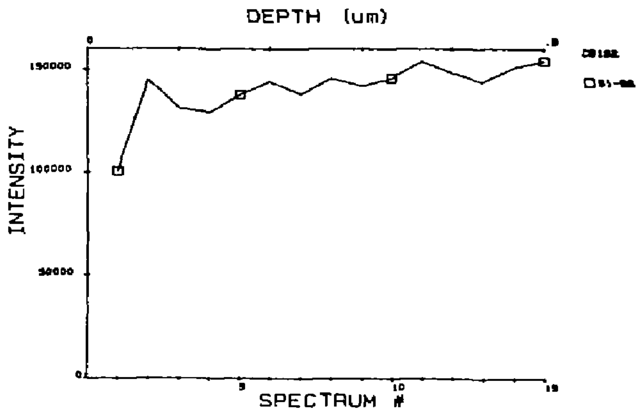
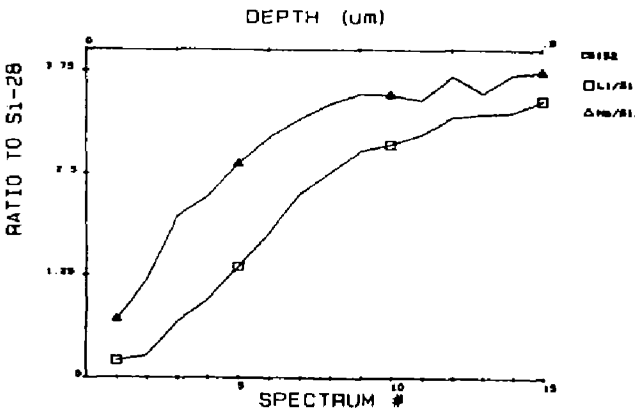


Fig. 26a. SIMS Profile of SRL Black Frit Glass After the Hydration Layer has been Removed. The glass has been reacted for 14 days in saturated water vapor at 187°C.





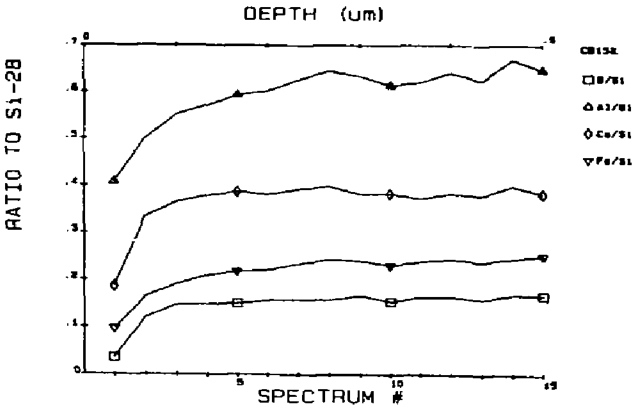


Fig. 26b. SIMS Profile of SRL Black Frit Glass After the Hydration Layer has been Removed. The glass has been reacted for 28 days in saturated water vapor at 187°C.

