♻EPA

Quantitative Mineral Assessment and Radionuclide Retention Potential of Atlantic 3800-Meter Nuclear Waste Dumpsite Sediments

Biogenous Materials

LEGEND
■ — Contemporary Sediment
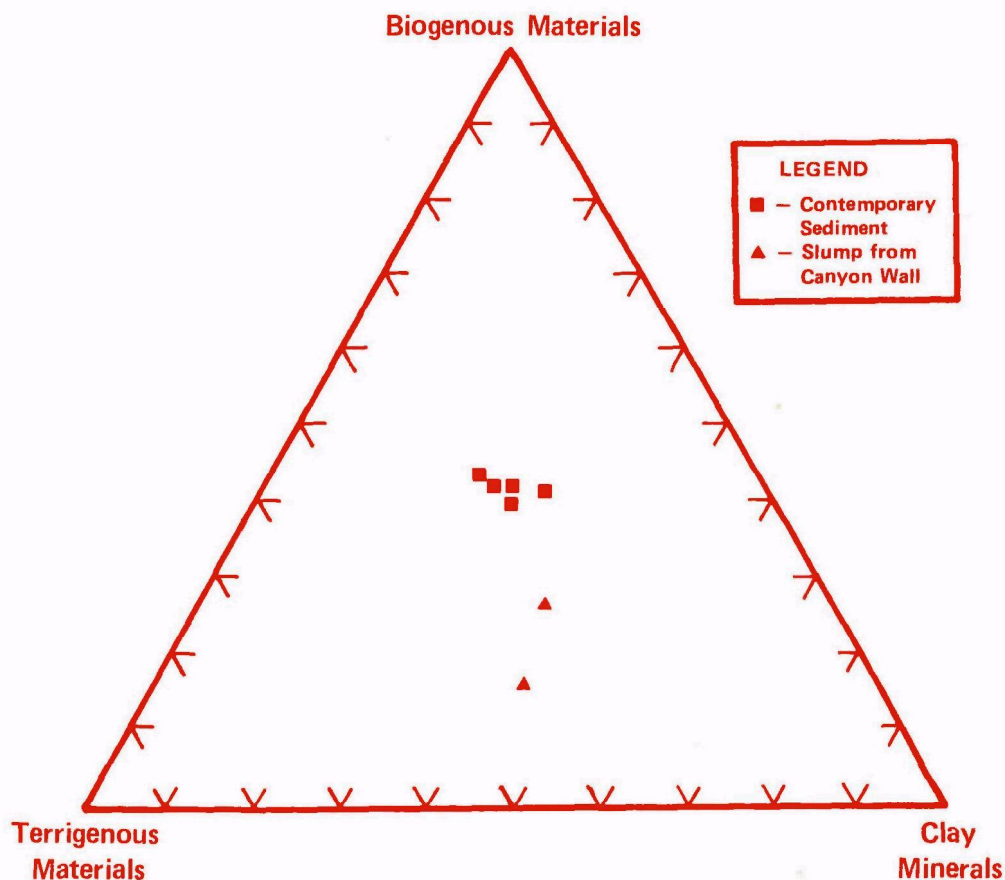▲ — Slump from Canyon Wall

Terrigenous Materials

Clay Minerals

Quantitative Mineral Assessment

and Radionuclide Retention Potential

of Atlantic 3800-Meter

Nuclear Waste Dumpsite Sediments
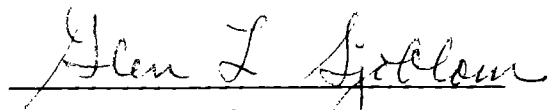

by

James Neiheisel

March 1983

FOREWORD

The Environmental Protection Agency (EPA) was given a Congressional mandate to develop criteria, standards, and regulations governing the ocean disposal of all forms of wastes pursuant to Public Law 92-532, the Marine Protection, Research, and Sanctuaries Act of 1972. Within this Congressional mandate, EPA has initiated a specific program to develop regulations and criteria to control the ocean disposal of radioactive wastes.

The EPA Office of Radiation Programs (ORP) initiated feasibility studies to determine whether current technologies could be applied toward determining the fate of radioactive wastes dumped in the past. After successfully locating radioactive waste containers in three of the primary radioactive waste disposal sites used by the United States in the past, ORP developed an intensive program of dumpsite characterization studies to investigate: (1) the biological, chemical, and physical parameters, (2) the presence and distribution of radionuclides within these sites, and (3) the performance of past packaging techniques and materials.

During the 1978 survey of the Atlantic 3800-meter radioactive waste disposal site, sediments from this waste disposal site were collected with a Soutar box corer to characterize the sediment geochemical properties and to obtain information regarding the capabilities of sediment to act as a natural barrier in the retention of radionuclides from the low-level radioactive waste. Under Interagency Agreement Number EPA-79-D-H0706, the U.S. Army Corps of Engineers, South Atlantic Division Laboratory, has assisted the EPA Office of Radiation Programs in analyzing the sediment samples using quantitative measurement techniques applicable to the precise requirements of this survey. This report presents the results of the laboratory analyses performed and considers the radionuclide retention potential of the sediment.

The Agency invites all readers of this report to send any comments or suggestions to Mr. David E. Janes, Director, Analysis and Support Division, Office of Radiation Programs (ANR-461), Washington, D.C. 20460.

Glen L. Sjoblom, Director
Office of Radiation Programs

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ACKNOWLEDGMENTS

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SUMMARY

In June 1978, seven box core sediment samples were obtained from the abandoned 3800-meter Atlantic low-level radioactive waste dumpsite. This site is located approximately 320 km east of the New York coast in the main axis of the Hudson submarine canyon. The sediments were characterized for assessment of their potential to act as a natural barrier to the migration of radionuclides.

An important first step in the sediment characterization is delineation of the highly sorptive materials which are concentrated in the fine fractions. A quantitative, state-of-the-art method was employed to obtain an accurate assessment of the sorptive minerals. This method combines the following: (1) textural grain-size accumulation curve; (2) separate mineral evaluation of sand, silt, and clay-size fractions to provide greater accuracy with x-ray diffraction; and (3) calculation of average composition of minerals by the sum of the weighted average on respective size fractions. The clay minerals, comprised of predominantly illite and lesser amounts of chlorite, kaolinite, and montmorillonite are the principal sorptive minerals of the 3800-meter site sediment. Two samples, containing divergent physical characteristics and montmorillonite as the dominant clay mineral, are believed to be slump block, Tertiary age, sedimentary units from the canyon wall.

An approximation of potential radionuclide retention that might be expected from the 3800-meter sediment can be calculated for cationic radionuclide species in which the sorption distribution coefficient (Kd) is known. Measured Kd values are known for cesium and strontium on pure mineral phases of quartz, feldspar, mica, illite, kaolinite, and montmorillonite, and approximations are made for chlorite and calcite. Calculations made using these data for the 3800-meter sediments approximate a Kd of 460 ml/g for cesium and 30 ml/g for strontium. Sufficient data are not available for other radionuclides of interest. However, approximations are made from similar Kd calculations with other ocean sediments that closely match the environmental conditions (pH, Eh) and chemical factors in the Atlantic 3800-meter nuclear waste dumpsite.

INTRODUCTION

The U.S. Environmental Protection Agency (EPA), in carrying out
Public Law 92-532, the Marine Protection Research and Sanctuaries Act, is
investigating abandoned nuclear waste dumpsites located in the Pacific and
Atlantic Oceans off the continental United States. The Atlantic 3800-meter
dumpsite, located approximately 320 km off the New York coast, was studied
in the summer of 1978. Sediment samples were recovered to characterize
the ability of the sediment to act as a natural barrier for the retention
of radionuclides. To assess this capability, quantitative techniques were
employed for precision in reporting the amount of sorptive minerals in the
sediment.

Korte, et al. (1976), have investigated the relative mobility of
heavy metals and trace elements in soils. They conclude that determining
the percent clay in the soil is the most useful means of predicting
whether a soil will retain a particular element. Onishi, et al. (1981),
and other investigators, reporting on the mobility of radionuclides in
soil and ocean sediment, have also cited the importance of clay minerals,
as well as chemical factors, as they affect the retention of radionuclides.

The purpose of this paper is to present a quantitative mineral
evaluation technique to delineate the precise amount of the highly
sorptive clay minerals, as well as the lesser sorptive materials, in the
sediment of the 3800-meter Atlantic nuclear waste dumpsite and to evaluate
the potential of these clay minerals for retention of specific radio-
nuclides found in low-level radioactive waste.

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SITE DESCRIPTION

The 3800-meter Atlantic nuclear waste site is located approximately 320 kilometers off the New York coast and comprises an area of about 256 square kilometers (Figure 1). The area is centered at 37°50'N and 70°35'W. From 1957 to 1959, in excess of 14,500 drums of low-level radioactive waste were dumped at this site (Dyer, 1976). This amounts to approximately 40 percent of all waste dumped in the Atlantic (Holcomb, 1982). In 1962, the United States ceased ocean disposal practices, and low-level radioactive waste is disposed of in shallow land burial sites on the continent.

The 3800-meter site is physiographically part of the lower continental rise in the region of the main axis of the Hudson Canyon (Figure 1). During the 1978 site survey of this area, the submersible, DSRV Alvin, was used to recover waste drums and to investigate the physiographic and sediment conditions at the site. Hanselman and Ryan (1983), from observations made aboard the DSRV Alvin, describe the canyon floor as gently sloping and about one kilometer wide covered with fine-grained sediment and local claystone slump blocks of various sizes and shapes. Adjacent canyon walls rise from the canyon floor along sloping-to-vertical surfaces to heights up to 200 meters in relief; channel thalwegs in contact with channel walls apparently provide the cutting mechanism that activates slumps or gravity slides (Hanselman and Ryan, 1983).

Figure 1. Location of the Atlantic 3800 m radioactive waste dumpsite and Soutar boxcore sediment sample locations.
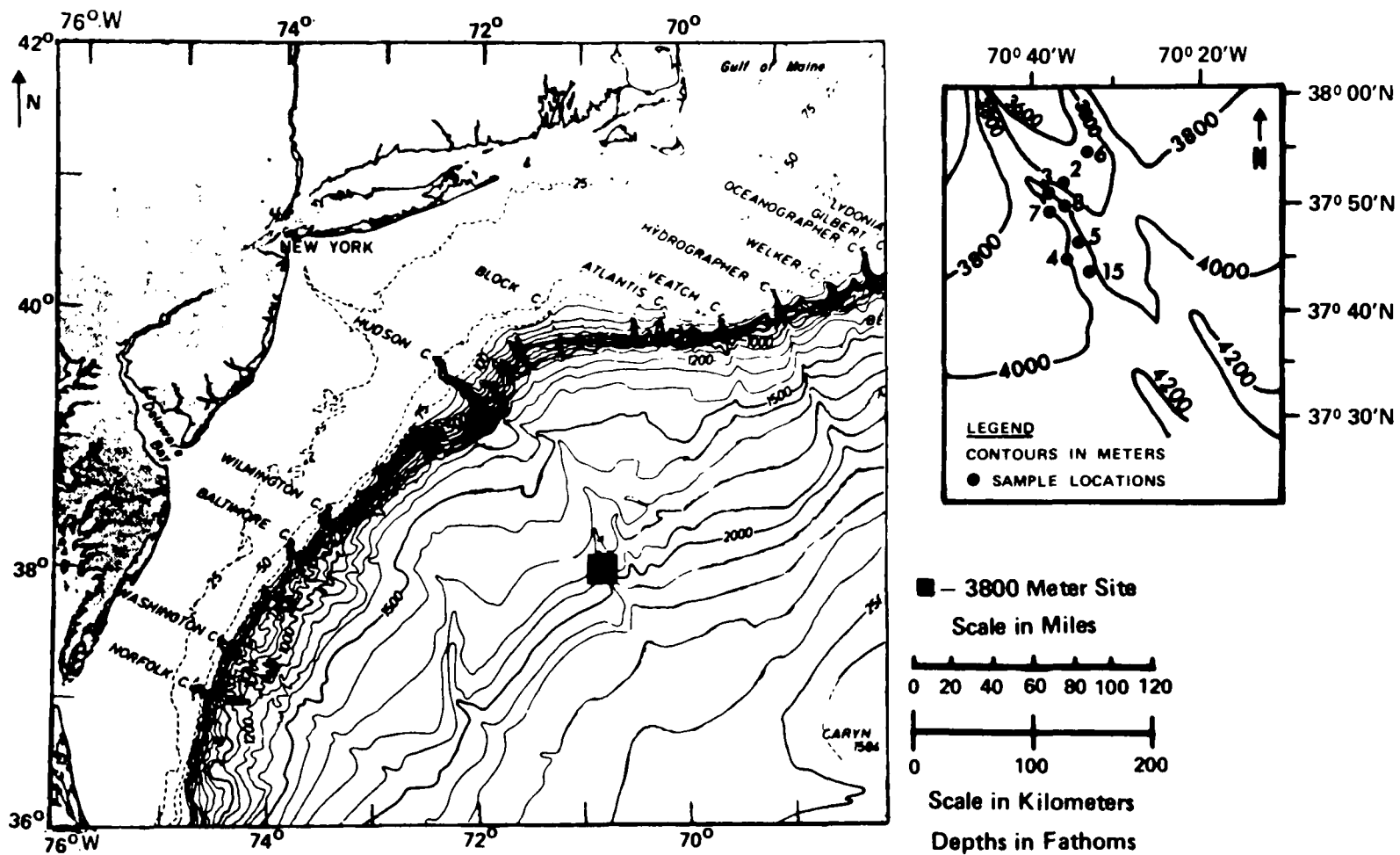
FIELD AND LABORATORY METHODS

Sediment Sampling

In June 1978 the sediment samples from the 3800-meter site were obtained by using the Soutar Box Corer from the SS Advance II. The bottom sediment locations are depicted in Figure 1. Geographic coordinates of the sample locations obtained by Loran navigational fix are listed as follows:

Field Location 2	37° 50.83' N	70° 35.50' W
Field Location 3	37° 49.30' N	70° 36.71' W
Field Location 4	37° 45.03' N	70° 35.75' W
Field Location 5	37° 46.75' N	70° 34.01' W
Field Location 6	37° 54.65' N	70° 32.69' W
Field Location 7	37° 48.10' N	70° 37.11' W
Field Location 8	37° 49.79' N	70° 36.13' W
Field Location 15	37° 43.81' N	70° 32.38' W

Plexiglass tube sub-cores were obtained as relatively undisturbed samples from the large-volume Soutar Box Corer as soon as the sample arrived on deck. The samples were visually inspected, and those selected for sediment and physical property analysis were frozen in dry ice to prevent physical or chemical change. Samples, numbered 5 and 7, appeared more consolidated and desiccated with numerous bore holes from organisms than the typical, plastic, less consolidated samples.

