Laboratory Studies of Radionuclide Distributions Between Selected Groundwaters and Geologic Media

October 1, 1979—September 30, 1980

Compiled by

W. R. Daniels

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LABORATORY STUDIES OF RADIONUCLIDE DISTRIBUTIONS
BETWEEN SELECTED GROUNDWATERS AND GEOLOGIC MEDIA

Annual Technical Progress Report for
October 1, 1979 through September 30, 1980

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ABSTRACT

This annual report presents the Los Alamos Scientific Laboratory contribution to the Waste/Rock Interactions Technology program, Tasks 3 and 4, for FY-1980.

SUMMARY

During FY-1980, Los Alamos Scientific Laboratory contributions to the Waste/Rock Interactions Technology program were primarily in the areas of migration-rate studies using crushed rock, whole core, and fractured core columns; parametric studies of variables which may influence radionuclide sorption-desorption behavior; and initial studies of actinide chemistry in near-neutral solutions and Eh control.

Batch experiments in both air and a controlled atmosphere (nitrogen, ≤ 0.2 ppm oxygen, ≤ 20 ppm carbon dioxide) for the sorption of several radionuclides on granite and argillite were completed. These data also provided information on the effects of other parameters, such as particle size and contact time. All nine elements studied had different sorption ratios for argillite when measured under the controlled atmosphere than when measured in air, except possibly for americium where any effect was smaller than the standard deviations. Technetium sorption ratios were higher for argillite, granite, and tuff when measured under controlled-atmosphere conditions. Interestingly, sorption of plutonium and americium on granite is much lower under the controlled-atmosphere conditions, while sorption of plutonium on tuff is actually higher under the controlled atmosphere. As expected, strontium, cesium, and barium are least affected by the presence or absence of oxygen and carbon dioxide. Batch studies of the effects of varying the solution-to-solid ratio and the element concentration showed that there is considerable variation in behavior depending upon the element involved. Other batch experiments indicate a small but measurable sorption of iodine on argillite with sorption ratios between 2 and 6 ml/g.

Columns of crushed rock and solid and cracked cores were used to study the migration of radionuclides through such materials. In general, sorption ratios measured by batch techniques are 2 to 3 times greater than those for columns; however, a wide

variation in behavior was observed, depending upon the element and the mineralogy. Results indicate a need to study the mechanisms causing retardation before an understanding of the relationship between behavior in a dynamic column experiment in the laboratory (and, ultimately, behavior in the field) and the many available batch sorption data can be achieved. Work has begun on a system wherein traced groundwater is circulated through a crushed rock column; this should provide a link between the usual, single-pass, crushed rock columns and the batch experiments.

Materials characterization has continued, and techniques for the determination of Fe(II) in silicate rocks and groundwater have been made operational.

Work on the fundamental solution chemistry of the actinides has been started. Thus far, efforts have been confined to preliminary considerations of the problems involved in developing an understanding of the precipitation and dissolution behavior of actinide compounds under environmental conditions. Attempts were made to calculate solubility as a function of Eh and pH using the appropriate thermodynamic data; results have been presented in terms of "contour maps" showing lines of constant solubility as a function of Eh and pH. Investigations of the measurement and control of the redox potential of rock-groundwater systems have been started. For the latter, the use of both Eh buffers (redox couples) and a potentiostat is being investigated.

I. INTRODUCTION

This report covers the technical activities on Waste/Rock Interactions Technology (WRIT) contracts B-A2377-AK and 78996-AK to the Los Alamos Scientific Laboratory for FY-1980. Based on their applicability to the WRIT project, some results on tuff have been included from research supported by the Nevada Nuclear Waste Storage Investigations program and the Radionuclide Migration project, both managed by the Nevada Operations Office of the Department of Energy.

II. PROJECT OBJECTIVE

The Los Alamos Scientific Laboratory (LASL) contribution to the Waste-Rock Interactions Technology project (formerly Waste Isolation Safety Assessment Program) in FY-1980 had several principal objectives. The first was to perform migration rate studies using three different types of columns: 1) crushed rock, 2) whole cores, and 3) cores containing natural fractures. Second, the LASL batch sorption methodology¹⁻³ 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 technique⁴ currently utilized at LASL 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 (non-pulverized) systems. Finally, initial studies of the chemistry of several radionuclides in the pH $\cong$ 8 solutions that frequently occur in natural environments were performed.

Most of the sorption 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. Many detailed analytical and mineralogical analyses of all materials were made.

III. PROGRESS REPORTED PREVIOUSLY

The results obtained by the LASL program since its beginning in September, 1977, have been summarized in several reports.¹⁻¹² Proper methods for performing batch sorption measurements were developed. These methods were applied to studies of the sorption behavior of various radionuclides on alluvium, granite, argillite, and tuff. The effects of particle size, surface area, contact time,

temperature, water composition, and sampling location were investigated for strontium, technetium(VII), cesium, barium, cerium(III), europium(III), uranium(VI), plutonium, and americium. Studies of the sorption of strontium, cesium, barium, cerium, europium, technetium, and uranium(VI) on granite and argillite were made under controlled-atmosphere (nitrogen, ≤ 0.2 ppm oxygen, ≤ 20 ppm carbon dioxide) conditions and the results were compared with earlier measurements made under atmospheric conditions. Several sorption isotherms were measured.

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 argillite² and tuff¹² were measured.

Measurements of migration rates in crushed granite, argillite, and tuff columns were made and compared with batch results. Infiltration experiments involving the forced injection of activity into intact and fractured cores were also performed.

A microautoradiographic technique was used to identify the specific sorption sites for actinides on ground and polished surfaces of petrographic thin-sections. A modification of this technique was used to assess the amount of "aggregation" of actinides that occurred in some of the sorption studies.

Additional physical and chemical characterizations of the materials used in these studies were made, and new analytical techniques were developed.

IV. GEOLOGIC MEDIA - NUCLIDE INTERACTION STUDIES IN THE REPORTING PERIOD

Much of the activity during FY-1980 involved those sorption studies needed to extend the current sorption data base, to continue studies of sorption isotherms, to continue chemical analysis and characterization techniques, to continue studies using the microautoradiographic technique, and to continue measurements of migration rates in crushed, fractured, and porous materials.

A. Sorption of Plutonium and Americium - Atmospheric and Controlled-Atmosphere Conditions (W. R. Daniels, F. O. Lawrence, P. Q. Oliver, and S. Maestas)

1. Experimental. The measurement of the sorptive behavior of plutonium and americium on granite and argillite involved geologic materials and groundwaters described earlier.^{1,2} The equipment utilized to achieve controlled-

atmosphere conditions (nitrogen, ≤ 0.2 ppm oxygen, ≤ 20 ppm carbon dioxide), the calculational methods, and, in general, the experimental techniques have also been described.⁸ For the current studies tracers were dried in air at room temperature. After dissolution of the tracers in the appropriate ground-water in the desired atmosphere, the traced feed solutions were centrifuged and passed through 0.4- and then 0.05- μm Nuclepore filters. All contacts were at 32°C for controlled-atmosphere and 22°C for atmospheric experiments. Contact times for sorption were 3, 6, and 12 weeks with the corresponding desorptions being 12, 9, and 3 weeks. The final separation of phases after contact was accomplished by three consecutive centrifugings at 12 000 rpm (28 000 g) for 1, 1, and 2 hours, respectively. Transfers were performed by pipetting. The final centrifuged solutions were aliquoted for counting and then passed through 0.05- μm Nuclepore filters. They were then aliquoted again for comparison with the unfiltered results.

2. Results and Conclusions. The results for the batch measurements of the sorptive behavior of ^{241}Am and ^{237}Pu under both atmospheric and controlled-atmosphere conditions are given in Tables I-V. The results, especially for ^{237}Pu , suffer from the low concentrations of tracer remaining in solution after contact. This is a consequence of the americium solubility limits in the original feed solutions, the small amount of ^{237}Pu available and its short half-life, and the generally large sorption ratios. In many cases, especially for ^{237}Pu , only R_d limits could be set. It was previously reported⁸ that the current centrifuging procedure gave plutonium, but not americium, solutions from which no additional tracer is removed by filtering. In general, these observations have been confirmed by additional measurements;¹³ however, some solutions which have extremely low concentrations of plutonium apparently lose plutonium when filtered (see Tables I and II). This effect could be due to removal of some minute amounts of solid phase remaining in the aqueous phase. As stated previously, if the results for unfiltered solutions are in error, it is probably in the conservative direction (i.e., R_d values too low) so data from these have been used to calculate the average sorption ratio values given in Table V. These data have been averaged over three contact times and two particle sizes.

The current results for normal atmospheric conditions tend to give somewhat higher R_d values for unfiltered solutions than those reported previously.^{1,8} This is reasonable because the improved phase-separation technique removes

TABLE I
²³⁷Pu SORPTION RATIOS, ATMOSPHERIC CONDITIONS^a

Medium	Core	Fraction (μm)	Approximate Pu Molarity ^b	Time(d)		R _d (mℓ/g)		pH		
				Sorption	Desorption	Unfilt	Filt	Initial	Final	
Granite	CS-7	<75	2.8 x 10 ⁻¹²	20.9		5 900	8 900	8.35	7.45	
					89.9	>9 000	>9 000	8.40	8.33	
				41.8		13 000	26 000	8.35	7.67	
					67.8	>10 000	>10 000	7.45	8.15	
		75-500		83.8		>15 000	>15 000	8.35	8.30	
					20.9	>11 000	>11 000	7.75	8.07	
				20.8		6 700	11 000	8.35	7.32	
					89.9	>9 000	>9 000	8.40	8.28	
				41.8		>28 000	>28 000	8.35	7.63	
					67.8	>10 000	>10 000	7.45	8.11	
				83.8		>15 000	>15 000	8.35	8.21	
					20.9	>11 000	>11 000	7.75	8.08	
Argillite	CN-3	<75	4.2 x 10 ⁻¹²	20.7		90 000	84 000	8.53	7.52	
					83.9	>26 000	>26 000	8.52	8.25	
				41.7		37 000	>71 000	8.53	7.56	
					62.9	>26 000	>26 000	8.48	8.36	
		75-500		82.7		>35 000	>35 000	8.53	7.68	
					21.7	>27 000	>27 000	7.85	8.43	
				20.7		32 000	59 000	8.53	7.55	
					83.9	>26 000	>26 000	8.52	8.40	
				41.7		21 000	39 000	8.53	7.73	
					62.9	>26 000	>26 000	8.48	8.41	
				82.7		>36 000	>36 000	8.53	8.77	
					21.7	26 000	>28 000	7.85	8.49	

^aMeasurements were made at ambient temperature (~22°C).

^bFeed solutions were filtered through 0.4- and 0.05-μm Nuclepore filters.

TABLE 11
 ^{237}Pu SORPTION RATIOS, CONTROLLED-ATMOSPHERE CONDITIONS^a

Medium	Core	Fraction (μm)	Approximate Pu Molarity ^b	Time (d)		R_d (mg/g)		pH	
				Sorption	Desorption	Unfilt	Filt	Initial	Final
Granite	CS-7	<75	1.1×10^{-13}	94.0		980	>2 300	9.00	8.48
				95.0		>2 000	>2 000	9.00	8.27
				100.0		655	830	9.00	8.88
			5.8×10^{-12}	21.7		34	35	9.53	9.12
					89.9	540	520	9.12	8.77
				42.7		150	180	9.53	9.19
					65.7	10 000	12 000	8.98	--
				83.7		190	240	9.53	8.88
					24.8	4 700	3 800	8.82	--
		75-500	1.1×10^{-13}	94.0		780	1 200	9.00	8.48
				100.0		540	1 050	9.00	8.90
				101.0		640	>1 700	9.00	9.03
			5.8×10^{-12}	21.7		22	22	9.53	9.06
					89.9	950	1 100	9.06	8.95
				42.7		110	120	9.53	9.21
					65.7	3 600	8 900	8.98	--
				83.7		220	280	9.53	8.93
					24.8	10 000	>16 000	8.82	--
Argillite	CN-3	<75	5.5×10^{-15}	94.0		>90	>90	8.75	8.16
				95.0		>50	>50	8.75	8.12
				100.0		>90	>90	8.75	8.44
			1.2×10^{-12}	26.7		>26 000	>26 000	8.56	8.68
					75.7	>8 000	>8 000	8.58	8.51
				41.7		>20 000	>20 000	8.56	8.20
					62.7	>7 100	>7 100	8.99	8.50
				82.7		8 100	9 100	8.56	8.99
					19.8	>8 000	>8 000	8.48	8.47
		75-500	5.5×10^{-15}	95.0		>60	>60	8.75	8.19
				101.0		>100	>100	8.75	8.35
				101.0		>100	>100	8.75	8.29
			1.2×10^{-12}	26.7		>21 000	>21 000	8.56	8.54
					75.7	>8 100	>8 100	8.58	8.52
				41.7		15 000	>21 000	8.56	8.19
					62.7	>7 400	>7 400	8.99	8.57
				82.7		>10 000	>10 000	8.56	8.77
					19.8	>8 300	>8 300	8.48	8.45

^aNitrogen, ≤ 0.2 ppm oxygen, ≤ 20 ppm carbon dioxide. Measurements were made at 32°C .

^bFeed solutions were filtered through 0.4- and 0.05- μm Nuclepore filters.

TABLE III
²⁴¹Am SORPTION RATOS, ATMOSPHERIC CONDITIONS^a

Medium	Core	Fraction (μ m)	Approximate Pu Molarity ^b	Time(d)		R _d (mL/g)		pH					
				Sorption	Desorption	Unfilt	Filt	Initial	Final				
Granite	CS-7	<75	8.3×10^{-8}	20.8		33 000	48 000	8.12	8.25				
					82.8	32 000	320 000	7.95	8.38				
				43.7		48 000	59 000	8.12	7.99				
					61.8	52 000	170 000	7.81	8.32				
				84.7		99 000	190 000	8.12	7.94				
					20.8	43 000	720 000	--	8.30				
				20.8		20 000	43 000	8.12	8.19				
					82.8	144 000	260 000	7.95	8.30				
		75-500		43.7		21 000	72 000	8.12	7.95				
					61.8	69 000	250 000	7.81	8.40				
				84.7		26 000	118 000	8.12	8.04				
					20.8	20 000	80 000	--	8.41				
				Argillite	CN-3	<75	1.4×10^{-7}	21.9		19 000	44 000	8.33	7.55
									86.9	18 000	170 000	--	8.19
								42.8		47 000	140 000	8.33	8.08
									63.7	66 000	290 000	7.42	8.12
83.8		81 000	310 000					8.33	8.20				
	28.7	120 000	430 000					8.02	8.42				
21.9		130 000	380 000					8.33	7.71				
	86.9	34 000	1100 000					--	8.18				
75-500	42.8		36 000			97 000		8.33	8.18				
		63.7	140 000			2200 000		7.42	8.12				
	83.8		61 000			200 000		8.33	8.29				
		28.7	170 000			250 000		8.02	8.43				

^aMeasurements were made at ambient temperature (~22°C).

