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**Basalt-Radionuclide  
Distribution Coefficient  
Determinations  
FY-1979 Annual Report**

L. L. Ames  
J. E. McGarrah

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September 1980

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Pacific Northwest Laboratory  
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BASALT-RADIONUCLIDE DISTRIBUTION  
COEFFICIENT DETERMINATIONS  
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## SUMMARY

Experimental radionuclide distribution coefficients ( $K_d'$ ) were determined for Pomona, Flow E, Umtanum basalts, and secondary mineralization associated with the Pomona basalt at 23°, 60° and 150°C. Radionuclides used were  $^{75}\text{Se}$ ,  $^{85}\text{Sr}$ ,  $^{99}\text{Tc}$ ,  $^{125}\text{I}$ ,  $^{135}\text{Cs}$ ,  $^{226}\text{Ra}$ ,  $^{237}\text{Np}$ ,  $^{238}\text{U}$ ,  $^{241}\text{Am}$ , and  $^{241}\text{Pu}$ . Two tracer concentration levels and two solid weight to solution volume ratios were run in triplicate. Solution oxygen contents were controlled by the basalt/groundwater system ( $E_h = 600$  to  $700$  mv), and were high (8.2 to 8.4 mg/l) at 23°C. Oxygen contents and pH changed little in contact with basalt.

The effects of temperature changes on radionuclide  $K_d'$  results varied depending upon the radionuclide involved, solution-solid reactions, and the relationship of the radionuclide to these reactions. For example, cesium  $K_d'$  values decreased from 3100 ml/g for Umtanum basalt at 23°C to 120 ml/g at 150°C. At the same time, strontium  $K_d'$  values increased for Umtanum basalt from 105 ml/g at 23°C to complete removal at 150°C and 40 days.

Radionuclide adsorption coefficient measurements at higher temperatures and pressures were made in addition to the 23°C, solution-solid contact time-conditional  $K_d$  ( $K_d'$ ) measurements. These included  $K_d'$  measurements with Umtanum basalt, Pomona basalt, Flow E basalt and secondary mineralization and radioisotopes of americium, cesium, iodine, neptunium, plutonium, radium, selenium, strontium, technetium and uranium. The additional temperatures involved were 60°C, 150°C, and 300°C. At 150°C, argon pressures of 6.9, 13.8, 20.7, and 27.6 MPa will be used to ascertain the effects of pressure changes on  $K_d'$  values. So far only the 6.9 MPa argon pressure has been investigated. The upper temperature of 250°C is where thermal breakdown of dioctahedral smectites (secondary mineralization) begins (Eberl et al. 1978). The present predicted maximum temperature is 300°C for the thermal regime of repository mined in basalt. Hence, the basalts (along with reconstitution to new mineral phases) on radionuclide  $K_d'$  values will be determined at 300°C.



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## INTRODUCTION

The objective of the work described in this annual report is to assist the Basalt Waste Isolation Program in completing a safety assessment of potential radionuclide migration from a repository mined in basalt to the biosphere. The time period covered by this report is February 1, 1979 to August 30, 1979.

Several parameters have been recognized as significant in the transport of radionuclides by groundwater through basalt. One of the most important parameters is the  $K_d$  (equilibrium distribution coefficient). A  $K_d$  may be defined as the tendency of a solute to distribute in equilibrium concentration between two immiscible phases at a constant temperature. Nernst first clearly stated this law in 1891. The ideal distribution law can be given as  $K = A/B$ , where A and B are the activities of the solute in the respective solvents, and K is the ideal equilibrium distribution coefficient. In very dilute solutions, the activities of the solute in the two phases may be replaced by their molar concentrations. The ideal distribution law is a limiting case and holds only for ideal solutions. The distribution law is not confined to liquid solutions, but also is applicable to systems involving more than one physical phase such as the basalt-groundwater system. Factors affecting the  $K_d$  include temperature and pressure.

Pressure generally has little effect on the distribution ratio, while temperature can show a large effect in nonideal solutions or if the temperature coefficients of solubility of the solute are unequal in the two phases. Hence, the concept of a radionuclide ideal equilibrium distribution coefficient ( $K_d$ ) is a valid one only within the narrow limits of the system: 1) at equilibrium, 2) reversible, 3) nearly ideal, and 4) isothermal.

To take these conditions in order, in systems that include basalt as the solid phase, the approach to equilibrium is very slow below temperatures of 100°C. Also, demonstrating that equilibrium has been attained is very difficult. Silicate solubilities and reaction kinetics are very slow at room temperature.

The sorption reaction resulting in the distribution coefficient is not always reversible. The sorption mechanism may involve the collapse of a 10 Å layer structure, trapping the radionuclide in an energy well for many days. Another possibility is radionuclide precipitation due to exceeding the solubility limits of the hydration products. Americium and plutonium often yield high  $K_d$  values as a result of partial precipitation.

The near ideal conditions refer to the trace level of radionuclide concentration in this case. Above about  $1 \times 10^{-7} \text{ M}$  cesium, for example, the  $K_d$  concept is no longer valid due to a cesium concentration dependence. The upper limit of the trace concentration level must be determined for each radionuclide. All of the  $K_d$  values must be determined isothermally because the final solution composition is a function of the temperature.

Due to the above considerations, the radionuclide distribution coefficients discussed in this report are constrained by system temperature, contacting solution composition including pH and Eh, radionuclide concentration and species and the basalt-solution approach to equilibrium. The last constraint led to the association of each radionuclide distribution coefficient with a solution-solid contact time. This coefficient is referred to as a  $K_d'$  with the dimensions of ml of solution/g of basalt. If the surface area/unit of the basalt is known, the  $K_d'$  also could have the dimensions of ml of solution/m<sup>2</sup> of basalt.

The immediate objective of this work is to determine the  $K_d'$  values for americium, plutonium, neptunium, uranium, radium, cesium, strontium, selenium, technetium and iodine with basalt under conditions simulating those predicted for a repository in basalt. This report contains improvements in distribution coefficient precision and experimental  $K_d'$  results at 23°C, 60°C and 150°C.

Additional work on the basalt characterization includes surface area determinations and quantitative mineralogy of Flow E and Pomona basalts (Appendix A). Preparation and some physical and chemical characteristics of the secondary mineralization used in the  $K_d'$  determinations are given in Appendix B. The mechanics of an ethylene glycol adsorption surface area

determination are recorded in Appendix C. Outlines of the 150°C and 300°C experiments in the pressure vessels are given in Appendices D and E, respectively.

The Umtanum basalt was sampled at a surface location near Priest Rapids dam on the Columbia River (Hodge and Grutzeck 1978). As a surface outcropping, it has been subjected to a certain amount of weathering. The nature of this basalt surficial weathering is reported in Appendix F.

## CONCLUSIONS

Several general conclusions may be drawn from the 23°, 60° and 150°C Kd' results obtained to date. These conclusions are as follows:

- Iodine, neptunium and uranium Kd' values for basalt ranged from 0 to 10 ml/g at 23°C and remain at nearly the same values to 150°C. Secondary mineralization Kd' data presently are insufficient to allow general conclusions. Technetium Kd' values changed little from 23°C to 60°C for secondary mineralization or basalt.
- Cesium Kd' values for basalts decreased from 3100 ml/g at 23°C to 120 ml/g at 150°C, probably due to increased basalt solubility and solution ionic strength with increased temperature. Strontium Kd' values increased with temperature probably due to sorption and burial on forming secondary mineral products.
- Plutonium Kd' values increased for the Pomona basalt and decreased for Flow E and Umtanum basalt from 23°C to 60°C. At 150°C, the Umtanum basalt Kd' increased sharply from 180 ml/g at 60°C and 36 days to complete removal at 150°C.
- Americium Kd' values for basalt decreased by about an order of magnitude from 23°C to 60°C (500 to 1000 ml/g to 35 to 63 ml/g).
- Selenium Kd' values for basalt increased from 3 ml/g at 23°C to 360 ml/g at 150°C and 45 days.
- Solutions in contact with basalt at 23°C tended to increase in pH with time from approximately pH 7 to 8 to pH 8 to 9.
- Oxygen contents of the solutions in contact with 0.30 to 0.85-mm mesh basalts changed little in 31 days.
- Certain of the radionuclides are more readily removed by one basalt than by another. Technetium, for example, shows a Kd' of 12 to 15 ml/g at 23°C and 30 to 40 ml/g at 60°C with Umtanum basalt. Flow E basalt technetium Kd' was steady at 2 ml/g for 23°C and 60°C. Pomona basalt Kd' varied from 1 to 0 ml/g at 23°C and 60°C for technetium.

- The empirical nature of  $K_d'$  measurements becomes readily apparent as the affects of temperature changes on resulting  $K_d'$  changes is observed.  $K_d'$  values rise and fall in response to presently unknown reactions between the solution, basalt and radionuclide.

## DISTRIBUTION COEFFICIENT PRECISION IMPROVEMENT

One of the primary goals of the laboratory distribution coefficient work is to improve the precision of the  $K_d'$  data obtained with the batch contact methodology used in these determinations. There are two ways to improve  $K_d'$  values. These are through improvements in the laboratory techniques used in  $K_d'$  determinations and through the use of replication of  $K_d'$  determinations.

### EXPERIMENTAL METHODOLOGY IMPROVEMENT

A batch  $K_d'$  measurement is made by contacting a known volume and composition of solution containing a radionuclide at trace level concentration with a weighed solid for a known length of time. At the finish of solid-solution contact, an aliquot of the solution is separated from the solid by centrifugation or filtration, and the radionuclide is counted and compared to a blank solution (an equal volume of the original solution containing no solids). The radioactivity on the solid is not usually directly counted, but is determined by subtracting the radioactivity in a volume of equilibrium solution from the radioactivity in an equal volume of blank solution. The  $K_d'$  (based on mass) is the radionuclide concentration per gram of solid divided by the radionuclide concentration per milliliter of equilibrium solution at time  $t$ , and has dimensions of ml/g.

One of the problem areas of batch  $K_d'$  measurement is that of solids-solution separation prior to counting. Certain radionuclides, such as those of cesium, can become adsorbed on colloidal and larger-size particles, remain in the solution through the solids separation procedure, and result in a much lower computed  $K_d'$  value for the radionuclide. If the radionuclide is not strongly adsorbed by the very fine to colloidal particulates, a poor solid-solution separation procedure have little to no effect on the derived  $K_d'$  value because no high activity solids are contained in the counting aliquot. Cesium is one of the elements that have shown a direct relationship between suspended solids concentration and the percentage of the total cesium in the system adsorbed on them (Eichholz et al. 1967).



An example of difficulties with solid-solution separations is given in Table 1 and Figure 1, where the total amounts of cesium and suspended solids in the system were varied by changing the solution volume to clay weight ratio used. The less than two micrometer ( $<2 \mu\text{m}$ ) nontronite, a common basalt weathering product, was purposely inadequately separated from its contacting solution before cesium-137 counting. The resulting cesium  $K_d'$  values varied considerably with the solution volume to solid weight ratio. The actual cesium  $K_d'$  value obtained with a good solution-solid separation was about 1380 ml/g. Later filtration of the solids-contaminated, 10 ml to 1 g solution volume to solid weight ratio solution volume yielded a cesium 30-day  $K_d'$  value of  $1339 \pm 166$  ml/g. Hence, with proper solid-solution separations, it is possible to obtain the same cesium  $K_d'$  value. Filtration of the 80 ml to 1 g ratio aliquot did not appreciably change its cesium  $K_d'$  value, probably because this aliquot contained 8 times as much cesium as the 10 ml to 1 g ratio aliquot and the same weight of clay. Although the clay adsorbed as much cesium in both aliquots, the fraction of the total cesium in the system adsorbed by the clay in the 80 ml to 1 g ratio aliquot was minor.

The same problem with poor solid-solution separations also was encountered using basalt rocks as the solid. Umtanum basalt cesium  $K_d'$  values were checked with the same variable solution volume to solid weight ratio procedure with the results shown in Table 2 and Figure 2. Much larger solution volume to solid weight ratios were required to approach the true cesium  $K_d'$  value of about 3100 ml/g shown as a dotted line in Figure 2. Filtration through a 0.015- $\mu\text{m}$  filter did not appreciably change any of the cesium  $K_d'$  values, which suggests that the suspended particulates were colloidal in size. Since the 20- to 50-mesh (0.85 to 0.30 mm) Umtanum basalt was thoroughly washed before use on a 50-mesh screen, it must be assumed that the colloidal particulates were generated by abrasion during sample agitation. The greater the weight of basalt per unit volume (the lower the solution volume to solid weight ratio), the more frequent were the collisions between basalt solids per unit time and the more colloidal particulates produced. As the solution volume to solid weight ratio increased, the collision frequency between basalt solids decreased; the total amount of cesium in the system also increased until a true cesium  $K_d'$  value was approached at 3100 ml/g.