The frozen sediment samples were analyzed by the South Atlantic Division Laboratory for physical, textural, and mineral properties. Scanning electron micrograph (SEM) and cation exchange capacity (CEC) sediment test samples were also delivered in frozen condition to the Georgia Institute of Technology for analysis.

Method of Analysis

The sediments were examined for physical, chemical, and mineralogical properties with special methodology employed to characterize selected phases of the sediment for radionuclide retention. Radionuclide retention factors will be described in detail in a later section.

The cation exchange capacity was determined by a method similar to that of Zaytseva, as described by Sayles and Mangelsdorf (1977). The samples were squeezed into a stainless steel device, and the pore water was collected and analyzed for Na^+, K^+, Mg^{++}, and Ca^{++}; the remaining partially dewatered cake was split into two parts. One part was used for determining the residual water content ($110^\circ C$ drying), and the other was leached of residual seawater and exchange cations, using a succession of washes (80 percent methanol, $1\underline{N}$ NH_4Cl adjusted to pH 8 with NH_4OH). The exchange cations were calculated by subtracting the seawater contribution from the total leach solution. This procedure thus circumvented the exchange cation-seawater reequilibrium (Donnan effect) that occurs during the washing step which precedes the exchange in the more traditional approach. The pH adjustment and the use of methanol minimized the solution of $CaCO_3$ during leaching.

The grain-size analysis, bulk specific gravity, porosity, and Atterberg Limits tests were performed in accordance with standard soil testing procedures described by the U.S. Army Corps of Engineers (1970) in EM-110-2-1906. In preparing the grain-size accumulation curve by the sieve-hydrometer method, the clay-size fraction is reported as that material less than 2 micron size; the division between silt and sand-size material occurs at the 50 micron size. Sediment texture description is based on the percentages of sand, silt, and clay-size fractions in accordance with the nomenclature of Shepard (1954); this is depicted in the ternary plot of Figure 2. In determining porosity, it was assumed that no compaction occurred and that the sample volume, upon receipt in the laboratory, was the same as the volume of the _in situ_ sediment sample; as such, the value obtained is considered reasonably accurate.

Quantitative Mineral Analysis

Several quantitative or semiquantitative techniques to identify clay minerals have been described by Johns, et al. (1954), Schultz (1960), Brindley (1961), Griffin and Goldberg (1963), Biscaye (1965), Neiheisel and Weaver (1967), Devine (1972), and others. These methods and the variables involved have also been evaluated by Gibbs (1968), Pierce and Siegel (1969), and others. An understanding of the capabilities and limitations of each of these methods enables one to design a method applicable to the need. In this context, the method used in this investigation builds upon established concepts, but its application provides greater accuracy in the semiquantitative to quantitative results derived.

The method employs separate x-ray diffraction analysis of representative portions of both the silt and clay-size fractions to eliminate some of the phases. With fewer phases, there is greater accuracy in the analysis of the clay minerals for reasons inherent in the x-ray diffraction procedure. The powder press mounting technique, endorsed by Gibbs (1965), is used to eliminate errors due to segregation. The resulting diffractograms are superior to those which combine the silt and clay-size fractions, commonly referred to as "fines" by some investigators; this is especially true where several phases are involved.
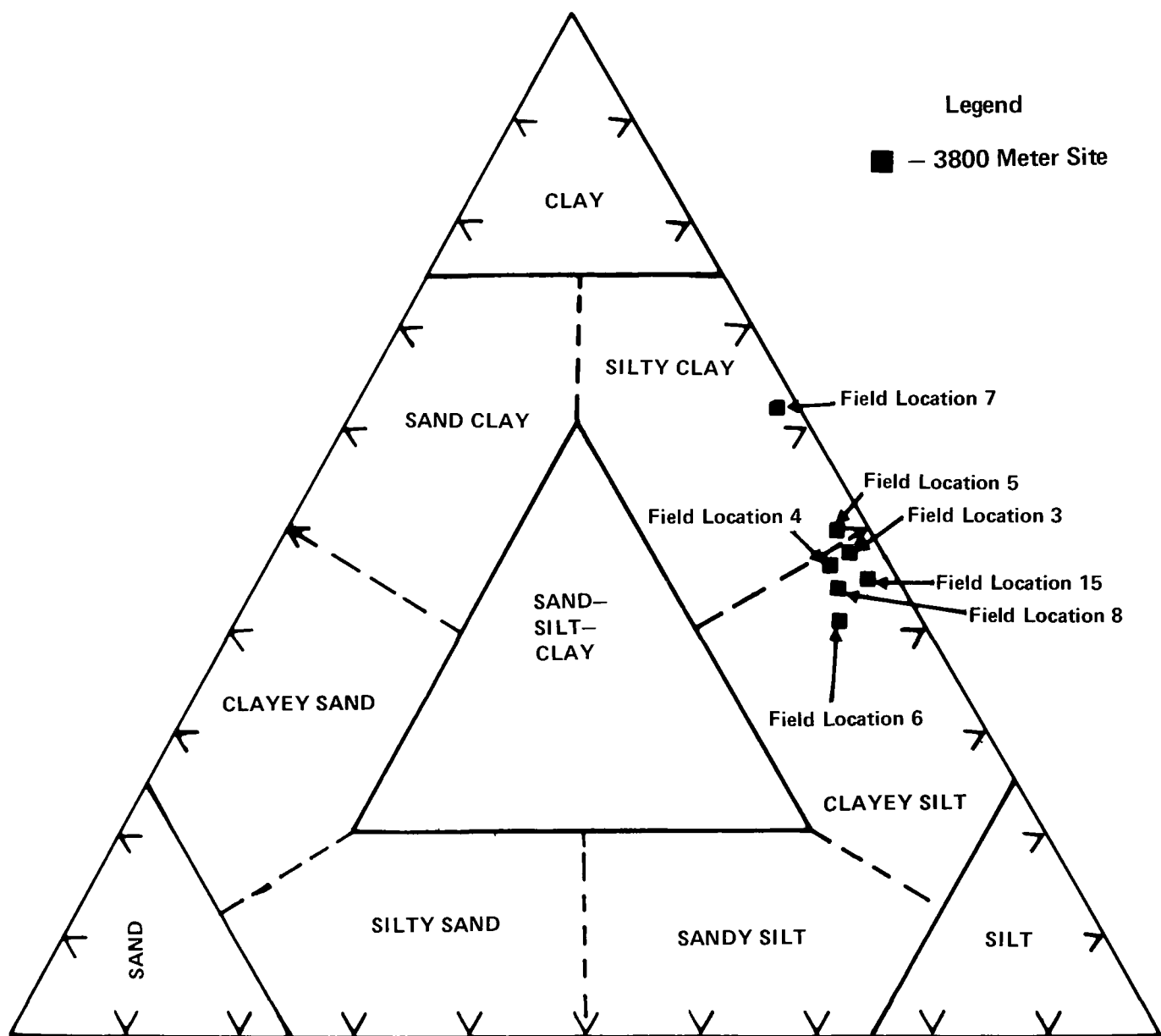
Figure 2. Percentage of sand, silt, and clay in the Atlantic 3800 meter site bottom sediments.

Fast x-ray diffraction scans and diagnostic tests (glycolation and heat treatments at 300° C and 500° C) identify the clay-mineral suite present by standard methods before determining the percent of clay minerals from powder press samples. The more difficult separation of kaolinite and chlorite is performed by the slow scan method after Biscaye (1964); the peak height intensity of the kaolinite peak at 3.58A and the chlorite peak at 3.54A are proportioned to determine their quantity represented in the 7.2A peak. The clay minerals in the clay-size fraction are then calculated by the peak area method (Biscaye, 1965) or the peak height intensity method on the diffractograms generated from the powder press mounted sample. The calcite may be determined independently of the clay minerals on a separate sample by the dilute acid leach (1:4 HCl) method.

The x-ray diffractograms of silt-size sediment contain predominantly quartz, feldspar, and calcite, and minor aggregations of clay minerals. While there are no quantitative methods to evaluate the percentages of these minerals, reasonably accurate percentage evaluations exist in the following:

(1)   Determination of carbonate (calcite) by dilute acid leach (1:4 HCl) of a separate representative sample.

(2)   After a first estimate of quartz, feldspar, and minor other minerals by peak intensity estimates, prepare laboratory mixtures to duplicate the diffractogram such as described by Buck (1972). The "best fit" matching diffractogram defines the percentages of the admixture.

Again, precision is gained by eliminating the conflicting phases such as occur if all size fractions were pulverized into one sample; a separate silt-size diffractogram provides this advantage.

The sand-size fraction is analyzed by standard petrographic techniques using at least a statistical 300 grain count. The calcite (biogenous) fraction can be separated from the insoluble terrigenous fraction by dilute acid (1:4 HCl) separation techniques.

The percentages of mineral composition are recorded for the sand, silt, and clay-size fractions, and these are multiplied by the weighted fractions of the grain-size accumulation curve. The sum of the various components from each of the respective size fractions represents the calculated percentages of each material in the total sample. The materials may now be grouped into categories of low, medium, and high sorptive materials.

The quantitative mineral method identifies the percentages of minerals in relation to their radionuclide retention potential. This method combines the following: (1) textural grain-size accumulation curve; (2) separate mineral evaluation of sand, silt, and clay-size fractions to provide fewest phases for greatest accuracy with x-ray diffraction; and (3) calculation of average composition of minerals by the sum of the weighted average on respective size fractions. The grouping of sorptive minerals will be described in later sections.

SEDIMENT TEXTURE AND PHYSICAL PROPERTIES

Sediment samples of the 3800-meter Atlantic waste dumpsite consist of olive grey to brown-colored fine-grained, clayey silt comprising the canyon floor and compact silty-clay and claystone samples, possibly derived from canyon or slump blocks from the canyon wall. This sediment description is based on the percentages of sand, silt, and clay-size fractions (Figure 2). The weight percent of the respective size fractions is obtained from the grain-size accumulation curve. As shown in Table 1, a comparison of the average texture between the top and bottom portions of the cores show that it is relatively uniform throughout the entire vertical length of each core. This is also reflected in the phi units for the median and standard deviation of the sediment samples (Table 1). Field samples 5 and especially 7, of probable canyon wall origin, show the most deviation from the standard (Table 1).

The bulk density and porosity were measured on five of the more typical sediment samples (Table 1). The bulk density ranges between 1.38 g/cm^3 and 1.55 g/cm^3 and the porosity between 0.67 and 0.76. These parameters are used along with the distribution coefficient (Kd) of a radionuclide of interest to determine the retardation factor of a radionuclide in sediment, as will be considered in a later section.

The Atterberg Limits are relatively inexpensive parameters to reflect upon the uniformity of the sediment properties. They are useful in describing quantitatively the effect of varying water content on the consistency of fine-grained sediments. The boundaries are defined by the water content which produces a specified consistency. The liquid limit (LL) defines the water content at which the sediment closes with standard mechanical manipulation, and the plastic limit (PL) is the water content at which the sediment begins to crumble or break apart. The difference between the plastic and liquid limits, termed the plasticity index (PI), represents the range in water contents through which the sediment is in a plastic state and is inversely proportional to the ease with which water passes through the sediment. The liquid limit is especially diagnostic in that the clayey-silt sediments have a relatively narrow range between 72 and 88, whereas the two silty-clay sediments, samples 5 and 7 (probably canyon wall materials), have values of 94 and 100 (Table 1). This correlation is as significant for mineral composition as it is for texture, as will be shown in a later section.

Table 1. Texture and Physical Properties of Sediment Samples
from the 3800 Meter Atlantic Nuclear Waste Disposal Site

Sample No.	Depth (cm)	Percent Dry Weight			Phi Units		Bulk Density g/cm3	Porosity	Atterberg Limits		
		Sand	Silt	Clay	Median	Std. Dev.			LL	PL	PI
2	10-20	3	48	49	8.9	3.6	---	---	82	44	38
3	0-26	3	50	47	8.8	3.3	1.55	0.67	85	37	48
3	26-40	3	50	47	8.6	3.7	---	---	86	45	41
4	0-26	3	49	48	8.5	3.5	1.50	0.69	83	43	40
4	26-40	4	49	47	8.7	3.3	---	---	88	36	52
5	0-13	4	48	48	8.8	2.8	---	---	94	40	54
6	0-26	8	51	41	8.2	3.1	1.38	0.70	78	36	42
6	26-40	7	52	41	8.3	3.9	---	---	72	36	36
7	0-18	2	36	62	9.2	2.2	---	---	100	41	59
8	0-26	5	50	45	8.2	3.2	1.39	0.76	85	34	51
8	26-40	5	52	43	8.3	3.1	---	---	85	34	51
15	0-26	2	52	46	8.8	3.6	1.44	0.71	81	41	40
15	26-40	2	53	45	8.5	3.5	---	---	78	37	41

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SEDIMENT COMPOSITION

Introduction

The sediment composition in this investigation was determined by a methodology designed for specific assessment of the highly sorptive minerals capable of radionuclide retention. The methodology builds upon established practices, but is more refined in (1) determination of mineral composition on separate sand, silt, and clay-size fractions for greater accuracy in the fewer phases involved, (2) requirement of a texture grain-size accumulation curve to calculate the weighted average of mineral species within each size fraction, and (3) calculation of the percent of each mineral species in the total sample. The most highly sorbent minerals are the clay minerals which occur in the smaller grain-size fractions, and the least sorbent phases occur in the larger grain-size materials. The biogenous materials occupy a position somewhere between these extremes as will be considered in more detail in a later section.

