DR. 956

LA-8088-PR

Progress Report

324
3/26/80

MASTER

Laboratory Studies of Radionuclide Distributions Between Selected Groundwaters and Geologic Media

Annual Report, October 1, 1978—September 30, 1979

University of California

LOS ALAMOS SCIENTIFIC LABORATORY

Post Office Box 1663 Los Alamos, New Mexico 87545

LA-8088-PR
Progress Report
UC-70
Issued: February 1980

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F. O. Lawrence
S. Maestas
P. Q. Oliver
J. L. Thompson
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LABORATORY STUDIES OF RADIONUCLIDE DISTRIBUTIONS BETWEEN SELECTED GROUNDWATERS AND GEOLOGIC MEDIA

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ABSTRACT

Extensive studies of the behavior of plutonium and americium in pH ≅ 8 groundwaters were made, particularly with respect to container sorption, filtering, and centrifugation. Significant improvements in the method used for measuring sorption ratios for these elements were developed, and their sorption-desorption ratios on argillite and tuff were measured. Effects of particle size, temperature, sampling location, mineralogy, and time were investigated for these elements. The chemical composition of the water was found to be a major factor that governs sorption behavior. Studies of the sorption of strontium, cesium, barium, cerium, europium, uranium, and americium on Hainesville salt dome materials were made under aerobic and anoxic (<0.2 ppm oxygen) conditions using two synthetic groundwaters: One represented the Wilcox aquifer in the Hainesville region and the second was a dilute brine. Studies of the sorption of strontium, cesium, barium, cerium, europium, and uranium(VI) on granite and argillite were made under anoxic (<0.2 ppm oxygen) conditions and the results were compared to earlier measurements made under aerobic conditions. The sorption of uranium(VI) on argillite under atmospheric conditions was investigated. Measurements

of migration rates in crushed granite, argillite, and tuff were made and compared with batch results. Infiltration experiments involving the forced injection of activity into intact and fractured cores were also performed. Microautoradiographic techniques were used to detect specific sorption sites. This latter technique was also used to characterize the sorption of plutonium and neptunium on polished thin-sections of alluvium, granite, tuff, and argillite and to assess the amount of "aggregation" that occurred. Additional physical and chemical characterizations of the materials used in these studies were made, and new analytical techniques were developed.

I. INTRODUCTION

The Los Alamos Scientific Laboratory (LASL) contribution to the Waste Isolation Safety Assessment Program (WISAP), Task 4, in FY-79 had five principal objectives. The first was to perform migration rate studies using three different types of columns: 1) crushed rock, 2) whole rock, and 3) cores containing natural fractures. Second, the LASL batch sorption methodology[1-3] was used to obtain data on several additional variables that influence sorption-desorption behavior and to perform studies on several new radionuclide-geomedia systems. Third, the microautoradiographic technique currently utilized at LASL[4] was used for further studies of the sorption of radionuclides on polished or ground surfaces of mineral grains and for identification of the specific sorbing surfaces in natural (nonpulverized) systems. Fourth, studies of sorption behavior in systems related to salt domes were performed. Finally, studies of the chemistry of several radionuclides in the pH $\cong$ 8 solutions that frequently occur in natural environments were performed.

Most of these studies were limited to three geologic types - granite, argillite, and tuff - usually from, but not limited to, the Nevada Test Site (NTS). Natural groundwaters or waters having a chemical composition related to the phreatic water were used for all studies. Detailed analytical and mineralogical analyses of all materials were made.

II. SORPTION OF PLUTONIUM AND AMERICIUM ON ARGILLITE (W. R. Daniels, F. O. Lawrence, S. Maestas, and P. Q. Oliver)

The measurement of the sorption behavior of americium and plutonium on argillite under atmospheric conditions involved geologic materials and groundwaters described earlier[1].

A. Measurement Techniques

1. Preparation of Tagged Solutions. Most of the traced waters used in these studies were prepared using the pretreated synthetic groundwater described in Ref. 1, ^{237}Pu tracer produced at Argonne National Laboratory under contract with Battelle Pacific Northwest Laboratories (PNL), and isotopically pure ^{241}Am tracer obtained from Oak Ridge National Laboratory. Tracer purities were checked by both alpha and gamma spectroscopy. (Feed solutions were prepared so as to contain $\cong 10^{-12}$ M Pu or $\cong 10^{-6}$ M Am at 100% yield of tracer in water; actual concentrations can be calculated from the yields given in Table I.) Stock tracer solutions were in 3 M HCl, which resulted in an added chloride concentration of $<10^{-2}$ M. The ^{237}Pu tracer was treated with $NaNO_2$ so that the plutonium was in the IV oxidation state at the beginning. This step resulted in the addition of $\cong 10^{-4}$ M sodium to the feed solutions containing plutonium. In general, feed solutions were prepared by drying the tracers at room temperature and then dissolving them in the appropriate groundwater. The chloride added with the tracers was normally $\cong 5 \times 10^{-3}$ M.

Some samples were run using one of two feed solutions containing both ^{241}Am and ^{239}Pu, partially in order to examine the effect of a large change in plutonium concentration. (The concentration at 100% yield would have been $\cong 10^{-6}$ M Am and $\cong 10^{-5}$ M Pu; actual concentrations can be estimated using the data in Table I.) One such feed solution was prepared by drying the tracer, and one was prepared by adding the tracer solution directly to the water and then readjusting the pH to its original value by adding NaOH solution. The latter step resulted in the addition of $\cong 1 \times 10^{-3}$ M sodium to the feed solution.

In order to examine the difference in apparent sorption resulting from filtering the feed solutions, solutions were centrifuged for one hour at 12 000 rpm (28 000 g's) and then portions were used in the batch experiments both before and after filtering through a 0.4-μm Nuclepore filter (all plastic

TABLE I

TRACER YIELDS IN FEED SOLUTIONS

Tracer	Temperature(°C)	Yield (%)	
		Unfiltered	Filtered
^{237}Pu	22	54	48
^{237}Pu	70	30	6
^{241}Am	22	38	22
^{241}Am	70	42	15
$^{241}Am+^{239}Pu$	22	11[b]	0.2[b]
$^{241}Am+^{239}Pu$[a]	22	19[b]	0.4[b]

[a]Tracer was not dried; pH readjusted with NaOH.

[b]Americium yield; other experiments indicated that the plutonium yield was probably approximately the same, at least for the unfiltered solutions.

parts). The filters always retained activity which had not been removed by centrifuging. The tracer yields in the feed solutions were determined by gamma-counting aliquots and are given in Table 1.

2. Sorption Measurements. Crushed rock from cores 1 (548 m) and 2 (717 m) from the Eleana formation at the NTS were used for batch sorption studies at both ambient (22 ± 2°C) and elevated (70 ± 1°C) temperatures. Three particle sizes were used: 106-150, 150-180, and 355-500 μm. The material was pretreated by shaking weighed 1-g quantities with 20-mℓ portions of synthetic groundwater for periods of at least two weeks. The samples were contained in pre-washed, capped, 40-mℓ, polypropylene tubes. The phases were separated by centrifuging at 12 000 rpm (28 000 g's) for one hour. The weight of the wash solution remaining with the solid phase was obtained by weighing the tube and solid before and after pretreatment.

Twenty-mℓ portions of traced feed solution of known pH were added to the tubes containing crushed rock. The solutions were dispersed by vigorous shaking and the mixtures were agitated gently for selected times: 1, 2, 4,

and 8 weeks. The shaking rates were 200 oscillations per minute for the ambient temperature samples and 80 oscillations per minute for the 70°C samples.

At the end of a shaking period, the aqueous phases were separated from the solids by centrifuging, usually four times, each time transferring the water to a new tube, for one hour at 12 000 rpm (28 000 g's). Usually the final solution was aliquoted and the remainder was then passed through a 0.4-μm Nuclepore filter, sometimes twice, and aliquoted again in order to observe the effect of filtering on the observed sorption ratio. An improved technique was used for later measurements (see below). Any errors in the data for unfiltered solutions in the argillite measurements would result in the reported R_d (see below) values being too low.

A number of rock-water mixtures were transferred to clean tubes before the first centrifuging. The original tubes were then checked for activity in order to determine the gamma activity sorbed on the walls. This was found to be negligible (<2% of total input activity). All other solid phases were left in the original tubes and counted directly, after centrifuging.

Earlier comments[1-3] concerning the use of "control" samples with traced aqueous phase but no solid are applicable here. The activity in the control samples was found to sorb on the walls much more readily than when rock was also present.

Desorption experiments were performed by adding pre-equilibrated synthetic groundwater to the solid phases from the sorption experiments and continuing as for the sorption measurements.

3. Assay of Radioactivity. Solid samples were normally gamma-counted for ^{241}Am or ^{237}Pu on a NaI(Tl) detector utilizing a single-channel analyzer and a scaler. Counting standards were prepared using known amounts of ^{241}Am or ^{237}Pu in the same geometries and conditions as the experimental samples.

Liquid samples were usually gamma-counted with a NaI well counter (Packard Auto-gamma Scintillation Spectrometer). Standards were prepared in the appropriate geometry.

The ^{239}Pu was determined radiochemically[7] after sample dissolution.

4. Calculations. Since both solid and liquid phases were counted directly for ^{241}Am and ^{237}Pu, or analyzed separately for ^{239}Pu, the sorption ratio, R_d, can be calculated directly as

$$R_d = \frac{\text{activity in solid phase per unit mass of solid}}{\text{activity in solution per unit volume of solution}} .$$

The activities in the control tubes were not used in the calculations; container effects are considered negligible (see above).

B. Results and Conclusions

The results for the batch measurements of the sorption behavior of ^{241}Am, ^{237}Pu, and ^{239}Pu on argillite under atmospheric conditions are given in Tables II-V. Data for the desorption of ^{239}Pu from four argillite samples are not yet available.

Observations made later during sorption measurements with tuff (see below) tend to confirm that little or no sorption (at least for plutonium) occurs on the filter membranes and to suggest that most of the activity removed by filtering the final solutions during the argillite experiments consisted of particulates. The "unfiltered" data, therefore, probably provide lower limits for the sorption ratios since particulates remaining with the solutions after centrifuging would tend to lower the calculated R_d values. The "filtered" data perhaps provide more accurate sorption ratios; however, the use of "unfiltered" data would err in the conservative direction. The later experiments (see below) showed that the large differences between results from unfiltered and filtered final solutions and the large variations between replicate samples can be greatly reduced by use of a very cautious technique for transferring solutions between centrifugings.

For the argillite experiments, sorption ratios based on data from unfiltered solutions tended to decrease with increasing temperature, but for filtered solutions the calculated ratios tended to increase with increasing temperature. This effect is probably related to the size of the particles which form at the different temperatures and which behave differently when centrifuged or filtered. Less activity was removed by centrifuging solutions contacted at 70°C but more activity was removed by filtering these same solutions.

Several general conclusions can be made for the plutonium and americium results: Very little americium or plutonium sorbs on the container walls when crushed argillite is present (see below). There was no significant effect

TABLE II

^{241}Am SORPTION RATIOS (ARGILLITE)

Core Sample	Fraction (μm)	Temp. (°C)	Filtered[a] Feed ?	Sorp. Time (d)	Desorp. Time (d)	R_d (mℓ/g) Unfilt.	R_d (mℓ/g) Filt. 1[a]	R_d (mℓ/g) Filt. 2[a]	pH Initial	pH Final
1	106-150	22	yes	6.8		b	57 000		8.65	8.57
					28.7	24 000			8.3	8.58
			yes	12.7		b	450 000		8.65	8.61
					28.7	51 000	540 000		8.3	8.60
			yes	27.6		91 000[b]	320 000		8.65	8.66
					28.7	71 000	740 000		8.3	8.65
			yes	27.6		54 000[b]	170 000		8.65	8.57
					28.7	59 000	520 000		8.3	8.59
			yes	54.7		99 000[b]	420 000		8.65	8.21
					28.7	53 000	930 000		8.3	8.59
1	355-500	22	yes	12.7			62 000		8.65	8.69
					31.7	21 000	400 000		8.3	8.67
			yes	27.6		26 000[b]	120 000		8.65	8.59
					28.7	28 000	270 000		8.3	8.59
			yes	27.6		54 000	180 000		8.65	8.63
					31.7	33 000	280 000		8.3	8.68
			yes	54.7		35 000[b]	210 000		8.65	8.47
					28.7	36 000	280 000		8.3	8.53
			yes	54.7		28 000	260 000		8.65	8.66
					31.7	76 000	590 000		8.3	8.66

TABLE II (cont).

^{241}Am SORPTION RATIOS (ARGILLITE)

Core Sample	Fraction (μm)	Temp. (°C)	Filtered[a] Feed ?	Sorp. Time (d)	Desorp. Time (d)	R_d (mℓ/g) Unfilt.	Filt. 1[a]	Filt. 2[a]	pH Initial	pH Final
1	355-500	70	yes	6.8			55 000		8.33	8.39
					32.9	14 000	$> 10^6$		8.3	8.69
			yes	12.7			67 000		8.33	8.44
					32.9	31 000	$> 10^6$		8.3	8.71
			yes	26.7		1 600	410 000		8.33	8.53
					32.9	40 000	$> 10^6$		8.3	8.64
			yes	55.7		7 300	810 000		8.33	8.02
					32.9	33 000	$> 10^6$		8.3	8.61
2	355-500	22	yes	6.8		b	52 000		8.65	8.56
					28.7	61 000	330 000		8.3	8.56
			yes	12.7		b	62 000		8.65	8.61
					31.7	60 000	210 000		8.3	8.65
			yes	12.7			85 000		8.65	8.68
					33.9	47 000	470 000		8.3	8.65
			no	13.0		12 000	83 000		8.65	8.78
					31.9	68 000	400 000		8.3	8.67
			yes	26.7		34 000	270 000		8.65	8.65
					33.9	79 000	450 000		8.3	8.63
			yes	27.6		12 000[b]	77 000		8.65	8.63
					31.7	160 000	400 000		8.3	8.54

TABLE II (cont).

^{241}Am SORPTION RATIOS (ARGILLITE)

Core Sample	Fraction (μm)	Temp. (°C)	Filtered[a] Feed ?	Sorp. Time (d)	Desorp. Time (d)	R_d (mℓ/g) Unfilt.	R_d (mℓ/g) Filt. 1[a]	R_d (mℓ/g) Filt. 2[a]	pH Initial	pH Final
			yes	27.6		57 000[b]	190 000		8.65	8.58
					31.7	180 000	420 000		8.3	8.67
			no	27.9		25 000	210 000		8.65	8.72
					33.9	69 000	490 000		8.3	8.63
			yes	29.7		70 000	280 000	330 000	8.65	8.72
					33.9	59 000	450 000		8.3	8.64
			yes	54.7		84 000[b]	270 000		8.65	8.39
					31.7	71 000	650 000		8.3	8.67
			yes	54.7		140 000	560 000	790 000	8.65	8.36
					33.9	59 000	520 000		8.3	8.64
			no	54.9		150 000	620 000		8.65	8.68
					33.9	110 000	730 000		8.3	8.63
			yes	55.6		230 000	590 000		8.65	
					33.9	77 000	420 000		8.3	8.63
2	355-500	70	no	12.7		3 300	130 000		8.33	8.50
					32.9	7 300	$> 10^6$		8.3	8.63
			yes	12.7			94 000		8.33	8.41
					32.9	26 000	$> 10^6$		8.3	8.66
			no	26.7		10 000	150 000		8.33	8.16
					32.9	27 000	$> 10^6$		8.3	8.45
			yes	26.7		1 700	160 000		8.33	8.48
					32.9	38 000	450 000		8.3	8.33

TABLE II (cont).

^{241}Am SORPTION RATIOS (ARGILLITE)

Core Sample	Fraction (μm)	Temp. (°C)	Filtered[a] Feed ?	Sorp Time (d)	Desorp. Time (d)	R_d (mℓ/g) Unfilt.	Filt. 1[a]	Filt. 2[a]	pH Initial	pH Final
			no	55.7		15 000	370 000		8.33	7.88
					32.9	60 000	170 000		8.3	8.37
			yes	55.7		5 800	760 000		8.33	7.78
					32.9	20 000	$> 10^6$		8.3	8.39
			yes	55.7		3 700	300 000	380 000	8.33	7.73
					32.9	250 000	$> 10^6$		8.3	8.42

[a]Through 0.4-μm polycarbonate membrane.

[b]Crushed rock was pretreated with groundwater for ≅276 d, as opposed to the usual 14 d.

TABLE III

^{237}Pu SORPTION RATIOS (ARGILLITE)

Core Sample	Fraction (μm)	Temp. (°C)	Filtered[a] Feed ?	Sorp. Time (d)	Desorp. Time (d)	R_d (mℓ/g) Unfilt.	R_d (mℓ/g) Filt. 1[b]	R_d (mℓ/g) Filt. 2[b]	pH Initial	pH Final
1	355-500	22	yes	13.7		c	37 000	63 000	8.47	8.49
					14.9	11 000	68 000		8.27	8.60
			no	13.7			15 000		8.47	8.56
					14.9	3 800	41 000		8.27	8.64
			yes	13.7			15 000		8.47	8.53
					14.9	1 400	25 000		8.27	8.65
			no	13.7			19 000	19 000	8.47	8.57
					14.9	2 500	17 000		8.27	8.66
			no	27.6		3 300	7 000		8.47	8.55
					14.9	3 300	41 000		8.27	8.58
			yes	27.6		2 300	6 100		8.47	8.59
					14.9	2 300	27 000		8.27	8.61
			yes	27.6		2 400	31 000	33 000	8.47	8.60
					14.9	3 200	4 800		8.27	8.64
			no	55.7		4 700	69 000		8.47	8.64
					21.0	2 900	36 000		8.20	8.43
			yes	55.7		1 300	2 100		8.47	8.64
					21.0	3 600	35 000		8.20	6.98
			yes	56.7		2 700	41 000	46 000	8.47	8.56
					21.0	1 700	33 000		8.20	8.39

TABLE III (cont).

^{237}Pu SORPTION RATIOS (ARGILLITE)

Core Sample	Fraction (μm)	Temp. (°C)	Filtered[a] Feed ?	Sorp. Time (d)	Desorp. Time (d)	R_d (mℓ/g) Unfilt.	R_d (mℓ/g) Filt. 1[b]	R_d (mℓ/g) Filt. 2[b]	pH Initial	pH Final
			no	56		2 200	36 000		8.47	8 60
					21 0	2 700	30 000		8.20	8.54
			yes	56.7		33 000[c]	27 000	47 000	8.47	8.56
					21.0	1 300	44 000		8.20	8.52
1	355-500	70	no	13.7			100 000		8.26	8.50
					15.9	1 100	>100K		8.19	8.63
			yes	13.8			15 000		8.26	8.46
					15.9	3 000	40 000		8.19	8.64
			no	27.6		2 600	>100K		8.26	8.52
					15.9	1 700	>100K		8.19	8.42
			yes	27.6		2 500	6 000		8.26	8.55
					15.9	2 000	15 000		8.19	8.57
			no	56.7		1 900	>100K		8.26	8.46
					21.1	1 300	67 000		8.25	8.42
			yes	56.7		1 800	18 000	>100K	8.26	
					21.1	2 200	>100K		8.25	8.39
2	150-180	22	yes	13.7			11 000	38 000	8.47	8.54
					14.9	7 200	38 000		8.27	8.62
			yes	55.7		8 000	22 000		8.47	8.54
					21.0	19 000	>100K		8.20	8.52

TABLE III (cont).

