Distribution, Regional Variation, and Geochemical Coherence of Selected Elements in the Sediments of the Central Gulf of Mexico

GEOLOGICAL SURVEY PROFESSIONAL PAPER 928

Distribution, Regional Variation, and Geochemical Coherence of Selected Elements in the Sediments of the Central Gulf of Mexico

By CHARLES W. HOLMES

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An evaluation of semiquantitative
data used in the determination
of trace-element distribution
and abundances in marine sediments

UNITED STATES DEPARTMENT OF THE INTERIOR

THOMAS S. KLEPPE, *Secretary*

GEOLOGICAL SURVEY

V. E. McKelvey, *Director*

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METRIC-ENGLISH EQUIVALENTS

Metric unit		English equivalent
Length		
millimetre (mm)	= 0.03937	inch (in)
metre (m)	= 3.28	feet (ft)
kilometre (km)	= .62	mile (mi)
Area		
square metre (m²)	= 10.76	square feet (ft²)
square kilometre (km²)	= .386	square mile (mi²)
hectare (ha)	= 2.47	acres
Volume		
cubic centimetre (cm³)	= 0.061	cubic inch (in³)
litre (l)	= 61.03	cubic inches
cubic metre (m³)	= 35.31	cubic feet (ft³)
cubic metre	= .00081	acre-foot (acre-ft)
cubic hectometre (hm³)	= 810.7	acre-feet
litre	= 2.113	pints (pt)
litre	= 1.06	quarts (qt)
litre	= .26	gallon (gal)
cubic metre	= .00026	million gallons (Mgal or 10⁶ gal)
cubic metre	= 6.290	barrels (bbl) (1 bbl=42 gal)
Weight		
gram (g)	= 0.035	ounce, avoirdupois (oz avdp)
gram	= .0022	pound, avoirdupois (lb avdp)
tonne (t)	= 1.1	tons, short (2,000 lb)
tonne	= .98	ton, long (2,240 lb)
Specific combinations		
kilogram per square centimetre (kg/cm²)	= 0.96	atmosphere (atm)
kilogram per square centimetre	= .98	bar (0.9869 atm)
cubic metre per second (m³/s)	= 35.3	cubic feet per second (ft³/s)

Metric unit		English equivalent
Specific combinations—Continued		
litre per second (l/s)	= .0353	cubic foot per second
cubic metre per second per square kilometre [(m³/s)/km²]	= 91.47	cubic feet per second per square mile [(ft³/s)/mi²]
metre per day (m/d)	= 3.28	feet per day (hydraulic conductivity) (ft/d)
metre per kilometre (m/km)	= 5.28	feet per mile (ft/mi)
kilometre per hour (km/h)	= .9113	foot per second (ft/s)
metre per second (m/s)	= 3.28	feet per second
metre squared per day (m²/d)	= 10.764	feet squared per day (ft²/d) (transmissivity)
cubic metre per second (m³/s)	= 22.826	million gallons per day (Mgal/d)
cubic metre per minute (m³/min)	= 264.2	gallons per minute (gal/min)
litre per second (l/s)	= 15.85	gallons per minute
litre per second per metre [(l/s)/m]	= 4.83	gallons per minute per foot [(gal/min)/ft]
kilometre per hour (km/h)	= .62	mile per hour (mi/h)
metre per second (m/s)	= 2.237	miles per hour
gram per cubic centimetre (g/cm³)	= 62.43	pounds per cubic foot (lb/ft³)
gram per square centimetre (g/cm²)	= 2.048	pounds per square foot (lb/ft²)
gram per square centimetre	= .0142	pound per square inch (lb/in²)
Temperature		
degree Celsius (°C)	= 1.8	degrees Fahrenheit (°F)
degrees Celsius (temperature)	= [(1.8×°C)+32]	degrees Fahrenheit

DISTRIBUTION, REGIONAL VARIATION, AND GEOCHEMICAL COHERENCE OF SELECTED ELEMENTS IN THE SEDIMENTS OF THE CENTRAL GULF OF MEXICO

By Charles W. Holmes

ABSTRACT

A semiquantitative six-step spectrographic method was used to analyze 2,482 sediment samples from 50 piston cores, averaging 6 m in length, from the Gulf of Mexico. Of the 30 elements scanned for, 20 (B, Ba, Be, Ca, Co, Cr, Cu, Fe, La, Mg, Mn, Nb, Ni, Pb, Sc, Sr, Ti, V, Y, Zr) occurred in a sufficient number of samples for valid statistical analysis.

Paleontological studies of some cores provided a basis for determining differences between the distributions of elements in Holocene and Pleistocene sediments. The abundances of these elements as estimated for all 2,482 samples and for each age group, show significant differences for only 6 of the 20 elements. Boron, titanium, vanadium, and zirconium are more abundant in sediments of Pleistocene age, whereas calcium and strontium are more common in the Holocene sediments. These distributional differences reflect the mechanical erosion and rapid deposition of the glacial epochs of the Pleistocene and the dominant pelagic deposition of the Holocene.

A statistical measure of the geochemical coherence of the elements suggests that they fall into three geochemical groups or associations. One group, containing iron and vanadium, was associated with clay-size particles; a second group, containing calcium and strontium, was associated with the carbonate component of the sediments. The third group, containing beryllium, niobium, and lead, was seemingly unrelated to anything, possibly because its distribution is severely censored by the analytical method.

The analytical method used in this investigation permitted rapid analysis of large numbers of samples. Although the analytical resolution fails to provide definition of the chemical species, the data nevertheless provide sufficient information to aid in solving major geochemical problems.

INTRODUCTION

In 1968 the U.S. Geological Survey began a reconnaissance study of the trace-element composition of the surface and nearsurface sediments in the Gulf of Mexico. The purpose of the study is to begin to build the background of geochemical data that will provide a better knowledge of (1) the sedimentary processes by which trace elements are both dispersed and concentrated in the marine environment; (2) the mechanics and rapidity of diagenesis after deposition and burial; (3) the general crustal abundance of the elements in the recent sediments of the world's oceans, more specifically for the Gulf of Mexico; and (4) the influence of salt tectonics on geochemical cycles within the sediments. Such knowledge is essential for determining the magnitude and extent of impact of the increasingly large volumes of waste being introduced into coastal waters and for determining baselines against which increasing levels of anthropogenic pollution in sediments can be measured.

The elemental composition of the surface sediments of the continental shelf has been described in an earlier report (Holmes, 1973); the present report is based on the semiquantitative spectrographic analysis of 2,482 samples selected from 50 cores from the Gulf of Mexico. The cores were obtained during a study sponsored jointly by the U.S. Geological Survey and the U.S. Naval Oceanographic Office. The analytical data were evaluated to determine the extent that its semiquantitative nature limits its usefulness in solving geochemical problems. This was accomplished by treating the data as quantitative, and then by comparing the results of the analyses with published chemical studies.

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Siems and Gordon Day, who made the spectrographic analyses, are recognized. A special thanks is extended to A. P. Marranzino and D. J. Grimes who arranged to place a spectrograph aboard the ship, and also to Lamont Wilch and Glenn Allcott for aid in the computer analyses. The laboratory analyses were done by J. J. Dillon, C. Duerr, and Mike Dorsey.

GEOLOGIC SETTING

The Gulf of Mexico basin is almost completely surrounded by a land mass of diverse geologic history. It covers approximately 1.6 million km² and has a maximum water depth of more than 3,600 m. (See fig. 1.)

The continental interior of the United States via the Mississippi river is the major source of clastic material found in the gulf basin. This sediment covers the entire eastern portion of the basin and spreads westward onto the abyssal plain. Sediment from other river systems that border the northern gulf is deposited on the broad shelves of this region. The rivers entering the gulf along the southwestern margin of the basin contribute little sediment to the gulf basin due to their relatively small drainage basins. Significant clastic deposits are absent on exposed lands adjoining the Florida shelf and Campeche shelf; the extreme width of these shelves inhibit any contribution of noncarbonate clastic material from the Florida or Yucatan peninsulas. Davies (1968), however, has shown that the Campeche shelf may have been an important source of clastic carbonate sediment on the abyssal plain; there is no evidence, though, of any Florida shelf sediment in the basin.

Textural analyses show that the predominant sediment in the central basin of the gulf is silty clay having an average clay content of 71 percent. In the eastern gulf, a veneer of light-brown to reddish-
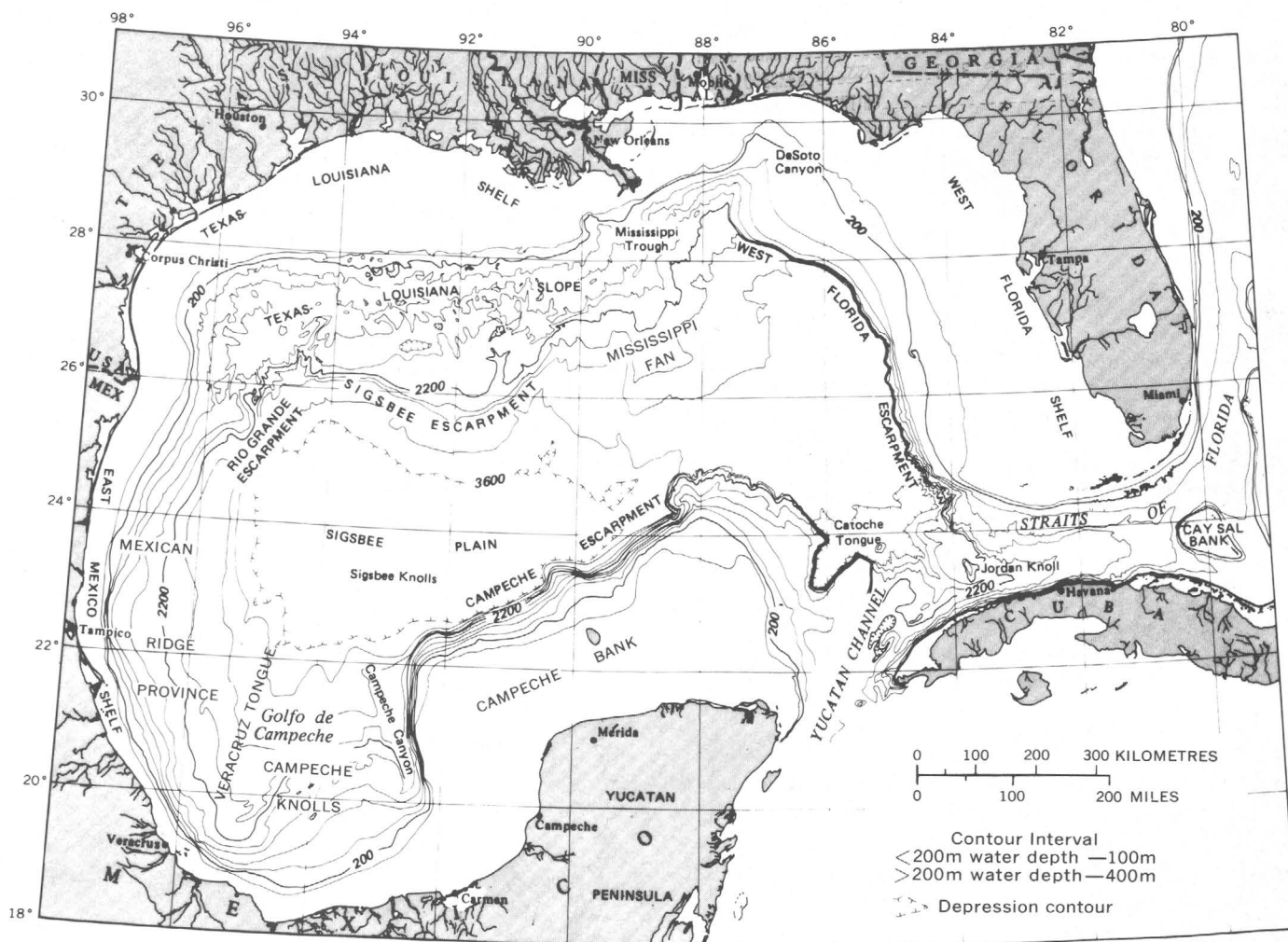
FIGURE 1.—Physiographic provinces of the Gulf of Mexico basin (from Garrison and Martin, 1973).

brown sandy clay ranging from 50 to 150 cm in thickness overlies gray silty clays. The sand-sized material is composed principally of foraminiferal tests. Cores in the western gulf exhibit layers of sand-sized carbonate detritus from Campeche Bank, volcanic ash from Mexico, and pelagic foraminiferal tests. Figure 2 is a map of the sediment distribution in the central gulf.

SAMPLING PROCEDURE

Core sites were selected to give a representative sampling of the major physiographic provinces of the gulf. These 50 cores, taken by a modified Ewing piston corer (fig. 3 and table 1), ranged in length from 16 to 1,122 cm, averaging 703 cm. Thirty-nine cores scattered throughout the basin were at least 6 m in length (fig. 4), giving a representative section of at least 6 m in each physiographic province.

After each core was taken, it was immediately split, described, photographed, and sampled. For the geochemical analyses, 1-g (wet) samples were taken every 20 cm from the center of the split core at the surface and from above and below major changes in lithologic character. This sampling procedure yielded a total of 2,482 samples.