^bFeed solutions were filtered through 0.4- and 0.05- μ m Nuclepore filters.

TABLE IV
 ^{241}Am SORPTION RATIOS, CONTROLLED-ATMOSPHERE CONDITIONS^a

Medium	Core	Fraction (μm)	Approximate Pu Molarity ^b	Time(d)		R _d (ml/g)		pH		
				Sorption	Desorption	Unfilt	Filt	Initial	Final	
Granite	CS-7	<75	7.3×10^{-10}	20.7		2 100	4 600	9.53	9.60	
					83.3	8 500	9 400	8.97	8.14	
				42.7		3 500	5 400	9.53	8.90	
					61.9	5 100	5 600	8.99	8.88	
		75-500		84.7		>14 000	>14 000	9.53	9.21	
					26.8	1 800	4 200	8.60	8.71	
				20.7		950	1 400	9.53	9.44	
					83.3	2 700	>9 000	8.97	8.00	
				42.7		1 000	1 500	9.53	8.94	
					61.9	8 600	>12 000	8.99	9.47	
				84.7		>12 000	>12 000	9.53	9.20	
					26.8	6 400	>11 000	8.60	8.99	
Argillite	CN-3	<75	4.6×10^{-8}	20.7		39 000	620 000	9.30	8.30	
					86.9	46 000	>930 000	--	8.06	
				41.6		34 000	240 000	9.30	8.47	
					66.9	180 000	>980 000	8.69	7.76	
		75-500		83.7		58 000	230 000	9.30	8.18	
					25.7	72 000	830 000	8.13	7.97	
				20.7		81 000	400 000	9.30	8.33	
					86.9	230 000	>970 000	--	8.04	
				41.6		45 000	190 000	9.30	8.48	
					66.9	360 000	>1000 000	8.69	7.79	
				83.7		48 000	240 000	9.30	8.09	
					25.7	115 000	>980 000	8.13	7.95	

^aNitrogen, ≤ 0.2 ppm oxygen, ≤ 20 ppm carbon dioxide. All measurements were made at 32°C .

^bFeed solutions were filtered through 0.4- and 0.05- μm Nuclepore filters.

TABLE V
AVERAGE^a SORPTION RATIOS (ml/g) FOR Am AND Pu,
ATMOSPHERIC AND CONTROLLED-ATMOSPHERE^b CONDITIONS

Medium	Tracer	Sorption		Desorption	
		Atmospheric	Controlled	Atmospheric	Controlled
Argillite	²⁴¹ Am	63 000(17 000) ^c	51 000(6 900)	92 000(25 000)	170 000(48 000)
	²³⁷ Pu	>32 000	>14 000	>26 000	>7 600
Granite	²⁴¹ Am	41 000(12 000)	>3 200	59 000(18 000)	5 500(1 200)
	²³⁷ Pu	>6 200	120(33)	>9 700	5 000(1 700)

^aSorption ratios for unfiltered solutions after contact have been averaged over two particle sizes and three contact times.

^bNitrogen, ≤ 0.2 ppm oxygen, ≤ 20 ppm carbon dioxide.

^cStandard deviations (absolute) of the means for six measurements are given in parentheses.

essentially all solid material from the aqueous phase. The current data are, therefore, considered to be more accurate. Current data for filtered solutions are consistent with earlier results; in both cases americium apparently sorbed on the filter membrane.

The following observations can be made. The R_d values for the sorption of plutonium on granite are significantly less under controlled-atmosphere conditions. Because of the limit values on the desorption results, it can only be said that the plutonium R_d values for controlled-atmosphere conditions appear to be somewhat less. Such a change with a change in atmosphere is not surprising considering the known⁸ speciation effects of plutonium. Americium also appears to have lower R_d values for granite for both sorption and desorption when under controlled-atmosphere conditions. As reported⁸ previously, americium has also exhibited a tendency toward large variations in behavior when experimental conditions are changed. This, also, is probably due to speciation effects even though the oxidation state remains unchanged.

Although the large number of limit values on the sorption ratios for plutonium on argillite restrict a comparison of the effects of changing the atmosphere, R_d values appear to be somewhat less than those for the air. Within the errors on the data there appears to be no variation of americium sorption on argillite with atmosphere.

Also within the errors on the data, particle-size effects appear to be minimal, as, for the most part, do changes with contact time. Where any contact-time effects can be observed the trend, as usual, is an increase in R_d values with increasing time.

In general, all sorption of americium and plutonium on argillite and granite is high, except for plutonium on granite under controlled-atmosphere conditions.

B. Measurements with Technetium (E. N. Vine)

The ^{95m}Tc tracer received from Argonne National Laboratory (ANL) under contract to the WRIT project was studied by solvent extraction techniques to determine the amount of pertechnetate present. Small aliquots of the ANL tracer were added to several aqueous solutions (dilute H_2SO_4 and tuff groundwaters) and Tc(VII) was extracted into CHCl_3 containing tetraphenylarsonium ion. It was found that 25 to 30% of the ^{95m}Tc tracer was not pertechnetate, i.e., did not extract into the organic phase. Addition of Ce(IV) to the aqueous solutions prior to extraction resulted in complete extraction of ^{95m}Tc .

It was hoped that any reduced technetium added to the groundwaters would gradually oxidize on standing in air; however, even after one week a reduced form of technetium was still present. Filtering through a 0.4- μ m membrane removed more than 50% of the reduced form. In J-13 well water pretreated with YM-38 tuff, ~94% of the ^{95m}Tc was present as pertechnetate in a solution which was filtered after standing for one week, and in J-13 water pretreated with YM-46 tuff ~88% of the ^{95m}Tc was present as pertechnetate after filtering a solution which had stood 4 days.

Since the use of solutions containing ^{95m}Tc initially in more than one oxidation state could lead to difficulty in interpretation of experimental results, the ^{95m}Tc tracer which we had obtained from New England Nuclear (and which was found to contain only pertechnetate) was mainly used.

Batch measurements of the sorption ratios for ^{95m}Tc on samples of Climax Stock granite (CS-7) and Eleana argillite (CN-3) under controlled atmosphere conditions (≤ 0.2 ppm oxygen, ≤ 20 ppm carbon dioxide) were completed. Particle-size fractions of <75 μ m and 75-500 μ m were used. The sorption and desorption R_d values obtained are given in Table VI along with the final pH value in each solution. The initial pH values were 8.80 and 8.10 for the granite and argillite samples, respectively. The sorption ratios tended to increase with time, particularly for the <75 - μ m fractions.

Additional Eleana argillite was crushed in the controlled-atmosphere boxes for batch measurements of ^{95m}Tc in conjunction with solvent extractions to determine the amount (if any) of reduced technetium present in solution at the time of the sorption (or desorption measurement). Although sorption experiments for approximately 6- and 12-week contacts have been terminated, data analysis is not complete.

C. Measurements under Controlled-Atmosphere Conditions - Cesium, Strontium, Barium, Cerium, and Europium (S. J. DeVilliers and A. J. Mitchell)

The sorption of strontium, cesium, barium, cerium, and europium on Eleana argillite and Climax Stock granite under controlled-atmosphere conditions was studied. Early results, measurement techniques, calculational techniques, solid materials, groundwaters, and equipment for controlling the atmosphere were described previously.^{1,2,8}

The results of the measurements are given in Tables VII and VIII. Table IX gives the starting and final pH values of each of the solutions.

TABLE VI
TECHNETIUM SORPTION RATIOS, GRANITE AND ARGILLITE,
CONTROLLED-ATMOSPHERE^a CONDITIONS

Sample	Fraction (μm)	Sorption Time (d)	Desorption Time (d)	R _d (ml/g)	Final pH
CS-7	<75	20.67		40	8.58
			83.98	60	8.91
		41.67		80	8.79
			62.98	140	8.90
	75-500	83.67		120	8.88
			20.98	280	8.90
		20.67		15	8.95
			83.98	20	8.80
		41.67		4.0	8.75
			62.98	32	8.76
		83.67		4.2	8.65
			20.98	12	8.94
CN-3	<75	20.67		170	7.93
			83.98	480	8.10
		41.67		330	8.17
			62.98	1 100	8.14
	75-500	83.67		830	8.10
			20.98	730	8.07
		20.67		180	8.11
			83.98	300	8.06
		41.67		200	9.82
			62.98	170	8.32
		83.67		330	7.70
			20.98	220	8.21

^a Ambient temperature (32°C), nitrogen atmosphere, ≤ 0.2 ppm oxygen, ≤ 20 ppm carbon dioxide.

TABLE VII
Cs, Sr, Ba, Ce, AND Eu SORPTION RATIOS, CS-7 GRANITE,
CONTROLLED-ATMOSPHERE^a CONDITIONS

Fraction (μm)	Sorption Time (h)	Desorption Time (d)	R_d (ml/g) ^b				
			Cs	Sr	Ba	Ce	Eu
<75	20.63		1 780 (2.7)	69.8 (2.5)	1 720 (1.7)	>2 640	1 140 (13.3)
		24.63	2 790 (7.8)	92.4 (8.7)	2 120 (8.7)		>9 070
	41.63		2 060 (3.5)	76.6 (2.5)	2 170 (2.0)	>2 970	>8 560
		41.63	2 540 (7.3)	86.6 (8.3)	2 320 (7.8)	>3 350	>8 620
	83.63		2 570 (3.7)	82.5 (2.5)	2 590 (2.1)		>6 350
75-500	20.63		752 (2.4)	19.4 (3.8)	245 (1.4)	>1 450	>5 320
	41.63		788 (2.5)	22.1 (3.8)	289 (1.4)		>1 240
		41.63	2 650 (7.2)	27.6 (8.3)	322 (7.6)		>5 890
	83.63		1 060 (2.8)	19.5 (4.0)	269 (1.5)		>6 810

^a Ambient temperature (32°C), nitrogen atmosphere, ≤ 0.2 ppm oxygen, ≤ 20 ppm carbon dioxide.

^b 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 for change of variables in a moment matrix assuming independence of the variables.

TABLE VIII
Ce, Sr, Ba, Ce, AND Eu SORPTION RATIOS, CN-3 ARGILLITE,
CONTROLLED-ATMOSPHERE^a CONDITIONS

Fraction (μm)	Sorption Time (d)	Desorption Time (d)	R_d (ml/g) ^b				
			Ce	Sr	Ba	Ce	Eu
<75	20.63		1 190 (2.2)	32.1 (3.1)	288 (1.4)	>110 000	>401 000
		20.63	1 690 (7.4)	32.8 (8.1)	524 (7.9)	>83 600	23 500 (11)
	41.63		1 250 (2.4)	39.1 (3.0)	372 (1.5)	>101 000	>354 000
		41.63	2 310 (7.5)	43.5 (8.3)	498 (8.1)	>73 500	>223 000
	91.63		1 670 (2.6)	29.3 (3.3)	397 (1.5)	>7 310	7 640 (5.7)
75-500	20.63		1 020 (2.6)	31.9 (3.2)	209 (1.6)	>128 000	>442 000
		20.63	2 370 (7.3)	30.2 (8.0)	306 (7.6)	>111 000	>486 000
	41.63		1 280 (2.5)	27.3 (3.4)	223 (1.3)	>98 700	35 000 (15)
		41.63	1 990 (7.5)	41.2 (8.1)	307 (8.1)	>118 000	46 400 (16)
	91.63		1 380 (2.5)	28.7 (3.4)	256 (1.5)	>107 000	6 980 (4.5)

^a Ambient temperature (32°C), nitrogen atmosphere, ≤ 0.2 ppm oxygen, ≤ 20 ppm carbon dioxide.

^b 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 for change of variables in a moment matrix assuming independence of the variables.

TABLE IX
pH VALUES, Cs, Sr, Ba, Ce, AND Eu STUDIES,
CONTROLLED-ATMOSPHERE CONDITIONS

Sample	Fraction (μ m)	Sorption Time (d)	Desorption Time (d)	pH Values	
				Initial	Final
CS-7	<75	20.63		8.43	8.56
			24.63	8.43	9.06
		41.64		8.43	8.45
			41.63	8.43	8.45
		83.63		8.43	9.24
	75-500	20.63		8.43	8.52
			24.63	8.43	8.66
		41.63		8.43	8.36
			41.63	8.43	8.66
		83.63		8.43	9.12
CN-3	<75	20.63		8.43	8.40
			20.63	8.43	8.06
		41.63		8.43	8.71
			41.63	8.43	8.11
		91.63		8.43	8.37
	75-500	20.63		8.43	8.80
			20.63	8.43	8.01
		41.63		8.43	8.80
			41.63	8.43	8.22
		91.63		8.43	8.31

The sorption ratio values obtained for cesium, strontium, and barium on the Climax Stock granite are nearly the same as those obtained under atmospheric conditions. The R_d values were also found to be strongly dependent on the particle size (surface area) as observed under atmospheric conditions. The sorption ratios for cerium and europium are higher than those obtained under atmospheric conditions, perhaps because of the absence of carbon dioxide in the controlled-atmosphere studies. Also, the R_d values for all elements increased with time.

The sorption values obtained for argillite under controlled-atmosphere conditions are somewhat different from those obtained under atmospheric conditions. The cesium, strontium, and barium values are smaller by factors of about 2, 10, and 50-100, respectively, while those for cerium and europium are larger by about a factor of 10. These results are not understood; however, it should be noted that the carbon dioxide concentration in the controlled-atmosphere

boxes was ≤ 20 ppm, which possibly results in a lower carbonate concentration in solution. Again, the R_d values for all elements increased with time.

D. Comparison of Batch Studies Made under Atmospheric and Controlled-Atmosphere Conditions (B. P. Bayhurst, W. R. Daniels, S. J. DeVilliers, B. R. Erdal, F. O. Lawrence, E. N. Vine, R. D. Aguilar, S. Maestas, A. J. Mitchell, and P. Q. Oliver)

Under the generally reducing conditions that may be expected for some groundwaters not in contact with the atmosphere, it can be anticipated that the sorptive behavior of some elements will be different from that under normal atmospheric conditions. One could also expect differences in the sorptive capacity of a rock if its surface had been altered by exposure to air. These effects were investigated by comparing the results of studies performed in a pure nitrogen atmosphere having ≤ 2.0 ppm oxygen and ≤ 20 ppm carbon dioxide present with similar measurements made under natural atmospheric conditions on the same geologic materials. It should be emphasized that the controlled-atmosphere studies are perhaps not truly representative of the conditions to be found in deep geologic systems because essentially no carbon dioxide was present and bicarbonate may have been lost from solution. This could be particularly important for uranium(VI), which is strongly complexed by carbonate ions. However, the pH values observed⁸ when rock was present were not appreciably different from those observed under atmospheric conditions, indicating that the rocks themselves may have supplied some bicarbonate ion buffering.