TABLE 1. The Less Than Two Micrometer, Freeze-Dried Nontronite/Cesium 30-Day  $K_d'$  Variations With Solution to Solid Ratio and Equilibrium Solution Treatment

<u>Solution Volume to Solid Weight Ratio, ml/g</u>	<u>Centrifuged, 1000 grav., 15 min.</u>	<u>Filtered, 0.015 <math>\mu</math>m</u>	<u>Initial Cs Concentration, Moles/l</u>
10/1	755 $\pm$ 115	1339 $\pm$ 166	$1.83 \times 10^{-9}$
30/1	1135 $\pm$ 237	-	$1.83 \times 10^{-9}$
60/1	1349 $\pm$ 26	-	$1.83 \times 10^{-9}$
80/1	1407 $\pm$ 22	1392 $\pm$ 43	$1.83 \times 10^{-9}$

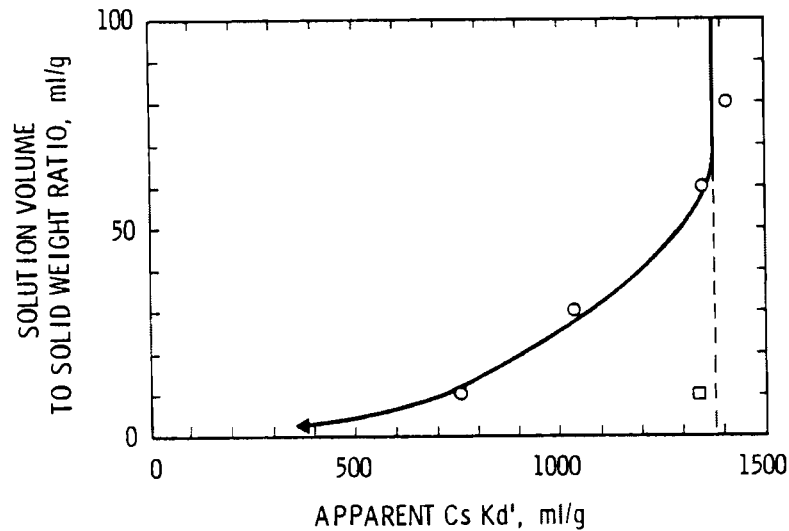


FIGURE 1. Apparent Cesium  $K_d'$  Variation of  $<2 \mu$ m Nontronite at Several Solution to Solid Ratios and 30 Days Equilibrium Time With Shaking. The square represents  $K_d'$  value of the 0.015- $\mu$ m filtered sample. (Agitation Rate = 125 cycles/min)

Another area of study was the minor element chemistry of synthetic ground-water equilibrated with 0.85 to 0.30 mm Umtanum basalt. Experiments suggested that suspended colloidal particles generated during the agitation used in solution-solid equilibrations were the source of iron in the ICP solution analysis as well as the cesium  $K_d'$  variation. The inductively coupled plasma spectrographic (ICP) analytical results are shown in Table 3. The solution was filtered through a 0.45- $\mu$ m filter to remove the larger suspended particles and allow determination of any suspended colloids during the ICP analysis.

TABLE 2. Umtanum Basalt 23°C Cesium Kd' Variation With Solution Volume to Solid Weight Ratio (Agitation Rate = 125 cycles/min)

<u>Solution Volume to Solid Weight Ratio, ml/g</u>	<u>30-Day Cs Kd', 23°C, 0.45 μm Filtered, ml/g</u>	<u>Initial Cs Concentration, Moles/l</u>
10/1	321 ± 39	1.83 x 10 <sup>-9</sup>
30/1	828 ± 36	1.83 x 10 <sup>-9</sup>
60/1	1624 ± 121	1.83 x 10 <sup>-9</sup>
80/1	2203 ± 53	1.83 x 10 <sup>-9</sup>
200/1	2876 ± 232	1.83 x 10 <sup>-9</sup>
400/1	3126 ± 1048	1.83 x 10 <sup>-9</sup>
600/1	3048 ± 749	1.83 x 10 <sup>-9</sup>

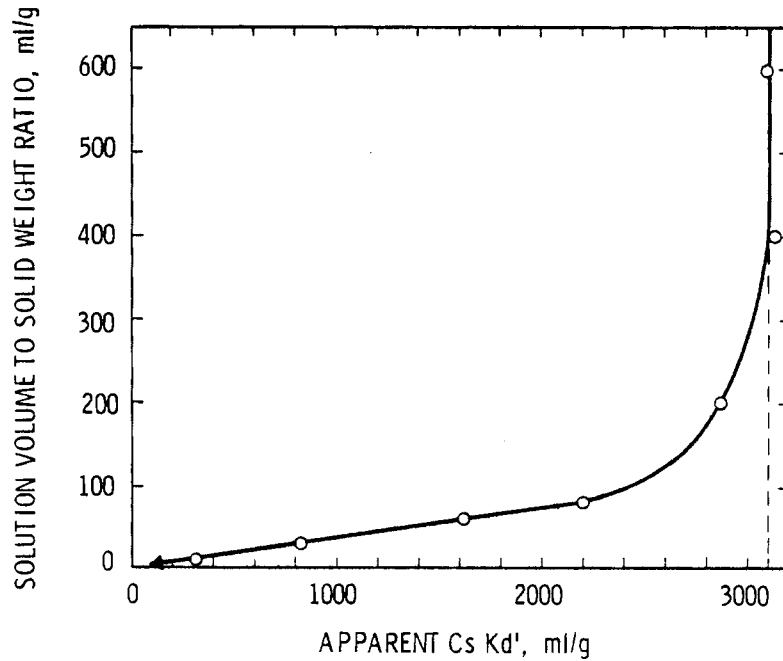


FIGURE 2. Apparent Cesium Kd' Variation for Umtanum Basalt at Several Solution to Solid Ratios and 30 Days Equilibrium Time With Shaking (Agitation Rate = 125 cycles/min)

Iron and manganese apparently increased in concentration in the equilibrium solution as seen in Table 3. The solubility of ferric iron in pH 8.0 solutions ( $K_{so} = -38.6$ , Sillen 1971) is rather low at approximately  $10^{-20}M$  at 25°C, while the 0.2 mg Fe/l given in Table 3 is  $3.58 \times 10^{-6}$  in molarity. The solubility of ferrous iron is much greater at pH 8.0, but in this oxygenated solution, the life of ferrous iron can be assumed to be very short. The 108-day equilibration solution, therefore, should have contained no measurable iron in solution. A colloid consisting at least partly of hydrated ferric oxide-hydroxide and similar manganese solids probably was present in the solution. The cesium would adsorb on these high surface area materials producing a low Cs  $K_d'$  value due to failure to separate these materials from the final solution to be counted.

TABLE 3. ICP Trace Element Analysis of the Original and 108-Day Equilibrating Solution With Umtanum Basalt. Solution volume to basalt weight ratio was 5 ml/g. Fluorine analysis was by ion chromatography. A general wt% error for all analyses was  $\pm 10$ .

<u>Original Solution</u>		<u>108-Day Solution, 0.45 <math>\mu</math>m Filtration</u>	
<u>Constituent</u>	<u>Content, ppm</u>	<u>Constituent</u>	<u>Content, ppm</u>
Al	<0.10	Al	0.10
As	<0.01	As	0.02
B	0.01	B	0.02
Ba	<0.01	Ba	0.01
Fe	<0.01	Fe	0.20
P	<0.05	P	0.10
Sr	0.01	Sr	0.03
Mn	<0.01	Mn	0.40
Se	<0.10	Se	<0.10
Th	<0.10	Th	<0.10
U	<0.01	U	<0.01
F	0.06	F	0.30
pH = 8.0		pH = 8.0	

Several revisions to the experimental technique for solution-solid equilibration were investigated to avoid the particulates generation problem, but the simplest was to lower the shaker agitation rate from 125 cycles/min to 50 or 60 cycles/min. The lower agitation rate was still adequate to maintain good solution-solid contact while preventing particulate generation. Sorption data for cesium on the same Umtanum basalt at the lower agitation rate is presented in Table 4.

#### REPLICATION

Another way to improve precision of the radionuclide distribution coefficient results is by replication of  $K_d'$  measurements. Six samples were equilibrated in the 23°C, 60°C and anoxic experiments in two sets of three samples each. Differing experimental conditions were represented by the two sets. One set contained relatively high concentrations of radionuclides while the other set contained relatively low radionuclide concentrations, although both were within the trace level of concentration where the  $K_d'$  remains the same.

The solution volume to solid weight was 100 ml/g for one set and 10 ml/g for the other set. Neither the changes in solution volume to solid weight ratio nor the changes in tracer concentration level should affect Cs or Sr  $K_d'$  values on basalts. If  $K_d'$  effects are noted between the two sets, they are due to experimental problems. Hence, the two data sets furnish a method of checking the experimental procedure as well as furnishing additional replicates to improve  $K_d'$  precision.

An example of such a dual set of experiments is shown in Table 4 and Figures 3 and 4. The mean cesium  $K_d'$  value for Umtanum basalt was about 3100 ml/g and the mean strontium  $K_d'$  value about 105 ml/g. The mean  $K_d'$  values were approached slowly, and later measured  $K_d'$  values tended to oscillate about them.

One problem with  $K_d'$  determinations that is inherent in the system can be discerned in Figure 3. Counting statistics becomes a major factor when the  $K_d'$  values are much above 1000 or close to zero, especially with matrix-corrected values such as those represented in Figure 3. The matrix-corrected

TABLE 4. Kd' Values for Umtanum Basalt at 23 C Under Two Sets of Experimental Conditions

Condition I

100 ml Solution/1 g Basalt, Contained in 202 m Polyethylene Mesh, 50 Cycles/Min Agitation, 2580 cpm <sup>137</sup>Cs + 360 cpm <sup>85</sup>Sr, Mean of 3 Samples And a Standard Deviation Estimate (1 s).

Radionuclide	Kd', ml/g						
	5 Days	10 Days	15 Days	20 Days	25 Days	36 Days	41 Days
<sup>137</sup> Cs	280 ± 49	2022 ± 44	2903 ± 210	2755 ± 168	2789 ± 104	2780 ± 105	3058 ± 214
<sup>85</sup> Sr	27 ± 0.6	85 ± 18	82 ± 9	88 ± 5	98 ± 7	97 ± 3	111 ± 12

Condition II

10 ml Solution/1 g Basalt, No Sample Containment, 50 Cycles/Min Agitation, 60,000 cpm <sup>137</sup>Cs + 21,300 cpm <sup>85</sup>Sr, Mean of 4 Samples Plus a Standard Deviation Estimate (1 s).

Radionuclide	Kd', ml/g				
	7 Days	14 Days	21 Days	27 Days	32 Days
<sup>137</sup> Cs	714 ± 55	1408 ± 126	1828 ± 56	2869 ± 252	3216 ± 187
<sup>85</sup> Sr	57 ± 1	72 ± 2	78 ± 3	88 ± 3	92 ± 2

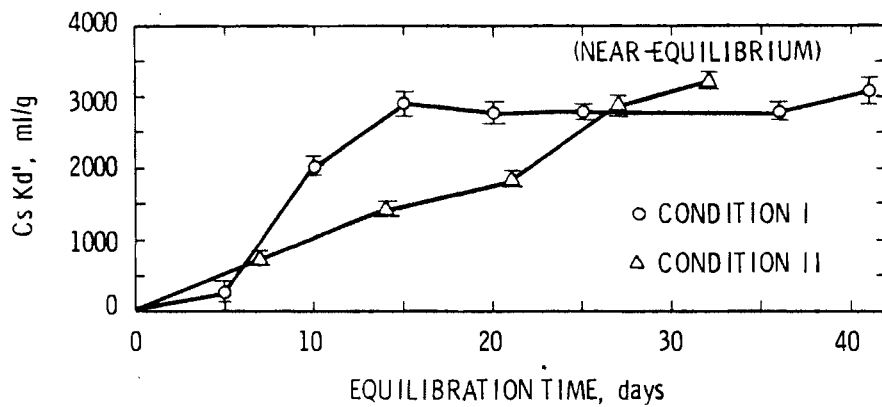


FIGURE 3. Cesium  $K_d'$  Values Versus Equilibration Time at 23°C for Umtanum Basalt and Synthetic Groundwater GR-1. The two sets of experimental conditions are given in Table 4.

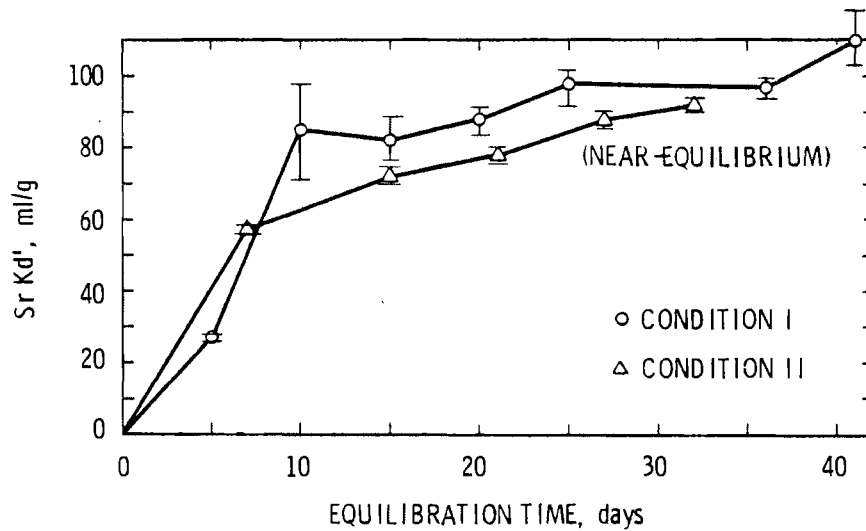


FIGURE 4. Strontium  $K_d'$  Values Versus Equilibration Time at 23°C for Umtanum Basalt and Synthetic Groundwater. The two sets of experimental conditions are given in Table 4.

$^{137}\text{Cs}$  value for the nonagitated samples, for example, was 200,000 counts/200 sec mean for the blank solutions and 560 counts/200 sec mean for the equilibrated solutions. A variation of 10 counts in the latter mean yields a variation of nearly 100 ml/g in the  $K_d'$  values. Hence, with very high and very low radionuclide adsorption, care must be taken to include several  $K_d'$  measurements to improve precision.