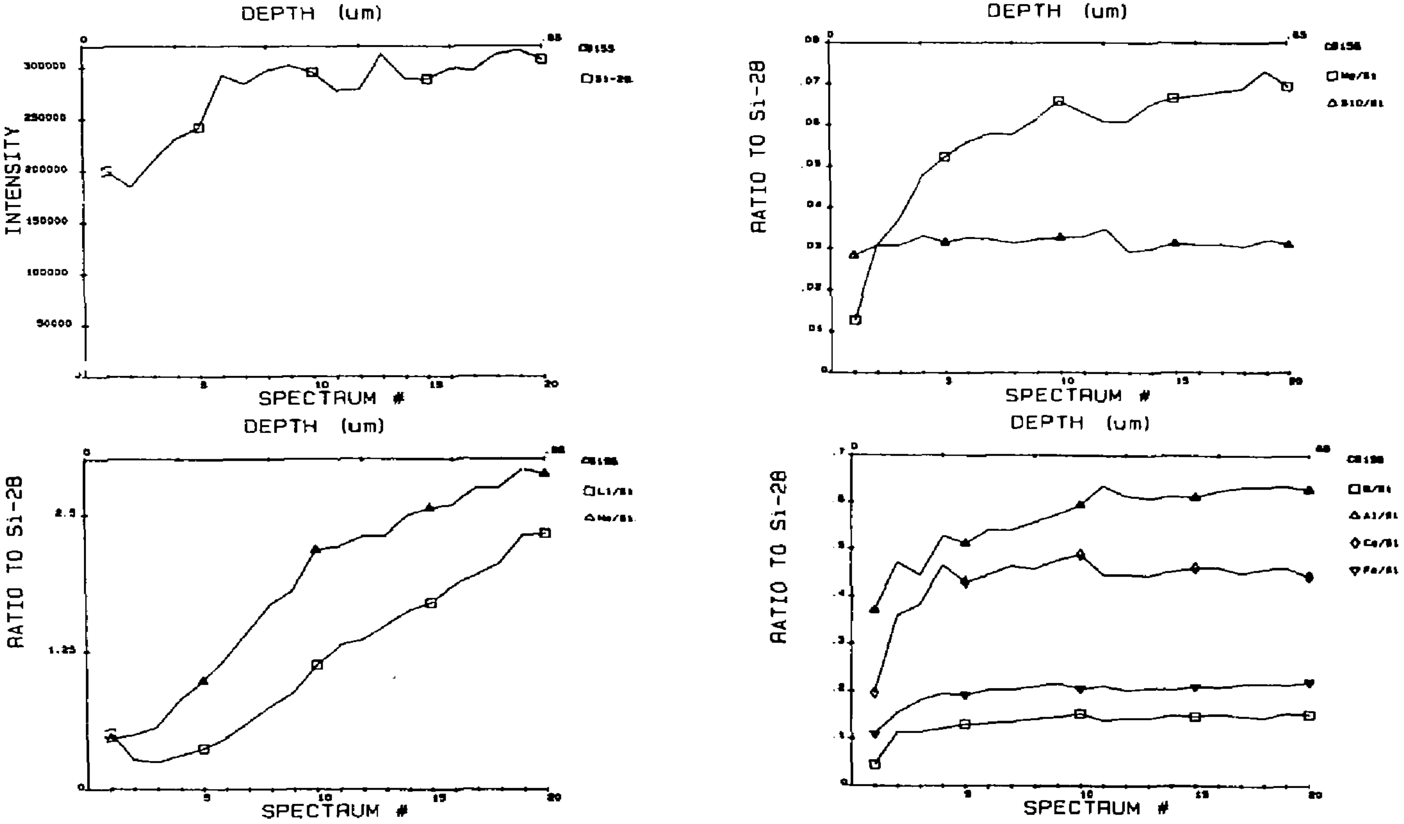


Fig. 26c. SIMS Profile of SRL Black Frit Glass After the Hydration Layer has been Removed. The glass has been reacted for 56 days in saturated water vapor at 187°C.

increase with time but for sample 155 are constant for the first several spectra. Note, however, that the profile of SiO vs. Si (Fig. 26c) is constant, supporting the observation that the Si profile actually is increasing more slowly than the other elements. Thus, the profiles suggest that while all elements are depleted just below the removed reaction layer B, Al, Ca, and Fe quickly reach the bulk glass values, while Si is depleted to a greater depth, which does not appear to depend with reaction time. Lithium and sodium are depleted to the greatest extent and the depth of depletion increases with reaction time.

Thus, while the reaction layers formed during the reaction process are quite thick, the diffusion front that has been referred to as the transition zone, is not much different from that observed in experiments of similar duration but where the reaction temperature is ~100°C less [ABRAJANO-1].

VII. NNWSI VAPOR HYDRATION EXPERIMENTS

A. Development of the Vapor Reaction Method

An extensive series of vapor hydration experiments are planned in which Savannah River Laboratory and West Valley glass formulations will be reacted with deionized water vapor at various temperatures.

These experiments are being conducted because it is likely that extensive contact between water vapor and glass will occur in the repository environment [BATES-8] prior to contact with liquid water. If the vapor reaction process results in significant alteration of the glass, it is possible that the eventual release of radionuclides from the glass will be different than observed for unaged or "fresh" glass. It is important to demonstrate whether the aging process will significantly affect the radionuclide release from glass.

In anticipation of these experiments, preliminary experiments have been performed in order to familiarize ourselves with the necessary experimental techniques. Experiments involve suspending glass disks by Teflon thread from a steel rod inside a Parr bomb. Enough deionized water is added to the vessel to assure a saturated vapor phase. A sketch of the reaction vessel is shown in Fig. 27. Vessels are placed in an oven for a

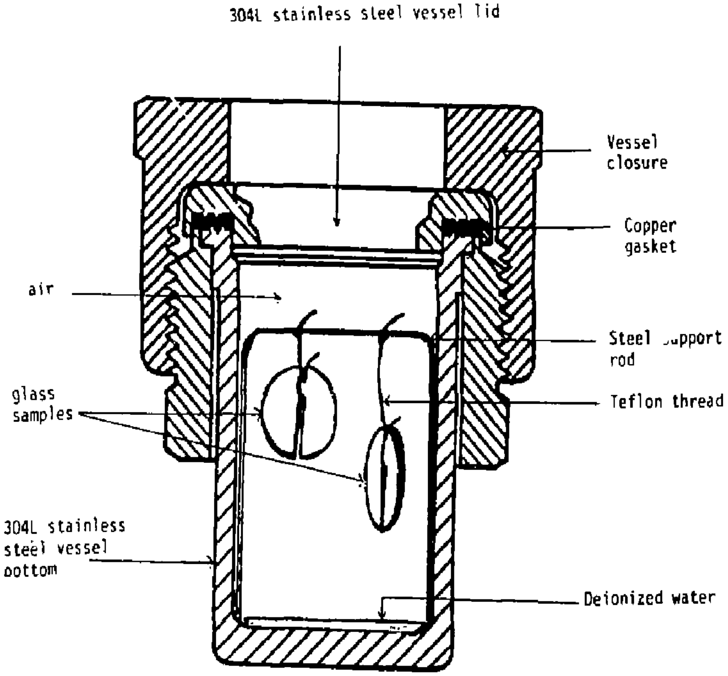


Fig. 27. Schematic Drawing of Vessel Assembly Used for Vapor Hydration Experiments