ANALYTICAL PROCEDURE

Samples taken from the center of the split core were analyzed for 30 elements by the 6-step semi-quantitative method of Grimes and Marranzino
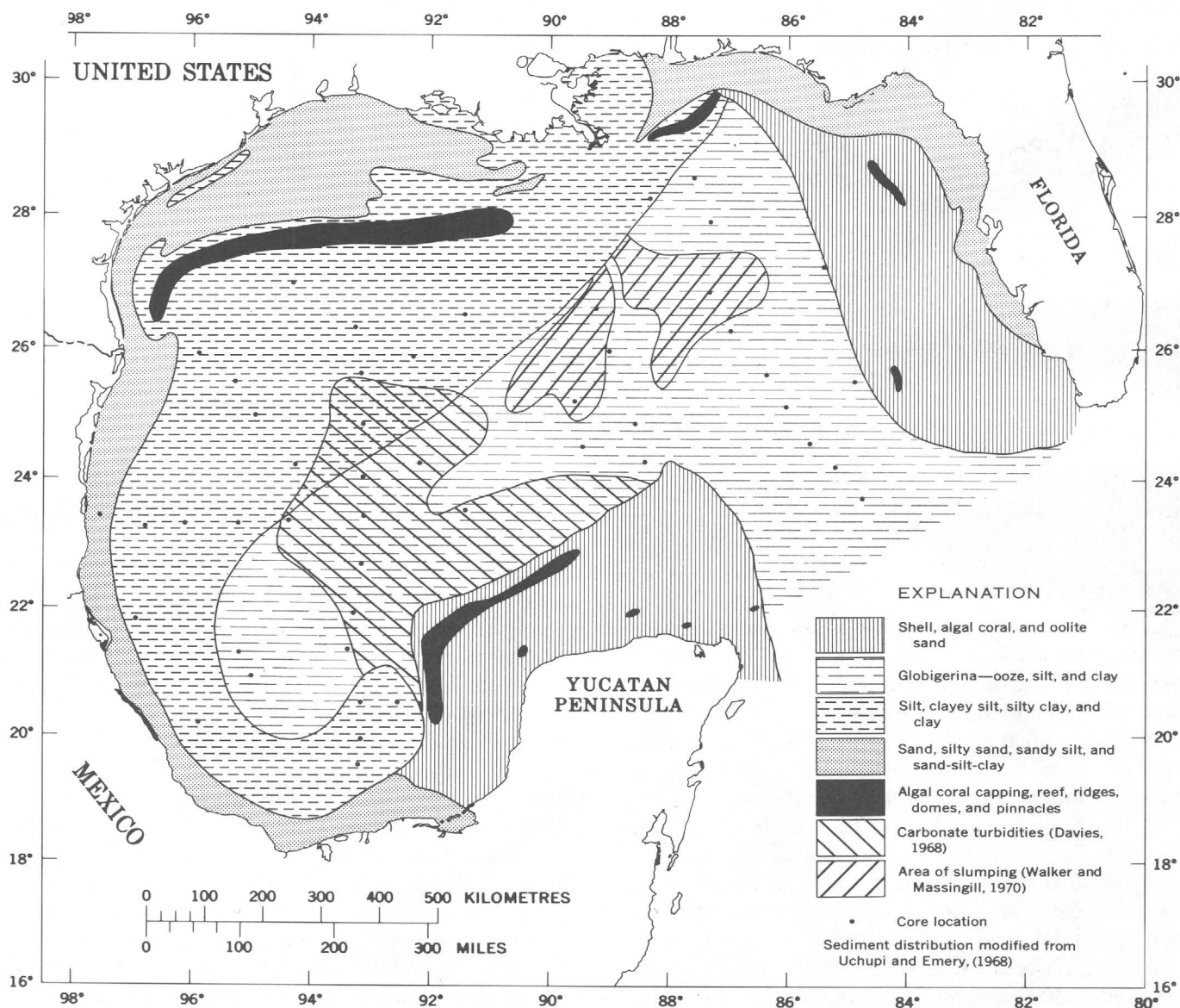
FIGURE 2.—Generalized surficial sediment distribution and location of core holes in the Gulf of Mexico basin.
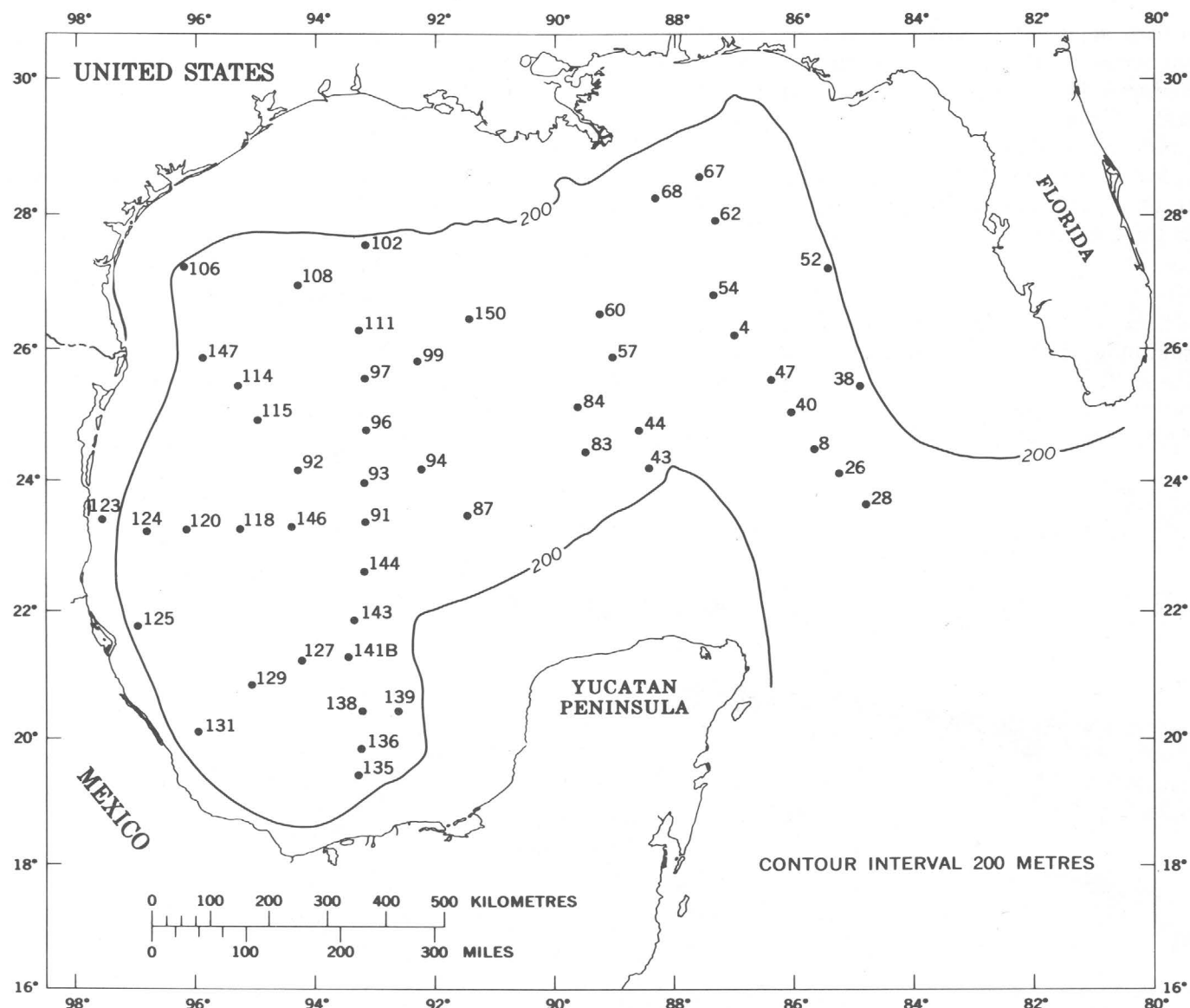
FIGURE 3.—Location of sampling stations. (See table 1.)

(1968). The results are given as the geometric mid-point (such as 0.1, 0.15, 0.2, 0.3, 0.5, 0.7, and 1.0 percent or parts per million) of the geometric brackets having the boundaries of 0.083, 0.12, 0.18, 0.26, 0.38, 0.56, 0.83, 1.2, and so forth. This precision of a reported value is approximately plus or minus two brackets at the 95 percent confidence level.

Of the 30 elements looked for (table 2), 19 were found to be within the limits of detection (table 4) in over 50 percent of the samples. Data on the 11 elements detected in less than 50 percent of the samples or not detected at all are listed in table 3.

Atomic absorption methods were used to analyze 150 additional samples for "authigenic" iron, manganese, and calcium. These samples were air dried,

ground in an agate mortar and pestle, and shaken for approximately 12 hours in a 50-ml solution of 1 M hydroxylamine-hydrochloric and 25 percent (v/v) acetic acid. This procedure dissolves the nonsilicate ferromanganese minerals and the carbonate minerals, and it extracts adsorbed trace elements but does not affect detrital-silicate or authigenic-sulfide minerals (Chester and Hughes, 1967). Replicate analyses of selected samples established the analytical precision of this method to be below 10 percent.

Uranium and thorium content and isotopic composition of selected carbonate samples were determined by alpha spectroscopy after chemical separation (Holmes, 1965). The pH was estimated with a flat-bulb combination electrode, standardized with

TABLE 1.—*Core locations*

Core. No.	Latitude	Longitude	Water depth (m)	Geographic area	Core length (cm)
4 --------	26°17.1'	87°00.1'	3,035	Toe Mississippi Fan	780
8 --------	24°32.8'	85°40.5'	3,346	----do -----------------	988
26 --------	24°08.0'	85°16.1'	3,340	----do -----------------	925
28 --------	23°40.0'	84°40.0'	3,320	Sill-Florida Straits	940
38 --------	25°29.0'	84°55.5'	3,320	Florida Scarp	960
40 --------	25°05.0'	86°02.1'	3,162	Mississippi Fan	859
43 --------	24°17.1'	88°28.5'	3,541	Canyon in Campeche Scarp	342
44 --------	24°50.1'	88°37.1'	3,505	Sigsbee Plain	870
47 --------	26°35.0'	86°25.0'	3,233	Mississippi Fan	978
52 --------	27°13.0'	85°26.8'	3,114	Florida Rise	841
54 --------	26°52.2'	87°24.8'	2,805	Mississippi Fan	380
57 --------	25°57.0'	89°03.9'	3,105	----do -----------------	200
60 --------	26°34.8'	89°18.0'	2,863	----do -----------------	176
62 --------	27°55.8'	87°20.7'	2,763	----do -----------------	840
67 --------	28°30.6'	87°39.2'	2,365	De Soto Canyon	752
68 --------	28°15.0'	88°22.0'	3,389	Mississippi Fan	920
83 --------	24°29.7'	89°30.9'	3,572	Sigsbee Plain	920
84 --------	25°11.0'	89°38.0'	3,573	----do -----------------	260
87 --------	23°32.7'	91°29.8'	3,685	----do -----------------	817
91 --------	23°27.0'	93°11.0'	3,760	----do -----------------	965
92 --------	24°14.1'	94°20.5'	3,750	----do -----------------	876
93 --------	24°04.8'	93°12.0'	3,762	----do -----------------	927
94 --------	24°14.7'	92°15.0'	3,749	----do -----------------	1,122
96 --------	24°04.8'	93°12.0'	3,706	----do -----------------	933
97 --------	25°37.0'	93°12.0'	3,408	----do -----------------	835
99 --------	25°53.0'	92°23.0'	2,388	Sigsbee Rise	880
102 --------	27°34.0'	93°12.0'	379	Texas Continental Slope	600
106 --------	27°13.6'	96°14.0'	275	----do -----------------	16
108 --------	26°59.7'	94°18.7'	1,796	Texas-Louisiana Continental Slopes	780
111 --------	26°19.0'	93°18.3'	2,450	Texas Continental Slope	610
114 --------	25°29.9'	95°23.5'	1,626	Louisiana Continental Slope	465
115 --------	24°59.9'	95°00.9'	3,576	Sigsbee Rise	447
118 --------	23°17.8'	95°15.2'	3,450	----do -----------------	775
120 --------	23°17.8'	96°10.8'	2,537	Mexico Ridges	920
123 --------	23°25.0'	97°36.1'	46	Mexico Shelf	27
124 --------	23°15.9'	96°45.0'	1,827	Mexico Continental Slope	754
125 --------	21°50.0'	96°59.0'	1,245	Mexico Ridges	710
127 --------	21°18.0'	94°23.0'	3,360	Vera Cruz Tongue	757
129 --------	20°56.7'	95°05.7'	3,108	----do -----------------	666
131 --------	20°11.2'	95°59.3'	2,001	Mexico Ridge	788
135 --------	19°33.5'	93°17.9'	580	Campeche Knolls	822
136 --------	19°58.9'	93°15.0'	1,215	----do -----------------	767
138 --------	20°31.5'	93°13.4'	1,711	----do -----------------	820
139 --------	20°30.0'	92°37.0'	2.462	Campeche Canyon	880
141 B--------	21°23.7'	93°27.9'	3,169	Campeche Knolls	917
143 --------	21°54.0'	93°20.8'	3,393	----do -----------------	884
144 --------	22°40.3'	93°13.0'	3,720	Sigsbee Plain	714
146 --------	23°22.9'	94°25.8'	3,755	----do -----------------	910
147 --------	25°42.5'	95°56.0'	1.086	Texas Continental Slope	373
150 --------	26°28.0'	91°28.0'	2,127	Sigsbee Scarp	199

commercially available buffers. In like manner, the redox potential was estimated using a combination platinum electrode calibrated with Zobell solution (Garrells, 1960).

DATA REDUCTION

The large volume of data that was generated required the use of a computer for efficient data reduction. For this report the "Geosum" program, a U.S. Geological Survey program designed specifically for semiquantitative spectrochemical analysis was used. The printout from this program gives, for each element for all samples, the maximum and minimum abundance values, a histogram plot, a tabulated frequency distribution, and a statistical summary (the geometric mean and geometric deviation). These statistics were determined on four data sets: (1) all 2,482 samples, (2) those samples taken below the Holocene veneer, (3) those samples containing more than 1,000 ppm manganese, and (4) all samples in each core, core by core (table 4).

The geometric mean and geometric deviation are antilogs of the arithmetic mean and standard deviation, respectively, of the logarithms of the analytical values. In samples with elemental concentrations less than the lower limit of detection (table 2), the geometric mean and deviation were estimated by a censored-distribution method presented by Cohen
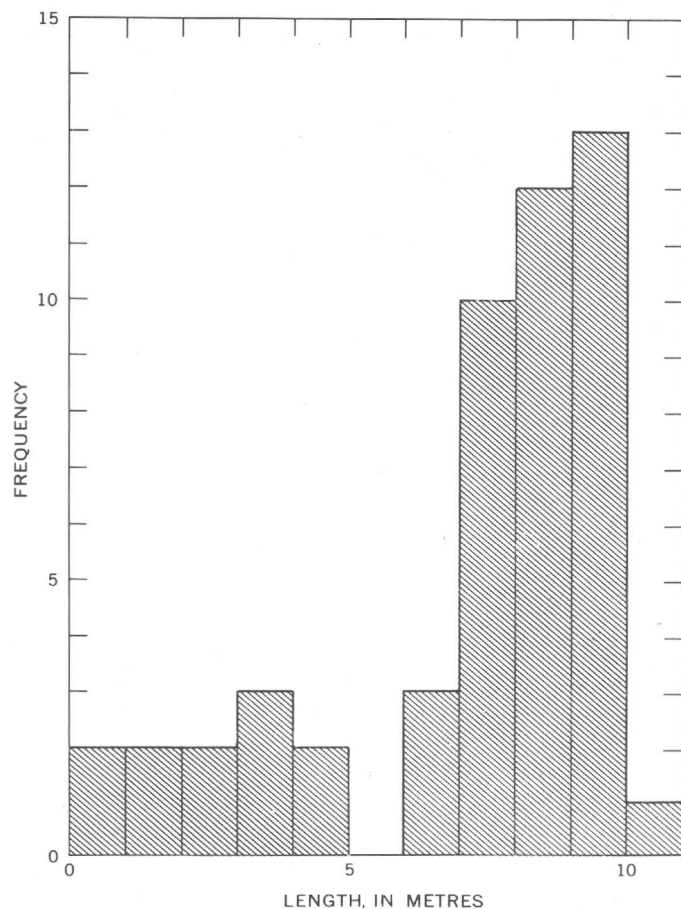
FIGURE 4.—Histogram showing the number of cores of various lengths.

TABLE 2.—*Analytical ranges of detection, in parts per million*

Element	Lower limit	Upper limit
Ag	0.5	5,000
As	200	10,000
Au	10	500
B	10	2,000
Ba	20	5,000
Be	1	1,000
Bi	10	1,000
Ca	500	200,000
Cd	20	500
Co	5	2,000
Cr	5	5,000
Cu	5	20,000
Fe	500	200,000
La	20	1,000
Mg	200	100,000
Mn	10	5,000
Mo	5	2,000
Nb	10	2,000
Ni	5	5,000
Pb	10	20,000
Sb	100	10,000
Sc	5	100
Sn	10	1,000
Sr	100	5,000
Ti	20	10,000
V	10	10,000
W	50	10,000
Y	10	200
Zn	200	10,000
Zr	10	1,000

TABLE 3.—*Elements detected in less than 50 percent of the samples or not detected at all*

Element	Lower limit of detection (ppm)	Percentage of samples in which element was found	Range (ppm)
Ag	0.5	2	0.5–15
As	200	.1	200–2,000
Au	10	0	-------
Bi	10	0	-------
Cd	20	0	-------
Mo	5	6.1	5–150
Nb	10	27.4	10–70
Sb	100	0	-------
Sn	10	1.7	10–30
W	50	0	-------
Zn	200	.7	200–5,000

(1959). The geometric mean is a more consistent measure of the central tendency of a frequency distribution than the arithmetic mean and thus is a better estimate of the typical or most common concentration of the element. The arithmetic mean, on the other hand, is a more accurate expression of elemental abundance than the geometric mean (Miesch, 1967). The arithmetic means were computed from the estimated geometric means and deviations by the method described by Miesch (1967), which is based on the technique of Cohen (1959) and Sichel (1952).

The frequency distribution of the elements in individual cores is depicted by a circular histogram (a histogram whose base has been shaped into a circle). This graphical method makes it easier to see shifts in dominant modes from one core to another. Rotation of a modal arm to the right in a succession of cores indicates an increase of the mode in the direction one is observing (pl. 1). Only 17 elements of the 19 measured in more than 50 percent of the samples were mapped in this manner; the remaining 2 showed so little variation that this type of presentation was unwarranted.

