MEASUREMENT OF PENETRATION DEPTHS OF PLUTONIUM
AND AMERICIUM IN SEDIMENT FROM THE OCEAN FLOOR

MASTER

by

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MEASUREMENT OF PENETRATION DEPTHS OF PLUTONIUM AND AMERICIUM IN SEDIMENT FROM THE OCEAN FLOOR*

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INTRODUCTION

The clay-like sediment covering the ocean floor constitutes the last barrier that shields the biosphere from contamination by radionuclides stemming from the nuclear wastes of a subseabed repository. In the event of a failure of the engineered barriers the mobility of the released radionuclides in the sediment determines the rate and the extent of entry into the water of the ocean. In this article we present the initial results of measurements designed to determine the mobility of transuranium elements in sediment from the ocean floor. Our data indicate very low migration rates and imply strong chemisorptive interaction with the sediment.

EXPERIMENTAL PROCEDURE

The method chosen to explore the diffusion behavior of selected radionuclides in the ocean floor sediment consists of the direct measurement of the penetration depth into samples of the sediment from a supernatant solution. Figure 1 shows the makeup of a sediment sample for the diffusion experiment. The sediment is contained in the center hole of a paraffin collar of 22 mm outer diameter and forms a cylinder of 13 mm diameter and

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FIG. 1.
DIAGRAM OF SEDIMENT SAMPLE
FOR MIGRATION MEASUREMENTS

approximately 15 mm height. Care is taken to pack the sediment into the collar in such a way that no voids or bubbles exist in the sample. The paraffin collar is supported by a brass holder to which it has been attached by melting of the paraffin. A short rod extends from the bottom of the brass holder by which the sample can be mounted on the stage of a microtome.

After the sediment has been packed into the collar, the surface is smoothed and made flush with the paraffin rim. A short, approximately 8 mm high paraffin extension ring is then fused onto the wax collar so that the sediment can be covered with solution. The samples were left in contact with 0.2 to 0.3 cm³ of artificial sea water (1) for an extended period to saturate the sediment with liquid and equilibrate it with the sea water. For a diffusion experiment the sea water covering the selected sample was replaced by a solution containing one or more of the radionuclides ²³⁷Pu, ²⁴¹Am, ²²Na and ¹²⁵I in sea water. The total amount of an individual tracer element applied to a sediment sample was of the order of 0.3 microcurie. The tracer solutions were left in contact with the samples for time periods varying from 1 hour to 100+ days. Evaporation of the solution was inhibited by closing the top of the samples with cover glasses fused onto the paraffin extension ring. A photograph showing samples in various stages of preparation is shown in Fig. 2. During the time allowed for contact of the sediment with tracer solutions the samples were stored at ambient temperature varying no more than ± 1 K.

After an appropriate contact time the diffusion experiments were terminated by removal of the solution without disturbance of the surface of the sediment. The extent to which the tracer elements had penetrated into the sediment cylinders was determined by sectioning of the cylinders with a refrigerated microtome. With few exceptions the samples were sectioned after freezing, a procedure which generally yielded dry, crumbling material. Each section of approximately 0.050 cm thickness was collected on a small piece of tissue paper and transferred to a plastic counting vial. In the case of sections obtained from non-frozen sediment the material had to be collected by wiping it off the blade of the microtome.

The concentration of the radioactive tracers in each section was measured by placing the counting vials in the well of a sodium iodide crystal scintillation counter and by determining the pulse rate of γ - or X-radiation characteristic for the individual tracers by pulse height analysis.

Fig. 2

RESULTS AND DISCUSSION

Of 15 sediment samples that have been sectioned to date 12 have yielded usable results for the penetration behavior of plutonium, americium, sodium and iodide ions. A listing of the types of sediment used, the type of radioactive tracers, and the time span for which each sample was left covered with solution is presented in Table I. The sediment used to make up the samples stemmed from two sources, the lower end of a 10 foot long core of 4.5 inch diameter taken in the mid-Pacific ocean ($30^{\circ}47.0'N$, $157^{\circ}42.9'W$) from a depth of 5821 meters, and a sample labeled "TT-141-II #7G", presumably from a deeper horizon of the sediment*. The former core contains illite clay minerals and is therefore designated in Table I as "illitic, core 11", the latter material contains smectites and is referred to as "smectic, TT-141-II".