predetermined length of time. At the termination of the experiment, the bottom inch of (the outside of) the vessel is quenched to condense the water vapor inside the vessel. The samples are then removed from the vessel and the amount of water remaining in the vessel and its pH are measured. The reacted glass surfaces are analyzed for precipitates formed and leaching depths measured in the polished cross-section.

The purpose of these preliminary experiments is to gain an appreciation for the rate at which these glasses react under various conditions in order to generate a reaction matrix scheme which will properly monitor the reaction progress. The reacted glasses have been analyzed using SEM/EDS analysis to identify the precipitates formed and nature of the alteration layer.

Vapor hydration experiments performed in the past have frequently shown residue of water droplets on the lower parts of the suspended samples. Such drops result from condensation of water on the sample in the early stages of the experiment. When the vessel is placed in the oven, the sample has the coolest surface as it is furthest removed from the heat source and somewhat insulated by the air. The presence of condensed water on the glass surfaces changes the experimental conditions and produces anomalous results. In an effort to prevent water condensation, the glass samples used in these preliminary experiments were preheated to 200°C (the temperature at which they were to be hydrated) before the final vessel assembly. The glass samples were tied to the support rod and placed in the vessel. The vessel top was put in the oven as well. After heating for 2-4 hours the vessel was removed from the oven. The outside of the bottom 1/2-1 inch of the vessel was quenched in water then dried and placed in a balance and water was added to the vessel. Contact with the vessel sides was avoided to prevent excess evaporation. An amount of water in excess of that necessary to saturate the air in the vessel at the reaction temperature (which is about 0.16 g at 200°C for the 22 mL vessels used) was used to allow for some evaporation and water loss during the experiment through vessel leakage. Vessel leakage has been a major problem in these experiments. The closure fittings must be completely tightened to sufficiently seal the vessels. Copper gaskets were used in these experiments. The vessel bottom and vessel lid have been machined to provide knife edges for proper sealing.

The reacted samples preheated in this manner showed no evidence of droplet formation, while samples reacted without being preheated showed definite drop formation. Preparation of samples in this way is time consuming as vessels must be removed individually from the oven, have the bottoms quenched and dried, have water added and be sealed and replaced in the oven. The reproducibility of the experiments should improve since drop formation is avoided. The extra few hours the samples are in the oven are not expected to alter the samples since the natural humidity is so low at the reaction temperatures.

The reproducibility of the experiments performed to date has suffered because of vessel leakage. This has developed an appreciation as to how tight the vessel closures must be to form a tight seal. The samples reacted in vessels that were found not to leak showed uniform reaction over the entire surface. The thicknesses of the alteration layers measured in polished cross-sections were uniform from the top of the sample to the bottom. The West Valley (WV) 50 glass reacted much faster than the SRL U glass, producing an alteration layers tens of microns thick after only a few days. These layers flake off the remaining glass making handling of the samples very difficult. The delicacy of these layers was evidenced in the polished cross-sections which showed a high degree of fragmentation of the layer due in a large part to the procedure of breaking the reacted sample into two pieces for surface and cross-section analysis.

The reacted SRL U samples had reacted layers that were much thicker than those found on the leached samples in the FY 1986 leaching experiments but much thinner than the reacted WV 50 samples. Good cross-sections were obtained for these reacted SRL U samples. The layer thicknesses were typically 10-20 μm after 5-10 days at 200°C, while the WV 50 layers were on the order of 1000 μm after 10 days at 200°C.

A number of relatively large precipitates were found to form on both the SRL U and WV 50 samples. These included sodium aluminosilicates, sodium calcium aluminosilicates, and calcium aluminosilicates on both glass types. Uranium-containing precipitates were very abundant on both glass types, though the precipitates had distinct morphologies depending on the glass type. Precipitates ranged in size from submicron to tens of microns in cross-section. Many of the precipitates were seen in the polished cross-sections though neither they nor the alteration layers have been semi-quantitatively analyzed. Samples that were vessel mates showed a common extent of reaction.

