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CHARACTERIZATION OF ACTINIDE
BEARING SOILS:
TOP SIXTY CENTIMETERS OF 216-Z-9
ENCLOSED TRENCH

Battelle

Pacific Northwest Laboratories
Richland, Washington 99352

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by

L. L. Ames

Water and Land Resources Department

February 1974

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CHARACTERIZATION OF ACTINIDE BEARING SOILS:
TOP SIXTY CENTIMETERS OF 216-Z-9 ENCLOSED TRENCH

L. L. Ames

INTRODUCTION

Under pre-1965 waste disposal practices at Hanford, certain actinide-bearing solutions were discharged to the soil in covered trench facilities; e.g., 216-Z-9.⁽¹⁾ The soil response to the influx of acidic, actinide-bearing solutions has pertinence to the present and future locations of the actinides. In order to understand present and future soil-actinide relationships, the following tasks were investigated.

1. Identification of the soil minerals and soil rock types.
2. Location of the actinides.
3. Determination of the present actinides form.
4. Characterization of the soil-solution chemical reactions that resulted in the present form and location of the actinides.

This document presents the results of work on the above tasks through examination of samples from the upper 60 centimeters of the 216-Z-9 covered trench.

SUMMARY

A program to examine the soil-actinide relationship in sediments from a disposal facility was initiated in March 1973. Initial work has been done using samples from the 216-Z-9 covered trench.

Soil mounts were made of soil recovered from a core of an uncontaminated well drilled alongside Z-9 trench. The mounts were made by plastic-impregnating smaller, 1-inch diameter cores taken from the original 4-inch diameter cores. The uncontaminated mounts showed that the less than 30 mesh soil was composed of predominately metamorphic rock fragments of the Belt Series, brought down from northern Washington and Idaho by the ancestral Columbia River.

Two 4-inch diameter cores, 2 feet in length, were taken from the floor of Z-9 trench. Smaller contaminated mounts were made from these original cores in the same manner as with the uncontaminated samples. Overlying one of these cores (4-11), was a sludge layer of silica, alumina and water. The other core (4-5) had no sludge layer.

At least two types of plutonium were found in cores 4-11 and 4-5 by autoradiographic and microprobe examination. The plutonium particles (up to 10 μm in diameter and 60 wt% PuO_2) were the most conspicuous form. These occurred near the top of the core 4-11, but extended down nearly to the bottom of core 4-5. It is probable that the sludge layer over core 4-11 acted as a filtering media to remove and concentrate the plutonium particles.

The second form of plutonium occurred in lesser concentration (<0.4 wt% PuO_2) but was found throughout the lengths of both cores associated with silicate hydrolysis. Silicate hydrolysis was investigated with microprobe chemical analysis. Loss of alkalies and alkaline earths, along with the absence of several metamorphic minerals found in the uncontaminated mounts, indicated extensive chemical attack of soil rock fragments by acidic influent solutions.

The locations of the base of the silicate hydrolysis zone, and associated plutonium deposition, are presently unknown.

UNCONTAMINATED SOIL EXAMINATION

Initial work was concerned with the identification of the original rock fragments that made up the 216-Z-9 trench soil. The minerals and rock types comprising the original uncontaminated sediment were obtained from a core well drilled alongside Z-9 trench. Plastic-impregnated mounts made from this soil and several rock fragments were randomly chosen for identification as to rock type. The results of the examination of a typical uncontaminated soil mount are given here. A composite photograph of the mount is shown in Figure 1. The large photograph was taken with reflected, polarized light. The black areas are not rock grains but bubbles or gas holes in the plastic. The smaller black areas in the rock grains are vesicles or holes, and in some instances, black or dark minerals.

Seven rock fragments in this typical soil mount were checked for their primary mineral composition.

Rock Fragment Number One

The first rock fragment is diabase, with the same general composition as a basalt but of medium grain size (Table 1).

The composition of the feldspars is of primary importance in determining a rock type from rock mineralogy. Plagioclase compositions near 50 percent albite - 50 percent anorthite, such as the feldspars in this rock fragment, indicate that the rock

FIGURE 1. A Composite Photomicrograph of an Uncontaminated Soil Mount Magnified Eight Times in Size. The rock fragments examined are identified by number.

TABLE 1. Major Mineral Constituents of Rock Fragment Number One.
An = anorthite, Ab = albite, Or = orthoclase

Feldspars

Crystal No. 1

Ca 2.163	An = 51.7 mol %
Na 1.976	Ab = 47.2
K 0.046	Or = 1.1
Σ 4.185	
Si 9.955	Labradorite
Al 5.942	
Σ 15.897	

Crystal No. 2

Ca 1.812	An = 43.9 mol %
Na 2.197	Ab = 53.3
K 0.114	Or = 2.8
Σ 4.123	
Si 10.172	Andesine
Al 5.791	
Σ 15.963	

Groundmass

No. 3

SiO ₂	75.6 wt %
Al ₂ O ₃	13.7
CaO	0.3
MgO	<0.3
BaO	<0.2
FeO	1.0
TiO ₂	<0.2
Na ₂ O	<1.3
K ₂ O	6.2
	<u>96.8</u>

No. 4

	67.4 wt %
	13.3
	0.6
	0.6
	0.3
	3.6
	0.8
	2.9
	6.3
	<u>95.8</u>

Pyroxene

Crystal No. 5

Ti 0.032	Mn 0.013	Augite
Mg 0.835	Σ 2.018	
Ca 0.650	Al 0.100	
Fe 0.484	Si 1.901	
K 0.004	Σ 2.001	

Crystal No. 6

Ti 0.040	Mn 0.006	Augite
Mg 0.808	Σ 2.018	
Ca 0.773	Al 0.130	
Fe 0.386	Si 1.874	
K 0.005	Σ 2.004	

TABLE 1
(Continued)

Metallic Oxides

Crystal No. 7

Fe 1.959
Mn 0.027 Ilmenite
 Σ 1.986

Ti 2.007

Crystal No. 8

Fe 1.978
Mn 0.022 Ilmenite
 Σ 2.000

Ti 2.000

Apatite

Mg 0.308		
Fe 0.208	PO ₄ 6.000	OH and F were assumed to sum to
Ca 9.579		two.
Σ 10.095		

Rock fragment one also contained a clay mineral. Computation showed that the clay was contaminated by excess hydrous iron oxides.

is a member of the basalt clan. The augites, ilmenites and apatites substantiate the original basalt classification, and the medium grain size points to diabase as the specific basalt clan species.

The composition of a specific mineral is determined from the microprobe chemical analysis. The weight percent oxides in the mineral chemical analysis are divided by their respective equivalent molecular weights, recomputed to 100 percent, the associated oxygens derived and summed, and the cation proportions derived by referring the summed oxygens to the number of oxygens found in a standard mineral "unit cell." For example, feldspars are referred to a "unit cell" containing 32 oxygens.

The method of doing this outlined in Table 2. The mole equivalents are determined from the as-received chemical analysis and from these, the mole percents of the various constituents. The associated oxygens are then computed for each constituent. The sum of the associated oxygens is divided by 32, and this value is used to divide the various mole percents to yield the numbers of atoms of each constituent associated with 32 oxygen atoms. The reason for computing this reference to 32 oxygens is to allow comparison of each analysis to a standard. The criterion of the chemical analysis adding up to 100 wt % is helpful, but the most important aspect of a chemical analysis of a mineral is whether or not the molar ratios between constituents are correct. If the molar ratios are correct, the total wt % of the analysis is of little consequence.

TABLE 2. Method of Referring the As-Received Chemical Analysis to a Feldspar "Unit Cell" Containing 32 Oxygen Atoms.

<u>Oxides</u>	<u>Analysis, wt %</u>		<u>Mole Equivalents</u>	<u>Mole %</u>	<u>Oxygen Factors</u>	<u>Atoms/32 Oxygens</u>
SiO ₂	54.2	÷ 60.06	0.945	52.021 x 2	104.042	10.203
Al ₂ O ₃	26.0	÷ 50.97	0.534	29.405 x 1.5	44.108	5.767
CaO	10.6	÷ 56.1	0.198	10.892 x 1	10.892	2.136
FeO	0.7	÷ 71.9	0.010	0.561 x 1	0.561	0.110
K ₂ O	0.5	÷ 47.1	0.011	0.612 x 0.5	0.306	0.120
Na ₂ O	3.5	÷ 31.0	0.118	6.508 x 0.5	3.254	1.276
					163.163/32	

Other "unit cells" are given under the mineral headings in the tables. If the analysis were a perfect one, the cations and anions in the given mineral would exactly sum to these "unit cell" contents. Ilmenites, for example, would all be (Fe,Mn)₂(Ti)₂O₆. No chemical analysis is perfect, however, so a limit of some kind must be imposed on deviations from the ideal "unit cell," usually plus or minus 5 percent. Any chemical analyses that do not fit the "unit cell" are so-indicated.

Rock Fragment Number Two

The feldspars in this rock fragment were a labradorite and an andesine, indicating a basalt composition again. Table 3 also indicates two magnesium pigeonites as the pyroxenes, and a high-iron groundmass. All metamorphic rock types can be eliminated because pigeonites are unknown in metamorphic rocks. Pigeonites invert to an orthopyroxene and an augite, providing that their

TABLE 3. Major Mineral Constituents of Rock Fragment Number Two.

Feldspars

Crystal No. 1

Ca 1.809	An = 46.6 mol %
Na 1.936	Ab = 49.8
K 0.139	Or = 3.6
Σ 3.884	
Si 10.466	Andesine
Al 5.482	
Σ 15.948	

Crystal No. 2

Ca 2.091	An = 52.2 mol %
Na 1.823	Ab = 45.5
K 0.092	Or = 2.3
Σ 4.006	
Si 10.222	Labradorite
Al 5.671	
Σ 15.893	

Groundmass

	<u>No. 3</u>	<u>No. 4</u>
SiO ₂	60.2 wt %	59.6 wt %
Al ₂ O ₃	13.2	12.5
CaO	4.9	6.6
MgO	1.0	2.1
BaO	0.2	<0.2
FeO	10.0	13.0
TiO ₂	2.2	2.1
Na ₂ O	<1.3	4.0
K ₂ O	2.4	2.1
P ₂ O ₅	0.6	0.5
	<u>94.7</u>	<u>102.5</u>

Pyroxene

Crystal No. 5

Ti 0.005	Al 0.034
Mg 1.328	Si 1.958
Ca 0.146	Σ 1.992
Fe 0.535	
K 0.004	
Mn 0.012	Magnesium
Σ 2.030	Pigeonite

Crystal No. 6

Ti 0.005	Al 0.034
Mg 1.303	Si 1.971
Ca 0.168	Σ 2.005
Fe 0.516	
K 0.003	
Mn 0.009	Magnesium
Σ 2.004	Pigeonite

cooling history allows the inversion. Rapid cooling permits the metastable persistence of pigeonites. The presence of pigeonites, plus the failure of iron to segregate in metallic oxides, indicates a rapidly-cooled, basalt-composition rock.

Rock Fragment Number Three

Number three was a quartzite fragment consisting almost entirely of quartz (Table 4). It looks like a typical milky-white quartz metamorphic rock under the microscope.

TABLE 4. Major Mineral Constituents of Rock Fragment Number Three.

<u>Quartz</u>			
SiO ₂			
SiO ₂	99.1 wt %	98.9 wt %	
Al ₂ O ₃	1.2	0.5	
K ₂ O	0.4	0.2	
MgO	0.6	<0.3	
FeO	<u>0.3</u>	<u><0.1</u>	
	101.6	99.6	

Rock Fragment Number Four

This fragment is a somewhat more complex metamorphic rock than has been encountered before. The minerals in this fragment are chiefly feldspars, some of which are high in potassium, and a titanium mineral (Table 5). The feldspars are an iron-rich, potassium feldspar, microcline, and albite. The first analysis, probably also a microcline, was not up to standard, or did not fit within a 5 percent deviation from the ideal formula. This not too surprising because the minerals in metamorphosed rocks tend to be rather "dirty." Analysis 7 does not fit any titanium-bearing mineral such as sphene, $\text{CaTiSiO}_4(\text{OH},\text{F})$, or perovskite, CaTiO_3 . It probably is an impure anatase, the lower temperature form of rutile, TiO_2 .

Albite is typical of the Belt Series plagioclases, which vary from albites to oligoclase,⁽²⁾ or toward the high sodium end of the plagioclase series. Microcline also is typical of the Greenschist metamorphic facies. In higher metamorphic grades, the potassium feldspar is a perthite. It not unusual for albite and microcline to occur together in the same metamorphic rock.