The measurement techniques and calculational methods have been reported earlier (Refs. 1, 2, 8, 10, and Section A above). The radionuclides used were ^{85}Sr , ^{137}Cs , ^{133}Ba , ^{141}Ce , ^{152}Eu , ^{95m}Tc , ^{237}U , ^{237}Pu , and ^{241}Am . The rock samples were Climax Stock granite core¹ CS-7, Eleana argillite core² CN-3, and Yucca Mountain tuff cores¹² YM-22, YM-38, and YM-54. The groundwaters utilized in the determinations in air and nitrogen atmospheres had the same initial composition for a given rock type. The $<75\text{-}\mu\text{m}$ and $75\text{-}500\text{-}\mu\text{m}$ fractions were used for the controlled-atmosphere studies on all media.^{8,9} For the tuff samples¹⁰ under atmospheric conditions, the $<106\text{-}\mu\text{m}$ and $106\text{-}500\text{-}\mu\text{m}$ fractions were used in some experiments. Several different particle-size fractions were used for the granite¹ and argillite² studies under atmospheric conditions.

1. Results and Observations. The R_d values from both sorption and desorption studies were reported earlier. Atmospheric R_d values for

argillite, granite, and tuff were reported in Refs. 1, 2, 3, and 12. Results obtained under controlled-atmosphere conditions were reported in Refs. 8 and 13 and Sections IV.A, B, and C above.

a. Cesium. The R_d values for sorption of cesium on granite are quite dependent on particle size, the smaller fraction having a higher R_d value. There is an increase in sorption with time. Dependences of the R_d value on particle size and contact time were observed for both air and nitrogen measurements. There is very little variation in the overall cesium sorption ratios for granite between atmospheric and controlled-atmosphere conditions. It seems that the changes that take place in granite with time are more effective in changing the sorption of cesium than are the low oxygen and carbon dioxide concentrations present in the controlled-atmosphere experiments.

The R_d values for cesium on argillite increase slightly with time. For some reason, the values obtained in the controlled-atmosphere experiments are somewhat lower (by a factor of ~2) than the atmospheric values.

The cesium R_d values for the three tuff samples studied in the controlled-atmosphere experiments are higher for the smaller particle size than for the larger; however, this dependence on particle size is less than that observed in the measurements carried out under atmospheric conditions. The sorptive behavior of cesium on tuffs appears to have been independent of the atmosphere involved.

b. Strontium. For both air and nitrogen atmospheres, the strontium R_d values for granite are dependent on particle size and have essentially no dependence on time. The strontium sorption ratios for granite were essentially the same when measured under atmospheric or controlled-atmosphere conditions.

There is very little dependence on particle size or time for strontium on argillite under controlled-atmosphere conditions; however, a small increase with time was observed under atmospheric conditions. In the latter experiment, it is possible that there was a change in mineralogy with time which had some effect on strontium sorption. The R_d values for argillite are smaller (by a factor of ~5) under controlled-atmosphere conditions than when measured in air. This fact may be related to the low carbon dioxide concentration in the controlled-atmosphere studies.

A small dependence on particle size was observed for the sorption of strontium on Yucca Mountain tuffs under controlled-atmosphere conditions.

There did not seem to be a time dependence of sorption ratios for either atmosphere. The strontium R_d values for the tuff samples were essentially the same for atmospheric and controlled-atmosphere conditions.

c. Barium. The barium R_d values for granite are quite dependent on particle size and time for both atmospheric and controlled-atmosphere experiments. The dependence on time is more noticeable for the smaller particle size for which the mineralogy might be expected to change faster with time. The values for granite were nearly the same for atmospheric and controlled-atmosphere conditions.

The sorption ratios for barium on argillite are lower (by a factor of 10 or more) in the controlled-atmosphere experiments than in the atmospheric ones. There is not much dependence on particle size or contact time in either type of measurement. It is possible that the lower carbon dioxide concentration is responsible for lower R_d values observed under the controlled-atmosphere conditions if solubility is the controlling factor.

The controlled-atmosphere determinations show a particle-size effect for barium sorption on the three tuff samples used. This dependence was not observed in the atmospheric measurements. Changing the atmospheric conditions did not seem to have any effect on the sorptive behavior of barium on tuffs.

d. Cerium and Europium. The cerium and europium R_d values are higher for granite and argillite when measured under controlled-atmosphere conditions than when measured under a nitrogen atmosphere; however, the difference is more noticeable on granite because all of the cerium and europium sorption ratios on argillite are very high. The low carbon dioxide concentration in the controlled-atmosphere experiments may be responsible for these higher R_d values but it is not clear in what manner.

The R_d values for the tuff samples are similar for the two different atmospheres.

The sorption of cerium and europium may be strongly dependent on the formation of insoluble substances of these elements (e.g., precipitates or colloids).

e. Technetium. The technetium R_d values are higher when measured under controlled-atmosphere conditions than when measured under atmospheric conditions for all three geologic media studied. The sorption ratios for argillite are higher than for the other two media under both types of atmospheric conditions. A strong time dependence for sorption of technetium on

argillite under controlled-atmosphere conditions was observed. Perhaps the reduction of Tc(VII) to Tc(IV) in the presence of argillite results from the time dependent release of some reducing agent or perhaps the rate of reduction itself is slow.

The sorption ratios for technetium on zeolite containing tuffs are about 15 times larger when measured under controlled-atmosphere conditions than when measured in air. The values for microgranite-like tuffs are 10 to 25 times larger when measured under the controlled-atmosphere conditions.

f. Uranium. The uranium(VI) sorption ratios for granite and argillite are somewhat lower under controlled-atmosphere conditions than when measured in air. Under controlled-atmosphere conditions the sorption ratios for the tuff samples are similar for YM-22 and YM-54 samples but somewhat higher for YM-38 (zeolitized tuff). It was anticipated that U(VI) might be reduced to U(IV) under the controlled-atmosphere conditions and that more sorption might take place; apparently this did not happen. The U(VI) may remain strongly complexed, probably by carbonate, in all of these groundwaters.

g. Plutonium. The R_d values for the sorption of plutonium on granite are significantly lower ($\geq$ factor of 50) under controlled-atmosphere conditions than in air. In contrast to the granite results, the sorption of plutonium on tuff appears to be slightly higher (factor of 2) under the controlled-atmosphere conditions. These results are probably attributable to speciation effects resulting from interaction with the different media. Although the large number of limit values on the sorption ratios for plutonium on argillite (Section A above) restrict a comparison of the effects of changing the atmosphere, the controlled-atmosphere values appear to be somewhat less than those for air.

Particle-size effects are minimal, as, for the most part, are changes with contact time. Where any contact-time effects can be observed the trend appears to be an increase with increasing time.

h. Americium. The R_d values for the sorption of americium on granite are lower ($\geq$ factor of 15) under controlled-atmosphere conditions than in air. For the sorption of americium on tuff and argillite, no real trend can be discerned; however, sorption on argillite may be slightly less in the controlled atmosphere, while sorption of tuff appears to show a slight dependence on the mineralogy of the tuff.

No significant dependence of sorption behavior on particle size or contact time could be discerned.

2. General Conclusions. The effects of atmosphere on the R_d values for the three geologic media and nine elements studied are summarized in Table X. Of the three geologic media studied, it seems that the sorptive behavior of argillite is most affected by the atmospheric conditions, except for plutonium and americium where the difference was greater for granite. All radionuclides studied have different R_d values for argillite when measured under the controlled atmosphere than when measured in air, except possibly for americium where any effect was smaller than the errors on the R_d values. The R_d values for technetium on all three media and for plutonium and americium on granite are most strongly dependent on the presence or absence of oxygen and carbon dioxide. The technetium sorption ratios are higher for all three media when measured under controlled-atmosphere conditions. Interestingly, sorption of plutonium and americium on granite is much lower under controlled-atmosphere conditions, while the sorption of plutonium on tuffs is actually higher under the controlled atmosphere. As expected, strontium, cesium, and barium are least affected by the presence or absence of oxygen and carbon dioxide.

E. Dependence of Sorption on the Solution to Solid Ratio (S. J. DeVilliers and A. J. Mitchell)

Batch sorption measurements have been started to determine the dependence of the sorption ratio on the solution to solid ratio. Previous batch sorption measurements were made at a 20 to 1 solution to solid ratio. In the current experiment the ratios were 5, 10, and 30 to 1. One-gram aliquots of two fraction sizes, $<75\ \mu\text{m}$ and $75\text{--}500\ \mu\text{m}$, of CS-5 (Climax Stock) granite were used. Contact times were 3 and 6 weeks at ambient temperature and under atmospheric conditions. The 6-week experiments are still in progress. The procedures for batch determinations have been described elsewhere.¹ The radionuclides used for these studies were ^{85}Sr , ^{137}Cs , ^{133}Ba , ^{141}Ce , and ^{152}Eu . The concentrations of the tracers in the feed solutions for the granite samples were 2.49×10^{-9} , 2.06×10^{-7} , 2.74×10^{-7} , 1.21×10^{-7} , and 1.38×10^{-7} M for cesium, strontium, barium, cerium, and europium, respectively.

The results for 3-week contacts are given in Table XI. It can be observed that the sorption ratios of cesium and strontium were more affected by the change in solution to solid ratio than those of the other elements. Sorption ratios for barium, cerium, and europium are essentially constant over the three solution to solid ratios. For cesium and strontium, sorption ratios tend to

TABLE X
COMPARISON OF SORPTION RATIOS (R_d) MEASURED
UNDER ATMOSPHERIC AND CONTROLLED-ATMOSPHERE (CA) CONDITIONS^a

Element	Granite	Argillite	Tuff
Cs	No effect	Lower in CA (factor of 2)	No effect
Sr	No effect	Lower in CA (factor of 5)	No effect
Ba	No effect	Lower in CA (factor of 10 or more)	No effect
Ce	Higher in CA (factor of 10 or more)	Higher in CA (factor of 10)	No effect
Eu	Higher in CA (factor of 10 or more)	Higher in CA (factor of 10)	No effect
Tc	Higher in CA (factor of 5-10)	Higher in CA (factor of 10)	Higher in CA (factor of 10 or more)
U	Lower in CA (factor of 10)	Lower in CA (factor of 10)	Higher in CA ^b (factor of 2-3)
Pu	Lower in CA (factor of 50)	Lower in CA?	Higher in CA (factor of 2)
Am	Lower in CA (factor of 15)	Lower in CA?	No effect ^c

^aNitrogen, ≤ 0.2 ppm oxygen and ≤ 20 ppm carbon dioxide.

^bYM-38 zeolitized tuff only; otherwise no effect.

^cMay depend on mineralogy.

increase with the solution to solid ratio. In general, sorption ratios were larger for the smaller fraction size. Further discussion of the results will await additional data.

F. Dependence of Sorption on Element Concentration - Isotherm Measurements (S. J. DeVilliers and A. J. Mitchell)

Experiments have been performed to determine the effect of element concentration on the sorptive behavior of some rock types. Studies involving

TABLE XI
 VARIATION OF SORPTION RATIO WITH SOLUTION TO SOLID RATIO^a

Sample	Fraction (μm)	Solution:Solid Ratio	R_d (ml/g)				
			Cs	Sr	Ba	Ce	Eu
CS-5	<75	5:1	797(6.5) ^b	61.0(2.5)	1 450(2.5)	160(9.5)	513(9.6)
		10:1	1 250(4.5)	44.8(2.3)	1 170(1.5)	118(6.7)	403(6.6)
		30:1	2 280(2.9)	122(2.2)	1 190(1.2)	158(4.7)	585(4.3)
CS-5	75-500	5:1	679(5.8)	34.5(2.6)	885(2.1)	105(8.6)	434(9.0)
		10:1	1 010(4.1)	19.8(2.9)	839(1.5)	92.3(6.1)	320(5.9)
		30:1	2 090(4.5)	160(2.1)	806(1.1)	158(4.7)	554(4.2)

^aGranite, 3-week contacts.

^bThe 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.

strontium, cesium, barium, and europium have been completed. Cerium studies have just been started.

1. Experimental. The synthetic groundwaters and solid materials are the same as those previously described.^{1,2} The <75- and 75-500- μm fractions of Climax Stock granite core CS-5 and the 250-355- μm fractions of Eleana argillite cores CN-1 and CN-2 were used. All contacts were for 3 weeks at ambient temperature under normal atmospheric conditions with our usual batch technique^{1,2,8} for ^{85}Sr , ^{137}Cs , ^{133}Ba , ^{152}Eu , and ^{141}Ce .

Carrier stock solutions of strontium and barium were prepared by dissolving the nitrate salts in the desired, rock-pretreated, synthetic groundwater. For cesium the chloride was used. Concentrations were calculated from the weights. A relatively concentrated solution of europium was prepared by dissolving $\text{Eu}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ in deionized water. The europium concentration was determined to be $8.92 \times 10^{-3} \text{ M}$ by means of a Spectrometric Incorporated, 20-channel, direct current, plasma-source, emission spectrometer. Subsequent dilutions of the europium carrier solution were made with the appropriate rock-pretreated groundwater.

To prepare individual tracer stock solutions the radionuclides were dried in plastic bottles, then dissolved in the appropriate granite or argillite rock-pretreated water, shaken for a few days, and passed through 0.45- μm Millipore filters. For each element, five solutions of different concentrations were prepared for batch contacts by mixing appropriate volumes of carrier and tracer stock solutions and the appropriate rock-pretreated waters. Unfortunately, the concentrations of the elements being studied in the groundwaters were not known at the time the experiments were started. They were determined later utilizing the plasma-source, emission spectrometer. Concentration data and pH values for the solutions before contact with the rocks are given in Table XII. It is apparent that in some cases the element concentration in the groundwater is much larger than the amount added. Because of concern over the possible precipitation of europium at the higher concentrations, five "control" samples were also prepared. Aliquots of the five different concentrations were placed in empty tubes and shaken for 3 weeks at the same time as the regular samples.