Mineral composition of the various size fractions and the calculated amount in the total sample are listed in Table 2. The weight percent of sand, silt, and clay-size fractions used to calculate the weighted average shown in column D of Table 2 are listed in Table 1. Each of the percentages of respective materials for the sand-size fraction (column A), silt-size fraction (column B), and clay-size fraction (column C) listed in Table 2 may also be used to reflect on the differences between the older slump material from the canyon wall and contemporary sediment. For example, note the high representation of quartz in the sand-size fraction of field sample 5 (40%) and field sample 7 (27%) as compared to the quartz in the sand-size of the other field samples (3 to 14%); in these same samples, note the relatively low carbonate content of the sand-size of field samples 5 and 7 (10%) as compared to 80 to 94% carbonate in the other field samples. These and other comparisons of physical and chemical factors enable deduction of slump materials from the contemporary sediments of the Hudson canyon floor. Mineral composition of individual clay mineral species is listed in Table 3. Mineral groupings, applicable to radionuclide retention, are also listed in Table 3 as terrigenous, biogenous, and clay minerals; these are depicted in the ternary plot of Figure 3. Each of these groupings will be considered in the following sections.

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Table 2. Mineral Suite of Sand-Silt-Clay Size Fractions and Average
Sediment Composition from the 3800 Meter Atlantic Nuclear Waste Disposal Site

Sample No.	Depth (cm)	Lab. No.	Carbonate				Quartz				Feldspar				Mica				Clay Minerals				Misc.		
			A	B	C	D	A	B	C	D	A	B	C	D	A	B	C	D	A	B	C	D	A	B	C
2	0-20	102	94	36	44	42	3	35	--	17	1	12	--	6	1	11	--	5	--	5	55	29	1	1	TR
3	0-26	74-75	80	31	46	40	12	44	--	22	4	14	--	7	2	7	--	4	--	3	54	27	2	1	TR
3	26-40	76	80	39	41	40	12	30	--	15	4	15	--	8	2	10	--	5	--	5	59	30	2	1	TR
4	0-26	77-78	91	29	45	39	5	36	--	18	2	7	--	4	1	18	--	9	--	7	55	30	1	1	TR
4	26-40	79	95	37	47	44	4	35	--	17	1	10	--	5	TR	13	--	7	--	4	53	27	TR	TR	TR
5	0-13	80	10	30	25	27	40	40	--	21	8	12	--	6	2	12	--	6	--	3	80	40	40	TR	TR
6	0-26	81-82	90	37	46	45	6	45	--	23	3	8	--	4	1	8	--	4	--	2	55	24	TR	TR	TR
6	26-40	83	84	37	40	42	10	39	--	21	4	8	--	4	1	11	--	6	--	5	60	27	1	TR	TR
7	0-18	84	10	8	21	16	27	60	--	22	8	10	--	4	5	17	--	6	--	5	79	52	50	TR	TR
8	0-26	85-86	80	43	39	44	13	37	--	17	4	8	--	4	1	7	--	4	--	4	61	30	2	1	TR
8	26-40	87	80	47	36	42	12	38	--	16	5	6	--	3	1	6	--	3	--	3	65	35	2	1	TR
15	0-26	88-89	80	40	48	43	14	36	--	19	4	9	--	5	1	10	--	5	--	4	52	28	1	1	TR
15	26-40	90	85	35	35	37	10	35	--	17	3	11	--	6	2	18	--	9	--	5	65	31	1	1	TR

Notes: 1 A = Sand-Size Fraction; B = Silt-Size Fraction; C = Clay-Size Fraction; D = Weighted Average
2 Clay minerals are illite, kaolinite, chlorite, montmorillonite and minor other (See Table 4).
3 Miscellaneous includes heavy minerals, pyrite,glauconite,radiolarians, diatoms, and minor other;
   Field samples 5 and 7 contain appreciable pyrite in miscellaneous fraction.

TR = present only in trace amounts.

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Table 3. Average Bulk Composition and Clay Mineral Suite of
Sediment from 3800-Meter Atlantic Site

	Average Bulk Composition				Clay Mineral Fraction			
Field Sample Number	Biogenous Materials	Terrigenous Materials	Clay Minerals		Illite	Kaolinite	Chlorite	Montmor-illonite
3	40	31	29		53	19	10	18
4	42	29	29		51	24	10	15
5	27	33	40		30	10	10	50
6	43	32	25		47	13	7	33
7	16	32	52		5	9	3	83
8	43	24	23		53	10	10	27
15	40	31	29		53	18	8	21

Notes: 1. Average bulk composition materials are depicted in triangular plot of Figure 3.

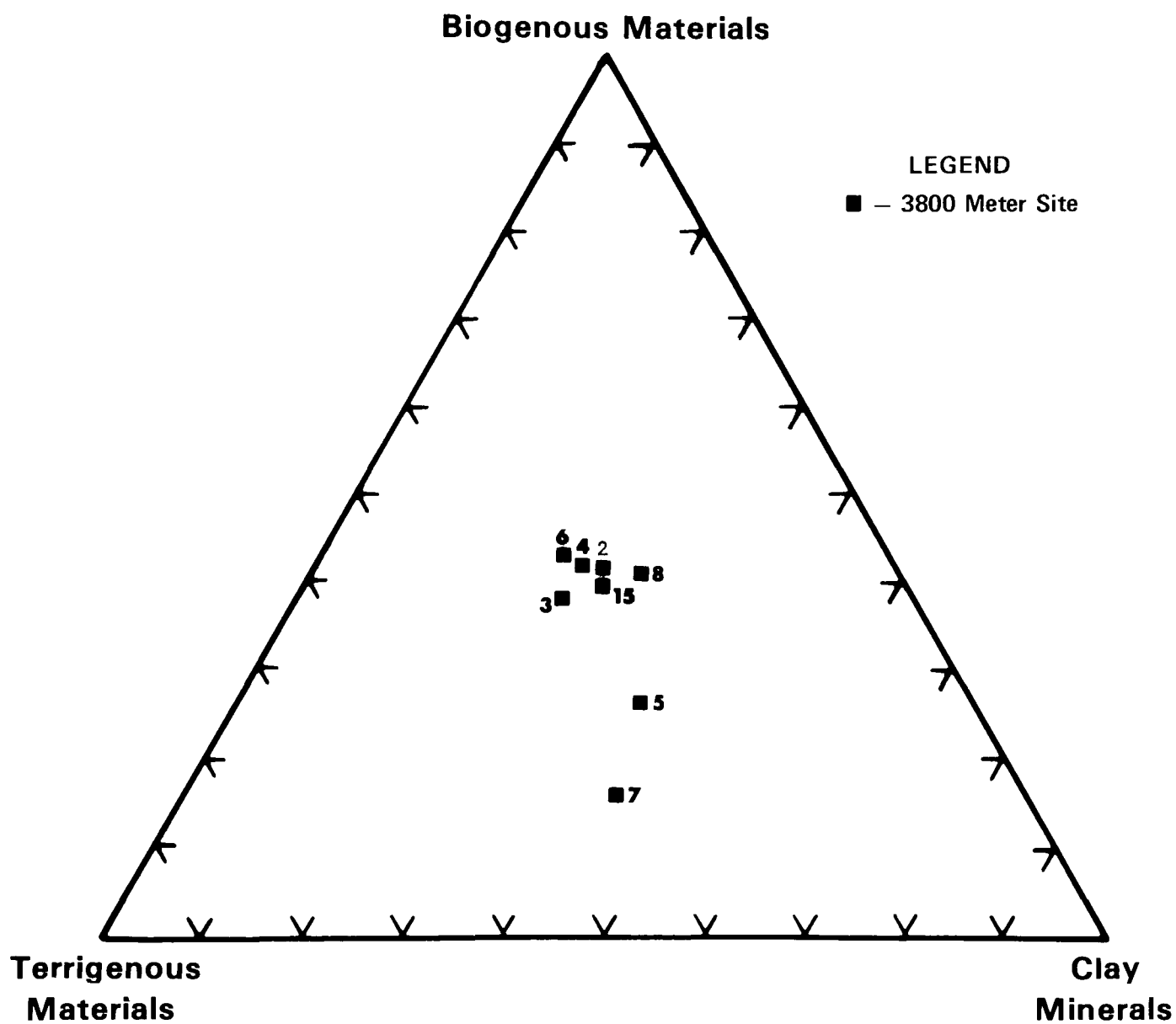2. Average clay minerals are depicted in triangular plot of Figure 7.

Figure 3. Percentage of terrigenous, biogenous, and clay minerals
in the 3800 meter site bottom sediments.

Biogenous Materials

Biogenous materials, originating from hard parts (calcareous, siliceous) secreted by microorganisms, comprise 40 to 43 percent of the contemporary sediment and 16 to 27 percent of the canyon wall slump material analyzed (Figure 3). The biogenous material is comprised predominantly of calcareous foraminifera and coccoliths and very minor siliceous radiolarian and diatom tests. The textural relationship of the various biogenous groups is depicted in Figure 4. As a result of foraminifera abundance in the larger size fractions and coccoliths in the fines, calcite is similar in distribution on all size fractions, with the greatest abundance in the sand-size, as depicted in Figure 4.

The calcareous foraminifera comprise from 80 to 94 percent of the sand-size fraction which constitutes 2 to 7 percent of the contemporary sediment. The foraminifera of the contemporary sediment are calcareous and comprised predominantly of Globigerina (Figure 5), whereas arenaceous tubular foraminifera occur in relative abundance in the slump block material comprising samples 5 and 7 (Figure 5). Some of the tubules contain appreciable pyrite replacement which oxidizes readily to red iron oxide when exposed to the atmosphere. The striking difference in faunal biogenic material in field samples 5 and 7 compared to contemporary sediment is highly significant when combined with clay mineral composition and other physical parameters in relating this material to a slump source from the canyon wall.

The calcareous coccoliths range from middle silt-size into clay-size as depicted in Figure 4. The scanning electron micrograph of Figure 6 illustrates the morphology of typical coccoliths in the silt-size fraction. The coccoliths comprise the major portion of the total carbonate reported for the average sample (Table 2); calcareous foraminifera dominate the sand-size and upper-silt size materials (Table 4), but the weight percent as regards total sample is less.

Siliceous radiolarian and diatom tests are restricted to the sand and upper-silt size sediment and occur in very subordinate amounts (generally less than one percent) in these sediment fractions (Figure 4). A scanning electron micrograph of a radiolarian from field sample number 8 is depicted in Figure 7.

The general increase of biogenous materials in a seaward direction from the upper to the lower continental slope is apparent if one compares the average 30 percent reported by Neiheisel (1979) for the 2800-meter site with the 42 percent at the 3800-meter site. This also corroborates the observations of Turekian (1971) regarding the general gradual decrease in calcium carbonate with increasing depth until about 4,500 meters; at 4,500 meters, the calcium carbonate goes into solution.