The tracer nuclides were dissolved in artificial sea water that had been prepared according to a formula reported by Kester et al. (1). Concentration levels of the radionuclides in the original solutions ranged from approximately 10^{-6} mol/l for ^{241}Am to 10^{-8} mol/l for ^{237}Pu . The choice of the particular isotope of each radionuclide that was applied as tracer was made by type of radiation. The nuclides listed in Table I are all distinguished by emission of characteristic X- or γ -radiation.

The electromagnetic radiation permits identification and assay of samples by scintillation counting without prior chemical purification. The contact times during which the samples were covered with the solution of tracers ranged from approximately 1 hour for the iodide sample no. 200605 to nearly 120 days for sample no. 210503. By sectioning samples after varying time periods it was hoped that coefficients for the effective diffusivity could be determined.

The activity of a given radionuclide observed in each section of a sample was converted to specific activity by referring it to a constant section thickness of usually 1 mm, and was corrected to 100% cross-sectional area in cases in which only part of the cross-section was removed by the microtome. The specific activities were used to generate histograms representing the relative variation of the tracer concentration with depth, and were scaled in such a manner as to obtain unity relative concentration near the top of the sample.

*The smectic sediment was supplied by R. Heath of Oregon State University, Eugene, Oregon.

Table I: Summary of Sectioned Samples of Ocean Floor Sediment

Sample Identification Number	Type of sediment	Type of tracer	Contact time in seconds
090301	illitic, core 11	$^{22}\text{Na} + ^{237}\text{Pu}$	3.89×10^6
100701	smectic, TT-141-11	$^{125}\text{I} + ^{241}\text{Am} + ^{237}\text{Pu}$	1.533×10^6
100702	smectic, TT-141-11	$^{125}\text{I} + ^{241}\text{Am} + ^{237}\text{Pu}$	4.640×10^6
200605	illitic, core 11	^{125}I	0.00426×10^6
210501	illitic, core 11	^{241}Am	0.0756×10^6
210502	illitic, core 11	^{241}Am	2.412×10^6
210503	illitic, core 11	$^{125}\text{I} + ^{241}\text{Am} + ^{237}\text{Pu}$	10.356×10^6
210504	illitic, core 11	^{241}Am	1.193×10^6
210606	illitic, core 11	$^{125}\text{I} + ^{241}\text{Am} + ^{237}\text{Pu}$	2.401×10^6
300301	illitic, core 11	$^{22}\text{Na} + ^{241}\text{Am} + ^{237}\text{Pu}$	4.15×10^6
300303	illitic, core 11	$^{125}\text{I} + ^{241}\text{Am} + ^{237}\text{Pu}$	0.52×10^6
300304	illitic, core 11	$^{125}\text{I} + ^{241}\text{Am} + ^{237}\text{Pu}$	0.69×10^6

A histogram showing the relative concentration of iodide ion as a function of distance from the top surface of the sediment is shown in Fig. 3. The data are those obtained from the sectioning of sample 200605, and the width of the individual bars indicates the width of each section. Also plotted in Fig. 3 are the relative concentrations of iodide observed for sample no. 210606. Even though there is considerable scatter of the data points it is obvious that after 2.4×10^6 sec the iodide has permeated the sample 210606 and is at a nearly uniform concentration. This is not the case for the sample 200605 which was sectioned after only 4260 s of contact with the tracer. The variation of the iodide concentration can best be approximated by the curve calculated for a diffusion coefficient of $D_I = 2.5 \times 10^{-4} \text{ cm}^2 \cdot \text{s}^{-1}$. By comparison, the coefficient of self-diffusion of iodide ion has been measured by Friedman and Kennedy (1) who found a value of $2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ for D_I in 0.5 molar solutions. The aggregate information on the mobility behavior of iodide-ion gathered through the sectioning of seven iodide-containing samples shows clearly that the iodide ion diffuses in the sediment without retardation and at approximately the same rate as in sea water alone.

The sectioning data of americium and plutonium do not yet permit quantitative evaluation of the mobility in terms of an effective diffusion coefficient. An example for the variation of the tracer element activity with depth is shown in Fig. 4. Plotted is the observed specific counting rate, i.e., the counting rate per unit thickness of each section, for sample no. 210503, which had been in contact with a sea water solution containing ^{125}I , ^{241}Am and ^{237}Pu in small concentrations.

In order to facilitate comparison of the sectioning data obtained on different samples, the specific activity was converted into a relative concentration by multiplication of each section's specific activity with a constant factor that differed from sample to sample. This factor was chosen in such a manner as to obtain values near unity for the relative concentration near the top surface of the sediment cores. Since, the first few sections are likely to be more affected by uncertainties than the deeper ones, the reduction factor was estimated on the basis of sections taken at 0.2 and 0.4 mm depth.