^{237}Pu SORPTION RATIOS (ARGILLITE)

Core Sample	Fraction (μm)	Temp. (°C)	Filtered[a] Feed ?	Sorp. Time (d)	Desorp. Time (d)	R_d (mℓ/g) Unfilt.	R_d (mℓ/g) Filt. 1[b]	R_d (mℓ/g) Filt. 2[b]	pH Initial	pH Final
2	355-500	22	yes	13.7			22 000		8.47	8.53
					15.9	8 100	28 000		8.27	8.43
			yes	55.7		11 000	>100K		8.47	8.65
					21.0	17 000	44 000		8.20	8.44
3	355-500	70	yes	13.7			3 600		8.26	8.40
					15.9	1 700	33 000		8.19	8.58
			yes	56.7		1 500	23 000		8.26	8.33
					21.1	3 000	21 600		8.25	8.32

[a]Through 0.4-μm polycarbonate membrane.

[b]All calculated R_d values >100 000 indicated as >100K because of poor counting statistics on the ^{237}Pu solutions, which had very low count rates.

[c]Crushed rock was pretreated with groundwater for ≅276 d, as opposed to the usual 14 d.

TABLE IV

^{239}Pu SORPTION RATIOS FOR ARGILLITE CORE #2, 150-180 μm, AMBIENT TEMPERATURE, FILTERED FEED[a]

Tracer Prep	Sorp. Time (d)	R_d (mℓ/g)[b]	pH Initial	pH Final
dried	14.7	8 200	8.60	8.53
	30.6	27 000	8.60	8.59
	55.6	39 000	8.60	8.45
pH adjust	14.7	5 100	8.39	8.45
	30.6	16 000	8.39	8.42
	55.6	81 000	8.39	8.10

[a]Through 0.4-μm polycarbonate membrane.

[b]Values from unfiltered final solutions were used.

TABLE V

REPRESENTATIVE SORPTION RATIOS FOR Am AND Pu

	R_d (mℓ/g)[a] 22°C	R_d (mℓ/g)[a] 70°C
Am sorption		
unfiltered[b]	75 000(15 000)[c]	6 500(1 900)
filtered	300 000(42 000)	450 000(120 000)
Am desorption		
unfiltered	68 000(8 100)	29 000(4 300)
filtered	480 000(35 000)	> 106
^{237}Pu sorption		
unfiltered	4 200(1 100)	2 100(220)
filtered	37 000(12 000)	75 000(38 000)
^{237}Pu desorption		
unfiltered	5 700(1 400)	2 000(250)
filtered	34 000(3 700)	97 000(50 000)
^{239}Pu sorption		
unfiltered	25 000(9 000)	

[a]All data are for feed solutions prepared by drying the tracers (see text).

[b]Indicates whether final solutions were filtered after centrifuging and before counting.

[c]Values in parentheses are standard deviations of the means (absolute values).

related to particle size or core sample within the ranges examined. Filtering the initial feed solutions appears to have had little effect except possibly with filtered final solutions which had been contacted at 70°C. At ambient temperature, americium R_d values for desorption are roughly the same as the values for sorption, while the R_d values for the elevated temperature appear to be higher for desorption than for sorption. Within the rather large errors in the data, there is no significant difference in ^{237}Pu R_d values for sorption and desorption at a given temperature. The data in Table 4 indicate that there was little difference in the observed R_d values for ^{239}Pu between the two methods of preparing the traced feed solutions, i.e., drying the tracer or adding an acid tracer solution and readjusting the pH. The average values are 25 000 ± 9 000 mℓ/g and 34 000 ± 24 000 mℓ/g, respectively. The results of ^{237}Pu and ^{239}Pu indicate that there is a difference in R_d values, which probably results from the $\cong 10^7$ difference in plutonium concentration and may well be a solubility effect. Based on data from unfiltered final solutions the average R_d value for the more concentrated ^{239}Pu was significantly higher than for ^{237}Pu, 25 000 ± 9 000 mℓ/g vs. 4 200 ± 1 100 mℓ/g. The ^{237}Pu data for filtered solutions, however, give an average R_d value for sorption of 37 000 ± 12 000 mℓ/g. No ^{239}Pu data are available for filtered final solutions.

III. SORPTION OF PLUTONIUM AND AMERICIUM ON TUFF (W. R. Daniels, F. O. Lawrewnce, S. Maestas, and P. Q. Oliver)

The measurement of the sorption behavior of americium and plutonium on tuff under atmospheric conditions involved geologic materials and groundwater described in Ref. 3.

A. Measurement Techniques

1. Preparation of Traced Feed Solutions. The traced waters used in these studies were prepared using the pretreated waters described earlier[3], isotopically pure ^{241}Am tracer obtained from Oak Ridge National Laboratory, ^{239}Pu tracer (weapons grade) from Los Alamos Scientific Laboratory, and ^{237}Pu tracer produced at Argonne National Laboratory under contract with Battelle (PNL). Tracer purities were checked by both alpha and gamma spectroscopy. The ^{237}Pu tracer was treated with $NaNO_2$ so that the plutonium was in the IV

oxidation state at the beginning; this resulted in the addition of $\cong 10^{-4}$ M sodium to the feed solutions containing ^{237}Pu. Feed solutions were prepared* by two methods: Most of the solutions for Experiments 1, 2, and 3 were prepared by drying the tracers at room temperature and then dissolving them in the appropriate groundwater. This operation resulted in the addition of $\cong 5 \times 10^{-3}$ M chloride to the feed solutions. In Experiment 4 the traced feed solutions were prepared by adding ^{237}Pu or ^{241}Am tracer solution to the pre-treated groundwater and readjusting the pH to the original value by adding NaOH solution. This step added $\cong 1 \times 10^{-3}$ M sodium and $\cong 5 \times 10^{-3}$ M chloride to the feed solutions. Feed solutions were prepared so as to contain (at 100% yield) $\cong 1 \times 10^{-6}$ M americium, $\cong 1 \times 10^{-5}$ M plutonium when ^{239}Pu was used, and $\cong 4 \times 10^{-13}$ M plutonium when ^{237}Pu was used. After allowing for the yield through preparation of the traced feed solutions, the concentrations were $\cong 4 \times 10^{-7}$ M americium, $\cong 1 \times 10^{-13}$ M plutonium with ^{237}Pu, and $\cong 4 \times 10^{-7}$ M plutonium with ^{239}Pu, but these varied significantly from one feed solution to another.

2. Sorption Measurements. Crushed rock[3] from cores JA-18, JA-32, and JA-37 was used for sorption studies at both ambient (22 ± 2°C) and elevated (70 ± 1°C) temperatures. The material was pretreated by shaking weighed 1-g quantities with 20-mℓ portions of water from well J-13 for periods of at least two weeks. The samples were contained in prewashed, capped, 40-mℓ polypropylene tubes. The phases were separated by centrifuging at 12 000 rpm (28 000 g's) for one hour. The weight of the wash solution remaining with the solid phase was obtained by weighing the tube and solid before and after the pretreatment.

Twenty-mℓ portions of traced feed solution of known pH were added to the tubes containing crushed rock. The solids were dispersed by vigorous shaking, and the mixtures were agitated gently for selected times: 1, 2, 4, and 8 weeks. A few contacts are being continued for ≅6 months to examine long-term effects. The shaking rates were 200 oscillations per minute for the ambient temperature samples and 60 oscillations per minute for the 70°C samples.

At the end of a shaking period, the aqueous phases were separated from the solids by four centrifugings, each in a new tube, for one hour at 12 000 rpm (28 000 g's). Solutions were transferred by decanting the first three times and by transferring with a plastic pipet the last time. In Experiment 4

*Additional details are given in Refs. 5 and 6.

three centrifugings were normally used (1, 1, and 2 h), and the solutions were transferred by pipet each time. Extreme care was taken to avoid transferring any particulates from the bottoms of the tubes or in surface films. Aliquots of the final solutions were taken for pH measurements, gross gamma counting, and gamma spectroscopy. The solid phases were left in the tubes and counted directly. The activity sorbed on the walls is considered negligible (see below). The comments[1-3] concerning control samples with a traced aqueous phase but no solid are applicable here. Such samples run with plutonium and americium showed much higher wall sorption on the container when no solid was present.

Desorption experiments were performed by adding pretreated groundwater to the solid phases from the sorption experiments and continuing as for the sorption experiments.

In Experiment 4, the effects of a number of different variables related to experimental technique were examined. The results are described below.

3. Assay of Radioactivity. Solid samples were normally gamma-counted for ^{241}Am or ^{237}Pu on a NaI(Tl) detector utilizing a single channel analyzer and a scaler. Liquid samples were usually gamma counted with a NaI well counter (Packard Auto-gamma Scintillation Spectrometer). Both liquid and solid samples were sometimes counted using a calibrated, 23%, coaxial Ge(Li) detector. The 1024-channel spectra were recorded in a multichannel analyzer connected to a PDP-9 computer.

A minimum of two counts were taken for each sample. Counting standards were prepared using known amounts of ^{241}Am or ^{237}Pu in the same geometries and conditions as the experimental samples.

The ^{239}Pu was determined radiochemically[7] after sample dissolution. Some analyses are not yet complete.

4. Calculations. Since both solid and liquid phases were counted directly for ^{241}Am and ^{237}Pu, or analyzed separately for ^{239}Pu, the sorption ratio, R_d, can be calculated directly as

$$R_d = \frac{\text{activity in solid phase per unit mass of solid}}{\text{activity in solution per unit volume of solution}} .$$

The activities in the control tubes were not used in the calculations; container effects are considered negligible (see below).

B. Results and Conclusions

The results to date for the batch measurements of the sorption behavior of ^{241}Am, ^{237}Pu, and ^{239}Pu on tuff under atmospheric conditions are given in Tables VI-X. Data for samples that were contacted for six months and for some samples that were traced with ^{239}Pu are not yet available. The initial and final pH values are also listed in the tables.

The quoted R_d values were calculated from direct counts of the solids and aliquots of the aqueous phases after they were centrifuged but before they were filtered. Average sorption ratios for both "dried" and "pH adjusted" methods of preparing the traced feed solutions are listed in Table X. These ratios were averaged over 1-, 2-, 4-, and 8-week contact times, 106-150 and 355-500 μm particle sizes, and $\cong 10^{-6}$ and $\cong 10^{-13}$ M plutonium concentrations. The errors quoted are the standard deviations of the means.

For comparison purposes, the results for Experiment 4 are presented in Table XI. Although more limited in scope, these data are probably more reliable than those from earlier experiments because of an improved experimental technique.

Several general conclusions can be made for the plutonium and americium results: The sorptive properties tend to vary with the mineralogy; the R_d values are highest for the zeolitized tuff (JA-37). At least qualitatively the americium R_d value for sorption or desorption tends to increase slightly with increasing particle size, while the plutonium value shows a slight decrease. The R_d values show very little increase with longer contact times; the plutonium values tend to increase more than do the americium values. The R_d values for sorption tend to increase with increasing temperature, while those for desorption tend to decrease with increasing temperature, at least for americium. The method of preparing the traced feed solutions appears to have influenced the observed sorption ratios, the "pH adjusted" method giving somewhat higher R_d values than the "dried" method for sorption but approximately the same for desorption. However, the improved procedure used in Experiment 4 (pH adjusted) for centrifuging and transferring solutions after contact may have resulted in the removal of more particulates from solution, which would result in the observation of higher R_d values. Five different feed solutions of ^{241}Am and two of ^{237}Pu were used in Experiment 4 with no observable differences in their behavior for a given element. This indicates that the feed preparation, at

TABLE VI

Am AND Pu SORPTION RATIOS, TUFF SAMPLE JA-18, AMBIENT TEMPERATURE

Experiment Number	Fraction (μm)	Tracer Prep	Time (d)		R_d		pH	
			Sorp	Desorp	Am	Pu	Initial	Final
1	106-150	dried	7.0		200	170[a]		8.19
1			7.0		250			8.29
				14	270	160[a]	8.30	
2			7.6		96	70[a]	8.56	7.43
2			7.6		310			7.52
				59.8	810		8.51	8.58
3			13.8			110[b]	8.38	8.30
				13.7		710[b]	8.43	8.51
2			14.6		86		8.56	8.42
				34.7	440		8.51	8.53
2			14.6		310			8.29
				59.8	710		8.51	8.57
2			28.6		120	81[a]	8.56	8.55
2			28.6		200		8.53	8.58
				34.7	1 200		8.51	8.15
2			28.6		360			8.60
				59.8	790		8.51	8.58
2			28.6		220		8.52	8.60
3			28.9			120[b]	8.38	8.41
				14		450[b]	8.44	8.56
3			55.7			220[b]	8.38	8.42
				17.8		97[b]	8.35	8.45
2			56.6		57	68[a]	8.56	8.36
2			56.6		100		8.52	8.57
				34.7	2 000		8.51	8.36
2			56.6		85			8.57
				59.8	2 300		8.51	8.52
2			56.6		85		8.53	8.49
4	106-150	pH adjust	32.9		450		8.55	8.42
				41.8	1 000		8.50	8.59
4			32.9		440		8.55	8.43
				41.8	930		8.50	8.64
4			60.9		420		8.55	8.27
				43.8	950		8.50	8.62
4			61.9		430		8.55	8.44
				44.8	970		8.50	8.65

[a] Approximately 10^{-6} M ^{239}Pu.

[b] Approximately 10^{-13} M ^{237}Pu.

TABLE VII

Am AND Pu SORPTION RATIOS[a], TUFF SAMPLE JA-32, AMBIENT TEMPERATURE

Experiment Number	Fraction (μm)	Tracer Prep	Time (d)		R_d		pH	
			Sorp	Desorp	Am	Pu	Initial	Final
2	106-150	dried	7.6		110		8.50	7.60
				34.7	2 800		8.58	8.56
2			14.6		110	110	8.50	8.60
2			28.6		140		8.50	8.63
2			28.6		230		8.50	8.63
				34.7	1 500		8.58	8.34
2			56.6		79		8.50	8.64
1	106-150	pH adjust	7		1 600	1 200	7.92	8.26
1			14		1 000	1 800	7.92	8.19
1			28		1 100		7.92	8.32
				14	2 100	920	8.30	
1	355-500	pH adjust	7		890	1 000	7.92	8.19
4			13		1 300		8.59	8.49
				47.8	2 100		8.46	8.64
1			14		640		7.92	7.94
				14	920	580	8.30	
4			14		1 400		8.59	8.45
				47.8	3 900		8.46	8.69
1			28		490	820	7.92	8.23
4			61.9		1 200		8.59	8.50
				44.8	2 100		8.46	8.67
4			62.9		1 700		8.59	8.52
				47.8	2 600		8.46	8.69

[a]Approximately 10^{-6} M ^{239}Pu.

TABLE VIII

Am AND Pu SORPTION RATIOS, TUFF SAMPLE JA-37,
AMBIENT TEMPERATURE

Experiment Number	Fraction (μm)	Tracer Prep	Time (d)		R_d		pH	
			Sorp	Desorp	Am	Pu	Initial	Final
2	106-150	dried	7.6		430	390[a]	8.64	7.53
2			14.6		365		8.64	8.52
				34.7	14 000		8.60	8.47
2			28.6		430	180[a]	8.64	8.67
2			28.6		1 500		8.64	8.62
				34.7	21 000		8.60	8.28
2			56.6		640		8.64	8.56
1	106-150	pH adjust	7		7 200	7 200[a]	7.92	8.53
1			14		5 200		7.92	8.23
				14	2 700	890[a]	8.30	
4			14		11 000		8.60	8.48
				47.8	12 000		8.58	8.64
4			14.7		10 000		8.59	8.44
				47.8	8 900		8.58	8.63
1			28		7 500	12 000[a]	7.92	7.94
				14	5 200	1 600[a]	8.30	
4			27.7			750[b]	8.35	8.33
				40.8		5 300[b]	8.58	8.60
4			27.7			720[b]	8.35	8.33
				40.8		8 600[b]	8.58	8.59
4			33.9		14 000		8.60	8.52
				42.8	11 000		8.58	8.56
4			34.7		14 000		8.59	8.57
				42.8	9 500		8.58	8.55
			54.7			1 900[b]	8.35	8.30
				43.8		5 500[b]	8.58	8.56
4			60.9		12 000		8.60	8.31
				43.8	12 000		8.58	8.57
4			62.6		11 000		8.59	8.54
				44.8	10 000		8.58	8.59
4			63.6		13 000		8.59	8.56
				47.8	9 700		8.58	8.61
1	355-500	pH adjust	7		3 700	5 400[a]	7.92	8.38
1			14		2 800	7 200[a]	7.92	8.19
1			28		3 800		7.92	8.29
				14	5 800	670[a]	8.30	
4			32.9		12 000		8.60	8.50
				41.8	17 000		8.58	8.58

TABLE VIII (cont).

Am AND Pu SORPTION RATIOS, TUFF SAMPLE JA-37, AMBIENT TEMPERATURE

Experiment Number	Fraction (μm)	Tracer Prep	Time (d)		R_d		pH	
			Sorp	Desorp	Am	Pu	Initial	Final
4			33.9		13 000		8.60	8.51
				42.8	17 000		8.58	8.55
4			60.9		14 000		8.60	8.37
				43.8	18 000		8.58	8.58
4			62.9		12 000		8.60	8.53
				47.8	33 000		8.58	8.60
4			27.7			280[b]	8.38	8.40
				40.8		6 500[b]	8.58	8.61
4			27.7			320[b]	8.38	8.40
				40.8		3 600[b]	8.58	8.59
4			54.7			450[b]	8.38	8.28
				43.8		1 000[b]	8.58	8.59
4			54.7			470[b]	8.38	8.46
				43.8		1 900[b]	8.58	8.56

[a]Approximately 10^{-6} M ^{239}Pu.
[b]Approximately 10^{-13} M ^{237}Pu.

least for the pH adjusted method, is fairly reproducible. For americium, the R_d values were greater for desorption than for sorption, except possibly at 70°C.

Comparison of results for ^{239}Pu ($\cong 4 \times 10^{-7}$ M) and ^{237}Pu ($\cong 1 \times 10^{-13}$ M), at least for "pH adjusted" feed solutions, shows higher sorption R_d values for ^{239}Pu but higher desorption R_d values for ^{237}Pu. Also, for ^{239}Pu the sorption R_d values are greater than the desorption, but for ^{237}Pu the desorption R_d values are greater than the sorption.