2. Results and Conclusions. Tables XIII and XIV list the sorption ratios obtained for strontium, cesium, barium, and europium on Climax Stock granite and Eleana argillite. The R_d values were calculated from counts of

TABLE XII
INITIAL CONCENTRATIONS AND pH VALUES OF SOLUTIONS
FOR ISOTHERM MEASUREMENTS

Element	Solution	Granite			Argillite		
		Element Concentration (M)		pH	Element Concentration (M)		pH
		Added	Total		Added	Total	
Sr(II)	1	1.27×10^{-3}	1.27×10^{-3}	7.59	1.44×10^{-3}	1.44×10^{-3}	8.36
	2	1.31×10^{-5}	1.36×10^{-5}	7.72	1.72×10^{-5}	2.42×10^{-5}	8.55
	3	1.91×10^{-7}	7.11×10^{-7}	7.70	1.98×10^{-7}	7.20×10^{-6}	8.51
	4	2.07×10^{-8}	5.41×10^{-7}	7.71	1.97×10^{-8}	7.02×10^{-6}	8.33
	5	2.35×10^{-9}	5.22×10^{-7}	7.77	2.16×10^{-9}	7.00×10^{-6}	8.28
Cs(I)	1	1.87×10^{-3}	1.87×10^{-3}	7.69	2.42×10^{-3}	2.42×10^{-3}	8.32
	2	1.87×10^{-5}	1.87×10^{-5}	7.76	2.32×10^{-5}	2.32×10^{-5}	8.34
	3	1.89×10^{-7}	1.89×10^{-7}	7.80	2.16×10^{-7}	2.16×10^{-7}	9.43
	4	1.02×10^{-9}	1.02×10^{-9}	7.81	1.95×10^{-9}	1.95×10^{-9}	8.13
	5	1.02×10^{-10}	1.02×10^{-10}	7.81	1.95×10^{-10}	1.95×10^{-10}	8.22
Ba(II)	1	1.12×10^{-3}	1.12×10^{-3}	7.40	1.08×10^{-4}	1.08×10^{-4}	7.93
	2	1.12×10^{-5}	1.17×10^{-5}	7.76	1.08×10^{-5}	1.15×10^{-5}	8.18
	3	1.29×10^{-7}	6.29×10^{-7}	7.76	1.26×10^{-7}	8.56×10^{-7}	8.23
	4	2.82×10^{-8}	5.28×10^{-7}	7.75	2.95×10^{-8}	7.60×10^{-7}	8.05
	5	2.82×10^{-9}	5.03×10^{-7}	7.83	2.95×10^{-9}	7.32×10^{-7}	8.25
Eu(III)	1	2.54×10^{-4}	2.54×10^{-4}	6.06	7.88×10^{-5}	7.88×10^{-5}	7.81
	2	2.53×10^{-6}	2.53×10^{-6}	7.81	5.96×10^{-6}	5.96×10^{-6}	8.01
	3	9.64×10^{-8}	9.64×10^{-8}	7.95	1.11×10^{-7}	1.11×10^{-7}	8.10
	4	9.78×10^{-9}	9.78×10^{-9}	7.99	5.30×10^{-8}	5.30×10^{-8}	8.13
	5	2.67×10^{-9}	2.67×10^{-9}	7.98	7.45×10^{-9}	7.45×10^{-9}	8.18

TABLE XIII
SORPTION RATIOS (ml/g) FOR Sr, Cs, Ba, AND Eu
ON GRANITE^a - ISOTHERM STUDIES

Solution Number ^b	Sr		Cs		Ba		Eu	
	<75 μ m	75-500 μ m	<75 μ m	75-500 μ m	<75 μ m	75-500 μ m	<75 μ m	75-500 μ m
1	147	33.3	6.86	4.54	10.7	4.88	15 700	12 300
2	44.0	18.1	58.3	16.9	553	116	1 330	1 520
3	67.5	24.1	895	465	1 320	348	1 720	2 400
4	61.8	25.8	1 760	971	1 140	330	1 880	1 170
5	55.6	23.8	1 320	817	1 490	400	1 550	---

^aClimax Stock Core CS-5.

^bTotal element concentrations including the groundwater contribution are given in Table XII.

TABLE XIV
SORPTION RATIOS (ml/g) FOR Sr, Cs, Ba, AND Eu
ON ARGILLITE^a - ISOTHERM STUDIES

Solution Number ^b	Sr		Cs		Ba		Eu	
	CN-1	CN-2	CN-1	CN-2	CN-1	CN-2	CN-1	CN-2
1	13.2	19.5	19.8	30.7	107	505	6 160	10 500
2	17.2	38.7	127	238	174	532	7 980	14 400
3	17.5	34.8	742	924	122	394	15 300	29 600
4	16.8	33.2	759	1 170	109	524	27 900	77 800
5	17.6	33.6	985	989	103	501	15 400	---

^aEleana argillite, particle size 250-355 μm .

^bTotal element concentrations including the groundwater concentration are given in Table XII.

both the solid and liquid samples. In general, the R_d values became essentially constant when the amount of an element added became small relative to the concentration of the element in the groundwater, as was to be expected since the total concentration remained virtually unchanged.

For the granite samples, a high R_d value was observed for the highest strontium concentration. This might indicate that the solubility product of a strontium compound, e.g., SrCO_3 , was exceeded.

Strontium sorption ratios for the argillite samples were all very close to the same value. Since the strontium concentration in the argillite water is 7.0×10^{-6} M, little change in sorption ratio was expected for small changes in added strontium concentration.

A strong correlation between cesium concentration and cesium sorption ratio was observed. The sorption ratios increase as the cesium concentration decreases although in some cases the R_d value was slightly lower at the 10^{-10} M level than at 10^{-9} M level. This relationship between sorption ratios and cesium concentrations seems to indicate an ion exchange mechanism for the cesium sorption on granite and argillite.

As did those for strontium, the sorption ratios for barium on granite increase as the barium concentration decreases, while the sorption ratios for barium on argillite are rather constant.

Sorption ratios for europium on granite are rather constant except at the highest europium concentration where some precipitation might have taken place. At this initial added concentration of 2.54×10^{-4} M the sorption ratio is about ten times larger than at the lower concentrations. The control solution at this concentration showed no change in activity after 3 weeks of shaking time, so a precipitation may have occurred due to some component of the rock which was going into solution during the contact time.

Sorption ratios for europium on argillite increase as the concentration decreases. All of the control solutions showed the same concentration at the end as they did at the beginning of the shaking time.

3. Sorption Isotherm Measurements. The element concentrations in the equilibrium solutions (moles/l) and on the solid (moles/g) were calculated from the amounts added, the concentrations in the original groundwaters, and the R_d values, assuming that the solid had no natural content of these elements. Plots of these data on a log-log scale are given in Figs. 1-4, and the concentration data are given in Tables XV and XVI.

Fig. 1. Cesium sorption isotherm data for granite and argillite.

CLIMAX STOCK GRANITE
AMBIENT TEMPERATURE

□ 0 - 75 μ m
Δ 75 - 500 μ m

ELEANA ARGILLITE
AMBIENT TEMPERATURE

□ CN-1
Δ CN-2

Fig. 2. Strontium sorption isotherm data for granite and argillite.

Fig. 3. Barium sorption isotherm data for granite and argillite.

Fig. 4. Europium sorption isotherm data for granite and argillite.

TABLE XV
FINAL Sr, Cs, Ba, AND Eu CONCENTRATIONS FOR
ISOTHERM MEASUREMENTS ON GRANITE^a

Element	<75- μ m Fraction		75-500- μ m Fraction	
	Solution ^b	Solid ^c	Solution ^b	Solid ^c
Sr	4.38	5.22	3.76	5.24
	5.44	6.79	5.14	6.88
	6.74	7.91	6.68	8.30
	6.88 ^d	8.08 ^d	6.90 ^d	8.48 ^d
Cs	2.82	4.99	2.80	5.14
	5.42	6.66	5.11	6.80
	8.42	8.47	8.29	8.62
	10.92	10.69	10.83	10.85
	11.92	11.80	11.76	11.85
Ba	3.08	5.06	2.99	5.30
	6.55	6.80	5.96	6.89
	8.03	7.91	7.60	8.05
	8.08	8.01	7.68	8.16
	8.15	8.04	7.73	8.12
Eu	6.52	5.33	6.46	5.37
	7.40	7.28	7.60	7.41
	9.14	8.88	9.16	8.78
	9.98	9.71	9.92	9.85
	10.38	10.19	--	--

^aClimax Stock core CS-5.

^bThe concentration in the solution is reported as the negative log(moles/l).

^cThe concentration in the solid is reported as the negative log(moles/g).
This calculation was made assuming no natural contribution.

^dAverage values for solutions which had essentially the same final concentrations because of large contributions from the groundwater.

TABLE XVI
FINAL Sr, Cs, Ba, AND Eu CONCENTRATIONS FOR
ISOTHERM MEASUREMENTS ON ARGILLITE^a

Element	Core CN-1		Core CN-2	
	Solution ^b	Solid ^c	Solution ^b	Solid ^c
Sr	3.19	5.00	3.18	4.84
	4.90	6.67	5.14	6.51
	5.44 ^d	7.20 ^d	5.56 ^d	6.97 ^d
Cs	2.93	4.64	3.04	4.55
	5.58	6.47	5.57	6.39
	8.25	8.37	8.40	8.44
	10.35	10.47	10.46	10.39
	11.40	11.41	11.42	11.42
Ba	4.83	5.80	5.25	5.55
	6.02	6.78	6.41	6.68
	6.93	7.84	7.34	7.74
	6.94 ^d	7.89 ^d	7.39 ^d	7.67 ^d
Eu	6.64	5.85	6.99	5.97
	7.95	7.05	8.03	6.87
	9.93	8.74	10.03	8.57
	10.55	9.10	10.92	9.03
	11.06	9.87	--	--

^aEleana argillite, particle size 250-355 μm .

^bThe concentration in the solution is reported as the negative log(moles/l).

^cThe concentration in the solid is reported as the negative log(moles/g).
The calculation was made assuming no natural contribution.

^dAverage values for solutions which had essentially the same final concentrations because of large contributions from the groundwater.

It is evident that a simple Freundlich isotherm does not entirely describe the strontium, cesium, barium, and europium data. The data plotted in this manner should be on a straight line since the Freundlich equation is $y = kc^n$, where y is the element concentration on the solid and c is the concentration in solution. The logarithm of this equation results in a straight line.

The nonlinearity of the data shown in Figs. 1-4 may indicate that different processes are occurring simultaneously. In particular, isotopic exchange processes would explain the relative lack of sensitivity to the amount of strontium in the rocks ($>3 \times 10^{-7}$ moles/g). The nonlinearity of the data may also be an artifact of the measurements since the concentrations of the element in solution and on the solid were not measured directly.

If, in spite of these difficulties, one fits the Freundlich isotherm equation to the data, the parameter values given in Table XVII are obtained. For some applications this may be adequate. It is striking that the values for n are all near unity, indicating that the sorption ratios (R_d) should be somewhat independent of concentration, as observed.

G. Sorption of Iodine on Argillite (K. Wolfsberg)

1. Measurement Technique. The sorptive behavior of iodine on Eleana argillite (core CN-2) was investigated in a procedure similar to that used for iodine sorption on alluvium¹⁴ and tuff.³ The iodine in an alluvial water sorbs quantitatively on anion resin and can be eluted with hypochlorite; therefore, it is probably present as iodide in the water. The initial solution for these batch experiments was made by leaching a sample from an underground nuclear test containing volatile fission products with synthetic Eleana argillite groundwater.² In addition to ^{131}I , the water also leached small but measureable quantities of ^{74}As , ^{99}Mo , ^{103}Ru , and ^{237}U . Sorption times were 13 and 26 d, and desorption times were 7 and 21 d, respectively. Separate 7-day sorption experiments were performed with the supernates from the earlier 13-day sorption experiments. The purpose of these later experiments was to investigate whether a single iodine species could be sorbed by the argillite from solution, assuming slow rates of change in solutions species. The pH values of all initial and final solutions were in the range of 8.55 to 8.65. Solutions are being retained for chemical analyses. The experiments were performed under atmospheric conditions at ambient temperature.

TABLE XVII
FREUNDLICH ISOTHERM PARAMETERS^a

<u>Rock Type</u>	<u>Fraction (μm)</u>	<u>Element</u>	<u>n</u>	<u>-log (k)</u>
CS-5	<75	Sr	1.11	0.52
		Cs	0.73	2.72
		Ba	0.58	3.20
		Eu	1.17	-1.92
	75-500	Sr	0.99	1.62
		Cs	0.73	3.00
		Ba	0.60	3.41
		Eu	1.23	-2.34
CN-1	250-355	Sr	0.98	1.88
		Cs	0.80	2.11
		Ba	0.99	0.95
		Eu	0.87	0.05
CN-2	250-355	Sr	0.88	2.03
		Cs	0.82	1.85
		Ba	1.02	0.17
		Eu	0.79	0.46

^aFreundlich isotherm, $y = kc^n$, where y is the concentration on the solid in moles/g and c is the concentration in solution in moles/l.

2. Results and Conclusions. The experimental results for iodine show (Table XVIII) small but measurable sorption of iodine on the argillite with R_d values between 2 and 6 ml/g. This represents sorption of 10 to 20 percent of the iodine. Values for alluvium¹⁴ and tuff³ are 20 and 0 ml/g, respectively. As usual, values for desorption are significantly higher. This observation is consistent with the probable presence of more than one species of iodine, some of which sorb and some of which do not.

The experiments with the aqueous phases from previous sorption studies gave approximately the same values as the original sorption measurements. If preferential sorption of one (or more) species of iodine occurred during the initial sorption experiments, it must have reformed from the other species present before the second set of measurements was made.

TABLE XVIII
SORPTION RATIOS FOR I, As, Mo, Ru, AND U ON ARGILLITE (CN-2),
ATMOSPHERIC CONDITIONS, 22°C

Fraction (μm)	Sorption Time (d)	Desorption Time (d)	R_d (m ℓ /g) ^a				
			I	As	Mo	Ru	U
106-150	13.0		2.18 (13)	46 (30)	4 (48)	12 (60)	16 (25)
		7.1	59 (27)				
	25.6		3.72 (7)	48 (21)		14 (38)	
		20.9	19 (42)				
	7.1 ^b		3.0 (26)				
355-500	13.0		4.8 (8)	44 (21)	3 (70)	13 (42)	7 (45)
		7.1	46. (28)				
	25.6		5.8 (8)	62 (22)		14 (38)	
		20.9	24. (39)				
	7.1 ^b		4.1 (13)				

^aThe 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 for change of variables in a moment matrix assuming independence of the variables.

^bThe measurements were made using the supernatant solution from the 13.0-d experiment for the same fraction.

Sorption ratios for molybdenum, ruthenium, and uranium are also low; arsenic values are somewhat higher. Not enough activity was present to allow desorption determinations to be performed.

Only the activity of the aqueous phases was measured since container effects have not been observed for iodine, molybdenum, ruthenium, and uranium.

H. Migration-Rate Studies on Crushed Materials - Comparison with Batch Studies (E. N. Vine, B. P. Bayhurst, and A. J. Mitchell)

1. Measurements. The migration of radionuclides through crushed rock columns of granite, argillite, and tuff has been studied. The geologic materials chosen were those on which batch sorption ratio (R_d) measurements had previously been made in order to provide a comparison with results obtained on the columns. The waters used for infiltration were described in Refs. 2 (argillite), 1 (granite), and 12 (tuff). Descriptions of the columns themselves and of the water delivery system(s) have also been previously reported (Refs. 8 and 12).