It is evident from Fig. 4 and from the scatter of the tabulated relative concentration data that the precision of the observed activities suffers from experimental errors. Sources for these errors are among others are the difficulty in determining the exact thickness of a section, the distortion of the original shape of the sediment cylinder during freezing, and the statistical uncertainty inherent in low counting rates. The

Fig. 3. Diffusion of iodide-ion in illitic sediment.
 Solid line - iodide concentration after 4260 seconds.
 Black squares - iodide concentration after 2.4×10^6 seconds.
 Dashed lines - concentration profiles calculated for selected values of the diffusion coefficient.

Fig. 4. Tracer concentrations measured in a sample of illitic sediment after 119.85 days ($= 10.36 \times 10^6$ seconds). For ^{237}Pu the ordinate scale has to be divided by 5.

numbers tabulated in Tables II, III and IV, can be considered most reliable in the range from 0.01 to 0.50. Relative concentrations as low as 0.001 or less indicate counting rates equal to background activity within experimental error.

The data given in the three tables can be approximated by curves that are calculated as solutions to the linear diffusion equation

$$\frac{\partial c}{\partial t} = D \cdot \frac{\partial^2 c}{\partial x^2}$$

with the following boundary conditions: The diffusion takes place in a one-dimensional bounded region of 30 mm total length. The initial distribution of the diffusing material is such that the concentration in arbitrary relative units has the value 2 in the left half of the region and zero in the right half. The concentration curves as functions of the time for the right half compartment will be representative of the variation of the relative concentration with distance and time in a homogeneous sample of sediment of uniform cross section and 15 mm length, in close approximation of the length of the actual samples.

The characteristic shape of the concentration curves over the 15 mm distance is a function of the product of diffusion coefficient and time as a parameter.

In Fig. 5 the data for the samples 300304, 210606 and 210503 are plotted as histograms for the first two millimeters, and two curves calculated for values of the product $D \cdot t$ of 5×10^{-8} and $2 \times 10^{-7} \text{ m}^2$, respectively, are also shown. These two curves seem to bracket the experimental data.

The first feature to be noted is the absence of any significant difference as regards the concentration variation of the experimental data. The three histograms refer to the observed activity of ^{237}Pu in illitic ocean floor sediment after having been in contact with the tracer for 0.69×10^6 , 2.40×10^6 , and 10.36×10^6 seconds. There is no clear evidence for diffusion of the plutonium, since the shape of the concentration curves is similar in all three cases. By the time the sectioning has progressed beyond a 2 mm distance, the activities observed are too close to background to yield reliable information. It is important to note that the data for 10.36×10^6 sec show a curve shape that is no shallower than those for 2.40×10^6 seconds.