With the two sets of radionuclide  $K_d'$  data, six replicates of each  $K_d'$  value were generated, leading to improvements in  $K_d'$  value precision for the 23° and 60°C experiments. The 150°C and 300°C experiments are expected to reach near-equilibrium relatively rapidly (30 to 45 days). Successive, single  $K_d'$  values at 150° and 300°C serve the same purpose of improving  $K_d'$  precision as do replicate experiments at 23° and 60°C.



## EXPERIMENTAL RESULTS

Radionuclide distribution coefficients were determined in Inconel 300 ml pressure vessels at  $150^{\circ} \pm 2^{\circ}\text{C}$ . The  $60^{\circ}\text{C}$  experiments were performed in incubator-shakers with heated, recirculated atmospheres. An investigation of  $300^{\circ}\text{C}$  radionuclide distribution coefficients also is under way, but no experimental  $K_d'$  results were obtained in FY-1979. Two 500 ml Inconel pressure vessels are on order for the  $300^{\circ}\text{C}$  work with basalts and secondary minerals. The  $K_d'$  results that were obtained are reported under their respective temperatures. The 20 to 50 mesh (0.85 to 0.30 mm) crushed basalts were used in the  $K_d'$  work unless otherwise specified.

### 23°C STATIC $K_d$ EXPERIMENTS

The methodology used in the  $23^{\circ}\text{C}$  experiments was given in PNL-3103 (Ames and McGarrah 1979). The synthetic groundwater-formulation used in the  $K_d$  determinations is given in Table 5. Briefly, a weighed solid was contacted with a known volume of solution containing a radionuclide. After a known contact time, the solution and solid phase were separated and the solution activity counted. The radionuclide concentration remaining in this solution was compared to that contained in a blank solution which never contacted a solid sample (basalt or secondary mineralization), and a  $K_d'$  value was computed. Two solid weight to solution volume ratios were used: 1 g/10 ml and 1 g/80 ml. The 1 g/80 ml ratio contained a greater radionuclide concentration as the 1 g/10 ml ratio experiments. The  $K_d'$  values from both ratios should eventually converge, provided that both radionuclide concentrations are within the stable  $K_d'$  range and the experimental conditions are otherwise comparable.

The initial  $K_d'$  results are shown in Tables 6, 7 and 8 for several contact times. Each  $K_d'$  value is a mean of three  $K_d'$  experiments, and the plus or minus value is an estimate of the standard deviation (1 s).

Many of the 58- and 83-day  $K_d'$  values shown in Table 6 were quite similar. Most of the radionuclides that yielded similar 58- and 83-day  $K_d'$  values were those little affected by system macrochemistry changes such as the

TABLE 5. Synthetic Groundwater Formulation GR-1

<u>Constituents</u>	<u>Concentration, mg/l</u>	<u>Chemical Compound</u>	<u>Wt, mg/l</u>
Na <sup>+</sup>	30.7	NaHCO <sub>3</sub>	112.2
K <sup>+</sup>	9.0	K <sub>2</sub> SO <sub>4</sub>	20.1
Ca <sup>2+</sup>	6.5	CaCl <sub>2</sub> · 2H <sub>2</sub> O	23.8
Mg <sup>2+</sup>	1.0	MgCl <sub>2</sub> · 6H <sub>2</sub> O	8.4
Cl <sup>-</sup>	14.4	SiO <sub>2</sub> (Amorphous)	25
CO <sub>3</sub> <sup>2-</sup>	0		
HCO <sub>3</sub> <sup>-</sup>	81.5		
F <sup>-</sup>	0		
SO <sub>4</sub> <sup>2-</sup>	11.1		
SiO <sub>2</sub>	25		

pH = 8.0

anionic species of selenium, technetium, iodine, and uranium. The contact times for the 1 g basalt/80 ml solution ratio K<sub>d</sub>' values and those for the secondary mineralization are too short to draw similar conclusions based on the data of Tables 7 and 8.

Even though the 2.00 to 0.85 mm and 0.30 to 0.85 mm Pomona basalts are considerably different in grain size range, they are nearly comparable in surface areas (see Appendix A). In most cases, the K<sub>d</sub>' values of the two Pomona grain size ranges for specific radionuclides also are very similar. Only the cesium, americium, and plutonium experiments of Table 5 are still monitored on a monthly basis. Monthly monitoring of the 1 g basalt/80 ml solution samples (Table 7) and the secondary mineralization samples (Table 8) also is continuing.

Except for cesium, americium, and plutonium, the radionuclide experiments reported in Table 6 were set aside and the pH of randomly selected blanks and basalt-containing solutions was taken. The pH values are reported in Table 9. In general, the pH values of the basalt-containing solutions tended to rise

TABLE 6. The 23°C, 1 g/10 ml Solution Kd' Values for Basalts and Synthetic Groundwater GR-1

Radionuclide	Kd', ml/g				Contact Time, Days	Tracer Initial Conc., M
	Umtanum Basalt	Flow E Basalt	Pomona Basalt, 2.00 to 0.85 mm	Pomona Basalt, 0.30 to 0.85 mm		
<sup>75</sup> Se	5 ± 0.3	2 ± 0.3	0	0	31	1.74 × 10 <sup>-12</sup>
	5 ± 0.3	3 ± 0.6	0	0	58	
	4 ± 0.4	3 ± 0.3	0	0	83	
<sup>85</sup> Sr	92 ± 2	72 ± 2	102 ± 14	102 ± 14	31	1.26 × 10 <sup>-12</sup>
	103 ± 3	96 ± 3	133 ± 11	138 ± 11	58	
	105 ± 3	102 ± 3	136 ± 2	137 ± 7	83	
<sup>99</sup> Tc	15 ± 5	2 ± 1	0.2 ± 0.1	0.2 ± 0.1	31	4.19 × 10 <sup>-6</sup>
	13 ± 4	2 ± 1	0.1 ± 0.04	0.1 ± 0.1	58	
	12 ± 3	2 ± 1	0	0	83	
<sup>125</sup> I	1.3 ± 0.3	0.3 ± 0.03	0.3 ± 0.1	0.3 ± 0.1	31	7.24 × 10 <sup>-13</sup>
	1.8 ± 0.2	0.4 ± 0.1	0.7 ± 0.2	0.7 ± 0.2	58	
	3.1 ± 0.5	0.5 ± 0.3	0.7 ± 0.1	0.5 ± 0.4	83	
<sup>137</sup> Cs	1247 ± 306	600 ± 111	1581 ± 90	1917 ± 332	31	1.83 × 10 <sup>-9</sup>
	1927 ± 92	920 ± 144	2437 ± 219	3166 ± 202	58	
	1663 ± 31	753 ± 79	2057 ± 124	2408 ± 203	83	
<sup>226</sup> Ra	67 ± 2	52 ± 4	56 ± 1	58 ± 5	31	1.31 × 10 <sup>-7</sup>
	39 ± 2	32 ± 7	32 ± 2	36 ± 2	58	
	64 ± 3	48 ± 3	52 ± 3	54 ± 2	83	
<sup>237</sup> Np	8 ± 1	3 ± 1	4 ± 0	5 ± 1	31	1.62 × 10 <sup>-6</sup>
	10 ± 2	5 ± 1	4 ± 0.3	6 ± 1	58	
	9 ± 1	4 ± 0.3	4 ± 0.6	5 ± 0.8	83	
<sup>238</sup> U	0	5 ± 3	0	0	31	1.01 × 10 <sup>-6</sup>
	0	4 ± 0	0	0	58	
					83	
<sup>241</sup> Am	2113 ± 689	738 ± 336	904 ± 637	883 ± 173	31	2.31 × 10 <sup>-8</sup>
	658 ± 294	578 ± 331	278 ± 65	625 ± 14	58	
	1265 ± 1230	536 ± 458	467 ± 173	831 ± 116	83	
	418 ± 189	213 ± 72	341 ± 115	732 ± 109	107	
<sup>241</sup> Pu	660 ± 682	142 ± 33	64 ± 44	83 ± 3	5	1.50 × 10 <sup>-10</sup>
	602 ± 113	748 ± 194	88 ± 27	77 ± 47	32	
	790 ± 280	147 ± 60	17 ± 2	68 ± 31	57	
	2597 ± 77	254 ± 345	45 ± 22	90 ± 23	107	

TABLE 7. The 23°C, 1 g/80 ml Solution Kd' Values for Basalts and Synthetic Groundwater GR-1

Radio-nuclide	Kd', ml/g			Contact Time, Days	Initial Cs Conc., M
	Umtanum Basalt	Flow E Basalt	Pomona Basalt,		
<sup>75</sup> Se	0.8 ± 0.7	0	0	14	3.03 x 10 <sup>-12</sup>
	0	9 ± 2	0	39	
	0	8 ± 1	0	63	
<sup>85</sup> Sr	95 ± 7	76 ± 4	152 ± 4	14	1.48 x 10 <sup>-12</sup>
	126 ± 13	99 ± 2	180 ± 8	39	
	134 ± 14	99 ± 3	183 ± 10	63	
<sup>99</sup> Tc	1.6 ± 0.4	2.3 ± 1.4	1.0 ± 0.2	14	1.07 x 10 <sup>-5</sup>
	0	0	0.7 ± 3	39	
	1.9 ± 1.0	1.1 ± 0.3	0.8 ± 0.5	63	
<sup>125</sup> I	8 ± 0.4	9 ± 4	0	14	1.39 x 10 <sup>-12</sup>
	2.1 ± 1.5	0	0	39	
	7.3 ± 2.4	1.3 ± 0.5	5.5 ± 1.9	63	
<sup>137</sup> Cs	911 ± 87	355 ± 21	1,346 ± 85	14	3.52 x 10 <sup>-9</sup>
	1,524 ± 195	500 ± 11	1,868 ± 159	39	
	1,837 ± 187	526 ± 14	2,183 ± 119	63	
<sup>226</sup> Ra	178 ± 89	108 ± 8	150 ± 26	14	1.91 x 10 <sup>-7</sup>
	241 ± 2	161 ± 2	201 ± 5	39	
	211 ± 2	146 ± 4	172 ± 2	63	
<sup>237</sup> Np	20 ± 5	14 ± 3	14 ± 3	14	2.43 x 10 <sup>-6</sup>
	27 ± 2	19 ± 4	11 ± 4	39	
	28 ± 2	17 ± 4	11 ± 3	63	
<sup>238</sup> U	0	6 ± 1	0	14	1.86 x 10 <sup>-6</sup>
	34 ± 15	8 ± 4	4 ± 2	39	
	5,800 ± 3,000	3,700 ± 1,700	3,300 ± 1,300	14	
<sup>241</sup> Am	20,300 ± 5,000	29,200 ± 8,000	15,800 ± 6,300	39	1.50 x 10 <sup>-8</sup>
	28,900 ± 4,100	38,400 ± 25,100	28,400 ± 11,600	63	
	2,141 ± 605	1,260 ± 316	518 ± 188	14	
<sup>241</sup> Pu	4,425 ± 700	2,699 ± 419	262 ± 154	39	1.83 x 10 <sup>-10</sup>
	4,199 ± 697	2,548 ± 267	171 ± 115	63	

TABLE 8. The 23°C Kd' Values for Secondary Mineralization and Synthetic Groundwater GR-1

Radionuclide	Kd', ml/g		Contact Time, Days	Tracer Concentration
	1 g/10 ml	1 g/80 ml		
<sup>75</sup> Se	3.2 ± 0.6	18 ± 3	14	1.74 × 10 <sup>-12</sup>
	0	7 ± 2	37	
<sup>85</sup> Sr	368 ± 18	881 ± 35	14	1.26 × 10 <sup>-12</sup>
	439 ± 109	745 ± 55	37	
<sup>99</sup> Tc	0	0	14	4.19 × 10 <sup>-6</sup>
	0	0	37	
<sup>125</sup> I	3.3 ± 0.3	9.8 ± 1.3	14	7.24 × 10 <sup>-13</sup>
	3.3 ± 0.2	20 ± 3	37	
<sup>137</sup> Cs	8,750 ± 4,860	42,100 ± 7,000	14	1.83 × 10 <sup>-9</sup>
	225,000 ± 345,000	35,100 ± 3,300	37	
<sup>226</sup> Ra	117 ± 0.3	553 ± 12	14	1.31 × 10 <sup>-7</sup>
	46 ± 1	224 ± 2	37	
<sup>237</sup> Np	12 ± 2	50 ± 1	14	1.62 × 10 <sup>-6</sup>
	12 ± 3	49 ± 6	37	
<sup>238</sup> U	12 ± 4	61 ± 10	14	1.01 × 10 <sup>-6</sup>
<sup>241</sup> Am	14,300 ± 4,300	17,300 ± 4,000	14	2.31 × 10 <sup>-8</sup>
	22,500 ± 752	76,400 ± 32,000	37	
<sup>241</sup> Pu	2,740 ± 3,100	2,830 ± 1,800	14	1.50 × 10 <sup>-10</sup>
	1,621 ± 354	9,500 ± 1,700	37	

slightly with time. The solution in contact with the Pomona basalt tended to increase the most. Very slow reactions between the basalt and solution would have to be the cause of any differences in pH between the blank and the basalt-containing solutions. The reproducibility of pH measurements was ±0.1 pH unit. Those experiments in Table 6 that were set aside will be measured in 4 to 8 months.

The dissolved oxygen measurements in the 23°C solutions showed little change due to the presence of the basalt at 31 days contact time. The one

TABLE 9. The 23°C, 1 g Basalt/10 ml Synthetic Groundwater Solution pH Values at 83 Days of Contact Time. The various blank pH GR-1 values are due to addition of radionuclides in differing chemical media to the solutions.