RESULTS AND DISCUSSION

GEOCHEMICAL ABUNDANCE AND DISTRIBUTION OF ELEMENTS

Estimating the abundance of constituents in major rock units of the earth is necessary in solving a range of geologic problems from mining to geochemical balances. The most reliable statistic in this regard is the arithmetic mean, that value which is

TABLE 4.—*Geometric mean (GM) compositions and geometric deviations (GD) of samples of sediment cores in the central Gulf of Mexico*

[Geometric means are given in percent for Fe, Mg, Ca, and Ti; values for all other elements are given in parts per million. ID=insufficient data for mean calculation]

Core no.	No. of samples in core	Fe GM GD	Mg GM GD	Ca GM GD	Ti GM GD	Mn GM GD	B GM GD	Ba GM GD	Be GM GD	Co GM GD	Cr GM GD	Cu GM GD	La GM GD	Ni GM GD	Pb GM GD	Sc GM GD	Sr GM GD	V GM GD	Y GM GD	Zr GM GD
4	46	2.17 1.31	1.62 1.32	1.77 1.64	0.16 1.57	789 1.36	75.6 1.27	268 1.43	1.46 1.23	14.1 1.38	54.2 1.49	17.3 1.29	20.1 1.33	27.4 1.40	9.39 1.48	11.28 1.33	117 1.69	135 1.28	16.8 1.22	106 1.58
8	50	1.83 1.29	1.23 1.32	1.17 1.77	0.15 1.26	654 1.44	79.7 1.24	274 1.33	1.25 1.24	15.2 1.43	52.2 1.50	20.5 1.31	ID ID	27.8 1.34	9.79 1.36	9.83 1.37	ID ID	95 1.35	15.9 1.19	86 1.50
26	68	3.81 1.49	2.16 1.35	3.15 1.92	0.26 1.32	1161 1.35	70.3 1.32	485 1.31	1.08 1.23	24.5 1.36	114 1.40	25.8 1.30	46.7 1.23	45.4 1.27	14.3 1.32	14.5 1.24	265 1.80	242 1.38	26.7 1.22	143 1.23
28	49	1.90 1.22	1.21 1.29	1.59 2.29	0.15 1.23	680 1.44	96.3 1.27	248 1.44	1.03 1.20	10.5 1.48	54.4 1.41	20.2 1.39	14.1 1.32	26.2 1.35	9.53 1.58	8.61 1.28	ID ID	91.5 1.31	13.8 1.24	83.8 1.46
38	54	1.73 1.32	1.16 1.66	1.27 1.81	0.14 1.38	589 1.59	85.0 1.28	199 1.78	1.21 1.26	12.7 2.01	48.1 1.53	18.8 1.52	19.9 1.30	26.9 1.58	12.5 1.58	8.91 1.34	ID ID	91.5 1.50	14.9 1.17	87.4 1.41
40	61	1.79 1.32	1.52 1.27	1.73 1.86	0.16 1.30	596 1.45	68.9 1.38	288 1.41	1.20 1.30	11.1 1.43	43.9 1.49	14.5 1.52	19.1 1.35	23.5 1.37	8.06 1.26	8.45 1.34	134 1.69	86.6 1.49	16.1 1.27	120 1.66
43	22	1.55 1.67	1.60 1.23	4.18 3.61	0.09 1.94	752 1.36	49.9 1.72	148 2.00	1.35 1.19	15.3 1.65	42.6 1.77	14.9 1.70	15.3 1.56	25.2 1.42	8.03 1.40	7.55 1.87	592 5.81	44.7 3.16	14.4 1.23	39.1 2.60
44	55	2.00 1.29	1.64 1.17	2.58 2.36	0.14 1.29	709 1.25	67.1 1.18	277 1.41	1.29 1.26	12.4 1.30	50.1 1.40	17.5 1.33	21.6 1.26	25.9 1.24	10.1 1.40	9.23 1.25	198 2.40	113 1.39	15.6 1.14	113 1.55
47	48	2.01 1.30	1.51 1.18	1.67 1.50	0.15 1.19	692 1.20	79.5 1.23	266 1.27	1.45 1.12	12.8 1.35	59.0 1.39	17.5 1.34	20.8 1.20	25.9 1.25	9.63 1.29	9.71 1.30	ID ID	129 1.25	15.4 1.17	90.3 1.43
52	45	2.05 1.33	1.56 1.16	2.33 1.49	0.15 1.15	734 1.17	70.9 1.20	286 1.41	1.47 1.09	13.3 1.86	51.2 1.42	17.5 1.31	19.4 1.22	28.0 1.26	9.98 1.31	9.67 1.26	128 1.46	113 1.32	15.5 1.13	110 1.42
54	21	1.94 1.21	1.43 1.18	1.61 1.84	0.16 1.23	757 1.31	78.9 1.23	219 1.28	1.36 1.19	12.8 1.39	52.4 1.37	18.4 1.31	17.0 1.26	26.7 1.21	8.24 1.30	10.4 1.27	ID ID	131 1.26	15.2 1.06	92.2 1.28
57	10	2.22 1.56	1.78 1.16	2.63 2.23	0.15 1.21	725 1.12	81.1 1.30	346 1.55	1.32 1.22	12.1 1.49	49.0 1.45	18.0 1.26	19.9 1.19	27.9 1.32	10.1 1.28	10.5 1.33	ID ID	128 1.31	14.8 1.18	90.9 1.42
60	24	2.28 1.29	1.83 1.30	3.86 2.08	0.16 1.15	918 1.43	78.8 1.19	291 1.20	1.40 1.17	18.4 1.38	64.1 1.34	23.9 1.41	28.2 1.40	31.4 1.41	11.6 1.35	10.2 1.27	287 1.72	114 1.28	19.2 1.28	124 1.29
62	42	2.02 1.32	1.42 1.25	2.12 1.69	0.14 1.27	943 1.58	68.9 1.11	242 1.30	1.42 1.14	17.1 1.39	49.1 1.48	19.2 1.35	16.4 1.36	25.6 1.28	12.2 1.54	10.4 1.27	122 2.08	116 1.39	15.7 1.17	82.5 1.53
67	40	1.81 1.41	1.36 1.81	3.36 1.83	0.13 1.45	689 1.70	63.9 1.41	218 1.48	1.29 1.26	14.6 1.67	41.4 1.58	17.7 1.39	20.0 1.40	27.5 1.41	8.52 1.32	9.05 1.37	216 2.06	84.1 1.52	15.9 1.19	73.0 1.91
68	72	3.40 1.40	2.22 1.39	5.12 1.81	0.25 1.39	1224 1.48	76.8 1.26	570 1.30	1.15 1.23	26.9 1.33	133 1.33	26.2 1.29	46.7 1.20	47.1 1.26	14.9 1.33	15.3 1.18	279 1.50	252 1.43	28.3 1.20	123 1.50
83	66	3.41 1.64	2.00 1.23	3.49 2.03	0.22 1.51	1032 1.46	69.8 1.35	419 1.93	1.00 1.15	19.8 1.43	99.3 1.44	24.9 1.59	36.6 1.38	42.4 1.44	13.5 1.45	13.2 1.38	321 2.26	192 1.66	23.8 1.29	116 1.67
84	28	1.88 1.29	1.54 1.30	3.21 1.94	0.16 1.35	651 1.49	68.8 1.22	268 1.40	1.40 1.18	13.0 1.52	44.9 1.48	23.2 5.95	24.5 1.28	24.7 1.31	8.34 1.55	9.55 1.27	152 1.97	107 1.38	16.5 1.19	85.2 1.80
87	48	3.06 1.37	1.86 1.16	2.64 2.01	0.23 1.52	838 1.38	88.9 1.25	328 1.77	0.99 1.15	17.6 1.33	114 1.33	25.9 1.42	29.0 1.23	44.2 1.30	11.9 1.29	13.2 1.34	219 2.12	217 1.74	21.0 1.21	101 1.70
91	50	4.30 1.42	2.47 1.28	4.47 1.81	0.28 1.48	1305 1.46	95.2 1.25	488 1.51	1.08 1.20	24.1 1.73	132 1.26	28.7 1.19	47.6 1.34	48.8 1.29	14.0 1.29	15.8 1.17	297 1.83	230 1.54	25.9 1.23	118 1.52
92	52	2.35 1.57	1.42 1.27	2.61 1.61	0.16 1.27	785 1.45	40.0 1.46	356 1.40	1.43 1.14	21.9 1.50	107 1.39	26.8 1.23	32.1 1.30	43.9 1.47	15.8 1.17	13.6 1.28	214 1.96	151 1.60	20.1 1.15	91.4 1.28
93	53	2.95 1.40	2.04 1.28	3.40 2.05	0.22 1.33	1168 1.60	72.4 1.31	318 1.41	1.03 1.17	18.0 1.32	87.3 1.43	27.2 1.34	35.0 1.27	38.8 1.36	12.6 1.45	13.1 1.24	299 2.21	180 1.15	22.9 1.26	102 1.40
94	69	3.55 1.54	2.54 1.27	3.50 1.81	0.26 1.48	1128 1.43	81.8 1.23	433 1.62	1.05 1.22	19.8 1.34	99.7 1.43	26.1 1.30	40.5 1.34	39.7 1.29	11.9 1.31	14.3 1.24	237 1.90	202 1.57	24.9 1.29	116 1.54
96	101	3.24 1.43	2.73 1.31	5.66 1.54	0.28 1.36	1137 1.52	78.4 1.24	438 1.38	1.01 1.13	20.3 1.30	91.7 1.34	23.8 1.38	38.8 1.29	40.3 1.32	11.9 1.28	14.1 1.19	233 1.48	176 1.38	27.6 1.19	141 1.32
97	48	2.61 1.45	2.27 1.36	5.14 1.68	0.22 1.49	1368 1.42	73.3 1.24	374 1.56	1.11 1.20	20.1 1.56	81.2 1.62	26.2 1.30	34.8 1.24	40.1 1.43	12.5 1.35	12.9 1.29	258 1.60	166 1.61	22.4 1.34	94.3 1.68
99	54	2.99 1.62	2.35 1.32	4.52 1.79	0.18 1.38	893 1.57	65.0 1.33	313 1.53	1.01 1.14	16.7 1.78	82.6 1.43	21.4 1.88	31.4 1.32	32.4 1.41	14.3 1.76	12.4 1.36	259 1.86	163 1.52	20.3 1.34	93.6 1.48
102	29	2.08 1.34	1.70 1.16	3.62 1.39	0.16 1.36	583 1.52	43.3 1.32	291 1.11	1.43 1.17	20.5 1.33	93.7 1.33	25.9 1.26	27.0 1.21	41.1 1.29	14.7 1.13	11.8 1.30	187 1.34	132 1.47	19.1 1.23	101 1.48
108	44	2.36 1.39	1.52 1.14	3.44 1.30	0.16 1.21	907 1.33	46.1 1.39	451 1.70	1.48 1.60	23.6 1.35	92.1 1.44	23.6 1.31	30.3 1.08	45.4 1.32	14.8 1.21	13.3 1.22	267 1.32	130 1.42	19.9 1.09	88.5 1.19
111	44	1.97 1.16	ID ID	4.53 1.68	0.13 1.36	698 1.59	42.1 1.30	280 1.24	1.44 1.13	22.5 1.35	81.7 1.53	24.9 1.82	29.1 1.09	38.0 1.35	14.6 1.17	10.7 1.22	251 1.69	112 1.43	18.7 1.13	85.8 1.35
114	35	1.76 1.36	1.41 1.30	4.71 1.67	0.16 2.06	683 1.35	40.7 1.46	259 1.25	1.26 1.23	20.7 1.55	60.1 1.65	21.8 1.59	29.4 1.32	33.8 1.43	13.6 1.31	10.9 1.41	251 1.41	112 1.62	19.0 1.24	112 1.44
115	60	2.20 1.39	1.31 1.48	3.26 1.55	0.15 1.27	808 1.78	38.3 1.74	366 1.46	1.20 1.23	24.5 1.50	57.0 1.51	21.2 1.86	27.8 1.26	34.1 1.42	12.6 1.30	11.4 1.34	269 1.64	87.1 1.36	19.0 1.19	75.3 1.27
118	77	2.06 1.40	1.32 1.41	2.65 1.80	0.12 1.32	895 1.49	40.5 1.59	244 1.43	1.30 1.24	20.1 1.52	47.9 1.89	21.4 1.67	25.2 2.22	31.8 1.66	12.9 1.31	9.87 1.39	202 1.42	84.6 1.49	17.2 1.28	69.5 1.49
120	95	2.44 1.46	1.10 1.47	3.41 1.79	0.12 1.41	909 1.73	41.6 1.56	258 1.34	1.33 1.21	18.8 1.54	56.7 1.97	14.7 1.67	24.2 1.23	30.2 1.71	12.3 1.29	10.6 1.42	266 1.49	92.0 1.68	17.4 1.36	73.9 1.64
124	76	2.19 1.51	1.43 1.29	4.84 1.84	0.13 1.30	926 1.37	48.4 1.51	311 1.38	1.21 1.25	21.6 1.68	49.8 2.09	21.1 1.56	26.5 1.26	33.9 1.60	13.0 1.38	11.0 1.36	293 1.50	94.0 1.65	18.4 1.33	79.9 1.58
125	50	2.28 1.41	1.40 1.20	4.89 1.37	0.14 1.39	769 1.42	48.4 1.35	278 1.25	1.31 1.21	17.0 1.45	56.6 1.57	17.1 1.45	27.7 1.24	33.9 1.35	13.9 1.21	11.4 1.35	265 1.29	96.6 1.52	20.1 1.33	84.8 1.50
127	71	2.30 1.43	1.29 1.52	4.93 1.63	0.13 1.58	882 1.39	48.1 1.41	279 1.40	1.30 1.22	20.9 1.77	70.7 1.94	23.0 1.63	29.3 1.23	40.9 1.87	13.7 1.22	11.6 1.36	307 1.37	97.3 1.67	17.2 1.21	86.1 1.49
129	56	1.99 1.52	1.31 1.50	3.86 2.10	0.11 1.44	899 1.50	39.5 1.43	236 1.66	1.43 1.19	22.5 1.97	63.0 2.28	23.5 1.68	28.3 1.32	38.9 1.83	14.7 1.26	10.6 1.42	276 1.63	82.0 2.05	17.8 1.19	74.1 1.47
131	68	1.77 1.55	1.07 1.70	3.41 2.49	0.12 1.41	562 1.40	ID ID	304 1.50	1.19 1.24	14.8 2.06	51.5 2.41	19.0 1.71	27.1 1.24	30.0 1.97	14.0 1.18	10.7 1.41	298 1.64	74.4 1.99	17.6 1.26	83.1 1.48
135	41	2.73 1.41	1.37 1.23	4.37 1.34	0.20 1.32	493 1.18	43.5 1.26	266 1.21	1.45 1.11	19.8 1.32	146 1.60	21.6 1.28	28.9 1.17	65.8 1.18	14.7 1.09	14.3 1.18	323 1.20	116 1.33	19.0 1.12	96.6 1.31
136	38	1.97 1.27	1.31 1.21	3.52 1.27	0.13 1.27	731 1.40	39.4 1.33	244 1.23	1.07 1.17	21.4 1.31	127 1.30	20.5 1.16	26.6 1.21	62.3 1.25	14.3 1.13	13.7 1.21	351 1.37	117 1.34	18.2 1.15	79.2 1.28
138	52	2.06 1.42	1.37 1.21	5.38 1.28	0.11 1.39	779 1.36	41.7 1.29	270 1.25	1.17 1.22	19.2 1.53	111 1.55	20.7 1.31	26.4 1.21	54.3 1.39	14.2 1.16	12.6 1.27	499 1.39	101 1.46	17.7 1.18	77.1 1.35
139	76	1.45 1.50	1.36 1.25	6.64 1.66	0.09 1.58	386 1.65	24.0 1.34	127 2.48	1.08 1.23	14.4 1.44	118 1.80	12.1 1.52	23.2 1.22	50.0 1.45	11.1 1.28	9.42 1.49	1152 2.11	67.7 1.54	16.4 1.29	51.9 1.63
141	79	1.29 1.57	1.18 1.26	8.84 1.55	0.07 1.89	484 1.85	22.5 1.40	104 2.86	1.01 1.12	14.8 1.67	91.0 1.79	13.0 1.81	24.3 1.23	41.4 1.74	11.0 1.37	7.93 1.55	1305 2.21	50.9 1.82	15.1 1.29	38.5 1.59
143	79	1.30 1.44	1.28 1.27	6.70 1.29	0.13 1.44	584 2.48	19.7 1.41	109 2.60	ID ID	17.4 1.51	69.1 1.54	14.4 1.82	25.9 1.22	39.6 1.55	11.2 1.34	8.50 1.57	1357 1.82	56.7 1.68	16.0 1.20	46.8 1.55
144	48	1.31 1.62	1.23 1.31	6.62 1.83	0.08 1.77	546 1.68	23.6 1.71	120 2.69	1.07 1.20	14.5 1.51	75.0 1.70	12.9 1.79	27.2 1.25	33.9 1.64	12.7 1.31	8.62 1.58	936 2.86	57.9 2.26	16.5 1.25	49.6 1.86
146	50	1.82 1.23	1.33 1.20	2.46 1.63	0.15 1.58	802 1.51	42.5 1.47	291 1.16	1.44 1.13	19.2 1.33	78.6 1.93	21.1 1.30	30.4 1.16	41.8 1.29	14.9 1.11	12.5 1.29	215 1.66	129 1.42	19.1 1.11	86.4 1.40
147	28	1.55 1.32	1.35 1.23	3.30 1.36	0.14 1.21	1044 1.60	52.4 1.32	290 1.21	1.07 1.17	15.0 1.23	48.7 1.49	13.2 1.53	25.5 1.22	31.4 1.29	12.2 1.23	9.19 1.27	184 1.30	87.2 1.26	16.4 1.33	81.9 1.31
150	10	2.07 1.33	1.38 1.19	4.58 1.38	0.15 1.31	1002 1.40	86.7 1.20	240 1.35	1.54 1.10	15.1 2.19	52.5 1.54	21.9 1.36	27.5 1.22	25.7 1.36	10.1 1.17	10.1 1.37	187 1.72	105 1.33	15.2 1.21	91.1 1.47
MN 1000	456	2.87 1.55	2.00 1.44	4.73 1.78	0.19 1.67	1700 1.30	67.5 1.44	369 1.64	1.16 1.24	23.3 1.57	89.6 1.60	25.8 1.40	33.8 1.43	43.1 1.38	13.9 1.39	13.0 1.34	290 1.73	158 1.78	22.2 1.35	96.5 1.63
TOTAL	2482	2.20 1.59	1.53 1.50	3.53 2.11	0.15 1.75	788 1.70	52.0 1.75	272 1.87	1.20 1.26	17.9 1.58	71.7 1.82	20.1 1.68	27.3 1.50	36.2 1.55	12.1 1.40	11.0 1.43	286 2.22	112 1.87	18.6 1.33	86.5 1.70