Table 11: Penetration of Illitic Sediment by Americium

Distance mm	Sample No. Contact Time, 10 ⁶ seconds	Relative Concentration				
		210501	300304*	210504	210606*	210502 210503
0.025	---	4.987	---	4.095	---	4.231
0.075	---	0.734	---	1.256	0.989	1.189
0.125	---	0.921	1.118	0.992	---	1.096
0.175	---	1.124	---	0.567	0.363	0.578
0.225	0.989	0.263	---	0.399	0.217	0.800
0.275	---	---	---	0.200	0.188	0.195
0.325	---	0.031	0.857	0.029	0.229	0.068
0.375	---	---	---	0.226	---	0.063
0.425	---	0.058	0.441	0.243	0.166	0.031
0.475	---	0.065	---	<0	0.139	0.028
0.525	0.274	0.037	0.264	0.004	0.207	0.022
0.575	---	0.019	0.276	0.115	0.153	0.010
0.625	---	0.046	0.276	0.257	0.246	0.005
0.675	---	0.008	0.192	0.068	0.159	0.008
0.725	0.357	0.007	0.123	0.116	0.080	0.004
0.775	---	0.004	0.109	0.006	0.121	0.006
0.825	---	0.00	0.038	0.250	0.043	0.001
0.875	---	0.003	0.016	0.018	0.046	2x10 ⁻⁴
0.925	0.326	0.002	0.009	0.231	0.022	0.008
0.975	---	---	0.003	0.141	0.005	---
1.025	---	0.004	0.003	0.129	0.001	---
1.075	0.235	0.---	0.005	0.103	0.001	---
1.125	---	---	0.006	---	5x10 ⁻⁴	---
1.175	---	0.031	0.031	0.328	---	---
1.225	---	0.003	0.027	0.050	---	---
1.275	0.316	---	0.016	0.071	---	---
1.325	---	<0	0.006	0.136	---	---
1.375	---	---	0.001	0.010	---	---
1.425	---	---	6x10 ⁻⁴	(0.072)	---	---
1.475	0.190	---	3x10 ⁻⁴	(0.072)	---	---
1.525	0.190	---	0.001	0.206	---	---
1.575	0.180	---	6x10 ⁻⁵	0.041	---	---
1.625	0.141	---	2x10 ⁻⁵	0.205	---	---
1.675	0.141	---	1x10 ⁻⁴	0.041	---	---
1.725	0.124	---	2x10 ⁻⁴	0.097	---	---
1.775	0.124	---	7x10 ⁻⁵	0.045	---	---
1.825	0.188	---	3x10 ⁻⁵	0.093	---	---
1.875	0.188	---	5x10 ⁻⁴	0.067	---	---
1.925	0.114	---	1x10 ⁻⁴	0.026	---	---
1.975	0.080	---	6x10 ⁻⁴	0.146	---	---
2.025	0.117	---	1x10 ⁻⁴	0	0.005	---
2.075	0.104	---	---	0.101	---	---
2.125	0.116	---	---	0	---	---
2.175	0.059	---	---	0.122	---	---
2.225	0.036	---	---	0.020	---	---
2.275	0.034	---	---	---	---	---
2.325	0.043	---	---	0.051	---	---
2.375	0.013	---	---	0.026	---	---
2.425	0.004	---	---	0.069	---	---
2.475	0.001	---	---	0.052	---	---
2.525	0.001	---	---	---	---	---
2.575	4x10 ⁻⁴	---	---	0.066	---	---

Table III: Penetration of Illitic Sediment by Plutonium

Distance mm	Sample No. Contact Time, 10 ⁶ seconds	Relative Concentration					
		300303	300304	210606	090301	300301	210503
		0.52	0.69	2.401	3.89	4.15	10.356
0.025		11.741	0.796	4.884	---	1.164	7.739
0.075		2.704	0.175	2.147	0.995	0.858	0.875
0.125		1.161	0.165	1.630	0.132	0.675	0.983
0.175		---	0.341	1.106	0.208	0.594	0.401
0.225		---	0.126	0.466	0.120	0.253	0.695
0.275		---	---	0.556	0.103	0.124	0.204
0.325		---	0.013	0.383	0.276	0.032	0.155
0.375		---	---	0.376	0.061	0.037	0.179
0.425		---	0.035	0.294	---	0.016	0.087
0.475		---	---	0.287	0.063	0.018	0.088
0.525		---	0.041	0.197	0.022	0.016	0.071
0.575		---	0.030	0.238	0.040	0.025	0.096
0.625		---	0.029	0.196	0.032	0.025	0.079
0.675		---	0.018	0.153	0.029	0.052	0.058
0.725		---	0.017	0.121	0.017	0.027	0.046
0.775		---	0.010	0.125	0.021	0.070	0.048
0.825		---	---	0.139	0.015	0.014	0.039
0.875		---	0.020	0.179	0.020	0.098	0.026
0.925		---	0.013	0.165	0.015	0.026	0.028
0.975		---	---	0.125	---	0.044	0.021
1.025		---	0.010	0.103	---	---	0.024
1.075		---	---	0.041	---	---	0.027
1.125	0.053	---	0.009	0.088	---	---	0.018
1.175	0.036	---	0.008	0.006	---	---	0.014
1.225	0.064	---	---	0.046	---	---	0.011
1.275	0.073	---	---	0.055	---	---	0.015
1.325	0.040	---	0.011	0.034	---	---	0.016
1.375	0.059	---	---	0.030	---	---	0.014
1.425	0.045	---	0.011	0.028	---	---	0.012
1.475	0.054	---	---	0.031	---	---	0.016
1.525	0.221	---	---	0.030	---	---	0.013
1.575	0.259	---	---	0.023	---	---	0.010
1.625	0.014	---	---	0.029	---	---	0.010
1.675	0.020	---	---	0.024	---	---	0.010
1.725	0.017	---	---	0.024	---	---	0.010
1.775	0.016	---	---	0.027	---	---	0.009
1.825	0.014	---	---	0.026	---	---	0.008
1.875	0.009	---	---	0.019	---	---	0.005
1.925	---	---	---	0.009	---	---	0.006
1.975	---	---	---	0.015	---	---	0.002
2.025	---	---	---	0.013	---	---	0.005