Radionuclide	pH				
	Blank	Umtanum Basalt	Flow E Basalt	Pomona Basalt, 10-20 Mesh	Pomona Basalt, 20-50 Mesh
<sup>75</sup> Se	8.90	8.90	8.90	9.05	9.05
<sup>85</sup> Sr	7.80	8.40	8.50	8.45	8.90
<sup>99</sup> Tc	9.00	9.00	9.00	9.05	9.10
<sup>125</sup> I	8.90	8.95	9.05	9.05	9.15
<sup>137</sup> Cs	8.10	8.15	8.15	-	8.30
<sup>226</sup> Ra	7.50	7.85	8.05	8.40	8.50
<sup>237</sup> Np	8.05	8.50	8.50	8.65	8.80
<sup>238</sup> U	8.25	8.55	8.65	8.50	8.90
<sup>241</sup> Am	8.00	7.90	7.95	-	8.05
<sup>241</sup> Pu	7.60	7.40	7.45	-	7.80

TABLE 10. Dissolved Oxygen in the Solution Contacting 0.30 to 0.85-mm Basalt Samples at 23°C

Basalt Wt/Solution Volume, g/ml	Dissolved Oxygen, mg/l at 23°C			
	16 Days Contact Time			
	Blank	Umtanum	Flow E	Pomona
1/10	8.25	8.00	8.30	8.20
1/80	8.25	8.25	8.25	8.30
	31 Days Contact Time			
1/10	8.25	8.15	8.30	8.30
1/80	8.25	8.35	8.20	8.20

exception is the Umtanum basalt. The oxygen measurements are good to within +2% of the value given in Table 10. The dissolved oxygen values at 16 and 21 days contact are not for the same samples. Once an oxygen measurement was made, the sample was discarded. The minor changes in oxygen content indicate that all of the 23°C experiments, except those in the controlled atmosphere glovebox, were in an oxidizing environment with the Eh approximately +600 to 700 mv.

### 60°C STATIC Kd EXPERIMENTS

The 60°C experiments were conducted in agitated, controlled air temperature chambers. Temperature control was within  $\pm 0.5^\circ\text{C}$  of the desired 60°C. Essentially the same procedure was used as at 23°C, with the samples and blank solutions at 1 g solid/10 ml solution and 1 g solid/80 ml solution ratios in polypropylene, 50-ml centrifuge tubes sealed with Teflon tape on the tube cap threads to avoid solution evaporation. Pipette tips were stored in the chamber along with the samples at 60°C to ensure that the same volume was pipetted each time for counting. A set of six samples (3 blank solutions + 3 solids-solution samples) was removed from the chamber and aliquots rapidly taken to avoid sample cooling. Temperature changes result in concomitant volume changes in the solution, in turn causing counting errors affecting Kd' results.

Initial results of the 60°C Kd' determinations are shown in Tables 11, 12 and 13. Elapsed solution-solid contact times are not adequately long in many cases to allow any firm conclusions. However, it appears that selenium, technetium, iodine, neptunium and probably uranium Kd' values will remain as low as they were at 23°C. There is some evidence for an increase of strontium and radium Kd' with a temperature increase, and a decrease in cesium Kd' with a temperature increase. The decrease in cesium Kd' may be due to an increase in contacting solution ionic strength, while the strontium and radium Kd' increase may be due to the formation of secondary mineral phases at higher temperatures that remove strontium and radium from solution. Only two Kd' values are available for each radionuclide with the secondary mineralization. However, these tend to be higher than the basalts for the simple cations strontium and cesium, probably because of the high cation exchange capacity and surface area of the smectite clay that is the main mineral constituent of the secondary mineralization.

### 150°C STATIC Kd EXPERIMENTS

The 150°C experiments were performed in 300-ml-capacity Inconel 600 pressure vessels. Purified argon was used to sparge dissolved oxygen from the solution and atmosphere above it before pressurization with Ar. Thus, the solution and basalt sample were low in oxygen and CO<sub>2</sub> content before the

TABLE 11. The 60°C Kd' Values for 0.30- to 0.85-mm Basalts and Synthetic Groundwater GR-1 at 1 g Basalt/10 ml Solution

Radionuclide	Kd', ml/g			Contact Time, Days	Radionuclide Initial Conc., M
	Umtanum Basalt	Flow E Basalt	Pomona Basalt		
<sup>75</sup> Se	9 ± 1	4 ± 0.1	2 ± 0.4	11	1.08 × 10 <sup>-12</sup>
	10 ± 0.3	7 ± 1	2 ± 0.3	36	
	10 ± 0.8	7 ± 0.8	4 ± 0.2	59	
<sup>85</sup> Sr	82 ± 10	58 ± 1	82 ± 11	11	5.74 × 10 <sup>-13</sup>
	178 ± 22	130 ± 10	156 ± 43	36	
	237 ± 37	171 ± 20	225 ± 58	59	
<sup>99</sup> Tc	39 ± 15	0.7 ± 0.5	0	11	4.32 × 10 <sup>-6</sup>
	35 ± 20	0	0	36	
	36 ± 26	0	0	59	
<sup>125</sup> I	0	0	0	11	4.35 × 10 <sup>-13</sup>
	0	0	0	36	
	0	0	0	59	
<sup>137</sup> Cs	209 ± 5	122 ± 3	294 ± 7	11	2.28 × 10 <sup>-9</sup>
	468 ± 82	221 ± 9	652 ± 29	36	
	550 ± 49	251 ± 16	938 ± 71	59	
<sup>226</sup> Ra	125 ± 23	110 ± 12	147 ± 40	11	1.21 × 10 <sup>-7</sup>
	57 ± 1	51 ± 6	59 ± 0.2	36	
	66 ± 6	53 ± 3	67 ± 3	59	
<sup>237</sup> Np	9 ± 1	3 ± 3	10 ± 9	11	1.62 × 10 <sup>-6</sup>
	16 ± 4	6 ± 1	7 ± 1	36	
	13 ± 1	6 ± 1	6 ± 1	59	
<sup>238</sup> U	69 ± 54	17 ± 11	17 ± 12	36	1.01 × 10 <sup>-6</sup>
<sup>241</sup> Am	126 ± 29	103 ± 33	56 ± 15	11	1.50 × 10 <sup>-8</sup>
	35 ± 2	48 ± 42	63 ± 39	36	
	69 ± 22	84 ± 47	235 ± 187	59	
<sup>241</sup> Pu	118 ± 75	68 ± 25	52 ± 17	11	6.65 × 10 <sup>-11</sup>
	187 ± 76	229 ± 18	139 ± 45	36	
	282 ± 108	565 ± 489	646 ± 108	59	



TABLE 12. The 60°C Kd' Values For Basalts and Synthetic-Groundwater GR-1 at 1 g Basalt/80 ml Solution

Radionuclide	Kd', ml/g			Contact Time Days	Radionuclide Conc., M
	Umtanum Basalt	Flow E Basalt	Pomona Basalt		
<sup>75</sup> Se	14 ± 4	14 ± 3	2 ± 1	11	1.66 x 10 <sup>-6</sup>
	17 ± 7	20 ± 5	7 ± 5	36	
	23 ± 3	26 ± 3	10 ± 4	59	
<sup>85</sup> Sr	126 ± 17	91 ± 3	158 ± 12	11	9.93 x 10 <sup>-13</sup>
	164 ± 43	102 ± 5	176 ± 15	36	
	173 ± 22	102 ± 5	161 ± 10	59	
<sup>99</sup> Tc	7 ± 5	0	0	11	1.02 x 10 <sup>-5</sup>
	10 ± 7	0	0	36	
	9 ± 6	0	0	59	
<sup>125</sup> I	0	0	0	11	7.66 x 10 <sup>-13</sup>
	0	0	0	36	
	0	0	0	59	
<sup>137</sup> Cs	447 ± 30	153 ± 14	528 ± 28	11	3.72 x 10 <sup>-9</sup>
	669 ± 48	171 ± 19	759 ± 60	36	
	712 ± 32	175 ± 21	792 ± 25	59	
<sup>226</sup> Ra	348 ± 41	310 ± 71	656 ± 201	11	2.90 x 10 <sup>-7</sup>
	310 ± 43	210 ± 23	243 ± 10	36	
	323 ± 36	232 ± 29	277 ± 20	59	
<sup>237</sup> Np	24 ± 8	15 ± 5	17 ± 1	11	2.69 x 10 <sup>-6</sup>
	37 ± 4	27 ± 0	25 ± 3	36	
	38 ± 4	0	14 ± 6	59	
<sup>238</sup> U	0	0	0	36	1.86 x 10 <sup>-6</sup>
<sup>241</sup> Am	5,621 ± 2,272	3,609 ± 99	2,361 ± 376	11	3.81 x 10 <sup>-8</sup>
	11,587 ± 470	775 ± 395	566 ± 52	36	
	429 ± 179	293 ± 134	247 ± 156	59	
<sup>241</sup> Pu	1,174 ± 128	580 ± 80	812 ± 211	11	1.10 x 10 <sup>-10</sup>
	1,596 ± 698	593 ± 93	473 ± 173	36	
	1,322 ± 467	636 ± 38	483 ± 159	59	

TABLE 13. The 60°C Kd' Values for Secondary Mineralization and Synthetic Groundwater GR-1. Initial radionuclide concentrations are the same as those given in Table 12.

Radionuclide	Kd', ml/g		Contact Time, Days
	1 g/10 ml	1 g/80 ml	
<sup>75</sup> Se	1.1 ± 0.8	7.1 ± 4.7	14
	0	4.2 ± 3.9	37
<sup>85</sup> Sr	772 ± 580	906 ± 46	14
	499 ± 167	997 ± 14	37
<sup>99</sup> Tc	0	0	14
	0	0	37
<sup>125</sup> I	0	0	14
	0	0	37
<sup>137</sup> Cs	22,200 ± 18,500	15,300 ± 4,300	14
	1,701 ± 1,099	17,000 ± 1,000	37
<sup>226</sup> Ra	212 ± 17	1,220 ± 180	14
	90 ± 7	613 ± 79	37
<sup>237</sup> Np	14 ± 2	63 ± 5	14
	17 ± 4	66 ± 21	37
<sup>238</sup> U	25 ± 13	349 ± 79	14
<sup>241</sup> Am	4,700 ± 2,500	16,200 ± 1,400	14
	7,275 ± 3,100	20,000 ± 7,400	37
<sup>241</sup> Pu	767 ± 228	2,200 ± 1,144	14
	1,536 ± 750	611 ± 270	37

experiments began. Temperatures and pressure were continuously recorded to ensure that pressure vessel operation was uninterrupted during the experiment duration. Samples were taken, via a 1/8-in. Inconel sample line that extended below the liquid level in the vessel, at the vessel operating temperature and pressure. The part of the sample line exterior to the vessel was cooled to collect a liquid sample. A few ml of solution were passed through the sample line each time to flush the line and avoid contamination of the sample with

the portion of the last sample remaining in the sample tubing. All of the samples taken for counting were pipetted at the same temperature to obtain equal sample volumes.

The vessels were lined with machined Teflon to hold vessel wall adsorption to a minimum. A comparison between  $K_d'$  values due to vessel wall adsorption with lined and unlined vessels is shown in Table 14. No basalt was present. A solution sample taken before the vessels were pressurized and heated was used for the original solution radionuclide solution count. Strontium, cesium, iodine, and selenium showed reduced  $K_d'$  values indicating reduced wall adsorption, while lining apparently has little effect on plutonium adsorption. Much of the remaining adsorption may be due to the low ionic strength of the blank solution and adsorption on sample line tubing.

When a basalt is added to the solution, plutonium adsorption is considerably lowered as seen in Table 15. Plutonium  $K_d'$  values with the Teflon liner have not been completed. Iodine, on the other hand, increased considerably in  $K_d'$  in the Teflon lined vessel, which indicate that an iodine reaction with the Teflon liner occurs in the lined vessel. Strontium and plutonium increase together suggesting that growth of a new mineral phase may be removing both of these elements. Cesium changes little between the lined and unlined vessels as shown in Figure 5.

TABLE 14. Measured Blank Solution Kd' Values at 150°C and 6.9 MPa Ar With and Without a Teflon Liner Present in the Pressure Vessels. The initial radionuclide concentrations were the same as those at 23°C and 1 g basalt/10 ml solution.

