URANIUM AND THORIUM SERIES ISOTOPES IN NEARSHORE MARINE SEDIMENTS

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Measurements of U and Th series isotopes have been made on sediments most often as a means of estimating sediment accumulation rates. Therefore data are available for long half-life isotopes such as ^{230}Th and ^{231}Pa on slowly depositing deep-sea sediments, and for the short half-life isotopes such as ^{228}Th, ^{234}Th, and ^{210}Pb mostly on rapidly accumulating coastal sediment. ^{210}Pb analyses of Mississippi Delta sediments have been used by Shokes (1976) to estimate sedimentation rates and bioturbation rates for the delta. We are also in the process of measuring ^{210}Pb on samples of Gulf of Mexico sediments collected for this study in order to improve our ability to interpret the Pu profiles in the Gulf.

Studies of U and Th series nuclides in sediments of rivers entering the Gulf have been described in a previous section of this progress report. The isotopic decay series are out of equilibrium at several steps in the series. The activity ratio of $^{234}U/^{238}U$ is greater than 1 in sediment and water samples in a few cases, and the $^{230}Th/^{234}U$ ratio is greater than 1 in most instances. In the case of the Mississippi River suspended sediment, an average of 0.93 dpm/gm ^{230}Th is present in excess of the amount of its parent ^{234}U. This excess ^{230}Th clearly must be added to the Gulf of Mexico by the river. The Gulf of Mexico sediments have been reported by Sackett et al. (1973) to have unusually high U concentrations. We have therefore begun a study of U, Th, Pa, Ra, and Pb isotopes in the sediments of this system, including the nearshore marine area of the Mississippi River Delta. The preliminary results are discussed in this report.

Uranium and Th isotope analyses have been completed on two cores from the delta, 78-G-8, Stations 8 and 9 (Table 1; Figure 1). Both cores show disequilibrium among the U and Th isotopes as well as evidence for chemical reactions involving the U in the sediment.

By far the dominant source of sediment to this part of the Gulf of Mexico is the suspended sediment carried by the Mississippi River. An "average" Mississippi River suspended sediment sample contains the following: 2.74 ppm U, $^{234}U/^{238}U = 1.02 \pm .07$; 11.3 ppm Th; $^{230}Th = 2.90$ dpm/gm, $^{230}Th_{xs} = 0.93$ dpm/gm. These values are based on the Mississippi River suspended sediment samples analyzed for this project. Comparison of average river sediment to the marine sediment values in Table 1 shows some obvious differences. The uranium content of the 0 - 2 cm interval of marine sediment cores is the same or slightly less than average river sediment. Below that depth both cores show significant enrichment of U with depth, up to 4.33 ppm in the 102 - 106 cm interval of the gravity core from Station 8 (Figure 2). These sediments have been shown to be reducing below the top few centimeters, and to have undergone remobilization of Fe and Mn. The enrichment of U in the cores is probably related to the process described by Veeh (1967) in which sea water U is reduced to its relatively insoluble +4 state by organic-rich, reducing, nearshore sediments. In the case of the delta sediments the reducing conditions are brought about by the rapid sedimentation rate, which quickly removes organic matter from contact with oxygenated sea water. The organic matter content of the sediments is not especially high, about 0.5% (Shokes, 1976).

According to this interpretation the incorporation of sea water uranium should be reflected by an increase in the $^{234}U/^{238}U$ activity ratio, because average sea water U has a ratio of 1.14 (Ku et al., 1977). It