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"the correct expression of abundance—or an unbiased estimate of abundance—under all conditions" (Miesch, 1967). Table 5 lists the estimated geochemical abundances for the combined strata of Holocene and Pleistocene age and may be compared directly to arithmetic means (geochemical coverages) reported in the literature (Schacklette and others, 1971).

As the arithmetic mean or geochemical abundance is important in determining geochemical cycles, geochemical variation is important in understanding the chemistry of the elements and in evaluating the statistics used to classify them. The method used in calculating the arithmetic mean is based on the assumption that the population of values from which the sample values were drawn is lognormal. Figures 5 and 6 show the distribution of each element; the base is the log scale used in reporting the results. From analyses for normality of the logs of each class for each element, using the procedure outlined by Krumbein and Graybill (1965, p. 177), it may be concluded that for all of the samples analyzed, iron, boron, cobalt, and nickel are lognormally distributed; for the Pleistocene samples, iron, calcium, titanium, cobalt, chromium, nickel, scandium, vanadium, and zirconium are lognormally distributed. The remaining elements either lack sufficient data for such analyses or are close approximations of normal distributions, as determined graphically (Krumbein and Graybill, 1965, p. 177). These analyses demonstrate that the distribution of the elements in the surficial sediment column of the Gulf of Mexi-

co all appear to approximate lognormality, and thus the procedure used for calculating the arithmetic mean apparently is valid.

The Pleistocene sediments show statistically significant higher abundances for only four elements: boron, titanium, vanadium, and zirconium; the Holocene sediments show significantly higher abundances for only calcium and strontium. The pattern of elemental concentration in some way reflects the sedimentological regime acting at the time of deposition. For example, the calcium and strontium enrichment in Holocene sediments indicates the known increase in pelagic sedimentation at this time, whereas the higher boron, vanadium, titanium, and zirconium values reflect the higher influx of hemipelagic sediment during Pleistocene glacial periods.

Comparison of the calculated average elemental abundances in this report and geochemical abundances reported in the literature shows significant differences. The sediments in the gulf basin may be classed as dominantly hemipelagic, but only the magnesium and the chromium concentrations approach the values listed for hemipelagic sediments by Horn and Adams (1966). Some of the remaining elemental concentrations compare on an individual-element basis with mobile belt sediments, shale, or pelagic sediments listed by Horn and Adams (1966). However, the concentrations of calcium, titanium, vanadium, or zirconium in these samples do not approximate the concentration values of any of the sediment types characterized by Horn and Adams.

TABLE 5.—*Average element content in central Gulf of Mexico sediments*
[Data in parts per million; each average represents arithmetic means]

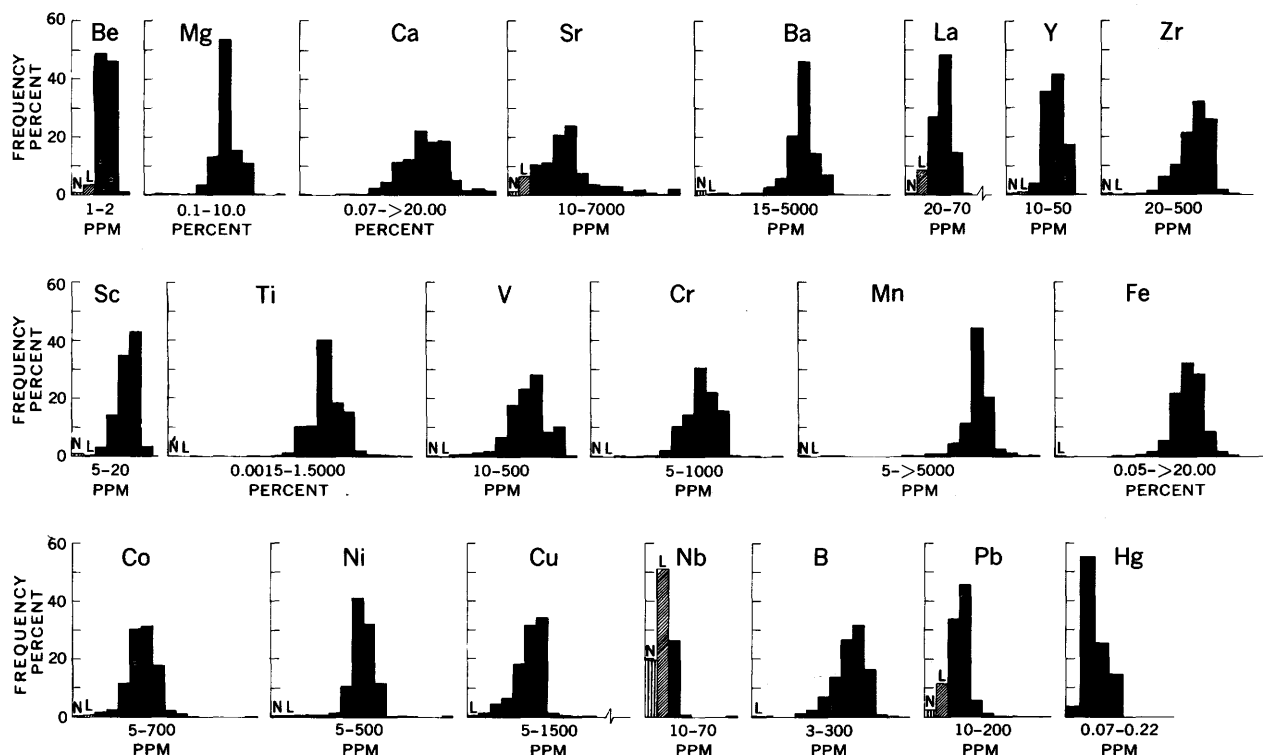| Element	Central basin sediments (This report)			Worldwide averages of major sedimentary units (Horn and Adams, 1966)					
	Total number of samples	Holocene samples	Upper Pleistocene samples	Carbonate	Shale	Sandstone	Mobile belt sediments	Hemipelagic	Pelagic
B	59	47	62	12	79	25	56	11	71
Ba	319	291	327	35	263	199	233	881	634
Be	1	1	1	0.2	2	0.3	1	6	3
Ca	45,090	69,100	43,130	272,000	22,000	22,200	26,900	27,700	83,300
Co	20	21	20	0.2	8	0.5	5	38	26
Cr	84	74	87	7	427	121	295	92	60
Cu	23	20	23	4	47	15	34	150	106
Fe	24,650	22,050	25,230	8,660	39,600	21,000	31,100	50,100	32,400
La	27	23	28	6	25	11	18	83	55
Mg	16,570	15,310	16,890	45,500	16,600	8,760	13,900	16,400	10,900
Mn	899	892	959	385	300	10	188	3,650	2,310
Ni	40	36	40	13	33	3	21	152	110
Pb	11	7	12	6	20	7	15	41	27
Sc	12	9	12	1	11	1	7	23	14
Sr	363	1,054	388	544	242	24	168	881	792
Ti	1,840	1,570	1,900	389	4,520	2,100	3,430	5,660	3,670
V	133	95	142	13	102	21	68	207	161
Y	19	18	20	6	12	2	8	83	56
Zr	97	87	100	18	144	206	160	145	121

FIGURE 5.—Frequency distribution of 21 elements for all samples taken on the central gulf basin. The horizontal scale is a log scale in which the values are reported by the analyst. L=less than the lower limit of detection by the analytical procedure, but present. N=none detected.
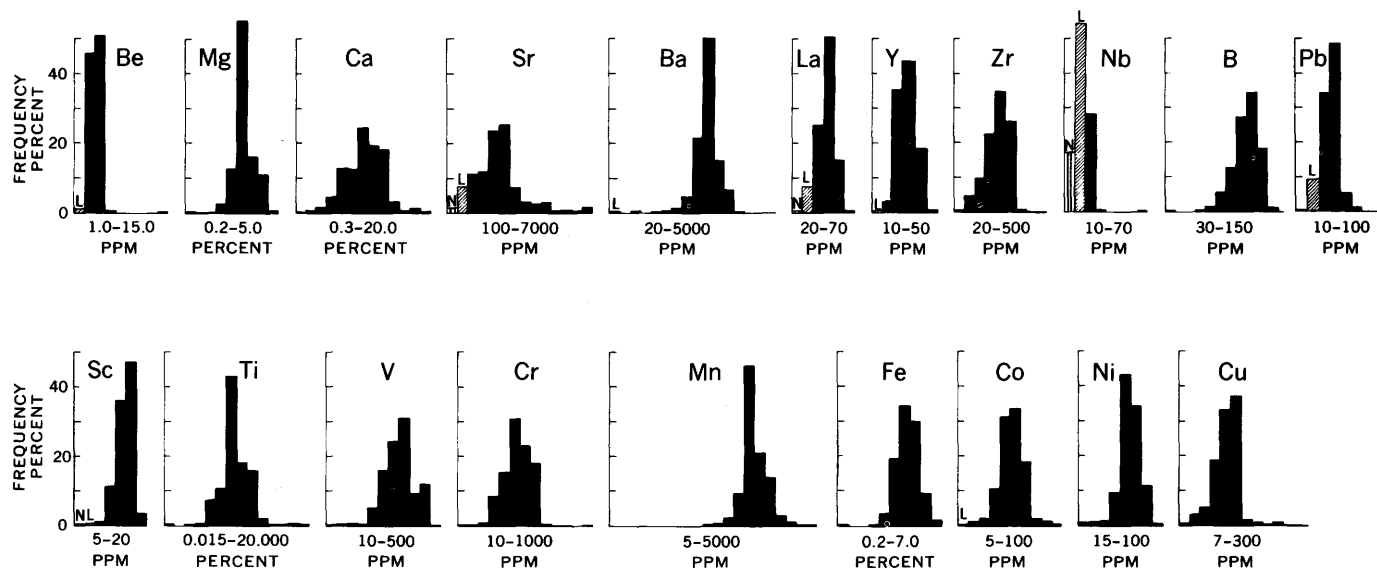

FIGURE 6.—Frequency distribution of 20 elements for samples of Pleistocene age in the central gulf basin. The horizontal scale is a log scale in which the values are reported by the analyst. L=less than the lower limit of detection by the analytical procedure, but present. N=none detected.

REGIONAL VARIATIONS AND GEOCHEMICAL COHERENCE

The chemical character of marine sediments is determined by nonequilibrium processes which complicate the solving of sedimentary geochemical prob-
lems. The factors presently considered to be responsible for the chemical imprint of sediments are: the nature of the source rock, the environment at the source, the nature of the transporting medium, the environment at the depositional site, the nature and

activity of the biomass at the site of deposition, tectonic activity, and diagenetic redistribution. Of these, probably the most important are the source rock and environment at the source. Hirst (1962), Jenne (1968), Krauskopf (1956, 1957), and Carroll (1958) have shown that, once in transit, most metals tend to remain physically associated with clay-size material. Thus, regional concentration patterns of metals associated with the clay-size materials may provide information about the source.

The data presented in this report show some regional variations of elemental abundances in the basin sediments of the Gulf of Mexico. For some of the mapped elements, however, the variation is only a matter of one "bracket of determination," in which case the value of these elements as a source indicator is considered poor. On the other hand, those elements whose distribution is spread, more or less evenly, through several brackets of determination have considerable potential as source indicators. Of the 17 elements mapped, only 4—calcium, strontium, chromium, and vanadium—appear to meet this requirement. However, before these elements can be definitely defined as source indicators, some understanding of the geochemistry of these elements is necessary. The determination of the geochemical coherence of the elements aids in this by relating these elements to major elements whose marine chemistry is better understood.