Contact Time, Days	Kd', ml/g, No Teflon Liner				
	<sup>85</sup> Sr	<sup>137</sup> Cs	<sup>125</sup> I	<sup>75</sup> Se	<sup>237</sup> Pu
1.0	6.9	1.0	~0	2.4	>10,000
2.0	7.0	0.8	~0	9.6	>10,000
3.0	6.5	1.7	~0	195.0	>10,000
7.0	7.9	1.5	~0	>10,000	>10,000

Contact Time, Days	Kd', ml/g, Teflon Liner				
	<sup>85</sup> Sr	<sup>137</sup> Cs	<sup>125</sup> I	<sup>75</sup> Se	<sup>237</sup> Pu
1.1	8.0	~0	~0	~0	>10,000
4.1	3.5	~0	~0	159	>10,000
6.1	0.7	~0	~0	72	>10,000

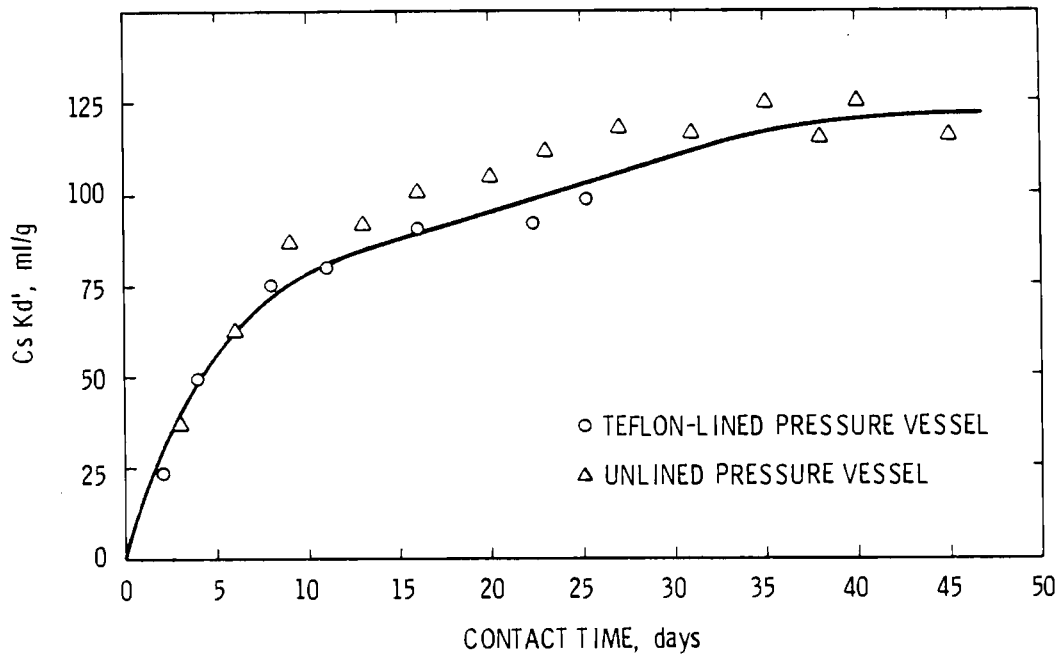


FIGURE 5. Cesium Kd' Value Versus Contact Time in Days for Umtanum Basalt at 150°C and 6.9 MPa Ar, 1 g Basalt/10 ml of Synthetic Groundwater

TABLE 15. Radionuclide Kd' Values Obtained With 0.30 to 0.85-mm Umtanum Basalt at 150°C and 6.9 MPa Ar, 1 g Basalt/10 ml Solution. Initial radionuclide concentrations are the same as those given for 1 g/10 ml and 23°C.

<u>Contact Time, Days</u>	<u>Kd', ml/g, No Teflon Liner</u>				
	<u><sup>85</sup>Sr</u>	<u><sup>137</sup>Cs</u>	<u><sup>125</sup>I</u>	<u><sup>75</sup>Se</u>	<u><sup>237</sup>Pu</u>
3.0	54	37	0.8	120	88
6.1	72	63	0.1	106	68
9.1	85	87	0.2	122	115
13.1	88	92	0.5	105	168
16.2	91	101	0.8	126	195
20.0	92	105	0.4	136	189
24.6	922	112	~0	119	123
28.6	896	118	0.1	86	123
32.5	393	117	0.2	125	370
36.6	3613	124	~0	155	>10,000
39.6	>10,000	116	0.3	158	>10,000
42.6	>10,000	125	0.7	166	>10,000
45.6	>10,000	116	0.3	360	>10,000

<u>Contact Time, Days</u>	<u>Kd', ml/g, Teflon Liner</u>				
	<u><sup>85</sup>Sr</u>	<u><sup>137</sup>Cs</u>	<u><sup>125</sup>I</u>	<u><sup>75</sup>Se</u>	<u><sup>237</sup>Pu</u>
2.0	212	23	9	19	-
3.9	4423	49	16	33	-
7.9	>10,000	75	16	100	-
11.0	251	80	21	311	-
16.0	1468	91	20	95	-
22.3	232	92	16	126	-
25.2	340	98	12	75	-
30.2	536	102	~0	82	-
36.2	946	101	~0	85	-
39.2	406	92	~0	73	-
46.2	>10,000	97	~0	105	-

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APPENDIX A

CHARACTERIZATION OF FLOW E AND POMONA BASALTS

APPENDIX A

CHARACTERIZATION OF FLOW E BASALT

(Ames 1978)

Whole Rock Chemical Analyses

<u>Constituent</u>	<u>Wt. %</u>	
SiO <sub>2</sub>	53.96	54.02
Al <sub>2</sub> O <sub>3</sub>	13.89	13.89
TiO <sub>2</sub>	1.94	1.95
FeO	12.27	12.29
MnO	0.20	0.20
CaO	8.46	8.39
MgO	4.33	4.37
K <sub>2</sub> O	1.20	1.19
Na <sub>2</sub> O	3.43	3.39
P <sub>2</sub> O <sub>5</sub>	0.32	0.31
Total	100.00*	100.00*

\*Analyses total 100% due to normalization of the X-ray fluorescence data by a computer program.

Major Mineral Phases Found by X-Ray Diffraction

Feldspar, Clinopyroxene

Microprobe Chemical Analyses and Computed Mineral Compositions

	<u>Wt. %</u>												
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>	<u>9</u>	<u>10</u>	<u>11</u>	<u>12</u>	<u>13</u>
SiO <sub>2</sub>	60.5	58.7	49.4	52.6	46.9	51.8	36.4	0.2	0.2	0.3	55.3	76.3	76.9
Al <sub>2</sub> O <sub>3</sub>	24.4	26.1	0.8	1.1	1.0	0.9	--	0.2	0.9	2.2	6.3	12.9	11.6
TiO <sub>2</sub>	--	--	0.6	0.4	0.6	0.4	--	51.8	27.9	28.1	0.1	0.7	--
FeO	0.9	0.8	21.6	11.5	17.0	29.8	52.0	45.5	68.8	68.4	27.6	1.9	1.4
MnO	--	--	0.4	0.2	0.2	0.5	0.7	0.4	0.3	0.4	--	--	--
CaO	9.3	11.9	11.9	19.1	20.2	8.2	0.4	--	--	--	1.3	0.5	0.4
MgO	--	--	12.1	15.1	11.3	8.3	12.1	--	0.5	1.4	5.0	--	--
K <sub>2</sub> O	0.9	0.5	--	--	--	--	--	--	--	--	0.6	6.9	6.5
Na <sub>2</sub> O	5.8	4.7	--	--	--	--	--	--	--	--	--	--	--
P <sub>2</sub> O <sub>5</sub>	--	--	--	--	--	--	--	--	--	--	--	--	--
TOTAL	101.8	102.7	96.8	100.0	97.2	99.9	101.6	98.1	98.6	100.8	96.2	99.2	96.8



### Resulting Formulations

---

1.  $(\text{Na}_{1.99}, \text{Ca}_{1.77}, \text{K}_{0.20})(\text{Al}_{5.11}, \text{Si}_{10.74})\text{O}_{32}$
2.  $(\text{Na}_{1.62}, \text{Ca}_{2.26}, \text{K}_{0.12})(\text{Al}_{5.45}, \text{Si}_{10.40})\text{O}_{32}$
3.  $(\text{Mg}_{0.72}, \text{Fe}_{0.72}, \text{Ca}_{0.51}, \text{Ti}_{0.02}, \text{Mn}_{0.01}, \text{Al}_{0.03})$   
 $(\text{Al}_{0.03}, \text{Si}_{1.97})\text{O}_6$
4.  $(\text{Mg}_{0.84}, \text{Fe}_{0.36}, \text{Ca}_{0.77}, \text{Ti}_{0.01}, \text{Mn}_{0.01}, \text{Al}_{0.02})$   
 $(\text{Al}_{0.03}, \text{Si}_{1.97})\text{O}_6$
5.  $(\text{Mg}_{0.68}, \text{Fe}_{0.57}, \text{Ca}_{0.87}, \text{Ti}_{0.02}, \text{Mn}_{0.01})$   
 $\text{Al}_{0.05}, (\text{Si}_{1.88})\text{O}_6$
6.  $(\text{Mg}_{0.47}, \text{Fe}_{0.95}, \text{Ca}_{0.33}, \text{Ti}_{0.01}, \text{Mn}_{0.02}, \text{Al}_{0.04})$   
 $(\text{Si}_{1.96})\text{O}_6$
7. ---
8.  $(\text{Fe}, \text{Mn})_{1.98}(\text{Ti})_{2.00}\text{O}_6$
9. ---
10. ---
11.  $(\text{Al}_{0.15}, \text{Mg}_{0.49}, \text{Fe}_{1.53})(\text{Al}_{0.34}, \text{Si}_{3.66})\text{O}_{10}(\text{OH})_2$
12. Ground mass
13. Ground mass

Note: The dashes indicate that constituent was below detection limits.

#### Ethylene Glycol Sorption Surface Area, 20 to 50 Mesh

$$10.3 \pm 1.0 \text{ m}^2/\text{g}$$

#### Strontium Cation Exchange Capacity, 20 to 50 Mesh

$$4.7 \pm 0.2 \text{ meq}/100 \text{ g}$$

Estimation of Quantitative Mineralogy on the Quantimet  
(electronic point counting)

<u>Major Minerals</u>	<u>Wt. %</u>
Plagioclase (Ab <sub>55</sub> -Ab <sub>40</sub> )	44
Clinopyroxenes	32
Groundmass (including glass)	13
Metallic Oxides	6
Clays	5

CHARACTERIZATION OF POMONA BASALT

(Deju et al. 1978)

Whole Rock Chemical Analyses

<u>Constituent</u>	<u>Wt. %</u>					
SiO <sub>2</sub>	52.98	51.87	52.39	52.01	52.78	52.04
Al <sub>2</sub> O <sub>3</sub>	15.63	15.02	14.92	14.88	15.50	15.11
TiO <sub>2</sub>	1.58	1.55	1.58	1.55	1.60	1.61
Fe <sub>2</sub> O <sub>3</sub>	2.00	2.00	2.00	2.00	2.00	2.00
FeO	8.99	8.89	8.21	8.99	8.90	8.95
MnO	0.19	0.19	0.18	0.19	0.19	0.20
CaO	8.89	10.58	10.94	10.62	8.73	10.44
MgO	6.79	7.08	6.94	7.17	7.22	6.97
K <sub>2</sub> O	0.65	0.39	0.53	0.35	0.53	0.34
Na <sub>2</sub> O	2.07	2.23	2.09	2.02	2.24	2.22
P <sub>2</sub> O <sub>5</sub>	0.25	0.19	0.22	0.21	0.31	0.23

Major Mineral Phases Found by X-Ray Diffraction

Feldspar, Clinopyroxene

Ethylene Glycol Sorption Surface Areas

<u>0.85 - 0.30 mm</u>	<u>2.00 - 0.85 mm</u>
31.2 ± 1.4 m <sup>2</sup> /g	27.4 ± 0.7 m <sup>2</sup> /g

Estimate of Quantitative Mineralogy by Point Counting

<u>Major Minerals</u>	<u>Volume %</u>
Plagioclase, laboradorite to andesine	33.9 to 28.7
Pyroxene, mainly augite	37.2 to 30.8
Olivine	2.8 to 1.4
Metallic Oxides	5.5 to 2.8

Other Phases

Tachylyte (nearly anhydrous basaltic glass)	34.5 to 17.1
Opal	3.5 to 1.8

APPENDIX B

CHARACTERIZATION OF SECONDARY MINERALIZATION

## APPENDIX B

### CHARACTERIZATION OF SECONDARY MINERALIZATION

#### SAMPLE TREATMENT

During excavation of the Near-Surface Test Facility on the Hanford Site, about 10 kg of Pomona basalt secondary mineralization was recovered and stored in plastic bags to avoid loss of water. The larger chunks of fracture mineralization showed dark green exterior surfaces and light blue centers. These characteristics suggest that oxidation had been occurring since exposure to the atmosphere. Nontronite normally is green in color, but contains ferric iron ( $\text{Fe}^{3+}$ ) as a part of its structure. The ferric iron is already fully oxidized so that the nontronite color is stable. The color change of the secondary mineralization may be due to admixed ferrous or manganous ion-containing materials.

Distilled water was added to the as-received secondary mineralization sample, and a blender used to physically disperse the sample to an overall mayonnaise consistency. Of the 10 kg total weight, 1.2 kg were admixed Pomona basalt fragments of various dimensions. The large basalt fragments were removed before blending or later by forcing the sample through a 50-mesh stainless steel screen. Approximately 20% of basalt-free fracture mineralization were finally obtained, homogenized by stirring in a large vessel and placed in 1-l polyethylene containers. The filled containers were frozen at minus 20°C. The frozen containers were dried under vacuum to produce a freeze-dried product. This treatment method in preparation for use of the fracture mineralization in  $K_d$  determination work caused the least damage to any of the smectite clays present in the sample (van Olphen 1965).

After freeze-drying, the various fractions were remixed into a single sample and placed in a dessicator so that the same amount of sample containing the same amount of water could be weighed out each time the secondary mineralization was used.

## X-RAY DIFFRACTION RESULTS

Tracings of the as-received and potassium-based secondary mineralization Cu K $\alpha$ , x-ray diffraction patterns are shown in Figure B.1. The air-dried, as-received material, taken from the homogenous clay after dispersion and before freezing, is shown in curve a of Figure B.1. A large basal peak at  $5.5^{\circ}2\theta$  is the main feature. No kaolinite, chlorite, illite, vermiculite or mica are present. Vapor glycolation of the as-received sample at  $60^{\circ}\text{C}$  resulted in a normal 17Å smectite or expanding layer silicate as shown in curve b. Potassium basing with gentle heating results in collapse of nontronite-beidellite mixtures to a 10Å mica spacing (van Olphen 1965), as seen in curve c of Figure B.1. The low temperature collapse is caused by the large percentage of lattice charge due to substitution in the tetrahedral layer and the presence of potassium on exchangeable cation positions (Weaver 1958).