Rock Fragment Number Five

Rock number five was probably originally an igneous rock, dioritic to granodioritic in composition. Only andesine feldspars and a few metallic oxides, mostly impure hematites, were found in the examines area (Table 6). The

TABLE 5. Major Mineral Constituents of Rock Fragment
Number Four.
An = anorthite, Ab = albite, Or = orthoclase

Feldspars

Crystal No. 1

Substandard
Analysis

Crystal No. 2

K 3.185
Fe 0.609
 Σ 3.794 Microcline
Si 9.894
Al 6.675
 Σ 16.569

Crystal No. 3

Ca 0.018 An=0.5 mol %
Na 3.883 Ab=98.4
K 0.042 Or=1.1
 Σ 3.943
Si 11.940 Albite
Al 4.093
 Σ 16.033

Crystal No. 4

Ca 0.070 An=1.7 mol %
Na 3.848 Ab=95.7
K 0.104 Or=2.6
 Σ 4.022
Si 11.754 Albite
Al 4.295
 Σ 16.049

Analyses 5 and 6 were quartz.

No. 7

SiO₂ 29.6 wt %
Al₂O₃ 6.9
MgO 1.9
CaO 0.1
FeO 0.4
K₂O 0.1
Na₂O 6.5
TiO₂ 59.5
105.0

Analysis seven is not a sphene or
perovskite because the calcium content
is far too low. It is probably and
impure anatase, the lower temperature
form of TiO₂.

TABLE 6. Major Mineral Constituents of Rock Fragment Number Five.

Feldspars

Crystal No. 1

Ca	1.648	An=42.8 mol %
Na	2.131	Ab=55.4
K	0.070	Or=1.8
Σ	3.849	
Si	10.413	Andesine
Al	5.616	
Σ	16.029	

Crystal No. 2

Ca	1.712	An=44.5 mol %
Na	2.067	Ab=53.7
K	0.071	Or=1.8
Σ	3.850	
Si	10.464	Andesine
Al	5.526	
Σ	15.990	

Groundmass

SiO ₂	78.7 wt %	71.4 wt %
Al ₂ O ₃	11.8	17.6
CaO	0.4	0.3
FeO	1.0	1.0
K ₂ O	5.1	5.0
Na ₂ O	1.5	3.9
	<u>98.5</u>	<u>99.2</u>

Metallic Oxides

SiO ₂	5.1 wt %	5.1 wt %
Al ₂ O ₃	1.8	2.8
MgO	0.6	1.0
CaO	0.5	0.6
Fe ₂ O ₃	83.0	74.8
TiO ₂	2.2	12.1
MnO	0.4	1.2
K ₂ O	0.2	0.1
	<u>93.8</u>	<u>97.7</u>

groundmass was higher in silica than the more basic rock types usually are. Also, the metallic oxides (hematite) were relatively low in TiO_2 content, as was the groundmass.

Except for a few percent Al_2O_3 and K_2O , the groundmass is practically a quartz.

The metallic oxides usually include magnetite ($\text{FeO} \cdot \text{Fe}_2\text{O}_3$) rather than hematite (Fe_2O_3). At some time during the history of this rock fragment, the ferrous iron was oxidized to ferric iron, probably during low-grade metamorphism.

Rock Fragment Number Six

This rock fragment still represents a relatively low grade of metamorphism, although probably on the upper side of the greenschist facies. The mineral assemblage depends to a large extent on the rock composition as well as the temperatures and pressures. The original rock in this case contained a considerable amount of calcium and iron, or this was added during the process of metamorphism (Table 7). Both the garnet and actinolite are fairly high in calcium and iron. The original rock also was obviously highly siliceous because quartz formed as a separate phase. Albite can be found over a considerable temperature range in metamorphic rocks, although it is abundant in the Belt Series greenschist facies. Actinolite also can be found in the greenschist facies along with garnets, but is more typical of the albite-amphibolite facies (300 to 400°C). The greenschist facies is typically 200 to 300°C.

TABLE 7. Major Mineral Constituents of Rock Fragment Number Six.

Amphiboles

Crystal No. 1

Ca 1.898	Al —
K 0.019	Si 8.088
Σ 1.917	Σ 8.088
Al 0.446	OH + F = 2
Fe 1.860	
Mg 3.361	Actinolite
Mn 0.025	
Σ 5.692	

Crystal No. 2

Ca 1.820	Al 0.120
K 0.019	Si 7.880
Σ 1.842	Σ 8.000
Al 0.573	OH + F = 2
Fe 1.836	
Mg 3.506	Actinolite
Mn 0.025	
Σ 5.940	

Crystal number three is a quartz (SiO_2)

Feldspars

Crystal No. 4

Ca 0.072	An = 1.8 mol. %
Na 3.910	Ab = 97.7
K 0.020	Or = 0.5
Σ 4.002	
Si 10.858	Albite
Al 4.162	
Σ 16.020	

Crystal No. 6

Ca 0.072	An = 1.8 mol. %
Na 3.915	Ab = 97.7
K 0.022	Or = 0.5
Σ 4.009	
Si 11.988	Albite
Al 3.987	
Σ 15.975	

Garnet

Ca 3.7
Fe 1.8
Σ 5.5

Al 4.0

Si 6.3

Grossular-almandine garnet

Rock Fragment Number Seven

Number seven is also a metamorphic rock fragment. The mineralogy is interesting because the fragment contains garnets, as did rock number six, but with a chlorite, as shown in Table 8. The chlorite, ripidolite, is typically found in chlorite-albite, low grade schists of regional metamorphism. This is still in the greenschist facies, even with the garnets present.

The garnets found in rocks six and seven are close relatives, both being a mixture or "solid solution" of grossular, $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$, and almandine, $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$. Grossular is normally found in regionally metamorphosed rocks and in calcareous contact rocks, or skarns. Almandine is the common garnet and occurs everywhere in igneous and metamorphic rocks. Nearly all naturally-occurring garnets are mixtures of two or more compositional end-members.

Sphene also is widely distributed in igneous and metamorphic rocks. It is characteristic as an accessory in metamorphosed, impure, calc-silicate rocks, and is stable over a large pressure and temperature range.

Microcline is the characteristic potash feldspar of the greenschist facies, just as albite is the characteristic, soda-rich plagioclase.

Apatite and chlorite, both containing fixed amounts of hydroxyl or fluoride ions, are easily fitted to their respective "unit cells" from the microprobe analyses. In

TABLE 8. Major Mineral Constituents of Rock Fragment Number Seven.

Analyses one and two were quartz (SiO_2). Analysis three does not conform to any titanium mineral "unit cell". It is probably a mixture of ilmenite (FeTiO_3) and sphene ($\text{CaTiSiO}_4\text{OH}$)

Sphene

Crystal No. 4

Si 4.225
Ca 3.328
Al 0.628 sphene
 Σ 3.956
Ti 3.195
Fe 0.361
Mg 0.529
 Σ 4.085

Garnet

Crystal No. 5

Ca 3.86	Al 4.13	Si 6.21
Fe 1.50		
Σ 5.36	Grossular-almandine garnet	

Analysis six was also a garnet but did not conform to the garnet "unit cell" due to admixed impurities or the presence of hydrogrossular which contains hydroxyl groups substituting for SiO_4 groups. The presence of hydroxyl groups cannot be detected by the microprobe. A general formula for hydrogrossular is $\text{Ca}_3\text{Al}_2\text{Si}_2\text{O}_8 (\text{SiO}_4)_{1-m} (\text{OH})_{4m}$.

TABLE 8
(Continued)

Feldspars

Crystal No. 7

K	3.804	Si	12.059
Ba	0.027	Al	4.034
Σ	3.831	Σ	16.093
Microcline			

Crystal No. 8

K	3.677	Si	11.844
Ba	0.030	Al	4.239
Fe	0.139	Σ	16.083
Σ	3.846		
Microcline			

Chlorites

Crystal No. 9

Mg	7.90	
Fe	3.91	16OH assumed
Σ	11.81	
Si	5.52	
Al	2.48	Ripidolite
Σ	8.00	

Crystal No. 10

Mg	7.68	
Fe	4.19	16OH assumed
Σ	11.81	
Si	5.63	
Al	2.37	Ripidolite
Σ	8.00	

hydrogrossular, however, where $(\text{OH})_4$ substitutes for (SiO_4) , the situation is considerably changed. The $(\text{OH})_4$ substitution effects all of the other constituents in an unpredictable manner, and it is unproductive to attempt a fit to a "unit cell" with so many unknowns.

The results of the above examination are summarized in Table 9. The majority, more than 70%, are metamorphic in origin. They are relatively low-grade metamorphics, chiefly, if not wholly, of the greenschist facies typical of the Precambrian to Cambrian Belt Series. The Belt Series occurs in Northern Idaho, Montana and part of Northeastern Washington and Canada. Other similar metamorphic rocks occur in Okanogan County. The metamorphic rocks, then, must have been transported south by the ancestral Columbia River and deposited in their present locations.

TABLE 9. Summary of Rock Types Examined in Soil Mount.

<u>Rock Fragment</u>	<u>Rock Types</u>	
1	Diabase, igneous	
2	Chilled basalt, igneous	
3	Quartzite, metamorphic	] Greenschist Facies
4	Metamorphic	
5	Granodiorite to diorite, metamorphosed	
6	Metamorphic	
7	Metamorphic	

CONTAMINATED SOIL EXAMINATIONAutoradiographical and Optical Results

The contaminated 216-Z-9 trench soils were cored in the field and transported to the 325 Building. The original cores (4-11 and 4-5) were 10.2 centimeters in diameter and 60 cm in total length, subdivided into four 15 cm segments. Each of these 4-inch by 6-inch segments were recorded by J. L. Swanson⁽³⁾ by driving a 2.5 cm internal diameter stainless steel pipe vertically down the 15 cm core segment. The segments were designated A, B, C, and C, from each core top to bottom. Complete 2.5 cm diameter cores of the 15 cm segments were not always successfully obtained due to the presence of an occasional cobble exceeding the 2.5 cm core diameter. The vertical locations of the soil samples discussed are given in Table 10.

After drying and impregnating the 2.5 cm soil cores, mounts were made from sections cut and trimmed from the cores with a diamond saw. These mounts represent as close to sectioned, in situ, soil samples as it is practical to obtain. After grinding and polishing, alpha emission autoradiographs were taken of the mounts. The exposure times for the autoradiographs give a relative measure of the alpha emitters contained in the mounts. The film exposure times also are given in Table 10.

TABLE 10. Vertical Distances of the Soil Mounts from the Top of the Core, and the Exposure Times During Alpha Emission Radiography.

<u>Soil Mount</u>	<u>Vertical Location, centimeters</u>	<u>Exposure Times, hours</u>
4-5-A1	0 - 1.3	2.0
4-5-A2	1.9 - 3.8	2.0
4-5-A3	3.8 - 5.1	16.0
4-5-C2	36.2 - 38.1	16.0
4-5-A Fines	0 - 15.2	0.66 (40 min.)
4-11-A1	0 - 1.9	0.25 (15 min.)
4-11-A2	5.1 - 7.0	6.0
4-11-A3	10.2 - 12.1	16.0
4-11-C2	36.8 - 38.7	16.0
4-11-A Fines	0 - 15.2	0.66 (40 min.)

Core 4-5, 4-5-A1 Mount

The autoradiograph of mounts obtained from Core 4-5 are given on the following pages. The original autoradiograph, properly oriented and magnified three times in size (3x), is given first. This is a positive print with high alpha areas indicated in black. The impregnating plastic and most of the soil grains are free of alpha emitters. The alpha emitters (Pu and Am, average Am/Pu=0.0032) are concentrated on rock fragment surfaces and between rock fragments in patchy areas. The resulting radiograph neatly outlines rock fragment surfaces. The freedom of the impregnating plastic from contamination makes it very unlikely that the plutonium was admixed with, or transported by, the plastic during the impregnation process.

Enlargements of the original radiograph are used in the remainder of 4-5-A1 photos to show alpha emitter locations in relation to the rock fragments comprising the soil at this location. Matching optical photos also are given at the same magnifications. Each set of photo enlargements is designated by a letter. The plain letter of the set is the optical photo and the letter-prime, the corresponding autoradiograph.

There is considerable evidence of chemical attack of soil rock fragments in these photos. For example, a rock fragment relic is visible in the lower, right hand side of the optical photo A. This same relic may be seen in outline in the middle-right of radiograph A', although A' is slightly

A

B

C

D

4-5-A1
50X

3X

A'

B'

C'

D'

turned in relation to A. Most of this rock fragment has been chemically attacked leaving a dark groundmass relic in the optical photo. The relatively refractory and eroded crystals remaining in the relic groundmass are probably feldspars. The electron microprobe was used to determine the refractory mineral and remaining groundmass compositions. It may be noted that the concentration of alpha emitters in this relic are relatively small compared to those concentrations external to it.

The medium gray-colored matrix seen in the optical photo (A) is the impregnating plastic, and is relatively free of alpha emitting contamination. The dusty-looking, fine-grained material seen in photo A contains the bulk of the alpha emitters. This material also contains, or is associated with, the bulk of the alpha emitters in the remaining photos of 4-5-A1 mounts. The three oblong, black areas shown between the two large rock fragments in optical photo C are bubbles in the plastic.

Core 4-5, 4-5-A2 Mount

The exposure time here is the same as on 4-5-A1 mount (2 hrs) and the relative amounts of alpha emitters found within the chemically-attacked rock fragments are still very low. A single exception is the relatively large fragment shown in the middle-right of optical photo C. There is a single, high alpha spot seen in the radiograph C' of in the same rock fragment. The bent, pin-like

object is probably a fiber of some sort, although a microprobe analysis would be required for positive identification. In the upper-left corner of optical photo C, a badly-corroded rock fragment can be seen. The possibility of a rock fragment naturally weathering to such a shape is practically nil because no evidence for accelerated attack of this type was found in the uncontaminated soil mounts.

