PLUTONIUM IN THE GULF OF MEXICO

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Background

As part of our study of the geochemical behavior of plutonium in the Gulf of Mexico system, we have collected a series of sediment cores in a traverse from the deep Gulf of Mexico to the Mississippi Delta. (Fig. 1). The sediment samples thus represent a wide range of sedimentary and geochemical environments. The cores were taken with a box corer, then sub-cored with a 20 cm diameter stainless steel core barrel. The sub-cores were extruded and sliced into 1cm intervals for analysis. The analytical techniques we have used to analyze for Pu are summarized in progress report # ORO-3852-26. Basically, we are following the procedures of Chu (1971), de Bortoli (1967), Talvitie (1971) and Wong (1971).

A map of the physiographic provinces of the Gulf of Mexico (Fig. 2) shows that its sediments are dominated by the Mississippi cone, a large mass of detrital material delivered by the Mississippi River. This feature has been formed largely by bottom transport mechanisms such as turbidity currents. Sediments on the tops of the Sigsbee Knolls represent some of the only examples in the Gulf of Mexico of particle-by particle deposition of detrital debris. The Knolls were elevated above surrounding depths by intrusion of salt domes.

Sediments in the area from the deep sea floor adjacent to the Sigsbee Knolls have been deposited by a combination of turbidity current transport and pelagic deposition, with increasing dominance by the detrital material as the Mississippi River is approached. Sediments in the delta itself have been shown by Trefry and Presley (1976) to be reducing, more as a result of the very rapid sediment accumulation rates than the organic matter content, which is not particularly high (0.5%).

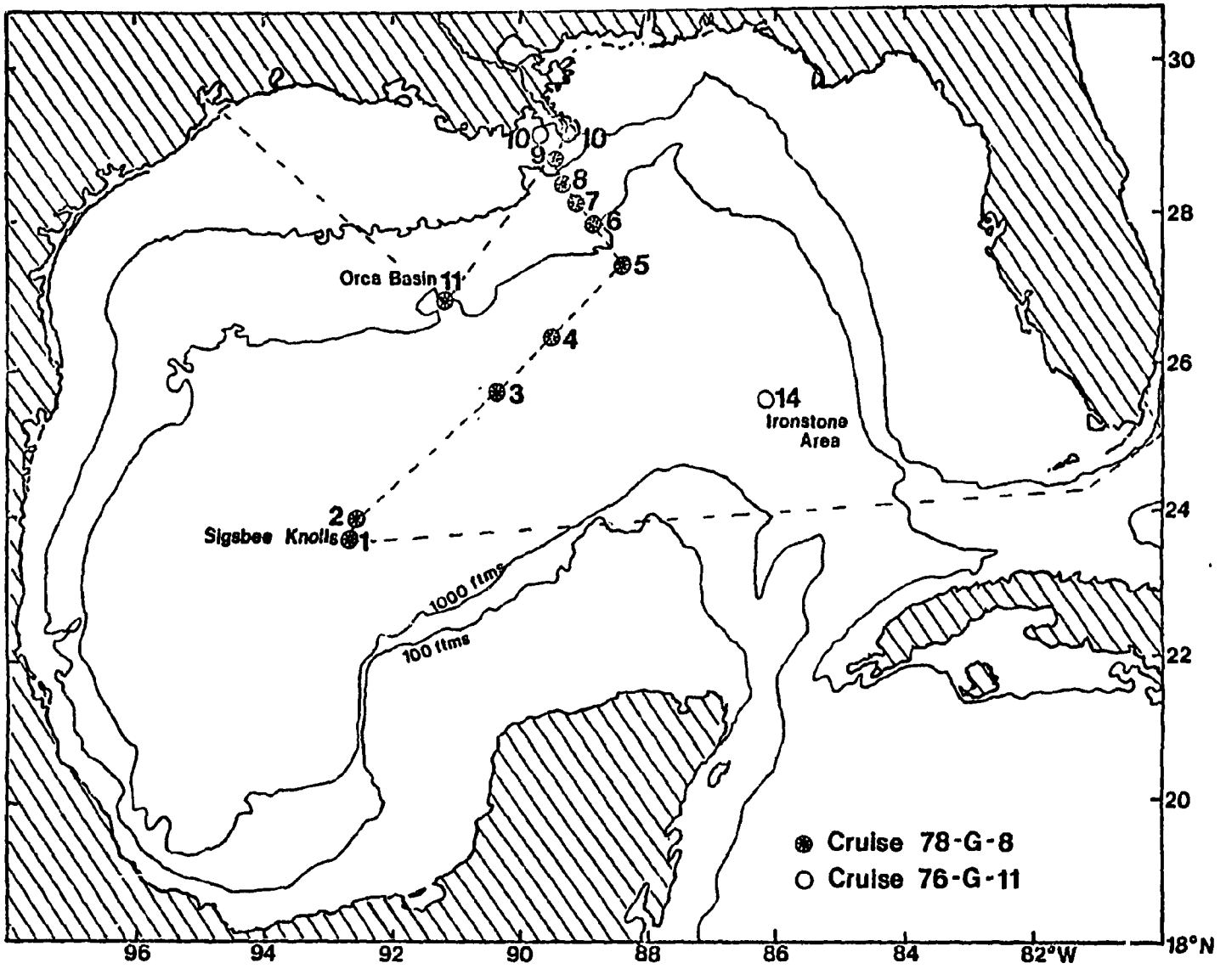

FIGURE 1. Location map of marine sediment cores analyzed in this study.

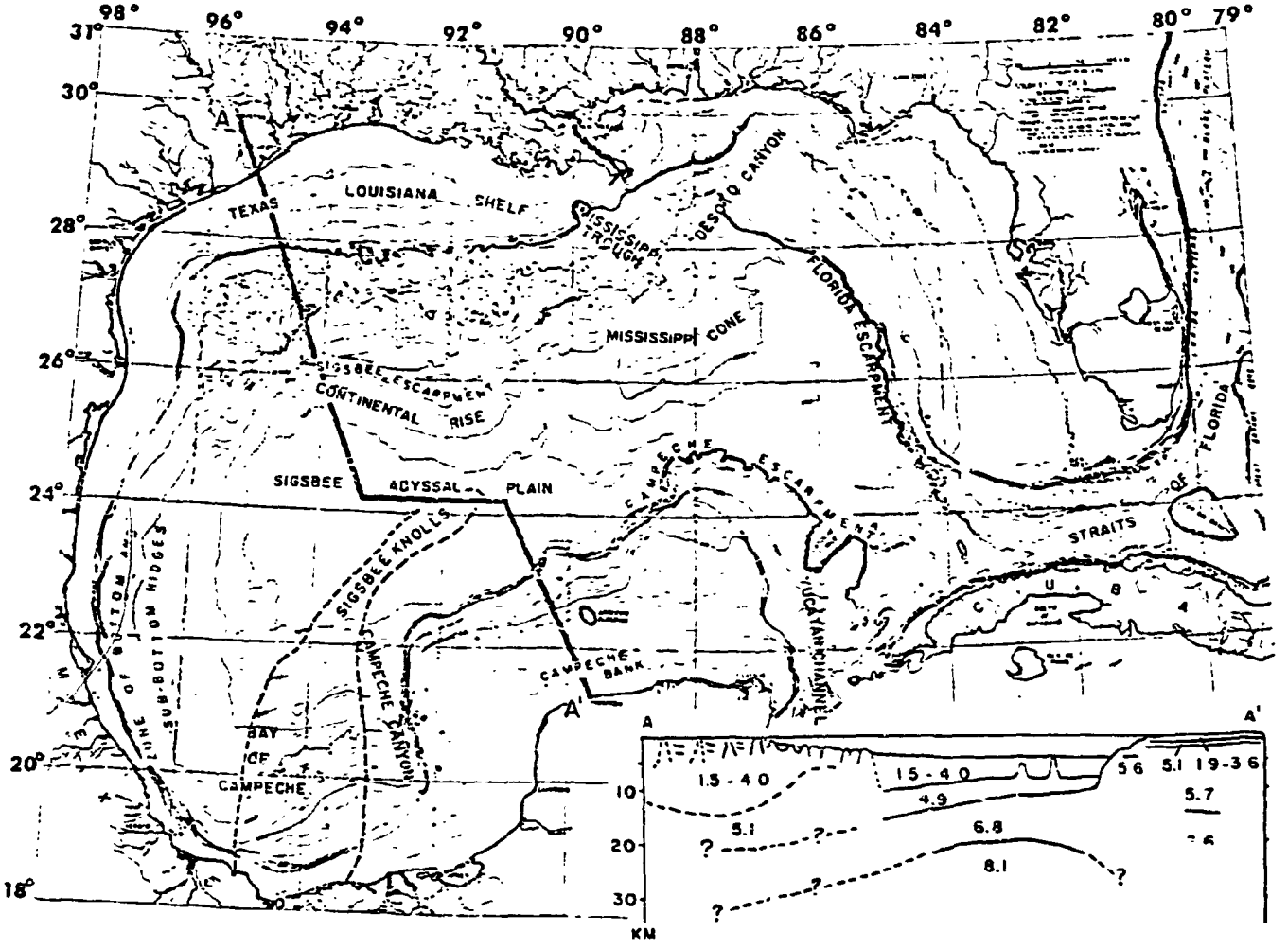

Figure 2. Physiographic provinces of the Gulf of Mexico. (El-Sayed et al., 1972)

The delta sediments have been divided into several distinct geochemical environments by Shokes (1976), partly on the basis of sediment accumulation rates determined by ^{210}Pb analysis. (Fig. 3). Near-river mouth sediments are deposited at the mouths of the major distributaries of the river at rates that exceed the utility of the ^{210}Pb method of measurement. The sediments in these areas tend to be sandier that the rest of the delta, and ^{210}Pb contents are nearly constant with depth, fluctuating to some degree as a function of grain size.

Mid-delta front sediments are deposited at very high rates, marginally within the appropriate range for the ^{210}Pb method. These sediments are deposited at rates greater than 1 cm/yr, and as a consequence are minimally influenced by bioturbation. Burrowing organisms are certainly present, but they are not able to thoroughly mix the large amounts of sediment being deposited annually.

Outer delta front sediments are deposited at 0.5-1 cm/yr in water depths of roughly 100 m. These sediments show sporadic evidence of redistribution of materials by bioturbation.

Delta front perimenter sediments have considerably lower sediment accumulation rates (.1-.4 cm/yr). The Pb profiles in these cores show well-defined bioturbation effects and evidence of slumping events. Water depths range from 150-500 m. Sediments in this area also show higher specific ^{210}Pb activities per gram, suggesting shoreward transport of ^{210}Pb from the open Gulf of Mexico waters (Shokes, 1976).

Sulfate reduction occurs in the delta sediments to an extent which is controlled by the sediment accumulation rates. In the more rapidly accumulating sediments of the delta (>1 cm/yr), Mn in the sediment has been reduced and has diffused into the overlying water. These sediments show a Mn loss of 45% compared to the river sediment delivered to the area (Trefry and Presley, 1976).