IV. BEHAVIOR OF PLUTONIUM AND AMERICIUM IN GROUNDWATER AT pH ≅ 8 (W. R. Daniels, F. O. Lawrence, S. Maestas, and P. Q. Oliver)

Although a considerable number of procedural variables were examined during batch sorption experiments with tuff[3], argillite[5,6], and granite[2], the following discussion will be primarily based upon tuff Experiment 4 (see the previous section). In this experiment improvements were made in the method used for separating solid and liquid phases after contact, presumably reducing

TABLE IX

Am AND Pu SORPTION RATIOS[a], TUFF SAMPLES JA-18, -32, and -37, 70°C

Core Sample	Experiment Number	Fraction (μm)	Tracer Prep	Time (d)		R_d		pH	
				Sorp	Desorp	Am	Pu	Initial	Final
JA-18	2	106-150	dried	7.6		220			7.19
					33.9	3 100		8.35	8.48
	2			7.6		190			7.32
	2			14.6		190			7.57
					33.9	3 600		8.35	8.42
	2			14.6		170			8.08
	2			28.6		290			8.61
	2			28.6		150			8.62
	2			28.6		340		8.60	
	2			28.6		370		8.57	8.50
	2			56.6		300			
	2			56.6		76			
JA-32	2	106-150	dried	7.6		120		8.46	7.33
	2			14.6		160		8.46	8.14
	2			28.6		130		8.46	8.57
	2			56.6		46		8.46	
JA-37	2	106-150	dried	7.6		520	240	8.58	7.33
	2			14.6		680		8.58	8.06
	2			14.6		2 100		8.58	8.18
	2			28.6		960		8.58	8.67
	2			56.6		800		8.58	
	2			56.6		730		8.58	8.52
JA-37	4	355-500	pH adjust	32.9		32 000		8.37	8.23
					41.7	3 800		8.41	8.59
	4			33.9		48 000		8.37	8.25
					42.7	7 200		8.41	8.46
	4			61.8		19 000		8.37	8.51
					44.7	5 500		8.41	8.58
	4			62.8		37 000		8.37	8.64
					47.8	4 800		8.41	8.58

[a]Approximately 10^{-6} M ^{239}Pu.

TABLE X

AVERAGE SORPTION RATIOS (mℓ/g) for Am AND Pu ON TUFF[a]

Element	Core	Temp (°C)	Dried		pH Adjusted	
			Sorption	Desorption	Sorption	Desorption
Am	JA-18	22	180(30)	1 100(260)	435(6)	960(15)
		70	230(30)	3 400(300)		
	JA-32	22	130(30)	2 200(650)	1 100(120)	2 300(310)
		70	110(30)			
	JA-37	22	670(210)	17 000(3 500)	8 800(1 100)	12 000(2 000)
		70	970(240)		34 000(6 000)	5 300(720)
Pu	JA-18	22	140(30)	350(140)		
	JA-32	22	≅110		1 200(210)	750(170)
	JA-37	22	280(100)		3 300(1 200)	3 800(950)

[a]Sorption ratios are given for both "dried" and "pH adjusted" methods of preparing the traced feed solutions. They are averaged over 1-, 2-, 4-, and 8-week contact times, 106-150 and 355-500 μm particle sizes, and ≅10^{-6} and ≅10^{-13} M plutonium concentrations. Values in parentheses are the standard deviations of the means (absolute values).

TABLE XI

AVERAGE SORPTION RATIOS FOR Am AND Pu ON TUFF, EXPERIMENT 4 DATA

Element	Core	Temp (°C)	R_d (mℓ/g)	
			Sorption	Desorption
Am	JA-18	22	435(6)	960(15)
	JA-32	22	1 400(110)	2 700(420)
	JA-37	22	12 000(500)	14 000(2 100)
		70	34 000(6 000)	5 300(720)
Pu	JA-37	22	700(210)	4 600(1 000)

[a]Sorption ratios are given for the "pH adjusted" method of preparing the traced feed solutions. They are averaged over 1-, 2-, 4-, and 8-week contact times and 106-150 and 355-500 μm particle sizes. Values in parentheses are the standard deviations of the means (absolute values).

the amount of particulates present in the aqueous phases and giving more accurate results. A few operations were added to examine container sorption for samples and controls, the fraction of centrifugible species in the controls, the effect of filtering successive portions of the same after-contact solution through the same filter membrane, the effects of filtering after-contact solutions through filter membranes with different pore sizes, and the effects of centrifuging after-contact solutions a different number of times and for different durations. A few contacts will be continued for ≅6 months to examine long-term effects. The procedure used for phase separation after contact was usually three centrifugings, for 1, 1, and 2 hours, at 12 000 rpm (28 000 g's). Extreme care was taken to avoid transferring any particulates from the bottoms of the tubes or in surface films. The centrifuged solutions were then filtered in various ways. In some cases, aliquots were taken for counting after each centrifuging and each filtering.

Sorption on container walls during tuff contacts was measured by transferring the contents after contact, without centrifuging, to new tubes and counting the original tubes. Sorption on the container walls when solids were present was measured for twenty-four ^{241}Am and seven ^{237}Pu samples. The amount of activity sorbed on the container, with the possibility of retention of a small amount of solid even after transfer, averaged 2.1% for americium and 2.5% for plutonium. For the controls, container sorption averaged 24% for nine americium solutions at room temperature, 74% for four americium solutions at 70°C, and 16% for two plutonium solutions at room temperature. The amount of plutonium or americium activity remaining on the container is obviously much lower for the samples than for the controls.

During earlier experiments container sorption for argillite samples was examined in essentially the same way except that the control samples were centrifuged and the aqueous phases were transferred to new tubes. The activity observed in a control tube therefore represented the sum of wall sorption and centrifugable species. Sorption on the container walls when solids were present was measured for thirteen ^{241}Am and nine ^{237}Pu samples. The amount of activity sorbed on the container, with the possibility of retention of a small amount of solid even after transfer, averaged 1.2% for americium and 0.6% for plutonium. For the controls, the americium activity remaining with the container averaged 13% for thirteen solutions at ambient temperature and 90% for four solutions at 70°C. For two plutonium controls at each temperature the

values were 43% at ambient and 88% at elevated temperature. Again, container sorption was much higher for the controls than for samples containing crushed rock.

The ratio of the activity on the bottom of a tube to that on the wall was measured for both tuff and argillite control tubes. For six tubes used with tuff controls, this ratio varied from 0.3 to 1.1 with an average of 0.7. Results for nine argillite controls gave a value of 1.2 for this ratio. The activity on both sets of control tubes appears to have been sorbed fairly evenly on the surface.

The above results for container sorption suggest that sorption is dependent on available surface area, so when crushed argillite or tuff is present container sorption is negligible.

For the tuff controls described above, the fraction of centrifugable species was measured by centrifuging the contents of the new tubes after the first transfer, again transferring the liquid, and counting the activity left in the tubes. The average fraction of the activity in the solution after contact that was removed by one 1-h centrifuging was 17% for nine americium controls at room temperature, 37% for four americium controls at 70°C, and 13% for two plutonium controls at room temperature. Since there was a significant amount of centrifugable species in the control solutions, presumably a similar fraction of the activity was also present with the samples where it would have been combined with the crushed rock and counted with the sorbed activity.

Each of three centrifugings (1h, 1h, 2h) removed additional activity from americium solutions after contact and, therefore, would appear to be necessary. (Such measurements were not made with plutonium solutions.)

In an experiment to see if effects related to the filtering process result in a change in the activity concentration of solutions after contact, three ≅3-mℓ portions of an after-contact solution were passed through the same 0.4-μm polycarbonate membrane. Each portion was aliquoted and counted after passing through the membrane. The averages for a number of samples of the relative concentrations of the solutions after filtering in this way are given in Table XII. Filtering successive portions of the same after-contact solution through the same filter membrane does not appear to result in a significant difference in the concentration of plutonium or americium in the solution.

TABLE XII

EFFECT OF CONSECUTIVE FILTERING OF TRACED SOLUTIONS THROUGH 0.4-μm MEMBRANES

	Ratio of Activity Concentrations of Different Portions	
	Second/First	Third/First
Sample		
^{241}Am		
22°	0.98	0.97
70°	0.97	0.93
Controls		
^{241}Am		
22°	0.94	0.92
70°	0.99	0.98
^{237}Pu		
22°	0.98	0.97

The effects of centrifuging the solutions after contact and then passing them through filters with various pore sizes were examined by counting aliquots of the solutions after each step. Data for a number of samples and controls are given in Table XIII. Filter sequences used were 1.0-0.4-0.05, 0.4-0.4, and 0.05-0.05 μm. The results indicate that the most recent procedure for centrifuging and transferring after contact gave plutonium solutions from which no additional plutonium was removed by filtering. This was not true for americium, where a factor of two or more of the activity was sometimes removed by filtering the centrifuged solutions, the results varying with the contact temperature. This plutonium result suggests that plutonium does not significantly sorb on polycarbonate filter membranes, at least in the time required for filtering. The activity present in a plutonium solution after it has been centrifuged three times is, therefore, probably the "true" value for calculating sorption ratios. For americium, centrifuging the solution after contact would appear to establish a lower limit to the sorption ratio since particulates remaining with the solution would tend to lower the calculated R_d.

In an attempt to clarify the mechanism by which americium is retained on filter membranes, 38 filters from the sequential filterings listed in Table XIII were examined by a microautoradiograpic technique. Approximately one-half to one-third of each filter membrane was mounted on a glass slide by coating with

TABLE XIII

AVERAGE ACTIVITY REMOVED[a] FROM SOLUTION BY CENTRIFUGING AND FILTERING (IN PERCENT)

Treatment	Samples			Controls		
	$^{237}Pu(22°)$	$^{241}Am(22°)$	$^{241}Am(70°)$	$^{237}Pu(22°)$	$^{241}Am(22°)$	$^{241}Am(70°)$
Centrifuge[b] 1 h (2nd)		22	51		14	8
Centrifuge 2 h (3rd)		24	26		6	8
Filter 1.0 μm	0	10		3	28	0
Filter 0.4 μm	0	13		2	26	0
Filter 0.05 μm	0	27		1	8	48
or						
Filter 0.4 μm		22		2	26	6
Filter 0.4 μm		11			24	3
or						
Filter 0.05 μm	0	39	70		40	
Filter 0.05 μm	0	21	6		32	

[a]Decreases in activity are in percent of input activity (just before addition to the rock) for a given operation removed by that operation.

[b]All centrifugings were at 12 000 rpm (28 000 g's).

a thin layer of parlodion (a 2% solution in isopentyl acetate). The slide was then alpha counted to determine the length of exposure time needed (calculated to give $\cong 10^7$ disintegrations) and clamped together with a second slide on which a Kodak AR.10 strippable emulsion had been mounted. It was found that mounting the emulsion directly onto the coated filter made visualization of single tracks very difficult. To get a good adherence of the emulsion on blank glass slides, the slides were first etched with a dilute solution of

hydrofluoric acid, then dried and coated with a 2% solution of parlodion in isopentyl acetate, dried again, and finally coated with a thin gelatin layer by dipping the slide in a water solution containing 0.5% gelatin and 0.06% $CrK(SO_4)_2 \cdot 12H_2O$.

Microautoradiography of the "sorption" membranes showed not only single-alpha tracks but also clusters and stars, indicating the presence of large complex species or polymers in the so-called solutions even after multiple centrifugings. Some "sorption" solutions were filtered through several membranes with the same or decreasing pore sizes (see Table 13). In general, all of these membranes were found to retain americium in clusters, stars, and single tracks. Americium species in these solutions probably exist in a broad range of particle sizes. In contrast, the "desorption" membranes generally showed only single-alpha tracks, suggesting that some americium sorbed on the membranes but that large particulates were not removed from the solids during desorption nor did they form in the aqueous phases during contact.

In related work B. M. Allard (Chalmers University, Göteborg, Sweden, personal communication) observed sorption ratios for Millipore filter paper comparable to those for rock-forming minerals during "batch" sorption experiments with americium in simulated groundwater.

Considering the above results, we have decided to take the conservative approach in calculating americium sorption ratios and use the results from the solutions after they have been centrifuged but not filtered.

It is important to emphasize that the measured sorption ratios for plutonium and americium include effects other than sorption. There may well be differences in the behavior of plutonium or americium even in supposedly identical solutions at pH $\cong$ 8 to 8.5, e.g., in the degree of polymerization and radiocolloid formation, and hydrolysis resulting in variations in species (including charge) and particle size. Grebenshchikova and Davydov[8] reported that the charge on colloidal Pu(IV) species may be either positive (at low pH values) or negative (at high) and that the isoelectric pH, or point of zero charge, is in the pH region 8.0 to 8.5. Polzer and Miner[9] presented a plot of effective charge (due to hydrolysis) of the americium species vs. pH for a 0.1 M $LiClO_4$ solution. Between pH 8.0 and 8.5 the average effective positive charge per atom of americium varied from $\cong$1.3 to essentially zero. Therefore, large variations in the behavior of both plutonium and americium could be expected in this pH range.

V. EFFECTS OF GROUNDWATER COMPOSITION OF SORPTION RATIOS (S. J. DeVilliers)

Since the composition of the groundwater may have a pronounced effect on the sorption ratio for many radionuclides, the first experiments to assess this dependence for granite and argillite have been initiated. The compositions of the two waters being used in the study were selected to represent extremes for the media being used. While the dependence of the sorption ratio on specific major ion concentrations cannot be determined in these experiments since the concentrations of several ions were varied, the overall effects can be distinguished. The same sieve fraction was used in all experiments. All measurements were made under natural atmospheric conditions.

A. Measurement Techniques

The approximate initial compositions of two waters selected for study are given in Table XIV. The dilute groundwater (labeled I) was prepared by adding 2.2 mℓ KCl solution (17.2 mg/mℓ), 13.2 mℓ NaOH solution (4.0 mg/mℓ), and 1.24 mℓ Na_2SO_4 solution (23.9 mg/mℓ) to 74 mg $Ca(OH)_2$ plus 19.2 mg $Mg(OH)_2$. The mixture was diluted to 4.0 ℓ with deonized water and then sparged with carbon dioxide for about 36 h. After the solution was sparged with nitrogen until a pH of 8 was reached, it was allowed to air-equilibrate for 2 d prior to use. The more concentrated groundwater (labeled II) was prepared in a similar manner using 370 mg $Ca(OH)_2$, 192 mg $Mg(OH)_2$, 2.2 mℓ KCl solution, 17.9 mℓ NaOH solution, 17.3 mℓ Na_2SO_4 solution, and 9.1 mℓ NaCl solution.

TABLE XIV

APPROXIMATE INITIAL GROUNDWATER COMPOSITION

	μg/mℓ	
Constituent	Water I	Water II
Na	10	50
K	5	5
Ca	10	50
Mg	2	20
SO_4	5	70
Cl	4.5	15

The 250-355 μm sieve fractions prepared earlier[1-3] were used. They were the Climax Stock quartz monzonite (CS-5 and CS-7) and the Eleana argillite (CN-1 and CN-2). Weighed 1-g quantities of these materials were pretreated for two weeks with 20 mℓ of each of the appropriate waters described earlier. The phases were then separated by centrifugation at 12 000 rpm (28 000 g's).

Four different rock-treated waters were prepared by shaking each of the two waters with the 250-355 μm fractions of CS-5 and CN-1. A 20 mℓ/g solution to solid ratio was used. The phases were separated by centrifugation at 6 000 rpm (20 000 g's) for 1 h followed by filtration through 0.45-μm Millipore filter membranes.

The ^{85}Sr, ^{137}Cs, ^{133}Ba, ^{141}Ce, and ^{152}Eu tracers were added to these rock-treated waters using the technique described (evaporation to dryness followed by dissolution) in Refs. 1-3. The concentrations due to the carrier added with the tracer are given in Table XV.

Each granite and argillite sample was treated with each of the corresponding tagged waters by the procedures described earlier[1-3] for measuring sorption ratios. All solutions and solids were assayed for radioactivity, and our standard calculation methods[1-2] were used. Contact times of 4 and 8 weeks were used.

Determination of the actual composition of the waters before and after contact with the rock is in progress.

B. Results and Conclusions

The results from these measurements are given in Table XVI. The initial and final pH values are given in Table XVII.

There is a strong general tendency for the sorption ratios for cesium, strontium, and barium to decrease when the more concentrated water is used. This is undoubtedly due to the effect of the increased amount of competing ions.

There is a large increase in the R_d values for cerium and europium when water II is used, especially for the granite samples. Since water II had an increased concentration of sulfate ions, perhaps the higher R_d values for cerium and europium can be explained by the greater tendency to form radiocolloids with increasing sulfate concentration. The values also increase greatly between 4 and 8 weeks. All of this is a further indication that the

TABLE XV

ESTIMATED ELEMENT CONCENTRATIONS

Material	Water	Molarity				
		Sr	Cs	Ba	Ce	Eu
Granite	I	5.8×10^{-8}	4.9×10^{-10}	1.0×10^{-8}	3.3×10^{-8}	1.9×10^{-8}
	II	6.4×10^{-8}	6.6×10^{-10}	1.2×10^{-8}	6.0×10^{-9}	3.5×10^{-8}
Argillite	I	5.1×10^{-8}	6.2×10^{-10}	6.4×10^{-9}	1.8×10^{-8}	1.5×10^{-8}
	II	6.4×10^{-8}	7.2×10^{-10}	8.3×10^{-9}	1.6×10^{-8}	1.8×10^{-8}

TABLE XVI

GRANITE AND ARGILLITE SORPTION RATIOS, AMBIENT TEMPERATURE

Mineral	Water	Sorption Ratio, R_d				
		27.63-d Contact Time				
CS-5	I	179(4.2)	8.2(7.3)	63.1(2.4)	184(7.1)	195(6.8)
	II	234(3.3)	5.0(10)	28.3(2.8)	>10 000	4 770(7.0)
CS-7	I	160(4.2)	10.3(6.2)	52.8(2.5)	130(6.7)	133(6.4)
	II	214(3.3)	6.4(8.6)	33.9(2.6)	>13 000	30 100(18)
CN-1	I	1 460(5.2)	227(2.5)	1 030(3.2)	1 890(9.6)	2 580(9.5)
	II	1 010(4.6)	91.7(2.6)	396(2.4)	2 760(14)	1 990(8.7)
CN-2	I	2 390(6.3)	703(2.8)	2 300(3.8)	5 810(12)	8 340(13)
	II	1 630(3.5)	173(2.4)	703(2.1)	12 400(13)	10 700(7.8)
		59.63-d Contact Time				
CS-5	I	591(3.7)	6.6(8.3)	59.4(2.4)	5 200(14)	3 290(6.1)
	II	366(3.4)	4.8(11)	39.7(2.5)	>13 000	17 800(17)
CS-7	I	409(3.7)	10.0(6.2)	74.2(2.2)	1 690(7.6)	1 550(5.2)
	II	289(3.4)	4.4(12)	31.6(2.7)	>9 500	20 600(20)
CN-1	I	1 410(3.8)	143(2.5)	822(2.4)	>68 000	>55 000
	II	1 070(3.4)	83.6(2.6)	428(2.1)	>55 000	>65 000
CN-2	I	2 980(4.2)	144(2.5)	2 570(2.7)	>73 000	>54 000
	II	1 760(3.6)	83.2(2.6)	767(2.1)	>60 000	>62 000

[a]Standard deviations of the means expressed in percent are given in parentheses.

TABLE XVII

pH VALUES IN THE WATER COMPOSITION STUDIES

Solid	Water	pH		
		Initial	28 d	60 d
CS-5	I	8.08	8.01	8.17
	II	8.58	8.44	8.50
CS-7	I	8.08	8.03	8.13
	II	8.58	8.50	8.50
CN-1	I	8.66	8.59	8.69
	II	8.76	8.72	8.76
CN-2	I	8.66	8.65	8.75
	II	8.76	8.65	8.78

sorption mechanism for cerium and europium is quite different than that for strontium, cesium, and barium.