A summary of the crushed rock columns studied and of the parameters measured is given in Table XIX. Each column was characterized in terms of the total column volume V (the size of the column calculated from column dimensions), 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. Upward-flow columns had relatively constant flow rates with a given syringe and pump setting, while gravity-flow columns tended to decrease in flow rate before a steady flow was established. Upward-flow rates generally ranged from 0.041 to 0.082 mL/h. (A flow rate of 0.045 mL/h for a 2.1-cm-long by 0.5-cm-diameter column with a free column volume of 0.224 mL corresponds to a flow velocity of ~ 37 m/y.)

The free column volumes of approximately one-third of the columns studied were determined by use of both HTO and $^{131}\text{I}^-$. 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 $^{131}\text{I}^-$, and all measurements for a given column were averaged irrespective of the method used. For example, the FCV for a YM-54 column obtained with iodide (breakthrough) was 0.177 mL and with HTO was 0.182 mL. On the YM-22 column, the iodide breakthrough method gave 0.249 mL and the iodide rinse

TABLE XIX
CRUSHED ROCK COLUMNS

Geologic Materials	Isotopes Studied	Column ₃ Size (cm)	Porosity (%)	Density (g/cm ³)	General Comments
Argillite:					
CN-1	⁸⁵ Sr, ¹³⁷ Cs	0.382	59.2	1.15	
CN-2#1	⁸⁵ Sr, ¹³⁷ Cs	0.386	64.4		
CN-2#2	^{95m} Tc, ¹³¹ I	0.616	68.8		
CN-3	^{95m} Tc, ¹³¹ I	0.732	77.9		<0.2 ppm oxygen conditions
Granite:					
CS-7	⁸⁵ Sr, ¹³³ Ba, ¹³⁷ Cs	0.412	59.2	1.26	Slow "peakless" elution of ¹³⁷ Cs
CN-5	⁸⁵ Sr, ¹³³ Ba, ¹³⁷ Cs	0.422	59.7	1.25	Slow "peakless" elution of ¹³⁷ Cs
CS-5#2	⁸⁵ Sr, ¹³³ Ba, ¹³⁷ Cs	1.026	55.8	1.25	Slow "peakless" elution of ¹³⁷ Cs; fast flow (5 ml/h)
Tuff:					
YM-54#1	⁸⁵ Sr, ¹³³ Ba, ¹³⁷ Cs	0.295	79.3	0.98	¹⁰ ⁻⁶ M ¹³⁷ Cs
#2	¹³⁷ Cs	0.294	61.2		¹⁰ ⁻⁹ M ¹³⁷ Cs
#3	⁸⁵ Sr, ¹³³ Ba, ¹³⁷ Cs	0.511	66.9		¹⁰ ⁻⁶ M ¹³⁷ Cs
YM-38#1	⁸⁵ Sr	0.785	39.9	0.90	Activity decayed before it was eluted
#2	¹⁴¹ Ce	0.266	35.7		Activity decayed before it was eluted
#3	¹³⁷ Cs	0.390	39.0		Fast flow rate (4.5 ml/h)
JA-32#1	⁸⁵ Sr	0.830	54.9	0.89	
#2	⁸⁵ Sr	0.432	67.8		
#3	⁸⁵ Sr	0.353	63.5		Fast flow rate (18 ml/h), continuous feed
JA-18#1	⁸⁵ Sr, ¹³⁷ Cs	0.251	56.2	0.98	
#2	¹⁴¹ Ce, ¹⁵² Eu	0.239	47.7		
#3	⁸⁵ Sr, ¹³⁷ Cs, ¹³³ Ba	1.004	54.5		
JA-37	⁸⁵ Sr, ¹³⁷ Cs	0.342	44.4	0.95	
YM-22	⁸⁵ Sr, ¹³³ Ba, ¹³⁷ Cs	0.373	65.4	1.16	
YM-45	¹⁴¹ Ce	0.264	31.8	1.08	Activity decayed before it was eluted
YM-54#4	²³⁷ U	0.353	48.7	1.09	

gave 0.239 mL. The values for the CS-5 and CS-7 granite columns, the CN-1 and CN-2#1 argillite columns, and the JA-18, JA-37, and YM-45 tuff columns were measured using ^{131}I only. However, since a small retardation factor (2 to 6 mL/g) had recently been measured (Section IV.G above) for "iodide" on argillite, columns CN-2#2 and CN-3 were run with both tritium and ^{131}I (as well as technetium). The tritium data have been analyzed for only one of these columns; however, the breakthrough curve was identical to that obtained for ^{131}I .

Several parameters have been investigated, to a limited extent, with crushed rock columns. Flow rates were varied from 0.082 mL/h to 18 mL/h on three JA-32 tuff columns loaded with ^{85}Sr . However, the fast flow column was run with ^{85}Sr tracer added to the groundwater, rather than loaded onto the column in a spike. Other fast flow columns were ^{137}Cs (spike) on tuff YM-38#3 run at ~4 mL/h and granite CS-5#2 loaded with ^{85}Sr , ^{137}Cs , ^{133}Ba (spike) and run at ~5 mL/h. Argillite columns, with ^{95m}Tc , ^{131}I , and HTO , were run under controlled atmosphere conditions (≤ 0.2 ppm oxygen, ≤ 20 ppm carbon dioxide) as well as in air. The effect of the cesium ion concentration on tuff was also investigated. Two YM-54 columns were loaded with ^{137}Cs in a 5- to 15- μL spike at a concentration of $\sim 10^{-6}$ M. Another YM-54 column was also run with a continuous feed of ^{137}Cs at a concentration comparable to that of the batch measurements, $\sim 10^{-9}$ M, to see if the R_d value of cesium increased with the decreased cesium ion concentration.

Since the sorption ratios measured for uranium(VI) are small, the retardation factor should also be small. With the columns now used in this laboratory, the volume of eluate of interest is small enough to require drop collection. A method to perform this has been devised using a syringe pump (Sage model 352) and a fraction collector (ISCO model 1200) used in drop mode. Aluminum planchets have been made to fit the collection holders.

The columns are loaded with ^{131}I and ^{235}U simultaneously. This eliminates any uncertainties caused by different conditions during determination of free column volume and radioisotope collection.

Some difficulty was encountered due to the loss of iodide when it was dried in carrier-free form. Experiments showed that the I^- can be "fixed" Filter paper disks were punched to fit the bottom of the planchets and were pretreated with 100 μL of NaHSO_3 (~1 mg) and 100 μL of NaI (~2 mg) and then were air dried. After sample collection, 50 μL of AgNO_3 (~0.5 mg) was added

to the paper disks, which were air dried again. These fixers made very stable samples which had good reproducibility.

Because of the slow drop rate and low humidity, the drops may evaporate on the column tip before collecting. Hence, the fraction collector and column were placed in a humidity box ("Manostat" glove box with the glove holes capped) where ~100% humidity was maintained. Thin tubing (0.15 cm) connected the syringe pump to the column.

The ^{131}I and ^{237}U on each planchet (1 drop) or in the scintillation vials are determined using a Ge(Li) detector in conjunction with an automatic sample changer. The 208-keV gamma from ^{237}U and the 364-keV gamma from ^{131}I are readily analyzed.

2. Data Collection and Analysis. Methods of sample collection, detection of radioisotopes, data analysis, and equations for calculation of retardation factors and corresponding distribution coefficients (R_d) have previously been described (Refs. 8 and 12).

3. Results and Conclusions. A description of the crushed rock columns studied is given in Table XIX. The calculated column distribution coefficients for the isotopes ^{85}Sr , ^{137}Cs , and ^{133}Ba are given in Tables XX-XXII, along with data from batch sorption measurements for comparison.

Several kinds of elution behavior have been observed: symmetric peaks where fifty percent of the activity eluted corresponds closely to the peak of the elution curve, asymmetric peaks, and "no peaks" - but instead a slow, usually uniform elution of activity. Plots of elution curves having symmetric and asymmetric peak shapes have been given in Refs. 8 and 12. With the exception of JA-18#1 and YM-38#1 tuff columns (see Table XIX), the elution curves of ^{85}Sr have fallen into the first category, i.e., "symmetric peaks", with the column R_d value being one to three times lower than the corresponding batch R_d value. Three JA-32 columns were loaded with ^{85}Sr to compare the effect of varying the flow rate from 0.082 ml/h to 18 ml/h. The effect of flow rate on the calculated distribution coefficients was negligible. However, as mentioned earlier, the fast-flow column was run with ^{85}Sr tracer added to the groundwater rather than loaded as a spike as were the slow-flow-rate columns. With two granite columns, CS-5#1 and CS-5#2, both loaded with a spike of activity, a considerable increase in R_d was observed when the flow rate was increased from 0.04 ml/h to 4.98 ml/h. Increases from 8.5 ml/g to 25 ml/g and from 32 ml/h to 165 ml/g were obtained for ^{85}Sr and ^{133}Ba , respectively.

TABLE XX
⁸⁵Sr: A COMPARISON OF BATCH AND COLUMN R_d VALUES

Column	R _d (ml/g)		Comments
	Batch	Column	
CS-5#1	14	8.5	
CS-5#2	14	25	Fast flow (4.98 ml/h), total vol = 2390 ml
CS-7	18	15	
YM-22	50	30	
JA-32	56	42	
YM-54	84	44	
CN-1	138	43	
CN-2#1	156	52	
JA-37	300	106	
JA-18#1	16 000	381(9%)	23% removed, 9% of which was in a peak
JA-18#3			In progress
YM-38#1	12 000	>460	Activity decayed prior to eluting

TABLE XXI
¹³⁷Cs: A COMPARISON OF BATCH AND COLUMN R_d VALUES

Column	R _d (ml/g)		Comments
	Batch	Column	
YM-54	247	97	Peak, with 90% ¹³⁷ Cs; average of 3 columns
YM-22	287	122	Peak, with 95% ¹³⁷ Cs (broad peak)
CS-7	328	>606	20% removed in 314 ml (52 weeks) ^a
CS-5#1	347	>665	8% removed in 352 ml (52 weeks) ^a
CS-5#2	347	"706"	50% removed in 908 ml, peakless
JA-37	740	>560	3.6% removed in 182 ml (26 weeks) ^a
CN-2#1	1580	>520	0% removed in 235 ml (40 weeks) ^a
CN-1	1830	>570	0% in 243 ml (40 weeks) ^a
YM-38#3	8600	>21 900	50% removed in 7680 ml, "peakless"
JA-18#1	6 600-15 000		13% removed in 100 ml (27 weeks) ^a
JA-18#3			In progress

^aIn progress.

TABLE XXII
¹³³Ba: A COMPARISON OF BATCH AND COLUMN R_d VALUES

Column	R _d (ml/g)		Comments
	Batch	Column	
CS-5#1	154	32	
CS-5#2		165	Fast flow, broad peak
CS-7	175	44	
YM-54	620	124	
YM-22	899	355	
JA-18#3	4 800		In progress

Only a partial (peakless) elution has been obtained for ¹³⁷Cs to date on the slow-flow rate column. A "peakless R_d" of 706 ml/g was obtained on the fast-flow column.

The YM-38#1 column was loaded with ⁸⁵Sr before the batch R_d measurement (12 000 ml/g) was completed. None of the strontium (t_{1/2} = 65.2 days) was eluted before the isotope decayed. A Polaroid film exposed to the YM-38 column several months after elution was started indicated that the ⁸⁵Sr remained in the top quarter of the column. Petrographic analysis on crushed rock from YM-38#1, as well as JA-32#1, was done both before and after elution. No change in YM-38 was observed, while there was a slight alteration of feldspar in the JA-32 tuff (M. L. Sykes, Los Alamos Scientific Laboratory, personal communication, 1980). The JA-18#1 column was the only other one loaded with ⁸⁵Sr for which a large batch R_d value (16 000 ml/g) had been measured. The strontium on this column was eluted at a rate of ~0.07%/day for ~72 days; then a small, sharp peak (R_d = 381 ml/g) containing 9% of the total activity was observed. Elution of the JA-18#1 column has continued for 95 days since the peak was observed, and the slow, uniform "leaking" has resumed. The JA-18 sample is a highly glassy tuff and the slow elution may be due to a gradual dissolution of the glass. This, however, would not explain the weak, sharp peak which seems to indicate that more than one "sorption" mechanism exists. The JA-18#1 and YM-38#3 columns were also loaded with ¹³⁷Cs and the same slow "leaking", without a sharp peak, was observed. Besides dissolution of the glass, the slow elution of ⁸⁵Sr and ¹³⁷Cs might also be the result of exchange of the sorbed radioactive species with stable isotopes in the pretreated waters

used, which contain $\sim 10^{-9}$ M cesium and $\sim 6 \times 10^{-7}$ M strontium. Another column, JA-18#3 was started about $3\frac{1}{2}$ months ago to see if the results obtained are reproducible.

Other cesium column data are given in Table XXI. The most straightforward results are from tuff columns of YM-54 (3 columns) and YM-22 (1 column), where the batch distribution coefficients are fairly small and values from desorption and sorption experiments are approximately equal. They are the only columns containing cesium analyzed to date where elution of the activity occurred in a peak. The three YM-54 columns were run at two ^{137}Cs concentrations, 10^{-6} M and 10^{-9} M, to see if the R_d value calculated for cesium was affected by the cesium ion concentration. No effect was observed. On two granite columns, CS-5#1 and CS-7, a slow elution of ^{137}Cs began at about day 48 and has continued for one year. A third (CS-5#2) column, run at ~ 5 ml/h, was completed. In that column ^{137}Cs was also removed in a slow, peakless, elution. On argillite, after 40 weeks, no ^{137}Cs has been eluted from either of two columns; however, the cesium batch R_d values on argillite are approximately five times larger than those for granite, and a similar slow elution behavior may still occur. On the JA-37 column, elution of ^{137}Cs began on day 95 and the activity has increased from 25 to 500 dpm/ml. In 184 days, 3.6% of the total cesium has been removed.

In another column, ^{137}Cs was loaded onto YM-38 tuff and run at a fast (4-5 ml/h) flow rate. The ^{137}Cs was not detected until 1150 ml had passed through the column. Fifty percent of the total ^{137}Cs was eluted in 7680 ml; in slowly increasing amounts. (If the average flow rate used on the majority of columns had been used in this case, about 29 years would have been required to collect the total of 10.5 l eluted.) Although a sharp peak was not observed, and the mathematical expressions relating distribution coefficients with retardation factors are not appropriate for such cases, one can calculate a "lower limit" column R_d value of $>21\,900$ ml/g from the volume required to elute 50% of the activity. This is a value well above that obtained from batch measurements (8600 ml/g), is indicative of the "complications" revealed by flow experiments, and is probably due in part to the fast flow rate used.