Table 1

Uranium and Thorium Isotopic Analyses of Mississippi Delta Sediments

	Interval cm	[illegible]	U ppm	Th ppm	^{234}U dpm/g	^{238}U dpm/g	^{232}Th dpm/g	^{230}Th dpm/g	$\frac{^{234}U}{^{238}U}$	$\frac{^{230}Th}{^{232}Th}$	$\frac{^{230}Th}{^{234}U}$	^{230}Th Excess
75-G-8, Station 9 [illegible] m, depth	0 - 2	75.97	2.87 ± .03	18.45 ± .16	2.12 ± .02	1.85 ± .02	4.54 ± .04	5.11 ± .04	0.89 ± .01	1.13 ± .01	2.72 ± .04	3.23 ± .05
	8 - 10	53.49	3.46 ± .04	10.88 ± .30	2.56 ± .03	2.34 ± .03	4.64 ± .07	5.19 ± .08	0.91 ± .02	1.12 ± .02	2.22 ± .04	2.85 ± .09
	22 - 26	51.45	3.16 ± .09	15.53 ± .29	2.33 ± .07	2.28 ± .06	3.82 ± .07	3.94 ± .07	0.98 ± .04	1.03 ± .03	1.73 ± .06	1.66 ± .09
	38 - 42	51.34	3.43 ± .06	13.79 ± .12	2.53 ± .04	2.48 ± .04	3.37 ± .03	3.54 ± .03	0.90 ± .02	1.05 ± .01	1.55 ± .03	1.26 ± .05
	54 - 58	47.09	3.16 ± .06	12.80 ± .15	2.33 ± .04	2.14 ± .04	3.15 ± .04	3.37 ± .04	0.92 ± .02	1.07 ± .02	1.57 ± .03	1.23 ± .06
	74 - 78	49.48	3.22 ± .06	13.96 ± .14	2.38 ± .05	2.10 ± .04	3.44 ± .03	3.60 ± .04	0.88 ± .03	1.05 ± .01	1.72 ± .04	1.51 ± .06
	102 - 106	50.60	3.07 ± .12	13.00 ± .09	2.27 ± .09	2.18 ± .09	3.20 ± .02	3.32 ± .02	0.96 ± .05	1.04 ± .01	1.52 ± .06	1.14 ± .11