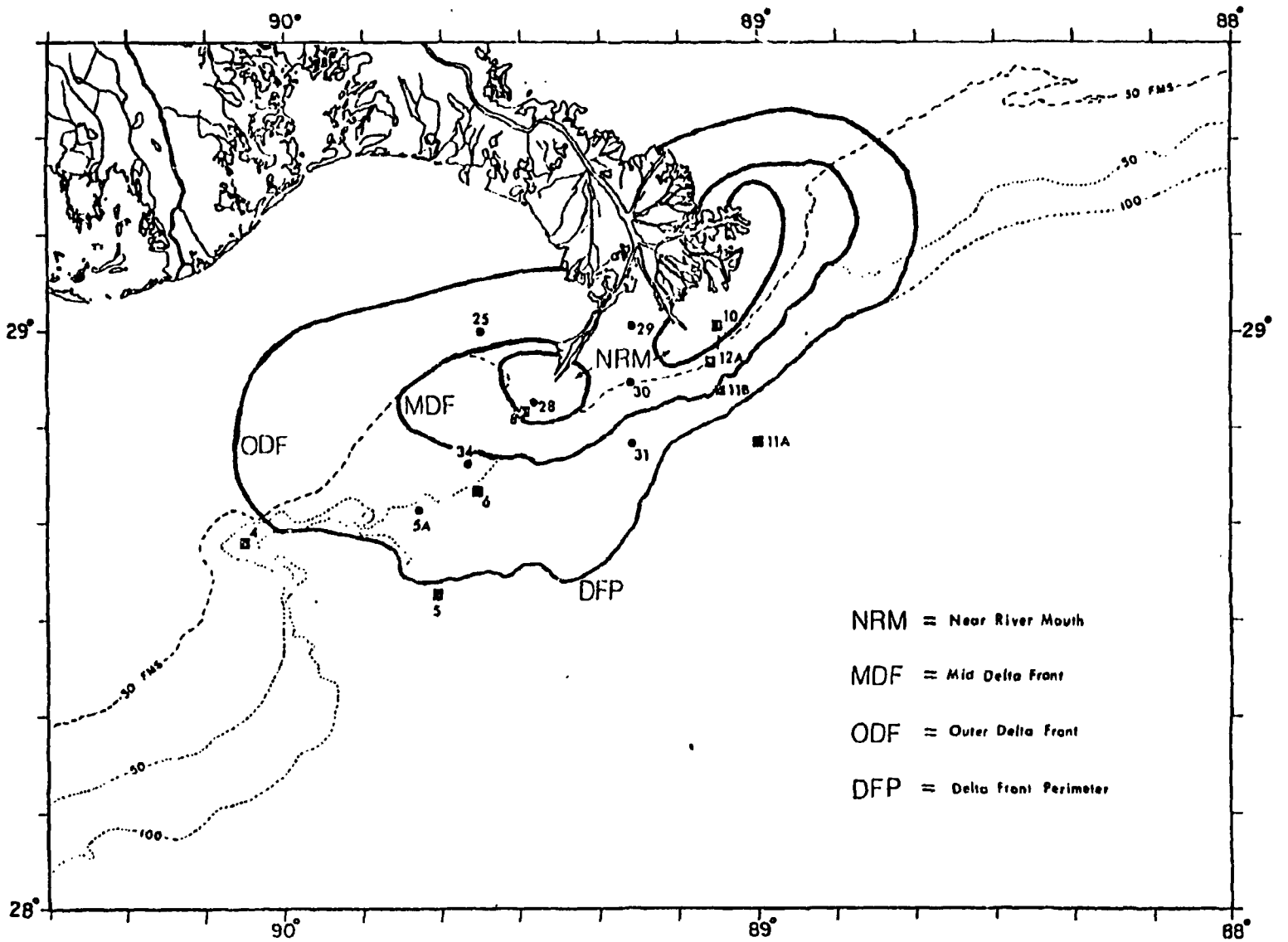

Figure 3. Mississippi Delta Front regions, after Shokes, 1976.

Much less remobilization of Fe occurs in these sediments, as shown by Trefry and Presley (1976) and by analyses in this work, discussed later. The reduction of Mn must take place essentially at the sediment-water interface because no Mn-rich oxidized layer is observed in the inner part of the delta. In areas with lower sedimentation rates, a Mn-rich layer is observed at the top of the core, and in deep Gulf of Mexico water, the sediments are enriched with Mn compared to river sediment input. According to Trefry and Presley (1976) this enrichment occurs by adsorption of the dissolved Mn from nearshore sediments onto particles which are then deposited in deep water sediments. It is on this pattern of sedimentary and geochemical processes that deposition of fallout plutonium is superimposed.

Plutonium in Gulf of Mexico Sediments

Table 1 is a compilation of the plutonium analyses completed on Gulf of Mexico sediments. Figures 4 through 12 show the distribution of Pu versus depth in the Gulf of Mexico cores analyzed so far. Cores 1, 2, 4 and 6 represent deep water cores, with water depth ranging from 3649 m to 1701 m. Core 7 represents an "intermediate" depth range of 786 m, and cores 8, 9 and 10 represent delta cores with depths ranging from 320 m to 106 m. Figure 13 shows the Fe/Al and Mn/Al ratios versus depth for most of these cores.

The deep water cores (1, 2, 4 and 6) show an abrupt decrease with depth in $^{239-240}$ Pu content typical for open ocean sediments. The sediment accumulation rate for core 1 was estimated by Ewing et al., (1958) for the same Sigsbee Knoll to be 3 cm/10^3y. This sediment is largely derived from particle by particle settling through the water column. Core 2, taken at the base of that Knoll is in an area estimated to have an accumulation rate of 10 cm/10^3y (Ewing et al., 1958). The sediment in the second site is derived to a

TABLE 1

Pu in Gulf of Mexico Sediments

Sample & Location	Water Depth meters	Sample Interval cm	H_2O	$CaCO_3$	$^{239,240}Pu$† dpm/kg	^{238}Pu† dpm/kg	$^{238}Pu/^{239,240}Pu$
78-G-8, Station 1 Box Core 1 23° 43.9'N, 92° 28.0'W Sigsbee Knolls	3402	0 - 1	92.6*	48.8	11.0 ± 1.4	3.2 ± .7	0.29 ± .08
		1 - 2	61.7	47.2	3.2 ± .3		
		2 - 3	61.4	43.9	1.2 ± .2		
		3 - 4	57.6		2.7 ± .2	0.31 ± .06	0.11 ± .02
		4 - 5	57.8	42.0	1.7 ± .1		
		5 - 6	54.1		2.0 ± .13	0.30 ± .05	0.15 ± .02
		6 - 7	55.3	42.6	1.4 ± .1		
		8 - 9	53.3	42.7	0.5 ± .1	0.8 ± .1	1.6 ± .4
		13 - 14	51.0	42.1	0.20 ± .04		
		16 - 17	49.7	40.1	0.13 ± .06	0.8 ± .1	6 ± 3
		21 - 22	49.8	39.9	0.02 ± .01	0.03 ± .01	2 ± 1
78-G-8, Station 2 Box Core 1 23° 57.1'N, 92° 19.9'W Abyssal Plain	3649	0 - 1	89.3*	34.5	6.3 ± .5	2.0 ± .3	0.31 ± .05
		2 - 3a	56.6	--	2.9 ± .4	0.4 ± .2	0.14 ± .06
		2 - 3b	61.1	41.1	4.8 ± .3	0.9 ± .3	0.20 ± .03
		4 - 5a	58.8	--	1.5 ± .2	1.0 ± .2	0.7 ± .2
		4 - 5b	56.4	41.9	1.1 ± .1	0.30 ± .06	0.25 ± .06
		6 - 7	57.0	41.3	0.47 ± .03	0.10 ± .01	0.22 ± .04
		8 - 9	55.4	37.4	0.63 ± .05	0.12 ± .02	0.20 ± .04
		12 - 13	54.2	39.4	1.3 ± .2	0.28 ± .06	0.22 ± .06
		16 - 17	52.0	33.5	0.08 ± .02	0.08 ± .02	1.0 ± .4
78-G-8, Station 4 Box Core 1 26° 34.0'N, 89° 11.3'W	2744	0 - 1	66.5*	--	13 ± 3	4 ± 2	0.3 ± .1
		1 - 2	63.1	34.0	10.3 ± .3	1.7 ± .1	0.019 ± .001
		3 - 4	58.0		3.1 ± .2	0.41 ± .05	0.13 ± .02
		4 - 5	57.0	33.1	0.92 ± .09	0.46 ± .06	0.48 ± .08
		5 - 6	56.3		1.8 ± .2	0.44 ± .08	0.25 ± .05
		8 - 9	54.3	31.2	0.34 ± .04	0.38 ± .04	1.1 ± .2
		9 - 11	54.6		0.16 ± .03	0.02 ± .01	0.13 ± .06
		14 - 16	51.7		0.03 ± .02	n.d.	--
		21 - 22	51.1	28.6	n.d.	n.d.	--
78-G-8, Station 6 Box Core 1 27° 57.5'N, 88° 47.7'W	1701	0 - 1	84.1*	20.9	8.9 ± .4	1.2 ± .1	0.13 ± .02
		2 - 3	63.5	20.9	2.30 ± .08	0.29 ± .03	0.12 ± .01
		4 - 5	63.0	18.6	3.1 ± .1	0.46 ± .04	0.15 ± .02
		6 - 7	59.9	16.4	1.16 ± .07	0.16 ± .02	0.14 ± .02
		8 - 9	58.4	22.4	0.67 ± .06	0.07 ± .02	0.11 ± .04
		12 - 13	59.4	26.0	0.10 ± .02	0.06 ± .01	0.5 ± .2
		16 - 17	59.7	30.0	0.10 ± .02	0.09 ± .02	0.9 ± .3
		21 - 22	58.1	24.1	0.02 ± .01	0.06 ± .01	3 ± 2
78-G-8, Station 7 Box Core 1 28°21.6'N, 89°09.0'W	786	0 - 1	65.7	5.4	17.7 ± .8	1.1 ± .2	0.06 ± .01
		2 - 3	68.9	5.2	8.2 ± .4	0.64 ± .09	0.08 ± .01
		4 - 5	60.0	4.8	8.4 ± .2	0.71 ± .06	0.08 ± .01
		6 - 7	57.1	4.6	2.6 ± .1	0.20 ± .03	0.08 ± .01
		8 - 9	58.0	4.8	2.0 ± .2	0.14 ± .04	0.07 ± .02
		14 - 16	58.7	4.7	0.33 ± .05	0.04 ± .02	0.12 ± .05
		22 - 24	58.4	6.6	0.16 ± .02	0.01 ± .01	0.08 ± .04
		30 - 32	55.7	6.7	n.d.	n.d.	--

* Includes the top few centimeters of overlying water.

† Concentrations have been corrected for salt content. All errors reported are 1σ counting errors.

TABLE 1

Pu in Gulf of Mexico Sediments

(continued)

Sample & Location	Water Depth meters	Sample Interval cm	H_2O	$CaCO_3$	$^{239-240}Pu$† dpm/kg	^{238}Pu† dpm/kg	$^{238}Pu/^{239-240}Pu$
78-G-8, Station 8 Box Core 1 Sub-Core B 28°32.1'N, 89°17.7'W	320	0 - 1	76.4*	6.5	89 ± 2	3.7 ± .3	0.041 ± .004
		2 - 3	68.9	4.4	90 ± 1	4.4 ± .2	0.049 ± .002
		4 - 5	64.2	4.5	88 ± 2	4.3 ± .2	0.049 ± .002
		6 - 7	65.0	4.7	108 ± 2	4.9 ± .2	0.045 ± .002
		9 - 10	59.5	5.2	108 ± 2	5.6 ± .2	0.052 ± .002
		14 - 16	59.7	[illegible]	41.6 ± 1.0	2.3 ± .1	0.055 ± .003
		20 - 22	59.3	4.0	12.0 ± .3	0.84 ± .06	0.070 ± .006
		26 - 28.5	58.2	4.0	2.0 ± .1	0.16 ± .02	0.08 ± .01
78-G-8, Station 9 Box Core 1 Sub-Cores A & B 28°44.0'N, 89°25.9'W Mississippi Delta	106	0 - 1a	75.1*	<1	90 ± 2	4.5 ± .2	0.049 ± .002
		0 - 1b	62.6*	<1	101 ± 4	5.8 ± .6	0.057 ± .006
		2 - 3a	64.6	<1	104 ± 2	4.8 ± .2	0.046 ± .002
		2 - 3b	65.6	<1	98 ± 3	5.3 ± .3	0.055 ± .004
		4 - 5a	58.3	<1	107 ± 2	4.8 ± .2	0.048 ± .003
		4 - 5b	58.8	<1	100 ± 3	5.3 ± .4	0.051 ± .004
		6 - 7a	60.5	<1	101 ± 2	4.9 ± .2	0.049 ± .002
		6 - 7b	58.4	<1	99 ± 2	5.0 ± .2	0.050 ± .002
		8 - 9b	60.5	<1	111 ± 3	5.2 ± .3	0.047 ± .003
		9 - 10a	61.1	<1	114 ± 2	5.5 ± .2	0.048 ± .002
		12 - 14b	57.1	<1	105 ± 4	4.5 ± .3	0.043 ± .003
		14 - 16a	56.6	<1	112 ± 4	4.4 ± .2	0.040 ± .003
		18 - 20b	54.1	<1	68 ± 1	2.9 ± .1	0.042 ± .002
		20 - 22a	53.7	<1	52.2 ± .8	2.35 ± .08	0.045 ± .002
		26 - 28.5b	57.3	<1	10.8 ± .3	0.59 ± .04	0.055 ± .004
		28 - 30.5a	53.5	<1	8.1 ± .2	0.37 ± .03	0.045 ± .004
78-G-11, Station 10 Box Core 1, Subcores A & B 28° 37.2'N, 89° 33.5'W Mississippi Delta	110	0 - 1a	73.3	13.6	24.4 ± .9	2.4 ± .2	0.10 ± .01
		0 - 1b	74.8	14.2	27 ± 2	1.2 ± .2	0.04 ± .01
		2 - 3a	73.1	13.3	22.6 ± .9	1.4 ± .1	0.06 ± .01
		2 - 3b	73.6	11.8	22 ± 1	0.9 ± .1	0.04 ± .01
		4 - 5a	73.8	12.3	21.0 ± .7	0.9 ± .1	0.04 ± .01
		4 - 5b	73.4	12.4	19 ± 1	0.7 ± .1	0.04 ± .01
		6 - 7b	66.5	8.9	16 ± 1	0.6 ± .1	0.04 ± .01
		8 - 9a	66.8	12.2	13.9 ± .5	0.9 ± .1	0.06 ± .01
		8 - 9b	69.5	11.7	12.0 ± .9	0.5 ± .1	0.05 ± .01
		11 - 13b	73.9	9.6	4.7 ± .2	0.20 ± .04	0.04 ± .01
		15 - 17b	70.4	11.3	1.3 ± .1	--	--
		19 - 22.5b	73.6	11.4	0.76 ± .04	0.07 ± .01	0.09 ± .01
79-L-316, Station 3 Box Core A & B 28°51.5'N, 89°27.9'W Mississippi Delta SW Pass	42	0 - 1a	81.66*	<1	25.3 ± .9	1.1 ± .1	0.044± .005
		2 - 3b	64.17	<1	27.7 ± .8	1.5 ± .1	0.056± .006
		4 - 5b	61.37	<1	22.9 ± .8	1.3 ± .2	0.058± .008
		6 - 7a	57.22	<1			
		6 - 7b	56.60	<1			
		8 - 9b	54.94	<1			
		10 - 11b	50.03	<1	13.0 ± .5	3.3 ± .3	0.25 ± .02