Assuming that uncontrolled variables are not important, the composition of the water seems to be a major factor that governs the observed sorption ratio. The possible influence of anions, other than in a complexing role, must be taken into account in future studies.

VI. SORPTION MEASUREMENTS ON HAINESVILLE SALT DOME MATERIALS (B. R. Erdal, B. P. Bayhurst, S. J. DeVilliers, and F. O. Lawrence)

Since salt systems are considered to be important as potential sites for nuclear waste repositories, it is necessary to begin sorption studies on materials from such areas. Two samples from the Hainesville area in east Texas have been received from Battelle (PNL). These samples are representative of two strata surrounding the dome. Recipes for two "typical" groundwaters were also supplied by Battelle.

Studies of the sorption of strontium, cesium, barium, cerium, europium, uranium, and americium were made under natural atmosphere (called "aerobic") and controlled-atmosphere ("anoxic", <0.2 ppm oxygen) conditions.

A. Measurement Technique

1. Preparation of Materials. The two different solid samples "representative" of the materials around the Hainesville salt dome were used as received from PNL. According to R. J. Serne and J. F. Relyea (PNL), these are mixtures of materials from the pertinent strata. The "aquifer" sample was an equal mixture of the Calvert Bluff and Carrizo strata, while the "aquitard" sample was an equal mixture of Hooper and Simsboro materials. The preliminary mineralogy indicated that all the samples were mainly quartz with minor amounts of secondary clays. Appreciable discoloring was observed. The detailed mineralogy will be done at PNL.

The groundwater compositions used were selected (R. J. Serne, J. F. Relyea) to represent two different scenarios for breach of the dome. The first water represents the Wilcox aquifer which is in the Hainesville region. It was made up to contain 1260 ppm $NaHCO_3$ and 7 ppm $CaSO_4$ (12.6 g $NaHCO_3$ plus 0.0885 g $CaSO_4 \cdot 2H_2O$ per 10.0 ℓ deionized water). The second water represents the high density brine as diluted by the Wilcox aquifer, and contains 10 000 ppm NaCl and ≅7 ppm $CaSO_4$ (100 g NaCl plus 0.0885 g $CaSO_4 \cdot 2H_2O$ per 10.0 ℓ deionized water).

The materials were pretreated by shaking weighed 1-g quantities with 30 mℓ of the appropriate groundwater for 4 d. The phases were separated by centrifuging at 12 000 rpm (28 000 g's) for 20 m. A second pretreatment using 20 mℓ was then done for 3 d, followed by a centrifugation at 12 000 rpm for 20 min. The weight of solution remaining with the solid phase was obtained by weighing the tube and solid before and after the pretreatment.

2. Preparation of Tagged Solutions. The appropriate volumes of the tracer solutions for ^{85}Sr, ^{137}Cs, ^{133}Ba, ^{141}Ce, and ^{152}Eu needed for a set of measurements were evaporated to dryness in a washed polyethylene bottle overnight on a steam bath. Concentrated hydrochloric acid was added and the mixture was taken dry again in order to convert the salts to chlorides. The appropriate volume of groundwater was added and the mixture was mixed for 3 d in an orbit shaker. The mixture was centrifuged for 1 h at 7 000 rpm, followed by filtration through a 0.4-μm Nuclepore filter. The resulting tracer solution was used for the sorption measurements within 0.2 d. An aliquot of the final solution was also removed for assay of the initial activity of each of the tracers in the solution. This aliquot was acidified with hydrochloric acid before assaying in order to stabilize the solution.

The ^{237}U used in these measurements was made by the $^{236}U(n,\gamma)^{237}U$ reaction in the HFIR at the Oak Ridge National Laboratory. The purification chemistry was done at Oak Ridge. It consisted of a dissolution in HCl-HNO_3, a conversion to the nitrate, an extraction with ethyl acetate, an anion column washed with 5M HCl-0.1M HF, and an elution with water. The ^{237}U thus prepared was used, after dilution, by simply adding an aliquot to the desired volume of the appropriate groundwater, and then the remainder of the procedure given earlier was followed.

The isotopically pure ^{241}Am tracer used in this study was obtained from Oak Ridge National Laboratory. For each preparation, the desired amount of tracer solution was evaporated at room temperature in a polypropylene tube. The dried activity was then contacted several times with 20-mℓ volumes of groundwater for a few minutes. The mixture was transferred to a large polyethylene bottle. Contacts were continued until no significant decrease in gamma-ray activity in the tube was observed. Generally three contacts were made. Groundwater was added to the bulk of the feed solution in the bottle to give the desired final volume. The solution was shaken in the bottle in an orbit shaker for >24 h and then passed through a 0.4-μm Nuclepore filter. An aliquot of the final solution was assayed to determine the initial ^{241}Am activity. The traced feed solution was used for the sorption measurements within about 1 h.

In all cases, the original evaporation of the tracers was done in air. The evaporated samples needed for the measurements under reduced oxygen conditions were then transferred to the anoxic boxes. The groundwaters used in the anoxic boxes were sparged with high-purity nitrogen gas prior to transfer to the glove box.

Table XVIII gives the estimated molarities for the tracers.

3. Sorption Measurements. Batch sorption experiments were performed by shaking the 1-g quantities of pretreated material with 30 mℓ of the tagged water, dispersing the solid by vigorous shaking, and agitating the mixture for about 20 d. At the end of the shaking period, the aqueous phase was separated from the solids by a single centrifuging for 1 h at 12 000 rpm (28 000 g's). An aliquot of the final solution was then removed and placed in a standard scintillation counting polyvial. This solution was acidified with hydrochloric acid, and it was then assayed for the remaining activities. The pH of the

TABLE XVIII

TRACER CONCENTRATIONS

	Concentration (molarity)			
	Wilcox		Dilute Brine	
	Aerobic	Anoxic	Aerobic	Anoxic
^{85}Sr	5.3×10^{-8}	6.2×10^{-8}	6.2×10^{-8}	6.4×10^{-8}
^{137}Cs	1.8×10^{-9}	2.7×10^{-9}	2.7×10^{-9}	2.7×10^{-9}
^{133}Ba	1.3×10^{-8}	1.2×10^{-8}	1.8×10^{-9}	1.6×10^{-8}
^{141}Ce	7.5×10^{-8}	4.0×10^{-8}	5.3×10^{-8}	6.9×10^{-8}
^{152}Eu	1.1×10^{-7}	1.4×10^{-7}	1.4×10^{-8}	3.0×10^{-8}
^{237}U	$\cong 1 \times 10^{-7}$	$\cong 1 \times 10^{-7}$	$\cong 1 \times 10^{-7}$	$\cong 1 \times 10^{-7}$
^{241}Am	4.9×10^{-7}	4.4×10^{-7}	4.3×10^{-7}	1.4×10^{-7}

solution before and after contact with the rock was also recorded. Three samples for each groundwater-solid combination were used.

The same sorption procedure was also preformed using three tubes for each water type that did not have a solid phase present. These control samples were used to indicate if any of the radionuclides were likely to be removed by the containers.

The samples were all assayed for radioactivity using the techniques described earlier[1-2].

The following equation was used to calculate the sorption ratios for strontium, cesium, barium, and uranium:

$$R_d = \frac{R \cdot A_c - A_t}{A_t} \cdot \frac{V}{W} \qquad (1)$$

where A_c is the average activity per mℓ of a given radionuclide in the control samples, A_t is the activity per mℓ in the supernatant solution after the required contact time, W is the weight (grams) of solid material used, V is the total final volume of supernatant solution, and R is the dilution factor to take into account the residual solution from the wash that remains with the solid. The amount of residual solution (V_r) left with the solid material was

calculated from the weight increase of the sample plus container (g_r) after the two prewashes and the measured density (ρ_r) of the solutions used ($V_r=g_r/\rho_r$).

For the barium and cerium cases, a different calculational method was used. Since sorption on the container has never been observed for cesium, the R_d value for cesium was used as in internal monitor. The activity of the element of interest and of cesium in the solid and liquid was measured. The sorption ratio is

$$R_d = \frac{A_s}{A_t} \cdot \frac{1}{W} \qquad (2)$$

where A_s is the activity on the solid. If a ratio of R_d values is calculated using Eq. 2 one has, after rearrangement,

$$R_{dx} = \frac{\left(\frac{A_{sx}}{A_{sm}}\right)}{\left(\frac{A_{tx}}{A_{tm}}\right)} R_{dm}$$

where the x and m refer to the element of interest and cesium, respectively. This equation was used to calculate the R_d value for the element of interest since the sorption ratio for cesium was measured in the same experiment and calculated using Eq. 1.

Eq. 2 was used to calculate the sorption ratio values for americium.

The standard deviation for each measurement was obtained from the errors associated with the activity measurements (usually less than 5%), 3% uncertainty assumed for g_r, a 10 mg uncertainty in W, and 0.5% uncertainty in the volumes, and, where applicable, the uncertainty associated with the reproducibility of the control measurements (A_c). The errors were propagated using the rule for change of variables in a moment matrix assuming independence of the variables.

B. Results and Conclusions

The results for the sorption ratio measurements under "aerobic" and "anoxic" conditions are given in Tables XIX-XXIV. The percent of the feed activity remaining in solution in the control samples is given in Tables XXV and XXVI while Tables XXVII and XXVIII give the pH values observed.

TABLE XIX

AEROBIC MEASUREMENTS FOR CESIUM, STRONTIUM, AND BARIUM

Solid	Water	Sample	Sorption Ratio, R_d (mℓ/g)[a] Cs	Sr	Ba
Aquifer	Wilcox	1	14 400 (3.8)	472 (1.9)	2 200 (2.2)
		2	13 900 (3.3)	451 (2.0)	2 120 (2.0)
		3	14 100 (3.1)	465 (2.0)	2 200 (1.9)
		Average[b]	14 100 [1.9]	463 [1.4]	2 170 [1.2]
Aquitard	Wilcox	1	5 960 (7.2)	418 (2.5)	837 (3.1)
		2	4 540 (6.2)	419 (2.6)	839 (3.1)
		3	4 260 (6.2)	409 (2.6)	821 (3.1)
		Average[b]	4 650 [9.1]	415 [1.5]	832 [1.8]
Aquifer	Brine	1	3 670 (3.0)	7.13 (8.8)	22.3 (3.7)
		2	3 730 (3.0)	7.84 (8.0)	24.2 (3.5)
		3	3 750 (3.0)	8.17 (7.9)	24.0 (3.5)
		Average[b]	3 720 [1.7]	7.70 [4.7]	23.5 [2.6]
Aquitard	Brine	1	4 810 (6.0)	9.18 (8.1)	15.7 (4.7)
		2	5 000 (3.3)	10.1 (6.9)	16.5 (4.4)
		3	5 940 (3.4)	11.2 (6.9)	18.4 (4.3)
		Average[b]	5 280 [6.3]	10.1 [5.6]	16.8 [4.6]

[a]The values in parentheses are the standard deviations for a single measurement of the R_d values expressed in percent; these were obtained from the errors associated with the activity measurements and estimated uncertainties for the various parameters entering into the calculation; these estimated uncertainties were propagated using the rule of change of variables in a moment matrix assuming independence of the variables.

[b]Weighted average; the error (%) given is the standard deviation of the mean for the three replicate experiments.

TABLE XX

ANOXIC MEASUREMENTS FOR CESIUM, STRONTIUM, AND BARIUM

Solid	Water	Sample	Sorption Ratio, R_d (mℓ/g)[a] Cs	Sr	Ba
Aquifer	Wilcox	1	8 950 (2.9)	657 (2.2)	3 400 (3.1)
		2	7 670 (2.9)	608 (2.3)	3 280 (3.0)
		3	9 090 (5.2)	635 (2.4)	3 290 (3.7)
		Average[b]	8 310 [5.6]	633 [2.3]	3 320 [1.9]
Aquitard	Wilcox	1	3 420 (2.1)	441 (1.9)	871 (1.8)
		2	3 200 (2.4)	427 (2.1)	822 (1.8)
		3	3 450 (2.3)	432 (2.1)	844 (1.8)
		Average[b]	3 360 [2.3]	434 [1.2]	845 [1.7]
Aquifer	Brine	1	3 800 (2.8)	7.91 (7.7)	25.7 (3.5)
		2	3 790 (2.8)	7.38 (8.3)	24.9 (3.6)
		3	3 200 (2.8)	7.62 (8.2)	24.5 (3.6)
		Average[b]	3 550 [5.8]	7.64 [4.7]	25.0 [2.1]
Aquitard	Brine	1	4 470 (3.1)	10.1 (6.6)	16.0 (4.6)
		2	4 170 (2.9)	9.98 (6.6)	15.8 (4.8)
		3	4 120 (2.9)	9.24 (7.7)	15.2 (4.9)
		Average[b]	4 230 [2.4]	9.80 [4.0]	15.7 [2.7]

[a]The values in parentheses are the standard deviations for a single measurement of the R_d values expressed in percent, these were obtained from the errors associated with the activity measurements and estimated uncertainties for the various parameters entering into the calculation; these estimated uncertainties were propagated using the rule of change of variables in a moment matrix assuming independence of the variables.

[b]Weighted average; the error (%) given is the standard deviation of the mean for the three replicate experiments.

TABLE XXI

AEROBIC MEASUREMENTS FOR CERIUM AND EUROPIUM

Solid	Water	Sample	Sorption Ratio, R_d (mℓ/g)[a] Ce	Eu
Aquifer	Wilcox	1	37 400 (18)	27 900 (11)
		2	40 700 (20)	32 600 (11)
		3	36 300 (19)	25 400 (11)
		Average[b]	37 900 [11]	28 000 [7.2]
Aquitard	Wilcox	1	5 860 (8.2)	2 780 (7.3)
		2	4 940 (7.2)	2 530 (6.6)
		3	6 440 (8.5)	3 020 (7.4)
		Average[b]	5 520 [7.9]	2 730 [5.2]
Aquifer	Brine	1	965 (5.1)	1 820 (11)
		2	1 190 (6.9)	2 640 (16)
		3	943 (5.0)	1 640 (9.4)
		Average[b]	988 [6.0]	1 780 [10]
Aquitard	Brine	1	300 (7.8)	333 (8.3)
		2	317 (7.6)	323 (8.2)
		3	333 (7.6)	364 (8.2)
		Average[b]	316 [4.4]	338 [4.8]

[a]The values in parentheses are the standard deviations for a single measurement of the R_d values expressed in percent; these were obtained from the errors associated with the activity measurements and estimated uncertainties for the various parameters entering into the calculation; these estimated uncertainties were propagated using the rule of change of variables in a moment matrix assuming independence of the variables.

[b]Weighted average; the error (%) given is the standard deviation of the mean for the three replicate experiments.

TABLE XXII

ANOXIC MEASUREMENTS FOR CERIUM AND EUROPIUM

Solid	Water	Sample	Sorption Ratio, R_d(mℓ/g)[a] Ce	Eu
Aquifer	Wilcox	1	17 100 (11)	15 200 (7.5)
		2	24 900 (16)	27 900 (9.3)
		3	25 100 (15)	23 700 (9.2)
		Average[b]	19 600 [13]	18 500 [19]
Aquitard	Wilcox	1	8 970 (6.5)	2 670 (5.8)
		2	8 790 (11)	3 970 (9.4)
		3	8 480 (10)	3 900 (8.2)
		Average[b]	8 810 [4.9]	3 030 [13]
Aquifer	Brine	1	956 (5.2)	1 730 (6.0)
		2	1 000 (5.2)	1 800 (6.0)
		3	967 (4.8)	1 650 (5.2)
		Average[b]	973 [2.9]	1 710 [3.3]
Aquitard	Brine	1	332 (5.4)	359 (5.4)
		2	330 (5.5)	354 (5.5)
		3	326 (5.2)	344 (5.2)
		Average[b]	329 [3.1]	352 [3.1]

[a]The values in parentheses are the standard deviations for a single measurement of the R_d values expressed in percent; these were obtained from the errors associated with the activity measurements and estimated uncertainties for the various parameters entering into the calculation; these estimated uncertainties were propagated using the rule of change of variables in a moment matrix assuming independence of the variables.

[b]Weighted average; the error (%) given is the standard deviation of the mean for the three replicate experiments.

TABLE XXIII

AEROBIC MEASUREMENTS FOR URANIUM(VI) AND AMERICIUM

Solid	Water	Sample	Sorption Ratio, R_d (mℓ/g)[a] U(VI)	Am
Aquifer	Wilcox	1	233 (8.1)	89 000
		2	86 (9.6)	134 000
		3	141 (8.6)	108 000
		Average	118 [29][b]	110 000 [12][c]
Aquitard	Wilcox	1	3.82 (67)	19 900
		2	3.37 (75)	17 400
		3	2.89 (85)	21 400
		Average	3.34 [43]	19 500 [5.6][c]
Aquifer	Brine	1	10 900 (7.2)	2 160
		2	9 320 (7.2)	2 190
		3	8 150 (7.2)	2 510
		Average	9 200 [8.3]	2 290 [4.9][c]
Aquitard	Brine	1	594 (7.5)	336
		2	566 (7.5)	319
		3	571 (7.6)	325
		Average	577 [4.4]	326 [1.5][c]

[a]The values in parentheses are the standard deviations for a single measurement of the R_d values expressed in percent; these were obtained from the errors associated with the activity measurements and estimated uncertainties for the various parameters entering into the calculation; these estimated uncertainties were propagated using the rule of change of variables in a moment matrix assuming independence of the variables.

[b]Weighted average; the error (%) given is the standard deviation of the mean for the three replicate experiments.

[c]The error (%) given is the standard deviation of the simple mean.

TABLE XXIV

ANOXIC MEASUREMENTS FOR URANIUM(VI) AND AMERICIUM

Solid	Water	Sample	Sorption Ratio, R_d (mℓ/g) U(VI)	Am[a]
Aquifer	Wilcox	1	7.13 (40)	96 800
		2	7.35 (37)	107 400
		3	7.10 (40)	76 800
		Average	7.20 [22][b]	93 500 [9.6][c]
Aquitard	Wilcox	1	1.48 (150)	19 600
		2	1.68 (140)	18 900
		3	1.17 (200)	21 400
		Average	1.44 [92][b]	19 900 [3.8][c]
Aquifer	Brine	1	7 300 (10)	3 790
		2	5 250 (10)	1 910
		3	5 390 (10)	2 330
		Average	5 730 [10][b]	2 680 [2.1][c]
Aquitard	Brine	1	232 (11)	334
		2	235 (11)	306
		3	244 (11)	319
		Average	237 [6.4][b]	319 [2.5][c]

[a]The values in parentheses are the standard deviations for a single measurement of the R_d values expressed in percent; these were obtained from the errors associated with the activity measurements and estimated uncertainties for the various parameters entering into the calculation; these estimated uncertainties were propagated using the rule of change of variables in a moment matrix assuming independence of the variables.

[b]Weighted average; the error (%) given is the standard deviation of the mean for the three replicate measurements.

[c]The error (%) given in the standard deviation of the simple mean.