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72-G-8, Station 8 [illegible] m, depth	0 - 2	88.19	2.56 ± .07	9.32 ± .30	1.89 ± .05	1.75 ± .05	2.23 ± .07	2.69 ± .08	0.93 ± .03	1.17 ± .05	1.54 ± .06	0.94 ± .09
	8 - 10	56.21	3.26 ± .08	14.50 ± .26	2.41 ± .05	2.29 ± .06	3.37 ± .06	3.81 ± .07	0.95 ± .03	1.07 ± .03	1.67 ± .05	1.52 ± .09
	22 - 26	53.29	4.00 ± .06	11.62 ± .39	2.96 ± .05	2.82 ± .05	2.86 ± .10	3.25 ± .10	0.95 ± .02	1.14 ± .05	1.15 ± .04	0.43 ± .12
	38 - 42	57.25	3.61 ± .08	11.44 ± .70	2.66 ± .06	2.55 ± .05	2.81 ± .18	2.77 ± .16	0.96 ± .03	0.98 ± .08	1.09 ± .08	0.22 ± .20
	54 - 58	57.90	4.05 ± .07	13.13 ± .19	2.99 ± .06	2.91 ± .05	3.23 ± .05	3.45 ± .05	0.97 ± .02	1.07 ± .02	1.18 ± .03	0.54 ± .07
	74 - 78	54.99	3.98 ± .06	11.61 ± .11	2.94 ± .05	2.80 ± .04	2.66 ± .03	3.14 ± .03	0.95 ± .02	1.10 ± .01	1.12 ± .02	0.34 ± .05
	102 - 106	54.30	4.33 ± .07	11.19 ± .20	3.20 ± .05	3.04 ± .05	2.75 ± .05	3.01 ± .05	0.95 ± .02	1.09 ± .03	0.99 ± .02	0.03 ± .07
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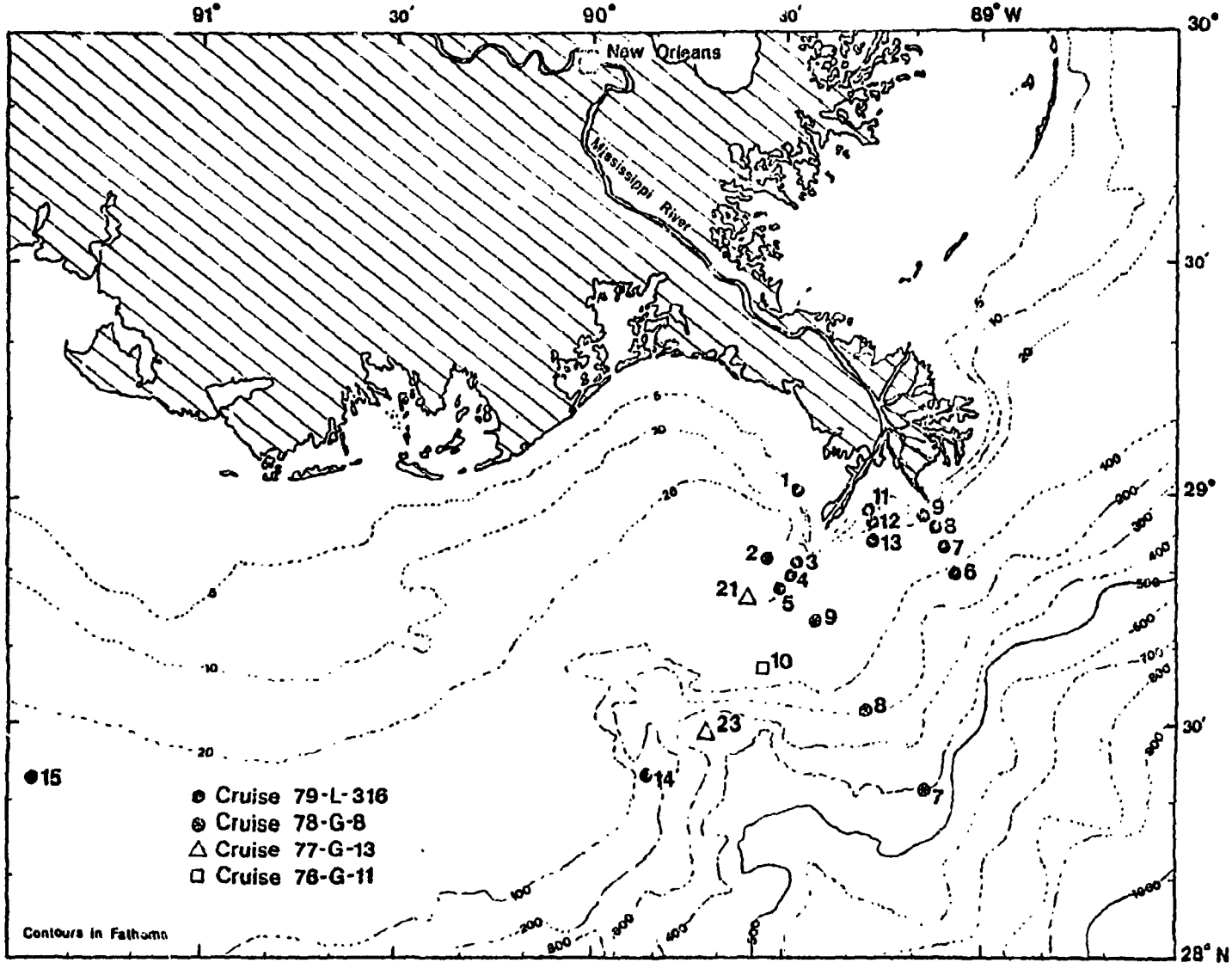