* Includes the top few centimeters of overlying water.

† Concentrations have been corrected for salt content.
All errors reported are 1σ counting errors.

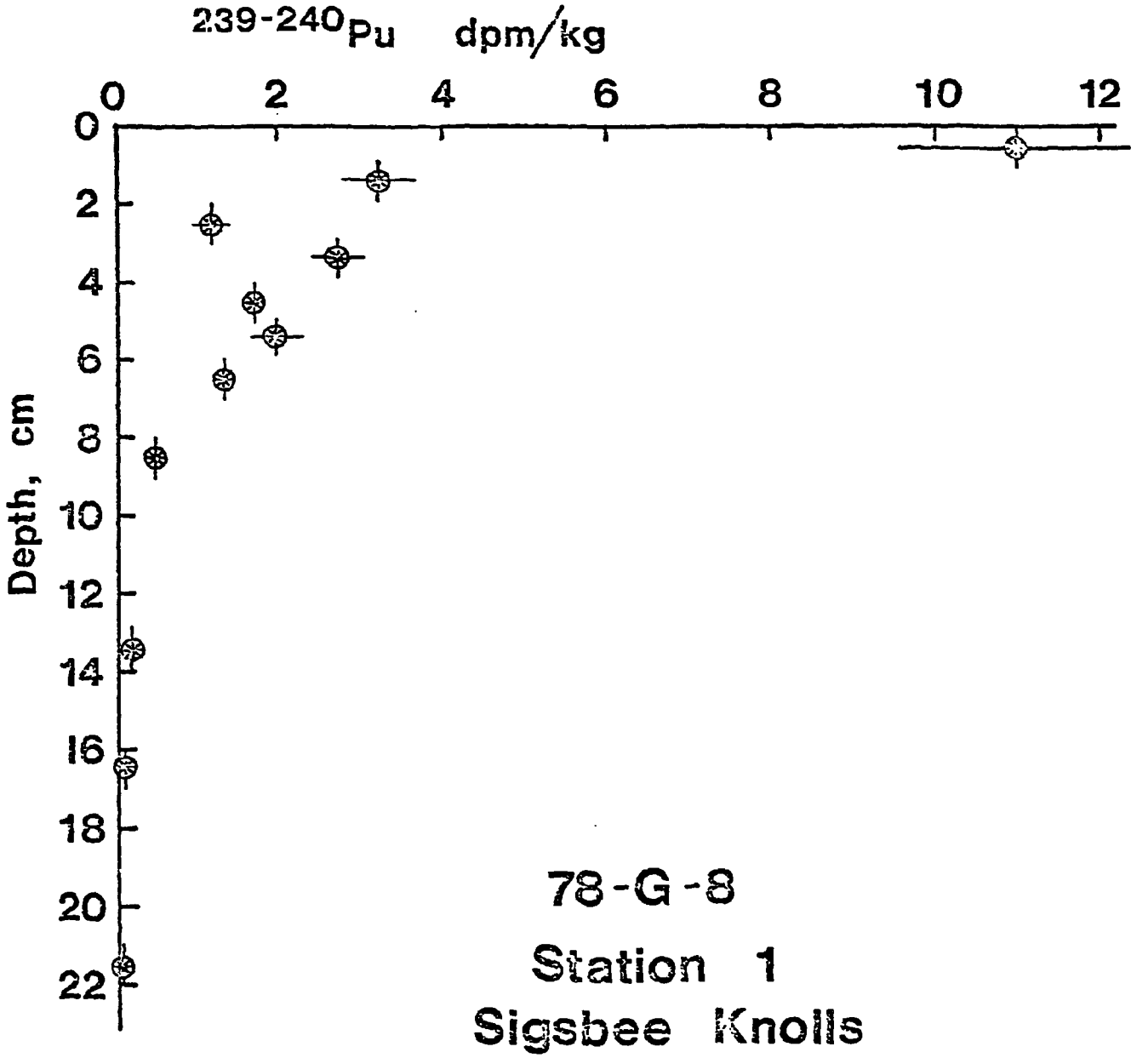

Figure 4. Distribution of Pu versus depth in core.

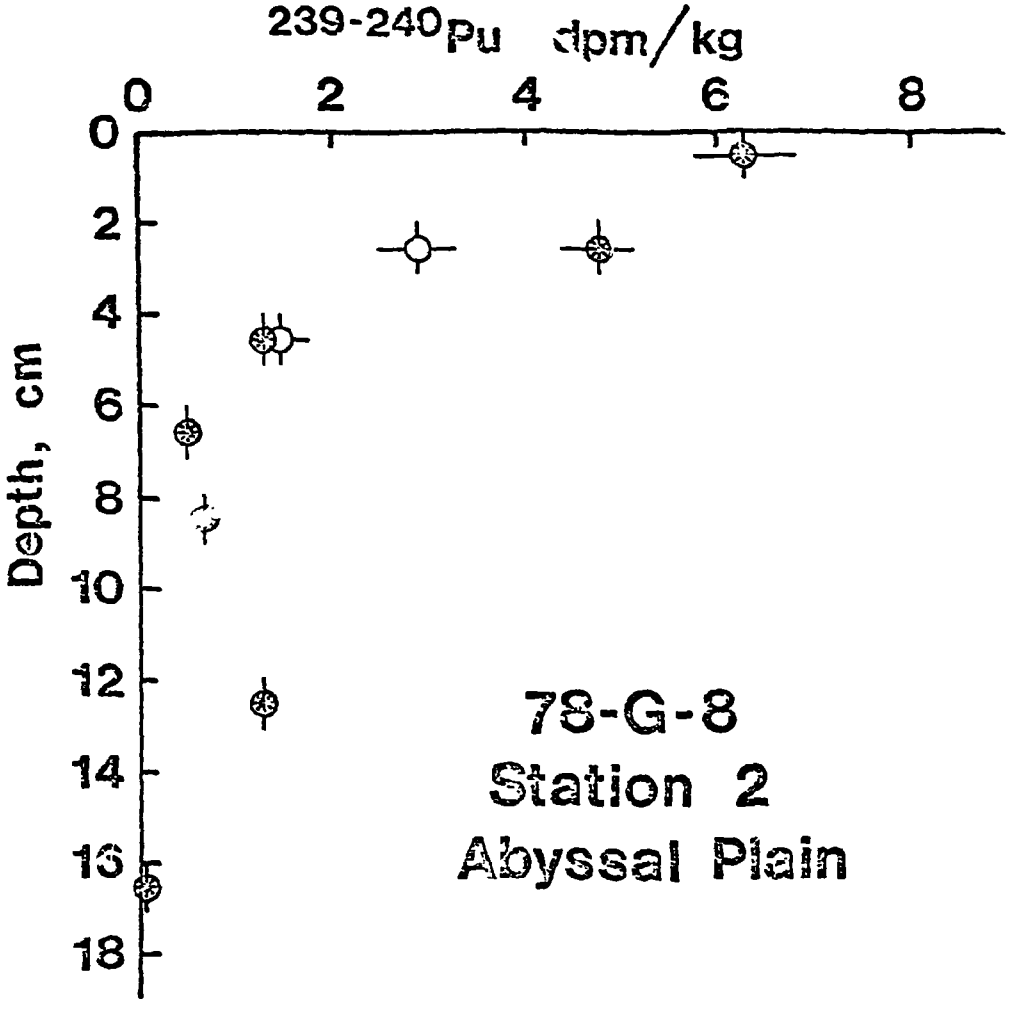

Figure 5. Distribution of Pu versus depth in core. Open circle points represent duplicate analyses done in this laboratory.

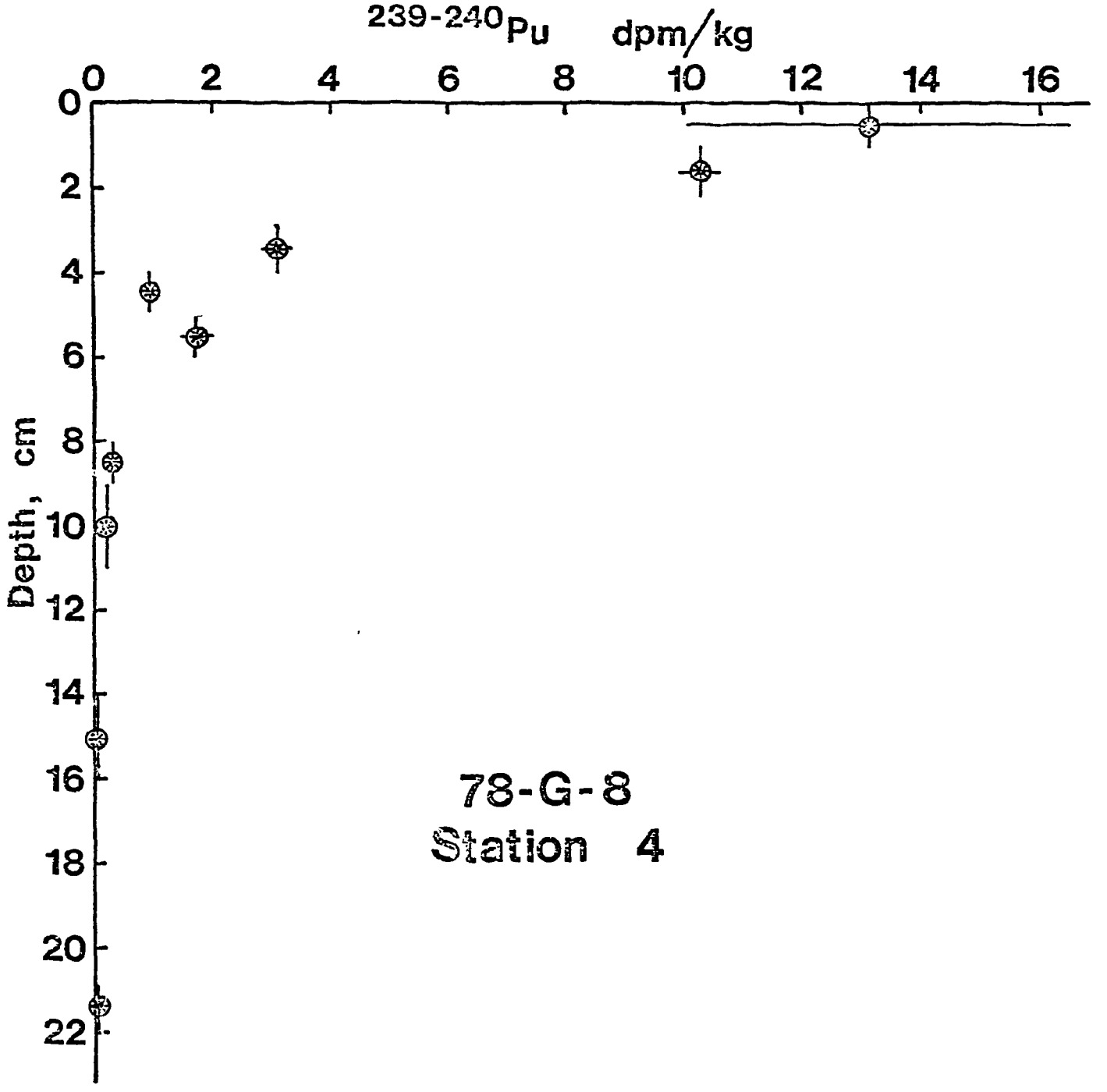

Figure 6. Distribution of Pu versus depth in core.