Geochemically coherent elements as described by Rankama and Sahama (1950) are those elements "which are always found together in nature." This relationship does not necessarily imply similarity of chemical behavior or chemical coherence in the environment in which the elements are or have been; all that is implied is that the elements do tend to be associated in the sediment. The degree of geochemical coherence is most conveniently obtained by the calculation of correlation coefficients—those statistical parameters which "measure" the reliability of one variable in predicting another. These parameters were calculated on the logarithms of the reported analytical values, and data pairs in which one or both of the values are beyond the limits of detection were ignored. In the cases where data have been skipped over, the data are derived from censored

TABLE 6.—Correlation coefficients among 20 elements based on all sediment samples taken during the cruise of the USNS Kane in 1969

[The numbers above the diagonal are the correlation coefficients (r); the numbers below the diagonal represent the number of element pairs on which r was calculated. The discrepancy between the total listed here and the total given in text is because this table is based on all samples including 51 grab samples]

	Fe	Mg	Ca	Ti	Mn	B	Ba	Be	Co	Cr	Cu	La		Ni	Pb	Sc	Sr	V	Y	Zr
	Fe	0.50	-0.08	0.59	0.43	0.52	0.52	0.03	0.51	0.52	0.44	0.46	-0.01	0.47	0.17	0.67	-0.28	0.76	0.62	0.55
Mg	2533	Mg	0.26	0.45	0.43	0.46	0.37	-0.14	0.32	0.47	0.40	0.37	0.03	0.37	0.10	0.49	-0.08	0.58	0.53	0.38
Ca	2496	2497	Ca	-0.18	0.08	-0.28	-0.17	-0.26	0.15	0.23	0.02	0.05	0.08	0.28	0.07	0.02	0.72	-0.16	0.10	-0.31
Ti	2533	2535	2497	Ti	0.34	0.51	0.54	0.04	0.30	0.37	0.41	0.43	0.06	0.33	0.05	0.56	-0.36	0.59	0.58	0.68
Mn	2515	2517	2479	2517	Mn	0.42	0.40	-0.02	0.34	0.23	0.40	0.28	0.01	0.23	0.16	0.36	-0.13	0.46	0.36	0.24
B	2531	2533	2495	2531	2513	B	0.39	0.10	0.10	0.15	0.42	0.27	0.06	0.10	0.02	0.36	-0.45	0.61	0.30	0.47
Ba	2500	2501	2467	2501	2483	2499	Ba	0.01	0.32	0.29	0.40	0.40	0.01	0.14	0.20	0.48	-0.43	0.59	0.53	0.63
Be	2431	2431	2420	2431	2415	2429	2413	Be	0.04	-0.10	0.07	-0.08	-0.03	0.03	0.07	-0.07	-0.27	0.05	-0.04	0.16
Co	2509	2510	2478	2510	2492	2508	2483	2415	Co	0.47	0.41	0.30	-0.03	0.65	0.28	0.52	-0.02	0.43	0.46	0.27
Cr	2521	2523	2486	2523	2505	2521	2491	2419	2502	Cr	0.32	0.37	0.01	0.72	0.14	0.62	0.11	0.58	0.53	0.29
Cu	2528	2530	2494	2529	2511	2528	2499	2428	2507	2518	Cu	0.25	0.03	0.38	0.34	0.47	-0.16	0.54	0.36	0.32
La	2308	2308	2282	2308	2293	2307	2279	2244	2292	2297	2305	La	0.02	0.27	0.24	0.43	-0.08	0.47	0.56	0.38
Ni	2528	2529	2492	2529	2511	2527	2497	2428	2509	2519	2525	2305	692	Ni	0.20	0.57	0.19	0.46	0.42	0.19
Pb	2193	2193	2176	2193	2177	2192	2190	2151	2182	2182	2191	2078	670	2191	Pb	0.23	0.00	0.18	0.24	0.10
Sc	2494	2494	2464	2494	2477	2493	2486	2413	2479	2484	2492	2283	694	2492	2188	Sc	-0.16	0.73	0.63	0.49
Sr	2261	2263	2232	2262	2244	2260	2249	2180	2242	2252	2256	2106	679	2258	2060	2245	Sr	-0.39	-0.14	10.51
V	2529	2531	2493	2531	2513	2527	2500	2429	2508	2521	2526	2306	693	2527	2190	2493	2261	V	0.63	0.65
Y	2523	2523	2486	2523	2505	2521	2496	2426	2506	2511	2519	2303	694	2520	2191	2492	2257	2521	Y	0.56
Zr	2526	2526	2490	2526	2508	2524	2498	2429	2504	2514	2521	2304	694	2522	2192	2494	2259	2523	2521	Zr

TABLE 7.—Correlation coefficients for the Pleistocene samples

[The numbers above the diagonal are the correlation coefficients (r); the numbers below the diagonal represent the number of element pairs on which r was calculated]

	Fe	Mg	Ca	Ti	Mn	B	Ba	Be	Co	Cr	Cu	La		Ni	Pb	Sc	Sr	V	Y	Zr
	Fe	0.55	0.00	0.61	0.38	0.48	0.56	-0.03	0.51	0.54	0.37	0.59	-0.01	0.44	0.15	0.66	-0.21	0.76	0.62	0.54
Mg	2072	Mg	0.24	0.48	0.42	0.40	0.51	-0.19	0.33	0.43	0.34	0.52	0.04	0.29	0.11	0.47	-0.07	0.55	0.59	0.44
Ca	2060	2060	Ca	-0.14	0.14	-0.35	-0.03	-0.23	0.25	0.29	0.05	0.14	0.11	0.34	0.13	0.10	0.72	-0.14	0.21	-0.22
Ti	2072	2072	2060	Ti	0.25	0.48	0.53	-0.02	0.28	0.35	0.32	0.53	0.06	0.28	0.09	0.53	-0.30	0.67	0.56	0.65
Mn	2062	2062	2050	2062	Mn	0.35	0.40	-0.07	0.32	0.15	0.32	0.34	0.01	0.16	0.14	0.31	-0.09	0.38	0.34	0.19
B	2072	2072	2060	2072	2062	B	0.40	0.06	0.06	0.06	0.30	0.29	0.08	-0.05	0.01	0.27	-0.48	0.54	0.25	0.49
Ba	2069	2069	2057	2069	2059	2069	Ba	-0.05	0.36	0.34	0.39	0.52	0.01	0.22	0.21	0.49	-0.33	0.61	0.56	0.61
Be	2046	2046	2040	2046	2036	2046	2043	Be	0.01	-0.14	0.04	-0.14	-0.03	-0.07	0.05	0.02	-0.24	-0.02	-0.11	0.11
Co	2070	2070	2058	2070	2060	2070	2067	2045	Co	0.52	0.39	0.40	-0.40	0.65	0.28	0.53	0.07	0.44	0.48	0.25
Cr	2070	2070	2058	2070	2060	2070	2067	2044	2068	Cr	0.26	0.49	0.01	0.72	0.19	0.63	0.19	0.53	0.55	0.28
Cu	2072	2072	2060	2072	2062	2072	2069	2046	2070	2070	Cu	0.31	0.06	0.33	0.35	0.39	-0.08	0.43	0.31	0.26
La	1917	1917	1906	1917	1907	1917	1914	1894	1916	1915	1917	La	0.02	0.38	0.25	0.57	-0.04	0.62	0.71	0.44
Ni	2072	2072	2060	2072	2062	2072	2069	2046	2070	2070	2072	1917	597	Ni	0.26	0.55	0.28	0.40	0.43	0.15
Pb	1862	1862	1852	1862	1852	1862	1862	1840	1861	1860	1862	1764	580	1862	Pb	0.22	0.05	0.18	0.23	0.10
Sc	2067	2067	2055	2067	2057	2067	2066	2041	2065	2065	2067	1912	597	2067	1860	Sc	-0.06	0.69	0.65	0.47
Sr	1853	1853	1843	1853	1843	1853	1853	1831	1851	1851	1853	1762	586	1853	1749	1853	Sr	-0.35	-0.02	-0.44
V	2072	2072	2060	2072	2062	2072	2069	2046	2070	2070	2072	1917	597	2072	1862	2067	1853	V	0.64	0.64
Y	2071	2071	2059	2071	2061	2071	2068	2046	2070	2069	2071	1917	597	2071	1862	2066	1852	2071	Y	0.52
Zr	2072	2072	2060	2072	2062	2072	2069	2046	2070	2070	2072	1917	597	2072	1862	2067	1853	2072	2071	Zr

distributions and the correlation coefficients should be considered as "indices of association" rather than true correlation coefficients (A. T. Miesch, written commun., 1970). The correlation coefficients for all samples and for those only of Pleistocene age are listed in tables 6 and 7, respectively.

Further evaluation for geochemical coherence may be made from R-mode (between variables) factor analysis (Imbrie, 1963). In this analysis, the data are assumed to be derived from a system which consists of a number of unknown causal influences, a notion of cause and effect which is treated strictly mathematically. However, geologic evaluation of the output of this analysis allows for the determination of the number of causal influences needed to account for the observed variations and for the identity of these influences. For a detailed discussion of factor analysis the reader is directed to the report of Imbrie (1963).

Based on the correlation coefficients and R-mode factor analysis, the element concentrations were classed into three geochemically coherent groups: the iron-vanadium group (I), the calcium-strontium group (II), and the beryllium-niobium-lead group (III). The strongest correlations in the total data set were found between iron and vanadium and calcium and strontium. Thirteen elements (B, Ba, Cr, Co, Cu, La, Mg, Mn, Ni, Sc, Ti, Y, and Zr) were found to have significant correlation with the iron-vanadium couple. Factor analysis indicated that a division of this group into four sub-classes could be made (fig. 7). All the elements in group I, except those in the manganese subclass, have high correlation with the iron-vanadium couple. The manganese subclass,
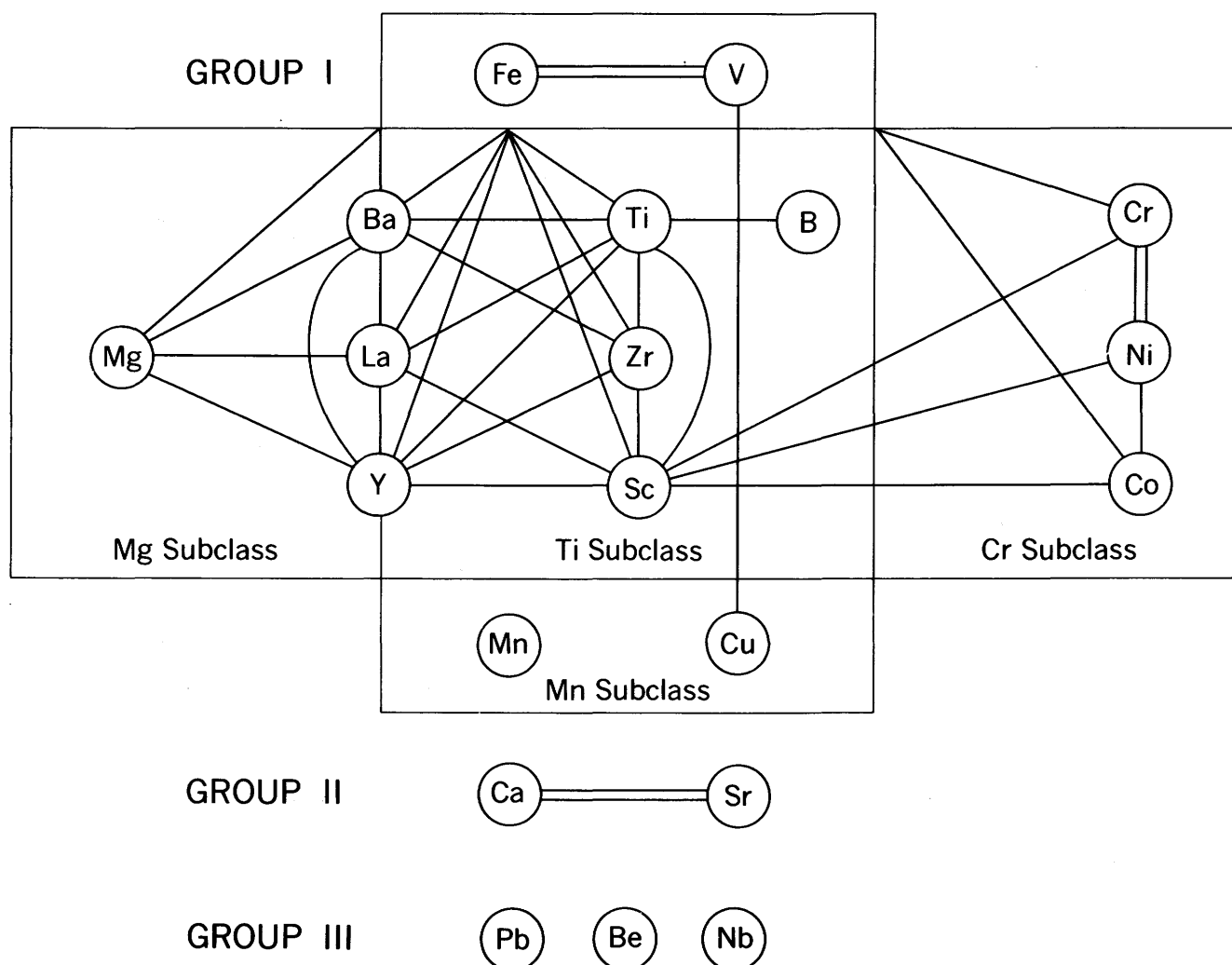
FIGURE 7.—Schematic of element associations based on the calculated correlation coefficients and factor analysis. Double line ties two elements having an (r) correlation coefficient for all samples greater than 0.70; a single line ties those elements with an (r) between 0.70–0.50.

the bastard of group I, shows only moderate correlation with iron or vanadium and is placed. in this group because of the reported association of iron and manganese (Krauskopf, 1956). The elements in group III, beryllium, niobium, and lead, have either no significant or very weak correlations between themselves and all other elements determined. The lack of correlation and geochemical coherence of the elements in the third group with any other element is probably because of their truncated distribution.

IRON-VANADIUM GROUP

The group I elements are predominantly associated with the detrital phases of marine sediments (Hirst, 1962). Categorizing the group I elements into the subclasses allows for geological judgment about the form in which these elements exist. For example, those elements in the magnesium subclass are most likely associated within clay minerals (Hirst, 1962) ; the titanium and the chromium subclasses, on the other hand, suggest an association with such detrital phases as heavy minerals.

The areal distribution of the group I elements is best represented by vanadium. On the Mississippi Fan, vanadium has an almost 150 ppm unimodal distribution (pl. 1). Next to the fan, in the lower reaches of the De Soto Canyon (core 67), the sediment has a significantly lower average vanadium content. Toward the Florida Straits the patterns become confused, the vanadium distribution in the core 40 at the base of the lower fan exhibiting a scattered distribution and a character similar to the sediment in the De Soto Canyon area. The sediments of these areas contain an abundance of reworked Cretaceous foraminifera (Huang, 1969) which does suggest a De Soto Canyon source, the material having been slumped into its present position. In the three remaining cores on the southeasterly line (8, 26 and 28), the sediments in the first and third have a chemical character similar to those of the Mississippi Fan. However, the sediment in core 26 has a chemical nature nearly identical to that of core 68, taken nearest the mouth of the Mississippi River. This suggests that, at least chemically, the sediments are similar at both sites and are possibly from a similar source. It is noted that these two cores also show a unique similarity in their clay mineralogy (Ferrell and others, 1971).

The vanadium map also shows that the sediments on the perimeter of the basin have the lowest vanadium content, whereas those in the abyssal section of the basin have the highest values, with the exception of sediment in the vicinity of the lower Campeche Canyon. These sediments, represented by cores 139, 141B, 143 and 144, have extraordinarily low vanadium values owing to dilution of carbonate-rich vanadium-poor detritus from the Campeche Bank. This influx of Campeche Bank sediment is also apparent in the sediments on the abyssal plain (43) at the northeastern edge of the Campeche Bank.

Examination of the maps of the rest of the group I elements shows that they have distributional patterns nearly identical to vanadium; that is, the sediments on the perimeter of the gulf basin have the lower concentrations of most elements, and the sediments in the abyssal region have the higher. The sediments near the western edge of the Campeche Bank reflect dilution by carbonate sediment. Cores 68 and 26 from the Mississippi River and Yucatan Straits, respectively, exhibit a chemical similarity which suggests similar origin. Also, on many maps 40 can be chemically differentiated.

Chemical composition of the sediment in the northern and eastern gulf does show significant regional variation, but is nevertheless a questionable basis for determination of the ultimate source of this area's sediment. As mentioned previously, the Mississippi River is the major source of sediment, and apparently has been for at least the past 2 million years, the maximum possible age of the sediment examined. If the variations in most of the cores do not reflect the source, the question arises as to what could produce the definite regional pattern of low elemental concentration on the perimeter to high in the central basin. As mentioned above, the elements of group I may be associated with different phases of detrital sediment. To a degree this is the case, but as pointed out by many investigations (Hirst, 1962; Chester, 1965), the clay-size material seems to be the detrital material with the highest concentration of these elements. If so, then the region with the highest content of clay-size material would have the highest concentration of metals in the Gulf of Mexico. Figure 8 shows the distribution of clay-size material based on data published by Bouma, Bryant, and Davies (1971). In general, the diagram shows that the cores from deeper, more central areas of the basin have a higher clay content, as well as high metal concentrations. This seems to uphold the findings of Hirst (1962) and Chester (1965).