Figure 1. Location of sediment cores analyzed.

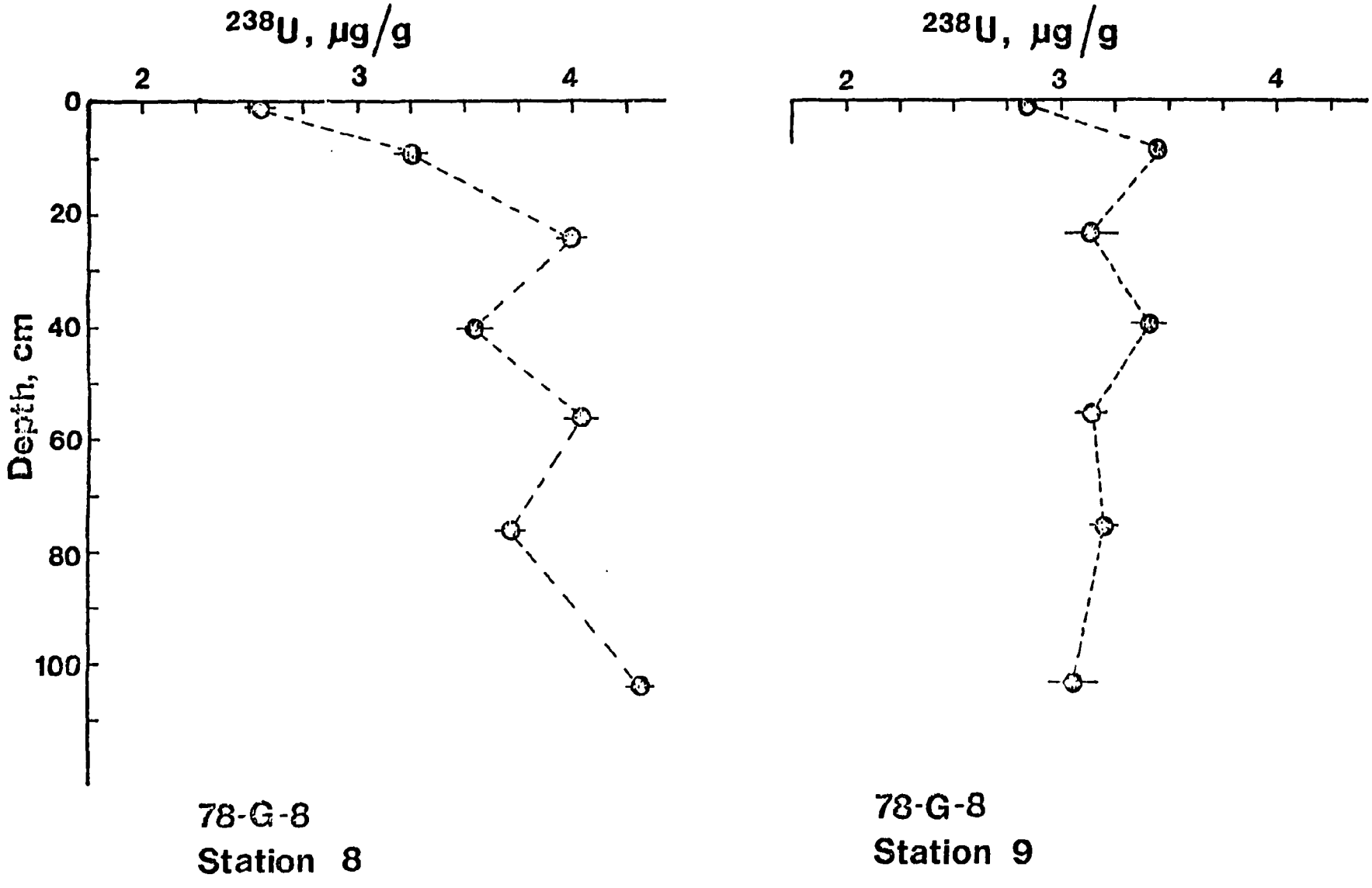

Figure 2. Distribution of uranium versus depth in cores.

is puzzling to note that this does not seem to be the case. As an extreme example, the 102 - 106 cm layer of the Station 8 core (Table 1) has 1.59 µg/g more U than average river sediment. If this were added with a sea water activity ratio of 1.14, the resulting ratio should be 1.06. Instead, the $^{234}U/^{238}U$ activity ratio is 0.95 $\pm$ .02. Clearly the behavior of U in this system is not so simple as hypothesized above.