TABLE XXV

PERCENT RECOVERY OF CESIUM, STRONTIUM, AND BARIUM IN THE CONTROL SAMPLES

			Percent in Solution		
Condition	Water	Sample	Cs	Sr	Ba
Aerobic	Wilcox	1	100	100	99.0
		2	101	101	99.6
		3	100	99.4	99.1
Anoxic	Wilcox	1	100	98.8	96.9
		2	101	99.5	97.8
		3	101	99.3	98.5
Aerobic	Brine	1	98.6	98.4	97.1
		2	99.0	98.5	97.7
		3	98.9	98.3	96.9
Anoxic	Brine	1	99.7	99.4	98.9
		2	101	99.2	98.9
		3	99.3	98.7	98.1

TABLE XXVI

PERCENT RECOVERY OF CERIUM, EUROPIUM, URANIUM(VI), AND AMERICIUM IN THE CONTROL SAMPLES

			Percent in Solution			
Condition	Water	Sample	Ce	Eu	U(VI)	Am
Aerobic	Wilcox	1	3.11	53.7	96.7	93.9
		2	7.04	55.9	95.7	92.1
		3	8.57	58.0	96.7	93.6
Anoxic	Wilcox	1	48.0	83.0	101	11.1
		2	56.8	85.9	101	7.2
		3	49.1	84.7	101	8.1
Aerobic	Brine	1	94.7	93.2	78.1	77.1
		2	94.6	92.4	77.2	75.6
		3	94.0	91.8	78.9	75.9
Anoxic	Brine	1	29.3	19.1	39.9	0.20
		2	52.9	40.6	35.6	0.30
		3	0.4	1.1	35.5	0.21

TABLE XXVII

pH VALUES, AEROBIC CONDITIONS[a]

Solid	Water	Sample	pH		
			Sr, etc.	U(VI)	Am
Aquifer	Wilcox	1	8.79	9.09	8.82
		2	8.75	8.54	8.86
		3	8.82	8.46	8.84
Aquitard	Wilcox	1	8.51	8.64	8.94
		2	8.72	8.77	8.89
		3	8.70	8.85	8.89
	Wilcox	1	8.98	9.05	9.05
		2	9.04	9.09	9.02
		3	9.16	9.17	9.01
	Wilcox[b]		8.72	9.07	9.32
Aquifer	Brine	1	7.60	8.15	5.12
		2	7.86	7.58	5.09
		3	7.44	7.26	5.12
Aquitard	Brine	1	5.94	7.42	4.43
		2	5.20	6.59	4.40
		3	4.92	6.07	4.40
	Brine	1	7.16	7.24	6.02
		2	6.86	7.10	5.91
		3	6.75	6.93	6.00
	Brine[b]		6.94	5.65	6.14

[a]Unless otherwise indicated the values are those obtained at the end of the measurement.

[b]The value for the feed solution.

TABLE XXVIII

pH VALUES, ANOXIC CONDITIONS[a]

Solid	Water	Sample	pH		
			Sr, etc.	U(VI)	Am
Aquifer	Wilcox	1	9.30	9.32	9.58
		2	9.30	9.43	9.58
		3	9.32	9.44	9.59
Aquitard	Wilcox	1	9.34	9.39	9.66
		2	9.31	9.37	9.52
		3	9.31	9.40	9.63
	Wilcox	1	9.45	9.39	9.66
		2	9.45	9.43	9.69
		3	9.45	9.40	9.64
	Wilcox[b]		9.47	9.52	
Aquifer	Brine	1	6.32	6.50	5.35
		2	5.20	6.43	4.93
		3	5.07	6.33	4.93
Aquitard	Brine	1	4.36	4.46	4.28
		2	4.34	4.08	4.30
		3	4.32	4.39	4.27
	Brine	1	6.24	6.09	6.53
		2	6.16	6.06	6.55
		3	6.32	6.11	6.51
	Brine[b]		7.97	5.83	6.42

[a]Unless otherwise indicated the values are those obtained at the end of the measurement.

[b]The value for the feed solution.

On examining Tables XIX-XXIV one can make several general conclusions. The sorption ratios for a given element are, with a few exceptions, significantly higher for the aquifer solid than for the aquitard samples. The R_d values for cesium are all rather high, independent of the medium, water, or atmospheric conditions. This may indicate that there is a mineral present which has a high capacity and selectivity for cesium. The values for strontium, cesium, and barium are not affected by the atmospheric conditions in the brine solutions the strontium and barium values are generally low. However, the R_d values for these elements in the bicarbonate water generally decrease when the measurements are performed under anoxic conditions. This may be a function of the absence of carbon dioxide in the anoxic studies which resulted in higher pH values (Tables XXVII and XXVIII). The R_d values for cerium and europium are not strongly affected by the atmospheric conditions except for the aquifer solid with the bicarbonate water. In this case, the sorption ratios decreased strongly when anoxic conditions were used.

The most surprising result from these measurements is the rather significant R_d values obtained for uranium(VI). The values obtained using the brine solutions are always high, independent of the atmospheric conditions. Those for the aquifer solid and the bicarbonate water are also larger than observed in other systems studied (Ref. 2; see below). Anoxic conditions, however, do result in somewhat lower sorption ratios. The reasons for these observations are not understood.

The sorption ratios for americium are all rather large. There does not seem to be any observable dependence on atmospheric conditions.

It is also important to further emphasize the need to assay both the solution and solid for radioactivity in order to obtain proper answers for some elements. For example, some of the americium numbers reported here are more than a factor of ten larger than those calculated using Eq. 1. Somewhat lesser effects were found for cerium and europium.

VII. SORPTION OF URANIUM(VI) ON ARGILLITE (B. P. Bayhurst)

A. Measurement Technique

The measurement of the sorption behavior of uranium(VI) on argillite under atmospheric conditions involved geologic materials and groundwaters

described earlier[1]. The procedure used for these measurements at ambient temperature was described before[2] except that the amount of wash solution left with the solid was measured. The estimated uranium(VI) concentration was $\cong 4.3 \times 10^{7}$ M.

B. Results and Conclusions

The results of the uranium(VI) sorption ratios and the final pH values are presented in Tables XXIX and XXX. The pH of traced feed for sorption was 8.58; that of the untraced feed for desorption was 8.59. The fraction of ^{237}U in the control samples for 1, 2, and 3 week contact times were 100%, 107%, and 98%, respectively.

As expected, uranium(VI) is poorly sorbed on argillite under the conditions used. This is presumably due to the rather high carbonate concentration in these waters, which would strongly complex the uranyl ion. For the smaller particle size (<75 μm), there is a decided increase in sorption ratio. This observation is not understood. However, one should note that the <75-μm particle size material is not a sieve fraction. It was prepared by repeated grindings of the material until the entire sample passed through the sieve. Essentially no iron was introduced in the grinding procedure (see section XII.A).

VIII. MEASUREMENTS UNDER CONTROLLED ATMOSPHERE CONDITIONS (B. R. Erdal, B. R. Bayhurst, and S. J. DeVilliers)

A. System Installation

The equipment needed to perform sorption measurements under reduced oxygen conditions or conditions having a specific atmosphere was purchased and made operational. The two-station controlled atmosphere boxes were manufactured by Vacuum/Atmospheres Co. (model DL-002-S-P). The oxygen concentration is measured by use of a Teledyne trace-oxygen analyzer (model 317-X, special modifications for LASL). The nitrogen gas is cleaned by a Vacuum/Atmospheres Co. gas purification system (model MO-40-2-H). The equipment works very reliably and the oxygen concentration is less than 0.2 ppm. Only measurements under ambient temperature conditions can presently be made.

TABLE XXIX

URANIUM(VI) SORPTION RATIOS, ELEANA ARGILLITE CN-1, AMBIENT TEMPERATURE[a]

Fraction (μm)	Sorption Time (d)	Desorption Time (d)	R_d (mℓ/g)[a]	Final pH
<75	6.810		21.5(14)	8.78
		19.703	21.3(24)	8.62
	13.807		24.9(12)	8.61
		13.734	31.3(17)	8.52
	20.804		21.2(14)	8.58
		7.905	34.1(18)	8.58
106-150	6.810		2.1(72)	8.56
		19.703	- 2.0(510)	8.13
	13.807		1.7(87)	8.53
		13.734	- 4.6(210)	8.56
	20.804		3.4(43)	8.64
		7.905	6.7(130)	8.62
250-355	6.810		1.9(81)	8.60
		19.703	- 2.4(460)	8.67
	13.807		1.4(105)	8.55
		13.734	- 5.9(180)	8.56
	20.804		3.1(48)	8.63
		7.905	7.4(140)	8.55
355-500	6.810		1.9(82)	8.67
		19.703	- 2.5(440)	8.59
	13.807		1.2(121)	8.50
		13.734	- 6.6(180)	8.52
	20.804		3.1(51)	8.66
		7.903	7.7(150)	8.66

[a]The values in parentheses are the standard deviations for a single measurement of the R_d values expressed in percent; these were obtained from the errors associated with the activity measurements and estimated uncertainties for the various parameters entering into the calculation; these estimated uncertainties were propagated using the rule of change of variables in a moment matrix assuming independence of the variables.

TABLE XXX

URANIUM(VI) SORPTION RATIOS, ELEANA ARGILLITE, CN2-4, AMBIENT TEMPERATURE[a]

Core and Fraction (μm)	Sorption Time (d)	Desorption Time (d)	R_d (mℓ/g)[a]	Final pH
CN-2, <75	6.810		15.4(16)	8.61
		19.703	16.2(31)	8.65
	13.807		13.6(17)	8.61
		13.734	15.7(34)	8.51
	20.804		16.8(15)	8.69
		7.905	22.8(25)	8.54
CN-2, 355-500	6.810		5.5(31)	8.62
		19.703	7.0(100)	8.61
	13.807		5.1(31)	8.61
		13.734	5.0(123)	8.53
	20.804		7.1(25)	8.69
		7.905	14.5(50)	8.59
CN-3, <75	6.810		95.5(8)	8.52
		19.703	84.2(11)	8.59
	13.807		94.9(8)	8.58
		13.734	86.9(11)	8.57
	20.804		107(8)	8.66
		7.905	108(10)	8.68
CN-4, <75	6.810		83.2(9)	8.61
		19.703	72.6(11)	8.67
	13.807		74.4(9)	8.61
		13.734	69.0(11)	8.88
	20.804		77.2(9)	8.61
		7.905	89.6(11)	8.62

[a]The values in parentheses are the standard deviations for a single measurement of the R_d values expressed in percent; these were obtained from the errors associated with the activity measurements and estimated uncertainties for the various parameters entering into the calculation; these estimated uncertainties were propagated using the rule of change of variables in a moment matrix assuming independence of the variables.

B. Preparation of Materials

The solids being used are the same as those previously described. These are the Climax Stock quartz monzonite[2] and Eleana argillite[1] (core CN-3). Solid samples of these materials were ground under anoxic conditions in a non-iron system using an agate mortar with a 50- or 70-mm agate ball (Tekmar Co., Pulverisette). Each material was graded by use of Tyler sieves (ASTM E-11 specification) into two size fractions, <75 μm and 75-500 μm. The entire sample was ground until it passed into one of these fractions.

The same groundwaters as previously described[1,2] were used to prepare the rock-treated waters for granite and argillite. The rock-treated waters were prepared by contacting batches of the groundwater, which had been sparged with high purity nitrogen for at least 1 h with pulverized material (20 to 40 g), that had not been sieved. The contact time was at least two weeks at ambient temperature with a solution volume to solid ratio of 50 mℓ/g. The phases were separated by centrifugation at 7 000 rpm for 1 h followed by filtration through a 0.4-μm Nuclepore filter membrane. All operations were performed in the controlled atmosphere boxes.

The solid samples were also pretreated with the appropriate oxygen-free groundwater by shaking weighed 1-g quantities of the crushed rock with 20 mℓ of the water for a period of two weeks at ambient temperature under anoxic conditions. The samples were contained in stoppered 40-mℓ polypropylene (Oak Ridge) screw-cap centrifuge tubes. All tubes were washed with deionized water prior to use. The phases were separated by centrifuging at 12 000 rpm (28 000 g's) for 1 h. The weight of the wash solution remaining with the solid phase was obtained by weighing the tube and solid before and after the pretreatment.

C. Sorption of Strontium, Cesium, Barium, Cerium, and Europium

The sorption of strontium, cesium, barium, cerium, and europium on argillite and granite under anoxic conditions (<0.2 ppm oxygen) was studied. This was done to see if there was any effect of reduced oxygen concentration on the solid since one would not expect any major effect of oxygen on these elements. However, there was also a reduction in the amount of carbon dioxide in the solutions used.

1. Preparation of Tagged Solutions. The appropriate volumes of the tracer solutions for ^{85}Sr, ^{137}Cs, ^{133}Ba, ^{141}Ce, and ^{152}Eu needed for a set of measurements were evaporated to dryness in a washed polyethylene bottle overnight on a steam bath. Concentrated hydrochloric acid was added and the mixture was taken dry again. The appropriate volume of groundwater was added to the bottle inside the controlled atmosphere box and the mixture was mixed for about 2 d in an orbit shaker. The mixture was filtered through a 0.45-μm Millipore filter and the resulting tracer solution was used for the sorption measurements within about 0.2 d. An aliquot of the final solution was also removed for assay of the initial activity of each of the tracers. This aliquot was acidified with hydrochloric acid before assaying in order to stabilize the solution. The estimated molarities of the tracers were Sr(7.9×10^{-8} M), Cs(3.3×10^{-9} M), Ba(2.4×10^{-8} M), Ce(3.1×10^{-8} M), and Eu(6.3×10^{-8} M) for the argillite samples, and Sr(8.3×10^{-8} M), Cs(1.8×10^{-9} M), Ba(2.5×10^{-8} M), Ce(9.5×10^{-10} M), and Eu(1.3×10^{-9} M) for the granite samples.

2. Sorption Measurements. Batch sorption measurements were performed using the techniques described earlier[1,2]. The contact times were 3, 6, and 12 weeks. At the end of the shaking period the samples were centrifuged for 1 h at 12 000 rpm (28 000 g's). The solid and aqueous phases were separated by transferring the liquid into a clean tube with a plastic transfer pipet. After centrifuging for another hour at 12 000 rpm, the solutions were again transferred into a clean tube by pipet and centrifuged for 2 h. An aliquot was then taken for assay of the radioactivity. The pH measurements were made on the remainder of the solution. A small amount of the solid was transferred to a counting vial for activity assay. All the handling of the solid or solution samples was made inside the controlled atmosphere boxes. The assay and calculational methods described earlier[1,2] were used.

3. Results and Conclusions. The results from the 3 week contact time measurements are given in Table XXXI. The other measurements are still in progress. The initial pH values were all 8.43 and the final granite pH values were 8.56 and 8.52 for the <75 μm and 75-500 μm samples, respectively, while the corresponding final argillite pH values were 8.55 and 8.68, respectively.

The R_d values obtained for strontium, cesium, and barium on the granite are all consistent with the values obtained under aerobic conditions[2], particularly when the differences in the particle sizes used are taken into account.

TABLE XXXI

MEASUREMENTS UNDER ANOXIC CONDITIONS,
20.63-d CONTACT TIME[a], 32°C

Sample	Fraction (μm)	R_d (mℓ/g) Cs	Sr	Ba	Ce	Eu
CS-7	<75	1 780(2.7)	69.8(2.5)	1 720(1.7)	>2 600	>1 100
	75-500	752(2.4)	19.4(3.8)	245(1.4)	>1 400	>5 300
CN-3	<75	1 190(2.2)	32.1(3.1)	288(1.4)	>110 000	>400 000
	75-500	1 020(2.6)	31.9(3.2)	209(1.6)	>128 000	>440 000

[a]The values in parentheses are the standard deviations for a single measurement of the R_d values expressed in percent; these were obtained from the errors associated with the activity measurements and estimated uncertainties for the various parameters entering into the calculation; these estimated uncertainties were propagated using the rule of change of variables in a moment matrix assuming independence of the variables.

However, the values for cerium and europium are significantly larger. Perhaps this is due to the absence of carbon dioxide in the controlled-atmosphere studies.

Similarly, the values for cerium and europium on the argillite are also larger than those observed under aerobic conditions[1]. However, the values for strontium and barium are lower. This must be due to the absence of carbon dioxide in the controlled atmosphere boxes. The values for cesium are consistent with the measurements under aerobic conditions.

D. Sorption of Uranium(VI)

The measurement of the sorptive behavior of uranium(VI) on argillite and granite under controlled-atmosphere conditions (<0.2 ppm oxygen) utilized the same geologic materials described earlier. The only change in the experimental method from that used in the aerobic studies (see earlier) was that the tracers were evaporated to dryness in air before being brought into the controlled atmosphere system.

The results from these measurements are given in Table XXXII. The ambient temperature was 32°C. The desorption measurements are in progress. No loss of ^{237}U from solution was observed in the control samples. It is surprising that no sorption of uranium(VI) was observed under these conditions since

TABLE XXXII

URANIUM(VI) SORPTION RATIO MEASUREMENTS
UNDER ANOXIC CONDITIONS, 32°C

Sample	Fraction (μm)	Contact Time (d)	R_d (mℓ/g)
CS-7	<75	6.755	0.99 (150)
		13.774	1.20 (130)
		20.803	1.28 (120)
	75-500	6.755	0.97 (150)
		13.774	-0.51 (270)
		20.803	0.35 (400)
CN-3	<75	6.755	6.61 (29)
		13.774	8.43 (24)
		20.803	8.91 (23)
	75-500	6.755	5.26 (35)
		13.774	5.76 (32)
		20.907	7.26 (27)

[a]The values in parentheses are the standard deviations for a single measurement of the R_d values expressed in percent; these were obtained from the errors associated with the activity measurements and estimated uncertainties for the various parameters entering into the calculation; these estimated uncertainties were propagated using the rule of change of variables in a moment matrix assuming independence of the variables.

it was felt that the reducing potential of these materials could have resulted in the formation of uranium(IV), which could be expected to sorb. This reduction must not be taking place. All values are consistent with the values obtained earlier[2,5].

IX. CRUSHED ROCK COLUMN MIGRATION RATE STUDIES (E. N. Vine)

A. Measurement Techniques

1. Preparation of Columns. Crushed rock column studies have been made on three types of media from the Nevada Test Site: tuff, argillite, and

granite. The geologic materials chosen were those on which batch R_d measurements had previously been made in order to provide a comparison with results obtained using columns. The pretreated waters used for the infiltration were prepared using techniques described elsewhere[1-3]

Water delivery rates were controlled by syringe pumps (Sage Instruments, Model 352). Initially the columns, 0.5 cm inside diameter by 2 to 4 cm long (Bio-Rad Econo-Columns), were run by gravity flow and the syringe pumps were used only to control the delivery rate of water to the top of the column. The actual flow rate through the column was not known. A simple, upflow, 0.4-0.5 cm x 2 cm column was then developed to maintain a known, steady flow rate controlled by the syringe pump. The columns were modified from Bio-Rad Econo-Columns by shortening them to ~2 cm, lining them with Teflon tubing, and placing polyethylene bed supports and a polypropylene Luer fitting on each end.