These preliminary experiments have shown the West Valley formulation to react to a much greater extent than the SRL U glass, at 200°C. Plans to place samples of each glass type in common vessels would appear to be improper for reaction times longer than a few days. Indeed, the WV glass should not be reacted longer than ten days at 200°C because of the rapid reaction. Preheating the samples to the reaction temperature before vessel assembly reduces the amount of water condensation such that no evidence of drop formation on the samples can be seen in the reacted glasses. Care must be taken to assure the vessel closure nuts are tightly fastened. Multiple vessels should be used for each reaction condition to be sure that at least one vessel that is properly sealed is included. Since samples that were vessel mates showed a similar extent of reaction, it is suggested that two samples of the same glass formulation be included in each vessel in order to increase the amount of analyzable surface area and measurable alteration layer.

B. Hydrothermal and Vapor Experiments on ATM-1c, WV 44, and Obsidian

A set of experiments was also performed on ATM-1c glass and obsidian to measure the difference between the layer thickness formed through hydrothermal leaching and that due to vapor hydration. It has been demonstrated previously [ABRAJANO-2] that at equivalent temperatures, hydrothermal leaching results in a thicker reaction layer which suggests that the reaction mechanism is different under the two conditions. The present experiments are being conducted to test the experimental vapor phase hydration method that will be used in the upcoming hydration matrix and to provide some additional data for a paper to be presented at the Spring MRS meeting.

ATM-1c glass is known to react rapidly under hydrothermal conditions, but in previous hydration tests [BATES-8], PNL 76-68 type glasses have appeared resistant to vapor hydration. Obsidian is of interest because the hydration rind dating method [MICHELS] uses a hydrothermal treatment to determine hydration rate constants for natural glasses. However, if vapor hydration results in a different rate constant then the accuracy of age dating measurements may be in question. WV 44 is similar to ATM-10 glass that will be used in the extended vapor phase experiments described in the previous section, and some idea as to its rate of hydrothermal reaction is required.

The experimental matrix is given in Table 18. The ATM-1c glass was supplied by the MCC and has been used previously in the gamma leach experimental matrix. The obsidian was obtained from a grab bag at Northwestern University and was analyzed using quantitative EDS. The WV 44 glass was supplied by Catholic University. The composition of the glasses is shown in Table 19.

The reaction progress was measured by weight loss and by determining the reaction layer thickness with SEM/EDS and SIMS. SEM/EDS was the primary technique because it is anticipated that the reaction layers will be thick (>2 μm) and will be easily observed. SIMS was used on an obsidian sample to determine whether the hydration process results in any measurable change in elemental profiles in obsidian. These profiles are directly comparable with the profiles of obsidian reacted at 75°C in the previously discussed RH experiments.

1. Obsidian

Hydrothermal Leaching

The samples were leached for periods of 1 to ~11 days. The extent of reaction was measured by weight loss, SEM/EDS examination, SIMS, and optical microscopy. The weight loss results are shown in Table 18. These results indicate that some leaching or etching of the obsidian has occurred. The effects of such leaching are also evident in the SEM and optical microscope where a white crust is evident on the circular edge of the glass after only 24.5 hours and on the glass surface after 72 hours of reaction. This white crust is what remains of the glass after considerable etching occurs. In the circular rims the etched pits are particularly evident as shown in Fig. 28. The thickness of the etched regions was measured, and layer thickness together with the weight loss plotted in Fig. 29 and 30. The sample reacted for 3 days was examined with SIMS. The profiles indicate a slight Si depletion in the first 0.1 μm with an equivalent Al enrichment in the same region. Sodium shows a depletion for the first 0.3 μm after which the profile is constant while K shows an

Table 18. Experimental Matrix for ATM-1c and Obsidian Experiments

Experiment	Sample #	Glass Type	Temp (°C)	Duration hours	Date IN	Time	Date OUT	Time	Sample Mass IN	Sample Mass OUT	Vessel #	Vessel Weight IN	Vessel Weight OUT	Δ Mass	pH Out	Δ Mass (gm x 10^6)
Hydrothermal	JKB 1	ATM-1c	100	24.5	12/17/87	11:30	12/18/87	12:00	0.23515	0.23026	1	1044.95	*	-	9.7	489
	JKB 2		100	48	12/17/87	11:30	12/19/87	11:30	0.20100	0.19462	2	1048.20	*	-	10.2	638
	JKB 3		100	72.5	12/17/87	11:30	12/21/87	12:10	0.21280	0.20647	3	1047.74	1047.64	0.10		633
	JKB 4		100	141	12/17/87	11:30	12/23/87		0.20630	0.19661	4	1066.72	1055.54	0.18	10.2	989
	JKB 5		100	261.5	12/17/87	11:30	12/28/87	9:00	0.23891	0.22679	5	1045.61	1045.31	0.20	9.1	1210
	JKB 11	Mazer	100	24.5	12/17/87	11:30	12/18/87	12:00	0.15634	0.15547	6	1045.26	*	-	7.8	87
	JKB 12	Obsidian	100	48	12/17/87	11:30	12/19/87	11:30	0.16051	0.15909	7	1045.27	1046.25	-	7.9	142
	JKB 13		100	72.5	12/17/87	11:30	12/21/87	12:10	0.16089	0.16464	8	1045.38	1045.28	0.10		225
	JKB 14		100	141	12/17/87	11:30	12/23/87		0.15872	0.15588	9	1046.29	1046.18	0.11	7.3	284
	JKB 15		100	261.5	12/17/87	11:30	12/28/87	9:00	0.13205	0.13222	10	1045.42	1045.11	0.31	9.0	473
Vapor Phase Hydration	JKB 6	ATM-1c	100	72	12/28/87	3:30	12/31/87	3:30	0.25167	0.25163	82					
	JKB 7		100	24	1/03/88	12:30	1/04/88	12:15	0.30406	0.30407	83					
	JKB 8		100	48	1/03/88	12:30	1/05/88	12:30	0.27213	ND	84					
	JKB 9		100	96	1/03/88	12:30	1/07/88	12:30	0.26407	ND	85					
	JKB 10		100	192	1/03/88	12:30	1/11/88	12:30	0.24881	ND	86					
	JKB 16	Mazer	100	72	12/28/87	3:30	12/31/87	3:30	0.14976	0.14967	82					
	JKB 17	Obsidian	100	24	1/03/88	12:30	1/04/88	12:15	0.15909	0.15914	83					
	JKB 18		100	48	1/03/88	12:30	1/05/88	12:30	0.16564	ND	84					
	JKB 19		100	96	1/03/88	12:30	1/07/88	12:30	0.16528	ND	85					
	JKB 20		100	192	1/03/88	12:30	1/11/88	12:30	0.16702	ND	86					