Aller and Cochran (1976) and Thompson et al. (1975) have also noted mobilization of U in nearshore sediments of Long Island Sound. They observe an apparent U loss from the core tops, and suggest that it is related to the activities of benthic organisms. These organisms irrigate the bottom sediments to provide an oxygen supply for themselves in reducing sediments. Luedtke and Bender (1979) have shown that such organisms transfer ^{22}Na at rates greater than possible by chemical diffusion. The irrigation may cause or enhance removal of U from the core top and addition of U in deeper parts of the sediment. This activity may be seasonally variable, and could result in complex patterns of depletion and enrichment (Aller and Cochran, 1976).

An examination of $^{230}Th/^{234}U$ activity ratios in the delta sediments also shows discrepancies. The "average" unsupported excess ^{230}Th in river sediment is exceeded in the delta sediments, even though the sediments have apparently been enriched in U in the marine environment. Figure 3 is a profile of ^{230}Th excess in Station 9 sediments versus depth. The stippled area represents the 0.93 dpm/gm ^{230}Th excess inherited from river sediment. If this amount of ^{230}Th is omitted, a total marine ^{230}Th excess of 57.8 dpm/cm^2 may be calculated, assuming a dry bulk density of 0.9 gm/cm^3. The water depth at this station was 106 m, so the total ^{230}Th in equilibrium with the ^{234}U in a 1 cm^2 column of water would be 29 dpm,