A summary description of the crushed rock columns studied and the parameters measured are given in Table XXXIII. Each column was characterized in terms of the total column volume (the size of the column calculated from the dimentions of the column), the free column volume (FCV) (measured and used to calculate the effective column porosity), the dry bulk density, the particle size, and the flow rate. Flow rates were determined by weighing the eluate sample delivered in a known time period. Gravity flow columns tended to decrease in flow rate before a steady flow rate was maintained. For example, the first and third YM-54 columns began with flow rates of ≅0.08 and 0.07 mℓ/h and decreased to ≅0.04 and 0.03 mℓ/h, respectively. However, the flow rates of the upward-flow columns were found to be relatively constant for a given column, syringe, and pump setting. Upward flow rates ranged from 0.041 to 0.082 mℓ/h. A flow rate of 0.045 mℓ/h for a 2.1-cm long column with a free column volume of 0.224 mℓ would correspond to a flow of ~34 m/y.

The free column volumes of approximately one-third of the columns studied were determined by use of both HTO and $^{131}I^-$. In the iodide case, the ^{131}I breakthrough (leading edge) curve and the rinse (trailing edge) were both used. There was essentially no difference in the values obtained with HTO or with $^{131}I^-$ and all measurements for a given column were averaged irrespective of the method used. For example, the FCV for YM-54 obtained with iodide (breakthrough) was 0.177 mℓ and with HTO was 0.182 mℓ. On YM-22, the iodide breakthrough method gave 0.249 mℓ and the iodide rinse gave 0.239 mℓ. Another YM-22

TABLE XXXIII

DESCRIPTIONS OF THE CRUSHED ROCK COLUMNS

Material	Particle Size (μm)	Column Size (cm)	Porosity	Bulk Density (g/mℓ)	Flow Rate (mℓ/h)	Expt. Type[a]
Tuff						
YM-54	35-106	1.50x0.50	0.793	0.98	0.037	S,G
	35-106	1.50x0.50	0.612		0.067	CF,G
	35-106	2.60x0.50	0.669		0.033	S,G
YM-45	106-500	2.10x0.40	0.318			S,U
YM-38	35-106	4.00x0.50			0.060	S,G
	106-500	2.12x0.40	0.357			S,U
	106-500	2.45x0.45	0.390			S,U
YM-22	35-106	1.90x0.50	0.654	1.16	0.077	S,U
JA-37	106-150	2.15x0.45	0.444			S,U
JA-32	35-106	4.40x0.49	0.549	0.89	0.131	S,G
	35-106	2.20x0.50	0.678		18.0	CF,G
	35-106	1.80x0.50	0.635		0.082	S,U
JA-18	106-150	2.00x0.40	0.562			S,U
Argillite						
CN-1	180-250	2.40x0.45	0.592	1.11	0.053	S,U
	180-250	2.43x0.45	0.644	1.18	0.054	S,U
Granite						
CS-5	35-106	2.15x0.50	0.597	1.25	0.041	S,U
	35-106	2.10x0.50	0.592	1.26	0.045	S,U

[a]U(upward flow); G(gravity flow); S(spike loading); CF(continuous feed).

column (not yet used or included in Table XXXIII) gave 0.208 mℓ with HTO, 0.205 mℓ by the iodide breakthrough method, and 0.199 mℓ by the water rinse method. The values for the CS-5 and CS-7 granite columns, the CN-1 and CN-2 argillite columns, and the JA-18, JA-37, and YM-45 tuff columns were measured using ^{131}I only.

The radionuclides studied were usually added to the column in a minimal (5 to 15 mℓ) volume or "spike." The radionuclides used were primarily ^{85}Sr, ^{137}Cs, and ^{133}Ba, although studies using ^{141}Ce and/or ^{152}Eu were recently begun. Rickert et al. (personal communication, Argonne National Laboratory) had previously noted a cesium concentration dependence for ^{137}Cs sorption on limestone, where the R_d value decreased with increasing concentration. The concentration of cesium in the batch measurements ($\cong 10^{-9}$ M) was $\cong 10^{-3}$ times less than that of the cesium spike added to two YM-54 columns. Another YM-54 column was, therefore, run with a continuous feed of ^{137}Cs at a concentration comparable to that of the batch measurements in order to determine if the cesium concentration effect also existed for tuff.

In addition to varying the radionuclide loading concentration (of ^{137}Cs) on crushed core columns, the flow rates were also varied for three JA-32 tuff columns loaded with ^{85}Sr. Flow rates were varied from 0.082 mℓ/h to 18 mℓ/h. Two of these columns were run by gravity flow and the third was run by the upward flow technique.

2. Data Acquisition and Analysis. Eluate fractions from each column were collected in closed pre-tared vials. The vials were replaced daily and weighed immediately after removal for determination of the eluate volume. At flow rates of ~0.03 to 0.08 mℓ/h, this represented $\leq$ 1 to 2 mℓ/d. Each sample was diluted to a known volume, sealed, and saved for measurement of radioactivity. Samples from a given column were counted with a NaI(Tl) detector until activity was observed. If more than one radioisotope had been placed on the column, all samples, beginning with the one in which activity was first detected, were counted on a calibrated, 14%, coaxial Ge(Li) detector. The 4096 channel spectra were recorded in multichannel analyzers and analyzed on-line with a PDP-9 computer by our in-house gamma-ray spectroscopy program, RAYGUN. If only one radioisotope had been added to a column, all eluate fractions were counted with a NaI(Tl) detector.

The activity per mℓ of each fraction collected (and of each tracer, if more than one was used) was plotted against the total volume which had been eluted at the time the sample was taken. An example of these plots is given in Fig. 1 (YM-54, third column). A main reason for utilizing column studies is that the behavior of a radionuclide can be observed directly as it flows through the rock. The relative velocity of the radionuclide with respect to the groundwater velocity, or the retardation factor, R_f, can then be related to the distribution coefficient, K_d:

$$R_f = K_d\ (\rho/\varepsilon) + 1$$

where ρ is the bulk density and ε is the porosity (FCV/V). Thus, the total volume eluted which corresponded to the peak of each radioisotope was compared to the free column volume (the volume corresponding to the peak of the $^{131}I^-$ or HTO curve) to obtain the retardation factor and, subsequently, the sorption ratio. Since K_d implies reversible equilibrium and batch studies have shown that equilibrium is frequently not attained in a few weeks or months for many cases, it may not be entirely correct to use this equation. However, for calculational purposes it is assumed that the sorption ratio R_d is the same as the distribution coefficient K_d.

Such data can also be represented by a breakthrough curve where the cumulative fraction of the total activity is plotted against eluate volume. If the breakthrough curve is symmetrical, the volume where 50% of the activity has been eluted should correspond to the peak of the elution curve. The elution and breakthrough curves from the first JA-32 column are plotted in Figs. 2 and 3.

B. Results and conclusions

The columns for which data are available are those begun initially to develop techniques. Seventeen columns are described in Table XXXIII. Ten of the columns are still running, with one or more isotopes yet to be eluted. Thus, the conclusions to date should be considered preliminary. The materials and isotopes chosen initially were those for which batch R_d values were known to be low. The exception, ^{85}Sr on YM-38, where the R_d values are about ≅14 000 and ≅22 000 mℓ/g for sorption and desorption, respectively, was begun before the

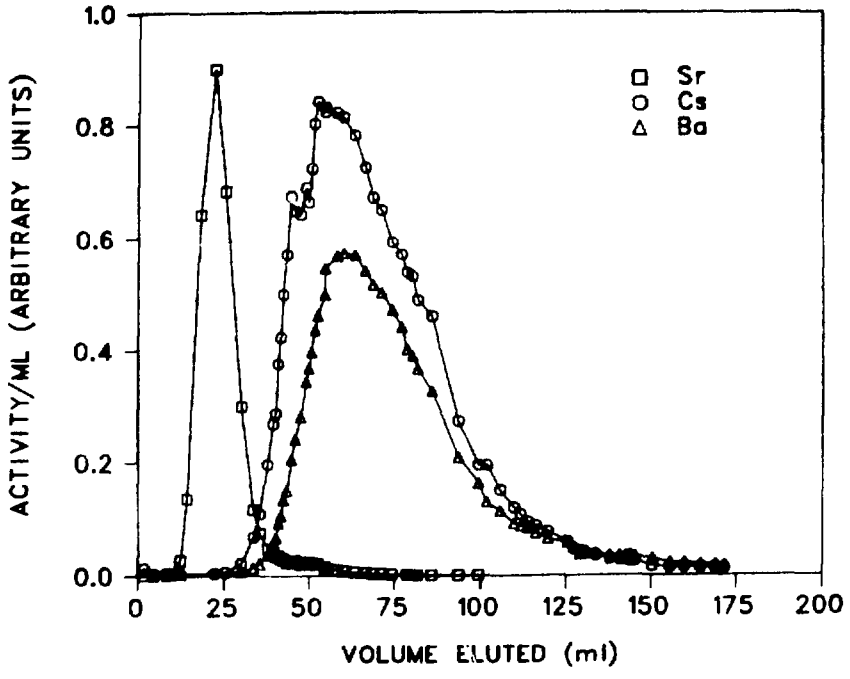

Fig. 1. Elution Curves, Third YM-54 Column.

batch measurements had been completed. It is therefore not surprising that no ^{85}Sr has been eluted in ≅240 days. The initial pH values for the waters were 8.12(YM-54), 8.17(JA-37), 7.76(JA-18), 7.90(argillite), and 7.99(granite). There was little or no pH change of the waters due to flow through the columns.

The R_d values which have been calculated from the column data are given in Table XXXIV. Generally, the peak shapes of the elution curves were reasonably symmetric and the point where 50% of the activity had been eluted corresponded closely to the peak of the elution curve. For example, in Figs. 2 and 3 for ^{85}Sr on the first JA-32 column, the 50% point was 41.5 mℓ and the peak of the elution curve was at 39.0 mℓ. For all three JA-32 columns, the average R_d value calculated from peak volumes was 41.6 mℓ/g and that obtained from the volumes at the 50% point was 43.3 mℓ/g. Since the other columns studied to date also had relatively symmetric peak shapes, the peak volumes were used for convenience to calculate the retardation factors. This made it unnecessary to rely on an external standard as a monitor of total activity, A_T, or to wait until all the activity had been eluted from a column to calculate A_T.

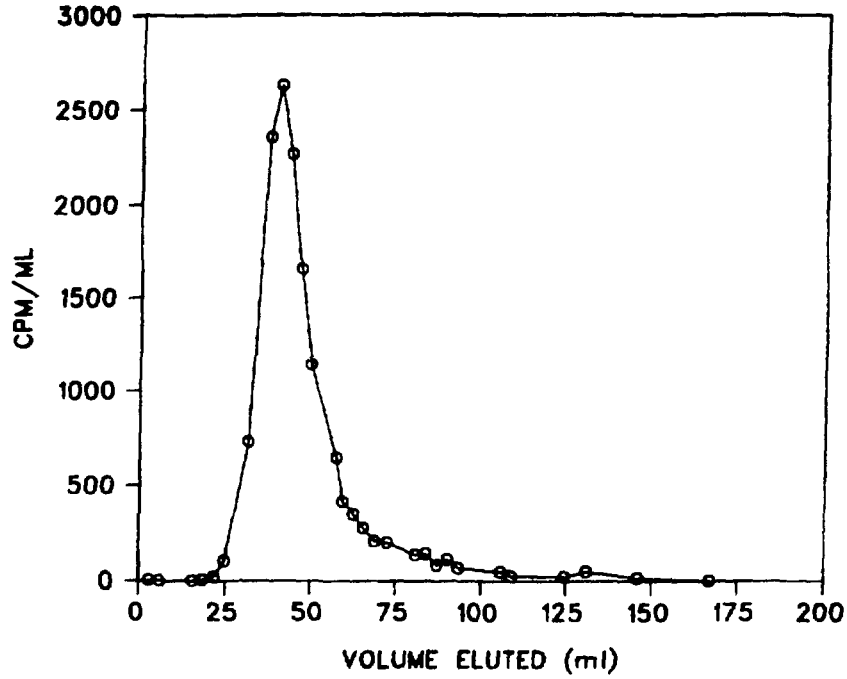

Fig. 2. ^{85}Sr Elution Curve, First JA-32 Column.

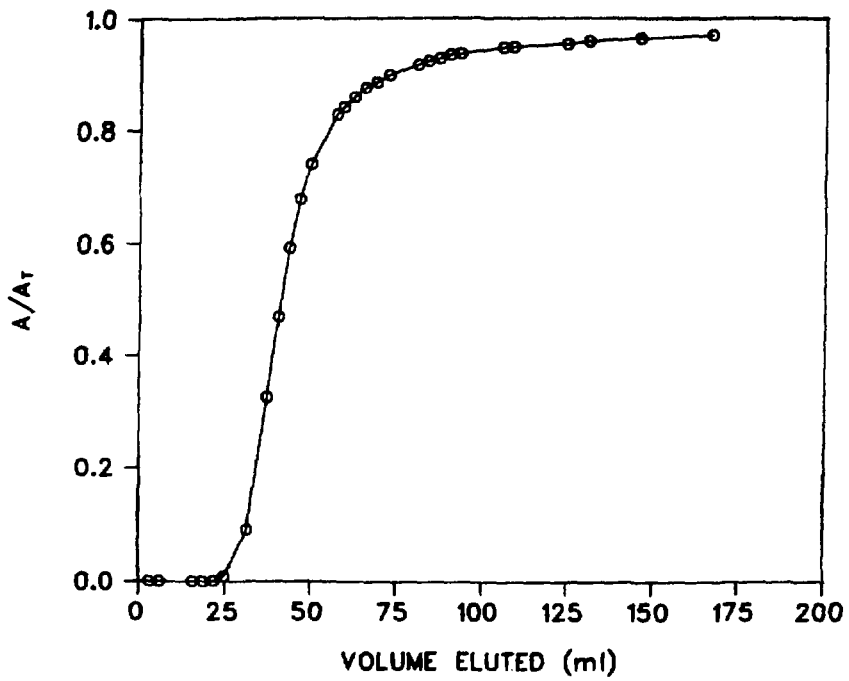

Fig. 3. Breakthrough Curve, First JA-32 Column.

TABLE XXXIV

COMPARISON OF BATCH AND COLUMN SORPTION RATIO (mℓ/g) VALUES

	Sr		Cs		Ba	
Column	Column[a]	Batch[b]	Column[a]	Batch[b]	Column[a]	Batch[b]
YM-54	44	84,82	92	247,321	126	652,632
			80			
	44		113		122	
YM-22	30	50,57	122	287,365	335	899,824
JA-32	52	56,47				
	37					
	35					
CN-1	43	138,133	NA	1830,3110	NA	4270,5530
CN-2	52	156,131	NA	1580,3810	NA	4900,5650
CS-5	8.5	14,19	NA	328,734	32	154,176
CS-7	15	18,22	NA	347,533	44	

[a] If no entry appears the corresponding element was not loaded onto the column; NA means that the elution is not yet complete.

[b] The two numbers for the batch results are the mean values obtained under ambient temperature conditions for sorption and desorption, respectively. They were obtained from the following sources: CS-5 and CS-7 granite, Ref. 2 (106-150, 250-355, and 500-850 μm fractions, ≅ 4 weeks contact time); CN-1 and CN-2 argillite, Ref. 1 (<75, 106-150, and 355-500 μm fractions, ≅ 8 weeks contact time); JA-32 tuff, Ref. 3 (106-150 μm fraction, ≅ 8 weeks contact time time for sorption and ≅ 11.5 weeks for desorption); YM-54 and YM-22 tuff, Ref. 5 (≦ 106 μm fraction, ≅ 6 week contact time).

Three general conclusions can be drawn from the results: The ^{85}Sr column R_d value, at least for JA-32 tuff is relatively independent of flow rate. Sorption ratios of 37 and 35 mℓ/g were obtained for the first JA-32 (gravity flow) column where the delivery rate was 0.131 mℓ/g. (The actual flow rate although unknown, was probably on the order of several mℓ/h.) The higher R_d value obtained for the first JA-32 column could perhaps be due to the column being twice as long as the other two, although two YM-54 columns, which also varied in length by close to a factor of two, gave identical R_d values for ^{85}Sr. Variations in rate constants and distribution coefficients with bed depth have been noted in the literature (see, for example, Ref. 10).

The effect of the cesium ion concentration on the R_d value appears to be negligible for the tuff crushed core studied (YM-54). Two columns, where ^{137}Cs was loaded at $\cong 10^{-6}$ M, gave R_d values of 113 and 92 mℓ/g. A third column, where the ^{137}Cs concentration was $\cong 10^{-9}$ M, gave an R_d value of 80 mℓ/g. All three values are approximately three times lower than the sorption ratio obtained by a batch technique.

The sorption ratio obtained using the columns analyzed so far were always found to be less than those obtained using the batch technique. The ratios of batch to column sorption ratios are given in Table XXXV. The biggest differences are factors of about five for ^{133}Ba. In most cases, the agreement between batch and column R_d values are within a factor of two to three. Given the variations in batch measurements themselves, this is fairly good agreement. The flow rates and column sizes used correspond to $\cong 10^{-4}$ cm/sec or ~30 m/y, which, although not slow by geologic standards, are within a reasonable range for flow rates in geologic media ($\sim 10^{-3}$ to 10^{-7} cm/sec). The fact that column sorption ratios (for materials with low R_d values) tend to be smaller could in part be due to the shorter residence times. Perhaps in batch experiments lasting weeks or months, diffusion contributes significantly in cases of low R_d values. This effect would be negligible in a comparatively short column experiment. (In fact, a significant difficultly with small crushed core columns, even given good agreement with batch R_d data, will be in relating such data, obtained over small distances in short contact times, to long distances and long contact times.)

Since preliminary data indicated that increasing flow rate did not significantly alter results, experiments were begun to look at isotopes having high R_d values on tuff. The elution of ^{85}Sr on a column of YM-38 (average batch R_d $\cong$18 000) should be done in $\cong$38 days at a flow rate of $\cong$3 mℓ/h. Since several liters of water will be required, the column has been prepared; however, ^{85}Sr has not been loaded, since the water is still being pretreated. It will also be important to measure how closely cerium and europium column R_d data agree with batch R_d values since sorption of these elements is most likely not by ion-exchange mechanisms. Such experiments are in progress (YM-38 and YM-45).

TABLE XXXV

R_d (BATCH) / R_d (COLUMN)

Column	Sr	Cs	Ba
YM-54	2.0	3.6	5.1
		3.1	
	2.0	2.5	5.3
YM-22	1.8	2.7	2.6
JA-32	1.0		
	1.4		
	1.4		
CN-1	3.1		
CN-2	2.8		
CS-5	1.9		4.8
CS-7	1.3		4.0

X. MICROAUTORADIOGRAPHY (J. L. Thompson and E. N. Vine)

Microautoradiography has been employed at LASL as an adjunct to other techniques for studying the sorption properties of certain elements on selected types of rocks. Whereas column or batch sorption methodologies yield information on sorption properties of gross rock, microautoradiography can indicate the specific mineral phase responsible for the sorption. Furthermore, this technique can give insight into the state of aggregation of the sorbed material. Since many of the transuranic elements tend to form polymeric or colloidal species in solution at groundwater pH values, observation of the amount of aggregation in adhering species is very important.