TEXTURE – MINERAL DISTRIBUTION – 3800 METER SITE
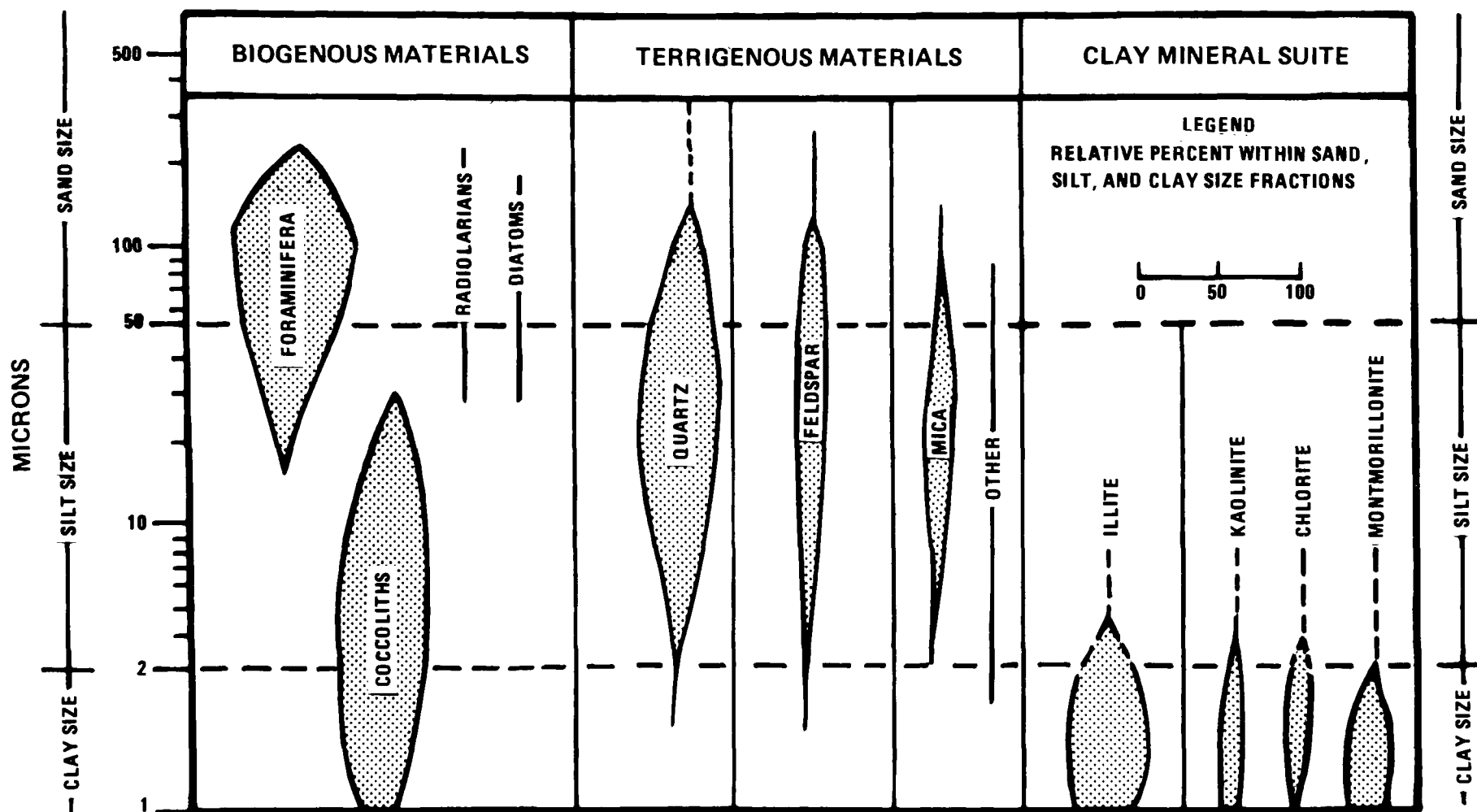
Figure 4. Relative mineral distribution for sand, silt, and clay-size fractions of contemporary sediment from the 3800 meter Atlantic nuclear waste dumpsite.
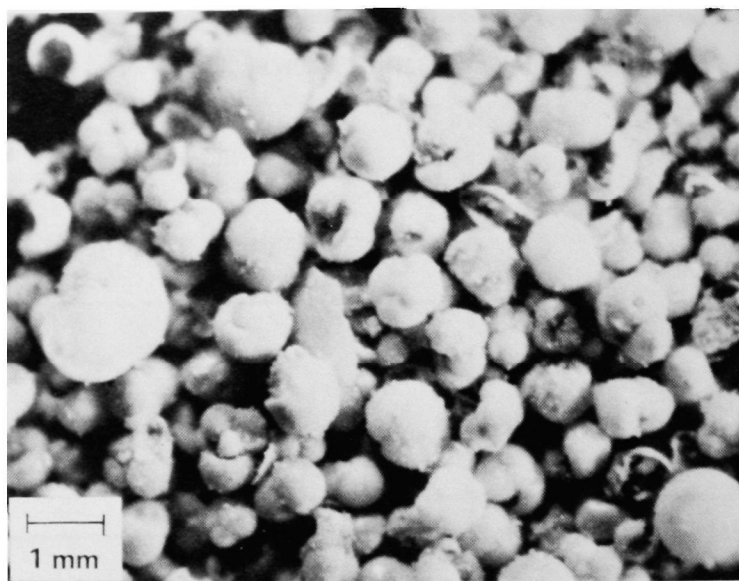
FIELD LOCATION 4
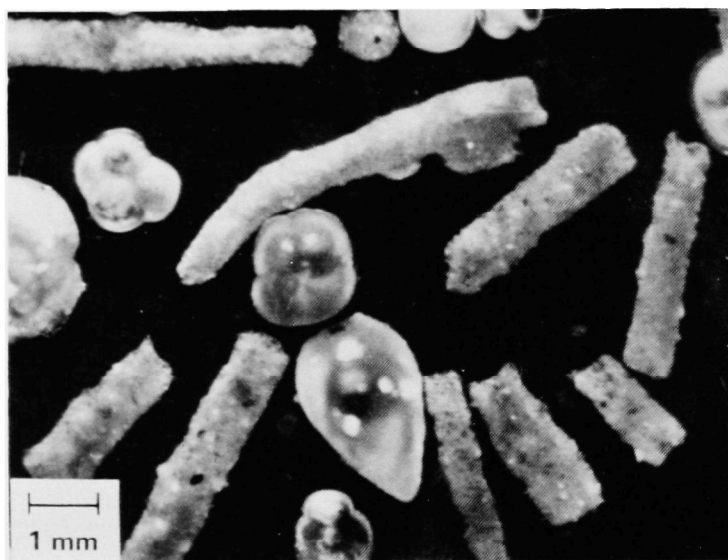
FIELD LOCATION 7

Figure 5. Photomicrograph (10x) of sand fraction from 3800 meter Atlantic site showing typical calcareous foraminifera of contemporary sediment (top) and sediment with arenaceous tubular tests of foraminifera from canyon slump claystone (bottom).

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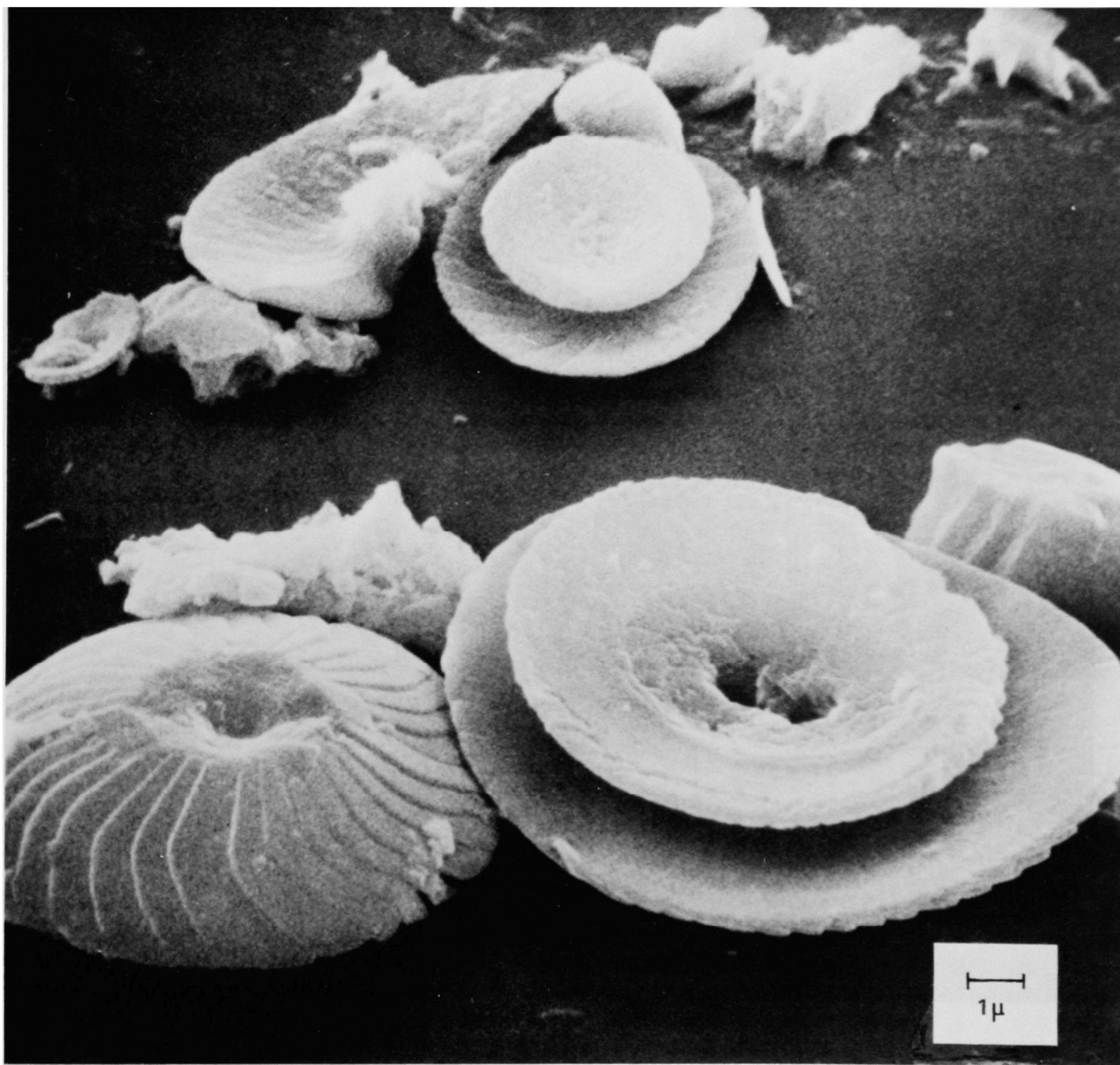
Figure 6. Scanning electron micrograph (9500 X) of coccoliths in silt fraction
of field sample number 8 at 3800 meter Atlantic nuclear waste site.
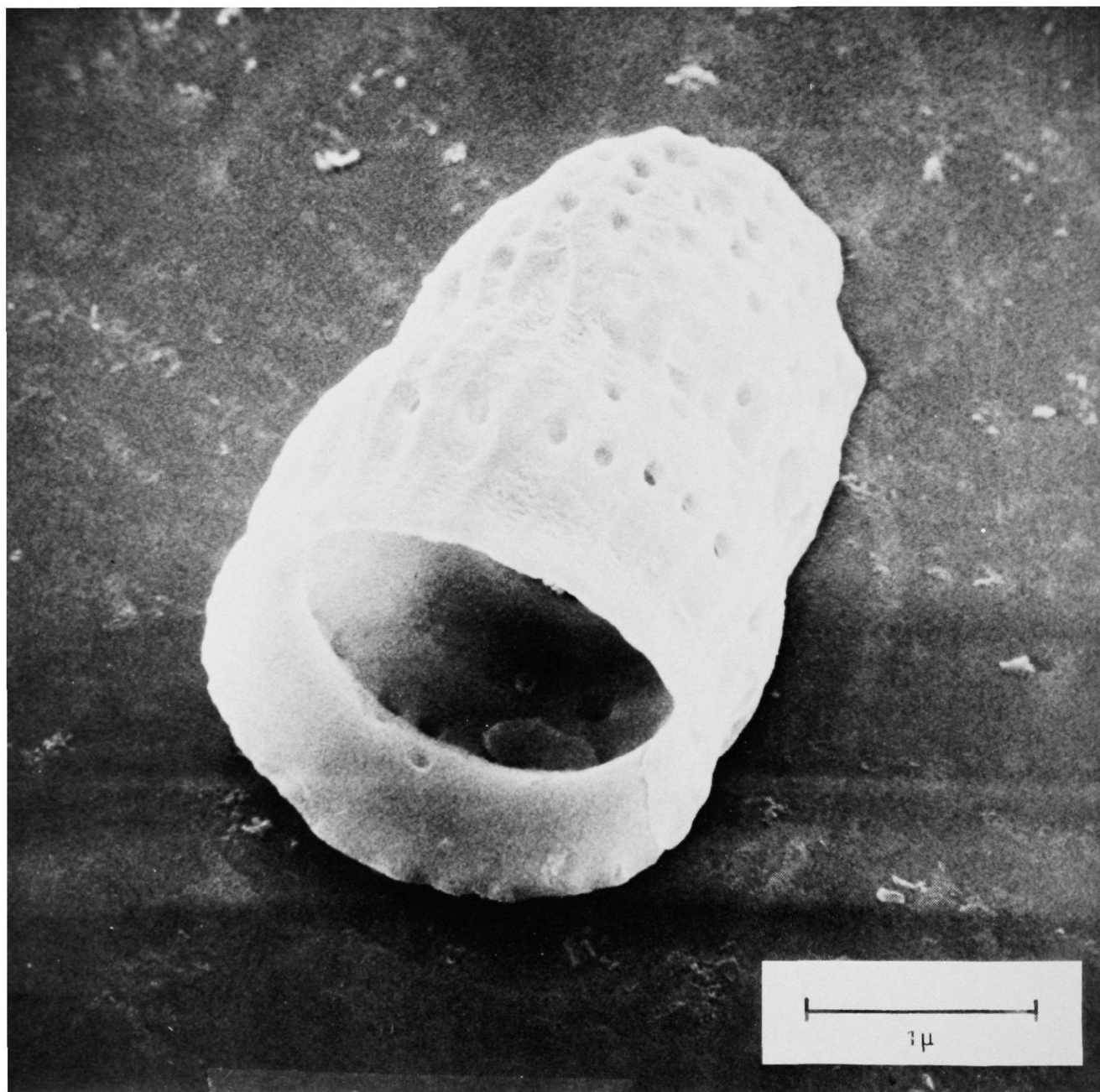
Figure 7. Scanning electron micrograph (2400 X) of radiolarian in silt fraction
of field sample number 8 at the 3800 meter Atlantic nuclear waste site.

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Table 4. Transparent Heavy-Mineral Suite of Sand-Size Sediment
from the 3800-Meter Atlantic Nuclear Waste Disposal Site and Vicinity

Sample Number	2	3	4	5	6	7	8	15
Lab No.	102	74-76	77-79	80	81-83	84	85-87	88-90

Percent Transparent Heavy-Mineral Fraction

Amphibole/Pyroxene	42	56	52	43	31	38	52	55
Garnet	29	10	18	20	30	18	14	10
Staurolite	5	2	3	3	6	3	2	2
Epidote Group	7	10	10	12	9	14	9	18
Zircon	4	7	5	5	7	5	7	5
Sillimanite	5	6	2	8	8	14	6	3
Kyanite	2	TR	2	2	2	4	2	1
Rutile	TR	1	1	TR	1	TR	1	1
Tourmaline	4	6	4	5	4	2	5	3
Monazite	1	1	1	1	1	1	1	1
Other (apatite, etc.)	1	1	1	1	1	1	1	1

Terrigenous Materials

Terrigenous material, as used in the sediment grouping, includes all other materials except the biogenous materials and the clay mineral species. The terrigenous materials comprise from 24 to 33 percent of the sediment (Table 3). These materials, in order of abundance, are quartz, feldspar, mica (biotite, muscovite, and chlorite), and less than one percent consists of minor detrital heavy minerals and glauconite. The terrigenous materials are shown to occur most abundantly in the silt-size fraction and to a lesser degree in the sand-size fraction (Figure 4). Most of this material probably originates from the continental shelf area off the New York Bight and is funneled down the Hudson Canyon by turbidity currents, while another minor contributing source is probably from southerly flowing countour currents (Keller and Shepard, 1978).

Clay Minerals

The clay minerals comprise 23 to 29 percent of the contemporary sediment and 40 to 50 percent of the canyon slump material. The clay minerals and the calcareous coccoliths constitute the major materials of the clay-size fraction (Figure 4). Some aggregates of clay particles also occur in the silt-size fraction (Table 2). The proportional amount of clay mineral species is depicted graphically in the ternary plot of Figure 8 and listed for individual species in Table 3.

The clay-mineral suite of the contemporary sediment consists of illite (51-53 percent), kaolinite (10-24 percent), chlorite (7-10 percent), montmorillonite (15-27 percent), and other minerals in very minor amounts (Table 3). In the ternary diagram of clay minerals shown in Figure 8, the kaolinite and chlorite are combined since these two clay minerals are generally similar in sorptive properties and are the most difficult to separate on x-ray diffractograms. The clay-mineral suite of the probable Tertiary age canyon wall sediment, consisting predominantly of montmorillonite, is observed to be markedly divergent on the ternary diagram of Figure 8.