The highest concentrations of alpha emitters are once again associated with the dusty-appearing patches between the soil rock fragments and on fragment surfaces. The composition and probable origin of this fine-grained material is found in the microprobe section of this report.

Core 4-5, 4-5-A3 Mount

The original autoradiograph of A3 mount is shown first at 3x magnification. The mount is properly oriented (top of mount is closest to top of original soil core), but film exposure time is eight times as long as that used on 4-5-A1 and 4-5-A2 mounts. The comparative exposure times must be kept in mind when comparing the apparent alpha emitter concentrations within rock fragments in these mounts. For example, the rock fragment relics shown in the D set of photos apparently indicate that the alpha emitter concentrations are higher within the rock fragment relics than those shown in the 4-5-A1 and 4-5-A2 mounts. The amount of alpha emitters within all of the relics could be the same, with the apparent differences in concentration caused by differences in exposure times. There

A

B

C

D

4-5-A 3
50 X

3X

A'

B'

C'

D'

Core 4-5

is an impression, however, that the concentration of alpha emitters within the chemically-attacked rock is increasing relative to the total concentration of alpha emitters present as one proceeds down the soil column beneath Z-9 trench.

Core 4-5, 4-5-C2 Mount

Evidence for chemical attack of the soil rock fragments is just as prevalent at this depth in the soil column (14 1/4-15 inches) as at the top of the soil column. It is also becoming increasingly evident that the fraction of alpha emitters within the attacked rock fragments is larger in relation to the fraction of the total alpha emitters external to the rock fragments as we proceed down this Z-9 crib soil column.

The lines on optical photo A are scratches on the plastic matrix probably caused during surface cleaning. They are not seen in the radiograph photo A'.

Optical photo B shows an area of chemical attack on a rock fragment in its upper right-hand quadrant. Little alpha contamination can be seen in this attacked area in the radiograph B'.

An interesting example of selective chemical attack of a large rock fragment is shown in optical photo C. The large fragment that occupies approximately the lower half of photo C shows an area just to the right of the middle that is discolored in relation to the rest of the fragment.

A

4-5-C2
50X

A'

B

3X

B'

C

C'

D

D'

D [200X]

Core 4-5

This same area is seen in radiograph C' to contain considerable alpha activity. The solution causing this attack must have dripped down onto the fragment from above.

Optical photo D shows a chemically-attacked rock fragment in the upper-right quadrant. The same fragment can be seen to contain considerable alpha activity in radiograph D'. A higher magnification of an area of the same rock fragment shows that even the relatively resistant feldspar crystals have been corroded by the attacking solutions.

Core 4-5, 4-5-A Fines Mount

J. L. Swanson used soil size fractionation as one step in his treatment of as-received 216-Z-9 trench soils. The 4-5-A fines mount represents the minus 230 mesh fraction from the first six inch segment of core 4-5. A sample of this fines material was obtained from J. L. Swanson,⁽³⁾ embedded in plastic, and sectioned and polished in the same manner as the other core samples. The reader should keep in mind that this is a sieved sample of the first six inches of core 4-5, and has been drastically disturbed. It is not directly comparable to the other mounts, where considerable care was taken not to disturb the as-received core samples.

The original autoradiograph is shown magnified three times. No orientation is possible in the case of this radiograph. The photos A and A' are not a matching set in this instance. They are not of the same areas or at the same magnification.

4-5-A

-230 Mesh Fraction

3 X

A

100 X

A'

50 X

Core 4-5, 4-5-A Fines Mount

Optical photo A shows that about half of the fines are made up of refractory mineral grains and the other half of chemically-attacked relics. The location of the alpha emitters required microprobe examination because these were not matching photos. The distribution of alpha emitters in discrete particles is noteworthy.

Core 4-11, 4-11-A1 Mount

The oriented, original autoradiograph of mount 4-11-A1 is shown at the top of the page. Exposure time was 15 minutes, indicating a relatively high concentration of alpha emitters. The soil does not begin until approximately three-fourths of the way down this mount. The top three-fourths is a fine-grained sludge not naturally found in a soil. Presumably the sludge was added during crib operation. Core 4-5 did not show the sludge layer overlying the soil column. According to J. L. Swanson,⁽³⁾ the water content of this overlying sludge is up to 35 wt %. Note the plastic-filled cracks in the autoradiograph. These are dessication cracks formed during the drying step prior to vacuum impregnation with plastic. The V-shaped outline on the top of the sludge layer was formed by a pebble washed in with the sludge. The alpha emitters occur in distinct layers within the sludge.

Two examples of rock fragment chemical attack are shown in the magnifications of the original autoradiograph and matching optical photos. In optical photo A, a rock

A

B

C

D

4-11-A1
50X

3X

A'

B'

C'

D'

Core 4-11, 4-11-A1 Mount

fragment relic is barely visible to the middle-right, but is plainly seen in the radiograph A'. Again, the fraction of the total alpha emitters within these corroded rock fragments is very low compared to the fraction exterior to rock fragments at this position in the soil column. The lighter gray area at the top of optical photo A is the impregnating plastic, and is seen to be free of contamination in radiograph A'. Another chemically-attacked rock fragment is visible in the upper-right quadrant of optical photo C. The contamination-free areas running vertically through the right side of optical photo B and near the middle of optical photo D are impregnating plastic in sludge dessication cracks.

Core 4-11, 4-11-A2 Mount

The original autoradiograph of 4-11-A2 mount is given first. It is properly oriented in the vertical direction and magnified three times. The vast majority of the rock fragments have been sectioned. Chances are very low that a given rock fragment in these mounts was flat, and that sawing, grinding and polishing occurred in a plane parallel to the original rock surface so that upon final polishing the original exterior surface of the rock was exposed.

Some of the strange-looking swirls in the higher magnification optical photos, such as photo A, probably occurred during reimpregnation of some of the mounts to get rid of bubbles in the original impregnating plastic.

Core 4-11, 4-11-A2 Mount

Slightly larger amounts of alpha emitters can be noted in partially corroded fragments such as in the C set of photos, but again this may be a function of exposure times. The bulk of the alpha emitters are still external to the soil rock fragments.

Core 4-11, 4-11-A3 Mount

An increasingly large fraction of the alpha emitters present here are located within the chemically-attacked rock fragments. This conclusion is even apparent in the original autoradiograph at three times magnification. Optical photo D, at a magnification of 50 times, shows a corroded rock fragment that preserves the original fragment outlines (a relic structure). A large fraction of the alpha emitters shown in the area represented by photos D and D' are contained in the corrosion products of the rock fragment relic. The 200 power magnification of this fragment shows that even the remaining refractory minerals have been corroded. This fragment is surrounded by plastic, which also contains a bubble seen in the 50x optical photo D.

Core 4-11, 4-11-C2 Mount

Severe soil rock fragment chemical attack, and a major fraction of the alpha emitters present within these rock fragments, characterize the soil mount at this soil

Core 4-11, 4-11-A3 Mount

A

B

C

D

4-11-C2
50X

3X

A'

B'

C'

D'

Core 4-11, 4-11-C2 Mount

column location. This does not mean that alpha emitter concentrations within the corroded rock fragments are greater here than at the top of the soil column, or that chemical attack of rock fragments at this level is any more prevalent than at the top of the column.

A characteristic common to all of the mounts is illustrated by the original, three power magnification of the 4-11-C2 mount autoradiograph. Note the alpha activity around 4-11-C2 mount. This was embedded in the edges of the plastic mount during grinding and polishing. Subsequent cleaning removed smeared activity on the mount surface. Another, and much worse, source of alpha activity movement was encountered during driving of the one inch core barrel into the contaminated soil sample. Note that three-quarters of an inch was the largest size of impregnated core recovered for mounting. The smearing of alpha activity at the point of soil-core barrel contact was trimmed off to yield an unsmeared relatively undisturbed sample toward the core-barrel center.

Optical photo C is of interest because it shows a corroded soil rock fragment at the bottom of the photo with only feldspar crystals remaining relatively resistant. Another soil rock fragment in the upper part of the photo is relatively untouched by chemical attack and free of alpha contamination in the fragment interior.

Core 4-11, 4-11-A Fines Mount

This mount was made from the minus 230 mesh fraction of the first six inch segment of core 4-11. The sieve fraction sample was furnished by J. L. Swanson. The optical and radiograph photos are not a matching set of the same area. Half, or more, of the soil fragments are relics produced by chemical attack of the original rock fragments. The refractory portion of the soil is composed chiefly of single mineral crystals, probably removed from larger rock fragments during chemical attack of these fragments. Even in this fine fraction, the alpha emitters can be seen to occur in discrete particles rather than in a homogeneous distribution. The refractory grains are generally smaller in 4-11-A fines than in 4-5-A fines, and relic sizes are about the same in both mounts.

4-11-A

-230 Mesh Fraction

3X

A

100 X

A'

50X

Core 4-11, 4-11-A Fines Mount

Electron Microprobe Results

Core 4-5

The microprobe results from examination of core 4-5 are presented in the following section. The chemical analyses are numbered and the location of each analysis is indicated on the sample in the electron scattering photos.

Core 4-5 differs from core 4-11 in that core 4-5 has no overlying sludge layer. The absence of the sludge layer affects the distribution of plutonium particles in core 4-5. Apparently the sludge acts as a filter to limit the downward migration of suspended plutonium particles. The sludge is probably thickest at the lowest surface elevations on the bottom of Z-9 trench. The higher elevations were covered only occasionally with waste solution.

The vertical locations of the soil mounts from core 4-5 are given in centimeters from the bottom of Z-9 trench in Table 11. Several of the same mounts used in the optical and autoradiographical work were also used in the microprobe examinations.

Microprobe chemical analyses of the plutonium and associated elements are listed in Table 12. They are similar to core 4-11 results in that considerable plastic is present with the plutonium, leading to total wt % values much below 100 wt %. The plastic constituents cannot be obtained with the microprobe. Associated elements include silicon, phosphorus and iron continuously present. Magnesium is always below the detection limit (<0.3 wt %), and the other elements vary in amount in a nonsystematic manner.

TABLE 11. Vertical Distances of the Soil Mounts from the Top of the 4-5 Core.

<u>Soil Mounts</u>	<u>Vertical Locations, Centimeters</u>
4-5-A1	0 - 1.3
4-5-A2	1.9 - 3.8
4-5-A3	3.8 - 5.1
4-5-B1	15.2 - 17.2
4-5-B2	19.7 - 21.6
4-5-B3	23.5 - 25.4
4-5-C1	30.5 - 32.4
4-5-C2	36.2 - 38.1
4-5-C3	41.3 - 43.2
4-5-D1	45.7 - 47.6
4-5-D2	48.3 - 50.2
4-5-D3	50.2 - 51.4
4-5A Agglomerate	0 - 15.2
4-5A Fines	0 - 15.2

TABLE 12. Analyses of Plutonium and Associated Elements.

Oxides, wt %	4-5-A1			4-5-A2		4-5-A3			4-5-B1	
	1 Pu	2 Pu	3 Pu	4 Pu	5 Pu	6 Pu	7 Pu	8 Pu	9 Pu	10 Pu
PuO ₂	4.2	8.8	5.5	16.8	4.5	2.7	3.8	6.4	3.6	3.1
SiO ₂	34.6	28.2	25.9	4.8	22.6	8.2	11.9	4.8	14.7	13.7
P ₂ O ₅	<0.2	2.6	1.5	0.5	0.9	1.3	1.8	6.7	1.9	4.4
FeO	0.5	1.6	2.5	1.0	0.2	2.2	4.4	3.5	3.5	4.0
TiO ₂	<0.2	--	--	0.3	--	0.8	3.8	1.3	0.5	0.5
CaO	0.1	0.4	0.8	0.6	0.6	0.3	0.4	0.5	0.5	<0.1
MgO	<0.3	--	--	--	--	--	--	--	--	--
K ₂ O	0.1	0.4	0.8	0.2	0.1	0.5	0.6	0.4	0.7	1.5
Na ₂ O	<1.3	--	--	--	--	5.3	4.9	--	--	--
Al ₂ O ₃	<0.1	3.4	5.4	1.1	2.2	2.9	2.9	--	2.5	4.8
S	<0.04	--	--	--	--	--	--	--	0.4	0.4
Total	39.5	45.4	42.4	25.6	31.1	24.2	34.5	23.6	28.3	32.4

Oxides, wt %	4-5A			4-5A Fines				
	4-5-B3 11 Pu	4-5-D1 12 Pu	4-5-D2 13 Pu	4-5A Agglomerate 14 Pu	15 Pu	16 Pu	17 Pu	18 Pu
PuO ₂	3.4	3.7	3.6	10.4	14.3	9.6	6.8	11.1
SiO ₂	27.2	0.3	2.4	27.2	42.1	6.1	8.5	7.4
P ₂ O ₅	--	0.4	3.3	0.2	0.3	5.5	4.7	5.3
FeO	0.6	1.3	1.9	0.7	0.7	1.5	2.2	1.9
TiO ₂	--	1.5	1.0	0.2	0.2	1.0	--	1.3
CaO	3.2	0.2	0.2	0.4	0.4	0.5	1.3	0.6
MgO	--	--	--	--	--	--	--	--
K ₂ O	0.4	0.08	0.3	0.3	0.2	0.2	0.2	0.2
Na ₂ O	--	--	--	--	--	--	--	--
Al ₂ O ₃	10.2	--	0.7	1.0	1.4	--	0.3	--
S	--	--	0.2	--	--	--	--	--
Total	45.0	7.48	13.6	40.4	59.6	24.4	24.0	27.8

The distribution of plutonium particles extends over a larger soil volume in core 4-5 and does not reach the 60 wt % PuO_2 concentration level found in core 4-11. The particles were found at 48.3 to 50.2 centimeters depth (4-5-D2) in core 4-5 while they were not found below 15.2 to 17.2 centimeters (4-11-B1) in core 4-11. The more generally-distributed type of plutonium is associated with silicate hydrolysis and is found throughout both cores. The concentration of this originally-soluble plutonium is generally below 0.3 wt % PuO_2 , the microprobe plutonium detection limit. This type of plutonium occurrence is discussed further in the silicate hydrolysis section.