A. Sorption of Plutonium and Neptunium of Thin-Sections

Techniques had been developed earlier[4] for preparing autoradiograms of ^{233}U and ^{241}Am on thin sections of rocks derived from NTS alluvium, tuff, granite, and argillite. In general, the same techniques were employed with ^{239}Pu and ^{237}Np.

An effort was made to prepare ^{239}Pu solutions of groundwaters with activity levels which would remain constant with time. All water used for these solutions was filtered through 0.4- and 0.05-μm filters, and the solutions were stored in capped Teflon tubes. The original plutonium stock solution (in $HClO_4$) was evaporated to dryness, the plutonium was dissolved in distilled water, taken to dryness, and redissolved in the groundwater derived from the alluvial, tuff or granite formation or, in the case of argillite, synthesized to represent the composition of the natural groundwater. It was found that plutonium disappeared from these solutions in a period of several days, but could be reproducibly reintroduced (probably in a colloidal form) by placing the Teflon tubes in an ultrasonic bath for a short time. It was thought that this "colloidal" plutonium would settle out on the thin-sections under the force of gravity, but experiments conducted with droplets of plutonium solution hanging suspended from the thin section did not produce less activity on the rock surface than when the droplets were sitting on top of the thin-section.

Microautoradiograms were prepared of ^{239}Pu on alluvium, JA-25 and JA-26 tuff, Climax Stock granite, and Eleana argillite. Complete petrographic analyses of these have not yet been done, but strong sorption by specific minerals seemed to be lacking. Generally the alpha-track distribution was fairly uniform, with a number of stars present (indicating aggregated species). It appears that plutonium sorbs rather indiscriminately on rock thin-sections and even on glass. However, it is also true that the amount of sorption on the various rock types varied significantly, with the tuffs showing the least sorption and granite the most. Perhaps some unidentified variable, such as the dissolved species in the groundwaters, is controlling the quantity of deposition on the thin-sections.

Attempts to sorb ^{237}Np on rock thin-sections were hampered by the rather low tendency of the neptunium to sorb (estimated to be lower than plutonium by at least a factor of ten) and by the presence of large amounts of the ^{233}Pa daughter in the radioactive source solution. The ^{233}Pa sorbed strongly on the thin-sections, and the beta radiation from this nuclide exposed the emulsions to the point of obscuring the alpha tracks generated by the ^{237}Np. Two procedures were exployed to purify the neptunium: a TTA extraction[11], and a fluoride precipitation followed by separation on an ion exchange column. Neither of these procedures gave a very complete separation. Autoradiograms

were prepared with alluvium, JA-26 tuff, Eleana argillite, and granite thin-sections using a high specific activity solution (~7 x 10^6 dps/mℓ) with the ^{233}Pa in secular equilibrium with the ^{237}Np. In general, the neptunium seemed to deposit in some aggregated form, as dense clumps of tracks were present on all the thin sections. In the case of the JA-26 tuff and the alluvium, there is possibly some association of the tracks with specific minerals. As always, individual alpha tracks were difficult to see against the dark background of the Eleana argillite, but with intense illumination a large number of dense clumps of tracks were visible. The granite showed a broad distribution of tracks and clumps, with no apparent tendency to sorb on specific minerals.

B. Beta Microautoradiography

A number of autoradiograms were prepared using ^{85}Sr, ^{63}Ni, ^{233}Pa, and ^{90}Sr. Kodak AR.10 strippable emulsion, Kodak liquid emulsions NTB-2 and NTB-3, and a film-backed emulsion "Ultrafilm ^{3}H" (manufactured by LKB, Rockville, Md.) were utilized. Beta tracks (generally spots) were readily visible at moderate surface densities against a clear background, but were difficult or impossible to identify except at very high densities against the mottled backgrounds typical of rock thin-sections. Thus it appears that beta autoradiography may be limited in geologic applications to situations in which high resolution is not required and in which rather large track density can be tolerated.

XI. INFILTRATION OF ROCK CORES (W. R. Daniels, J. L. Thompson, S. Maestas)

A. Sorptive Studies

Several experiments involving solutions of radionuclides pumped through solid rock cores were performed. An apparatus similar to the equipment used in FY-78 for permeability measurements was constructed for use as a high-pressure column apparatus. This may be somewhat of a misnomer because the net difference between the confining pressure and the driving pressure (which equals the effective pore pressure) is normally in the 50- to 100-psi range. The equipment design is based on that of Brace *et al.*[12] as modified by Potter[13] and is shown schematically in Fig. 4. The right circular cylindrical core sample 15.9 mm high and 25.4 mm in diameter is placed in a

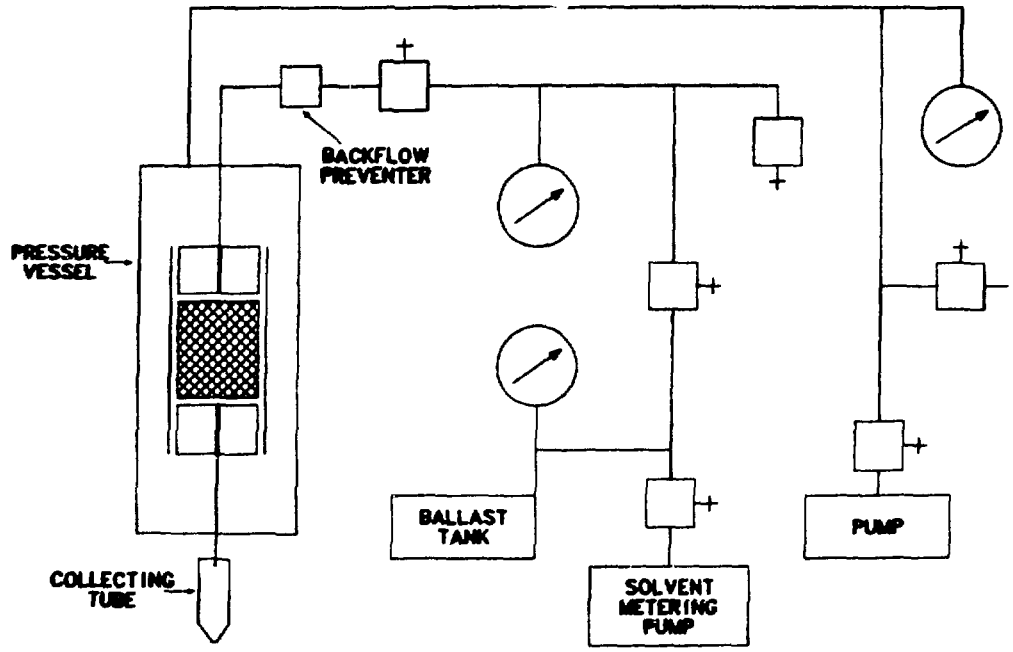

Fig. 4. Schematic of the High-pressure Column Apparatus.

Teflon sleeve and a porous disk of pressed stainless steel fiber is placed on each end of the sample. Steel cylinders of the same diameter as the sample, with pressure lines attached, are then inserted into the ends of the Teflon cylinder and the assembly is placed in a pressure vessel, which then is pressurized by a miniaturized, air-driven, hydraulic pump (Haskel, MCP-88). The stainless steel capillary tubing leading to the collecting tube has a 0.048-cm internal diameter. The delivery pressure is supplied by a metering pump (Altex, model 100A) capable of operation either as a constant-flow metering pump or as a constant-pressure source up to 10^4 psi. It has a minimum metered flow rate of 0.01 mℓ/m and is pressure limiting within the operating range without shut-off. Currently all tubing is stainless steel rated at 60 000 psi. Water was forced through the core at a controlled rate by a "driving" pressure significantly lower than the confining pressure. After the core had been flushed with the appropriate type of groundwater (filtered through 0.4- and 0.05-μm filters), the core was removed, and a small volume of high specific activity solution was placed on the top face. The core was again placed in the pressure assembly, and the rate of transport of the radioactive material through the core was determined by monitoring the activity in the effluent water.

1. ^{233}U in JA-26 Tuff. Two experiments were conducted with ^{233}U in the JA26 tuff cores from the Jackass Flats area of the NTS. These experiments were undertaken to allow development of techniques for handling the rock and preparing autoradiograms, rather than to yield much information on sorption characteristics of the rock. After placing the ^{233}U solution on the core and reassembling the pressure apparatus, water was pumped through the core only until appreciable amounts of activity appeared in the effluent. In the first experiment, using mixed isotopes of uranium, 4.8 mℓ of effluent passed through the core. In the second measurement, using isotopically pure ^{233}U, 13.4 mℓ of effluent passed through the column. The pumping rates were 0.3 to 0.7 mℓ/h. The rock cores were then sliced perpendicular to the direction of water flow using a small rock saw (Isomet, model 11-1180).

Several observations were obtained from these two experiments: The ^{233}U activity, which was placed at the center of the top faces of the tuff cores, was found to be spread laterally so that at a depth of about 1 mm there were no obvious concentration gradients across the diameter of the core. A substantial fraction of the activity was still on the top surface when some of the ^{233}U had passed completely through the core.

The stainless steel frits in contact with the top and bottom surfaces of the core showed some activity, though the amount relative to the total activity was small (see, however, the ^{233}U on granite experiments described below).

The surface activity on the rock cross-sections was measured using emulsions in one of two ways. In the first technique, a microscope slide was coated with Kodak NTB-2 or NTB-3 liquid emulsion, dried, placed against the rock for an appropriate time (until about 10^6 to 10^7 disintegrations had occurred), and developed using standard procedures. This yielded a transparent slide with the alpha tracks readily visible. However, it was difficult to correlate the tracks with their points of origin on the rock with a certainty of better than a few mm. Even with the use of a jig constructed to align the rock core and microscope slide, it was not possible to improve the registration significantly. A second technique involved coating the emulsion directly on the rock, then exposing and developing it while in place. To insure good adhension of the emulsion, an undercoating of parlodion and gelatin had to be applied. The liquid emulsions worked better than the strippable emulsion (Kodak AR.10) for this application. With the emulsion developed in place, registry with the underlying surface was no problem, but viewing the tracks

was difficult against the opaque background. The tracks could be illuminated with reflected, polarized light, but the underlying minerals could not be seen well. Thus, neither emulsion technique proved to be very useful for identifying specific sorption sites by mineral composition.

It proved to be impractical to slice the tuff cross-sections thinner than about 1.2 mm, as the saw tended to dislodge grains at lesser thicknesses. It was necessary to cool and lubricate the saw blade with a liquid which would not dissolve the uranium sorbed on the rock. Benzene was found to be satisfactory for this purpose.

2. ^{85}Sr in Climax Stock Granite. About 2 x 10^5 cpm of ^{85}Sr in 50 mℓ of solution was placed on the top face of a Climax Stock granite core on February 15, 1979, and filtered synthetic granite groundwater was pumped through the core until July 5, 1979 at an average rate of 0.17 mℓ/d. During the first few days the effluent had a specific activity of about 10^3 cpm/mℓ, and then it fell to about 10^2 cpm/mℓ and was more or less constant (allowing for the decay of ^{85}Sr) until the elution was stopped. The core had what appeared to be a crack running lengthwise through it. Attempts were made using a NaI(Tl) scintillation detector and collimated lead shields to measure enhanced radiation levels in the region of the crack. These efforts were not successful and showed only that the top of the core still contained more activity than other regions. It was found that ^{85}Sr could be detected with a proportional counter and with emulsions, probably because of Auger electron emission initiated by the electron capture decay. Kodak NTB-3 emulsions were used to determine the ^{85}Sr on the surfaces of several crosssectional slices of this core. No pattern of high concentrations in the vicinity of the "crack" or elsewhere could be found. The tracks produced in the emulsion were generally dots and were rather difficult to identify unless they were present in high concentrations. The granite could be cut in very thin slices ($\leq$ 0.5 mm), and even slices several mm thick were translucent. The distribution of activity through the core as measured with the NaI(Tl) detector is shown in Fig. 5. It appeared that this activity was distributed through the length of the core with a linear concentration gradient.

3. ^{233}U in Climax Stock Granite. Climax granite core "2d-3" was placed in the pressure apparatus and flushed with filtered synthetic granite water (about 0.7 mℓ) at a pumping pressure of 550 psi and confining pressure of

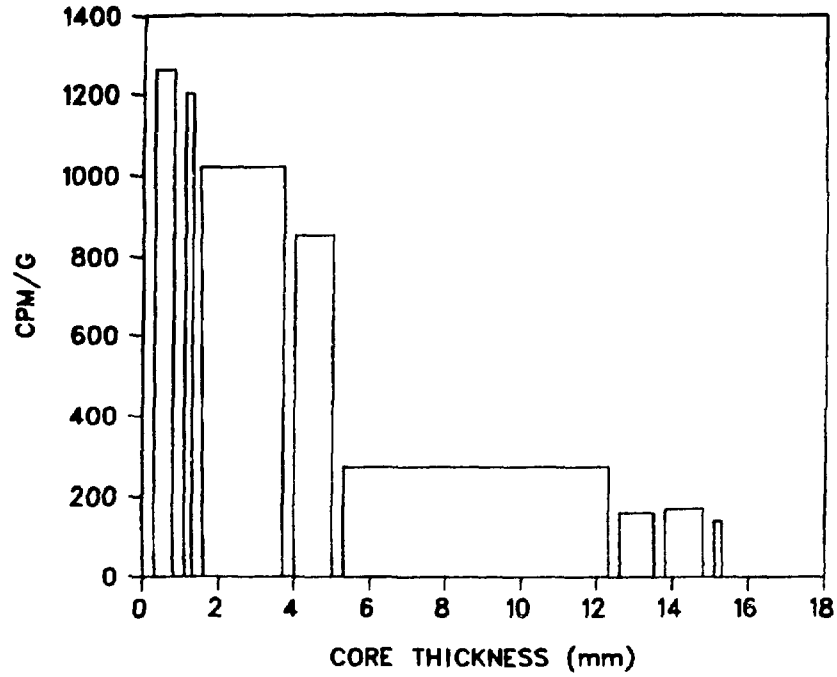

Fig. 5. Strontium Distribution in a Climax Stock Granite Core.

1000 psi. Then about 75 mℓ of isotopically pure ^{233}U solution containing about 7.6 μg of uranium and yielding nearly 10^8 disintegrations/m was applied to the top of the core and pumping was resumed at the same pressures previously used. The flow rate varied from 0.1 to 0.3 mℓ/d. About 60% of the activity was eluted in the first 0.5 mℓ, and about 35% in the next 0.6 mℓ. This effluent was concentrated to about 200 mℓ and reintroduced on the top of the core. Pumping was continued as before until about 0.2 mℓ of effluent was collected and the specific activity began to increase rapidly. The core was removed, several slices were taken from the top and bottom ends, and the surface activity on the slices was measured with both a proportional counter and with emulsions. Both the top and bottom surfaces of the core showed a high level of activity, as did the stainless steel frits in contact with them. Also, the sides of the core cylinder yielded a high count rate, indicating that some of the radioactive solution had penetrated the sleeve-core boundary. This activity

appeared to be evenly distributed over the surface. The activity in the frits was slowly released by rinsing with a large volume (about 170 mℓ) of water. Some radioactive contamination of the exit tube of the pressure apparatus was observed, though at a much lower activity level than the contamination of the frits.

The emulsions revealed that flow through the core was by means of a very few small cracks, with the majority of the rock mass not coming in contact with the radioactive solution. Some sorption by minerals along the path of flow was indicated (but not yet confirmed by petrographic examination). An apparent radiocolloid was detected at a site along a crack several mm into the core. These observations were documented on 35 mm color film.

A second experiment was performed as an attempt to measure an R_d value for a solid granite core which could be compared with R_d values determined on crushed granite. No activity peak in the eluate was observed, and there is considerably doubt that all of the eluent actually ran through the core. Climax core C-79-9a-1 was mounted in the pressure apparatus and about 0.15 mℓ of synthetic granite water was flushed through the core at 540 psi. The core was removed from the pressure apparatus and about 50 mℓ of ^{233}U solution was placed on the top surface. This solution had been prepared by taking to dryness 45 mℓ of isotopically pure ^{233}U solution containing about 47 μg of uranium (about 10^7 disintegrations per m), then redissolving it in filtered synthetic granite water. A 1-mm thick disc of the granite was placed on top of the core to provide a barrier between the radioactive material and the metal endpiece. (Unfortunately, some of the ^{233}U solution squeezed up around the edges of the disc.) This material was dried in air, the pressure apparatus was reassembled, checked for leaks, and pumping was initiated at the previous setting of 540 psi. No flow was observed until the pumping pressure was raised to 850 psi. The eluate was collected dropwise using a fraction collector (ISCO Model 1200) contained in a plastic bag with a water-saturated atmosphere. Without this container, it was found that the drops would evaporate rather than fall. The drop rate was about 5 drops per day for several days, then it increased to about 12 drops per day. The drops were collected in small glass cups, dried, and the activity measured with a methane flow proportional counter. Nearly 1.5 mℓ of effluent was collected, and the dropwise distribution of activity is shown in Fig. 6. Although there are a number of fluctuations in the activity level for individual drops, these may

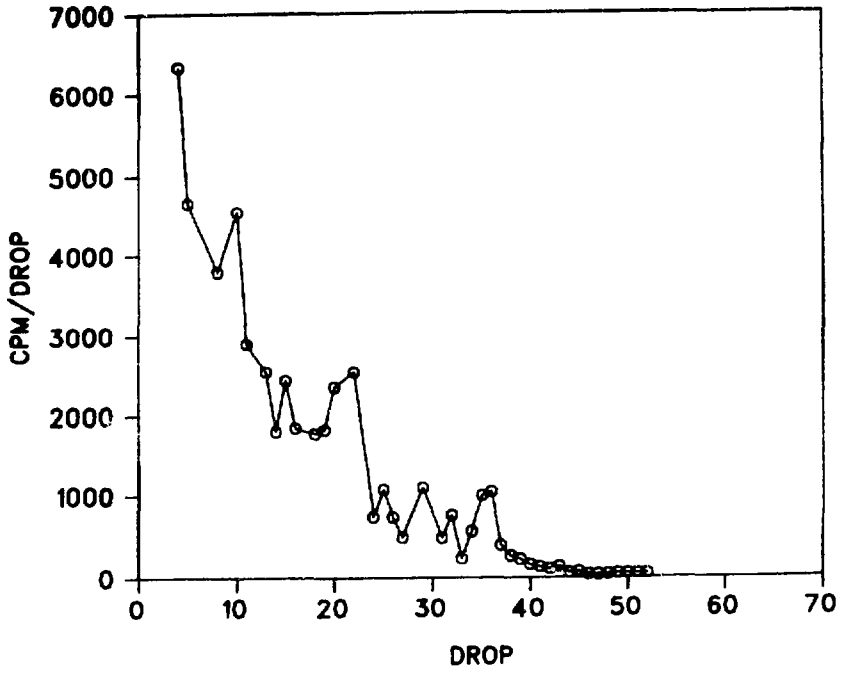

Fig. 6. ^{233}U from a Climax Stock Granite Core.

be due to uncertainties in the counting procedure used. In any event, there is no well-defined activity peak. The core was examined for residual activity, and it was found that the top, bottom, and sides had high levels of activity (about 10^4 counts per m). At a depth of about 1 mm inside from either the top or bottom, the activity level was reduced by a factor of about 30. The activity was spread more or less uniformly over the exterior surfaces but seemed to be confined to small crack systems in the interior. It was not possible to tell whether activity found in the interior had entered through the top face of the core or from the side. It may be that the confining pressure of 1000 psi was not sufficient to keep the eluting water (at 850 psi) from penetrating the Teflon-granite interface. Probably more than half of the activity initially introduced remained on the exterior surfaces of the core when the experiment was ended.