The distribution of the clay minerals and the characterized clay-mineral suite for the lower portion of the continental rise containing the 3800-meter site is in general agreement with the broader projections suggested by Hathaway (1972). The montmorillonite-rich, clay-mineral suite of the canyon wall slump material is also in proportions that correlate with Tertiary sediments of probable Miocene age from the formations comprising the canyon wall. The amount of montmorillonite reported in the sediment of the 2800-meter site situated on the upper continental rise between the Hudson and Wilmington Submarine Canyons (Neiheisel, 1979) is considerably less than that comprising the contemporary sediment of the 3800-meter site. This suggests that a significant portion of the montmorillonite found in the contemporary sediment may be derived from erosion of the canyon wall. The high illite, chlorite, and kaolinite appear more related to the clay-mineral suite of the glacial sediments which cover the adjacent continental shelf area.
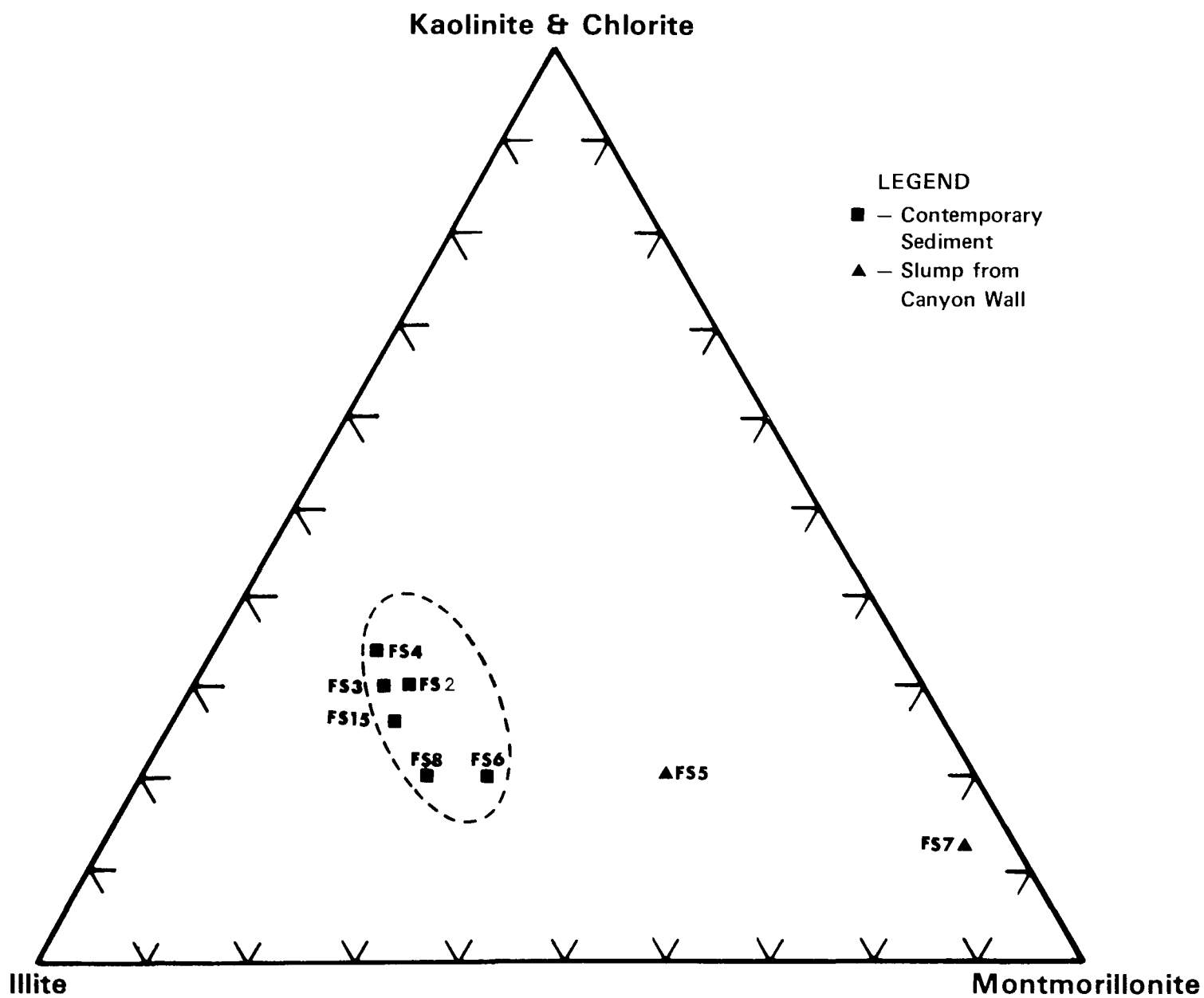
Figure 8. Clay mineralogy of the 3800 meter site sediment samples and probable originating source.

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CHEMICAL AND STRUCTURAL CONFIGURATION OF CLAY MINERALS

General Considerations

In order to consider some of the physicochemical relations associated with the relatively high radionuclide retention by clay minerals, it is necessary to have a general concept of the chemical and structural makeup of the clay-mineral suite of the 3800-meter site. The following information is presented for those readers having little familiarity with clay minerals.

The clay minerals are comprised of thin sheet-like structures as depicted in Figure 9. The tetrahedral layer is comprised of units of silica tetrahedrons, with each unit consisting of one silicon atom equidistant from four oxygen or hydroxyl atoms. The tetrahedral layer, made up of these units, are arranged in a sheet-like hexagonal network (Figure 9). The octahedral layer consists of units made up of an aluminum, iron, or magnesium atom equidistant from six oxygen or hydroxyl atoms. As depicted in Figure 9, the units form sheet-like layers by sharing of oxygen atoms between adjacent octahedrons.

Kaolinite

The varieties of clay minerals are a result of the number of tetrahedral and octahedral layers and associated cations. As diagrammatically shown in Figure 9, kaolinite is made up of one tetrahedral sheet and one octahedral sheet; the thickness of the structural unit is seven angstrom units (Figure 9).

Illite

Illite consists of one octahedral sheet between two tetrahedral sheets with the entire structural unit ten angstroms thick (Figure 9). The potassium ion (K+), fixed to the illite, does not add much thickness to the illite because it fits into the hexagonal hole in the top of the tetrahedral layer; this will be an important consideration in a later section regarding radionuclide retention potential.

Montmorillonite

The montmorillonite clay has a similar structural layering as illite, but in addition has one to two layers of water between tetrahedral sheets, with thickness depending on the variety of cationic species in the water interlayer (Figure 9). With the cation interlayer comprised predominantly

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KAOLINITE

ILLITE

CHLORITE

MONTMORILLONITE

EXPLANATION

= TETRAHEDRAL LAYER

= OCTAHEDRAL LAYER

KEY:
● OXYGEN OR HYDROXYL
○ ALUMINUM, IRON OR MAGNESIUM
● SILICON

Figure 9. Diagrammatic sketch of clay minerals of the 3800 meter Atlantic nuclear waste dumpsite.

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of Na+, the thickness of montmorillonite is 12 angstrom units. With Ca++ predominant in the interlayer, the structural thickness is 14 angstrom units thick (Figure 9). In ocean sediment, montmorillonite occurs with multiple layers. Ethylene glycol used in laboratory tests also swells the interlayer to a maximum structural thickness of 17.5 angstrom units for montmorillonite. Because of the interlayer accumulat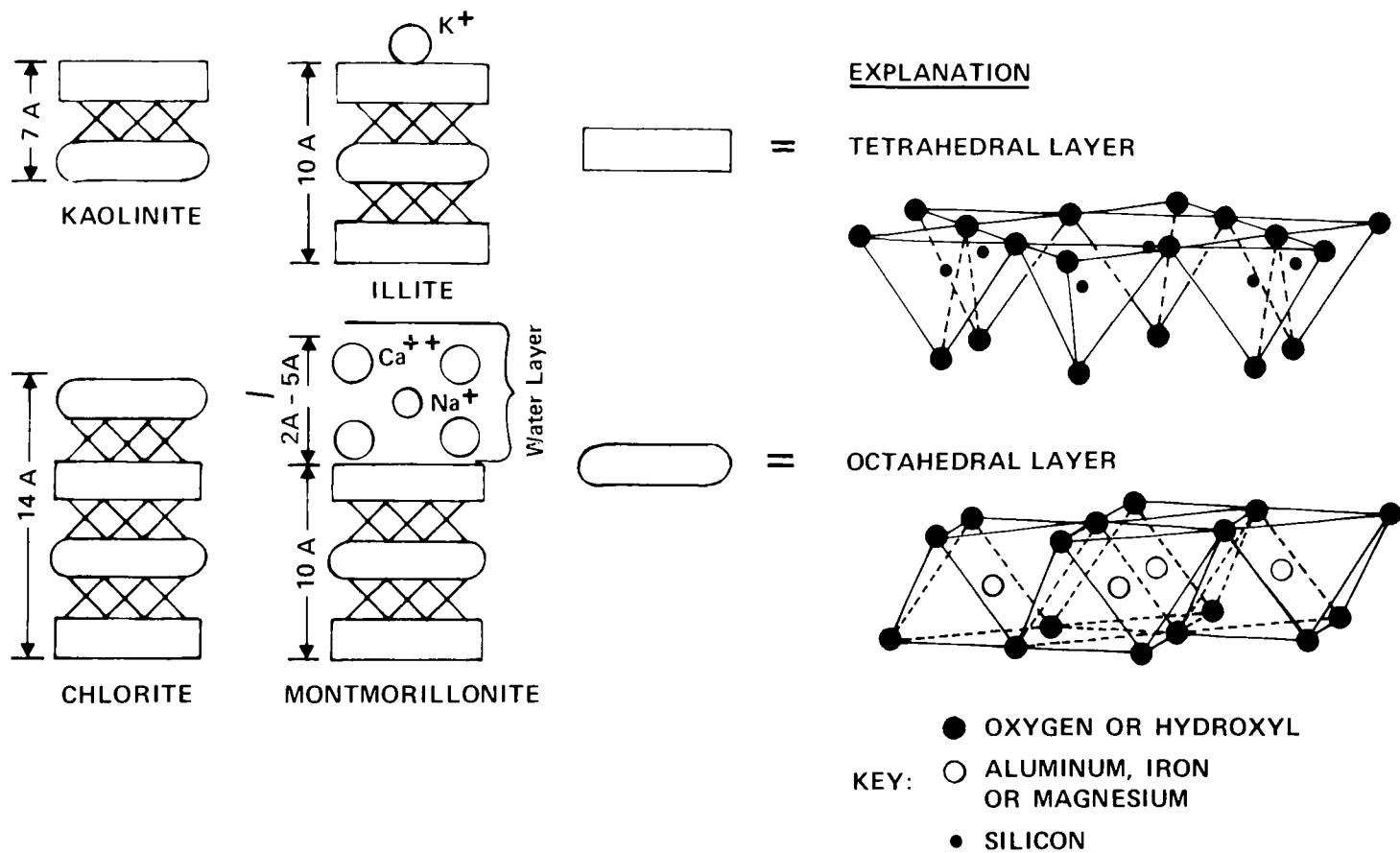ion of cations (H+, Mg++, Ca++, Na+, K+) and other factors of instability, montmorillonite has a higher cation exchange capacity and sorption potential for radionuclides than any of the other clay species.

Chlorite

The chlorite clay structure consists of two tetrahedral layers alternating with two octahedral layers (Figure 9). The structural thickness of chlorite is 14 angstrom units thick and matches that of the more common montmorillonite. However, the ability of ethylene glycol to displace the water layer in montmorillonite and increase the interlayer thickness to 17.5 angstrom units while the chlorite structure remains fixed at 14 angstrom units facilitates identification by x-ray diffraction analysis. Some chlorite varieties contain Mg++ and others Fe++ in the octahedral layer, which also affects the behavior of this mineral in relation to solubility and heat treatments. The magnesium chlorite is generally more stable than the iron chlorite varieties.

Size Considerations

The clay minerals in ocean sediments range in size from 2 microns to less than 0.1 microns in diameter. Average diameters in decreasing size for three common clay mineral varieties are depicted in Figure 10; kaolinite averages 1 micron diameter, illite averages 0.3 microns diameter, and montmorillonite 0.1 microns diameter (Krone, 1972). Clay minerals also occur in silt-size as aggregated particles in the ocean sediment; however, their presence is relatively minor in this size fraction (Figure 4 and Table 2). In general, the sorption potential of the clay minerals increases with increasing surface area, i.e., with decreasing diameters. The increased sorption with decreasing diameters is probably more related to the mineral structures and ionic bonding than any other factor.

Cation Exchange Capacity of Clay Minerals

In an important study of the behavior of trace element movement in soils, Korte, et al. (1976), concluded that knowledge of cation exchange capacity (CEC) does not improve the ability to predict the movement of ions through the natural soils. They state that the percentage of clay in the soil stands out as the most useful means of predicting whether a soil will retain a particular element. Surface area and the percentage of free iron oxides provide the next best correlation after the clay fraction.