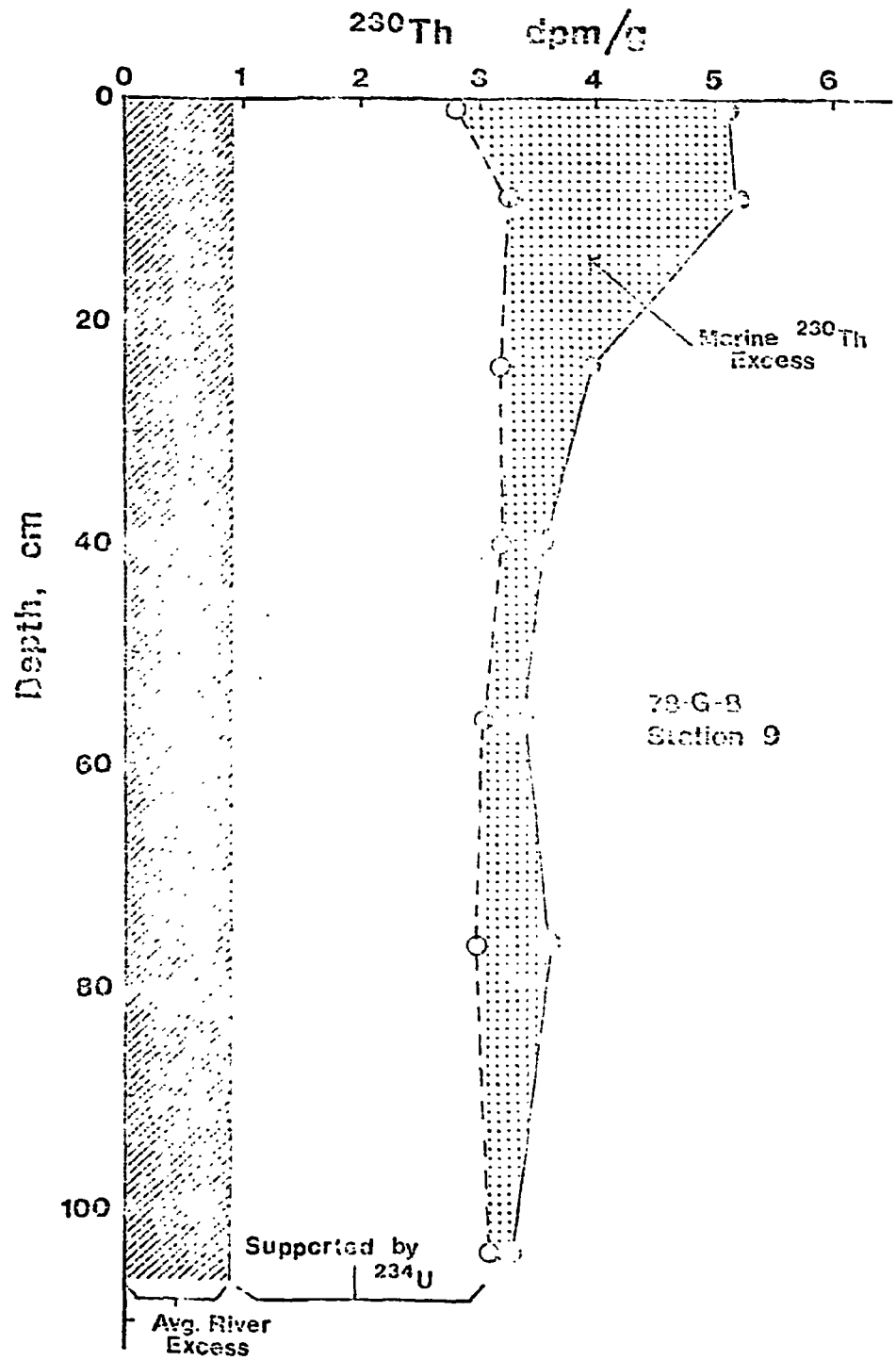

Figure 3. ^{230}Th excess versus depth for core 9, 78-G-8.

presumably entirely removed to the sediment. It is tempting to suggest that more "marine" ^{230}Th has been transported to these sediments than the amount generated by U in the overlying water. If so, the transport would probably involve shoreward movement of ^{230}Th-rich particles, as proposed by Bruland (1974) and Shokes (1976) to explain higher than expected ^{210}Pb values in nearshore sediments.

The ^{230}Th content of the sediment from Station 8 complicates the interpretation given above. The ^{230}Th distribution with depth in this core (Figure 4) shows very little excess ^{230}Th, and virtually no unexplained "marine" excess ^{230}Th. This situation is caused in part by the U enrichment of the sediment at this site, which directly affects the calculation of ^{230}Th excess. However, it is also apparent from Table 1 that the Station 9 sediment is richer in both ^{230}Th and ^{232}Th than is the sediment from Station 8. Scott (1968) has shown that although the difference in U in different size fractions of river sediments is slight, the difference in Th content may be significant. It is possible that the Station 9 sediments show an apparent Th enrichment because of size fractionation. The correlation between ^{230}Th and ^{232}Th was also seen in size fractionated river sediments, and was attributed to remobilization of both Th isotopes in the soil profiles during weathering processes. A strong positive correlation of Th/U weight ratios with $^{230}Th/^{234}U$ activity ratios is shown in Figure 5. Similar relationships were shown for river sediments (Scott, 1968) and for soils (Rosholt et al., 1966). It is probably that the delta sediments have inherited this trend in their land-derived constituents. Addition of U to the samples would move the data points toward the origin. Removal of U or addition of Th (or enhancement of Th content by size fractionation) would move the data points away from the