The phosphorus contained in TBP or DBBP, or their degradation products, is contained in the impregnating plastic. The same plastic used to impregnate core 4-11 also contained the organic-phosphorus. The original plastic contains no phosphorus that could be detected with the microprobe (<0.2 wt % P_2O_5).

The soil constituents of cores 4-11 and 4-5 have undergone intensive chemical attack by the influents entering Z-9 trench. These influents were much higher in hydrogen ion concentration than any natural soil solution, and resulted in very high rates of silicate hydrolysis. The apparent imbalance in soil mineral compositions caused by the rapid hydrolysis are reflected in the following silicate analyses.

The elemental compositions of feldspars found in core 4-5 are given in Table 13. The feldspar crystals from which the analyses were made are located on the electron scattering pictures

TABLE 13. Microprobe Analyses of Feldspars Referred to a "Unit Cell" of $(\text{Ca}, \text{Na}, \text{K}, \text{Fe}^{++})_4 (\text{Si}, \text{Al})_{16} \text{O}_{32}$

<u>4-5-A1</u>	<u>Si</u>	<u>Al</u>	<u>Σ</u>	<u>Ca</u>	<u>K</u>	<u>Na</u>	<u>Fe</u>	<u>Σ</u>	<u>Mineral</u>
1F	10.247	6.037	16.284	1.712	0.070	1.197	0.106	3.084	Plagioclase
2F	10.051	5.911	15.961	2.168	0.118	1.332	0.140	3.758	Plagioclase
<u>4-5-A2</u>									
3F	10.095	5.868	15.964	2.191	0.098	1.309	0.113	3.711	Plagioclase
4F	10.070	5.912	15.981	2.180	0.116	1.268	0.121	3.685	Plagioclase
<u>4-5-A3</u>									
5F	12.499	3.441	15.940	0.786	0.724	0.938	0.223	2.670	
6F	12.295	3.728	16.023	0.258	0.022	3.098	---	3.378	Albite
<u>4-5-B1</u>									
7F	10.167	5.957	16.123	2.181	0.144	0.767	0.095	3.187	Plagioclase
8F	10.054	5.945	15.999	1.918	0.093	1.806	0.107	3.924	Labradorite*
9F	10.228	5.871	16.099	2.066	0.072	1.052	0.110	3.299	Plagioclase
10F	10.208	5.894	16.102	2.055	0.118	1.073	0.093	3.338	Plagioclase
11F	11.928	3.699	15.627	---	5.191	---	---	5.191	Microcline
12F	12.939	2.567	15.506	0.041	4.460	---	---	4.501	Microcline
<u>4-5-B3</u>									
13F	10.558	5.525	16.083	1.878	0.114	1.144	0.090	3.225	Plagioclase
14F	10.101	5.887	15.988	2.155	0.093	1.347	0.092	3.687	Plagioclase
15F	10.343	5.806	16.148	2.094	0.069	0.772	0.091	3.027	Plagioclase
16F	13.158	2.980	16.138	0.078	2.150	---	0.061	2.290	
<u>4-5-C1</u>									
17F	10.328	5.653	15.981	1.974	0.120	1.349	0.157	3.599	Plagioclase
18F	10.438	5.572	16.010	2.178	0.120	0.803	0.126	3.228	Plagioclase
19F	10.235	5.823	16.058	2.139	0.089	1.019	0.102	3.349	Plagioclase
<u>4-5-C2</u>									
20F	10.360	5.523	15.883	2.111	0.119	1.369	0.140	3.739	Plagioclase
21F	10.049	5.942	15.991	2.171	0.116	1.274	0.122	3.684	Plagioclase
<u>4-5-C3</u>									
22F	10.108	5.829	15.937	2.256	0.091	1.211	0.134	3.692	Plagioclase
23F	10.240	5.800	16.040	2.154	0.115	1.009	0.105	3.383	Plagioclase
24F	10.181	5.998	16.179	1.860	0.067	1.258	0.117	3.303	Plagioclase
25F	10.079	5.927	16.006	2.126	0.071	1.331	0.124	3.652	Plagioclase
<u>4-5-D1</u>									
26F	10.284	5.834	16.118	2.097	0.093	0.773	0.152	3.114	Plagioclase
27F	9.906	6.083	15.988	1.926	0.116	1.796	0.182	4.020	Labradorite*
<u>4-5-D2</u>									
28F	12.117	3.970	16.087	---	3.621	---	---	3.621	Microcline
29F	10.355	5.669	16.023	1.991	0.137	1.247	0.105	3.480	Plagioclase
30F	10.186	5.703	15.889	2.149	0.120	1.417	0.157	3.843	Labradorite*
31F	10.223	5.839	16.062	1.992	0.117	1.213	0.138	3.461	Plagioclase
32F	10.125	5.793	15.918	2.121	0.140	1.493	0.123	3.876	Labradorite*
<u>4-5-D3</u>									
33F	10.478	5.522	16.000	1.927	0.182	1.277	0.104	3.490	Plagioclase
34F	10.257	5.810	16.067	2.073	0.114	1.042	0.120	3.350	Plagioclase
35F	10.144	5.848	15.992	2.129	0.140	1.237	0.122	3.628	Plagioclase
36F	10.163	5.761	15.924	2.145	0.141	1.389	0.123	3.797	Plagioclase
37F	10.243	5.705	15.948	1.927	0.156	1.727	0.088	3.898	Labradorite*
<u>4-5-A Agglomerate</u>									
38F	12.068	4.404	16.472	0.037	1.915	---	0.263	2.215	
39F	10.279	5.636	15.914	2.108	0.120	1.454	0.094	3.776	Plagioclase
40F	10.199	5.729	15.928	2.153	0.117	1.381	0.107	3.757	Plagioclase

*Analyses marked with an asterisk were the only analyses within the normal error limits.

in the appendix by number. In each case, the microprobe chemical analysis was referred to a feldspar "unit cell" containing 32 oxygen atoms. The normal limit imposed on the standard feldspar model is that the sum of Ca, Na, K and Fe atoms not exceed plus or minus five percent of the ideal value of 4.0, or the sum range between 3.8 and 4.2. Due to admixed impurities and other causes, 2 out of 25 feldspar analysis usually have to be discarded as substandard. Note that only 5 out of the 40 analyses in Table 13 could be retained as standard with this criterion. The majority of the feldspars have lost alkali and alkaline earth cations (and gained hydrogen ions) so that their compositions no longer correspond to those of normal feldspars. Except for the five standard analyses, all of these feldspars have been altered to some degree, although their appearance is that of normal feldspars in the electron scattering and optical photomicrographs.

The chemical compositions of the pyroxenes from core 4-5 referred to a pyroxene "unit cell" containing six oxygen atoms are given in Table 14. The limit imposed on the standard pyroxene is more stringent than that for the feldspars due to the absence of sodium in the pyroxene "unit cell." Sodium is the lightest element that can be determined with the microprobe used here, and its counting statistics are inherently poor. A limit of plus or minus two percent variation for the sum of the cations not in tetrahedral coordination (Si, Al) was used, or a range in this sum of 1.96 to 2.04. Less than five percent of the pyroxene

analyses of Table 14 are apparently substandard, again showing losses of alkaline earths and associated cations.

The compositions of metallic oxides analyzed in core 4-5 are given in Table 15. They are either ilmenite, FeTiO_3 , or magnetite ($\text{FeO} \cdot \text{Fe}_2\text{O}_3$) - ilmenite solid solutions. The metallic oxides are nearly as refractory as quartz in acidic solutions. Little evidence of alteration of the metallic oxides was found.

Several quartz (SiO_2) analyses were made during microprobe examination of core 4-5. The number of quartz analyses made on each mount is shown in Table 16. Quartz is a relatively common soil constituent over all of core 4-5. The quartz is derived from two sources. The bulk of the quartz comes from the metamorphic rocks that comprise a large fraction of the Z-9 trench soil at these elevations. Other metamorphic mineral phases accompanying the quartz include a hornblende, $(\text{Mg}, \text{Ca}, \text{Fe})_{3.52} \text{Ti}_{0.48} \text{Al}_{2.04} \text{Si}_{8.02} \text{O}_{22} (\text{OH})_{21}$ in 4-5-D1 and an almandine-grossular garnet, $(\text{Ca}, \text{Fe})_{6.02} \text{Al}_{3.95} \text{Si}_{6.00} \text{O}_{24}$, found in 4-5-A3. The other metamorphic minerals were apparently altered beyond recognition.

The other source of quartz is found in the basalts themselves, not as a primary phase but as secondary vug filling. This is a relatively minor source of soil quartz.

Part of core 4-5, segment A (0-15.2 centimeters) was found to be agglomerated in part. Examination of cementing material suggests that it was derived from iron compounds added to Z-9 trench during the course of operations. The cement is chiefly hematite (Fe_2O_3) which coexists with unaltered metallic oxides

containing ferrous oxide in their original crystalline forms. It is unlikely that there is any genetic relationship between the cement and original metallic oxides.

TABLE 14. Microprobe Analyses of Pyroxenes Referred to a "Unit Cell" of $(\text{Mg, Fe, Ca, Ti, K, Mg, Al})_2(\text{Al, Si})_2\text{O}_6$

<u>4-5-A1</u>	<u>Si</u>	<u>Al</u>	<u>Σ</u>	<u>Mg</u>	<u>Fe</u>	<u>Ca</u>	<u>Ti</u>	<u>K</u>	<u>Mn</u>	<u>Al</u>	<u>Σ</u>	<u>Mineral</u>
1P	1.998	0.002	2.000	0.866	0.393	0.575	0.022	0.005	0.012	0.072	1.945	Augite*
<u>4-5-A2</u>												
2P	2.026	---	2.026	0.701	0.619	0.479	0.029	---	0.010	0.055	1.963	Augite
3P	2.004	---	2.004	0.791	0.418	0.669	0.015	0.003	0.013	0.046	1.955	Augite*
4P	1.964	0.036	2.000	0.828	0.403	0.723	0.012	0.003	0.013	0.019	2.001	Augite
<u>4-5-B1</u>												
5P	2.036	---	2.036	0.746	0.399	0.682	0.020	0.005	0.010	0.032	1.894	Augite*
6P	1.980	0.020	2.000	0.882	0.389	0.638	0.022	0.004	0.013	0.028	1.976	Augite
7P	1.954	0.046	2.000	0.815	0.391	0.715	0.031	0.005	0.006	0.021	1.984	Augite
<u>4-5-B2</u>												
8P	2.004	---	2.004	0.804	0.442	0.625	0.019	0.003	0.009	0.048	1.950	Augite*
9P	1.995	0.005	2.000	0.770	0.420	0.693	0.017	0.004	0.006	0.052	1.962	Augite
<u>4-5-C1</u>												
10P	1.967	0.033	2.000	0.896	0.398	0.619	0.014	0.003	0.010	0.043	1.983	Augite
11P	1.966	0.034	2.000	0.785	0.412	0.633	0.034	0.014	0.010	0.068	1.956	Augite
<u>4-5-C2</u>												
12P	1.974	0.026	2.000	0.872	0.398	0.619	0.020	0.003	0.010	0.049	1.971	Augite
<u>4-5-C3</u>												
13P	2.074	---	2.074	0.717	0.352	0.590	0.016	0.004	0.006	0.103	1.788	Augite*
<u>4-5-D2</u>												
14P	1.927	0.030	1.957	1.111	0.366	0.589	0.016	0.003	---	---	2.085	Augite
15P	2.010	---	2.010	0.680	0.458	0.712	0.019	0.004	0.006	0.056	1.935	Augite*
16P	2.000	---	2.000	0.725	0.432	0.697	0.023	0.003	0.010	0.059	1.949	Augite*
<u>4-5-D3</u>												
17P	2.004	---	2.004	0.883	0.362	0.657	0.008	0.005	0.009	0.042	1.966	Augite
18P	2.056	---	2.056	0.684	0.551	0.580	0.021	0.005	0.010	0.037	1.888	Augite*
<u>4-5-A</u> <u>Agglomerate</u>												
19P	2.090	---	2.090	0.896	0.617	0.232	0.011	0.005	0.010	0.027	1.798	Intermediate Pigeonite*
20P	1.861	0.139	2.000	0.724	0.397	0.547	0.024	0.009	0.006	0.229	1.936	Augite*

*Analyses marked with an asterisk show loss of cations.