INCREASING Kd BY ADSORPTION

INCREASING SURFACE AREA

0.001 μ

|◄ 0.1 μ ►|

c. MONTMORILLONITE

0.01μ

|◄──── 0.3 μ ────►|

b. ILLITE

0.1 μ

|◄──────────────── 1μ ────────────────►|

a. KAOLINITE
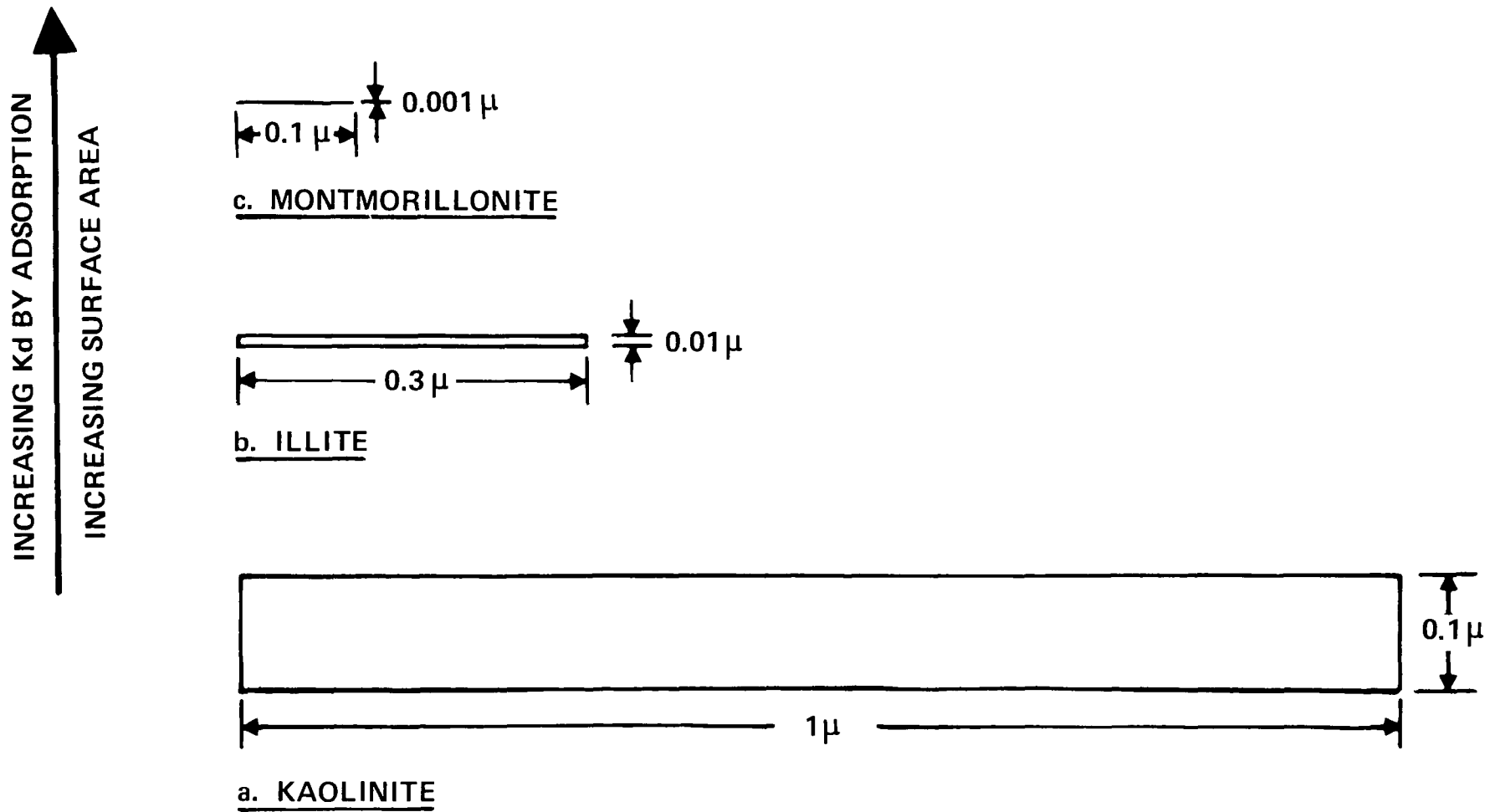
Figure 10. Relative size of clay minerals as they occur in nature
and general relationships to adsorption.

Radionuclides probably behave somewhat similar to some of the trace elements studied by Korte, et al. (1976), but the chemical environment in the marine sediments differs in that there is less divergence in pH but a marked change in Eh (redox) from oxidizing to reducing conditions over a few feet of sediment depth. The percentage of the element Mn in marine sediments is as important as the percentage of free iron oxides is to the soils. The role of cation exchange is probably similar in being of generally less significance in predicting radionuclide behavior than the determination of sorptive minerals and other chemical factors.

The cation exchange capacity, however, may be used as a correlation to clay mineral composition. The CEC is expressed in milliequivalents per 100 grams, and the general range of CEC for the clay minerals reported by several investigators for estuarine and marine sediments are: kaolinite 3-15; chlorite 10-40; illite 10-40; montmorillonite 80-150. The cation exchange capacity for sediment samples at the 3800-meter Atlantic site varies between 30.0 and 35.1 meq/100 g for the contemporary samples and 43.8 meq/100 g for sample number 7. The higher cation exchange capacity correlates with the higher montmorillonite clay occurrence in this sample.

WASTE FORM AND BACKGROUND CONSIDERATIONS

Waste Form

A waste form is a monolithic free-standing solid resulting from the incorporation of the low-level radioactive waste (LLW) into a matrix material which, in this case for the 3800-meter dumpsite, was concrete (Columbo, et al., 1982). The low-level radioactive waste discharged to the 3800-meter site contained both naturally occurring and man-made radionuclides. Many of the radionuclides in the waste form are short-lived and are not of long-term radiological concern. Three criteria used to identify radionuclides of concern are (1) half-life more than five years, (2) presence in comparatively significant quantities, and (3) biological toxicity (Wild, et al., 1981). Radioisotopes that meet one or more of these criteria are tritium, carbon-14, cobalt-60, nickel-59 and 63, strontium-90, niobium-94, technetium-99, iodine-129, cesium-135 and 137, uranium-235 and 238, neptunium-237, plutonium-238, 239, 240, and 241, americium-241 and 243, and curium-243 and 244 (Wild, et al., 1981). These radioisotopes will be considered in relation to factors affecting sorption by the sediment in a later section.

Natural Background Radiation

If one conducts an investigation to determine the radionuclides released from radioactive waste and retained by the sediment, it is necessary to first obtain background data. Sediment samples, free of waste release, must be analyzed for (1) the presence of naturally occurring radionuclides, and (2) elements that are isotopes of the radionuclides of interest. Since site specific samples are measured in the laboratory, it is necessary to determine the "blank." Gillham, et al. (1980), has shown that retardation of Cs-137 in hydrologic systems can be governed by the concentration of natural exchangeable cesium that occurs in the system, and that in order for laboratory distribution coefficient (Kd) values to provide an accurate representation of the field retardation potential, the total exchangeable cesium concentration in the batch test must duplicate the field condition. Nonradioactive isotopes of radionuclides of interest must therefore be determined in the site specific sediments for an accurate assessment of the distribution coefficient.

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At the 3800-meter site, the natural background radiation can be estimated by use of the quantitative mineral evaluation. As Joseph, et al. (1971), and other investigators point out, the source of radioactivity in ocean sediment is primarily from the radioactive materials occurring in the minerals of the sediment. Cosmic rays and radioactivity from atmospheric testing programs, however, while of lesser significance, are also part of the background radiation.

The naturally occurring radionuclide responsible for the major portion of the background radiation is undoubtedly potassium-40. The K-40 occurs in the following minerals at the 3800-meter waste site: K-feldspar, muscovite (mica), illite, montmorillonite, glauconite, and hornblende. Since K-feldspar comprises the major portion of the feldspar listed in Table 2, this source averages about 3 percent of the sediment. Illite clay mineral comprises approximately one-sixth of the sediment by volume and represents the largest source of K-40. Muscovite (least abundant of the mica group) approximates one percent of the total sediment. Both glauconite and hornblende occur in trace amounts (less than 0.5 percent) in the sediment. Thus, at least one-fifth of the total sediment by volume at the 3800-meter site contains K-40 as a primary constituent of the minerals comprising the sediment.

The minerals, zircon and monazite, reported in fractional amounts of the heavy-mineral suite (Table 4) contain naturally occurring radionuclides of uranium and thorium. These minerals, of terrigenous origin, are found only in the upper silt and sand-size fractions. Their amount as regards total sample is estimated at a fraction of one percent (trace amounts). Zircon contains both uranium and thorium which replace zirconium in the mineral structure (Berry and Mason, 1959). Monazite contains thorium in variable amounts in the range between 2 and 40 percent of the mineral composition (Berry and Mason, 1959). The amount of radiation from these two minerals is estimated at probably less than 10 percent of the background radiation in the sediment. The major radiation source is the potassium-40 as previously stated.

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DISTRIBUTION COEFFICIENT (Kd) OF RADIONUCLIDES

General

The ocean sediments have the capacity to sorb radionuclides from the leachate derived from the waste form with the amount dependent on the mineral composition and chemical factors of the sediment environment. The clay minerals are the most effective materials in the sediment for sorption of most radionuclides; however, it will be shown that other chemical factors may also control sorption.

A measure of sorptive behavior of a radionuclide under a specific set of conditions can be expressed as a distribution coefficient (Kd). The Kd is defined as the ratio of specific activity in the sediment phase to that in the liquid phase for the radionuclide of interest (Pietrzak, et al., 1981).

$$Kd = \frac{\text{sediment activity/weight of sediment}}{\text{liquid activity/volume of liquid}}$$

The distribution coefficients (Kd) of radionuclides obtained from laboratory measurements are the most accepted means of quantifying the radionuclide retention in a geologic media (Gillham, et al., 1980). While more than 5,000 experiments exist on measured Kd values for various radionuclides of the continents, few Kd measurements exist for ocean sediment. Those that have been reported for specific radionuclides in ocean sediment will be considered in a later section.

Factors Affecting Kd Values

In addition to the percent clay mineral fraction present in the sediment, several other factors inherent with the sediment and water phases of the ocean environment affect the Kd values of radionuclides. These factors include type and quantity of sorptive minerals, pH, Eh (oxidizing-reduction potential), surface area, complexing ligands and organics, amorphous oxides, cation exchange capacity, and competing ions. Onishi, et al. (1981), has reviewed a number of elements and the probable factors most strongly affecting their sorption in geologic media. Some of these factors are listed in Table 5 for the various radionuclides considered of importance in low level radioactive waste. These factors are presented in a general manner here and will be related to specific radionuclides in a later section. The method of determining type and quantity of sorptive minerals has been presented in earlier sections.

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Table 5. Factors Affecting Sorption of Radionuclides of Importance
in Low-Level Radioactive Waste
(Modified after Onishi, et al., 1981)

Element[1]	pH	Eh	CEC[2]	Sorptive Minerals	Competing Ions	Complex Ions Inorganic Ligands	Organic Constituents	Colloid[3] Formation	Probable Sorption Mechanisms
H^3	–	–	–	–	–	–	–	–	None
C^{14}	–	–	–	–	–	–	X	–	None
I^{129}	–	–	–	–	–	–	X	–	None
*Tc^{99}	–	X	–	–	–	–	X	–	Unknown
Sr^{90}	X	–	X	X	X	X	X	–	Ion Exchange
Cs^{137}	–	–	X	X	–	–	–	–	Ion Exchange
Co^{60}	X	X	–	X	–	X	X	X	Ion Exchange,[2]PPT,[2]OX
Ni^{63}	X	X	–	X	–	–	–	X	Ion Exchange, PPT, OX
*U^{238}	X	X	–	X	–	X	X	–	PPT, Ion Exchange
*Np^{237}	–	X	–	–	–	X	–	X	Unknown (PPT)
*Pu^{239}	X	X	X	X	–	X	X	X	Ion Exchange, PPT
Am^{241}	X	–	X	X	X	X	–	–	Ion Exchange, PPT
Cm^{243}	X	–	–	X	–	X	–	X	PPT

* Most dependent on oxidation-reduction condition.

Notes

[1]Radionuclides listed are present in significant quantities in LLW and have a half-life greater than 5 years (after Wild, et al., 1981).

[2]CEC = Cation Exchange Capacity; PPT = precipitation; OX = oxide.

[3]The controlling sorption mechanism for colloid is precipitation.

The pH and Eh of the _in situ_ ocean sediment are important factors regarding the stability of a radionuclide. The pH is important in controlling the solubility of many of the radionuclides, but this factor is less variable in the marine sediments than the continental deposits. The Eh is more variable in changing from an oxidizing environment in the first several centimeters of sediment to reducing below that depth for many parts of the ocean (Talbert, 1982). The pH and Eh were measured on a sediment from a depth of 2500 meters at a site located on the upper continental rise off the coast of Maine. These measurements by Schmidt (1979) indicated that the sediments were well oxygenated throughout the first 0.6 meters of the sediment, after which reducing conditions occur through depth. Similar conditions probably prevail at the 3800-meter Atlantic site. As indicated in Table 5, the radionuclides most strongly affected by the Eh are Tc, Np, U, and Pu which are rendered immobile in the reducing environment but have little retention in the oxidizing environment. Nickel and cobalt tend to be affected by Eh in their relationship to the presence of Mn and Fe, respectively; both Mn and Fe precipitate as hydrous oxides in oxygenated conditions and coprecipitate the Co and Ni. Jenne (1976) cites convincing evidence in which electron probe measurements of oceanic manganese nodules show nickel occurring in manganese bands and cobalt predominantly in iron rich areas. Schmidt (1979) reports manganese from the 2500-meter Atlantic site as the most mobile of the metals in the deep-sea sediments, with Mn precipitating near the surface due to oxidation following diffusive transport from deeper layers. Phase diagrams have also been assembled which are used to depict the mineral or solid phase form which will most likely prevail under a set of pH and Eh conditions; such stability field diagrams, however, should be used with caution since they contain many limitations.

The factors listed in Table 5 will be used as a guide in the discussion of the probable mechanisms affecting sorption. This list, modified after Onishi, et al. (1981), examines all the factors reported for each element, and a deduction is made as regards the probable principal sorption mechanism. A sorption sensitivity to cation exchange capacity, competing ions, and pH may indicate an ion exchange sorption mechanism such as shown for strontium (Table 5). Precipitation is probably the control mechanism for nickel and cobalt as coprecipitates with Mn and Fe oxides. Neptunium and plutonium in reducing conditions and curium may also be controlled by precipitation (Table 5). If the Eh environment allows it, Pu(IV) can be oxidized to Pu(V) or (VI), with precipitation or much lower plutonium sorption values resulting; additional investigation is required to determine if neptunium can be reduced to much less soluble Np(IV) forms by reducing sediments or if curium precipitation is the sorption control mechanism (Onishi, et al., 1981). The probable Kd that might be predicted for the 3800-meter site sediment will be based on the quantitative mineralogy and the chemical factors which affect the sorption mechanisms.