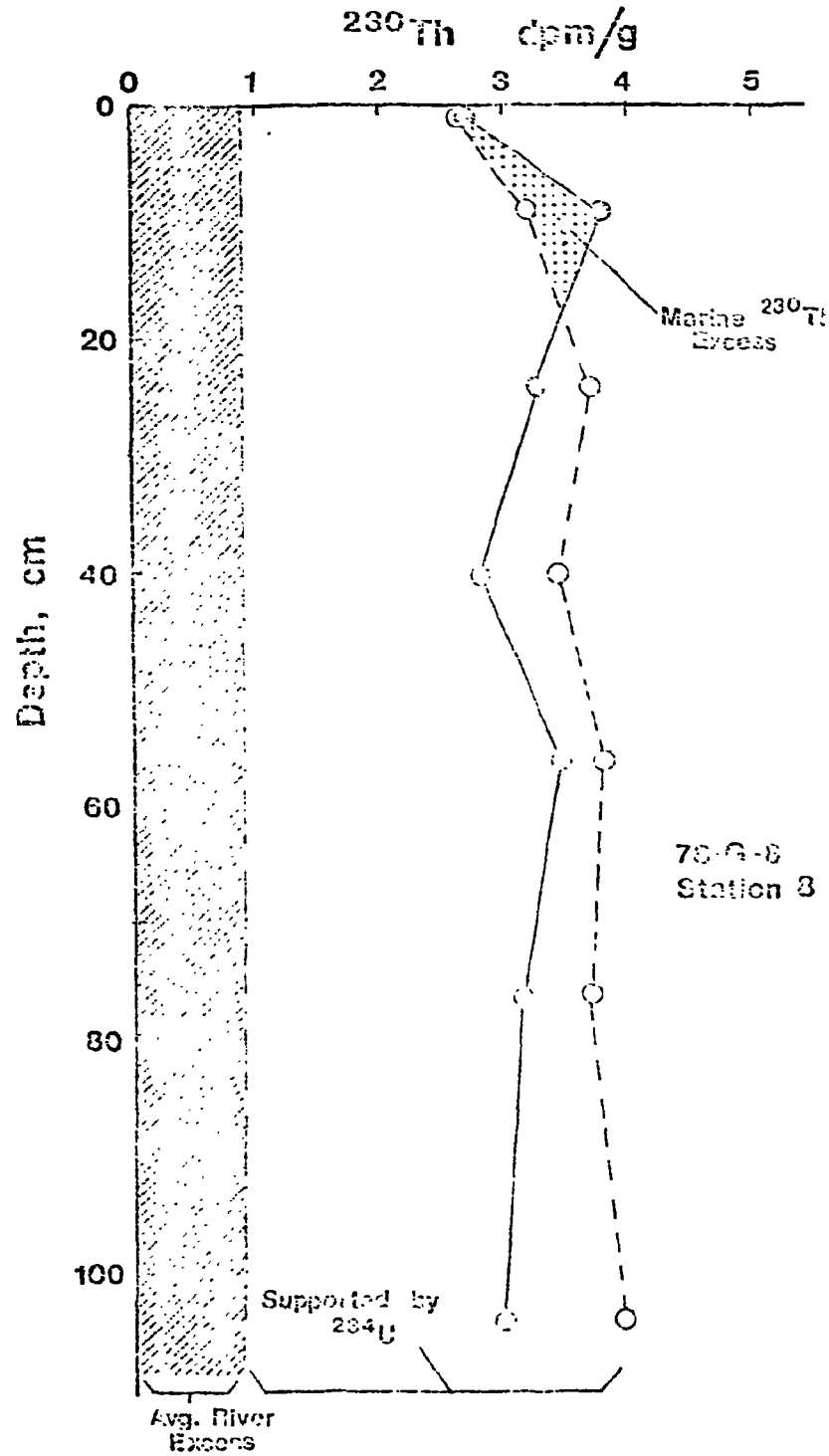

Figure 4. ^{230}Th excess versus depth for core 8, 78-G-8.