## CHEMICAL COMPOSITION

The chemical composition of the as-received secondary mineralization is given in Table B.1. An average of 25 wt.% water was contained in the analyzed samples. Six fragments of secondary mineralization were selected at random from the original material for mounting and electron microprobe chemical analysis.

Note that these analyses are relatively uniform, which suggests that the secondary mineralization is also relatively uniform in chemical composition. No attempts were made to determine a mineral formula from these analyses because the observed change in clay color from light blue to dark green upon exposure to the atmosphere strongly suggests an admixed phase or phases. Such an admixed material would be very difficult to quantify. In addition, up to 4 wt.% of the magnesium could be present as exchangeable cations rather than occupying an octahedral structural position. Further study of the clay would be required (exchangeable cations, etc.) before a probable formula could be derived.

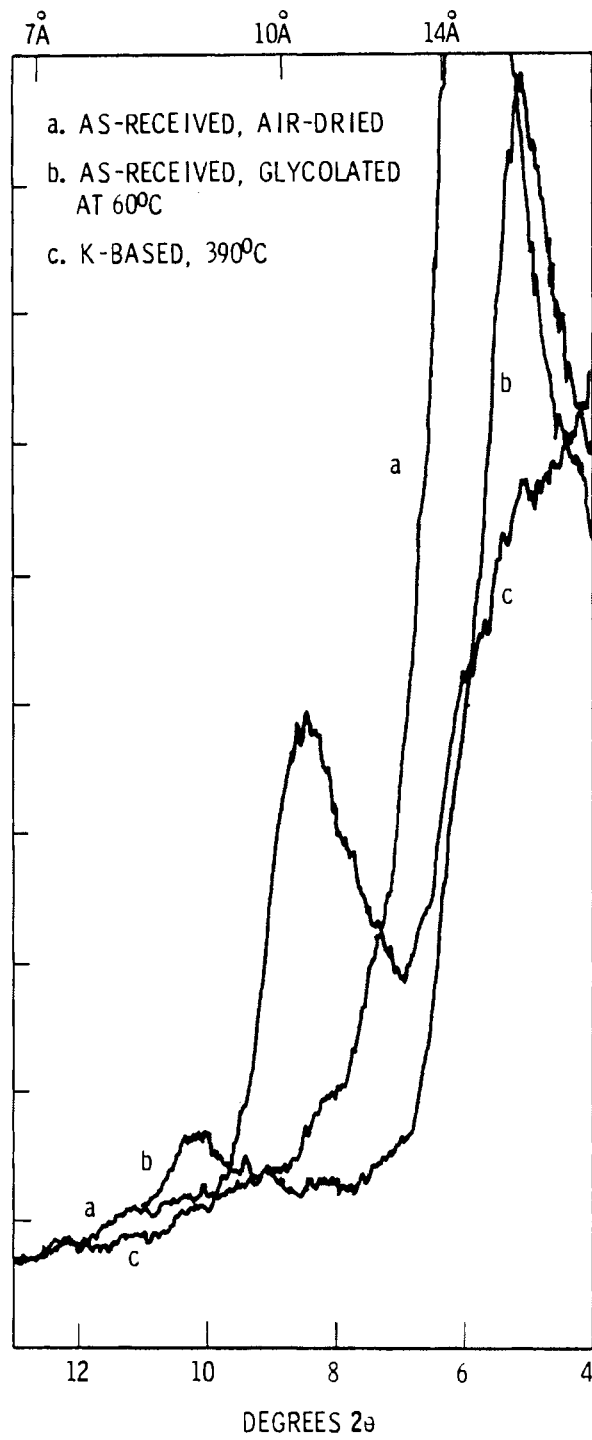


FIGURE B.1. X-Ray Diffraction Patterns of Treated and Untreated Secondary Mineralization

TABLE B.1. The As-Received Chemical Composition of the Secondary Mineralization Used in the Radionuclide Distribution Determinations. The remainder of the total wt% was water.

<u>Constituent</u>	<u>Wt. %</u>					
SiO <sub>2</sub>	43.2	45.5	44.5	44.3	45.3	43.2
Al <sub>2</sub> O <sub>3</sub>	6.5	6.6	6.6	6.5	6.9	6.4
TiO <sub>2</sub>	0.2	0.2	0.2	0.2	0.2	0.2
Fe <sub>2</sub> O <sub>3</sub>	9.8	9.6	9.7	9.4	9.6	9.0
CaO	1.2	1.0	1.1	1.0	1.0	1.3
MgO	12.4	12.8	12.6	12.7	13.0	12.4
K <sub>2</sub> O	<u>0.7</u>	<u>0.7</u>	<u>0.7</u>	<u>0.7</u>	<u>0.7</u>	<u>0.7</u>
Total	74.0	76.4	75.4	74.8	76.7	73.2

SURFACE AREA

The surface area of the secondary mineralization sample has not been determined at this time. However, based on its mineralogy, it should yield a value between 600 and 800 m<sup>2</sup>/g.



APPENDIX C

SURFACE AREA MEASUREMENT WITH ETHYLENE GLYCOL

## APPENDIX C

### SURFACE AREA MEASUREMENT WITH ETHYLENE GLYCOL

(Rai and Franklin 1978)

1. Prepare samples by saturating with  $\text{CaCl}_2$ : wash 15 grams of each sample with 200 ml of 2N  $\text{CaCl}_2$ , stir up, centrifuge and pour off supernatant, and repeat the washing. Then use distilled water to wash excess  $\text{CaCl}_2$  out of the samples. Stop washing with water when  $\text{AgNO}_3$  no longer precipitates with addition of the supernatant. Dry the samples either in an oven or by freeze drying.
2. Clean up aluminum moisture cans and place, without lids on, in  $105^\circ\text{C}$  oven. After an hour remove cans from the oven and place in a desiccator with drierite. Wait until cooled, then weigh each can; minimize the adsorption of atmospheric water by the cans, before the cans are weighed. (Put each sample into cans.) Return cans plus samples (lids removed) to  $105^\circ\text{C}$  oven; leave for several hours.
3. At least six hours after samples were placed in the oven, make up  $\text{CaCl}_2$  - glycol solvate. Weigh out three-105 gram aliquots of 40 mesh  $\text{CaCl}_2$  each in a 400 ml beaker. Place the beakers in a  $210^\circ\text{C}$  furnace. At the end of one hour reweigh the  $\text{CaCl}_2$  and return 100 grams of  $\text{CaCl}_2$  per beaker back into the furnace. Wait a few minutes before taking the  $\text{CaCl}_2$  out and mixing it with 20 grams of ethylene glycol. The heat of the  $\text{CaCl}_2$  plus vigorous mixing should result in a lump-free, well-mixed solvate, which is important. Place each beaker in separate, sealed desiccators to cool.
4. While the  $\text{CaCl}_2$  - glycol solvates are cooling, remove the cans from the oven, placing lids on them before putting them into the desiccator with drierite. After the cans have cooled weigh each can; again, it is important to minimize the adsorption of atmospheric water by the cans and samples before being weighed. At the completion of weighing place the cans on a bench top and wet each sample with minimum amount of glycol (1 ml or less) by applying dropwise over the surface of the samples.

5. Take the beakers of  $\text{CaCl}_2$  - glycol solvate and uniformly cover the bottom of three different culture chambers. Set circular pieces of 1/4" mesh hardware cloth on top of the  $\text{CaCl}_2$  glycol solvate. Rubber stoppers keep the hardware cloth slightly above the  $\text{CaCl}_2$  glycol solvate. With the culture chambers ready, place one of each sample (lids off) in the culture chambers, this will make each chamber have four different samples. Before putting the culture chambers in separate desiccators, place the culture chamber lids on top of the chambers; don't seal them. Now that each culture chamber is in a desiccator hook up the vacuum pump to each desiccator for 45 minutes. After 16-24 hours, again apply the vacuum pump to each desiccator for 45 minutes.
6. When the samples have been in the desiccators for at least 48 hours, carefully weigh out each sample. After weighing, apply vacuum to each desiccator for 45 minutes. Wait at least 8 hours before reweighing. Repeat the weighing procedures until two successive weighings agree within a few tenths of a mg.
7. Calculating the surface area:
  - $A = W_g / (W_s \times 0.00031)$
  - $A = \text{Surface area in } M^2/g$
  - $W_g = \text{Weight (grams) of glycol retained by the sample}$
  - $W_s = \text{Weight (grams) of sample.}$

0.00031 is Dyal-Hendricks value for grams of glycol required to form a monolayer on one  $M^2$  of surface.

Note: Care should be taken in handling the aluminum moisture cans; any amount of dirt or prolonged contact with the atmosphere will affect the calculated surface area.

8. Equipment Used:
  - 12 - aluminum boxes
  - 3 - 25 cm desiccators
  - 3 - culture chambers
  - desiccator with drierite

- vacuum pump
- 210°C furnace

#### Chemicals

- 40 mesh  $\text{CaCl}_2$
- 2N  $\text{CaCl}_2$
- Ethylene glycol

APPENDIX D

OUTLINE OF 150°C STATIC K<sub>d</sub> EXPERIMENTS

## APPENDIX D

### OUTLINE OF 150°C STATIC K<sub>d</sub> EXPERIMENTS

#### COMMON PROCEDURE

1. Weigh out proper amount of solid material.
2. Place in pressure vessel without abrasion and generation of fines.
3. Measure proper volume of solution and place in the pressure vessel pipette a 10 ml aliquot of each traced solution used identify solution with a date because there may be more than one solution traced with the same radionuclides.
4. Cover vessel.
5. With the gas exhaust valve through the cover open, gently purge the vessel contents of oxygen with argon make sure that enough is used to displace the atmosphere above the bomb contents as well.
6. Close exhaust valve bring vessel to proper temperature and pressure.
7. Take samples of desired volume at proper times by first purging sample line with solution don't waste the solution by over-purging pipette desired volume into a marked scintillation vial immediately.
8. Where the circumstances permit, only the Ar pressure need be adjusted before resampling at the new pressure after the proper time interval.
9. After sampling is completed, cool the vessel and vent Ar pressure-discard solids and solution unless specifically asked to save one or the other.
10. Clean the vessel walls of quartz and other silicates if necessary the need for cleaning will have to be established by experimentation.
11. Repeat procedure on another experiment.
12. Keep good records of each experiment by filling out an autoclave data sheet for each of the experiments in each of the pressure vessels - attach a xerox copy to each batch of samples taken for counting if

possible identify each sample with a label that allows us to go to the notebook and find the experimental conditions such as radionuclides in the solution, run temperature and pressure, solids, etc. identify each pressure vessel with a number or letter and use solutions containing the same radionuclides in the same vessels each time contact us if there are any questions.

### SPECIFIC EXPERIMENTS

1. Sr-Cs-Tc, Se-I, U, Pu; one group per vessel
  - a. blank solutions (no solids), 60 ml each sample
  - b. 150°C - 4000 psi Ar
  - c. 5 ml samples at 24, 48, 96 hours
  - d. total of 12 samples
2. Sr-Cs-Tc, Se-I, U, Pu; Umtanum 20 x 50 mesh basalt
  - a. 250 ml solution/20 g basalt, no stirring
  - b. 150°C - 4000 psi Ar
  - c. 5 ml samples every 3 days from startup to 30 days
  - d. total of 40 samples
3. Sr-Cs-Tc, Se-I, U, Pu; Flow E 20 x 50 mesh basalt
  - a. 200 ml solution/20 g basalt, no stirring
  - b. 150°C - 4000 psi Ar
  - c. 10 ml samples, 3 in succession each vessel at the optimal sampling time
  - d. total of 12 samples
4. Sr-Cs-Tc, Se-I, U, Pu; Pomona 20 x 50 mesh basalt
  - a. 200 ml solution/20 g basalt, no stirring
  - b. 150°C, 4000 psi Ar
  - c. 10 ml samples, 3 in succession each vessel optimal sampling time
  - d. total of 12 samples

5. Sr-Cs-Tc, Se-I, U, Pu; Secondary Mineralization
  - a. 250 ml solution/20 g clay, no stirring
  - b. 150°C, 4000 psi Ar
  - c. 5 ml samples every 3 days from startup to 30 days
  - d. total of 40 samples
6. Sr-Cs-Tc, Se-I, U, Pu; Umtanum 20 x 50 mesh basalt
  - a. 250 ml solution/20 g basalt, no stirring
  - b. 150°C, 1000 psi pressure Ar
  - c. 5 ml samples every 3 days from startup to 30 days
  - d. total of 40 samples
7. Sr-Cs-Tc, Se-I, U, Pu; Umtanum 20 x 50 mesh basalt
  - a. 200 ml solution/20 g basalt, no stirring
  - b. 150°C, 2000 psi Ar
  - c. 10 ml samples, 3 in succession each vessel at optimal sampling time
  - d. total of 12 samples
8. Sr-Cs-Tc, Se-I, U, Pu; Umtanum 20 x 50 mesh basalt
  - a. 200 ml solution/20 g basalt, no stirring
  - b. 150°C, 3000 psi Ar
  - c. 10 ml samples, 3 in succession each vessel at optimal sampling time
  - d. total of 12 samples
9. Sr-Cs-Tc, Se-I, U, Pu; Umtanum 20 x 50 mesh basalt
  - a. 200 ml solution/20 g basalt, no stirring
  - b. 150°C, 4000 psi Ar
  - c. 10 ml samples, 3 in succession each vessel at optimal sampling time
  - d. total of 12 samples
10. Sr-Cs-Tc, Se-I, U, Pu; Flow E 20 x 50 mesh basalt
  - a. 200 ml solution/20 g basalt, no stirring
  - b. 150°C, 1000 psi Ar
  - c. 10 ml samples, 3 in succession each vessel at optimal sampling time
  - d. total of 12 samples