All of the columns run to date with ^{133}Ba have shown peaks, followed in some cases by a gradual elution of activity. The R_d values calculated from the columns are given in Table XXII; they are 2.5 to 4.8 times lower than the corresponding batch R_d values, except for CS-5#2, run at a fast flow rate,

where the column R_d was 1.07 times higher than the batch R_d . The ^{133}Ba peak from CS-5#2 was also considerably broader than that from CS-5#1. It is also apparent from Table XXII, that only materials with relatively low distribution coefficients for barium have been used in columns. Thus, the more complicated situations, better revealed by high R_d values, have not yet been studied with barium. On YM-54 and YM-22 tuff, with batch R_d values of 620 and 899 ml/g, respectively, the batch sorption and desorption ratios for barium were found to be equal, implying a reversible interchange of ions. With "comparable" batch sorption R_d numbers (see Table XXI), cesium on columns of granite, JA-37 tuff, and argillite, did not elute in simple peaks. This was perhaps due to desorption R_d values at least a factor of two larger than the sorption R_d values. This suggests that more than one species and/or mechanism with different rates of reaction are present during sorption (and absent in batch desorption measurements), or that weathering in the batch studies and mineral alteration is affecting sorption vs desorption. For the granite columns the peaks of the barium elution curves represented less than half of the total activity and were followed by a slow, uniform elution. Barium batch desorption values were about twice those for sorption for this material.

Other isotopes studied, but not indicated in Tables XX-XXII, were ^{141}Ce , ^{95m}Tc , ^{237}U , and ^{131}I . The cerium which was loaded on a YM-45 tuff column [batch R_d of 730 ml/g (sorption), 5700 (desorption)] was not eluted in 165 days at a flow rate of ≤ 1.020 ml/days. Since the ^{141}Ce had decayed significantly in that period of time and the column could not be continued much longer, the flow rate was increased to ≤ 0.6 ml/h until a total of 250 ml had been collected from the column. No ^{141}Ce was detected, indicating that the R_d value is > 880 ml/g; however, counting the whole column loaded with ^{141}Ce , both before and after elution, indicated that $\sim 6\%$ of the ^{141}Ce had been removed from the column. The YM-38#2 column was run for 112 d at a flow rate of 0.911 ml/days with no ^{141}Ce detected in the eluate; it was stopped due to insufficient ^{141}Ce remaining on the column. The lower limit for the column R_d was 430 ml/g compared with batch values of 830 ml/g for sorption and 3800 ml/g for desorption. Another column, JA-18#2, was loaded with ^{141}Ce as well as ^{152}Eu . In nine months a small fraction of the ^{152}Eu was eluted.

A tuff column, YM-54#4, loaded with spikes of tritium, ^{131}I and ^{237}U gave an R_d value of 0.72 ml/g for uranium, compared with an average batch R_d value of 1.5 ml/g. The uranium peak was quite asymmetric, and the

concentration of uranium in the eluate slowly decreased. Again, the marked asymmetry could be related to the large difference between batch sorption (1.5 ml/g) and desorption (11 ml/g) ratios.

Technetium breakthrough occurred simultaneously with tritium and ^{131}I on argillite under both atmospheric conditions (CN-2#2) and controlled-atmosphere conditions (CN-3, nitrogen, ≤ 0.2 ppm oxygen, and ≤ 20 ppm carbon dioxide). The ^{131}I and HTO had identical breakthrough curves indicating no retardation of iodide on argillite, in contrast to that previously indicated by batch measurements. The column R_d values for ^{95m}Tc , 0.4 ml/g on CN-2 and 0.3 ml/g on CN-3, were considerably less than those obtained by batch techniques, 30.5 ml/g for CN-2 in air (Ref. 6) and 175 ml/g for CN-3 in ≤ 0.2 ppm oxygen, ≤ 20 ppm carbon dioxide (Ref. 9). However, the columns were run at a fast flow rate (~ 2 ml/h), reducing the time of contact between technetium and the rock by 80 to 700 times that of the batch measurements. The fast flow could also be responsible for the lack of effect of the ≤ 0.2 ppm oxygen atmosphere by limiting the time available for reduction of pertechnetate. Since the sorption of technetium on argillite has been shown to be strongly time dependent, particularly under ≤ 0.2 ppm oxygen conditions, (Section IV.B above) the observed difference between batch and column R_d values seems reasonable and can be easily checked by short-contact-time batch measurements.

A general conclusion based on these results, particularly the data for ^{85}Sr , ^{137}Cs , and ^{133}Ba on granite, argillite, and tuff, is that - except in the simplest of cases, where sorption coefficients are relatively low, and reversible ion-exchange is apparently the dominant mechanism for removal of radioisotopes from solution - the simple, theoretical relation between the distribution coefficient R_d or K_d and the relative velocity of radionuclides with respect to groundwater velocity does not accurately describe the actual retardation of radionuclides. We must study the mechanisms causing retardation in order to understand the relationship between sorptive behavior in dynamic laboratory experiments (and, ultimately, behavior in the field) and the many available batch R_d data.

I. Sorption Measurements Using a Circulating System (R. D. Aguilar, B. R. Erdal, and E. N. Vine)

It has been observed¹⁻¹² that frequently the sorption ratios determined by use of the batch technique increase slowly with contact time. One

possible explanation for this observation is that there is self-grinding of the crushed rock due to the shaking used to stir the rock-water mixture in the batch technique. A series of experiments have been initiated to determine whether the shaking results in a change in the R_d values. A circulating system is being used in which a 355-500- μm fraction of crushed rock is placed in a polycarbonate column (1.0 cm diam. x 5.0 cm long), and the appropriate groundwater is continuously circulated through the column in a closed loop as a substitute for the shaking in the usual batch experiment. The columns have polyethylene bed supports and polypropylene Luer fittings on each end. A peristaltic pump (Pharmacia model P-3) is used to produce flow rates of 0.6 ml/min.

Experiments have been started with columns containing five different types of crushed rock, each using the groundwater characteristic of that sample: CS-5 granite, CN-2 argillite, and JA-37, YM-22, YM-54 tuffs. The columns hold about 4.5 g of rock, and an initial solution-to-solid ratio of ~15 ml/g (compared to batch experiment ratios of ~20 ml/g) was used. First, the groundwater was circulated for two months to check out the system and to pretreat the rock samples. Rock-pretreated groundwaters were tagged with ^{85}Sr , ^{137}Cs , ^{133}Ba , ^{141}Ce , and ^{152}Eu by the usual evaporation-dissolution procedure. The circulation of these tagged groundwaters is now in progress. Since the sorptive capacity of some of the components in the systems is unknown, groundwaters are being circulated through similar systems without rock. Aliquots (5 ml) of the aqueous phases were removed at intervals of 4, 7, 9, and 12 weeks, and at least one more sampling will be done at ~16 weeks. Preliminary data are given in Table XXIII. The time dependence observed in the batch studies^{1,2} does not seem to be present in these early results.

J. Radionuclide Sorption Studies Using Solid Rock Cores (J. L. Thompson, W. R. Daniels, R. S. Rundberg, S. Maestas, and N. A. Raybold)

Radionuclide sorption on rocks is a surface phenomenon, and, therefore, the surface condition is a critical parameter in experiments involving partitioning of radionuclides between solutions and geologic media. Studies utilizing crushed rock involve mineral surfaces newly exposed to the atmosphere and to water; those utilizing geologic thin-sections involve surfaces exposed and possibly altered by grinding and polishing. In an attempt to work with unaltered rock surfaces, we have initiated experiments in which pumped groundwater is used to move radionuclides through rock cores.

TABLE XXIII
Sr, Cs, Ba, AND Eu SORPTION RATIOS
CIRCULATING COLUMNS

<u>Material</u> ^a	Contact <u>Time (d)</u>	<u>R_d (mℓ/g)</u>			
		<u>Sr</u>	<u>Cs</u>	<u>Ba</u>	<u>Eu</u>
Granite-1	26	8.2	421	54	372
	49	7.5	360	56	685
	63	6.2	339	52	
Granite-2	26	8.5	370	56	
	49	7.3	386	53	
	63	5.3	339	47	
Argillite	26	48	3 700	655	
	49	46	3 810	645	
	63	43	3 310	536	

^aGranite columns 1 and 2 contained 4.3 and 4.5 g, respectively.

The intent of these experiments is to achieve an understanding of the transport of radionuclides through rock by either porous or fracture flow. These studies represent an intermediate step in the extrapolation from batch to in situ studies.

The apparatus has been described previously.⁸ The rock cores are 15.9-mm-high by 25.4-mm-diameter right-circular cylinders. The confining pressure is usually 1000 psi. The groundwater for these experiments is first treated with the appropriate crushed tuff, then centrifuged and filtered through a 0.05-μm filter. Prior to the introduction of radionuclides to the rock cores, pretreated water is forced through the cores so as to minimize alteration of the rock during the actual elution experiment and, hopefully, to better simulate the actual, in situ, conditions.

1. ⁸⁵Sr in YM-22 Tuff. An experiment was conducted with ⁸⁵Sr sorbed on a core of YM-22 tuff. This tuff is devitrified and densely welded and has relatively low sorptive properties. The core was loaded with 20 μℓ of ⁸⁵Sr tracer solution, and water was then pumped through the core for a period of

12 months at an average flow rate of 0.8 ml/day. About 40% of the ^{85}Sr was eluted at a fairly constant rate; no peak was observed. The core was sectioned, and the residual ^{85}Sr concentration was found to be relatively low in the top few mm of the core. A peak occurred in the core midsection, and the concentration remained high throughout the remainder of the core (see Fig. 5). Based on the anticipated volume corresponding to elution of 50% of the ^{85}Sr , the R_d value for strontium on this YM-22 core was crudely estimated to be ~ 20 ml/g, which is less than the 53 ml/g value obtained from batch measurements.¹² This difference is similar to those obtained with crushed rock columns and batch results (Section IV.H above). More elution and distribution profile studies of this type will be conducted after modifications in our experimental methodology have been completed.

2. ^{241}Am in YM-45 Tuff. The movement of ^{241}Am through a YM-45 core was observed by monitoring the eluted solution and using microautoradiography on core slices. The column was run for 5 weeks with a flow rate of 0.8 ml/d. Approximately 0.2% of the ^{241}Am added to the column was collected.

On disassembly of the pressure apparatus, it was found that the metal end cap in contact with the top surface of the core showed a high level of radioactivity and that the bottom end cap showed almost none. The alpha activity on the core sides and bottom was measured using microautoradiography. Low to moderate levels of alpha activity due to ^{241}Am were found on these surfaces. The ^{241}Am seemed to have been deposited primarily in an aggregated form, as indicated by the high ratio of stars to single tracks. One giant colloidal particle was observed on the bottom surface.

The core was then sectioned with a rock saw, with three slices about 1 mm thick being cut from the top of the core and one such slice from the bottom of the core. The ^{241}Am in these slices was measured with a NaI(Tl) well crystal and an alpha proportional counter. The alpha activity on the top core surface was $10^3 - 10^4$ times greater than that on the bottom of the top slice and the other interior surfaces. The alpha activity levels on the exterior surfaces and on the interior slice surfaces were compared using a collimator with the proportional counter. The exterior surfaces had activity levels greater by a factor of five than the interior surfaces. The activity on the exterior surface was relatively uniform, differing from region to region by only a factor of two.

Fig. 5. Distribution of ^{85}Sr in a solid core of YM-22 tuff.

The results of this experiment indicate that almost all of the ^{241}Am originally placed on the top core face remained there. The small fraction of ^{241}Am which was mobilized by the water flow appears to have been deposited at higher concentrations on the exterior surfaces than in the interior of the core. This may imply that more flow occurred over these exterior surfaces than through the core, or alternatively that these surfaces were particularly sorptive. The fact that a large fraction of ^{241}Am was in an aggregated form on the exterior surfaces, however, suggests that this portion did not flow through the core.

3. ^{241}Am in Climax Stock Granite. Climax Stock granite core C-79-5b-1 was placed in a Teflon sleeve and fractured using a hammer and chisel. The crack occurred along an old fracture plane extending through the core. After initial attempts to force water through the core failed, the two core segments were displaced axially and then returned to the initial configuration. A reasonable flow rate was then achieved. Solution containing ^{241}Am was placed

on the top surface of the core at the crack. Water was pumped through the core for a period of five weeks with about 2% of the ^{241}Am being eluted.

On disassembly it was noted that both metal end caps showed extremely high levels of alpha activity. The whole core was counted in the NaI(Tl) well counter, then sectioned with the rock saw. The first three slices from the top of the core and the first slice from the bottom shattered into six to eight fragments during the sawing operation. These were recovered and counted in the well counter. The ^{241}Am activity for each of these slices is given in Table XXIV.

The second slice from the bottom was recovered intact and was coated with emulsion for examination using microautoradiography. Also, examinations of the interior surfaces of the core midsection and of a reconstructed mosaic of the second slice from the top were performed using glass slides coated with Kodak ETB-3 emulsion. The emulsions showed that a very large fraction of the ^{241}Am was confined in the major crack system. Some alpha tracks were readily visible along the Teflon sleeve-core interface, especially in the regions where cracks reached the core surfaces. The tracks not in the vicinity of the cracks were mostly single with a few stars and were present in rather low density. No colloids were observed.

The exterior (curved) surface of the core midsection was monitored using a collimator and the proportional counter. The ends of the midsection were coated with epoxy to facilitate handling and to prevent detection of alpha particles from the cut faces which were originally interior portions of the core. The surface alpha activity at various angles of rotation of the core under the counter is shown in Table XXV.

The counting data and microautoradiographs indicate that the ^{241}Am was strongly concentrated in those regions which the solution could readily penetrate, namely, the major crack system and the exit line of the cracks at the core surface. Although the ^{241}Am was distributed the length of the core, the concentration in the topmost slice was about a factor of three higher than elsewhere. It would appear that the ^{241}Am was deposited primarily on those surfaces initially contacted by the ^{241}Am tracer solution. In addition to the alpha activity on the surfaces near the cracks, there was significant activity on the other regions of the core surface, indicating exposure of these surfaces to the aqueous phase containing ^{241}Am .