TABLE 15. Microprobe Analyses of Metallics Referred to an Ilmenite "Unit Cell" of $(\text{Mg, Fe, Mn, Cr})_2\text{Ti}_2\text{O}_6$

<u>4-5-A1</u>	<u>Mg</u>	<u>Fe</u>	<u>Mn</u>	<u>Cr</u>	<u>Σ</u>	<u>Ti</u>	<u>Mineral</u>
1M	0.138	3.174	0.021	0.004	3.337	1.328	Magnetite-ilmenite*
2M	0.198	3.087	0.020	0.007	3.312	1.336	Magnetite-ilmenite
<u>4-5-A2</u>							
3M	0.166	3.100	0.010	---	3.276	1.362	Magnetite-ilmenite
4M	0.230	3.152	0.005	---	3.387	1.306	Magnetite-ilmenite
<u>4-5-B1</u>							
5M	0.053	3.028	0.025	---	3.106	1.447	Magnetite-ilmenite
6M	---	3.218	0.037	---	3.255	1.373	Magnetite-ilmenite
7M	0.113	1.809	0.017	---	1.939	2.030	Ilmenite
<u>4-5-B3</u>							
8M	0.129	1.805	0.022	---	1.956	2.022	Ilmenite
9M	0.035	3.045	0.025	---	3.105	1.447	Magnetite-ilmenite
<u>4-5-C1</u>							
10M	---	3.099	0.015	0.004	3.118	1.438	Magnetite-ilmenite
11M	---	3.196	0.026	---	3.222	1.389	Magnetite-ilmenite
<u>4-5-D1</u>							
12M	0.023	1.848	0.026	---	1.897	2.052	Ilmenite
<u>4-5-D2</u>							
13M	0.104	2.996	0.025	---	3.125	1.438	Magnetite-ilmenite
14M	0.062	3.005	0.015	---	3.082	1.459	Magnetite-ilmenite
15M	0.104	2.943	0.025	---	3.072	1.464	Magnetite-ilmenite
<u>4-5-D3</u>							
16M	0.044	3.431	0.030	---	3.505	1.247	Magnetite-ilmenite
17M	0.228	2.979	0.019	---	3.226	1.387	Magnetite-ilmenite
<u>4-5-A Agglomerate</u>							
18M	---	2.909	0.036	---	2.945	1.528	Magnetite-ilmenite
19M	---	3.110	0.031	0.011	3.152	1.413	Magnetite-ilmenite
<u>4-5-A Fines</u>							
20M	---	2.905	0.031	0.004	2.940	1.527	Magnetite-ilmenite
21M	---	3.076	0.041	---	3.117	1.441	Magnetite-ilmenite

*Magnetite-ilmenite are solid solutions of $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ and FeTiO_3 .

TABLE 16. Quartz Soil Fragments Analyzed in the
Core 4-5 Mounts During Microprobe Examination.

<u>Soil Mount</u>	<u>No. of Quartz Analyses</u>
4-5-A1	1
4-5-A2	1
4-5-A3	2
4-5-B1	2
4-5-B3	2
4-5-C1	2
4-5-C2	1
4-5-C3	0
4-5-D1	1
4-5-D2	2
4-5-D3	0

Core 4-11

The microprobe results for 4-11 core are presented in the following section. Specific analyses are identified by number on the electron scattering photo of each set in the appendix.

The vertical locations of the 4-11 core soil mounts are given in Table 17.

TABLE 17. Vertical Distances of the Soil Mounts
from the Top of the 4-11 Core.

<u>Soil Mounts</u>	<u>Vertical Location, Centimeters</u>
4-11-A1	0 - 1.9
4-11-A2	5.1 - 7.0
4-11-A3	10.2 - 12.1
4-11-B1	15.2 - 17.2
4-11-B2	19.7 - 21.6
4-11-B3	24.8 - 26.7
4-11-C1	30.5 - 32.4
4-11-C2	36.8 - 38.7
4-11-D1	45.7 - 47.6
4-11-D2	48.9 - 50.8
4-11-D3	51.4 - 53.3
4-11-A Fines	0 - 15.2

Microprobe chemical analyses of the plutonium and associated elements are listed in Table 18. The majority of the plutonium analyses are from soil mount 4-11-A1 because the bulk of the plutonium in core 4-11 is contained at the column top. Note that none of the plutonium analyses of Table 18 sum to 100 wt %. This is primarily due to the presence of the plastic impregnating medium. The microprobe cannot analyze for elements below sodium, and the plastic is composed of elements such as carbon, nitrogen and oxygen, all lighter in weight than sodium. The total weight percent sum of each analysis is a function of the quantity of admixed plastic.

TABLE 18. Analyses of Plutonium and Associated Elements

Oxides, wt %	4-11-A1										
	1 Pu	2 Pu	3 Pu	4 Pu	5 Pu	6 Pu	7 Pu	8 Pu	9 Pu	10 Pu	11 Pu
PuO ₂	29.3	28.1	17.2	2.8	2.5	31.7	50.8	27.5	15.8	28.0	31.4
SiO ₂	24.5	14.3	20.9	23.0	19.5	20.3	19.4	17.1	16.9	22.2	9.0
P ₂ O ₅	3.7	3.7	3.9	6.2	3.4	3.6	1.4	3.1	3.0	2.6	3.1
FeO	1.1	1.3	1.5	2.1	3.4	1.2	0.9	1.8	0.7	1.1	2.5
TiO ₂	0.4	<0.2	--	--	--	--	--	--	--	0.4	--
CaO	0.2	0.1	<0.1	0.3	0.2	0.2	0.2	0.2	0.3	0.2	0.1
MgO	<0.3	--	--	1.6	--	2.9	2.2	2.1	0.4	3.6	1.9
K ₂ O	0.2	0.3	0.09	1.3	0.5	0.2	0.2	0.2	0.2	0.1	0.1
Na ₂ O	<1.3	--	7.5	--	--	--	--	--	7.6	--	--
Al ₂ O ₃	0.2	<0.1	--	5.4	2.4	--	--	--	0.3	--	--
BaO	0.8	<0.2	0.6	--	--	--	--	--	--	--	--
S	<0.04	--	--	--	--	--	--	--	--	--	--
Total	60.4	47.8	51.69	42.7	31.9	60.1	75.1	52.0	45.2	58.2	48.1

Oxides, wt %	4-11-A2			4-11-A3		4-11-B1	4-11-C	4-11-A Fines			
	12 Pu	13 Pu	14 Pu	15 Pu	16 Pu	16 Pu		17 Pu	18 Pu	19 Pu	20 Pu
PuO ₂	3.8	4.6	3.6	0.4	3.5	3.5	<0.3	6.3	65.4	5.9	10.3
SiO ₂	0.5	11.8	13.2	35.0	0.2	0.2		11.9	3.3	5.7	11.2
P ₂ O ₅	<0.2	1.0	0.7	4.4	--	--		3.0	2.1	11.7	3.4
FeO	6.2	3.4	5.1	16.0	4.5	4.5		2.0	10.3	1.1	12.6
TiO ₂	<0.2	--	--	2.5	--	--		--	--	--	0.9
CaO	0.1	0.3	0.6	0.4	0.1	0.1		0.2	0.2	<0.1	0.4
MgO	<0.3	--	--	6.0	6.8	6.8		--	--	--	--
K ₂ O	0.6	0.3	0.4	0.2	<0.06	<0.06		3.7	0.3	0.1	0.3
Na ₂ O	<1.3	--	--	6.0	6.8	6.8		--	--	--	--
Al ₂ O ₃	<0.1	0.2	1.8	4.3	2.6	2.6		4.7	0.7	--	1.3
BaO	<0.2	--	--	--	--	--		--	--	--	--
S	<0.04	0.9	1.3	--	--	--		--	--	--	--
Total	11.2	22.5	26.7	69.2	17.7	17.7		33.2	82.3	24.5	40.4

Other probable soil constituents including other hydrocarbons and water are also below the range of the microprobe. However, these cores were originally dried at 105°C over a weekend before plastic impregnation. Water and low boiling hydrocarbon content are probably quite low. Hence, higher boiling point hydrocarbons and the plastic are the only constituents that would give the low total weight percents in Table 18. The reader would not be very much in error if he subtracted the plastic content of these analyses by recomputing the analysis to 100 wt %.

As pointed out in previous sections, there are at least two types of plutonium found in these soil mounts. One type is the discrete particles of plutonium, up to 10 micrometers in diameter, that occur chiefly in the upper 15.2 centimeters of this core and constitute the bulk of the plutonium. The other type of plutonium occurrence is as plutonium apparently precipitated from solution. The precipitated type occurs through the whole core in conjunction with chemical attack of soil rock fragments. The discrete plutonium particles may be the oxide, and were probably added to the trench soil in approximately their present form. A successful attempt was made to extract plutonium particles and obtain x-ray diffraction patterns of them. Techniques are available, and have been used to identify 5 micrometer air sampler particles by x-ray diffraction. A portion of the sludge overlying 4-11 core was spread on a flat surface and the plutonium particles in it located by autoradiography. The map of plutonium particles

was then examined and several were chosen for mounting on fine glass rods for x-ray examination. The results of the x-ray examination are given in Table 19.

TABLE 19. Plutonium Particle X-Ray Results.

<u>Particle Diameter, μm</u>	<u>Pattern Identification</u>	<u>Pattern Quality</u>
25	PuO_2	Excellent
100	PuO_2	Excellent
25	PuO_2	Good
50	PuO_2	Excellent
10	No Pattern Obtained	----

The five particles, or groups of particles, in Table 19 also were microprobed, and varied in Pu content from 62 to 84 wt % (70-95 wt % PuO_2). The ten μm particle on which no x-ray pattern was obtained after several tries, contained the 84 wt % Pu. The large plutonium content and lack of a pattern after several x-ray beam realignment attempts, suggests that a small portion of the particles may be noncrystalline polymer or hydroxide.

The plutonium associated with rock fragment chemical attack is generally low in concentration (0.5 wt % PuO_2 or less) but occurs over a rather large area. The particles, on the other hand, occupy a relatively small area, but are generally high in plutonium content (up to 90 wt % PuO_2). Most of the plutonium associated with soil rock fragment attack is not

detectable by microprobe analysis (<0.3 wt % PuO_2). Autoradiography was required to locate this plutonium in many cases. The analyses in Table 18 are nearly all of discrete particles of plutonium. Even in the 4-11-B section, 15.2 to 30.5 centimeters below the top of the core, there is only a rare discrete plutonium particle. The soil column and sludge layer must have acted as a filter to remove these plutonium particles, while the soluble plutonium went on down the column with the solution and was removed in small amounts during chemical attack of soil rock fragments.

The most persistent associated constituents with the plutonium are silica, phosphorus, iron, calcium and potassium, in that order of magnitude. There is an occasional high aluminum and sodium value. Most of the above constituents were added with the plutonium and constitute, along with water, the bulk of the sludge overlying the soil column. The phosphorus associated with the plutonium is of interest because its probable source was TBP, DBBP, or a similar organic product. This phosphorus is also associated with the impregnating plastic, as shown in Table 20. Note that the phosphorus content of the plastic is less at the bottom of the column (4-11-D1) than at the top (4-11-A1). This is consistent with the notion that the heavy phosphorus-containing organic remained in the soil during the drying step and was higher

in concentration near the top of the soil column. The phosphorus-containing organic was removed preferentially into the plastic during impregnation. The as-received plastic used in the impregnation contains less than 0.2 wt % P_2O_5 .

TABLE 20. Analyses of the Impregnating Plastic and Associated Elements.

Oxides, wt %	<u>4-11-A1</u>		<u>4-11-D1</u>
PuO_2	<0.3	--	--
SiO_2	0.6	0.6	<0.1
P_2O_5	3.1	1.7	0.6
FeO	0.1	<0.1	--
TiO_2	<0.2	--	--
CaO	<0.1	--	--
MgO	<0.3	--	--
K_2O	<0.06	--	--
Na_2O	<1.3	--	4.4
Al_2O_3	<0.1	--	--
BaO	<0.2	--	--
S	<0.04	--	--
Total	3.8	2.3	5.0

As shown previously, the bulk of the soil fragments of sand size or smaller were derived from metamorphic rocks. The minerals in the metamorphic rocks included chlorites, garnets, actinolite, albite, microcline and quartz. Only the last two minerals have been found in a microprobe examination of the contaminated 4-11 core. Either the ratio of metamorphic rock fragments to basalt rock fragments is much lower in the backfilled trench, or the basalt-derived rock fragments persist with less alteration in the environment of the Z-9 trench. Since about the same amount of quartzite fragments were located and analyzed in the contaminated core mounts as in the uncontaminated mounts, it is assumed that many of the metamorphic minerals were destroyed by chemical attack. Even microcline fragments are not numerous, and no albite fragments were found.