POTENTIAL RADIONUCLIDE RETENTION

Introduction

The potential radionuclide retention by the sediment of the 3800-meter site will be assessed for the radionuclides of concern in the low-level radioactive waste. The prediction is based on the concept of a diffusion release to a physical setting experiencing minimal sediment transport. The pH and Eh of the sediment in the absence of measured values will be considered to be similar to that existing on the adjacent continental rise at 2500-meter depth described by Schmidt (1979).

The sediment can only be an effective barrier if the drums containing the waste are surrounded by sediment. Leakage from any exposed area of the drum would "short circuit" the sediment trap by moving directly into the water column. Bioturbation could also "short circuit" radionuclide retention. This assessment of radionuclide retention considers the drum surrounded by sediment with no "short circuit" mechanisms in operation. Only the radionuclides considered important by virtue of greater than five-year half-life, abundance, and toxic nature are considered in this assessment.

Tritium, Carbon-14, and Iodine-129

Most investigators agree that tritium substitutes readily for the hydrogen in water and is not sorbed to any significant degree by sediment. The distribution coefficient (Kd) for tritium at the 3800-meter site would thus be close to zero. Any release of carbon-14 to the sediment would likewise result in transfer to the interstitial water system to form, most probably, a bicarbonate ion. The Kd for C-14 would probably be zero. Iodine-129 would also have minimal retention (probably zero), although under other circumstances it could combine with organic matter (Table 5).

Cesium-137 and Strontium-90

A considerable range of Kd values over orders of magnitude have been reported by numerous investigators for both cesium and strontium. The average Kd reported for cesium and strontium in saltwater is, respectively, 300 and 50 (Onishi, et al., 1981). Considering the fact that the most likely control mechanism affecting sorption may be ion exchange, the quantity and type of sorptive minerals could be profitably used to provide an approximation of the distribution coefficient of both Cs and Sr at the 3800-meter site.

The distribution coefficients (Kd) of cesium and strontium have been determined for pure mineral phases (Ames and Rai, 1979). Most of the Kd values for the common terrigenous minerals of sand and silt-size are on the order of 0-15, whereas clay minerals range from 15-4900 (Figure 11). In the absence of measured Kd values on pure phases of marine calcareous biogenous materials, the values reported for the Yucca Flat limestone by Norke and Fenske (1970) are used: a Kd of 0.2 for strontium and 13.5 for cesium thus approximates the biogenous carbonate fraction of the 3800-meter site. The Kd of chlorite is also considered to be similar to kaolinite for the purposes of this assessment of Cs and Sr retention.

The potential Kd values for strontium-90 and cesium-137 in the 3800-meter site contemporary sediment samples are calculated by multiplying the mineral percentages listed in Tables 2 and 3 by the Kd value of individual minerals in Figure 11. The resultant calculated values predict the following Kd for the contemporary sediment of the 3800-meter site:

	Kd (ml/g)
Strontium-90	30
Cesium-137	460

These values compare favorably with average measured values from saltwater sediments reported by Onishi, et al. (1981), who has reported an average Kd of 50 for strontium and a Kd value of 300 for cesium.

Cobalt-60 and Nickel-63

The principal sorption mechanism of cobalt and nickel in the marine sediments is the coprecipitation of these radionuclides with hydrous oxides of manganese and iron under controlling conditions of pH and Eh (Jenne, 1968). The average Kd of cobalt in the ocean sediment is listed by Onishi, et al. (1981), as 10,000 with the Atlantic Ocean values generally similar to those of the world oceans. The Kd values of nickel are not reported for ocean sediment; however, values for continental soils rich in montmorillonite and a generally alkaline pH have a Kd range between 1300-3000, and kaolinite-rich soils of acidic pH (6.0) have a Kd range between 130 and 330 (Swanson, 1982). An estimated Kd for nickel at the 3800-meter site might be 1000, whereas cobalt might approximate a Kd of 10,000.

Technetium-99

The average Kd for measurements of technetium-99 in oxidizing conditions in ocean sediments is zero (Onishi, et al., 1981). In soils with high organic matter and reducing conditions, Kd values as high as 900 have been reported. At the 3800-meter site, the Eh could be the main controlling factor, in which case this measurement should be made. At the expected depth of a drum in the sediments, it is probable that the Kd of technetium will be zero.

Typical Kd values of Sr and Cs on Pure Mineral Phases

TEXTURE	MINERALS	(1) DISTRIBUTION COEFFICIENT (Kd)	
		Sr	Cs
SAND-SIZE	CALCITE (FORAMINIFERA) QUARTZ FELDSPAR MICA	unknown 0 - 5 9 5	unknown 0 9 5 - 15
SILT-SIZE	CALCITE $\left(\begin{array}{l}\text{FORAMINIFERA}\\ \text{& COCCOLITHS}\end{array}\right)$ QUARTZ FELDSPAR MICA	unknown 0 - 5 9 5	unknown 0 9 5 - 15
CLAY-SIZE	CALCITE (COCCOLITHS) KAOLINITE ILLITE MONTMORILLONITE	unknown 15 100 150	unknown 45 400 4900

(1). Kd values after Ames and Rai (1978).

Figure 11. Distribution coefficients (Kd) for strontium and cesium on minerals typical of the 3800 meter Atlantic nuclear waste dumpsite.

Uranium-238

The Kd of uranium is controlled by the pH, Eh, inorganic ligands (carbonate), and organic constituents (Table 5); both precipitation in the reducing environment and ion exchange are probable sorption mechanisms. The average Kd reported for uranium in ocean sediment by Onishi, et al. (1981), is 500. In the presence of complexing anions such as carbonate, uranium tends to form soluble complexes.

The probable Kd that might be expected in the sediment at the 3800-meter Atlantic waste site is suggested as 500. This value is expected to be nearer to the average for ocean sediment since carbonate is the common constituent in most biogenous deep ocean sediments. The extreme values Kd up to 10,000 probably occur in highly organic, strongly reducing, or carbonate-free sediment.

Transuranic Elements

The important transuranic elements in the waste form are neptunium-239, plutonium-239, americium-241, and curium-243. The average Kd reported by Onishi, et al. (1981), for these radionuclides in ocean sediments are: Np – no data; Pu – 50,000; Am – 10,000; Cm – no data.

While little data exists on neptunium for ocean sediment, the Kd numbers are very low for oxygenated sediments on the continent. However, it is recognized that neptunium is rendered immobile in reducing environments with precipitation as the probable sorption mechanism (Table 5). Since the upper several centimeters of the 3800-meter site sediment are oxidizing, the Kd suggested might be on the order of 5.

The sorption of plutonium-239 on ocean sediment is affected by a number of factors, including sorptive minerals, Eh, pH, cation exchange, inorganic ligands, and organics, with ion exchange and/or precipitation the most probable sorption mechanism (Table 5). Strongest sorption occurs in the pH range of 4 to 8. Average Kd for plutonium in ocean sediment is 50,000 (Onishi, et al., 1981). Plutonium varies over two orders of magnitude depending on the oxidation state. The Kd for plutonium suggested for the 3800-meter Atlantic site is 50,000.

The factors affecting americium-241 sorption are sorptive minerals, pH, competing ions, cation exchange, and inorganic ligands, with ion exchange and/or precipitation the probable sorption mechanism (Table 5). The average americium Kd reported by Onishi, et al. (1981), for the marine environment is 10,000, with pH especially an important mechanism in marine environments. The Kd of americium is greater in freshwater than marine waters since the sorption of this radionuclide decreases with an increase in concentration of competing ions (Onishi, et al., 1981). The Kd for americium suggested for the 3800-meter Atlantic site is the marine environment value of 10,000.

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Although little data are available for curium-243, it is believed
that the principal sorption mechanism is by precipitation controlled
largely by pH and inorganic ligands (Table 5). Iron and manganese oxides
are believed to act as scavengers for curium (Onishi, et al., 1981). A
highly speculative Kd of 1000 is suggested for the 3800-meter Atlantic
site based on some limited observations of continental deposits reporting
an average Kd of 5000 (Onishi, et al., 1981).

COMPARISON WITH WORLD OCEAN CLAY SUITES

The clay-mineral suite of the North Atlantic Ocean to as far south as 35° N latitude has been characterized by Hathaway (1972) and others as an illite-chlorite suite (Figure 12). The illite at the 3800-meter site is the dominant clay mineral, and the ratio of kaolinite to chlorite is in general agreement with that mapped by Biscaye (1965). Montmorillonite is subordinate to illite in all of the contemporary sediment samples but slightly higher than that reported by Neiheisel (1979) for the upper continental rise or by Hathaway (1972) for the lower continental rise in this portion of the ocean. The slightly larger montmorillonite values are probably due to scour of the montmorillonite-rich portions of the Tertiary canyon wall effected by turbidity currents down the Hudson Canyon.

Except for the montmorillonite-kaolinite clay-mineral suite comprising the sediment of the southwest portion of the North Atlantic Ocean, the middle latitudes and equatorial Atlantic are dominated by kaolinite (Figure 12). The typical weathering in humid, tropical climates produces the kaolinite which is transported as detritus by winds and major discharge by rivers from the adjacent South American and African continents. The kaolinite is unique to the Atlantic Ocean because of the comparitively small size of the ocean basin in relation to the world ocean, the lack of trenches or volcanic activity on its margins, and the predominance of equatorial drainage from the continents to this basin of deposition. The lack of trenches, in particular, enable kaolinite to be transported to the ocean basins.

The sediment of the Pacific Ocean is dominated by a montmorillonite-suite in the middle latitudes and equatorial regions and illite-chlorite in the high latitudes (Figure 12). In addition, much of the Pacific Ocean sediment in the middle latitudes contains an abundance of zeolite minerals (Turekian, 1972) which have high sorption properties like the clay minerals. Both the montmorillonite and zeolites are presumed to be derived indigenously from the abundance of volcanic ash generated along the margins of the ocean basin and intrabasin locations. The illite, predominant in the clay-mineral suite of the high latitudes, is mainly detrital matter carried by winds and rivers (Figure 12). Chlorite occurs in fair abundance in the clay-mineral suite of the high latitudes where it can be preserved (Millot, 1979).

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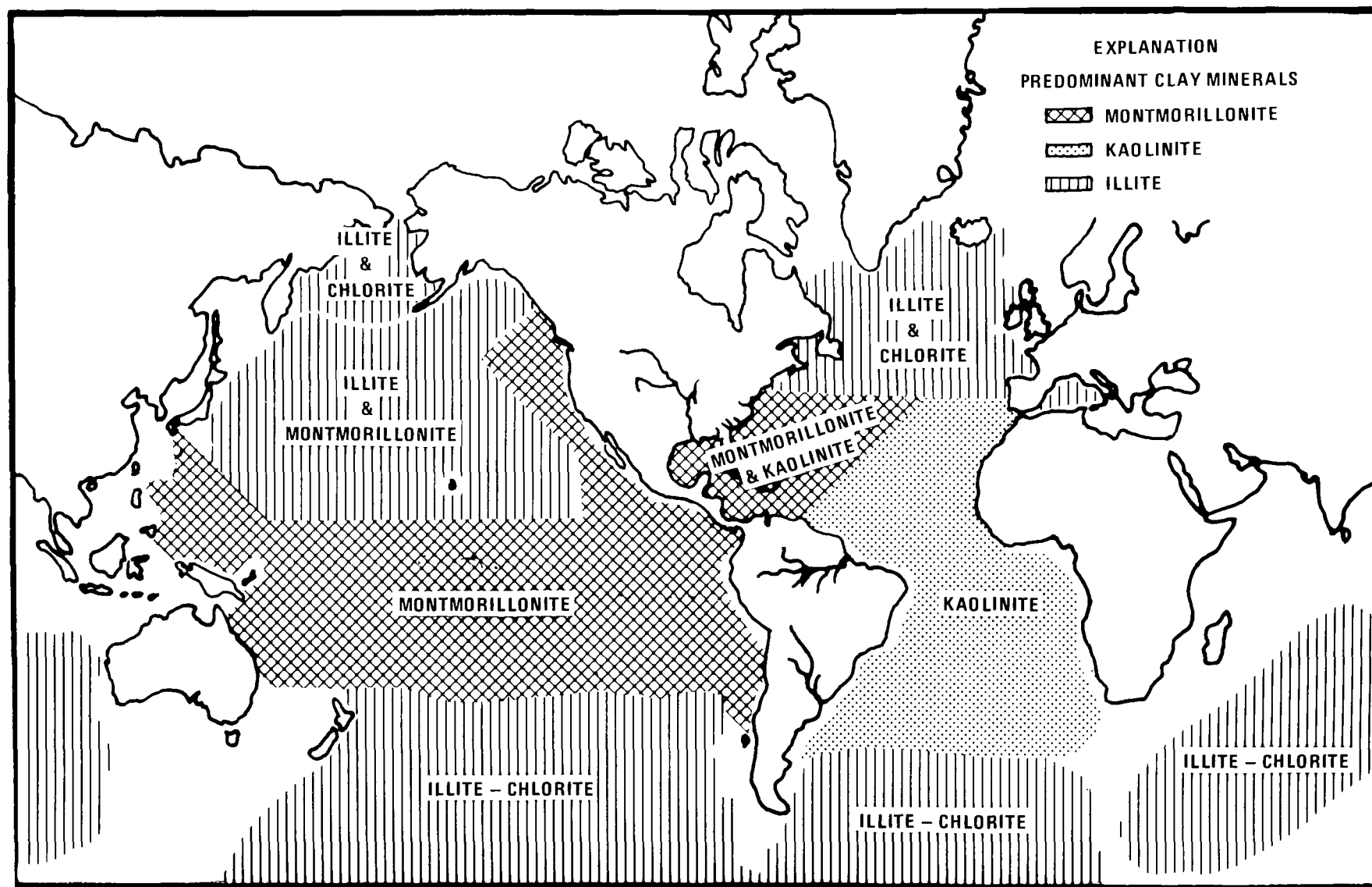
Figure 12. Generalized distribution of clay - mineral suites in the world ocean.