TABLE XXIV
²⁴¹Am IN VARIOUS SECTIONS OF A CLIMAX STOCK CORE

<u>Slice</u>	<u>Width</u>	<u>Activity (cpm/mm)</u>
1st	1 mm	6.5 x 10 ⁵
2nd	1 mm	2.3 x 10 ⁵
3rd	1 mm	1.4 x 10 ⁵
Midsection	8 mm	2.0 x 10 ⁵
2nd from bottom	1.5 mm	1.3 x 10 ⁵
1st from bottom	1.5 mm	1.5 x 10 ⁵

TABLE XXV
²⁴¹Am ACTIVITY vs ORIENTATION OF CORE SLICE

<u>Degrees of Rotation</u>	<u>Alpha Activity (c/m)</u>	<u>Comments</u>
0	187	
45	5 334	Crack visible
90	82	
135	4 286	Crack visible
180	56	
225	1 106	
270	57	
315	74	
360	172	

4. Encased Cores. The data in the preceding two experiments, as well as evidence from previous studies,⁸ strongly suggest that there is leakage of pumped water between the Teflon sleeve and the core surface. For example, higher alpha activity levels were sometimes found on the exterior surfaces of the core than on the interior surfaces of the core slices. Possible routes for this exterior flow were thought to be: (1) leakage along the top surface between the end cap and the core and then down the core sides and (2) flow from within the core to the side surfaces, then down the core sides. If the sorptive behavior of solid cores is to be compared with that of crushed rock

columns, it is imperative to be able to define with confidence the volume of rock exposed and the flow rate through this volume.

Experiments were performed to develop a method of completely encasing the cores in a material impermeable to water. A polyurethane and an epoxy were tested with and without confining pressure. The polyurethane was tried in two experiments with YM-45 tuff. One core was given a thin coating on the curved surfaces and was then inserted in a Teflon sleeve. The other was cast in a mold with both end caps; the polyurethane thickness was 4 to 8 mm. This second core was used with no confining pressure. The core with the thin coating was fitted with polyethylene washers, end caps, and a confining pressure of 5000 psi was imposed. The cores were treated with filtered, pretreated groundwater, and then ^{233}U was loaded on the top face of each core. Water was pumped through the cores at about 30 psi, which gave a flow rate of about 1 ml/d. Some ^{233}U appeared in the eluate after 2.5 to 3 ml of water passed through the cores, and the cores were then removed for analysis using microautoradiography. In the case of the core with the thin coating, substantial amounts of alpha activity were found on the exterior surfaces. It was not clear whether this was due to leakage from the top (although the washer did appear to confine most of the ^{233}U placed on the top face), flow through surface areas not completely coated with the polyurethane, or simply penetration by alpha particles of the very thin coating. The rock with the thick coating evidenced no leakage around the end caps, and the rock-to-resin bonds seemed to have maintained their integrity. Some variation in the alpha activity levels near the rock surfaces were observed.

Several granite cores were encased in epoxy by casting in a mold, and the epoxy pottings were tested for their ability to withstand pressure. One core was fitted with end pieces with a polished surface, and another with end caps which had been sand-blasted. These were attached to the high pressure column apparatus, and the pumping pressure was gradually increased (no confining pressure was employed). Both epoxy coatings held overnight at a pressure of 360 psi. A third granite core was placed under a confining pressure of up to 5000 psi with no leaks occurring. The confining pressure was dropped to 2000 psi, and a gradually increasing pumping pressure was imposed. The maximum imposed pressure of 880 psi was held for a period of 3 days with no leakage.

Several different types of rock cores were examined to determine the ^{233}U distribution in the core at the point at which it was just beginning to be eluted. Of particular concern were the extent of penetration of the epoxy into the core (which might inhibit the water flow) and the possibility that the ^{233}U might concentrate in regions containing the epoxy.

A core of YM-54 tuff was coated with epoxy and loaded with ^{233}U . With the aid of a small rock saw the end caps were removed and the core was sliced into several sections. Surface activity as measured with a proportional counter and by autoradiography revealed that most of the ^{233}U had penetrated only about 5 mm down into the core. Within this region of penetration there was not much spreading toward the perimeter of the core. At the top face of the core, the ^{233}U had been confined largely to the area in the center of the washer, and at a depth of 4.7 mm most of the ^{233}U was still concentrated in the center of the core. This flow pattern is in marked contrast to that previously observed for a JA-26 tuff core in which the ^{233}U was distributed uniformly below a depth of a few millimeters, showing no concentration gradients across the face of the core slices. Although the washer did prevent ^{233}U from spreading over the entire top face of the core, some penetration of washer-rock and washer-end cap interfaces was indicated, and the alpha activity levels on both surfaces of the washer were appreciable.

A granite core, C-79-9b-1, which had been coated with epoxy and tested for leaks under confining pressure, was treated with ^{233}U in an experiment similar to that described above for the YM-54 tuff. In this case, a pumping pressure of about 880 psi under a confining pressure of 2000 psi for a period of one day gave an eluant volume of 0.1 ml which contained about 3% of the initial 10^6 cpm of activity introduced onto the top of the core. As in previous experiments, the polyethylene washer confined most of the ^{233}U to the top center of the core face; however, this pattern was not maintained into the core. The alpha activity levels on the interior surfaces of slices taken through the core were very low. A system of cracks over about 25% of the slice area seemed to be responsible for all of the flow through a slice taken about 3 mm from the top face of the core. Similarly, the top side of the bottom slice had ^{233}U confined to two small areas; however, on the bottom of this slice (the bottom exterior of the core), the concentration level was nearly as high as on the top surface. Likewise, the bottom end cap was found to have nearly 60% as much ^{233}U as the top end cap. This would seem to

indicate that a "reservoir" of radioactive solution accumulated at the bottom face of the core, perhaps with the bottom washer inhibiting clean elution from this area. In neither the tuff nor the granite core was there any indication that the epoxy had penetrated appreciably into the core, nor were there regions of high track density near the core-epoxy interface.

K. Microautoradiography (E. N. Vine)

A microautoradiographic technique used to look at americium retained on filter membranes was described previously (Section IV, Ref. 8). Studies of the "sorption" membranes had shown that not only was americium uniformly sorbed on the filter but also that americium species in a large range of particle sizes were retained.

Most "desorption" membranes, however, showed only single alpha tracks, suggesting that large particulates were not removed from the solids (assuming they had been sorbed) nor were they formed in the aqueous phase during contact. Since it was not known if any of the complex species or polymers which were found to be present in the sorption solutions had been sorbed and were thus "available" to the desorption solutions, the microautoradiographic technique was used to look at the crushed rock itself, after completion of the desorption experiments. Five rock samples were examined and all had "clusters" present, indicating that large species were indeed sorbed. However, only in one case were clusters present in the corresponding desorption solution.

L. Materials Characterization (B. P. Bayhurst, E. N. Vine, N. L. Ott, G. E. Bentley, J. R. Smyth, A. J. Gancarz, W. R. Daniels, and F. O. Lawrence)

1. Determination of Iron(II) in Silicate Rocks. The presence of Fe(II) and Fe(III) has important effects on the oxidation potential in geological systems. Total iron can easily be determined; however, a good method for determination of Fe(II) in silicate rocks must involve careful techniques to keep the Fe(II) from being oxidized during preparation, dissolution, and determination. In most procedures, hydrofluoric acid is used, thus restricting the container composition. The method that we have selected is based on a procedure¹⁵ in which the silicate rock is dissolved in the presence of ICl. Dissolution results in the simultaneous oxidation of Fe(II) and formation of I₂. The I₂ is immediately extracted into carbon tetrachloride which is present in the dissolving vessel. Iodine monochloride has a lower oxidation

potential than either permanganate or dichromate, so the use of ICl as oxidant precludes interference by Mn(II) or Cr(III). Pertinent half-cell reactions are

The method described above has been modified and tested on several USGS "standard" rocks. The results (see Table XXVI) were usually within 2% of the stated Fe(II) concentration. The I_2 was determined by titration with a standardized KIO_3 solution in such a manner as to prevent the carbon tetrachloride containing the iodine from contacting air.

The concentration of Fe(II) in the CS-7 granite was determined to be 1.26%. A sample of the same granite, which had been crushed and analyzed in a nitrogen atmosphere (≤ 0.2 ppm oxygen), was found to contain 1.13% Fe(II). The small difference is probably due to sampling errors. No Fe(II) was detectable in YM-22, YM-38, and YM-46 tuffs.

TABLE XXVI
Fe(II) ANALYSES ON USGS^a "STANDARD" ROCKS

"Standard" Rock	% FeO		% Deviation
	LASL ^b	USGS ^a	
DTS-1 (Dunite)	7.26	7.23	+0.4
PCC-1 (Peridotite)	5.11	5.24	-2.5
BCR-1 (Basalt)	8.81	8.80	+0.1
GSP-1 (Granodiorite)	2.23	2.31	-3.5
AGV-1 (Andesite)	2.02	2.05	-1.5

^aUSGS = U. S. Geological Survey.

^bLASL = Los Alamos Scientific Laboratory.

2. Determination of Iron(II) in Groundwater. Knowledge of the Fe(II)/Fe(III) concentration ratio in solutions that have been in contact with rocks under various conditions should help in the interpretation of sorption results for multivalent elements and may substantiate Eh measurements. A method modified from that of Lee and Stumm¹⁶ is being used; the limit of detection is about 0.2 µg/ml. Correction is made for a small interference from Fe(III). The 4,7-diphenyl-1,10-phenanthroline reagent used is more sensitive and the color developed is more stable than other phenanthrolines. Iron-free reagents have been prepared for use in the analysis. Absorbance is measured at 533 mµ with a Hewlett-Packard model 8450A UV/VIS spectrophotometer.

3. Emission Spectrometric Analysis of Groundwaters. The Spectrometrics, Inc., twenty-channel, direct current, plasma-source, emission spectrometer described in Ref. 8 is being used to analyze the extensive suite of acid-stabilized solutions saved from the majority of our batch sorption studies.^{1,2,3,12} The samples are being analyzed for the elements on the first two cassettes described in Ref. 8 (the major ions plus representative minor elements). Selected samples are being analyzed for rare earth constituents using the fourth cassette.

The results will be summarized in a future report, as will the conclusions reached concerning the effect of water composition on sorption behavior. Data are being entered into a computer data base for future processing.

4. Analysis of the Clays in the Eleana Argillite. The analyses of the clays in Eleana samples CN-3 and CN-4 have been checked using a new Siemens diffractometer. Both samples are approximately 50% quartz. The principal clay mineral is kaolinite, comprising about 30% of each sample. The remaining 20% is approximately equal amounts of illite and smectite (montmorillonite), probably as a mixed-layer clay. All clays in this sample appear to be stack-disordered.

Using our previous methods,² it was impossible to distinguish illite from varieties of smectite (montmorillonite), particularly when they form only 50% of a sample. The Eleana clay was previously reported² as montmorillonite-kaolinite, which is reasonably close. The results of the current investigation indicate that it might be better termed "kaolinite-mixed-layer-montmorillonite-illite."

5. Assay of ²³⁷Pu. There has been some concern about the actual total plutonium concentration in the ²³⁷Pu samples received from ANL under contract to the WRIT project; therefore, the ²³⁷Pu sample received at LASL in January, 1980 was analyzed using mass spectrometry techniques. The results of these

measurements are given in Table XXVII. The actual plutonium concentration in solution as of April 11, 1980 was 5.14 times larger than the value originally calculated based on the ^{237}Pu activity alone.

V. CHEMISTRY STUDIES IN THE REPORTING PERIOD

A. Preliminary Considerations with Respect to Actinide Solubilities (T. W. Newton)

During the past year we have begun work on fundamental solution chemistry pertinent to the WRIT project.^{9,10,11} Thus far, work has been confined to preliminary considerations of the problems involved in developing an understanding of the precipitation/dissolution behavior of actinide compounds under environmental conditions. For the first step in gaining this understanding we have restricted our considerations to equilibrium solubilities in the absence of complexing agents and have limited the compounds to actinide oxides and hydrated oxides, or hydroxides.

In order to get a preliminary idea of the solubility behavior, we have attempted to calculate solubility as a function of Eh and pH using the appropriate thermodynamic data. The solubility of a substance is the sum of the concentrations of all the species that are in equilibrium with it; for an actinide oxide or hydrous oxide these will be all the hydrolyzed forms of the usual four oxidation states (the +7 states of Np and Pu can safely be ignored). For each oxidation state the concentrations of these hydrolyzed species depend on the hydrolysis constants and the concentration of the unhydrolyzed species (see the Appendix for the relevant equations). When the solid phase is the +4 oxide or hydrous oxide, the concentration of the unhydrolyzed species (An^{+4}) is determined by the value of the solubility product and the pH. The concentrations of the other three unhydrolyzed species will depend on the Eh, the pH, and the standard oxidation potentials in accord with the Nernst equation. Thus, if the solubility products, hydrolysis constants, and oxidation potentials are available, the solubilities can be calculated in a direct way. Unfortunately, almost none of the required data have been accurately determined, so we have used recently published estimates.¹⁷ Our results are presented in terms of "contour maps" showing lines of constant solubility as a function of Eh and pH. Calculations have been made for the +4 oxides and hydrous oxides of uranium, neptunium, and plutonium. As an example, the results for $\text{PuO}_2 \cdot n\text{H}_2\text{O}$

TABLE XXVII
ISOTOPIC ANALYSIS OF ^{237}Pu

<u>Mass</u>	<u>Atom %</u>	<u>Relative to ^{237}Pu</u>
236	19.3	0.992
237	19.5	$\cong 1.00$
238	16.8	0.862
239	25.6	1.32
240	17.4	0.894
241	1.4	0.073

are shown in Fig. 6. The diagrams were constructed under the assumption that conversions of the hydrated oxides to the more stable crystalline oxides are slow compared with the establishment of the solubility equilibria. In spite of the uncertainty in the input data we have found the results to be very instructive; they show that the Eh and pH dependences are certainly quite complex. In addition, these results will be of value in planning solubility experiments and in interpreting the data.

The solubility diagram for $\text{PuO}_2 \cdot n\text{H}_2\text{O}$ (Fig. 6) is divided into two regions by a solid diagonal line; below this line the solid phase is the +4 hydrated oxide, while above the line the +6 hydroxide is stable. It is not surprising that rather abrupt changes in solubility occur when crossing this line. The upper dotted line on the diagram represents the potential of the water/oxygen couple: $2\text{H}_2\text{O} = \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$; systems with apparent Eh values below this line are thermodynamically unstable in the presence of one atmosphere of oxygen. Reactions involving this couple are usually very slow, so the potential for the more rapid $\text{H}_2\text{O}_2/\text{O}_2$ couple, $\text{H}_2\text{O}_2 = \text{O}_2 + 2\text{H}^+ + 2\text{e}^-$, is also shown. Systems with potentials below this line are expected to react reasonably rapidly with oxygen.

The diagram shows that the calculated minimum solubility occurs at the bottom of a basin with approximately triangular contours. Three distinct principal solubility equilibria are associated with the regions showing diagonal, horizontal, and vertical contour lines, respectively. In the lower left of the diagram the contour lines show a slope of about -4×0.059 , and the plutonium half-reaction for the principal equilibrium is

Fig. 6. Lines of constant log(solubility) vs Eh and pH for plutonium hydrous oxides.