The elemental compositions of feldspars found in 4-11 core are given in Table 21. In each case, the microprobe chemical analysis was referred to a feldspar "unit cell" containing 32 oxygens. The standard for an acceptable chemical analysis used on the feldspars is that the sum of the Ca, Na, K and Fe^{+2} atoms/32 oxygens not exceed plus or minus 5 percent of the ideal value of four. With the hundreds of feldspar analyses from basalts, the average number of substandard analyses has been approximately 2 per 25. In Table 21, we have 19 apparently substandard analyses per 25. The apparently low Ca + Na + K + Fe values reflect some loss of alkalis and alkaline earths due to chemical attack.

The chemical compositions of the pyroxenes from 4-11 core are given in Table 22. The method used to refer the original

TABLE 21. Microprobe Analyses of Feldspars Referred to a Feldspar "Unit Cell" of $(\text{Ca}, \text{Na}, \text{K}, \text{Fe}^{++})_4 (\text{Si}, \text{Al})_{16} \text{O}_{32}$

<u>4-11-A1</u>	<u>Si</u>	<u>Al</u>	<u>Σ</u>	<u>Ca</u>	<u>K</u>	<u>Na</u>	<u>Fe</u>	<u>Σ</u>	<u>Mineral</u>
1F	10.203	5.767	15.970	2.136	0.120	1.276	0.110	3.643	Plagioclase
2F	10.805	5.243	16.048	1.555	0.046	1.865	0.015	3.482	Plagioclase
<u>4-11-A2</u>									
3F	10.404	5.530	15.934	2.260	0.144	0.876	0.126	3.407	Plagioclase
4F	10.498	5.560	16.058	2.110	0.145	0.771	0.095	3.121	Plagioclase
5F	10.047	5.920	15.967	2.231	0.142	1.262	0.093	3.728	Plagioclase
<u>4-11-A3</u>									
6F	10.072	5.883	15.955	2.093	0.111	1.590	0.087	3.881	Plagioclase*
7F	12.002	3.917	15.920	--	4.239	--	--	4.239	Microcline*
<u>4-11-B1</u>									
8F	10.444	5.717	16.160	1.756	0.135	1.162	0.133	3.186	Plagioclase
9F	10.330	5.793	16.124	1.710	0.113	1.410	0.178	3.411	Plagioclase
<u>4-11-B2</u>									
10F	10.170	5.721	15.891	2.249	0.113	1.368	0.088	3.819	Plagioclase*
<u>4-11-B3</u>									
11F	10.282	5.624	15.906	2.012	0.117	1.642	0.108	3.880	Plagioclase*
12F	10.189	5.745	15.933	2.150	0.116	1.167	0.214	3.648	Plagioclase
<u>4-11-C1</u>									
13F	10.403	5.671	16.074	1.840	0.092	1.332	0.136	3.400	Plagioclase
14F	10.455	5.699	16.154	1.849	0.116	1.057	0.106	3.128	Plagioclase
<u>4-11-C2</u>									
15F	10.305	5.752	16.057	2.052	0.161	1.016	0.121	3.350	Plagioclase
16F	11.456	4.884	16.340	0.133	2.042	0.620	0.297	3.092	Microcline
<u>4-11-D2</u>									
17F	10.403	5.685	16.088	1.937	0.144	1.095	0.110	3.287	Plagioclase
18F	9.982	6.010	15.992	2.126	0.070	1.447	0.137	3.779	Plagioclase
19F	10.109	5.945	16.055	1.970	0.093	1.482	0.107	3.651	Plagioclase
20F	10.276	5.670	15.945	2.019	0.112	1.502	0.118	3.752	Plagioclase
<u>4-11-D3</u>									
21F	10.151	5.872	16.023	1.969	0.094	1.532	0.108	3.702	Plagioclase
22F	10.242	5.714	15.956	1.884	0.119	1.814	0.094	3.911	Plagioclase*
23F	10.405	5.603	16.008	2.098	0.121	1.032	0.111	3.362	Plagioclase
<u>4-11-A Fines</u>									
24F	10.487	5.446	15.933	1.960	0.136	1.481	0.089	3.666	Plagioclase
25F	9.553	6.471	16.024	2.413	0.091	1.248	0.105	3.857	Plagioclase*

*The analyses marked with an asterisk are the only results that were within the plus or minus 5 percent of four for Ca, Na, K, and Fe^{++} .

TABLE 22. Microprobe Analyses of Pyroxenes Referred to a "Unit Cell" of $(\text{Mg, Fe, Ca, Ti, K, Mg, Al})_2(\text{Al, Si})_2\text{O}_6$

<u>4-11-A1</u>	<u>Si</u>	<u>Al</u>	<u>Σ</u>	<u>Mg</u>	<u>Fe</u>	<u>Ca</u>	<u>Ti</u>	<u>K</u>	<u>Mn</u>	<u>Al</u>	<u>Σ</u>	<u>Mineral</u>
1P	1.984	0.016	2.000	0.637	0.431	0.755	0.032	0.004	0.007	0.075	1.941	Augite
<u>4-11-A2</u>												
2P	1.907	0.093	2.000	0.811	0.406	0.661	0.044	0.004	0.006	0.049	1.981	Augite
3P	1.963	0.037	2.000	0.874	0.484	0.560	0.020	0.003	0.009	0.033	1.983	Augite
4P*	2.088	--	2.088	0.974	0.543	0.218	0.014	0.010	--	0.036	1.795	Magnesium pigeonite
<u>4-11-A3</u>												
5P*	2.059	--	2.059	0.636	0.596	0.396	0.027	0.032	0.012	0.114	1.813	Subcalcic augite
<u>4-11-B1</u>												
6P	1.923	0.077	2.000	0.748	0.367	0.733	0.050	0.004	0.006	0.054	1.962	Augite
7P	1.900	0.100	2.000	0.751	0.384	0.747	0.059	0.003	0.006	0.028	1.978	Augite
<u>4-11-B2</u>												
8P	1.955	0.045	2.000	0.725	0.425	0.706	0.034	0.003	0.006	0.061	1.960	Augite
9P	1.918	0.063	1.981	0.981	0.322	0.709	0.027	0.009	--	--	2.048	Augite
<u>4-11-B3</u>												
10P	1.971	0.029	2.000	0.840	0.465	0.612	0.024	0.003	0.009	0.026	1.979	Augite
11P	1.953	0.047	2.000	1.157	0.316	0.520	0.011	0.003	0.009	--	2.016	Subcalcic augite
<u>4-11-C1</u>												
12P	1.928	0.072	2.000	0.881	0.363	0.686	0.037	0.003	0.006	0.016	1.992	Augite
13P	1.976	0.024	2.000	0.796	0.566	0.556	0.023	0.004	0.010	0.025	1.980	Augite
<u>4-11-C2</u>												
14P	1.934	0.066	2.000	0.806	0.412	0.697	0.036	0.004	0.003	0.029	1.987	Augite
15P	1.914	0.086	2.000	0.848	0.390	0.688	0.025	0.003	0.006	0.040	2.000	Augite
<u>4-11-D1</u>												
16P	1.989	0.011	2.000	0.778	0.479	0.618	0.022	0.003	0.009	0.050	1.959	Augite
17P	1.951	0.049	2.000	0.877	0.423	0.656	0.024	0.003	0.003	0.011	1.997	Augite
18P	1.957	0.043	2.000	0.807	0.403	0.683	0.030	0.003	0.006	0.040	1.972	Augite
19P	1.952	0.048	2.000	0.883	0.407	0.619	0.026	0.005	0.006	0.037	1.983	Augite
<u>4-11-D2</u>												
20P*	2.014	--	2.014	0.720	0.433	0.628	0.032	0.003	0.010	0.077	1.903	Augite
21P	1.977	0.023	2.000	1.056	0.604	0.278	0.014	0.005	0.009	0.024	1.990	Magnesium pigeonite
<u>4-11-D3</u>												
22P*	2.029	--	2.029	0.881	0.338	0.621	0.014	0.004	0.006	0.044	1.908	Augite
23P	1.965	0.035	2.000	1.058	0.602	0.300	0.013	0.003	0.006	0.015	1.997	Subcalcic augite
24P*	2.006	--	2.006	0.793	0.509	0.524	0.029	0.005	0.007	0.064	1.931	Augite
<u>4-11-A Fines</u>												
25P*	2.039	--	2.039	0.742	0.434	0.632	0.019	0.003	--	0.050	1.880	Augite
26P	1.910	0.068	1.978	1.013	0.385	0.642	0.017	0.004	--	--	2.061	Augite

*Analyses marked with an asterisk especially show loss of cations.

chemical analysis to 6 oxygens is the same as that given for 32 oxygens in the feldspar section. Six of the analyses are identified as showing a loss of cations due to chemical attack.

The compositions of metallic oxides found in 4-11 core, referred to 6 oxygens, are given in Table 23. These are either ilmenites, FeTiO_3 , or ilmenite-magnetite solid solutions. No evidence was found that these analyses were anything but normal for metallic oxides occurring in basaltic rocks. Ilmenite and magnetite are soluble only with difficulty in hot HCl. The Z-9 environment should not effect ilmenite and magnetite chemically and apparently has not.

The several quartz analyses made during examination of the soil mounts are located in Table 24. The number of analyses per soil mount does not necessarily reflect the amount of quartz in that mount. The analyses are given only to show that quartz is a relatively common soil constituent over all of 4-11 core.

Many instances of chemical attack of soil rock fragments and their mineral phases have been pointed out in previous reports. Chemical analyses of similar altered minerals and rock fragments are given in Table 25. Ground mass areas are probably included as well, little changed by their contact with altering solutions. In some cases, it is possible to guess the identity of the original mineral. For example, 2A may have been a microcline fragment, 4A and 13A pyroxenes, and 12A and 14A, albites. In many other cases, however, the alteration has proceeded too far from the original composition to allow estimation of the original mineral. Many of

TABLE 23. Microprobe Analyses of Metallics Referred to an Ilmenite "Unit Cell" of $(\text{Mg}, \text{Fe}, \text{Mn}, \text{Cr})_2\text{Ti}_2\text{O}_6$

<u>4-11-A1</u>	<u>Mg</u>	<u>Fe</u>	<u>Mn</u>	<u>Cr</u>	<u>Σ</u>	<u>Ti</u>	<u>Mineral</u>
1M	0.092	2.254	0.022	--	2.368	1.816	Ilmenite-magnetite*
<u>4-11-A2</u>							
2M	0.031	1.946	0.018	--	1.995	2.002	Ilmenite
3M	0.032	1.956	0.014	0.003	2.005	1.994	Ilmenite
<u>4-11-A3</u>							
4M	--	1.968	0.023	--	1.991	2.004	Ilmenite
<u>4-11-B1</u>							
5M	0.091	1.827	0.021	0.006	1.945	2.021	Ilmenite
6M	0.262	3.074	0.026	--	3.362	1.319	Ilmenite-magnetite
<u>4-11-B2</u>							
7M	0.028	3.366	0.021	0.007	3.422	1.281	Ilmenite-magnetite
8M	0.256	3.262	0.016	0.004	3.538	1.228	Ilmenite-magnetite
9M	0.101	3.199	0.073	0.007	3.380	1.302	Ilmenite-magnetite
<u>4-11-B3</u>							
10M	--	3.178	0.027	0.004	3.209	1.392	Ilmenite-magnetite
11M	0.161	3.405	0.027	0.008	3.601	1.192	Ilmenite-magnetite
12M	--	3.141	0.026	0.004	3.171	1.411	Ilmenite-magnetite
13M	--	3.128	0.027	0.004	3.159	1.417	Ilmenite-magnetite
<u>4-11-C1</u>							
14M	--	2.008	0.017	--	2.025	1.987	Ilmenite
15M	0.075	1.921	0.017	--	2.013	1.994	Ilmenite
16M	--	3.311	0.021	0.004	3.336	1.328	Ilmenite-magnetite
<u>4-11-C2</u>							
17M	0.142	3.403	0.022	0.004	3.571	1.211	Ilmenite-magnetite
18M	0.093	1.943	0.022	--	2.058	1.971	Ilmenite
19M	0.192	3.350	0.026	0.007	3.575	1.205	Ilmenite-magnetite
<u>4-11-D2</u>							
20M	0.232	3.937	0.022	0.008	4.199	0.893	Ilmenite-magnetite
21M	0.198	2.845	0.020	0.003	3.066	1.463	Ilmenite-magnetite
22M	0.284	3.238	0.022	0.004	3.548	1.223	Ilmenite-magnetite
23M	0.078	1.910	0.013	--	2.001	1.999	Ilmenite
<u>4-11-D3</u>							
24M	--	3.217	0.026	0.015	3.258	1.356	Ilmenite-magnetite
25M	--	3.081	0.026	0.004	3.111	1.441	Ilmenite-magnetite
26M	0.083	3.344	0.026	0.007	3.460	1.262	Ilmenite-magnetite
27M	0.113	3.044	0.020	0.004	3.181	1.407	Ilmenite-magnetite
28M	0.284	2.804	0.023	0.003	3.114	1.440	Ilmenite-magnetite
<u>4-11-A Fines</u>							
29M	--	3.373	0.021	0.004	3.398	1.297	Ilmenite-magnetite
30M	0.108	3.096	0.015	0.007	3.226	1.379	Ilmenite-magnetite

*Ilmenite-magnetite analyses are solid solutions of magnetite, $\text{FeO} \cdot \text{Fe}_2\text{O}_3$, and ilmenite, FeTiO_3 .