Even though it is somewhat questionable to determine the ultimate source of the sediment in the eastern and northern gulf by the sediment's chemical character, in the southwestern gulf there is sub-
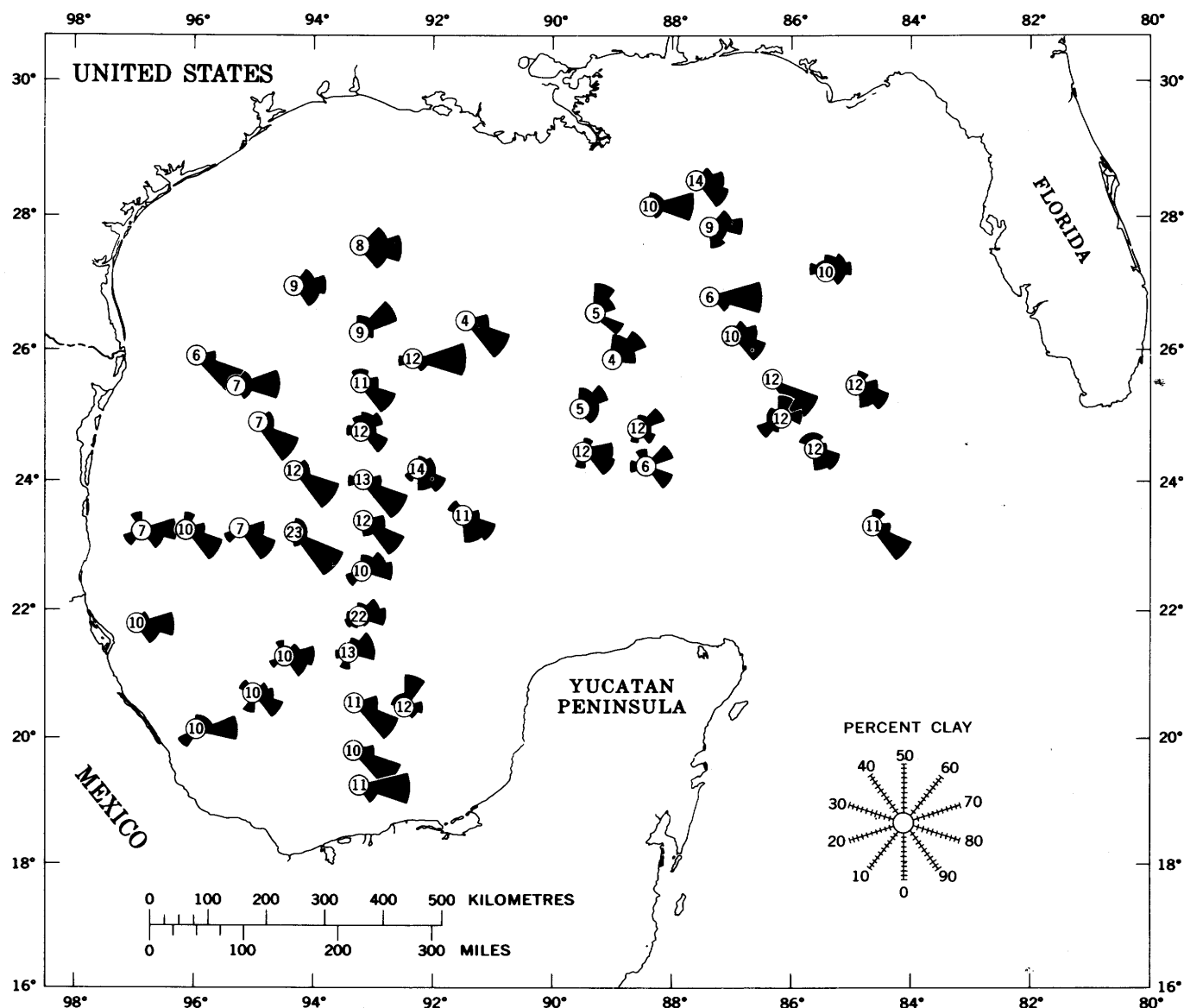
FIGURE 8.—Circular histogram of frequency versus clay percentage in cores from the central gulf basin. The number in the center of each graph is the number of analyses made for that core. The scale is present at the lower right. Data from Bouma and others, 1971.

stantial evidence that the elemental trends are indicative of source areas. In the Bay of Campeche the sediments nearest land have high chromium, nickel, and cobalt concentrations which decrease seaward. This gradient reflects a landward source in the volcanic fields on the isthmus of Tehuanatepec. Similarly, carbonate detritus low in trace metal from the Campeche Bank produces a dilution effect decreasing the concentration of all elements in sediments (Cores 139, 141, 143, 144) off the northwestern corner of the Campeche Bank. These trends, then, suggest that under some circumstances the semiquantitative data are of value as indicators of source regions, particu-

larly where the regions are significantly different in chemical character.

MANGANESE SUBCLASS

Distribution.—The weak correlation between manganese and the other elements of group I is not apparent when comparisons are made of their patterns of areal distribution (for example, comparing manganese with vanadium in pl. 1). The differences become apparent, however, when the vertical distribution of manganese is compared to that of other elements, for example, iron (figs. 9 and 10). A few
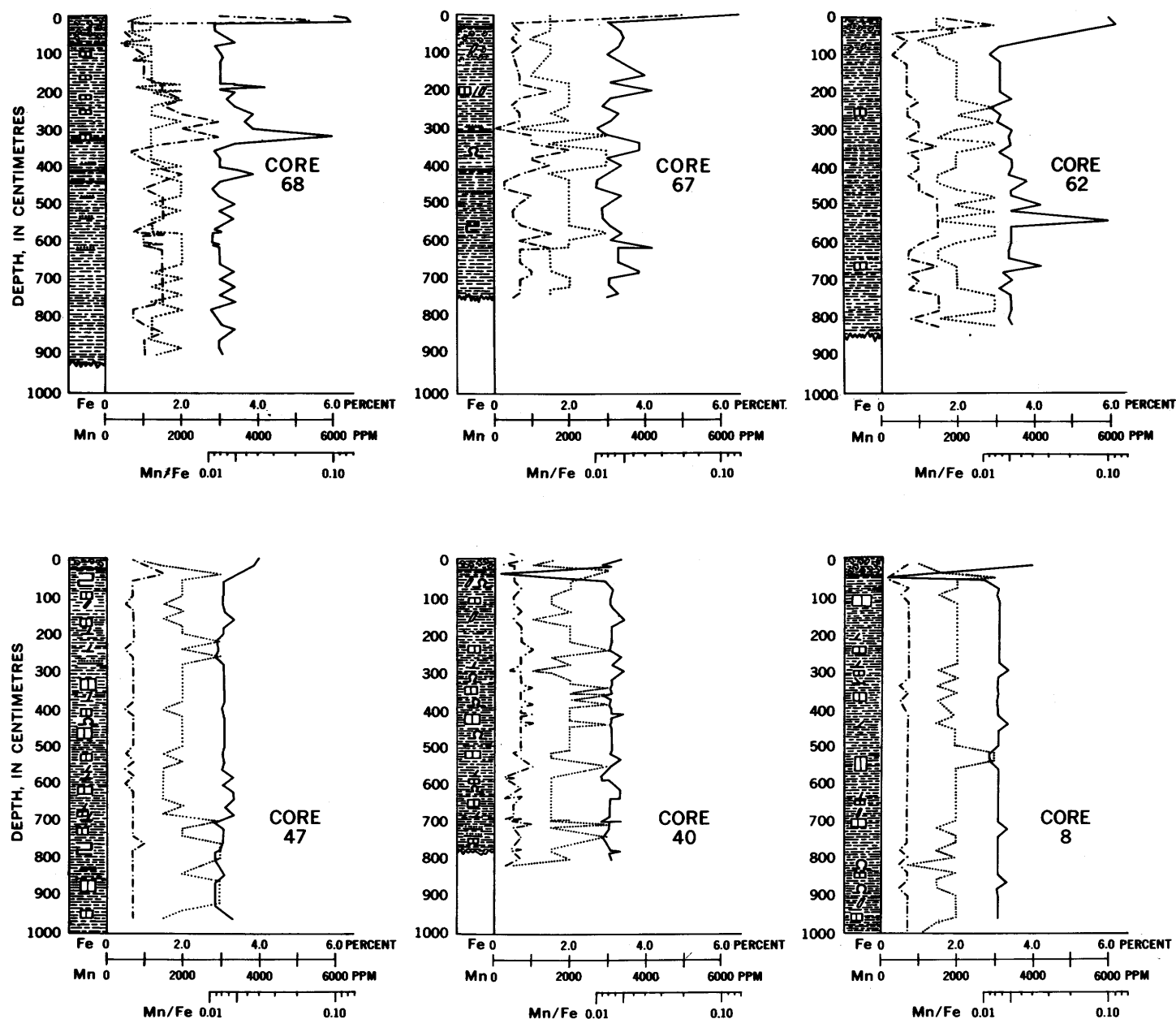
FIGURE 9.—The distribution of iron, manganese, and Mn/Fe ratio with depth in cores raised from a southeast-northwest transect in the eastern gulf basin.

cores (68, 97, 96, and 93) in addition to the more typical section which shows the highest manganese concentration in the upper metre have manganese-rich zones at depth. Those few cores which do not show the flag type of vertical manganese distribution (fig. 11) appear to be sedimentologically unique. For example, core 40 on the lower Mississippi Fan has been described as unique by Bouma, Bryant, and Davis (1971) and Huang (1969) because of its lack of Holocene surface sediment, its internal structure, and its texture. This core probably contains sediment implaced by mass transport rather than by the regular sedimentological processes of this section of the gulf. As a consequence, the chemical nature of the sediment is unique for the area and no high manganese concentrations are present. Similar descriptions may be applied to cores 139, 143, and 144 in the southwestern gulf and cores 102, 114, and 150 on the northern rim of the gulf basin, all of which lack the characteristic flag distribution of manganese.

Distribution over Holocene-Pleistocene boundary. —Based on paleontologic (Kennett and Huddleston, 1972; Ludwig, 1971), geochemical (Newman and others, 1973), and sedimentologic (Bouma and oth-
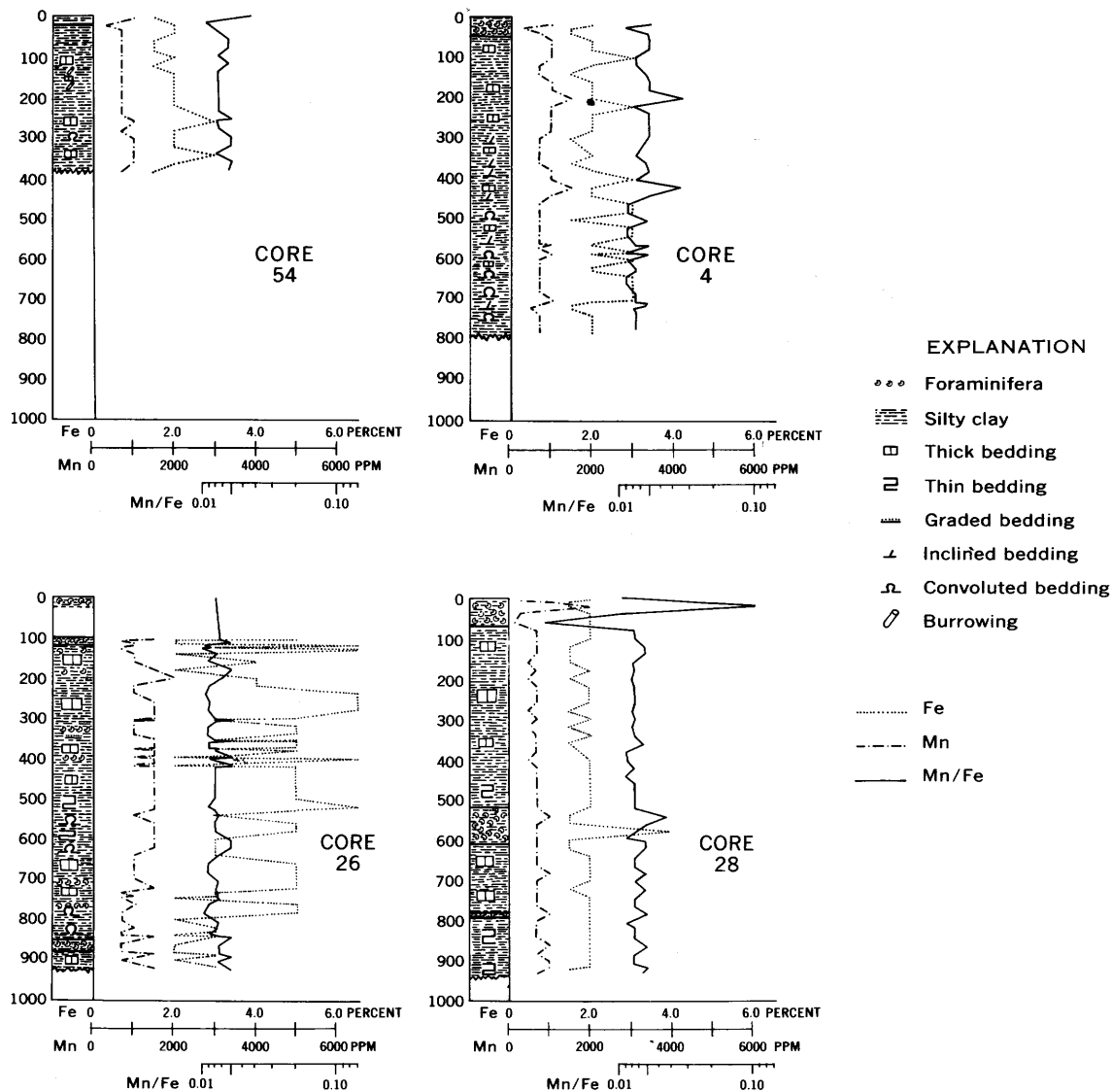
FIGURE 9. —Continued.

ers, 1971) evidence, the Holocene-Pleistocene boundary was estimated with confidence in 27 cores. Fortunately, these cores are spread throughout the basin, and chemical comparisons can be made with both age and different physiographic regions. In all but one of these cores (96), the spectrographically determined manganese was found to be highest in the Holocene sediments (table 8).

Regionally, the Holocene sediments highest in manganese concentration are adjacent to the Mississippi delta, in the southernmost sections of the Bay of Campeche, and in the western portion of the abyssal plain; the highest and most extensive concentrations occur in the area mentioned last. By contrast, the highest manganese concentration in the Pleistocene sediments occurs adjacent to the Mississippi delta and in the west-northwest region of the basin.

Selective leaching of manganese by the analytical procedure mentioned previously accounted for nearly all the manganese from the sediment. Comparison of spectrographically determined manganese and the authigenic manganese showed that most manganese is in a hydrogenous form (fig. 12).