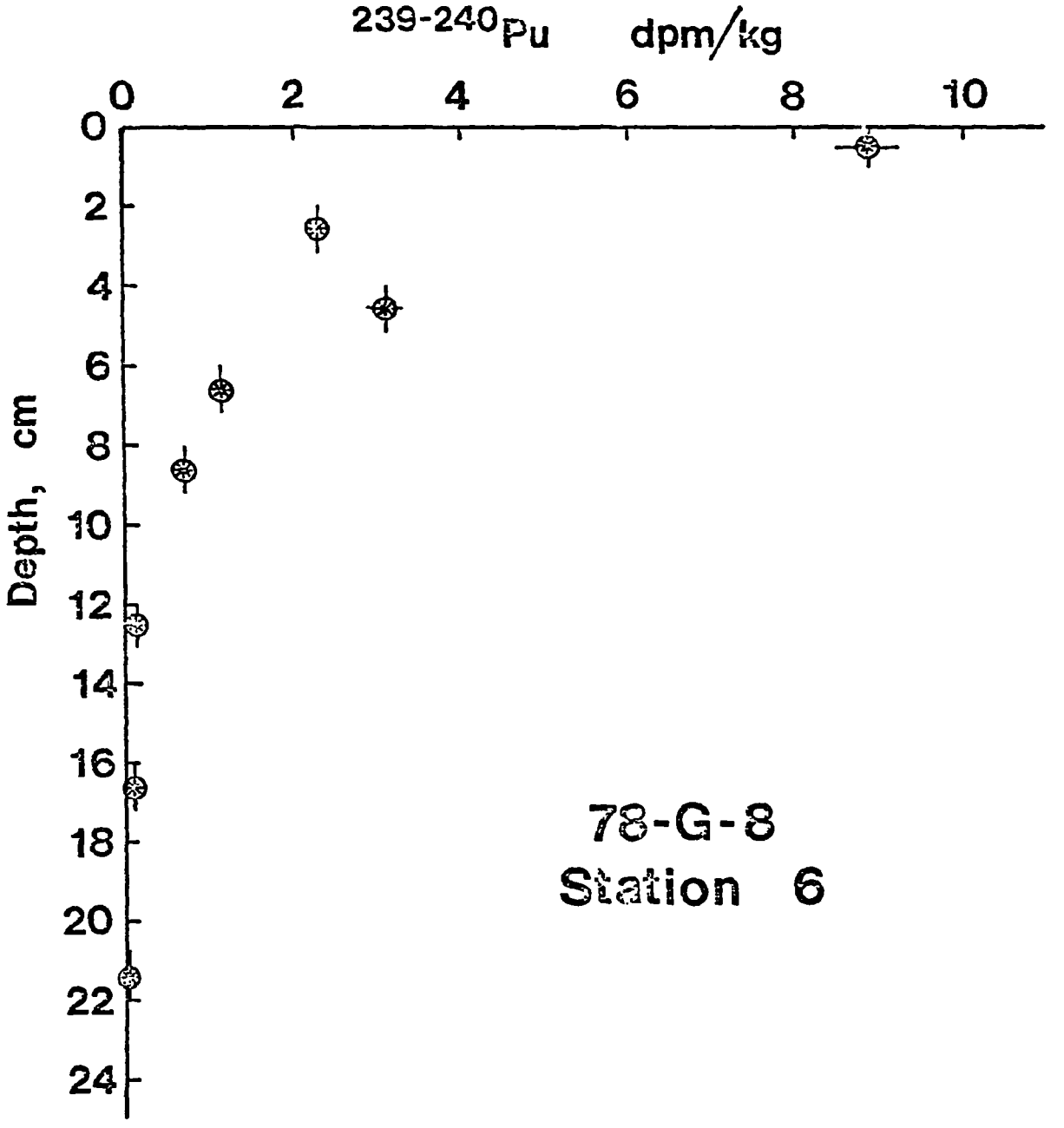

Figure 7. Distribution of Pu versus depth in core.

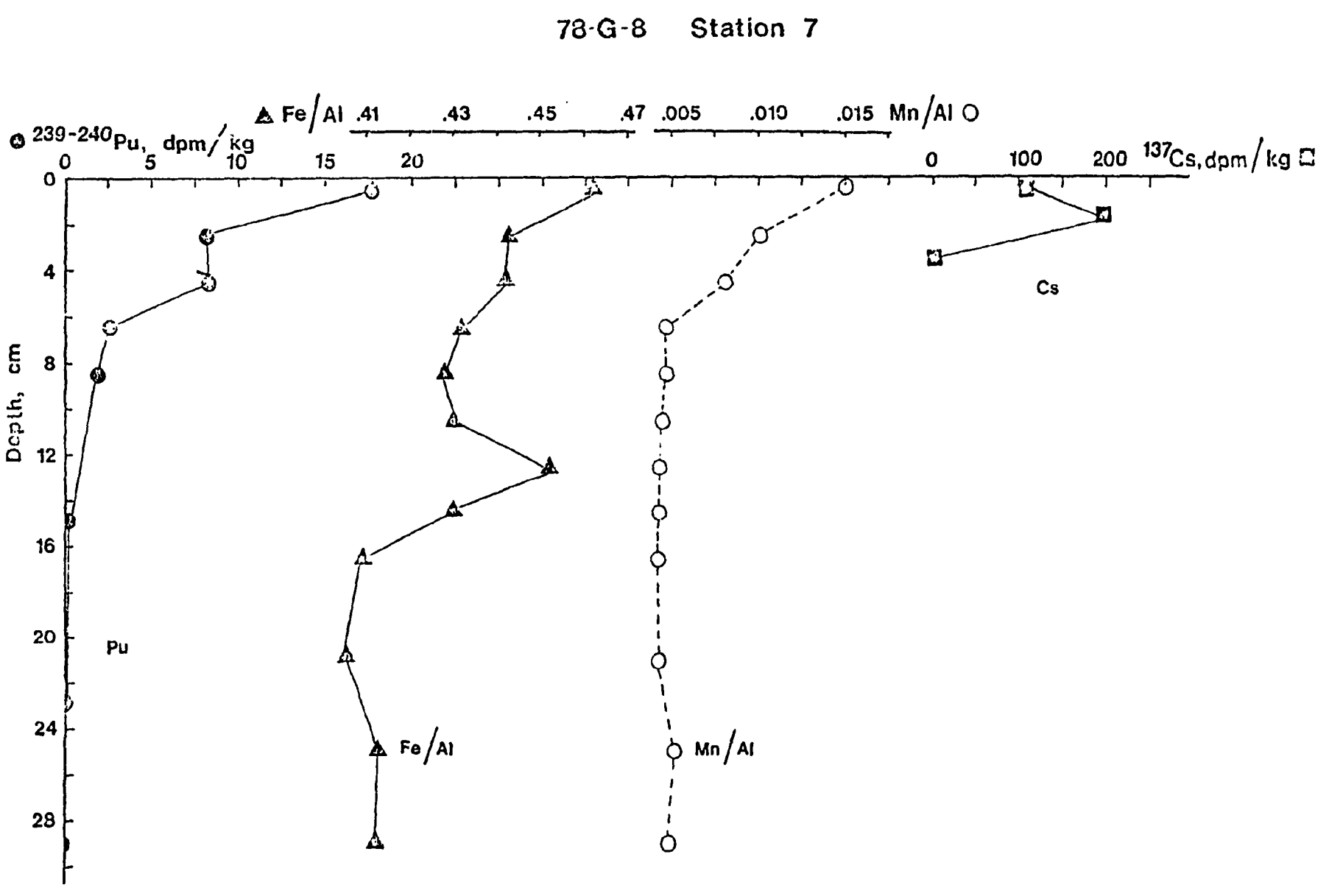

Figure 8. Distribution of Pu, Fe/Al ratios, Mn/Al ratios and ^{137}Cs versus depth in core.

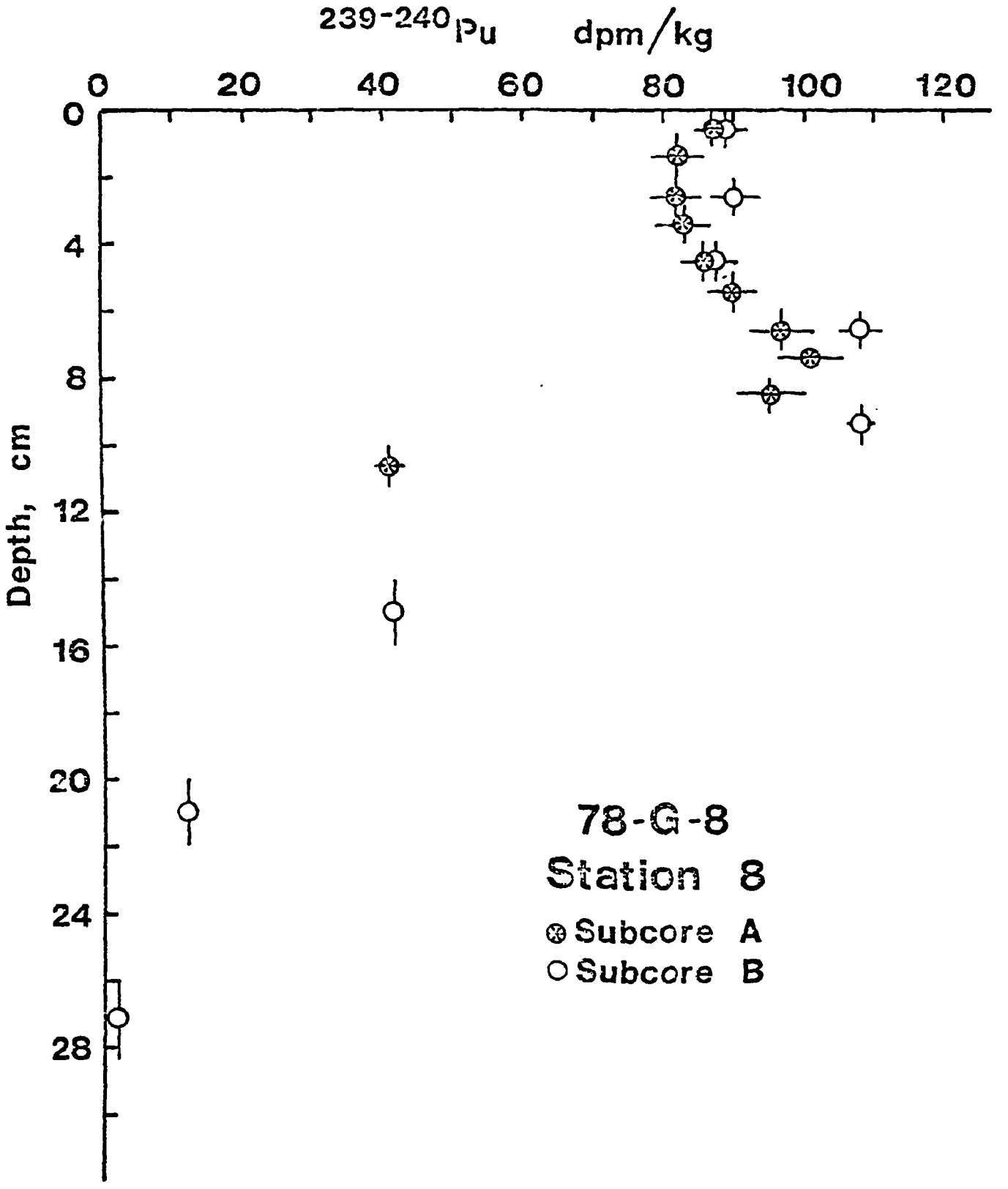

Figure 9. Distribution of Pu versus depth in core.