11. Sr-Cs-Tc, Se-I, U, Pu; Flow E 20 x 50 mesh basalt
  - a. 200 ml solution/20 g basalt, no stirring
  - b. 150°C, 2000 psi Ar
  - c. 10 ml samples, 3 in succession each vessel at optimal sampling time
  - d. total of 12 samples
12. Sr-Cs-Tc, Se-I, U, Pu; Flow E 20 x 50 mesh basalt
  - a. 200 ml solution/20 g basalt, no stirring
  - b. 150°C, 3000 psi Ar
  - c. 10 ml samples, 3 in succession each vessel at optimal sampling time
  - d. total of 12 samples
13. Sr-Cs-Tc, Se-I, U, Pu; Flow E 20 x 50 mesh basalt
  - a. 200 ml solution/20 g basalt, no stirring
  - b. 150°C, 4000 psi Ar
  - c. 10 ml samples, 3 in succession each vessel at optimal sampling time
  - d. total of 12 samples
14. Sr-Cs-Tc, Se-I, U, Pu; Secondary Mineralization
  - a. 200 ml solution/20 g clay, no stirring
  - b. 150°C, 1000 psi Ar
  - c. 5 ml samples, 3 in succession each vessel at optimal sampling time
  - d. total of 40 samples
15. Sr-Cs-Tc, Se-I, U, Pu; Secondary Mineralization
  - a. 200 ml solution/20 g clay, no stirring
  - b. 150°C, 2000 psi Ar
  - c. 5 ml samples, 3 in succession each vessel at optimal sampling time
  - d. total of 12 samples
16. Sr-Cs-Tc, Se-I, U, Pu; Secondary Mineralization
  - a. 200 ml solution/20 g clay, no stirring
  - b. 150°C, 3000 psi Ar
  - c. 5 ml samples, 3 in succession each vessel at optimal sampling time
  - d. total of 12 samples

17. Sr-Cs-Tc, Se-I, U, Pu; Secondary Mineralization
  - a. 200 ml solution/20 g clay, no stirring
  - b. 150°C, 4000 psi Ar
  - c. 5 ml samples, 3 in succession each vessel at optimal sampling time
  - d. total of 12 samples

Clean and Decontaminate All Four Vessels

Repeat (1) with Ra, Np, Am

18. Ra, Np, Am; Umtanum 20 x 50 mesh basalt
  - a. 250 ml solution/20 g clay, no stirring
  - b. 150°C, 4000 psi Ar
  - c. 5 ml samples 3 days from startup to 30 days
  - d. total of 40 samples
19. Ra, Np, Am; Flow E 20 x 50 mesh basalt
  - a. 200 ml solution/20 g clay, no stirring
  - b. 150°C, 4000 psi Ar
  - c. 10 ml samples, 3 in succession each vessel at optimal sampling time
  - d. total of 9 samples
20. Ra, Np, Am; Pomona 20 x 50 mesh basalt
  - a. 200 ml solution/20 g clay, no stirring
  - b. 150°C, 4000 psi Ar
  - c. 10 ml samples, 3 in succession each vessel at optimal sampling time
  - d. total of 9 samples
21. Ra, Np, Am; Secondary Mineralization
  - a. 250 ml solution/20 g clay, no stirring
  - b. 150°C, 4000 psi Ar
  - c. 5 ml samples every 3 days from startup to 30 days
  - d. total of 30 samples

22. Ra, Np, Am; Umtanum 20 x 50 mesh basalt
  - a. 250 ml solution/20 g clay, no stirring
  - b. 150°C, 1000 psi Ar
  - c. 5 ml samples every 3 days from startup to 30 days
  - d. total of 30 samples
23. Ra, Np, Am; Umtanum 20 x 50 mesh basalt
  - a. 200 ml solution/20 g clay, no stirring
  - b. 150°C, 2000 psi Ar
  - c. 10 ml samples, 3 in succession each vessel at optimal sample time
  - d. total of 9 samples
24. Ra, Np, Am; Umtanum 20 x 50 mesh basalt
  - a. 200 ml solution/20 g clay, no stirring
  - b. 150°C, 3000 psi Ar
  - c. 10 ml samples, 3 in succession each vessel at optimal sample time
  - d. total of 9 samples
25. Ra, Np, Am; Umtanum 20 x 50 mesh basalt
  - a. 200 ml solution/20 g clay, no stirring
  - b. 150°C, 4000 psi Ar
  - c. 10 ml samples, 3 in succession each vessel at optimal sample time
  - d. total of 9 samples
26. Ra, Np, Am; Flow E 20 x 50 mesh basalt
  - a. 200 ml solution/20 g clay, no stirring
  - b. 150°C, 1000 psi Ar
  - c. 10 ml samples, 3 in succession each vessel at optimal sample time
  - d. total of 9 samples
27. Ra, Np, Am; Flow E 20 x 50 mesh basalt
  - a. 200 ml solution/20 g clay, no stirring
  - b. 150°C, 2000 psi Ar
  - c. 10 ml samples, 3 in succession each vessel at optimal sample time
  - d. total of 9 samples

28. Ra, Np, Am; Flow E 20 x 50 mesh basalt
  - a. 200 ml solution/20 g clay, no stirring
  - b. 150°C, 3000 psi Ar
  - c. 10 ml samples, 3 in succession each vessel at optimal sample time
  - d. total of 9 samples
29. Ra, Np, Am; Flow E 20 x 50 mesh basalt
  - a. 200 ml solution/20 g clay, no stirring
  - b. 150°C, 4000 psi Ar
  - c. 10 ml samples, 3 in succession each vessel at optimal sample time
  - d. total of 9 samples
30. Ra, Np, Am; Pomona 20 x 50 mesh basalt
  - a. 200 ml solution/20 g clay, no stirring
  - b. 150°C, 1000 psi Ar
  - c. 10 ml samples, 3 in succession each vessel at optimal sample time
  - d. total of 9 samples
31. Ra, Np, Am; Pomona 20 x 50 mesh basalt
  - a. 200 ml solution/20 g clay, no stirring
  - b. 150°C, 2000 psi Ar
  - c. 10 ml samples, 3 in succession each vessel at optimal sample time
  - d. total of 9 samples
32. Ra, Np, Am; Pomona 20 x 50 mesh basalt
  - a. 200 ml solution/20 g clay, no stirring
  - b. 150°C, 3000 psi Ar
  - c. 10 ml samples, 3 in succession each vessel at optimal sample time
  - d. total of 9 samples
33. Ra, Np, Am; Pomona 20 x 50 mesh basalt
  - a. 200 ml solution/20 g clay, no stirring
  - b. 150°C, 4000 psi Ar
  - c. 10 ml samples, 3 in succession each vessel at optimal sample time
  - d. total of 9 samples

34. Ra, Np, Am; Secondary Mineralization
  - a. 250 ml solution/20 g clay, no stirring
  - b. 150°C, 1000 psi Ar
  - c. 5 ml samples every 3 days from startup to 30 days
  - d. total of 30 samples
35. Ra, Np, Am; Secondary Mineralization
  - a. 200 ml solution/20 g clay, no stirring
  - b. 150°C, 2000 psi Ar
  - c. 10 ml samples, 3 in succession each vessel at optimal sample time
  - d. total of 9 samples
36. Ra, Np, Am; Secondary Mineralization
  - a. 200 ml solution/20 g clay, no stirring
  - b. 150°C, 3000 psi Ar
  - c. 10 ml samples, 3 in succession each vessel at optimal sample time
  - d. total of 9 samples
37. Ra, Np, Am; Secondary Mineralization
  - a. 200 ml solution/20 g clay, no stirring
  - b. 150°C, 4000 psi Ar
  - c. 10 ml samples, 3 in succession each vessel at optimal sample time
  - d. total of 9 samples

APPENDIX E

OUTLINE OF 300°C STATIC Kd EXPERIMENTS

## APPENDIX E

### OUTLINE OF 300°C STATIC K<sub>d</sub> EXPERIMENTS

#### COMMON PROCEDURE

1. Weigh out proper amount of solid material.
2. Place in pressure vessel without abrasion and generation of fines.
3. Measure proper volume of solution and place in the pressure vessel - pipette a 10 ml aliquot of each traced solution used - identify solution with a date because there may be more than one solution traced with the same radionuclides.
4. Cover vessel.
5. With the gas exhaust valve through the cover open, gently purge the vessel contents of oxygen with argon - make sure that enough is used to displace the atmosphere above the bomb contents as well.
6. Close exhaust valve - bring vessel to proper temperature and pressure.
7. Take samples of desired volume at proper times by first purging sample line with solution - don't waste the solution by over-purging - pipette desired volume into a marked scintillation vial immediately. Secondary mineralization (clay) may not be removed by the 10  $\mu$ m line filter. Check sample for solids before pipetting.
8. Where the circumstances permit, only the Ar pressure need be adjusted before resampling at the new pressure after the proper time interval.
9. After sampling is completed, cool the vessel and vent Ar pressure-discard solids and solution unless specifically asked to save one or the other.
10. Clean the vessel walls of quartz and other silicates if necessary - the need for cleaning will have to be established by experimentation.
11. Repeat procedure on another experiment.

12. Keep good records of each experiment by filling out an autoclave data sheet for each of the experiments in each of the pressure vessels - attach a xerox copy to each batch of samples taken for counting if possible - identify each sample with a label that allows us to go to the notebook and find the experimental conditions such as radionuclides in the solution, run temperature and pressure, solids, etc. - identify each pressure vessel with a number or letter and use solutions containing the same radionuclides in the same vessels each time - contact us if there are any questions.
13. Radionuclide adsorption should be less on titanium and Zircaloy vessels than on the 100K area Inconel vessels. If not, these two vessels also may need to be Teflon-lined.

#### SPECIFIC EXPERIMENTS

1. Sr-Cs, Tc; one group per vessel
  - a. blank solutions (no solids), 100 ml each
  - b. 300°C - 4000 psi Ar
  - c. 3 successive 5 ml samples at 24, 48, 96 hours
  - d. total of 9 samples each for Sr-Cs and Tc
2. Sr-Cs, Tc; Umtanum 20 x 50 mesh basalt
  - a. 250 ml solution/20 g basalt, no stirring
  - b. 300°C - 4000 psi Ar
  - c. 3 successive 5 ml samples every 3 days from startup to 30 days
  - d. total of 30 samples each for Sr-Cs and Tc
3. Sr-Cs, Tc; Umtanum 20 x 50 mesh basalt
  - a. 500 ml solution/10 g basalt, no stirring
  - b. 300°C - 4000 psi Ar
  - c. 3 successive 5 ml samples each vessel at the optimal sampling time
  - d. total of 3 samples each for Sr-Cs and Tc



4. Sr-Cs, Tc; Pomona 20 x 50 mesh basalt
  - a. 250 ml solution/20 g basalt, no stirring
  - b. 300°C - 4000 psi Ar
  - c. 3 successive 5 ml samples each vessel at the optimal sampling time
  - d. total of 3 samples each for Sr-Cs and Tc
5. Sr-Cs, Tc; Flow E 20 x 50 mesh basalt
  - a. 250 ml solution/20 g basalt, no stirring
  - b. 300°C - 4000 psi Ar
  - c. 3 successive 5 ml samples each vessel at the optimal sampling time
  - d. total of 3 samples each for Sr-Cs and Tc
6. Sr-Cs, Tc; Secondary Mineralization
  - a. 250 ml solution/10 g basalt, no stirring
  - b. 300°C - 4000 psi Ar
  - c. 3 successive 5 ml samples every 3 days from startup to 30 days
  - d. total of 30 samples each for Sr-Cs and Tc

CLEAN AND DECONTAMINATE BOTH VESSELS

7. U, Ra; one per vessel
  - a. blank solutions (no solids), 100 ml each
  - b. 300°C - 4000 psi Ar
  - c. 3 successive 5 ml samples at 24, 48, 96 hours
  - d. total of 9 samples each for U and Ra
8. U, Ra; Umtanum 20 x 50 mesh basalt
  - a. 250 ml solution/20 g basalt, no stirring
  - b. 300°C - 3000 psi Ar
  - c. 3 successive 5 ml samples every day from startup to 30 days
  - d. total of 30 samples each for U and Ra
9. U, Ra; Pomona 20 x 50 mesh basalt
  - a. 250 ml solution/20 g basalt, no stirring
  - b. 300°C - 4000 psi Ar

- c. 3 successive 5 ml samples each vessel at the optimal sampling time
  - d. total of 3 samples each for U and Ra
10. U, Ra; Flow E 20 x 50 mesh basalt
- a. 250 ml solution/20 g basalt, no stirring
  - b. 300°C - 4000 psi Ar
  - c. 3 successive 5 ml samples each vessel at the optimal sampling time
  - d. total of 3 samples each for U and Ra
11. U, Ra; Secondary Mineralization
- a. 250 ml solution/10 g basalt, no stirring
  - b. 300°C - 4000 psi Ar
  - c. 3 successive 5 ml samples every day from startup to 30 days
  - d. total of 3 samples each for U and Ra

CLEAN AND DECONTAMINATE BOTH VESSELS

12. Se-I, Np; one group per vessel
- a. blank solutions (no solids), 100 ml each
  - b. 300°C - 4000 psi
  - c. 3 successive 5 ml samples at 24, 48, 96 hours
  - d. total of 9 samples each for Se-I, Np
13. Se-I, Np; Untamum 20 x 50 mesh basalt
- a. 250 ml solution/20 g basalt, no stirring
  - b. 300°C - 4000 psi Ar
  - c. 3 successive 5 ml samples every 3 days from startup to 30 days
  - d. total of 30 samples each for Se-I and Np
14. Se-I, Np; Pomona 20 x 50 mesh basalt
- a. 250 ml solution/20 g basalt, no stirring
  - b. 300°C - 4000 psi Ar
  - c. 3 successive 5 ml samples each vessel at the optimal sampling time
  - d. total of 3 samples each for Se-I and Np