Table 19. Composition of Reacted Glasses

Glass Type	Oxide wt %											
	Si	Na	Al	Ca	Fe[a]	K	Mg	Ti	Li	B	P	Others[b]
WV-44	44.8	9.9	6.5	0.9	11.6	3.2	1.2	0.9	2.8	9.0	2.3	6.9
Hawaiian Basalt	50.7	4.5	11.8	10.6	13.1	0.7	6.7	1.9	-	-	-	
Nevada Obsidian	77.0	3.4	13.6	0.7	1.0	3.7	0.4	0.2	-	-	-	
ATM-1c	41.0	12.4	0.7	2.4	9.1	0.7	0.2	2.9	-	9.1	0.6	20.9

[a] Fe as Fe_2O_3.

[b] Includes Ba, Ce, Cr, Cs, Mn, Nd, Ni, S, Th, U, and Zr.

Fig. 28. Cross-Section of an Obsidian Sample Reacted for 48 Hours in DIW at 187°C. The dark areas penetrating into the glass are where the glass has dissolved. Magnification = 200X.

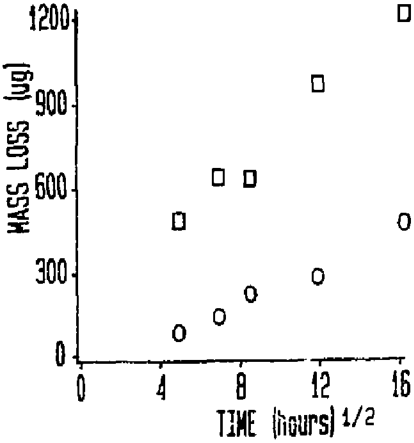


Fig. 29. Mass Loss during Hydrothermal Leaching Experiments for (□) ATM-1c Glass and (○) Obisidian. Reference Table 19.

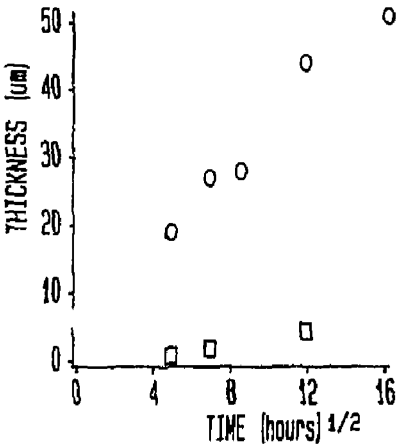


Fig. 30. Layer Thickness for Hydrothermal Leaching Experiments for (□) ATM-1c Glass and (○) Obsidian. Reference Table 19.

enrichment that levels off after ~1.3 μm of sputtering. The sample was sputtered to a total depth of ~6 μm to be assured of sputtering through the hydrated layer in an effort to see if there was a sharp interface of any type observed. No sharp interface was observed for the elements profiled.

Sample 13 and 15 were thin sectioned and examined using transmitted light to use the standard method of detecting the hydration layer in obsidian samples. This method resulted in clearly visible birefringent layers when observed under crossed-polarized light. The layer thicknesses were ~2 and 4 μm for samples 13 and 15, respectively.

Vapor Hydration

The glass surfaces when examined with optical microscopy and SEM appear quite unreacted. However, SIMS profiles indicate there is definite depletion of Ca and Na in the near-surface region extending ~0.3 μm into the glass. The extent of Na and Ca depletion appeared to be the same for both samples 18 and 19 (48 and 96 hours reaction).