Marine geochemistry.—The marine chemistry of manganese has been the subject of many recent re-reports (Krauskopf, 1957; Lynn and Bonatti, 1965; Boström, 1967; Chester and Hughes, 1967; Bender and others, 1970; Bender, 1971; Bonatti and others, 1971; Bischoff and Sayles, 1972). These and many previous studies provide a basic understanding of a general model of the marine chemistry of manganese. The element, either in the ionic form or as an hydroxide film adhering to fine detrital material, enters the sea via rivers. Once in the basic marine environment, manganese which is in the ionic state
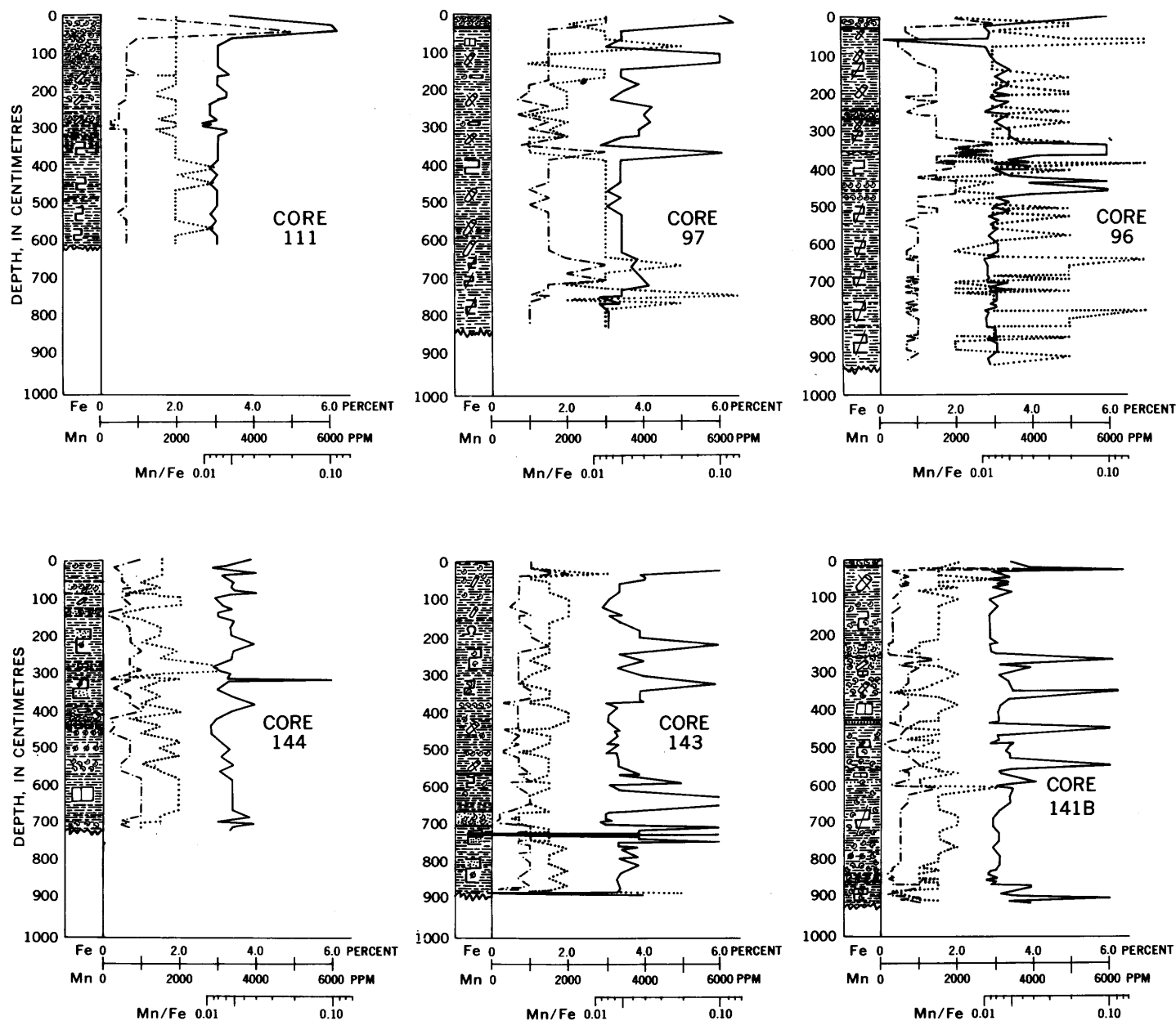
FIGURE 10.—The distribution of iron, manganese, and the Mn/Fe ratio with depth in cores raised from a north-south transect in the western gulf basin.

hydrolizes and precipitates to the sea floor and carries with it many metals it has scavenged. The high manganese concentration near the delta of the Mississippi is probably the result of this activity. The distribution of the adsorbed form of manganese will be wholly influenced by the sedimentologic environment; the regions of the highest clay concentration will have the highest manganese concentration.

Besides continental erosion, another source of manganese in the sea is volcanic activity. This source, however, may be neglected in the Gulf of Mexico because there is no evidence of any signifi-

cant basin and submarine volcanic activity in the later part of the Pleistocene.

The decay of organic detritus in the deposited sediment produces a reducing chemical environment. Under such conditions, manganese is reduced to the soluble Mn^{+2} species and migrates by ionic diffusion toward the surface. The other ions associated with manganese tend to form sulfides and remain nearly in place in the sediment column (unless the redox potential is extremely low). So manganese tends to be concentrated near the surface, the lower boundary of the enriched zone being marked by a decrease in
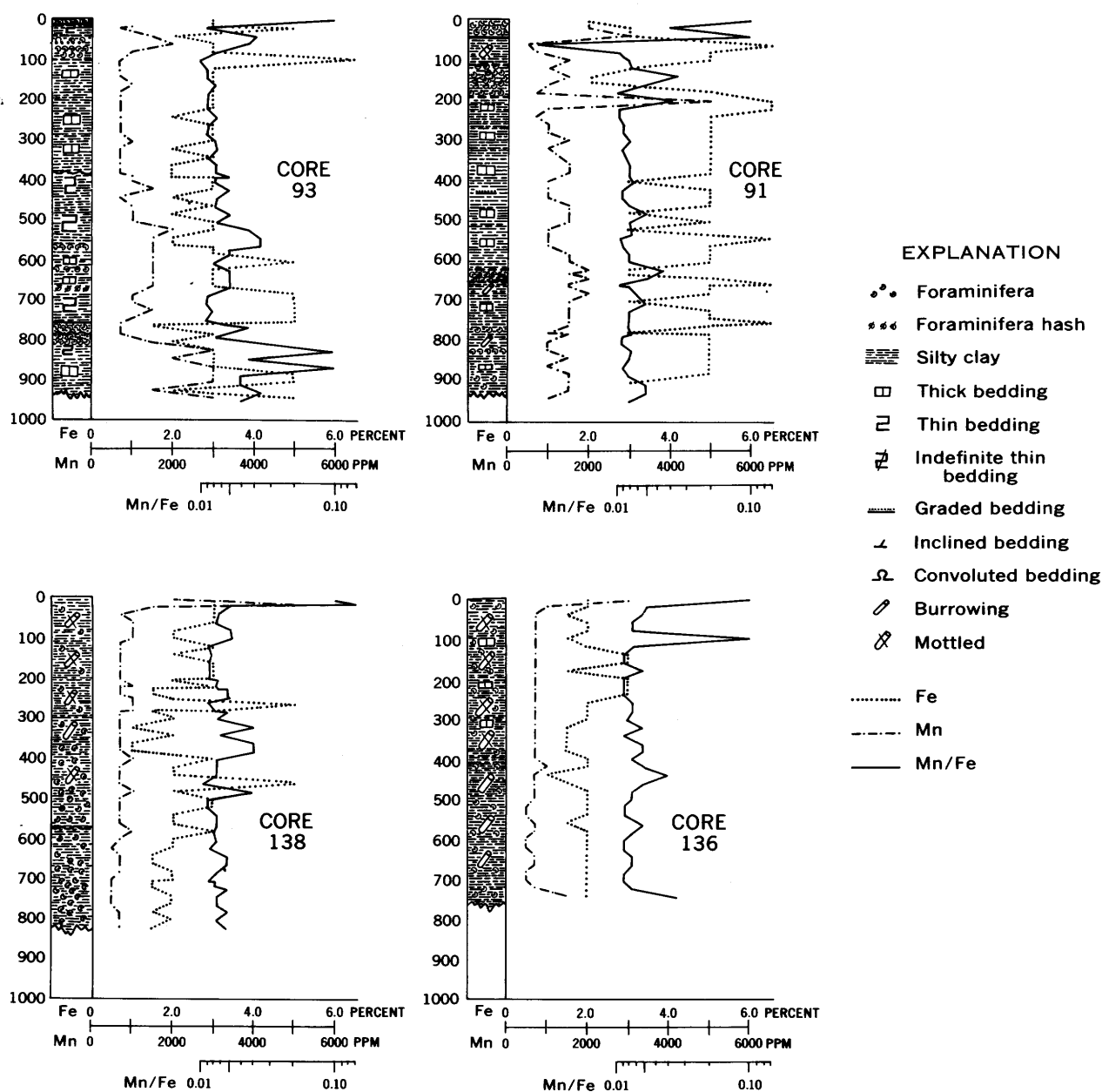
FIGURE 10.—Continued.

the oxidation potential. Estimates of the redox potential and manganese distribution in the sediments of the gulf show a general agreement with the model (fig. 13). Detailed manganese analyses in the upper metre of four representative cores from the major provinces of the gulf also demonstrate good agreement with the model (figs. 14 and 15). Figure 14 also shows the almost independent relationship of iron and manganese. Other elements in the sediments containing greater than 1,000 ppm manganese (table 4) undergo no significant enrichment in concentration in the high manganese sediments. In only one core in the western gulf is there the slightest evidence of comigration of iron and other elements with manganese.

In some cores, particularly in the western gulf, manganese-rich zones are found at depth (28 of fig. 9 and 93 and 96 of fig. 10). These are interpreted as "fossil" oxidized zones which were buried by rapid deposition during the glacial maxima of the Pleistocene.

CALCIUM-STRONTIUM GROUP

The distribution of these group II elements is intrinsically related to the distribution of carbonates, the predominant association of these elements. In the gulf basin the calcium content in the sediment
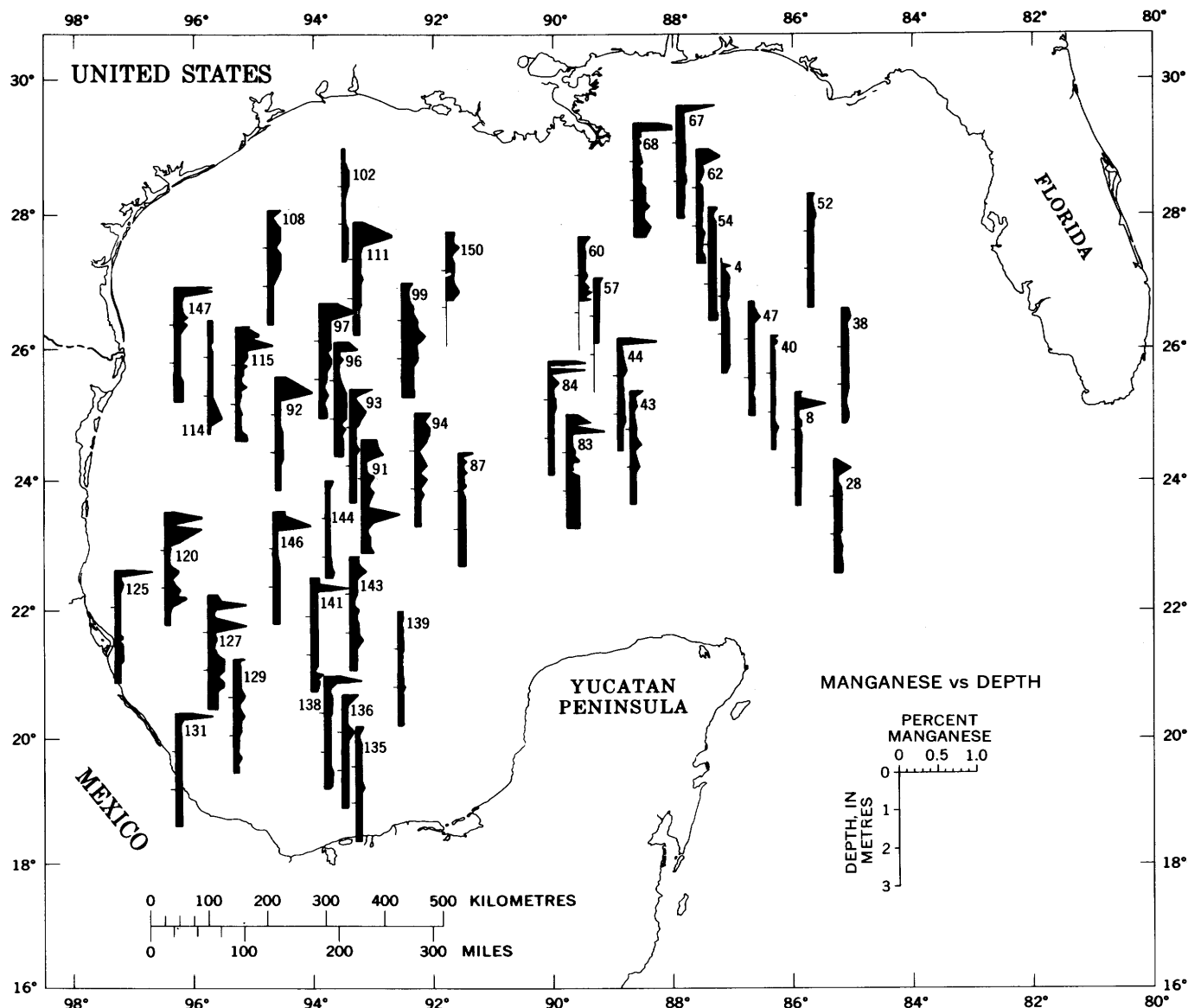
FIGURE 11.—Vertical distribution of spectrographically determined manganese from the top 3 m of 46 cores.

ranges from 0.25 to greater than 20 percent composition. The carbonates in the gulf basin were either deposited as carbonate detritus washed from the Florida or Yucatan shelves or derived from planktonic carbonate-secreting organisms. In the south-central abyssal region of the gulf, Davies (1968) found carbonate-rich zones in cores containing shallow-water organisms and suggested that much of the carbonate sediments in this region were derived from the Campeche Bank. The pelagic contribution of calcium to the sediment is primarily foraminiferal tests (Kennett and Huddleston, 1972) ; the tests of other carbonate secreting organisms (pterepods and coccoliths) are present in insignifi-

cant concentrations. The only detrital carbonate layers occur in the western gulf.

Like calcium, strontium in marine sediments is predominantly associated with carbonates. Chemically similar to calcium, strontium substitutes for calcium in carbonates; however, being somewhat larger than calcium (Ca^{+2} has an octahedral radius of 0.99 A, and strontium has a radius of 1.12 A), strontium is preferentially incorporated into the more open aragonite carbonate structure. Turekian (1964) reported that pelagic Foraminifera range from 700 to 1,500 ppm strontium, whereas coral and many other shallow-water carbonates average 8,000 ppm strontium. Mineralogically this is predictable because all pelagic Foraminifera are calcitic, and
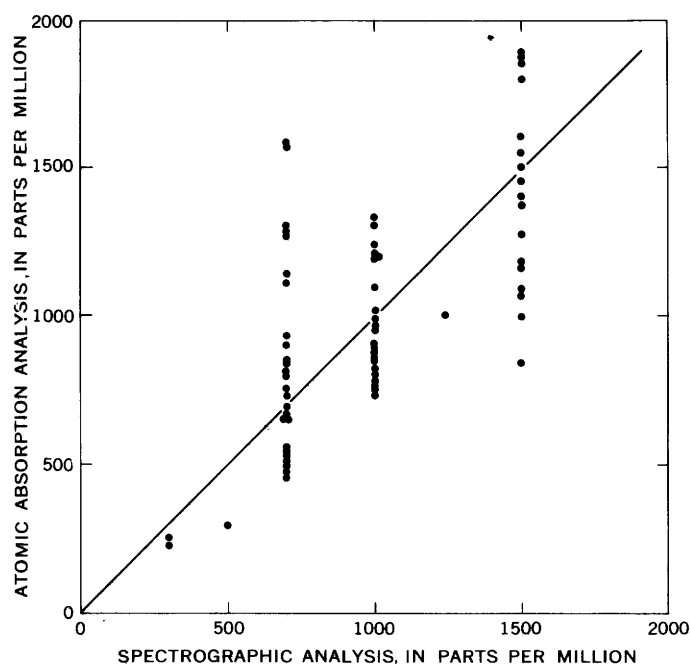
FIGURE 12.—Comparison of manganese determined by atomic absorption analysis of leached material and by spectrographic analysis of whole samples.