15. Se-I, Np; Flow E 20 x 50 mesh basalt
  - a. 250 ml solution/20 g basalt, no stirring
  - b. 300°C - 4000 psi Ar
  - c. 3 successive 5 ml samples each vessel at the optimal sampling time
  - d. total of 3 samples each for Se-I and Np
16. Se-I, Np; Secondary Mineralization
  - a. 250 ml solution/10 g basalt, no stirring
  - b. 300°C - 4000 psi Ar
  - c. 3 successive 5 ml samples every 3 days from startup to 30 days
  - d. total of 30 samples each for Se-I and Np

CLEAN AND DECONTAMINATE BOTH VESSELS

17. Am, Pu; one per vessel
  - a. blank solutions (no solids), 100 ml each
  - b. 300°C - 4000 psi Ar
  - c. 3 successive 5 ml samples at 24, 48, 96 hours
  - d. total of 9 samples each for Am and Pu
18. Am, Pu; Umtanum 20 x 50 mesh basalt
  - a. 250 ml solution/20 g basalt, no stirring
  - b. 300°C - 4000 psi Ar
  - c. 3 successive 5 ml samples every 3 days from startup to 30 days
  - d. total of 30 samples each for Am and Pu
19. Am, Pu; Pomona 20 x 50 mesh basalt
  - a. 250 ml solution/20 g basalt, no stirring
  - b. 300°C - 4000 psi Ar
  - c. 3 successive 5 ml samples each vessel at the optimal sampling time
  - d. total of 3 samples each for Am and Pu
20. Am, Pu; Flow E 20 x 50 mesh basalt
  - a. 250 ml solution/20 g basalt, no stirring
  - b. 300°C - 4000 psi Ar

- c. 3 successive 5 ml samples each vessel at the optimal sampling time
- d. total of 3 samples each for Am and Pu

21. Am, Pu; Secondary Mineralization

- a. 250 ml solution/10 g basalt, no stirring
- b. 300°C - 4000 psi Ar
- c. 3 successive 5 ml samples every 3 days from startup to 30 days
- d. total of 30 samples each for Am and Pu

APPENDIX F

EFFECTS OF WEATHERING ON SURFACES OF UMTANUM BASALT

## APPENDIX F

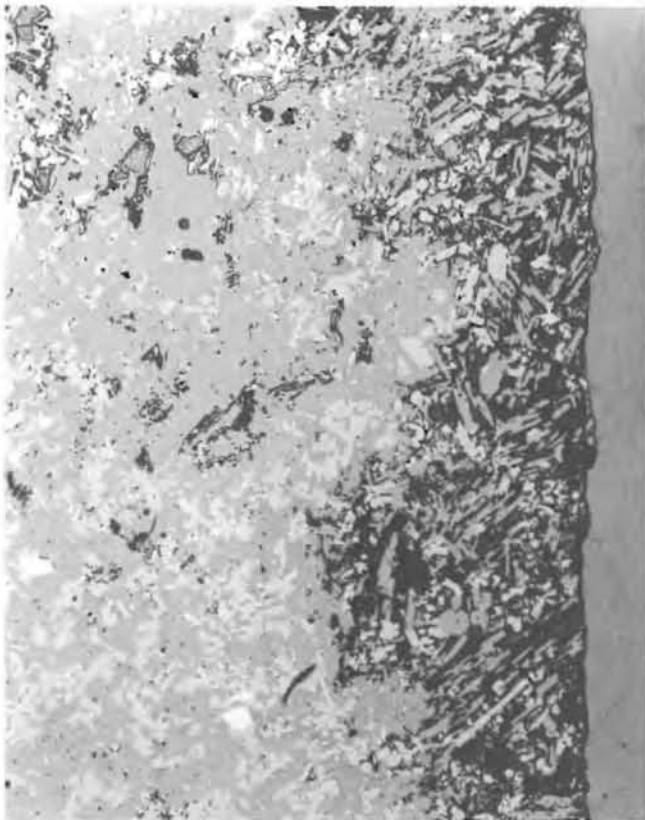
### EFFECTS OF WEATHERING ON SURFACES OF UMTANUM BASALT

Figure F.1 shows a 50 times magnification of a weathered zone perpendicular to a fissure in the surface-gathered Umtanum basalt. The weathered zone is compared to a similar magnification of hydrothermally treated (300°C, 13.8 MPa Ar, 21 days equilibration, 20 g Umtanum 20- to 50-mesh basalt/600 ml synthetic groundwater of Table 2) Umtanum basalt in Figure F.2. The results are very similar, with initial alteration of the glass phase in both cases.

Scanning electron micrograph (SEM) photos comparing the weathered and unweathered basalt areas are given in Figures F.3 through F.6. The two white fragments on the 500X unweathered photo are probably polishing agent and not a part of the basalt. The difference in the state of the glassy groundmass between the weathered and unweathered portions of the basalt are striking. In the weathered portion, parts of the glass are dissolved, leaving considerable porosity, and resulting in the synthesis of other, more stable mineral phases, such as the smectites.

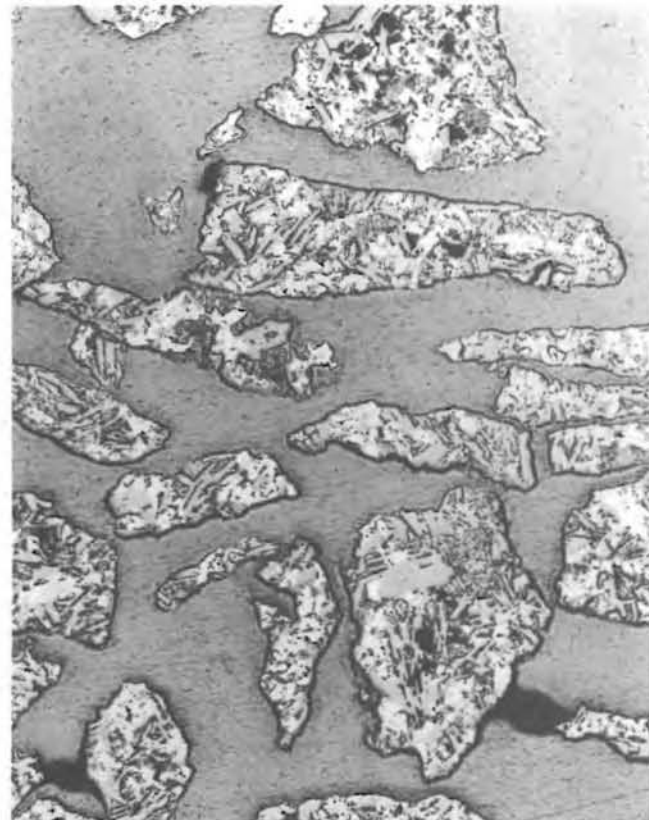
The glass phase is high in silica and potash. Electron maps of silicon and potassium are shown in the third glossy photo at a magnification of 100 across the weathered zone-unweathered zone contact. Note that the weathered zone is lower in silicon and potassium indicating that the glass phase is altering by weathering type reactions even in this relatively low rainfall area. The glass phase of the basalt very likely controls the groundwater composition that is in chemical equilibrium with it. Variations in glass composition could be reflected in some cases by radionuclide Kd variations.

F.2



50 X

FIGURE F.1. Weathered Basalt Section



50 X

FIGURE F.2. Hydrothermally Treated Basalt Section

F.3

500X

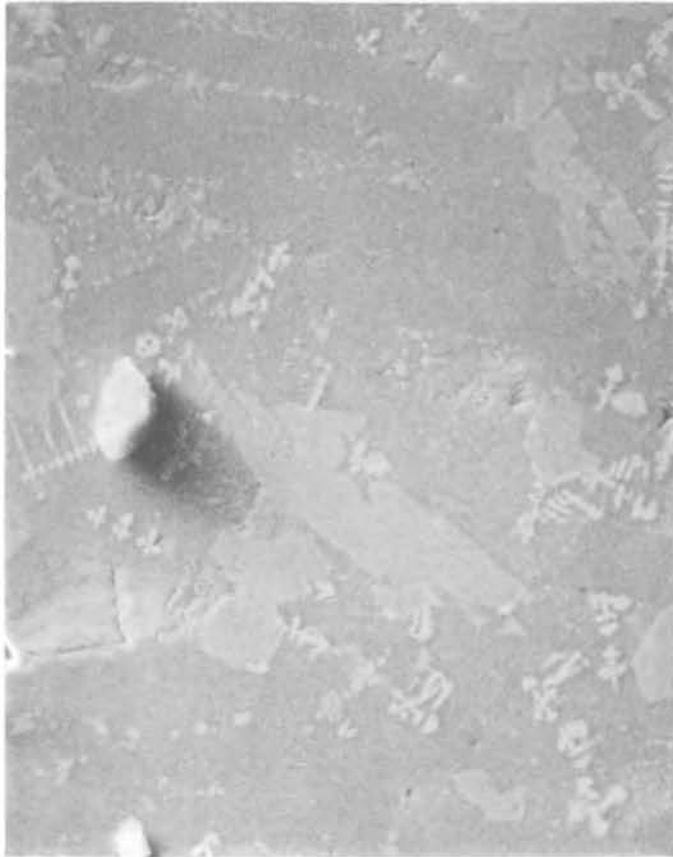


FIGURE F.3. Unweathered Basalt Section

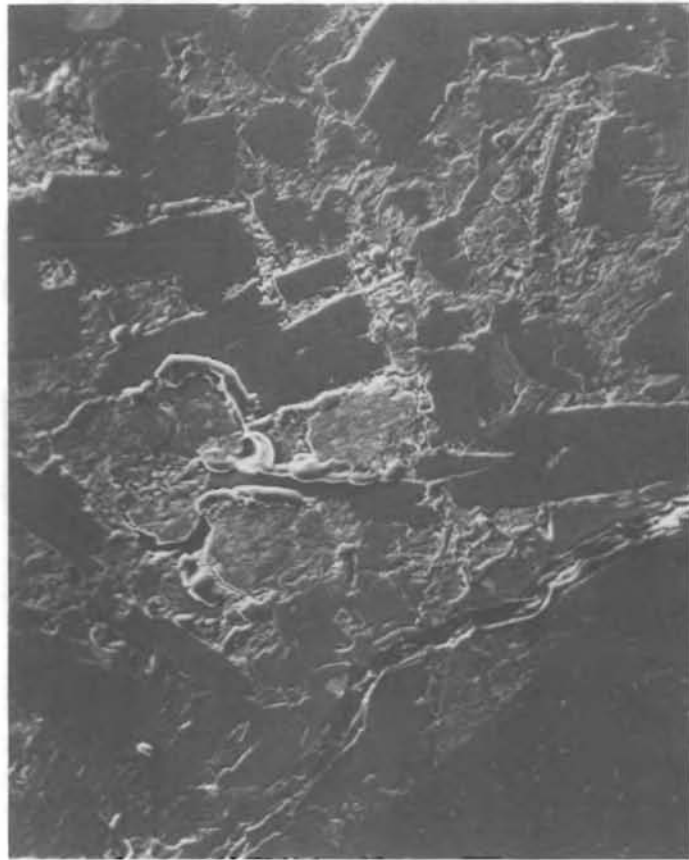


FIGURE F.4. Weathered Basalt Section



2000X



FIGURE F.5. Unweathered Basalt Section

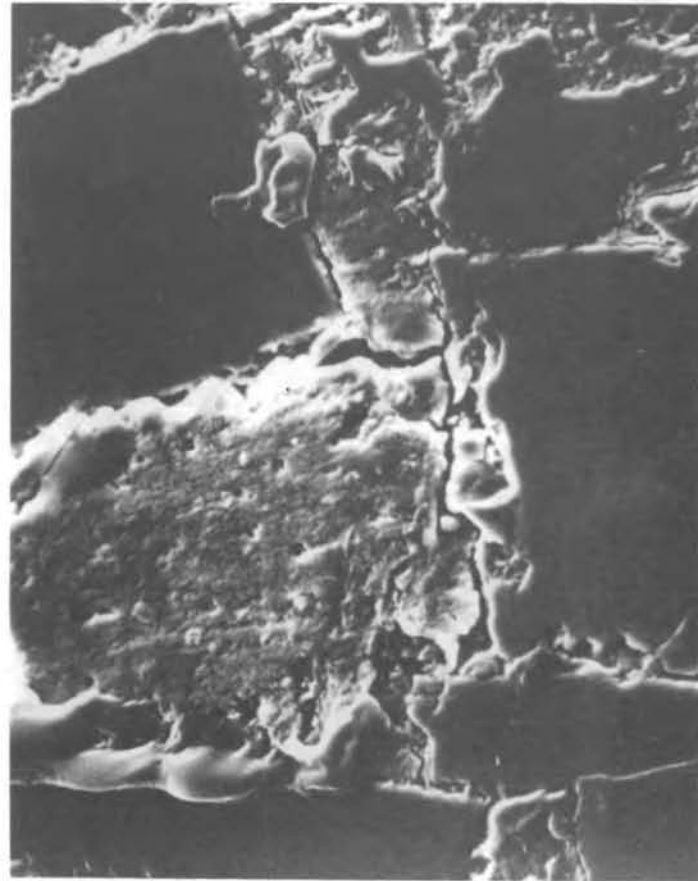


FIGURE F.6. Weathered Basalt Section



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