2. ATM-1c

Hydrothermal Leaching

Previous leaching experiments done at 90°C and higher temperatures indicate that ATM-1c glass reacts quite rapidly in a leaching environment. In the present experiments the extent of reaction was monitored by measuring weight loss and reacted layer thickness. Layer thickness and weight loss are shown in Fig. 29 and 30. Both give some indication that the growth of the reaction layer follows $t^{1/2}$ kinetics for throughout the test period, reaching a layer thickness of ~51 μm after 261.5 hours.

Vapor Hydration

The samples that were vapor hydrated showed little visible evidence for reaction. The exceptions were for those samples which were watermarked indicating that during the reaction period some water had condensed and collected near the bottom of the sample. These samples were examined in the optical microscope, SEM, and SIMS. Optical microscopy indicated that there was no formation of reaction products on the glass surface as is evident with SRL or WV glass under similar conditions. SEM examination verifies this to be the case with only the typical cross-hatched structure being evident (Fig. 31). Also evident in this figure are small white specks (<0.5 μm dia) that appear to be condensed regions. EDS spectra of these specks, while difficult to obtain due to the small volume of the region, are not radically different from spectra of the general reacted surface. Thus, both optical and SEM examination indicate the ATM-1c glass to be relatively unreacted in the vapor environment.

SIMS was used to profile individual element bheavior. Profiles for the samples reacted for one and two days are shown in Figs. 32 and 33, while the estimated depth at which bulk levels are reached is given in Table 20.

Several interesting features are evident in these profiles that bear further examination in the upcoming vapor hydration matrix. These include:

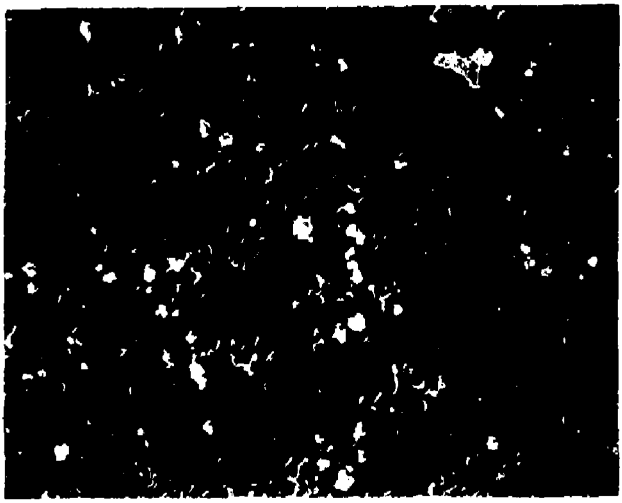


Fig. 31. SEM Micrograph of ATM-1c Glass That Has Been Reacted for 48 Hours at 187°C in 100% Water Vapor.