TABLE 24. Quartz or Quartzite Soil Fragments Analyzed
in the Core 4-11 Mounts During Microprobe
Examination.

<u>Soil Mount</u>	<u>No. of Quartz Analyses</u>
4-11-A1	4
4-11-A2	3
4-11-A3	1
4-11-B2	3
4-11-C1	1
4-11-C2	2
4-11-D2	1
4-11-D3	1

TABLE 25. Chemical Compositions of Some of the Altered Mineral Phases. The low total wt % values are due to the presence of impregnating plastic.

	<u>Na₂O</u>	<u>MgO</u>	<u>Al₂O₃</u>	<u>SiO₂</u>	<u>K₂O</u>	<u>CaO</u>	<u>TiO₂</u>	<u>FeO</u>	<u>BaO</u>	<u>PuO₂</u>	<u>Total</u>
<u>4-11-A1</u>											
1A	<1.3	<0.3	14.1	79.4	4.3	1.0	1.1	2.5	<0.2	<0.3	102.4
2A	--	--	18.9	73.7	8.5	0.1	<0.2	0.3	0.7	--	102.2
3A	--	0.8	31.6	55.8	4.7	<0.1	--	2.0	--	--	94.9
4A	--	7.2	18.2	42.0	3.1	0.1	1.0	21.8	--	--	93.4
5A	--	--	18.0	73.6	5.1	--	0.4	0.8	0.4	--	98.3
<u>4-11-A2</u>											
6A	--	--	14.4	76.3	1.8	2.4	0.7	4.5	--	0.4	100.5
7A	--	--	14.1	77.9	3.9	0.5	0.6	1.4	--	0.4	98.8
<u>4-11-A3</u>											
8A	1.2	--	13.3	58.3	1.8	3.7	5.0	12.0	--	--	94.1
9A	--	--	16.6	59.1	4.9	4.0	2.6	7.6	--	--	94.8
10A	--	--	16.8	84.3	0.1	1.2	--	0.2	--	--	102.6
<u>4-11-B1</u>											
11A	--	--	13.8	76.8	6.1	0.8	0.4	1.5	--	--	99.4
<u>4-11-B2</u>											
12A	4.2	--	13.3	75.4	4.0	0.9	--	2.3	--	--	100.1
13A	--	8.4	15.0	53.0	1.7	8.8	--	7.0	--	--	93.9
<u>4-11-D3</u>											
14A	5.8	--	18.3	74.8	1.7	0.9	--	0.7	--	--	102.2
<u>4-11-A Fines</u>											
15A	--	--	12.8	74.8	3.3	1.4	0.6	2.3	--	--	95.2

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the x-ray emission photos given in the appendix show some unusual changes. Note the changes apparent in the set of photos listed under 4-11-D3, for example.

SILICATE HYDROLYSIS

To better understand the process of aluminosilicate hydrolysis, and the persistence of silica in the originally low pH environment of the Z-9 trench, a rapid review of silica and alumina solubility may be of assistance.

Below pH 9, the solubility of silica in water is practically independent of pH, as can be seen on the silica solubility curve shown in Figure 2. The silica is present in true solution here. Below pH 9, it is in the form of monomolecules of monosilicic acid, H_4SiO_4^0 or $\text{Si}(\text{OH})_4^0$. Above pH 9, monosilicic acid dissociates to H_3SiO_4^- and $\text{H}_2\text{SiO}_4^{2-}$, and solubility increases. The important aspect of Figure 2 is to remember that silica solubility is relatively constant below pH 9.

The solubility of alumina is given in Figure 3. It is amphoteric in that it is soluble in both acidic and basic solutions. In acidic solutions, below pH 2, alumina exists as the cation Al^{+3} . From pH 2.85 to 4.07, another cationic form, $\text{Al}(\text{OH})_2^+$, exists. As the concentration of hydroxyl ions increases, $\text{Al}(\text{OH})_3$ is precipitated. In alkaline solutions, $\text{Al}(\text{OH})_3$ is redissolved as $\text{Al}(\text{OH})_4^-$, with the isoelectric point at pH 6.70.⁽⁷⁾

FIGURE 2. Solubility of Silica as a Function of pH at 25°C(4,5)

FIGURE 3. Solubility of Aluminum as a Function of pH at 25°C(7)

Thus when the two solubilities are compared:

- 1) Alumina is more soluble than silica in an acid environment,
- 2) Alumina is insoluble in a neutral environment while silica solubility is about the same as in an acid environment, and
- 3) The two solubilities increase together in an alkaline environment.

The above is consideration of silica and alumina solubilities acting separately rather than in a mixed alumina-silica-salt solution. In the mixed solution, solubilities are often modified.

The solubility of monosilicic acid in seawater, for example, is not affected by the ions in seawater except Al^{+3} . Twenty ppm Al^{+3} reduces the solubility of silica from about 140 ppm to 15 ppm at the seawater pH of 8 to 9.⁽⁶⁾ Magnesia and silica also coprecipitate between pH 10 to 12, a property that has been utilized for the past twenty years in desilicification of boiler feed water. The point here is that, due to coprecipitation phenomena, the solubility of silica cannot always be deduced from a consideration of its pure solubility curve.

Silicates can be considered as salts of the reaction of weak acids and strong bases. Thus hydrolysis reaction products are alkaline. The first step in a hydrolysis reaction between an albite ($\text{NaAlSi}_3\text{O}_8$) and water is contact between them. Without water contact, the silicate remains stable indefinitely. The second step is an exchange reaction between sodium ions in the albite and hydrogen ions in the contacting water. As a sodium

ion is released by exchange with hydrogen ions, it diffuses out into the water, yielding an increase in water pH. If the water film is not renewed, the hydrolysis, or silicate alteration process, comes to a standstill due to lack of hydrogen ions for further hydrolysis. Thermal agitation and molecular rotation assure that sodium ions are free to diffuse out of the silicate lattice and hydrogen ions free to diffuse into the lattice. Thus the alkalies and alkaline earths are exchanged for hydrogen ions in this initial phase of the silicate alteration process.

An attack on the aluminosilicate framework itself then proceeds by continuous leaching of silica and alumina. However, the proportions of leached silica and alumina are variable depending on the pH condition. There is more alumina than silica leached in an acid environment, more silica than alumina in a neutral environment and equal quantities in an alkaline environment. Al-O-Si bonds are more readily broken than Si-O-Si bonds by conversion to Al-OH and Si-OH. Hydrolysis proceeds much more rapidly with large polyhedra containing 12, 10 or 8-membered aluminosilicate rings. The last to be attacked are the tetrahedra containing Al or Si. If the framework is rich in cations, it can be easily broken down into fragments that can be transported away or dissolved.

There are three factors that effect the intensity of hydrolysis:

- 1) Temperature,
- 2) Leaching solution volume, and
- 3) Hydrogen ion concentration.

Temperature increases diffusion rates and thermal agitation. For an increase of 10°C , the dissociation of water and the reaction rate is about doubled. If the reaction rate is V at 10°C , it is $2V$ at 20°C , $3V$ at 25.85°C and $4V$ at 30°C . Hence, there is as much difference between 26 and 30°C as between 10 and 20°C .

Leaching solution volume controls the rate at which the sodium is removed at the end of the sodium diffusion path, as well as silicate fragments not in true solution and silica and alumina in solution. It also controls the renewal of hydrogen ions for diffusion into the silicate.

The hydrogen ion concentration effects the rate at which the hydrogen ions diffuse into the hydrolyzing silicate. Lowering the pH one unit increases the hydrogen ion concentration by a factor of ten, proportionally increasing the exchange portion of the hydrolysis process.

The effect of silicate composition on alteration rates also is easily understood. Olivine, $(\text{Fe}^{+2}, \text{Mg})_2 \text{SiO}_4$, is destroyed during the hydrolysis phase of silicate alteration, leaving SiO_4 fragments plus $\text{Si}(\text{OH})_4$ and Mg^{+2} in solution, and solid $\text{Fe}_2\text{O}_3 \cdot \text{XH}_2\text{O}$. Quartz (SiO_2), on the other hand, is only solubilized with difficulty in acid to neutral environments. Attack must proceed by the destruction of Si-O-Si bonds, and is very slow as evidenced by the high proportion of quartz in most sands and sandstones. The less the number of cations in the silicate lattice, the better able the silicate is to resist hydrolysis.

There are two types of pH changes during the hydrolysis process that could result in precipitation of plutonium and americium in

acidic solutions. The first type occurs within the soil rock and mineral fragments undergoing hydrolysis in the hydrolysis zone. Within each soil particle, a pH gradient occurs between the acidic solution on the particle exterior and the hydrolysis-unaltered mineral interface on the particle interior. This pH gradient occurs because the concentrations of alkali and alkaline earth cations are highest at the hydrolysis interface while the hydrogen ion concentration is lowest at the same location. At the exterior of the soil particle, the opposite case holds, with hydrogen ion concentration at its highest and alkali ion concentration at a lower value. If this concentration (and pH) gradient did not exist, ionic diffusion and hydrolysis would cease. Hydrolysis does cease at some depth in the soil column when the concentration of alkali and alkaline earth cations increases, and hydrogen ion concentration decreases, to the point where the required concentration gradients cannot be maintained, and the exchange and diffusion process (hydrolysis) ceases or becomes very slow. This is the second type of pH change that occurs, probably over some distance and at some depth in the soil column. Plutonium and americium in solution also may be precipitated at this point.

As shown in this report, hydrolysis of the silicates constituting the Z-9 trench soil was accelerated due to a high concentration of hydrogen ions. Silica is prevalent because its solubility remained low in relation to alumina in the low pH Z-9 environment. The originally soluble plutonium is found at all elevations in the soil column associated with silicate hydrolysis

probably because of the acidic-toward-basic pH change normally associated with the silicate hydrolysis process. The hydrolysis process should slow at some depth in the Z-9 trench soil column as the concentration of alkalies and alkaline earth ions increase with depth and the pH rises. The pH also rises within each silicate soil fragment as the interior cation-hydrogen ion active exchange surface is approached. Thus the plutonium can be found associated with the pH rise within each silicate soil fragment in the rapid silicate hydrolysis zone, and should also be effected by the pH rise associated with the base of the hydrolysis soil reaction zone located at some depth in the Z-9 trench soil column. At the latter zone base where hydrolysis becomes very slow because the pH of the contacting solution has risen in response to increased alkalies and alkaline earths concentration, plutonium (and Am) may be precipitated exterior to the soil silicate fragments. The location of the base of the rapid silicate hydrolysis zone, and the concentration and subsequent movements of the associated plutonium precipitated exterior to the soil grains near this zone base are presently unknown.

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APPENDIX

CORE 4-5

ELEMENTAL DISTRIBUTION

In this appendix, several sets of microprobe photos are presented. The first photo is an electron scattering photo, very similar to an electron microphotograph and obtained in nearly the same manner. The areas indicated in each electron scattering photo by a line and a number-letter designation refer to the chemical analyses given in the tables in the text of this report. The 75X under the electron scattering photo refers to the magnification.

The electron scattering photos are usually followed by a set of x-ray emission photos. The element is indicated under each x-ray emission photo. The density of the white dots, representing emitted x-rays as a result of electron excitation of the element, are a qualitative indication of the amount of the element present and its location in the sample. The magnification of the x-ray emission photos is the same as that of the corresponding electron scattering photo unless otherwise indicated. The areas shown in the x-ray emission photos are identical to those shown in the electron scattering photo.

The largest rock fragment is a basalt containing lath-shaped crystals of plagioclase feldspar and lighter gray areas of irregular-shaped pyroxene crystals. The large fragments of quartz, feldspar and metallic oxide crystals are imbedded in plastic. The highest concentrations of plutonium are associated with silica in the plastic. The lath-like crystal to the side of the large basalt fragment is the remains of a feldspar crystal. Note, that the bulk of the phosphorus is in the plastic.

4-5-A1 75X

Al

Ca

Fe

K

ELECTRON SCATTERING

1F
1M
1Pu
2Pu
2M

3Pu
Quartz
1P
2F

Pu

Si

Ti

The large rock fragment is a basalt containing lath-like plagioclase feldspar crystals, lighter gray pyroxene crystals and a few metallic oxides even lighter in color. This fragment has nearly disintegrated due to chemical attack of the groundmass matrix. Smaller fragments of quartz, feldspars and basalts surround the larger fragment. Small ($<2 \mu\text{m}$) plutonium particles are associated with the silica found in the plastic surrounding the fragments. The plutonium particles in this core tend to be much smaller in diameter than those in core 4-11.