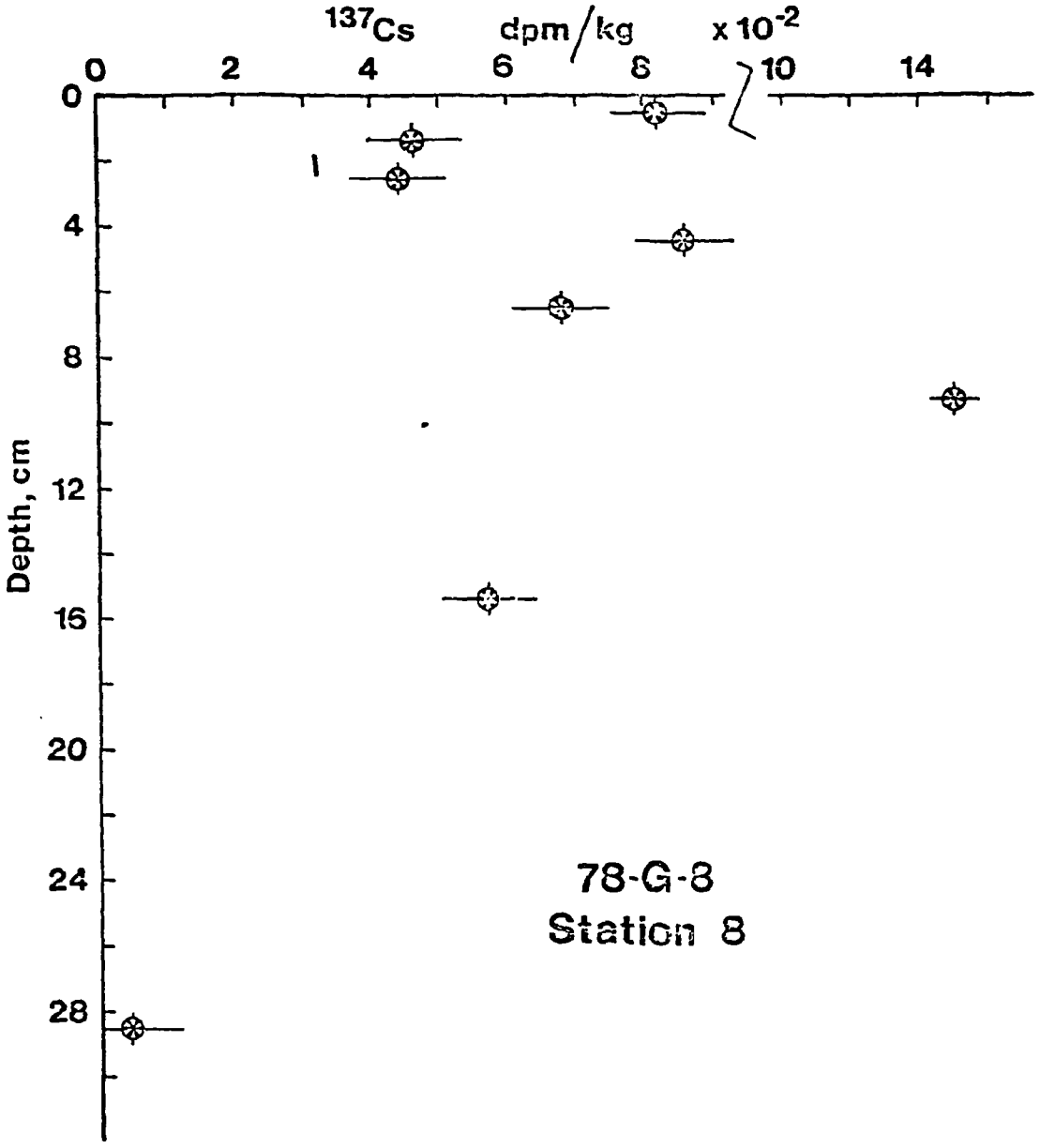

Figure 10. Distribution of ^{137}Cs versus depth in core.

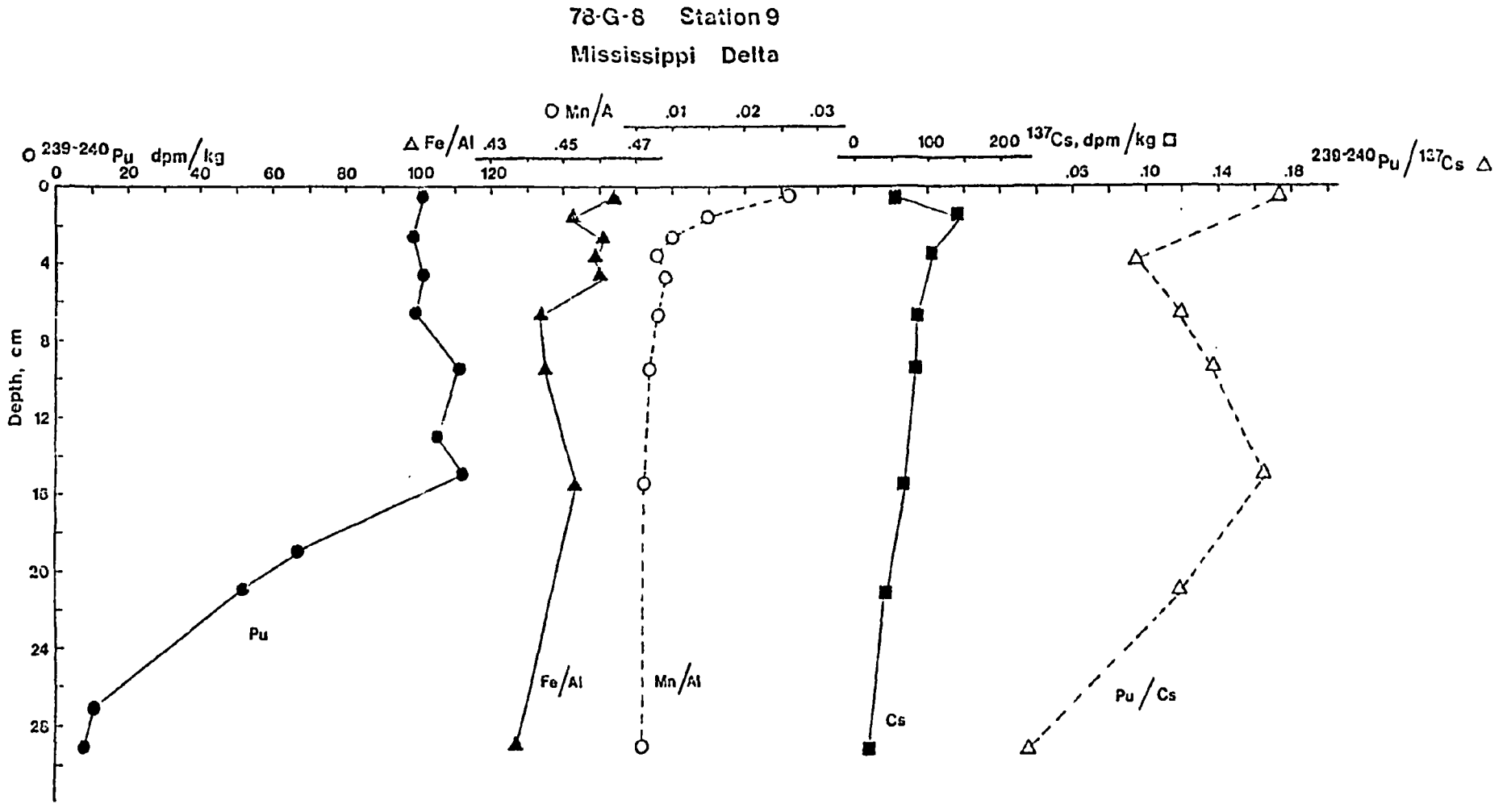

Figure 11. Distribution of Pu, Fe/Al ratios, Mn/Al ratios and ^{137}Cs versus depth in core.

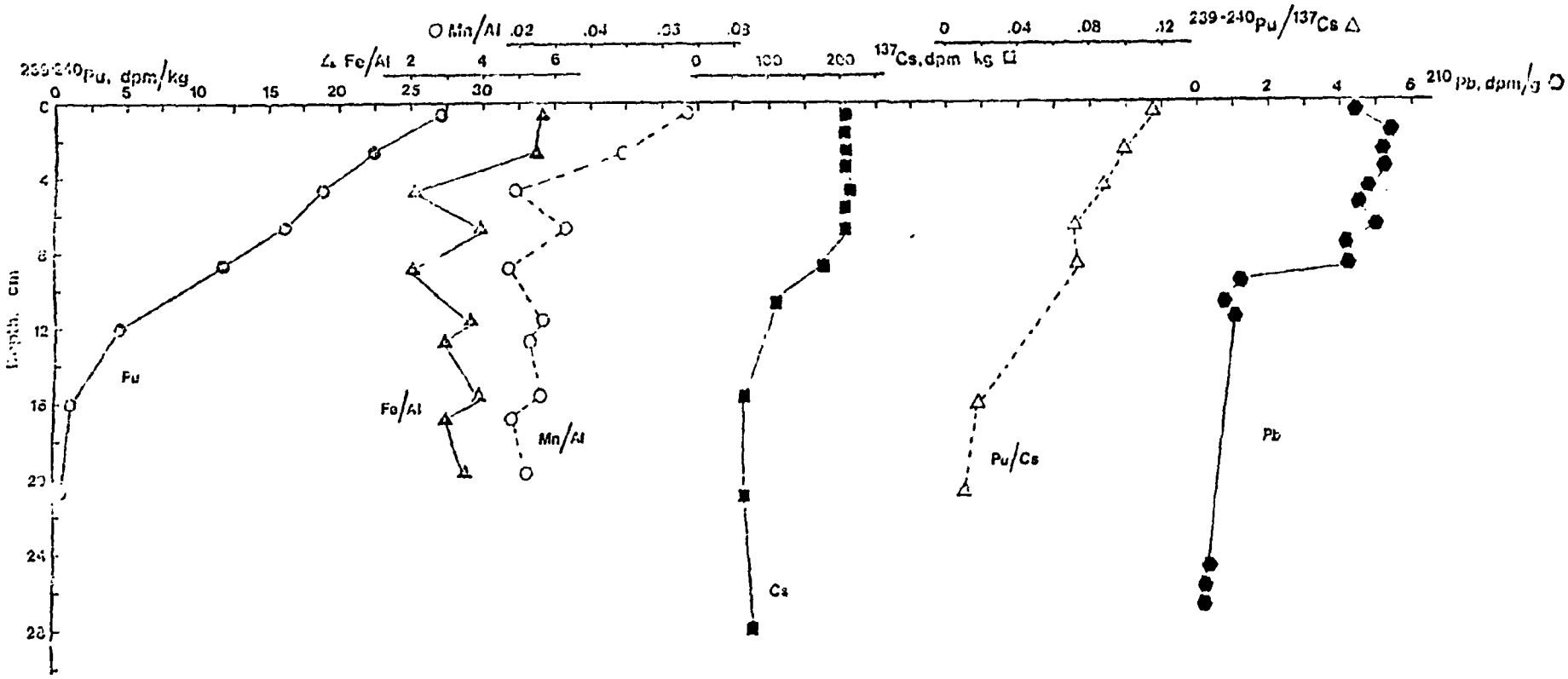

Figure 12. Distribution of Pu, Fe/Al ratios, Mn/Al ratios and ^{137}Cs versus depth in core.