Since penetration of solutions into small crack systems in granite cores had been observed, it was decided to attempt to study flow through a large crack known to extend through the core. An intact core, C-79-16a-3, was

selected because it had an apparent fracture plane extending the length of the core. A sharp rap with a hammer and chisel caused it to split cleanly along the old fracture. The inner surfaces of the fracture contained a number of small gold-colored particles (some of which fell out when the core split) which X-ray analysis showed to be iron pyrite. The core sections were recombined, inserted in a Teflon sleeve, and placed in the pressure apparatus as usual. The confining pressure was increased to the point (5000 psi) where water would not flow through the core under the force of gravity. About 3 mℓ of filtered synthetic granite water was then flushed through the core at a rate of 0.3 mℓ/h. At this point the Teflon sleeve ruptured along the bottom edge of the core where a chip was missing (not near the crack). The core was placed in a new Teflon sleeve, the chip void filled in with epoxy cement, a 1 mm granite disc inserted as a top endpiece, and about 4 mℓ more of granite water flushed through the core, again with a confining pressure of 5000 psi. A ^{233}U solution of the same composition as that used in the two previous experiments was again employed. About 50 μℓ was dried in the center of the top of the core, a distance of several mm from the crack. After reassembly in the pressure apparatus and pressurization to 5000 psi, pumping of water through the core was resumed. Activity was detected in the first 0.5 mℓ of effluent, so the flow was stopped and the core held in this condition for 3 days. Then the core was removed and slices (about 2 to 3 mm thick) were sawed from each end, with the Teflon sleeve holding the fracture pieces together. The slices, as well as the fracture surface of the smaller fragment, were coated with NTB-2 emulsion. The larger fragment was sawed so as to remove the fracture surface with about 2 mm of supporting rock, and it too was coated with emulsion. The top surface of the core showed regions of high track density in the middle and along one segment of the crack. At a depth of several mm tracks were found only along the large crack and along a small crack branching from the large crack and running almost the width of the core. The bottom surface of the core had activity distributed fairly uniformly over it. The interior surfaces of the large crack were difficult to observe with the microscope because of their roughness, but alpha tracks were found spread over most of this surface. There were several regions of very dense tracks on this surface. Identification of the minerals on the surface which appear to sorb ^{233}U strongly is in progress.

B. Porosity Measurements

The system described above for studying high-pressure columns was utilized for some preliminary measurements of connected pore space (i.e., free column volume or effective porosity) of tuff and granite cores. The volume of tritiated water required to fill the available pore space of a rock core 2.54 cm in diameter and 1.6 cm thick was measured by liquid scintillation counting. By comparison with the total core volume, the fraction of free space was determined. Three measurements on a tuff core from well J-13 at the NTS, JA-35, Core #3, gave values of 0.233, 0.247, and 0.239 for an average of 0.240 with a spread of ±3%. Measurements on two Climax granite cores gave values of 0.0015 for Core #6A and 0.0050 and 0.0081 for two measurements on Core #2A.

The tritiated water method appears to give satisfactory results for the available pore space in tuff and granite. Limited data suggest that measurement of the low values for granite is less reproducible than for the higher tuff values.

XII. MATERIALS CHARACTERIZATION (R. D. Aguilar, B. P. Bayhurst, and G. E. Bentley)

In order to be able to use the data bank of sorption information for the estimation of the migration behavior of a nuclide in any geologic material and type of water, one must gather the appropriate supporting information for the materials used. A method for rapidly analyzing the groundwaters for the major and minor elements was developed. Similarly, techniques were developed for determination of trace constituents of solids and solutions. Final determinations of surface areas by the ethylene glycol technique were also completed.

A. X-ray Fluorescence Analyses

Our in-house capability for chemical analysis via tube-excited X-ray fluorescence spectrometry has been used for samples utilized in previous studies (see above; Refs. 5, 6, 14). This technique is relatively simple and gives results for most major and semi-major elements. In our analysis system, either a tungsten or molybenum target can be chosen as the target for X-ray

production by high-voltage electrons. The X-rays from the sample are detected with a Si(Li) detector which is sensitive down to the 1-keV line of sodium. The linear data from the detector is stored in a multichannel analyzer from where it is read into a small computer (PDP-11/04) at the termination of a run. Data reduction programs to perform the analytical calculations have been written locally (T. Bornhorst) for both qualitative and quantitative analysis. The system is calibrated using samples having compositions similar to the unknowns. The results are given in Tables XXXVI-XXXIX. It is interesting that the total iron concentration is these materials does not change with the fraction used. One explanation for the observation[2] that Tc(VII) sorbed on the finer particle size material was that iron was concentrated in these fractions. This could still be the case if the fine fractions were enriched in the non-Fe(III) materials. This could happen if a clay fraction had some preference for Fe(II) and this clay was concentrated in the finer sieve fraction.

The observation that the total iron (Table XXXIX) concentration in the <75-μm fractions prepared by grinding in an agate system (see earlier) are not appreciably different than those prepared by grinding in a pulverizer is encouraging. This means that the iron introduced during the grinding operation was not significant and that the earlier measurements[1,2] were not perturbed by the addition of iron.

B. Ethylene Glycol Surface Area Measurements

Many sorption ratios are expected to scale with surface area. Table XL summarizes the measurements performed to date for all materials studied. The equilibrium glycol procedure[15-17] was used. Briefly, this procedure consists of wetting a dried and weighed sample of calcium-saturated material with ethylene glycol. This is then followed by equilibration in an evacuated desiccator containing an anhydrous calcium chloride-ethylene glycol solvate. The equilibration is repeated until the weights become constant, presumably indicating that only a monolayer remains.

Generally, the granites or granite-type material (Jackass Flats tuff JA-18) have low surface areas relative to argillites and tuff. This is presumably due to the high clay/zeolite content in the latter materials, which have considerable internal surface area. The surface areas do not scale

TABLE XXXVI

CS-5 GRANITE X-RAY FLUORESCENCE ANALYSES

Element	Fraction (μm)[a]			
	106-150	250-355	500-850[b]	
K_2O	4.63	4.23	4.67	4.63
CaO	2.98	3.20	3.33	3.32
TiO_2	0.50	0.40	0.44	0.43
Fe_2O_3	3.72	2.96	2.56	2.56
	mg/g			
V	58(9)	51(8)	46(7)	48(8)
Cr	19(11)	14(9)	11(7)	11(6)
Mn	495(7)	379(6)	403(6)	378(6)
Ni	16(5)	10(4)	10(4)	9(3)
Cu	31(6)	24(5)	30(6)	27(6)
Zn	78(9)	75(9)	74(9)	73(9)
Ga	<25	<25	<25	<25
Ge	1.29(0.06)	1.27(0.06)	1.28(0.06)	1.27(0.06)
As	<100	<100	<100	<100
Se	0.05(0.02)	0.04(0.02)	0.05(0.02)	0.04(0.02)
Pb	16(8)	16(8)	<16	18(9)
Rb	193(6)	169(5)	179(6)	181(6)
Sr	564(8)	626(9)	660(9)	657(9)
Y	25(9)	22(8)	24(9)	24(8)
Zr	196(20)	186(19)	178(18)	177(18)
Ba	1 181(118)	1 083(108)	1 103(110)	1 112(111)

[a]The numbers in parentheses are the errors given in μg/g. If no error is listed then it is less than 0.1%.

[b]Duplicate analyses are reported.

TABLE XXXVII

CS-7 GRANITE X-RAY FLUORESCENCE ANALYSES

Element	Fraction (μm)[a]				
	106-150[b]		250-355[b]		500-850
	Percent				
K_2O	3.46	3.42	3.25	3.25	3.93
CaO	3.23	3.20	3.29	3.29	3.14
TiO_2	0.35	0.35	0.29	0.29	0.43
Fe_2O_3	2.82	2.82	2.33	2.33	2.88
	μg/g				
V	46(7)	45(7)	42(7)	42(7)	45(7)
Cr	18(11)	19(11)	14(8)	13(8)	13(8)
Mn	358(5)	347(5)	401(6)	369(6)	659(10)
Ni	11(4)	12(4)	10(3)	9(3)	9(3)
Cu	18(4)	21(4)	19(4)	16(3)	18(4)
Zn	76(9)	76(9)	75(9)	75(9)	78(9)
Ga	<25	<25	<25	<25	<25
Ge	1.29(0.06)	1.30(0.06)	1.29(0.06)	1.28(0.06)	1.28(0.06)
As	<100	<100	<100	<100	<100
Se	0.04(0.02)	0.05(0.02)	0.04(0.02)	0.05(0.02)	0.04(0.02)
Pb	<16	19(9)	16	16	16
Rb	126(4)	124(4)	124(4)	122(4)	167(5)
Sr	547(8)	543(8)	585(8)	587(8)	601(8)
Y	24(8)	24(8)	20(7)	20(7)	23(8)
Zr	184(18)	184(18)	179(18)	180(18)	188(19)
Ba	690(69)	664(66)	770(77)	735(74)	860(86)

[a]The numbers in parentheses are the errors given in μg/g. If no error is present then it is less than 0.1%.

[b]Duplicate analyses are reported.

TABLE XXXVIII

ARGILLITE X-RAY FLUORESCENCE ANALYSES

Element	CN-1 Fraction (μm) 150-180	CN-1 Fraction (μm) 355-500	CN-2 Fraction (μm) 150-180	CN-2 Fraction (μm) 355-500
	Percent			
K_2O	1.11	1.12	1.79	1.78
CaO	0.99	0.94	0.85	0.84
TiO_2	1.31	1.30	1.20	1.18
Fe_2O_3	7.09	6.76	5.94	5.90
	μg/g			
V	66(11)	58(9)	52(8)	51(8)
Cr	51(31)	47(28)	44(27)	44(27)
Mn	1 236(19)	1 153(17)	507(8)	504(8)
Ni	29(10)	30(11)	29(10)	29(10)
Cu	45(9)	45(9)	47(9)	42(8)
Zn	94(11)	89(11)	96(12)	93(11)
Ga	<25	<25	<25	<25
Ge	1.33(0.06)	1.31(0.06)	1.26(0.06)	1.27(0.06)
As	<100	<100	<100	<100
Se	0.06(0.03)	0.05(0.03)	0.04(0.02)	0.04(0.02)
Pb	72(7)	60(6)	44(22)	51(5)
Rb	57(2)	59(2)	103(6)	124(4)
Sr	153(2)	154(2)	224(3)	222(3)
Y	36(12)	38(13)	35(12)	35(12)
Zr	272(27)	294(29)	176(18)	176(18)
Ba	<25	32(3)	<25	<25

[a]The numbers in parentheses are the errors given in μg/g. If no error is quoted then it is less than 0.1%.

TABLE XXXIX

X-RAY FLUORESCENCE ANALYSES FOR <75-μm FRACTIONS

Element	Sample[a] CN-3	CS-7
	Percent	
K_2O	1.58	3.55
CaO	0.60	3.55
TiO_2	1.39	0.38
Fe_2O_3	6.16	2.32
	μg/g	
V	30(5)	42(7)
Cr	40(24)	13(8)
Mn	399(6)	469(7)
Ni	31(11)	10(3)
Cu	77(15)	29(6)
Zn	85(10)	74(9)
Ga	<25	<25
Ge	1.30(0.06)	1.31(0.06)
As	<100	<100
Se	0.05(0.02)	0.05(0.02)
Pb	55(6)	23(12)
Rb	91(3)	141(4)
Sr	186(3)	589(8)
Y	35(12)	23(8)
Zr	201(20)	206(21)
Ba	180(18)	769(77)

[a]The numbers in parentheses are the errors given in μg/g. If no error is quoted then it is less than 0.1%.

TABLE XL

SURFACE AREA MEASUREMENTS

Identification	Core	Fraction (μm)	Treatment	Surface Area(m^2/g)
Climax granite	5	106-150	W	8
		250-355	W	4
		500-800	W	7
	7	106-150	W	7,11
		250-355	W	3
		500-850	W	3
Westerly granite			U	<1
Eleana argillite	1	106-150	W	50,47
		250-355	W	63
		355-500	W	45,49
		106-150	U	51,48
		355-500	U	64,64
	2	<75	U	75
	3	<75	U	99
	4	<75	U	92
Argillacious shale NY			U	46
Jackass Flats tuff	18	106-150	W	31
		355-500	W	46
	32	106-150	W	8,8
		355-500	W	9
	37	106-150	W	94,115
Umtanum basalt		355-500	U	3
Oolitic limestone			U	2

[a]W implies that the samples were briefly washed with distilled water to remove dust; U implies that the sample was not washed with distilled water.

strongly with particle size except perhaps for the granites. This is consistent with the observation[1-3] that the amounts of the various minerals in the sieve fractions are relatively constant.

C. Emission Spectrometry

The Spectrometrics Inc. twenty-channel direct-current plasma-source emission spectrometer allows the simultaneous determination, in a liquid sample, of up to twenty preselected elements. The suite of elements to be determined is selected by inserting a cassette into the instrument so that only certain atomic emission wavelengths are permitted to impinge upon the instrument's elements.

Four multielement cassettes are currently operational,. The cassettes are set up for the following elements: 1) Si, Al, Fe, Mg, Ca, K, Ti, Mn, Au, Ag, Ba, Rb, Sr, Li, V, Ga, and Sn; 2) Li, K, Na, Mg, Al, Rb, Mo, Ti, V, Sc, Bi, Pb, Tl, Hg, Cd, Sb, W, and Ga; 3) Li, K, Na, Mg, Al, Si, B, Be, Se, As, Ge, Ga, Zn, Cu, Ni, Co, Sr, and In; and 4) La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Tb, Ho, Er, Tm, Yb, Lu, Hf, Ta, Y, and Ga. If it is desired to determine an element not included in one of the multielement cassettes, it is possible to do so by using a variable single-element cassette.

Five water samples which had been analyzed[1-3] by the USGS by atomic absorption (AA) spectrophometry were subjected to analysis using the plasma emission spectrometer (ES). The results obtained by the two different methods are given in Table XLI. The sample identification numbers are those assigned to a Climax Stock (W-10) and Eleana argillite (W-5) ambient temperature pretreated waters, ambient temperature pretreated waters for JA-32 (W-14) and JA-37 (W-16) tuffs, respectively, and a 70°C pretreated water for JA-37 (W-17) tuff.

Regression calculations were performed for each set of analyses for each of the five samples. Perfect agreement between the two sets (AA and ES) is indicated by a correlation coefficient and slope of the regression line equal to one and an intercept of the regression line equal to zero. The values obtained are given in Table XLII.

It would appear that the USGS uses charge balance between major cations and anions as a primary quality control mechanism for the analysis of water samples. The ions used are Ca, Mg, K, and Na for the cations, and HCO_3, CO_3, Cl, F, and SO_4 as the anions. The milliequivalents per liter of each species

TABLE XLI

COMPARISON OF ATOMIC ABSORPTION AND EMISSION SPECTROSCOPY ANALYSES

	Sample[a]									
	W-5		W-10		W-14		W-16		W-17	
	ES	AA	ES	AA	ES	AA	ES	AA	ES	AA
Mg	2.1	2.0	2.1	2.0	0.92	0.8	0.91	0.9	0.40	0.30
SiO_2	18	22	61	58	51	39	33	27	45	39
Ca	10.1	11	12.8	13	6.2	7.2	7.7	8.9	4.4	5.2
Fe	0.2	0.1	0.06	0	0.6	0.5	0.05	0.04	0.04	0.02
Sr		0.03	0.04	0.06[b]	0.05	0.05	0.1	0.1	0.06	0.07
				0.04						
Ba		0.30	0.04	0.2	0.12	0.3	0.12	0.08	0.08	0.20
Li	0.06	0.02	0.05	0.05	0.04	0.06	0.03	0.06	0.03	0.05
K	3.6	2.9	4.6	4.7	5.6	6.0	8.4	8.6	5.1	5.6
Na	8.9	7.7	41	47	50	60	52	65	53	64

[a]All values are in ppm.

[b]Two values were reported by the USGS.

TABLE XLII

REGRESSION DATA AND EQUALITY CONTROL DATA

	W-5	W-10	W-14	W-16	W-17
R[a]	0.990	0.994	0.967	0.981	0.984
Slope	1.196	1.004	0.974	1.142	1.068
Intercept	-0.808	0.321	0.259	-0.657	-0.112
Σ meq$^+$	0.93	2.71	2.70	2.89	2.68
Σ meq$^-$	1.09	2.88	2.88	3.35	3.05
$(\Sigma+ + \Sigma-)/2$	1.01	2.80	2.79	3.12	2.86
% Diff.	7.8	3.0	3.2	7.4	6.6

[a]Correlation coefficient.

is calculated, and the anions and cations are summed separately. An average of the sums is taken and a percent difference is calculated by dividing the deviation from the average by the average and multiplying by 100. This was done for each of the five water samples compared in this study, using the USGS values for the anions, and the ES values for the cation values. These are also shown in Table XLII. A perfect analysis would have a percent difference equal to 0.

From these data, one may conclude that the emission spectroscopy technique gives results for these waters that are quite consistent with those achieved by the much more laborious atomic absorption method of analysis. Of the nine elements listed only barium was significantly different by the two methods. It may be speculated that this is due to a change in the water, as they were not preserved in any manner, or to an unknown deficiency in one or both techniques.

XIII. REPORTS AND PUBLICATIONS

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3. J. L. Thompson and K. Wolfsberg, "Applicability of Microautoradiography to Sorption Studies," Los Alamos Scientific Laboratory report LA-7609-MS (1979).

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XV. VISITORS

1. Prof. Ivars Neretnieks, Royal Institute of Technology, Stockholm, Sweden (University of California, Berkeley); Feb. 6-7, 1979.

2. Prof. Jan Rydberg, Chalmers Institute of Technology, Göteborg, Sweden; March 30, 1979.

3. W. R. Davison and D. Hanson, General Atomic Co., San Diego, CA; May 1, 1979.

4. T. T. Vandergraaf, Whiteshell Nuclear Research Establishment, AECL, Pinawa, Manitoba, Canada; May 14-15, 1979.

5. P. J. Shirvington, Environmental and Public Health Unit, Australian Atomic Energy Commission, Cliffbrook, Coogee, NSW, Australia; July 16-18, 1979.

6. B. M. Allard, Chalmers Institute of Technology, Göteborg, Sweden; August 16-17, 1979.

ACKNOWLEDGMENTS

The following Los Alamos Scientific Laboratory personnel are acknowledged for the efforts mentioned: P. A. Elder and M. E. Lark (sample counting and gamma-spectral analyses), P. Bussolini (quality assurance), and L. M. Mitchell (typing of drafts and final manuscript).

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