4-5-A2 75X

Al

Ca

Fe

K

Pu

Quartz

3P

3M

4Pu

5Pu

4P

4F

4M

3F

P

Si

Ti

ELECTRON SCATTERING

The large rock fragment in the center is quartz. Quartz is little affected by a low pH environment because, having no alkalies and alkaline earths, it does not undergo hydrolysis reactions. A small fragment of garnet and a part of an albite ($\text{NaAlSi}_3\text{O}_8$) crystal are contained in the surrounding area. Neither of these metamorphic minerals usually survive this low pH environment. Plutonium particles also can be seen surrounding the large quartz fragment.

4-5-A3 150 X

Al

Ca

Fe

K

ELECTRON SCATTERING

P

Pu

Si

Ti

Quartz
Garnet
Quartz

6 Pu
7 Pu
6 F

8 Pu

5 F

The large rock fragment is basalt again, with the lath-like plagioclase crystals outlined on the calcium x-ray emission photo, pyroxene crystals outlined as the lower iron content shown in the iron emission photo, and metallic oxides shown in the iron and titanium photos. The rock is badly attacked and at the point of disintegration. An interesting aspect of this particular rock is the location of the analyzed plutonium particle (9 Pu). It is inside of this rock fragment, probably in a solution pore or cavity. The location of this pore is shown on the silicon x-ray emission photo.

4-5-B1 75X

Al

Ca

Fe

K

5P
7F
9Pu
5M
6M

8F
7M
6P

Pu

Si

Ti

ELECTRON SCATTERING

The large rock fragment is a metamorphic rock consisting of quartz and microcline (KAlSi_3O_8). The surrounding fragments are pyroxenes and plagioclase feldspars, unrelated to the metamorphic rock fragment. The highest concentrations of plutonium occur among these smaller fragments.

4-5-B1 75 X

Al

Ca

Fe

K

ELECTRON SCATTERING

10F

7P

10Pu
12F

Quartz

11F
9F

P

Pu

Si

Ti

This is a basalt rock fragment. Again, a plutonium particle was carried into the interior of the rock (11 Pu) by solution circulation in a rock pore. Some of these particles may be rather difficult to extract.

4-5-B2 75X

9P
15F
13F
8P
Quartz
14F

16F
11Pu
8M
9M

Two rock fragments of different origin occur here. The left fragment consists of quartz and microcline, and is metamorphic in origin. The larger fragment on the right is basaltic in character consisting of pyroxenes, plagioclases and metallic oxides.

4-5-C1 75X

17F
11M
11P
10M
10P

ELECTRON SCATTERING

18F
Quartz
19F

The large, dark area in the center of the photo is mostly impregnating plastic, with silica, iron, titanium and aluminum mixed through it. The plutonium emission photo shows plutonium associated with this debris as well as in the surrounding rock fragments.

4-5-C2 75X

Al

Ca

Fe

K

ELECTRON SCATTERING

20F

12P

Quartz

P

Pu

Si

Ti

The large rock fragment is a basalt and the electron scattering photo is badly blurred on the right. Despite the poor quality, the plutonium emission picture shows very well that the plutonium here is low in concentration and found in the rock fragments.

4-5-C3 75X

Fe

P

Ti

Ca

ELECTRON SCATTERING

Si

Al

K

Pu

This electron scattering photo also is badly blurred on the right. The interesting aspect of this photo is the occurrence (or survival) of metamorphic hornblende. Also noteworthy is the coincidence of the highest phosphorus and plutonium concentrations.

The appearance of a single, large rock fragment in the center of the electron scattering photo is probably false. Quartz and microcline do not coexist with augite in nature in the same rock. It is most likely a group of rock fragments surrounded by plastic, silica and alumina. Plutonium particles (^{13}Pu) occur even at this depth in core 4-5.

A basalt fragment is shown here that has partially survived the low pH environment. It contains crystals of apatite, $(\text{Ca}, \text{Fe}^{+2})_5(\text{PO}_4)_3(\text{OH})$, and a clay mineral, $(\text{Fe}^{+3}_{1.833}\text{Mg}_{0.148}\text{Al}_{0.066})(\text{Si}_{3.675}\text{Al}_{0.325})_{10}(\text{OH})_2$, both commonly found in the local basalt flows. The apatites can be located on the calcium and phosphorus x-ray emission photos. The clay is an iron-rich member of the dioctahedral division of the smectite group of clay minerals. The smectite clays are formed under arid, alkaline conditions, and are easily destroyed in a low pH environment. Apatite, too, is easily destroyed in an acid solution. This is the first example of the survival of these two minerals in the many basalt soil fragments examined.

4-5-D2

Al

Ca

Fe

K

75 X

P

Pu

Si

Ti

The lower half of this basalt fragment has been chemically attacked with the loss of calcium and aluminum. Silica content appears to be higher in the lower half because silica would tend to be left behind as the calcium and aluminum were extracted. The plutonium is uniformly distributed and below the microprobe detection limit ($<0.3 \text{ wt\% PuO}_2$).

4-5-D3 75X

Al

Ca

Fe

K

ELECTRON SCATTERING

P

Pu

Si

Ti

This nodule is a variety of rock fragments apparently cemented with hematite (Fe_2O_3). Ilmenite-magnetite crystals are included in the cemented fragments, so the ferric iron probably originated in trench influents rather than from oxidized metallic oxides already present in the soil. Several particles of plutonium also were cemented into the mass of rock fragments.

4-5-A Agglomerate 75X

A sample of the minus 230 mesh fines from the top six inches of core 4-5 are shown here. The bulk of this size fraction is composed of crystal fragments of plagioclase feldspars with a few quartz and metallic oxide fragments. Several particles of plutonium are seen in the plutonium emission photo.

4-5-A Fines 75 X

Al

Ca

Fe

K

Si

P

Pu

Ti

18Pu
17Pu
16Pu
20M

21M
Quartz

ELECTRON SCATTERING

The area of the photo set is in the sludge overlying the Z-9 crib soil. There is an occasional soil rock fragment, such as that seen in the center of the electron scattering photo, but these are scarce. The general area of the x-ray emission photo for Pu is slightly to the left of the electron scattering photo, but includes the soil rock fragment in the upper right quadrant. The low Pu areas are plastic.

CORE 4-11

ELEMENTAL DISTRIBUTION

4-11-A 1
75 X

ELECTRON SCATTERING

Pu

Pu

[400X]

Quartz

ELECTRON SCATTERING

8 Pu

Pu

The area shown here is just below the soil-sludge contact. The most prominent feature is the precipitated hematite layer, cut perpendicularly, and the presence of considerable quartz (SiO_2). An optical photo by reflected light shows the same hematite layer at another location. On the x-ray emission photos, the Pu occurs in particles between the soil rock fragments in highest concentration. The quartz fragments can be seen in the Si photo and some potash feldspar fragments in the K photo. The iron precipitate contains no Ti. Also note the distribution of phosphorus within the impregnating plastic between the rock fragments and iron precipitate.

4-11-A 1

75 X

Al

Ca

Fe

K

P

Pu

Si

Ti

This is an area near the sludge-soil contact. A large corroded rock fragment is seen on the right side of the electron scattering photo. The curved structure near the center of the photo is a dessication crack filled with plastic. Much of the remainder of the soil mount also is plastic. The Pu concentration is high in this material. The Pu (400X) is again composed of particles and less concentrated Pu that at least originally was soluble. The rock fragment now consists of Si, Al and K, and little else. Note the Mg distribution suggesting a primary magnesium content in the sludge. A single feldspar fragment can be seen in the Ca emission photo in the upper right quadrant. Also the phosphorus is again largely associated with the impregnating plastic.

4-11-A1

75 X

Al

Ca

Fe

K

10 Pu 9 Pu

2 F

11 Pu

5 A

ELECTRON SCATTERING

Mg

P

Pu

Pu

400 X

Si

Ti

Three rock fragments are shown in the electron scattering photo, along with a dark, high plastic area. This is one of the few instances that show a high plutonium content in the soil rock fragments. Two of the attached rock fragments were probably metamorphic rock fragments originally based on their relatively high potassium content, suggesting the presence of a potash feldspar. The iron emission photo shows that the white-appearing material on the edges of the rock fragments is mainly iron.

4-11-A 2
75 X

Fe

Mg

Ti

Ca

ELECTRON SCATTERING

Si

Al

K

Pu

6 A
12 Pu
14 Pu
13 Pu
7 A

The soil rock fragment in the upper part of the electron scattering photo is metamorphic in origin, containing quartz and potash feldspar. The plutonium concentration is much lower than in the previous photos and is rather uniformly distributed. Most of the following photos also show the same lack of Pu particles that were found in the upper part of the soil column.

4-11-A2
75 X

Al

K

3M

4P

Ca Quartz

ELECTRON SCATTERING

Si

Fe

P

4F

5F

Quartz

Ti

Pu

Many smaller soil rock fragments are shown in the electron scattering photo, embedded in dark plastic. The fragments include potash feldspars and quartz. The larger rock fragments on the upper and lower right are basaltic in origin. Several of the smaller rock fragments also are basaltic in origin as indicated in the calcium emission photo. Plutonium is relatively low in concentration and fairly evenly distributed.

4-11-A3
75 X

Al

Ca

Fe

K

15P Quartz
ELECTRON SCATTERING 7F

Mg

P

Pu

Si

I

A large fragment of basaltic rock is shown in the electron scattering photo. The white areas are metallics, the light gray areas pyroxenes, and the dark gray crystals are feldspars. The rough areas within the fragment are groundmass, or represent chemical attack of the fragment in these areas. Some of the feldspars show a higher than usual potassium content.

Al

4-11-B1
75 X

Ca

Fe

ELECTRON SCATTERING

K

Mg

Pu

Si

Ti

A basaltic rock fragment and several smaller basaltic and metamorphic fragments are shown in the electron scattering photo. The metamorphic fragments include quartz and potash feldspar (microcline). The plutonium is fairly uniformly distributed and relatively low in concentration. The phosphorus is concentrated in the dark plastic areas shown in the electron scattering photo.

Al

Ca

Fe

K

4-11-B 2
75X

ELECTRON SCATTERING

Mg

P

Pu

Si

Ti

A large quartz soil fragment and basaltic rock fragments are shown in the electron scattering photo. High plastic areas are dark in color. The basaltic rock fragment on the right-hand side contains large feldspar crystals seen in the potassium and calcium emission photos. Pyroxene areas show in the magnesium emission photo. The bulk of the phosphorus is contained in the plastic between rock fragments. Plutonium is low in concentration and widely disseminated. This type of occurrence is typical of the less than 0.3 wt % of detectable PuO_2 .

The large rock fragment shown in the left-hand side of the electron scattering photo is a basaltic rock, while the rock fragment on the right-hand side is probably metamorphic in origin. Note how the metamorphic rock fragment is outlined in the iron emission photo by an exterior iron deposit.

Al

Ca

Fe

K

4-11-C2
75X

ELECTRON SCATTERING

Mg

P

Pu

Si

Ti

The electron scattering photo shows a large, chemically attacked rock fragment, probably a fine-grained rock of basaltic composition. Consideration of the x-ray emission photos show that the attacked areas have lost aluminum and calcium, and gained small amounts of phosphorus. Note, also, that the quartz fragment in the upper right is outlined by iron and potassium in the iron and potassium emission photos. There is no apparent accumulation of plutonium in the chemically attacked rock fragment area, but there is an unusually high concentration of plutonium near the exterior of the quartz fragment associated with the exterior iron coating.

Al

Ca

Fe

K

4-11-D2
75X

Quartz

20μ
ELECTRON SCATTERING

Mg

P

Pu

Si

Ti

A large, chemically attacked soil rock fragment is shown in the electron scattering photo. Only a small portion of the original rock fragment remains. This relatively unaltered portion is located on the upper side of the fragment. The unaltered portion is higher in iron content and the surviving plagioclase feldspar crystals are shown in the calcium emission photo. The unaltered area is also lower in potassium content than the altered portion constituting the bulk of the rock. Apparently this rock fragment was massively altered. Iron and calcium have been removed and potassium added in patchy areas. The small quartz area is probably secondary in origin (vug filling), and was originally present in the fragment. The various chemical reactions occurring between contacting solutions and soil rock fragment are a function of solution composition and rock fragment composition.

Al

Ca

Fe

K

4-11-D3
75 X

Mg

P

24M

Pu

Si

Ti

The electron scattering photo of the 4-11 column, section A, minus 230 mesh fines shows a group of crystal and rock fragments. Several plutonium particles are seen in the plutonium emission photo. The 500X plutonium emission photo shows a ten micrometer diameter plutonium particle whose chemical analysis is identified as 18 Pu. Plagioclase and microcline feldspars and pyroxenes can be identified among the fragments, although many of these have been partially-to-nearly totally altered.

**4-11-A Fines
150 X**

Al

Ca

Fe

K

ELECTRON SCATTERING

Mg

P

Pu

Pu

18 Pu

[400X]

Si

Ti

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