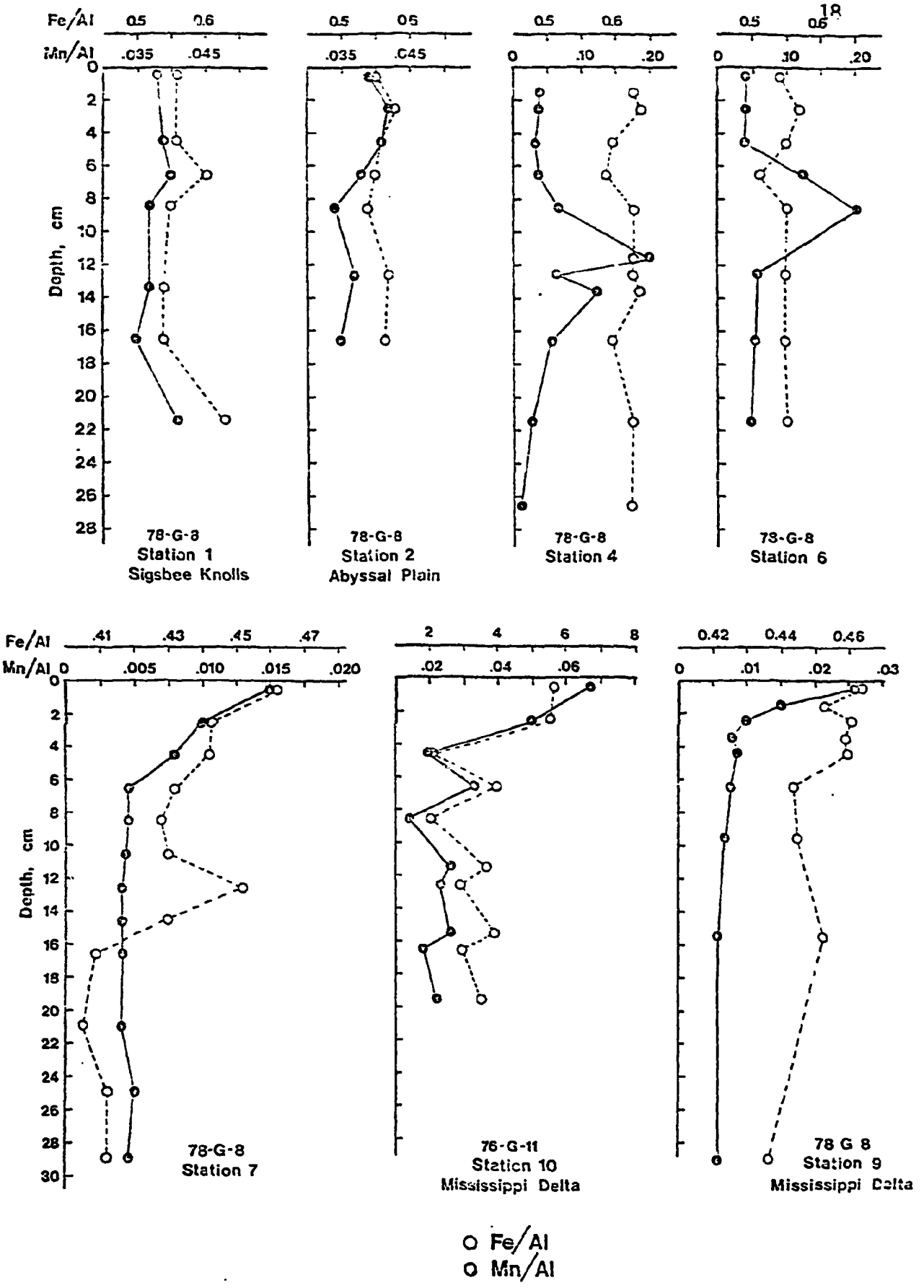

Figure 13. Plots of Fe/Al and Mn/Al ratios versus depth in Gulf of Mexico cores.

significant degree from turbidity current transport from the Mississippi cone sediments. The Pu profiles in these two cores do not differ markedly; both show evidence that the fallout Pu has been mixed downward by bioturbation processes. Cores from stations 4 and 6 show similar Pu profiles with depth indicating biological mixing of fallout Pu downward into older sediments. Note that none of the deep water cores show obvious remobilization of Fe and Mn (Fig. 13, Table 2). Comparison of core top values in Figures 4 and 5 with the river sediment data in Table 3 show that sediment from stations 1 and 2 are both enriched in Mn and Fe compared to Mississippi River sediments as predicted by Trefry and Presley (1976). Cores 4 and 6 are slightly depleted in these metals compared to river sediment; this observation is consistent with the fact that a majority of the detrital sediment in intermediate depths is delivered by turbidity flows from parts of the upper Mississippi cone sediments depleted in Fe and Mn (Trefry and Presley, 1976). High metal to Al ratios at depth in these cores suggest possible differences in the geochemistry of the Gulf at earlier times.

The core from station 7 (Figure 8) has a Pu versus depth distribution quite similar to that from station 6 (Figure 7). However, the Fe/Al and Mn/Al profiles for the upper part of the core indicates remobilization of both of those metals. The similarity of the Pu profiles shows essentially no interdependence of the geochemical behavior of Pu and Fe as suggested by Livingston and Bowen (1979) or of Pu and Mn as suggested by Means et al (1978).

The delta sediments show markedly different Pu concentrations (as discussed below) as well as depth distributions different from deep water sediments. Figure 9 shows distribution versus depth for $^{239-240}$ Pu in the core from station 78-G-8 station 8. The top 8 cm of the core appear to have been essentially homogenized by bioturbation, with some mixing of Pu to deeper

Table 2

Trace Metal Analysis of Gulf of Mexico Sediments

Sample & Location	Sample Interval cm	%H_2O	%$CaCO_3$	%Fe	%Mn	%Al	Fe/Al	Mn/Al
78-G-8, Station 1	0-1	92.6*	48.8	2.20	0.152	3.96	0.556	0.038
Box Core 1	1-2	61.7	47.2					
23°43.4'N, 92°28.0'W	2-3	61.4	45.9					
Sigsbee Knolls	3-4	57.6	--					
3402 m, depth	4-5	57.8	42.0	2.59	0.180	4.60	0.563	0.039
	5-6	54.1	--					
	6-7	55.3	42.6	2.72	0.181	4.52	0.602	0.040
	8-9	53.3	42.7	2.70	0.182	4.92	0.549	0.037
	13-14	51.0	42.1	2.71	0.184	5.02	0.540	0.037
	16-17	49.7	40.1	2.82	0.182	5.23	0.539	0.035
	21-22	49.8	39.9	2.73	0.234	4.92	0.555	0.046
78-G-8, Station 2	0-1	89.3*	34.5	1.99	0.142	3.62	0.550	0.039
Box Core 1	2-3	58.8	41.1	2.41	0.176	4.19	0.575	0.042
23°57.1'N, 92°19.9'W	4-5	57.6	41.9	2.56	0.175	4.32	0.558	0.041
Abyssal Plain	6-7	57.0	41.9	2.58	0.177	4.72	0.547	0.038
3649 m, depth	8-9	55.4	37.4	2.68	0.181	4.93	0.544	0.034
	12-13	54.2	39.4	2.77	0.179	4.88	0.568	0.037
	16-17	52.0	33.5	2.88	0.177	5.10	0.565	0.035
78-G-8, Station 3	0-1	80.6*	32.4					
Box Core 1	2-3	53.1	47.6	2.24	0.121	5.29	0.423	0.023
25°45.7'N, 90°12.9'W	4-5	52.3	46.1	2.28	0.123	5.27	0.433	0.023
3246 m, depth	6-7	50.6	44.0	2.36	0.125	5.17	0.456	0.024
	8-9	51.3	45.9	2.20	0.121	5.18	0.425	0.023
	10-11	49.4	38.7	2.60	0.132	5.81	0.448	0.023
	12-13	49.2	49.5	2.52	0.133	5.51	0.457	0.024
	14-15	48.5	37.3	2.53	0.128	5.69	0.445	0.022
	16-17	48.5	38.0	2.50	0.121	5.48	0.456	0.022
	18-19	48.9	40.2	2.55	0.119	5.75	0.443	0.021
	20-21	48.9	33.9	2.75	0.093	6.23	0.441	0.015
78-G-8, Station 4	0-1	86.5*	--	--	--	--	--	--
Box Core 1	1-2	63.1	34.0	2.39	0.165	4.13	0.579	0.040
26°34.0'N, 89°11.3'W	3-4	58.0						
2744 m, depth	4-5	57.0	33.1	2.60	0.158	4.71	0.552	0.034
	5-6	56.3						
	8-9	54.3	31.2	2.68	0.327	4.65	0.576	0.070
	9-11	54.6						
	14-16	51.7						
	21-22	51.1	28.6	2.89	0.168	4.98	0.580	0.031
78-G-8, Station 5	0-1	77.9*	17.7	3.00	0.075	6.49	0.462	0.012
Box Core 1	2-3	62.5	2.7	3.49	0.089	8.20	0.426	0.011
27°21.9'N, 88°12.7'W	4-5	56.1	1.9	3.57	0.071	8.07	0.442	0.009
2286 m, depth	6-7	49.7	2.8	3.58	0.062	8.77	0.408	0.007
	8-9	47.4	2.9	3.63	0.064	8.46	0.429	0.008
	10-11	49.0	3.1	3.58	0.068	8.32	0.430	0.008
	12-13	47.2	3.2	3.72	0.072	8.46	0.440	0.008
	14-15	51.6	3.0	3.68	0.073	8.53	0.431	0.009
78-G-8, Station 6	0-1	84.1*	20.9	2.80	0.231	5.74	0.490	0.040
Box Core 1	2-3	63.5	20.9	3.43	0.265	6.61	0.519	0.040
27°57.5'N, 88°47.7'W	4-5	63.0	18.6	3.48	0.273	6.98	0.499	0.039
1701 m, depth	6-7	59.9	16.4	3.61	0.854	7.18	0.463	0.123
	8-9	58.4	22.4	3.47	1.39	6.88	0.504	0.202
	12-13	59.4	26.0	3.14	0.262	6.35	0.494	0.057
	16-17	59.7	30.0	3.03	0.336	6.14	0.493	0.055
	21-22	58.1	24.1	3.34	0.324	6.62	0.505	0.049
78-G-8, Station 7	0-1	70.1*	5.4	3.87	0.126	8.38	0.462	0.015
Box Core 1	2-3	60.6	5.2	3.81	0.086	8.60	0.443	0.010
28°21.6'N, 89°09.0'W	4-5	62.3	4.8	3.86	0.071	8.73	0.442	0.008
786 m, depth	6-7	57.3	4.6	3.87	0.041	8.96	0.432	0.005
	8-9	58.8	4.8	3.81	0.041	8.90	0.428	0.005
	10-11	58.4	4.5	3.87	0.040	8.99	0.430	0.004
	12-13	58.2	5.3	3.93	0.036	8.70	0.452	0.004
	14-15	57.3	4.7	3.83	0.038	9.03	0.430	0.004
	16-17	57.8	5.8	3.65	0.037	8.92	0.409	0.004
	20-22	56.2	5.8	3.63	0.038	8.97	0.405	0.004
	24-26	57.8	7.5	3.52	0.043	8.54	0.412	0.005
	28-30	59.1	6.7	3.63	0.041	8.82	0.412	0.005

*Includes top few centimeters of overlying water

Table 2

Trace Metal Analysis of Gulf of Mexico Sediments
(continued)

Sample & Location	Sample Interval cm	%H_2O	%$CaCO_3$	%Fe	%Mn	%Al	Fe/Al	Mn/Al
78-G-9, Station 8	0-1	76.4	6.[illegible]					
Box Core 1, Subcore B	2-3	68.9	4.4					
28°32.1'N, 89°17.7'W	4-5	64.2	4.5					
320 m, depth	6-7	65.0	4.4					
	9-10	59.5	5.2					
	14-16	59.7	4.4					
	20-22	59.3	4.0					
	26-28.5	58.2	4.0					
78-G-8, Station 9	0-1	75.1*	<1	4.00	0.226	8.62	0.464	0.026
Box Core 1, Subcore A	2-3	64.6	<1	4.16	0.093	9.03	0.461	0.010
28°44.0'N, 89°25.9'W	4-5	58.3	<1	4.22	0.080	9.18	0.460	0.009
106 m, depth	6-7	60.5	<1	4.02	0.069	9.05	0.444	0.008
Mississippi Delta	9-10	61.1	<1	4.00	0.063	8.98	0.445	0.007
	15-16	56.6	<1	4.11	0.056	9.17	0.453	0.006
	20-22	53.7	<1	--	--	--	--	--
	28-30.5	53.5	<1	3.93	0.051	8.99	0.437	0.006
77-G-13, Station 21	0-1	66.4	3.4	4.08	0.144	7.80	0.523	0.018
Box Core 1	2-3	58.4	2.3	4.42	0.092	9.05	0.488	0.010
28°46.7'N, 89°36.5'W	4-5	53.9	2.1	4.35	0.075	8.00	0.544	0.009
230 m, depth	6-7	51.5	2.1	4.26	0.067	9.63	0.442	0.007
Mississippi Delta	8-9	51.6	1.6	4.04	0.061	8.45	0.478	0.007
	10-11	52.3	1.7	4.17	0.060	9.74	0.428	0.006
	12-13	53.9	1.7	4.27	0.059	9.74	0.438	0.006
	14-15	53.6	1.9	4.17	0.057	9.53	0.438	0.006
	16-17	54.9	1.7	4.26	0.056	9.84	0.433	0.006
	18-19	52.9	1.7	4.20	0.055	9.67	0.434	0.006
	20-21	54.2	1.7	4.12	0.054	9.67	0.426	0.006
	22-23	51.1	1.6	4.07	0.054	9.62	0.423	0.006
	24-25	44.9	1.5	3.95	0.056	9.40	0.420	0.006
76-G-11, Station 10	0-1	74.8	14.2	9.14	0.108	1.52	5.64	0.067
Box Core 1, Subcore B	2-3	73.6	11.8	20.40	0.182	1.71	5.50	0.049
28°37.2'N, 89°33.5'W	4-5	73.4	12.1	7.65	0.070	1.67	2.08	0.019
110 m, depth	6-7	66.5	12.2	10.80	0.090	2.74	3.94	0.033
Mississippi Delta	8-9	61.5	11.[illegible]	7.71	0.063	3.78	2.04	0.017
	11-13	73.3	9.[illegible]	9.10	0.070	2.84	3.24	0.025
	15-17	70.4	11.3	8.90	0.058	2.62	3.41	0.022
	19-22.5	73.5	11.4	9.00	0.062	2.76	3.48	0.022

*Includes top few centimeters of overlying water

Table 3. Representative Sediment Chemistry for the Mississippi Distributive Province.