Table IV: Penetration of Smectic Sediment by Americium and Plutonium

Distance mm	Relative Concentration			
	Tracer: Sample No. Contact Time, 10 ⁶ seconds	Americium 100701	100702	Plutonium 100701 100702
0.025		0.417	0.899	1.307 1.835
0.075		0.037	0.990	0.156 1.546
0.125		1.483	0.385	0.597 0.617
0.175		0.825	0.197	0.409 0.400
0.225		1.274	0.090	0.602 0.327
0.275		1.587	0.034	0.771 0.186
0.325		0.523	0.030	0.330 0.212
0.375		0.946	0.033	0.514 0.215
0.425		0.775	0.035	0.412 0.174
0.475		0.708	0.025	0.365 0.133
0.525		0.670	0.020	0.366 0.131
0.575		0.300	<0	0.116 0.108
0.625		0.050	0.008	0.230 0.105
0.675		0.020	0.007	0.122 0.097
0.725		0.016	0.003	0.100 0.059
0.775		0.009	0.005	0.070 0.056
0.825		0.004	4x10 ⁻⁵	0.027 0.044
0.875		0.033	0.008	0.211 0.044
0.925		0.016	6x10 ⁻⁴	0.095 0.040
0.975		0.008	<0	0.060 0.032
1.025		0.010	0.064	0.064 0.037
1.075		0.008	0.053	0.025 0.025
1.125		0.009	0.040	0.021 0.021
1.175		0.014	0.067	0.015 0.015
1.225		0.016	0.082	0.010 0.010
1.275		0.003	0.033	0.008 0.008
1.325		0.010	0.067	0.008 0.008
1.375		0.046	0.237	0.005 0.005
1.425		0.002	0.014	0.005 0.005
1.475		0.004	0.011	0.005 0.003
1.525		0.005	0.015	0.003 0.003
1.575		5x10 ⁻⁴	0.004	5x10 ⁻⁴
1.625		0.004	0.006	0.003
1.675		0.003	0.004	---
1.725		0.001	0.002	---
1.775		0.002	0.002	---
1.825		0.002	6x10 ⁻⁴	---
1.875		0.003	---	---
1.925		0.002	---	---
1.975		0.001	---	---
2.025		0.010	---	---
2.075		0.001	---	---
2.125		0.001	---	---
2.175		0.002	---	---
2.225		0.001	---	---
2.275		0.003	---	---
2.325		0.003	---	---
2.375		0.002	---	---
2.425		0.001	---	---
2.475		0.003	---	---
2.525		---	---	---
2.575		0.004	---	---
2.625		3x10 ⁻⁴	---	---

Fig. 5. Penetration of Illitic Ocean Floor Sediment by Plutonium. (Data from Table III.)

It follows that these data permit an estimate for the upper limit of the effective diffusion coefficient only. The numerical value for the effective diffusion coefficient of plutonium in illitic ocean floor sediment consistent with the two curves in Fig. 5 is

$$D_{\text{eff}}(\text{Pu}) = (1.2 \pm 0.7) \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}.$$

In a similar fashion as described for plutonium, the upper limit for the effective diffusion coefficient of americium can be estimated from the data of Table II. The result of the estimate is

$$D_{\text{eff}}(\text{Am}) = (1.1 \pm 0.8) \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}.$$

For the corresponding upper limits of the effective diffusion coefficients in smectic sediments the data of Table IV yield the values

$$D_{\text{eff}}(\text{Pu}) = (2.7 \pm 1.6) \times 10^{-10} \text{ cm}^2 \cdot \text{sec}^{-1}$$

and

$$D_{\text{eff}}(\text{Am}) = (1.2 \pm 1.0) \times 10^{-10} \text{ cm}^2 \cdot \text{s}^{-1}.$$

As judged by these numbers, the diffusivity of both americium and plutonium is less than that of the relatively unaffected iodide ion by a factor of one million. This dramatic reduction over the mobility in solution cannot be accounted for by the larger mass or the higher charge of the ions. It must be caused by either a chemical transformation of the simple cationic species in solution, such as a hydrolysis and the attendant formation of an insoluble hydroxide, or by a very strong interaction with the constituent minerals of the sediment. Whether it is one or the other, or perhaps a combination of these effects is currently being investigated in the laboratory.

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