Further up on the diagram where the contours are horizontal, the half-reaction is

This result is consistent with the observations of Rai and coworkers at Battelle Pacific Northwest Laboratory (PNL), who showed that where Pu(V) is the principal solution species in contact with $\text{PuO}_2 \cdot n\text{H}_2\text{O}$, the solubility depends on the Eh but is essentially independent of pH. In the lower part of the diagram where the contours are vertical, the solubility is independent of Eh, and the principal equilibrium is

This analysis shows that if the input for our calculations is reasonably correct, the only parameters that contribute significantly to the solubility

of $\text{PuO}_2 \cdot n\text{H}_2\text{O}$ are: (a) the solubility product, (b) the Pu^{3+} - Pu^{4+} standard potential, (c) the Pu^{4+} - PuO_2^+ standard potential, and (d) the fifth hydrolysis constant for Pu^{4+} .

This discussion indicates that only a limited number of properly chosen experiments are required to predict the solubility of $\text{PuO}_2 \cdot n\text{H}_2\text{O}$ over the whole range of Eh and pH. Since there is a fairly reliable value for the Pu^{3+} - Pu^{4+} standard potential,¹⁸ the solubility product could be determined from a set of solubility measurements in the $3 \leq \text{pH} \leq 4$ and $0.5 \leq \text{Eh} \leq 0.6$ V range where (1) is the principal equilibrium. Careful measurements in the $3.5 \leq \text{pH} \leq 6$ range where (2) is the principal equilibrium could be used for an independent determination of the solubility product with the difficulty that the estimated uncertainty in the required potential for the Pu^{4+} - PuO_2^+ couple is quite large.¹⁸ The equilibrium constant for (3) could be determined in any convenient region with $\text{pH} \geq 7$ or 8 and $\text{Eh} \lesssim 0.5$ V.

The diagram shows that careful measurement and control of the Eh will be required for meaningful solubility determinations in regions where (1) and (2) are the principal equilibria. A good way of doing this is probably to use Eh moderators or buffers together with a potentiostat. The requirements for such a moderator for use in actinide solubility studies are:

- (1) Formal potentials in the range -0.5 to 0.9 V, approximately.
- (2) Stable for many days with respect to decomposition in either the oxidized or reduced forms in the pH range from about 2 to about 9.
- (3) Relatively rapid redox reactions with actinide species, but no other reactions such as precipitation or complexation.
- (4) Reversible redox reactions at the working electrode of a potentiostat.

Bondietti and Lee at Oak Ridge National Laboratory have used redox indicators as Eh buffers in their work on technetium. They report that Nile Blue, Thionine, and 2,6-dichloroindophenol (DCIP) at concentrations of 10^{-6} M gave Eh values in agreement with the theoretical ones within 10 to 20 mV at a pH of about 8.25. The reported potentials¹⁹ for Thionine and DCIP are such that they might be useful for $\text{PuO}_2 \cdot n\text{H}_2\text{O}$ solubility studies in the regions where (1) and (2) are the principal equilibria, and for $\text{NpO}_2 \cdot n\text{H}_2\text{O}$ where equilibria analogous to (2) and (3) are predominant. However, DCIP probably would not be ideal for our purposes since it is insoluble in acid solutions, unstable in strongly alkaline solutions, and decomposes slowly even in neutral solutions.¹⁹ In addition, it forms anions that might complex actinide species.

Other dyes should be considered, e.g., Bindschedler's Green forms cations, shows Eh versus pH similar to that for DCIP, is useful in the $2 \leq \text{pH} \leq 9.5$ range, and shows instability only at the extremes of pH. In addition, it shows evidence for semiquinone formation, which may facilitate the one-electron steps required in the redox reactions of the actinides.

Rai and Strickert (PNL) have used quinhydrone as an Eh buffer in their study of $\text{NpO}_2(\text{c})$ solubility. Quinhydrone has an Eh-pH dependence that suggests its use in the region where (1) is the principal $\text{PuO}_2 \cdot n\text{H}_2\text{O}$ equilibrium. We have previously studied the rate of reaction between Pu(IV) and hydroquinone,²⁰ so it is possible to get an idea of how well the hydroquinone-quinone couple (quinhydrone) meets requirement (3) above.

The observed rate law in solutions with $0.2 \leq (\text{H}^+) \leq 1 \text{ M}$ indicates that the most important steps in the mechanism are

where H_2Q , $\text{HQ}\cdot$, and Q represent hydroquinone, the semiquinone radical, and quinone, respectively. The rate constants k_1 and (k_2/k_3) were measured in the experiments, and the overall equilibrium constant K is known from the potentials. The rate of approach to equilibrium for small displacements from equilibrium can be determined from these data; we find the half-time to be about 100 seconds for 10^{-4} M quinhydrone (see Appendix). Thus, the rate of reaction of quinhydrone with Pu^{3+} or Pu^{4+} is rapid enough to make it a satisfactory buffer for plutonium.

Inorganic couples also should be considered for use as redox buffers or moderators. Professor Henry Taube at Stanford University, who has had considerable experience with a wide variety of inorganic complexes, suggests that although many ruthenium complex couples have desirable potentials, they are probably not stable enough for our purposes (H. Taube, Stanford University, personal communication, 1980). Certain osmium complexes are much more stable, and Taube suggests that the II-III couples such as $\text{Os}(\text{bipyridyl})_3$ and $\text{Os}(\text{bipyridyl})_2(\text{CN})_2$ should be tried.

B. Redox Potential of Groundwaters (B. P. Bayhurst)

Investigations of the measurement and control of the oxidation-reduction potential of rock-groundwater systems have been started. Either platinum or gold electrodes, referenced to a standard calomel electrode, are currently being used to measure Eh. Standards of +430 mV and -388 mV are used to calibrate the electrodes.

Measurements of Eh made on unpoised systems are difficult to interpret when there are few electroactive redox couples present; the weak signal resulting can be unobservable because of electrical noise in the system. This is true of the groundwaters available, and Eh measurements may not be meaningful. Measurements of both oxygenated and oxygen-free solutions have failed to show negative potentials except in the case of YM-38 and YM-54 tuff suspensions which had been equilibrated for a year or more in a controlled atmosphere. Mixtures of powdered Yucca Mountain tuff samples and their appropriate groundwaters, which had been equilibrated for 24 days under oxygen free (≤ 0.2 ppm) conditions, also showed a slight reduction in measured potential compared to the waters alone.

Hydroxylamine hydrochloride was examined as a reducing agent. Solutions were sparged with N_2 gas for several hours to remove some of the oxygen, $NH_2OH \cdot HCl$ was added, and the pH was adjusted to neutral or slightly basic with dilute NaOH. Eh was measured as a function of pH. An approximately linear correlation was found: at pH 7 $Eh \cong +120$ mV and at pH 10.8 $Eh \cong -130$ mV.

Experiments under controlled-atmosphere conditions (≤ 0.2 ppm oxygen), using $NH_2OH \cdot HCl$ included studies of pH vs Eh in the presence of crushed rock and the effect of $NH_2OH \cdot HCl$ concentration on Eh.

Three ~1 g samples of <75- μ m granite (CS-7) were each mixed with 20 ml of pretreated, synthetic, granite water. Original Eh and pH values were approximately +120 mV and 8.65, respectively. A solution of $NH_2OH \cdot HCl$ (~50 mg) was added, and the pH was adjusted to the values listed below. The initial Eh measurements after pH adjustment are also given.

<u>Sample</u>	<u>pH</u>	<u>Eh (mV)</u>
1	7.04	+72
2	8.21	-8
3	9.01	-56

The absence of CO_2 and the buffering by the granite were enough to change the pH (and consequently Eh) to converging values. After 6 days, pH values were approaching ~9 and Eh values approximately -10 mV. After several weeks pH values were 9.38 ± 0.01 and Eh values were $-14 \pm 4\text{mV}$; these values remained essentially constant for 8 weeks.

The effect of hydroxylamine hydrochloride concentration on Eh was studied at three molarities. The pH values were ~8.7 initially. At each molarity samples of groundwater (synthetic granite) with and without rock were prepared. The molarity and pH were adjusted before adding the groundwater to the sample tubes. Initial conditions were:

<u>$\text{NH}_2\text{OH}\cdot\text{HCl}$ Concentration</u>	<u>pH</u>	<u>Eh (mV)</u>
0.023 M	8.8	-12
0.0047 M	8.7	+17
0.00095 M	8.5	+58

After 4 weeks equilibration, the samples with rock in each set showed no differences from those without rock. The pH values all increased to about 9.2. The Eh values did not change within the probable error of measurement; differences due to the $\text{NH}_2\text{OH}\cdot\text{HCl}$ concentration remained unchanged.

Nile Blue (10^{-6} M) was used in a sodium carbonate solution (10^{-3} M) for a preliminary experiment in Eh control. Ferrous ion was necessary to reduce the Eh to the Nile Blue theoretical value of -160 mV at pH 8.3. This reading was maintained for several hours with the addition of ferrous ammonium sulfate. Ottaway¹⁹ states that concentrations of $\leq 10^{-7}$ M Nile Blue are needed for true solution behavior.

A potentiostat cell has been fabricated similar to those of Harrar²¹ and Rai *et al.*²² The cell of Teflon is 3.6 cm in diameter and 7.5 cm in height. The working electrode is a 3.3-cm-diameter, platinum gauze cylinder. The counter electrode is a folded 5-cm-by-2-cm platinum gauze isolated in a glass cell with a porous Vycor frit making contact with the solution. A salt bridge contains a calomel reference electrode. Inlet and outlet tubes for inert gas sparging and a sample port with stopper are included.

The potentiostat will be used to reach various desired potentials. A study will be made of Eh buffers or moderators which might be used during long-term experiments to maintain a particular potential obtained by the potentiostat. Possible inorganic Eh moderators were discussed by T. W. Newton.¹¹ Ottaway¹⁹ discusses organic redox indicators in the applicable range. The

symbol E_m^7 is defined as the formal potential at pH 7. The formal potential, E_o' , is the potential of a solution containing equal concentrations (not necessarily molar) of the oxidized and reduced species under specified conditions of the other electrolytes. Possible indicators are listed in Table XXVIII, together with the corresponding E_m^7 (pH 7) values and the pH range under which they were investigated.

If it is determined that a potential buffer is reversible and does not interfere with sorption, then this method will be applied for studying sorption of elements such as plutonium, uranium, technetium, and neptunium under both controlled-atmosphere and controlled Eh conditions.

TABLE XXVIII
POSSIBLE ORGANIC REDOX INDICATORS^a

	E_m^7 (mV)	pH range
Induline Scarlet	-299	3.0 - 8.6
Rosinduline 2G	-281	4.8 - 11.4
Lissamine Blue BF	-253	1 - 11
N,N'-dimethyl Viologens	-446 ^b	8.4 - 13
Indigo Carmine	-125	<9 ^c
Pyocyanine	-34	1 - 12

^aData taken from Ref. 19.

^bPotentials of substituted viologens are independent of pH and follow the simple Nernst equation $E_h = E_o' + \frac{RT}{F} \ln \frac{Co}{Cr}$.

^cSemiquinone is formed above pH 9.

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VII. ORAL PRESENTATIONS

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2. G. Robbins, E. O'Donnell, and G. Birchard, U. S. Nuclear Regulatory Commission, Washington, DC.

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APPENDIX

CALCULATIONS RELATED TO ACTINIDE CHEMISTRY STUDIES

I. SOLUBILITY CALCULATIONS

The solubility, S , of an actinide oxide or hydrated oxide is given by the expression

$$S = \sum_{x=3}^6 \left((M_x) + \sum_{ij} iK_{xij} (M_x)^i (OH^-)^j \right),$$

where x is the oxidation state, $M_x = An^{x+}$ for $x = 3$ or 4 , and $M_x = AnO_2^{(x-4)+}$ for $x = 5$ or 6 . K_{xij} are the hydrolysis constants

$$K_{xij} = \frac{(M_x)_i (OH)_j}{(M_x)^i (OH)^j} \quad (\text{charges omitted for clarity}).$$

K_{xs} are the solubility products, e.g., $K_{4s} = (An^{4+})(OH)^4$

or $\log(M_4) = \log K_{4s} - 4 \log K_w - 4 \text{ pH}$.

From the Nernst equation, $\log(M_5) = (Eh - E_{45}^0)/\alpha + \log(M_4) + 4 \text{ pH}$

$$= (Eh - E_{45}^0)/\alpha + \log K_{4s} - 4 \log K_w,$$

$$\log(M_6) = 2(Eh - E_{46}^0)/\alpha + \log K_{4s} - 4 \log K_w,$$

$$\log(M_3) = (E_{34}^0 - Eh)/\alpha + \log K_{4s} - 4 \log K_w - 4 \text{ pH},$$

where $\alpha = (2.303)RT/F = 0.05916 \text{ V}$ at 25°C , $K_w = (H^+)(OH^-)$, the dissociation constant for water, and the E^0 's are the indicated standard potentials (for unit activity of H^+). The values for (M_x) calculated in this way are substituted into the above equation for S .

II. ESTIMATE OF THE HALF-TIME FOR APPROACH TO EQUILIBRIUM IN THE QUINHYDRONE Pu(III-IV) SYSTEM

The equilibrium constant for the reaction is given by

$$K = \frac{(Pu^{3+})^2 (Q) (H^+)^2}{(Pu^{4+})^2 (H_2Q)}.$$

Its value at zero ionic strength, calculated from the potentials, is $3.7 \times 10^{10} \text{ M}^2$, within a factor of about 1.5. This uncertainty is caused by the difference in the suggested values for the $Pu^{3+} - Pu^{4+}$ potentials.^{17,18} The rate constants k_1 and (k_2/k_3) were reported to be $9.6 \times 10^4 \text{ M}^{-1}\text{sec}^{-1}$ and $0.24 (H^+)$ at 25°C and unit ionic strength.²⁰ Terms k_1 and k_3 should be essentially independent of ionic strength, but it is reasonable to expect k_2 to decrease by a factor of about 8 on going from unit to zero ionic strength.

Extending a published derivation,²³ it can be shown that the reciprocal of the life-time for equilibration after a small displacement from equilibrium is given by

$$\tau^{-1} = \frac{k_1 (H_2Q) \left[4 + 4 / \sqrt{K(H_2Q)/(Q)/(H^+)^2} \right]}{1 + (k_2/k_3) \sqrt{K(H_2Q)/(Q)}}$$

Substituting values that might correspond to those in a typical experiment:
 $(H_2Q) = (Q) = 10^{-4} M$, $(H^+) = 10^{-3} M$, and the values given above for K , k_1 , and (k_2/k_3) , we find $\tau^{-1} = 6.6 \times 10^{-3} \text{ sec}^{-1}$ or $t_{1/2} = 104 \text{ sec}$. This estimate is probably good within a factor of 2 or 3.

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