	Mn, mg/g	Fe, %	$Mn/Al \times 10^{-4}$	Fe/Al
		Trefry and Presley		
Mississippi River Suspended Sediment	1300	4.61	150	.533
Nearshore Sediment	710	4.18	84	.495
Deep Gulf of Mexico Sediment	2200	4.38	240	.478
		This Work		
Mississippi River Suspended Sediment	1350	3.93	168	.489
Delta Core 78-G-8-9				
0-1 cm	2260	4.00	260	.464
9-10 cm	630	4.00	70	.445
Deep Gulf Core 78-G-8-1				
0-1 cm	1520	2.20	380	.556
8-9 cm (carbonate-rich)	1820	2.70	370	.549

depths by the same process. ^{137}Cs analyses have been done by Ronald C. Pflaum for some of the delta sediments using a GeLi detector and a 4000 channel analyzer. Pu/Cs ratios derived from those data are shown in Figure 10, also suggesting mixing of the upper part of the core although the data are more scattered. This core lies just outside the Delta Front Perimeter zone of Shoke's (1976) designation (Fig. 3) where ^{210}Pb profiles show abundant evidence of both bioturbation and slumping events.

Data from the cores from 78-G-8 station 9 and 76-G-11 station 10 are illustrated in Figures 11 and 12, respectively. Both of these cores lie within the outer delta front sediments (Shokes, 1976) described as showing sporadic evidence of bioturbation, and sedimentation rates of .5 - 1 cm/yr. We have no obvious explanation for why the Pu profile of core 10 is so different from the other two. That core was taken near the Mississippi trough, a feature of the shelf formed during the last glacial epoch that is known to funnel river sediment to the deep Gulf. The ^{210}Pb data in Figure 12 have not been corrected for ^{226}Ra parent, and Pb data on the other samples are now being collected. If the ^{226}Ra is assumed to constant with depth, a sedimentation rate of .8 cm/y is derived for the upper part of the core. Slumping is suggested by the abrupt change in ^{210}Pb values at 10 cm. We will direct part of our efforts during the next year toward a more detailed explanation of the individual profiles. Note that the Fe/Al and Mn/Al profiles fail to parallel the Pu versus depth profiles in these cores also.

The total inventories of Pu in the Gulf of Mexico cores is given in Table 4. The average predicted fallout of Pu for different parts of the Gulf is also listed. The cores from the deep and intermediate depths of the Gulf of Mexico all contain considerably less than 100% of the predicted amount (Cores 1, 2, 3, 4, 6, and 7, Table 4). The cores of delta sediments analyzed so far contain 48 to 745% of the predicted fallout inventory. Clearly

Table 4

Plutonium Inventory for the Gulf of Mexico

Station & Location	Water Depth m	Core Length cm	Measured Sediment Inventory dpm/cm^2	Predicted Fallout Inventory dpm/cm^2	% Fallout Pu Accounted For
78-G-8, Station 1 23°43.9'N, 92°28.0'W Sigsbee Knolls	3402	22	0.027	0.17	16
78-G-8, Station 2 23°57.1N, 92°19.9'W Abyssal Plain	3649	17	0.030	0.17	18
78-G-8, Station 4 26°34.0'N, 89°11.3'W	2744	22	0.041	0.25	16
78-G-8, Station 6 27°57.5'N, 88°47.7'W	1701	22	0.030	0.31	10
78-G-8, Station 7 28°21.6N, 89°09.0'W	786	32	0.080	0.33	24
76-G-11, Station 10 28°37.2'N, 89°335'W Mississippi Delta	110	22.5	0.16	0.33	48
78-G-8, Station 8 28°32.1'N, 89°17.7'W Mississippi Delta	320	28	1.39	0.33	421
78-G-8, Station 9 28°44.0'N, 89°25.9'W Mississippi Delta	106	30	2.46	0.33	745

sedimentary and/or geochemical processes are affecting the distribution of fallout Pu in the Gulf of Mexico.

There are several possible reasons for the non-deposition of fallout Pu in deep Gulf of Mexico sediments. Inventories low compared to predicted values are common (eg: Livingston and Bowen, 1979). They are ordinarily interpreted to mean that much of the Pu remains in solution in the ocean, or is associated with particles so small that the residence time in the water column is quite long.

The deep Gulf of Mexico cores analyzed in this study lie within the part of the Gulf commonly traversed by the Loop Current (El-Sayed et al, 1972), a part of the Gulf Stream which completely dominates the oceanography of the eastern Gulf of Mexico. The volume of water flowing through the Gulf in this current amounts to 800 times the amount added by annual runoff. The current which enters the Gulf at the Yucatan Straits arrives from low latitude regions characterized by minimal Pu fallout (Hardy, 1974). If the residence time of the Loop Current water in the Gulf of Mexico is short with respect to the deposition rates for particles, the Pu fallout arriving on the surface of the ocean in the Gulf of Mexico will quickly be removed from the area in the current. This process, operating over the entire time of fallout delivery of Pu could contribute to the low inventories observed in the deep Gulf of Mexico sediments. If this is the case, sediments from the western Gulf of Mexico may show higher average inventories of Pu, as the residence time of water in the western Gulf is thought to be about 100 years (El-Sayed et al, 1972).

The low Pu inventories in deep water sediments is in striking contrast to the inventories of the Mississippi Delta sediment (cores 8, 9, and 10, Table 4). The shallow water cores contain from 48 to 745% of the predicted fallout inventories. However, it should be noted that the sedimentary process

in rivers and estuaries commonly cause patchy distribution of fallout Pu inventories in bottom sediments. Simpson et al., (1976) have found evidence of this type of scour and fill phenomenon in the Hudson River estuary. By far the majority of Mississippi River sediment is being deposited in its delta, so that sedimentary processes may in part explain the differences in the observed inventories.

The really anomalous feature of the delta sediments is the observed high concentrations of Pu in cores 8 and 9 and to some degree 10. (Table 1). Previous work done on this contract has established the average content of $^{239-240}$Pu in Mississippi River sediments to be 14 dpm/kg (Scott and Salter, 1978 and ORO-3852-30). Values higher than 14.9 were never observed in any bottom or suspended sediments from the Mississippi River or any of its tributaries sampled for this project. The core top values for cores 8 and 9 are 90 to 100 dpm/kg, a factor of 6 to 7 higher than the average content of river suspended sediments. The core top values for core 10 is also high with respect to river sediments, having a value of 24-25 dpm/kg $^{239-240}$Pu. The 0-1 cm interval from 79-L-316 station 3 has been analyzed and has 27 dpm/kg $^{239-240}$Pu.

It is critically important to our understanding of the geochemical behavior of Pu to explain the high concentrations found in the nearshore sediments. Several explanations can be hypothesized: 1. Plutonium in solution in river water precipitates in the estuarine mixing zone and increases the content of Pu in the particulate phase. This suggestion can be tested by means of data collected last year on this project (ORO-3852-30). Analyses of Pu in Mississippi River suspended sediment for station 24 was 4.0±.1 dpm/$10^3\ell$ and on suspended sediment plus water was 5.4± 0.2 dpm/$10^3\ell$. The difference, 1.4± 0.2 dpm/$10^3\ell$ can be taken as an estimate of the amount of dissolved Pu delivered by the river. The error in this number is probably considerably larger than the 1σ counting statistics value listed. Nevertheless

it yields a K_D for Pu on river sediment (.295 g/ℓ) of about 10^4 which is slightly lower than the expected value of 10^5. Using the value of 1.4± 0.2 dpm/10^3ℓ one can quickly estimate that the sediment load of Pu in the river is accompanied by about 25% more Pu in the dissolved state. Precipitation of dissolved Pu in river water therefore could not account for delta sediment concentrations of 100 dpm/kg.

2. Plutonium is being scavenged from the open Gulf water, either in dissolved form or on particles, and is being preferentially deposited in the delta sediments. This suggestion is most attractive because it could easily provide enough fallout Pu to the delta sediments. The matter of transferring the material horizontally to the nearshore area is not particularly problematic. Horizonatal eddy diffusion coefficients for ocean water are 10^6 - 10^{10} cm^2/sec (Lerman, 1979).

In order for dissolved Pu to be scavenged by delta sediments, it would probably be necessary to have a change in its oxidation state to a more reduced form, which is consistent with the description of reducing conditions in these sediments by Trefry and Presley (1976). Reviews of the environmental chemistry of Pu have recently been published by Cleveland (1979) and by Aston (1980). Pu can occur in nature in several different oxidation states: +3, +4, +5, +6. The more reduced forms, +3 and +4, are generally believed to be least soluble in the environment, so that reduction of Pu to those states would tend to immobilize it in the sediment phase. Nelson and Lovett (1978) have published evidence that the stable oxidation states of Pu in sea water are +5 and +6. Cleveland (1979) points out that the least hydrolyzed form of Pu is +5, and it seems likely that it would tend to be more stable in solution than would the more hydrolyzed species. Bondietti and Trabalka (1980) have recently described evidence suggesting that Pu +5 is the dominant oxidized state in an alkaline lake. Aston has suggested the Pu species present in sea water is likely to be PuO_2CO_3OH. It seems possible, by analogy with U^{+6} and U^{+4}

chemistry that reduction of dissolved Pu in sea water might cause its removal to the reduced sediments. (The removal of sea water U to delta sediments is described in another section of this report). Alternatively the precipitation of Fe and Mn oxyhydroxides and organic matter that occur when river water mixes with the ocean (Sholkovitz, 1976) might serve to scavenge significant amount of Pu from sea water.

The chemistry of ^{210}Pb and ^{230}Th in Mississippi delta sediments also show unexplained "excess" concentrations. Similar observations for ^{210}Pb in coastal sediments have been made by Bruland (1974) and Shokes (1976) and were attributed to shoreward transport of particles that had scavenged the highly reactive Pb from the water. The amounts present in delta sediments are in excess of the theoretical amounts for the ambient water depth for ^{230}Th and for water plus atmosphere for ^{210}Pb. The high K_D ($\sim 10^5$) commonly observed for Pu in the environment suggests that it too may be transported shoreward by particles. There is no upwelling in this portion of the Gulf of Mexico, prevailing westerly winds during part of the year create a shoreward geostrophic flow.

3. A third suggestion that might be made to explain the high Pu concentrations in Mississippi River Delta sediments is that river-borne Pu is dissolved in the delta sediments and diffuses upwards to be reprecipitated at higher concentrations in the top part of the sediment. There is no consensus among scientists studying Pu in the environment concerning the extent to which the element can undergo dissolution and chemical diffusion once it is in the sediments. Livingston and Bowen (1975), Bowen et al. (1976) and Livingston and Bowen (1979) have described evidence for Pu migration in sediments. The migration was linked by Livingston and Bowen (1979) to sediments in which Fe is being remobilized as it is to a degree in the Mississippi Delta sediments. But the element commonly suggested as a chemical analogue of the Pu associated

with the solid phases is Th^{+4} (eg Bondietti et al. 1976), an element that is notoriously insoluble, and not readily mobilized in the environment. This factor was brought up in discussion following the presentation of Livingston and Bowen (1975) and was mentioned by Bondietti et al. (1976).