Legend (EXPLANATION — PREDOMINANT CLAY MINERALS):
- MONTMORILLONITE
- KAOLINITE
- ILLITE

Map labels:
- ILLITE & CHLORITE
- ILLITE & MONTMORILLONITE
- MONTMORILLONITE
- MONTMORILLONITE & KAOLINITE
- ILLITE & CHLORITE
- KAOLINITE
- ILLITE – CHLORITE
- ILLITE – CHLORITE
- ILLITE – CHLORITE

The Pacific Ocean sediments, by comparison with the Atlantic Ocean sediments, contain a higher order of sorptive minerals in the clay-mineral suite and, in addition, contain appreciable zeolites which also have high sorptive properties. The Pacific Ocean sediment could be expected to contain potentially greater radionuclide retention on this basis if other chemical factors are comparable. The few distribution coefficient measurements made in the world oceans have been summarized by Onishi, et al. (1981); to date, they show that Kd values of radionuclides range over orders of magnitude with most similarity in similar ocean basins. With site specific investigations similar to this investigation for detailed mineralogy and also including measurements of chemical factors, it is forseeable that predictions of radionuclide retention will be more meaningful.

CONCLUSIONS AND RECOMMENDATONS

Conclusions

The sediments of the abandoned 3800-meter Atlantic nuclear waste dumpsite are relatively uniform in textural, physical, and mineralogical composition. However, two samples differ markedly in the clay-mineral suite and physical properties indicating that they may be slump block material from the canyon walls. The contemporary sediment averages 42 percent biogenous materials, 29 percent terrigenous materials, and 29 percent clay minerals, while the Tertiary canyon wall material averages 21 percent biogenous material, 33 percent terrigenous material, and 37 percent clay minerals. The most diagnostic difference is the predominance of montmorillonite (50-83 percent) in the clay-mineral suite of the older Tertiary sediment versus an average of 24 percent in the contemporary sediment clay-mineral suite. There is also a noticeable difference in percent quartz in the sand-size fraction and the amount and type of biogenous material. Pyrite also occurs in the older, dessicated slump material, and the liquid limit (LL) ranges between 94 and 100 as compared with a range between 72 and 88 in the contemporary sediment.

Any assessment of the potential for the sediment to act as a barrier to radionuclide migration should consider the dynamics of sediment deposition, extent of burial of waste drums into the sediment, and potential "short circuits" of sorbed radionuclides to the surface of the sediment by bioturbation or other mechanisms. This assessment, for generic purposes, considers an ideal case in which the waste drums are buried in sediment and the radionuclides are retained in the sediment should radionuclide release occur from the waste form in the drums. In such an assessment, the percent of sorptive minerals constitutes the primary consideration along with chemical factors which affect the sorption mechanism of radionuclides in the sediment.

An important first step in the sediment characterization is delineation of the highly sorptive materials which are concentrated in the fines. A quantitative method was employed which consists of: (1) compiling a texture grain-size accumulation curve; (2) separate mineral evaluations of sand, silt, and clay-size fractions; and (3) calculation of the percent of each mineral in the total sample. With the percent of sorptive minerals known and the retention of a radionuclide known as a distribution coefficient (Kd) for the pure mineral phase, the radionuclide retention can be calculated for the sediment. The sorption

mechanism for some radionuclides may be affected by the concentration and oxidation state of the radionuclide, presence of amorphous Fe and Mn oxides, presence of organics or ligands, the pH and Eh of the pore water, and other factors. These must be known for a total assessment of all radionuclides of concern.

The fact that the sorption mechanisms of cesium and strontium are governed primarily by ion exchange, and the percent of each mineral in the sediment is known as well as the Kd for the pure mineral phase, makes calculation of their potential retention feasible. The Kd values obtained (Sr = 30 and Cs = 460) are nearer average values for the few Kd measurements made on ocean sediments; values differ by orders of magnitude in world ocean sediments.

<u>Recommendations</u>

It is recommended that site specific sediment samples be collected at existing and/or potential dumpsites and tested in the laboratory for the texture and quantitative mineral evaluation, as well as the sorption distribution coefficient (Kd) for each radionuclide of concern. The pH and Eh of the sediment should be determined as soon as the sediment is received aboard the survey ship since these are important factors affecting the sorption mechanism. Other laboratory measurements which should be made for assessment of sorption mechanisms of radionuclides include: quantity of Fe and Mn oxides, organic matter, quantity of ligands, measurements of naturally occurring radionuclides, and elements that have radioactive isotopes.

A predictive methodology for radionuclide retention in ocean sediment combines measurement of sorptive minerals, chemical factors, and the distribution coefficients (Kd) of radionuclides. With a sufficient number of measurements, a nomograph may be constructed that will provide an assessment of the Kd of radionuclides of interest.

REFERENCES

AMES, L.L., and RAI, D. 1979, Radionuclide interactions with soil and
rock media, EPA 520/6-78-007, v. 1, p. 253.

BERRY, L.G., and MASON, B. 1959, Mineralogy, W.H. Freeman and Company,
San Francisco, CA, p. 630.

BISCAYE, P.E. 1964, Distinction between kaolinite and chlorite in recent
sediments by x-ray diffraction, Amer. Mineralogist, v. 49, p. 1281-1289.

BISCAYE, P.E. 1965, Mineralogy and sedimentation of recent deep-sea clay
in the Atlantic Ocean and adjacent seas and oceans, Geol. Soc. Amer.
Bull., v. 76, p. 803-832.

BRINDLEY, G.W. 1961, Quantitative analysis of clay mixtures, p. 489-516,
in Brown, George, ed., X-ray identification and crystal structures of clay
minerals: Mineralogical Society, London, p. 544.

BUCK, A.D. 1972, Quantitative mineralogical analysis by x-ray
diffraction, U.S. Army Corps of Engineers, Waterways Experiment Station,
Miscellaneous Paper C-72-2, p. 25.

COLUMBO, P., FUHRMANN, M., NEILSON, R.M., and SAILOR, V.L. 1982,
Development of a working set of waste package performance criteria for
deepsea disposal of low-level radioactive waste, U.S. Environmental
Protection Agency, Office of Radiation Programs, Report No. 520/1-82-007,
p. 10.

DEVINE, S.B., FERRELL, R.E., JR., and BILLINGS, G.K. 1972, A quantitative
x-ray diffraction technique applied to fine-grained sediments of the deep
Gulf of Mexico, Jour. Sed. Petrology. v. 42, n. 2, pp. 468-475.

DYER, R.S. 1976, Environmental surveys of two deep-sea radioactive waste
disposal sites using submersibles, Proceeding of the International Atomic
Energy Agency, Vienna, Austria, pp. 317-338.

GIBBS, R.J. 1965, Error due to segregation in quantitative clay mineral
x-ray diffraction mounting techniques, Amer. Mineralogist, v. 50,
pp. 741-751.

GIBBS, R.J. 1968, Clay mineral mounting techniques for x-ray diffraction
analysis, Jour. Sed. Petrology, v. 38, pp. 242-243.

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GILLHAM, R.W., CHERRY, J.A., and LINDSAY, L.E. 1980, Cesium distribution coefficients in unconsolidated geological materials, Health Physics, v. 39, pp. 637-649.

GRIFFIN, J.J., and GOLDBERG, E.D. 1963, Clay-mineral distribution in the Pacific Ocean, pp. 728-741, in Hill, M.N., ed., The Seas: Ideas and Observations, v. 3, John Wiley and Sons, p. 963.

HANSELMAN, D.H., and RYAN, W.B.F. 1983, Atlantic 3800-meter radioactive waste disposal site survey - sedimentary micromorphologic and geophysical analyses, U.S. Environmental Protection Agency, Report under contract number 68-01-4836 (in press).

HATHAWAY, J.C. 1972, Regional clay mineral facies in estuaries and continental margin of the United States east coast, in Geological Society of American Memoir 133, B. Nelson, Editor, pp. 293-316.

HEATH, R.C. 1977, Barriers to radionuclide waste migration, Oceanus, v. 20, pp. 26-30.

HOLCOMB, W.F. 1982, A history of ocean disposal of packaged low-level radioactive waste, Nuclear Safety, v. 23, pp. 183-197.

JENNE, E.A. 1968, Controls of Mn, Fe, Co, Ni, Cu, and Zn concentrations in soils and water: The significant role of hydrous Mn and Fe oxides, pp. 337-387, in Trace Inorganics in Water, R.A. Baker, Editor, American Chemical Society, Advances in Chemistry Series 73, p. 387.

JOHNS, W.D., GRIM, R.E., and BRADLEY, W.F. 1954, Quantitative estimations of clay minerals by diffraction methods, Jour. Sed Petrology, v. 24, pp. 242-251.

JOSEPH, A.B., GUSTAFSON, P.F., RUSSELL, I.R., SCHUERT, E.A., VOLCHOK, H.L., and TAMPLIN, A. 1971, Sources of radioactivity and their characteristics, in Radioactivity in the Marine Environment, National Academy of Sciences, pp. 6-41.

KELLER, G., and SHEPARD, F.P. 1978, Currents and sedimentation processes in submarine canyons off the northeast United States. in: D.J. Stanley and G. Kelling (Editors), Sedimentation in submarine canyons, fans, and trenches. Dowden, Hutchinson and Ross, Stroudsburg, Pa., pp. 15-32.

KORTE, N.E., SKOPP, J., FULLER, W.H., NIEBLA, E.E., and ALESII, B.A. 1976, Trace element movement in soils: Influence of soil physical and chemical properties, Soil Science, v. 122, pp. 350-359.

KRONE, R.B. 1963, A study of rheological properties of estuarine sediments, U.S. Army Corps of Engineers, Committee on Tidal Hydraulics, Tech. Bull. No. 7, p. 41.

MILLOT, G. 1979. Clay, Scientific American, v. 240, n. 4, pp. 108-119.

NEIHEISEL, J. 1979, Sediment characteristics of the 2800-meter Atlantic nuclear waste disposal site: Radionuclide retention potential, U.S. Environmental Protection Agency, Technical Note ORP/TAD-79-10, p. 29.

NEIHEISEL, J. and WEAVER, C.E. 1967, Transport and deposition of clay minerals in southeastern United States, Jour. Sed. Petrology, v. 37, pp. 1084-1116.

NORKE, W.E., and FENSKE, P.R. 1970, Radioactivity in water - Project Rulison, NVD-1229-131.

ONISHI, Y., SERNE, R.J., ARNOLD, E.M., COWAN, C.E., and THOMPSON, F.L. 1981, Critical review: radionuclide transport, sediment transport, and water quality mathematical modeling; and radionuclide adsorption/desorption mechanisms, Battelle Pacific Northwest Laboratory, PNL-2901, p. 339.

PIERCE, J.W., and SIEGEL. 1969, Quantification in clay mineral studies of sediments in sedimentary rocks, Jour. Sed. Petrology, v. 39, pp. 187-193.

PIETRZAK, R.F., CZYSCINSKI, K.S., and WEISS, A.J. 1981, Sorption measurements performed under site-specific conditions - Maxey Flats, Kentucky, and West Valley, New York, disposal sites: Nuclear and Chemical Waste Management, v. 2, pp. 279-285.

RELYEA, J.F., SERNE, R.J., and RAI, D. 1980, Methods for determining radionuclide retardation factors: status report, Battelle Pacific Northwest Laboratory, PNL-3349, p. 80.

SAYLES, F.L., and Mangelsdorf, D.C. 1977, The equilibrium of clay minerals with seawater: exchange reactions, Geochem., Cosmochim. Acta, v. 41, pp. 951-960.

SCHMIDT, R.L. 1979, The chemistry of water and sediment from the benthic boundary layer at a site in the Northwest Atlantic Ocean, Battelle Pacific Northwest Laboratory, PNL-2842, UC 11, p. 23.

SCHULTZ, L.G. 1960, Quantitative x-ray determinations of some aluminous clay minerals in rocks, pp. 216-224 in Swineford, Ada, ed., Proc. Seventh National Conference on Clays and Clay Minerals.

SHEPARD, F.P. 1954, Nomenclature based on sand-silt-clay ratios: Jour. Sed. Petrology, v. 24, pp. 151-158.

SWANSON, J.L. 1982, Effect of organic complexants on the mobility of nickel and cobalt in soils: Status Report, Battelle Pacific Northwest Laboratory, PNL-4389.

TALBERT, D.M. 1982, Oceanographic studies to support the assessment of submarine disposal at sea: Vol. 1, Sandia National Laboratories, SAND 82-1005/1, p. 50.

TUREKIAN, K.K. 1971, Oceans: Prentice Hall, Inc., Englewood Cliffs, New Jersey, p. 120.

U.S. ARMY CORPS OF ENGINEERS. 1970, Laboratory soils testing, EM-110-2-1906, Appendix II, Washington, D.C.

WILD, R.E., OZTUNALI, O.I., CLANCY, J.J., PITT, C.J., and PICAZO, E.D. 1981, Data base for radioactive waste management, U.S. Nuclear Regulatory Commission, NUREG/CR-1759, Vol. 2.

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16. ABSTRACT

Seven box core sediment samples were obtained from the 3800-meter low-level radioactive waste dumpsite located 320 km off the New York coast in the main axis of the Hudson canyon. Sorptive minerals in the sediment were calculated from the texture grain-size curve and separate mineral evaluations of the sand, silt, and clay-size fractions. Two of the sediment samples, having marked differences in physical properties and mineralogy, are believed to be slump material from the Tertiary age canyon wall.

The contemporary sediment averages 42% biogenous calcite, 29% terrigenous materials, and 29% clay minerals. Clay mineral fractional composition averages 52% illite, 9% chlorite, 16% kaolinite, and 23% montmorillonite.

Calculations made from percentages of individual minerals and the distribution coefficients (Kd) of Sr and Cs on measured pure mineral phases suggests a potential Kd of 30 for Sr and 460 for Cs. The sorption mechanism of some of the other radionuclides are strongly influenced by pH, Eh (redox potential), presence of Fe and Mn, organics, and ligands. These factors should be known in addition to percentages of sorptive minerals for assessment of sediment retention potential of sediments for radionuclides of concern in the low-level waste form.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Ocean Dumping Sediment Characterization Sorptive Minerals Clay Minerals Radionuclide Retention Potential		

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