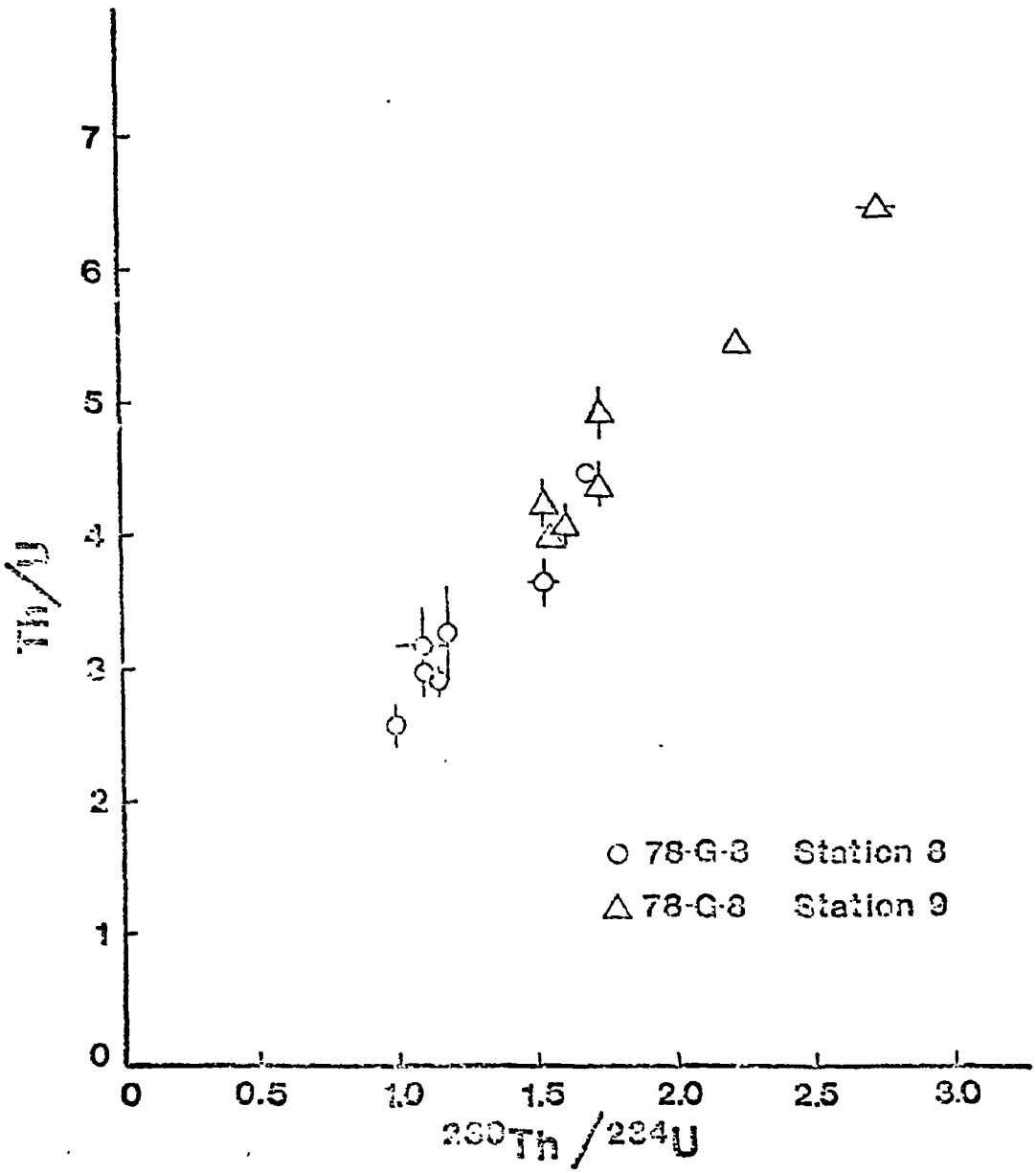

Figure 5. Plot of Th/U weight ratios versus $^{230}Th/^{234}U$ activity ratios for cores 8 and 9, 78-G-8.

origin along the same line. We will continue our studies of distribution of U and Th series nuclides in marine sediments during the coming year.

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