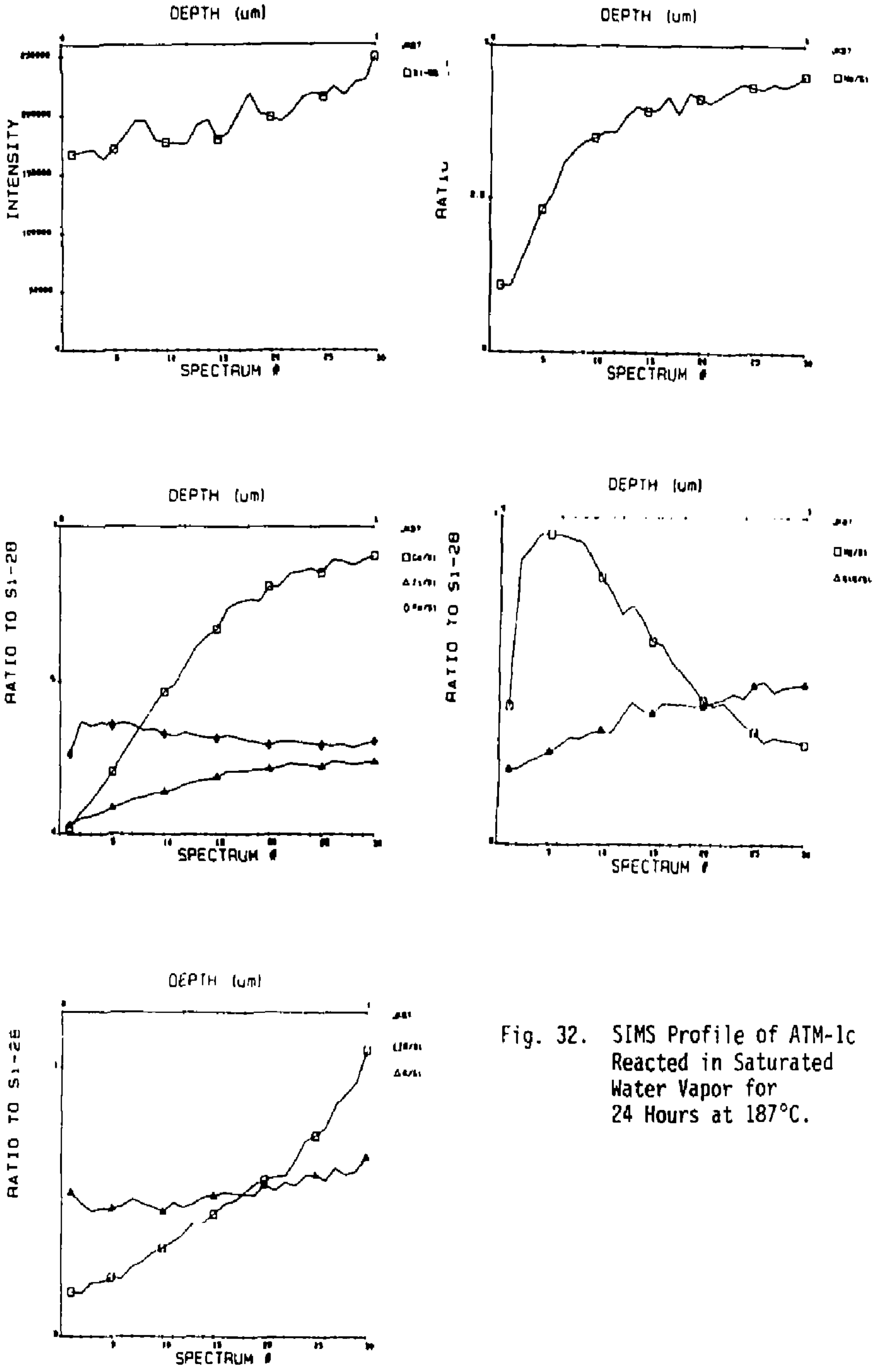


Fig. 32. SIMS Profile of ATM-1c Reacted in Saturated Water Vapor for 24 Hours at 187°C.