In order for Pu deposited in a marine sediment to be remobilized it would be necessary to have a change in its oxidation state to a more soluble form, and/or the presence of a significant amount of a ligand capable of complexing Pu in a soluble form. A number of environmentally important ligands are known to complex Pu, including CO_3^{-2}, PO_4^{-3}, and some organic compounds (Cleveland, 1979; Aston, 1980). However, there is considerable uncertainty about the correct values of the stability constants for these complexes, making it quite difficult to predict the behavior of Pu in a geochemically complex system such as the Mississippi River delta.

The association of Pu with soil organic matter has been investigated by several workers, including Bondietti et al, (1976), Cleveland (1979), and Nishita and Haug (1979). Both fulvic and humic substances appear to be able to complex Pu to a significant degree, and Nishita and Haug state that the complexes may mobilize Pu in the environment. But Cleveland (1979) discounts complexing by these substances as being an important means of solubilizing Pu. He cites evidence from his own work and that of Bondietti et al (1976) suggesting that Pu can actually be fixed in the soil by association with solid organic matter which is itself insoluble under most circumstances. It should be noted that Nishita and Haug worked with Pu which they added to the samples in the laboratory in soluble form shortly before the experiments. Cleveland's studies involved environmental samples contaminated accidentally years before the experiment, and thus might be more representative of the behavior of Pu now found in soil and sediment samples.

Several studies have indicated an association of Pu with solid hydrous oxide phases in the environment. Edgington et al (1976 a; b) have shown that much of the Pu in Lake Michigan sediment is extractable with citrate-dithionite leach, which removes Fe and Mn oxides. Means et al (1979) have concluded that the Mn oxides are more important the Fe oxyhydroxides in controlling Pu distribution in the solid phases. Previous work on river sediments for this contract (Scott and Salter, ORO-3852-30) has shown an association of Pu in river suspended sediments with Mn and Fe (Figs. 14 and 15). However, in the delta sediments analyzed for this report, remobilization of Fe and Mn was not accompanied by a parallel remobilization and diffusion of plutonium, as discussed above.

The effects of adsorption on the diffusion of dissolved material in sediment pore water has been studied by Schink and Guinasso (1978). An element like Pu with a K_D of 10^5 (gm Pu/gm sediment ÷ gm Pu/gm water) would have an effective diffusion coefficient of about $D = 10^{-10}$ cm^2/sec. The flux of Pu in the sediment would be determined by the diffusion coefficient and the chemical potential gradient in the pore water. In Irish Sea sediments with extremely high Pu, Heatherington (1978) has found the K_D of Pu on the sediment to be about 10^5, as in most other natural environments. At least in that instance no unusual mobility of Pu was noted. Consequently we expect the available chemical potential gradient for Pu in Mississippi Delta sediments to be quite small. The amount of migration that could have taken place in the last 30 years at a D of 10^{-10} cm^2/sec would be minimal. For this reason we favor explanation number 2, namely that the high concentrations of Pu in these sediments are being derived from open Gulf of Mexico waters.

In order to understand the distribution of Pu in Gulf of Mexico sediments we have undertaken a series of leaching studies of river sediment, delta

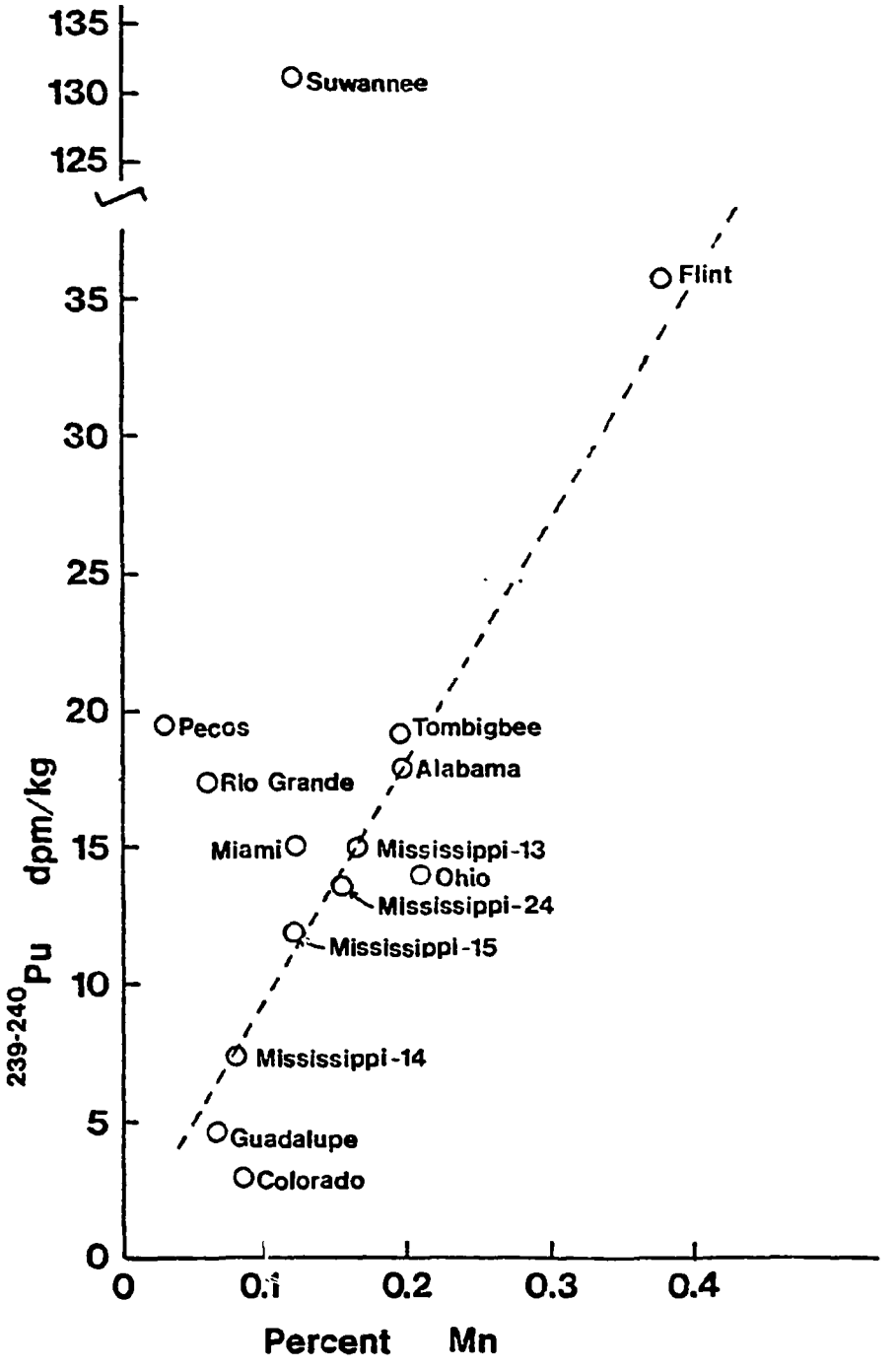

Figure 14. Plot of $^{239-240}Pu$ versus percent Mn in river suspended sediments.

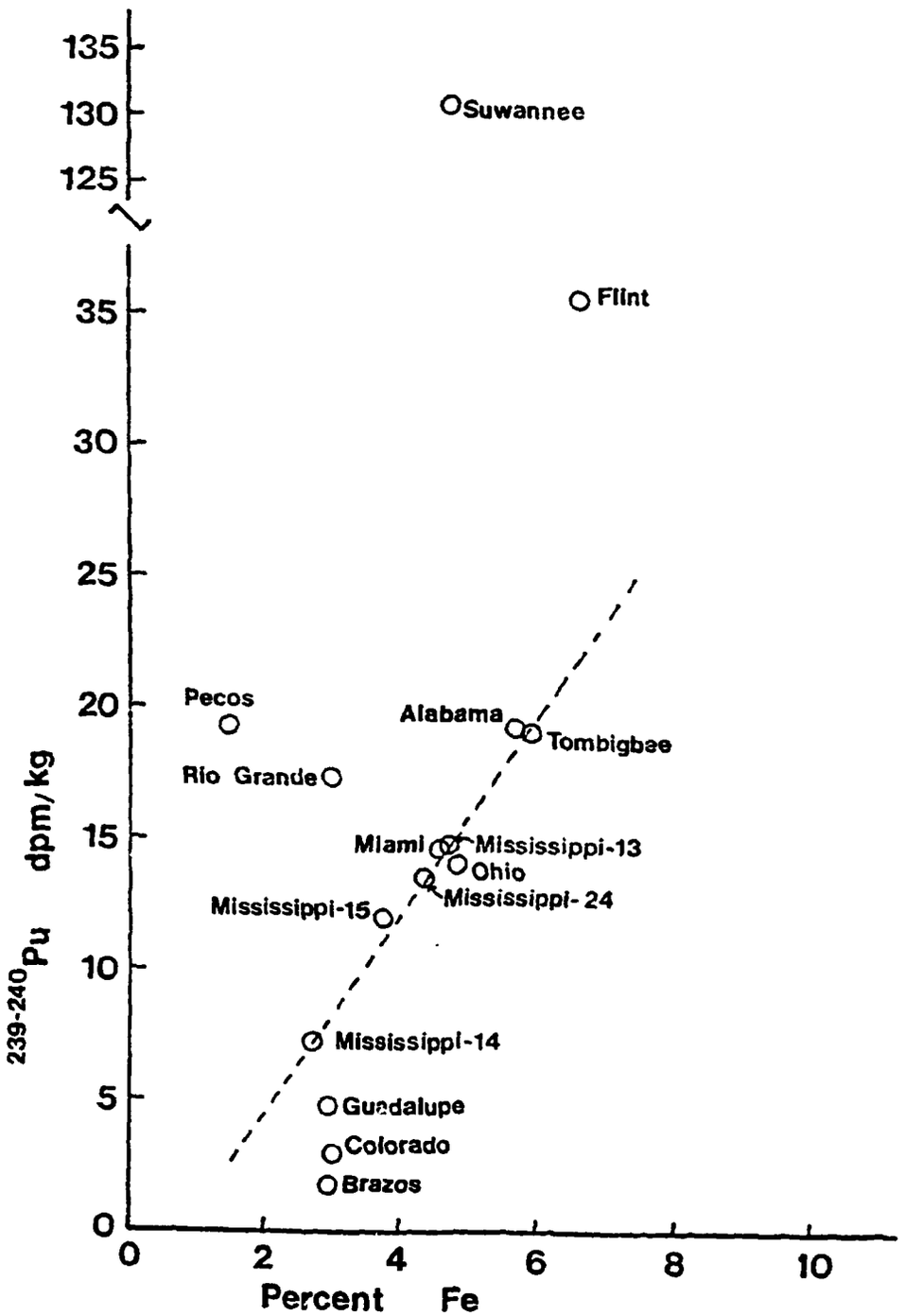

Figure 15. Plot of $^{239-240}Pu$ versus percent Fe in river suspended sediments.

sediments and marine sediments to determine the phases in each sediment type with which most of the Pu seems to be associated. The leaches will separate exchangeable ions, organic matter, Mn oxides, amorphous Fe hydroxides, crystalline Fe oxides and silicate residue. This work is not yet complete, and is described in another section of this progress report.

As pointed out by Trefry and Presley (1976), extensive loss of Mn from riverine sediment occurs in the reducing environment of the Mississippi Delta. The Mn diffuses out of delta sediments into the overlying water to be deposited ultimately in the deep Gulf sediments. Sediments in the nearshore parts of the delta exhibit this Mn loss starting at the very top of the sediment column, with no Mn-rich oxidizing layer at the surface. Because of the apparent association of Pu with Mn oxides in soils and sediments, this area seemed an interesting one for studying geochemical behavior of Pu. It should be noted that the remobilization of Fe from these sediments is minimal compared to that of Mn. Table 3 shows a comparison of the Fe, Mn, and Al data in this study with that of Trefry and Presley (1976). Clearly the data are in good agreement. None of our cores analyzed to date are in the Inner Delta area where the Mn-rich surface layer is absent. Samples taken on cruise 79-L-316 represent this area and are presently being analyzed. Much of the work proposed for next year will include detailed analyses of sediment samples from the inner part of the Mississippi Delta.

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