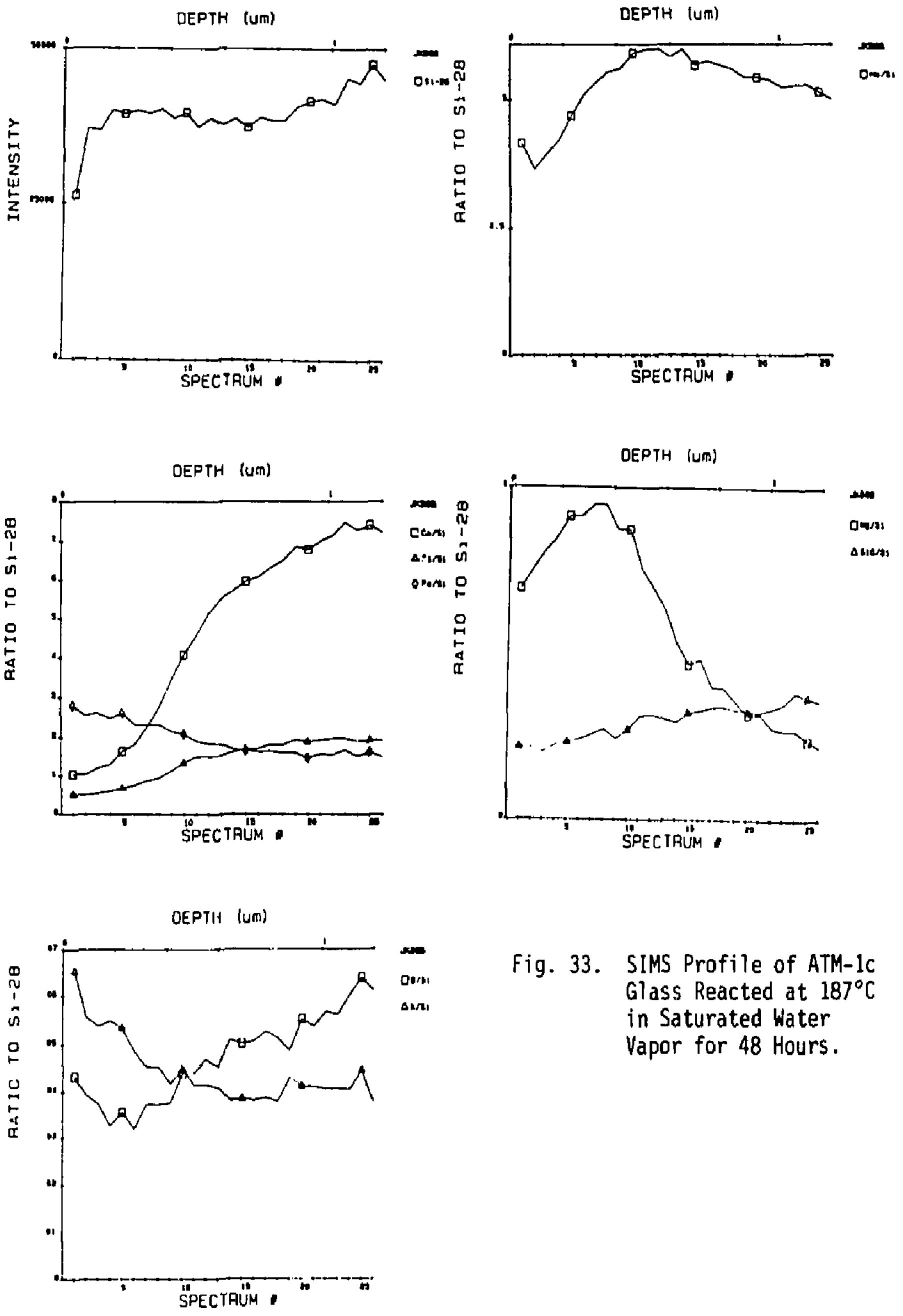


Fig. 33. SIMS Profile of ATM-1c Glass Reacted at 187°C in Saturated Water Vapor for 48 Hours.

Table 20. Elemental Depletion Depths for Vapor Phase Reacted ATM-1c Glass

Reaction Time (hrs)	Sample # (Table 19)	Depth to Reach Bulk Concentration (μm)			
		B	Na	Ca	SiOH (Data Not Presented)
24	7	$\geq$0.8	0.3	0.5	Considerable
48	8	$\geq$0.5	0.2	0.4	None
72	6	1.0	0.3	0.1	A Little
92	9	>0.7	0.1	0.2	Considerable

1) Sodium is depleted in the near-surface region but is depleted to neither the depth or extent (absolute Na signal) as is the hydrothermally leached samples, or in vapor reacted SRL glasses.
2) The depletion depth ranges from ~0.1 to 1 μm over a period of 96 hours while the equivalent depletion in the leached samples is ~51 μm (Fig. 30). The disparity in reaction, where the vapor reacted sample reacts to a lesser degree than in the hydrothermal solution, is far greater in ATM-1c glass than in SRL 165 glass.
3) In two of the samples (#s 7 and 9), there is a clear enhancement of the 45 AMU peak at the glass surface. This peak is, in part, attributable to SiOH.

Thus, while the extent of reaction has not appeared to increase in a uniform manner, it is clear that Na diffusion to the glass surface is less than would be expected from previous hydration of either basaltic or other types of nuclear waste glasses. One possible explanation is that the ability of a certain element to diffuse or ion exchange with H^+ or H_2O^+ depends on the chemical potential of that element at the glass surface. If a particular element as it is released from the glass is incorporated into a stable alteration product or goes into solution, the chemical potential for that element at the surface is lower than in the bulk glass and the element is released from the bulk. However, if during vapor phase hydration an element is released to the surface and collects in the surface film but is not incorporated into an alteration phase the chemical potential may exceed that in the glass thereby inhibiting further release of that element from the glass.

The surfaces of reacted glasses were examined as described above and no alteration phases were evident.

3. WV 44

Vapor Phase

The nuclear waste glass reacted to form a distinct altered layer penetrating into the glass with alteration products forming on the surface of the glass. The layer thickness increased with time as shown in Fig. 34. There was an initial period where no distinct layer was observed in the SEM and no alteration products formed on the glass. However, after four days at 200°C the glass began to react more rapidly, with extensive phase formation occurring as the layer became thicker. At least seven different phases formed, including analcime, apatite, and phases that incorporate both uranium and thorium.

Similar reaction trends have been observed for the early generation waste glasses SRL 211 and 131. For these glasses the more rapid reaction appears to correspond to the formation of tobermorite [$Ca_5Si_6O_{16}(OH)_2 \cdot 4H_2O$] on the glass surface [BATES-8].

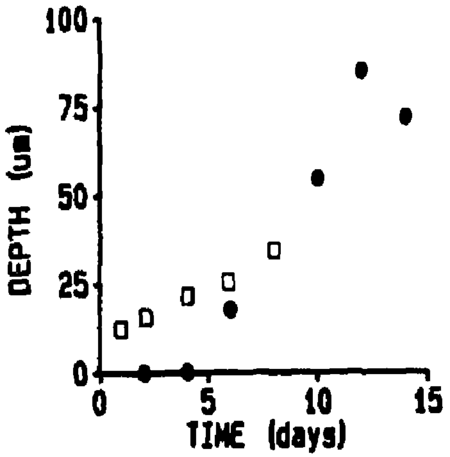


Fig. 34. Layer Thickness of Vapor and Hydrothermally Reacted WV 44 Glass (200°C); (□) hydrothermal, (●) vapor.

Hydrothermal

A distinct reaction layer also forms in the hydrothermal experiments. Unlike the vapor experiments, no distinct secondary phases form on the reacted surface. The layer increases in thickness at a fairly uniform rate (Fig. 34) and does not show the change in slope observed in the vapor experiments. Depending on the length of reaction, the layer thickness produced in the vapor experiments may exceed those formed hydrothermally.

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