FIGURE 13.—Manganese, emv, and pH in the upper section of core 28.

TABLE 8.—*Average manganese content of the total sediment and of the sediment on a carbonate-free basis (CFB) for those cores for which the Holocene-Pleistocene boundary has been defined*

[The investigator on whose data the Holocene boundary was primarily established: L=Ludwig (1971). K=Kennett and Huddleston (1972). N=Newman and others (1973).]

Core	Holocene Boundary	Holocene		Pleistocene	
		Total μg/g	CFB μg/g	Total μg/g	CFB μg/g
8	67 L	1,188	1,284	722	767
28	60 L	815	913	586	593
44	105 L	1,236	1,482	736	750
47	80 L	972	1,020	586	597
57	24 L	847	1,006	815	840
60	40 L	857	958	934	989
62	60 L	1,465	1,562	652	680
68	70 L	2,173	2,739	1,423	1,489
83	140 L	1,385	1,875	1,295	1,336
84	38 L	1,934	2,295	826	857
87	80 N	802	1,687	767	791
91	210 N	1,607	1,909	968	1,496
92	100 L	2,090	2,215	847	878
93	100 L	1,416	1,777	743	763
94	240 N	1,260	1,500	697	718
96	250 N	1,152	1,239	1,715	1,861
97	300 K	1,708	1,913	1,437	1,500
111	90 L	2,187	2,427	645	701
115	105 K	2,229	2,381	704	732
120	80 K	2,302	2,972	1,225	1,295
125	105 K	1,243	1,322	902	968
131	60 K	1,618	1,767	687	753
138	125 K	1,486	1,625	767	836
141	120 K	1,385	1,472	409	461
146	100 N	1,392	1,482	618	628
147	110 K	1,829	1,940	690	715
150	150 N	982	1,048		

most corals and shallow water carbonates are composed of aragonite. The shallow-water or pelagic origins of the carbonate layers in the gulf may be differentiated by the calcium/strontium ratio. High strontium content with a Ca/Sr ratio of approximately 50 is indicative of a shallow-water source; low strontium content with a Ca/Sr ranging between 250 and 600 is characteristic of a pelagic source.

The distribution of calcium and strontium in cores from the western gulf is shown in figure 16. These cores were taken along long 93° W. and represent a section across many environments: the northern Continental Rise (111); the abyssal plain (97, 96, 93, 91); the lower Campeche Canyon (144, 143, 141B); and the Mexican Continental Slope (138, 136). The average calcium content as represented in these cores is higher than those taken in the eastern gulf because of the reduced sedimentologic influence of the Mississippi River which allows pelagic processes to play a larger role. Seven of the 11 cores (10 of which are shown in fig. 16) have well-defined carbonate layers. In the cores taken near the Campeche platform, the strontium concentration exceeds the upper limit of detection. These strontium-rich layers are interpreted to contain carbonate turbidites similar to those reported by Davies (1968). In cores toward the north, some low-Ca/Sr-ratio zones are indicative of shallow-water material but are less numerous.

Samples from the southern cores having the highest strontium content were X-rayed to determine their aragonite/calcite ratios and their ages (table 9). These layers contained approximately twice as
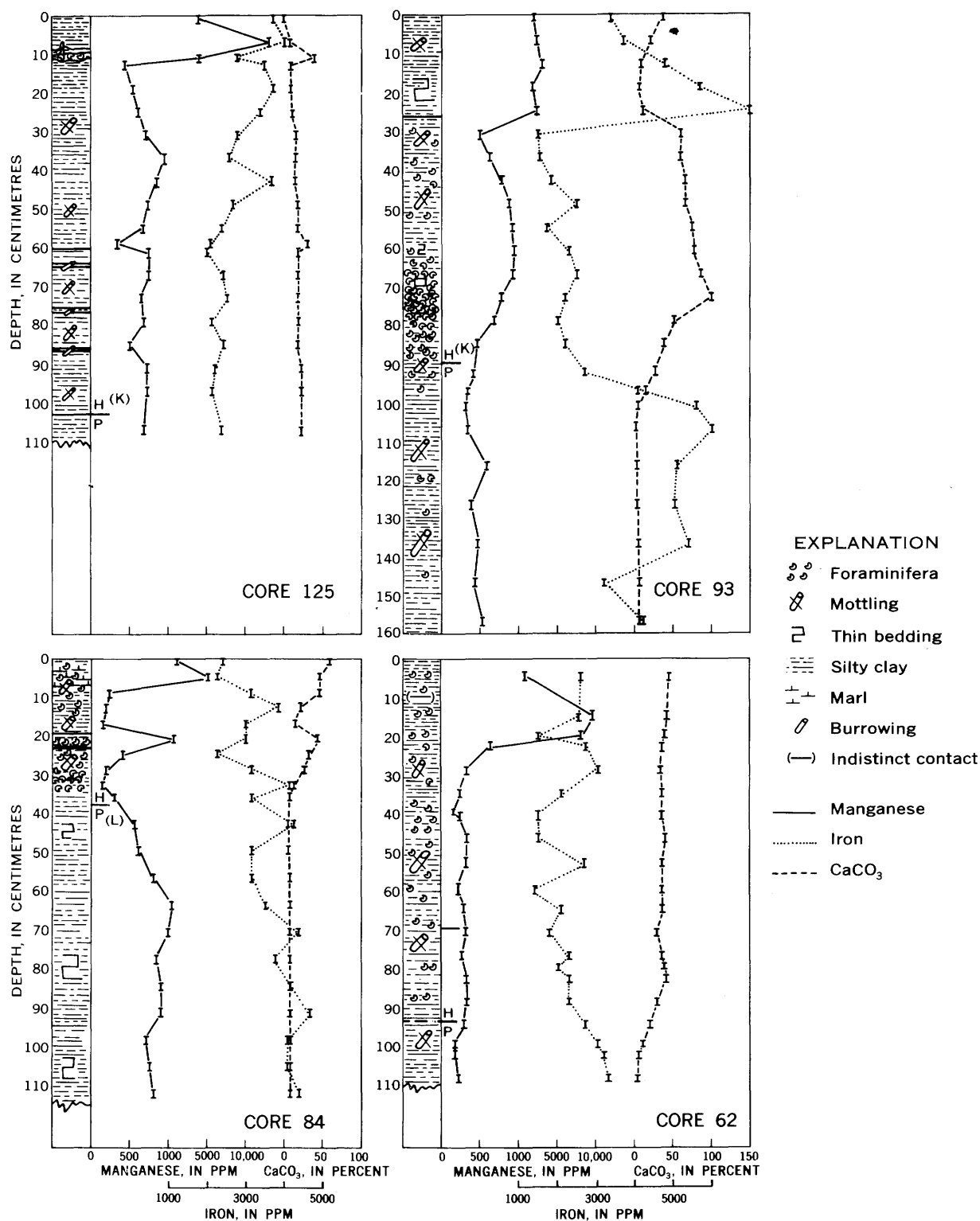
FIGURE 14.—Detailed analyses for manganese, iron, and calcium from the upper metre of four cores from the
major provinces of the Gulf of Mexico. The line H/P is the estimated position of the Holocene-Pleistocene
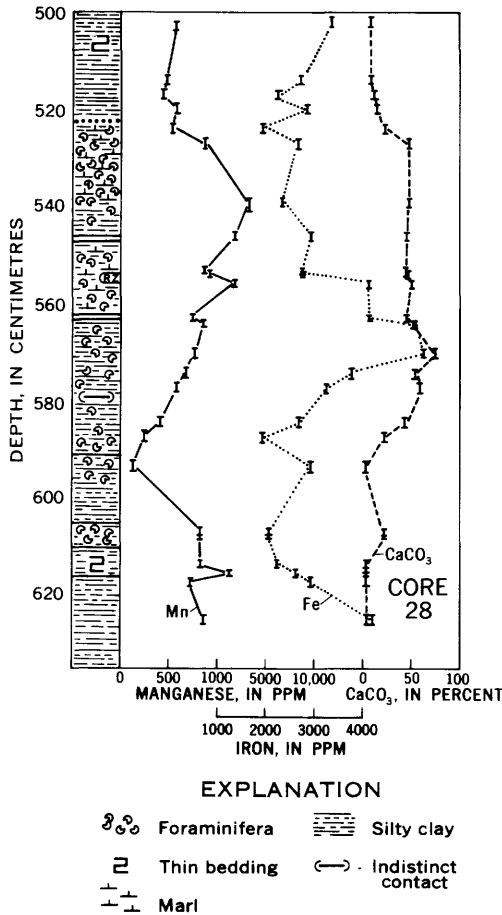boundary as determined by Ludwig (1971) (L) or Kennett and Huddleston (1972) (K).

FIGURE 15.—Distribution of manganese, iron, and calcium between 500- and 630-m depth in core 28.

much aragonite as calcite further evidence of a shallow-water origin of the carbonate. U^{234}/Th^{230} dating on these samples indicated an age of approximately 30,000 years. Those ages older than this can be brought into concordance by correcting for detrital thorium on the basis of the carbonate content. Thus, the carbonate layers in these cores were deposited at least 30,000 B.P. In core 141B, the synchronous deposition of nearly 6 m of carbonate must be the

result of mass transport processes. Paleontological work on this core (Kennett and Huddleston, 1972) shows that this zone is completely "reworked," thus supporting the mass-transport interpretation.

CONCLUSION

The semiquantitative analyses of sediments from the Gulf of Mexico have provided good and detailed data on the marine distribution of some trace and minor elements. The average elemental content of the sediment, as determined by this method, was found to be significantly different from that of similar sediment types reported in the literature (Horn and Adams, 1966). Whether or not this difference is due to the method of analysis cannot be evaluated at this time. However, these data do provide useful information for making comparisons of trace-element content between recent sediments and those of Pleistocene and Holocene age. Analyses of the distribution of individual elements of all samples demonstrate that most elements are approximately lognormally distributed; this is an important consideration in determining the geochemical cycle of elements and in deriving mathematical models to describe the elemental distribution.

Statistical analyses of the data allowed the grouping of elements according to geochemical coherence. The distribution of these groupings demonstrated that many elements (for example, iron, vanadium, chromium, magnesium, cobalt, titanium, and so forth) are intimately associated with detrital clay material. Manganese, an element showing a statistically weak association with the above elements, was found to be sensitive to postdeposition chemical pressures and was redistributed according to the chemical environment within the sediment. The distribution of calcium/strontium ratios provided useful criteria for determining the source of carbonate-rich sediments.

TABLE 9.—Carbonate uranium-thorium disequilibrium
[The ratio between uranium isotopes is in activity units, not mass]

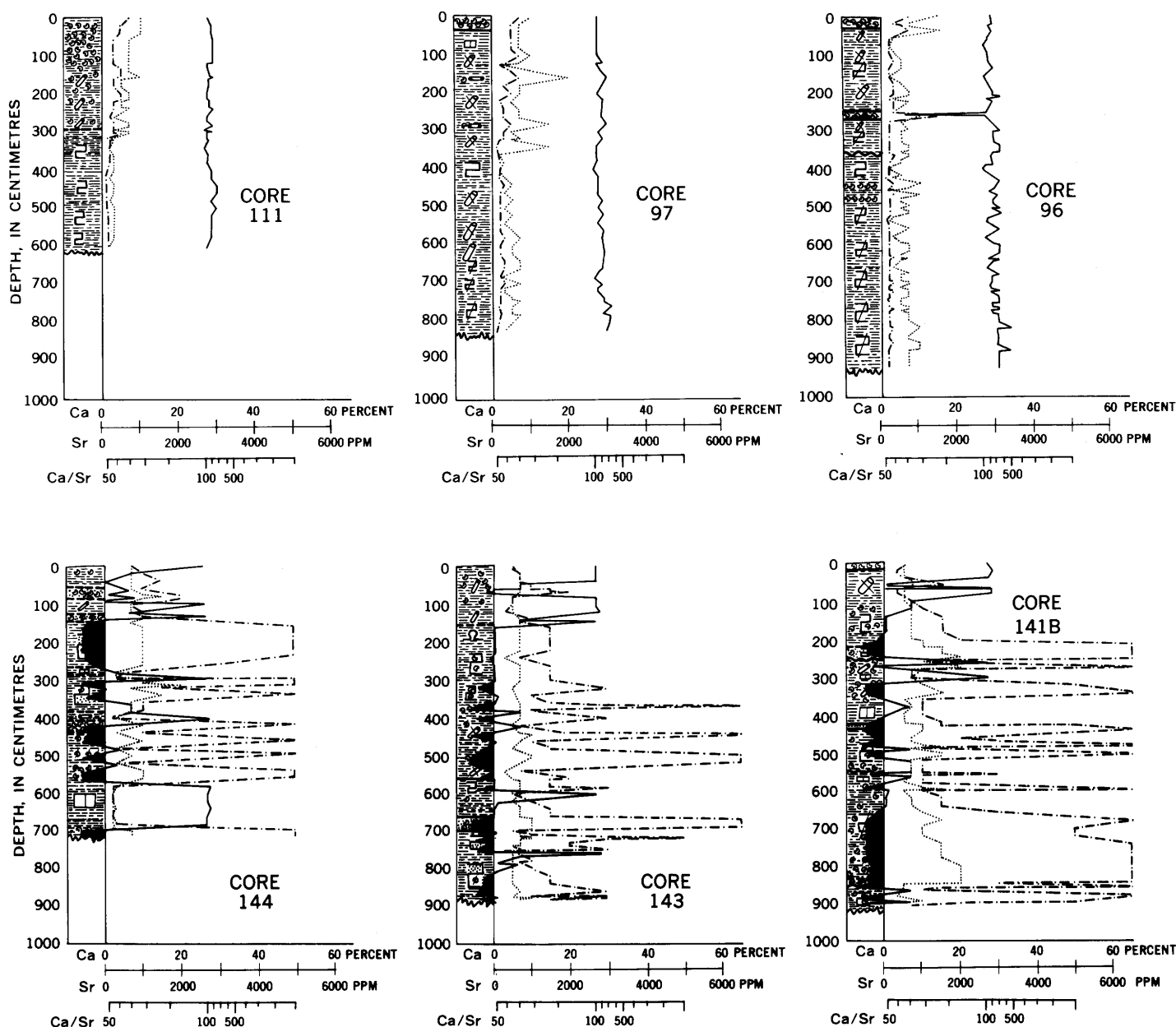| Depth (cm)	CO$_2$ (percent)	Arago- nite / Calcite ratio	U (ppm)	Th (ppm)	$\dfrac{U^{234}}{U^{238}}$	$\dfrac{Th^{230}}{U^{234}}$	Age (apparent)
				141B			
250	91.80	1.8	3.89± .81	0.50± .06	1.10±.06	0.26±.004	31,000±11,500
480	94.94	2.8	4.71± .04	.34± .03	.99±.10	.25±.10	30,500±11,000
845	79.80	2.0	3.33± .03	1.12± .10	1.12±.04	.41±.004	57,000±11,500
				143			
500	87.3	2.4	3.89±0.03	1.61±0.10	1.09±.01	0.39±.03	53,000± 5,000
685	91.4	2.0	4.48±0.03	.39± .09	1.04±.19	.26±.01	31,000± 2,000

FIGURE 16.—Calcium, strontium, and calcium/strontium ratio in cores from north-south transect in the western gulf basin.

Thus, the semiquantitative data used in this report have provided much information on the gross distribution of trace and minor elements in marine sediments of the gulf. The lack of precise definition which is inherent in rapid analyses, however, prevents specific analyses of the species in which the elements occur. More detailed and sophisticated analytical methods are necessary for these results. However, the data presented herein provide a basis on which such studies may be founded.

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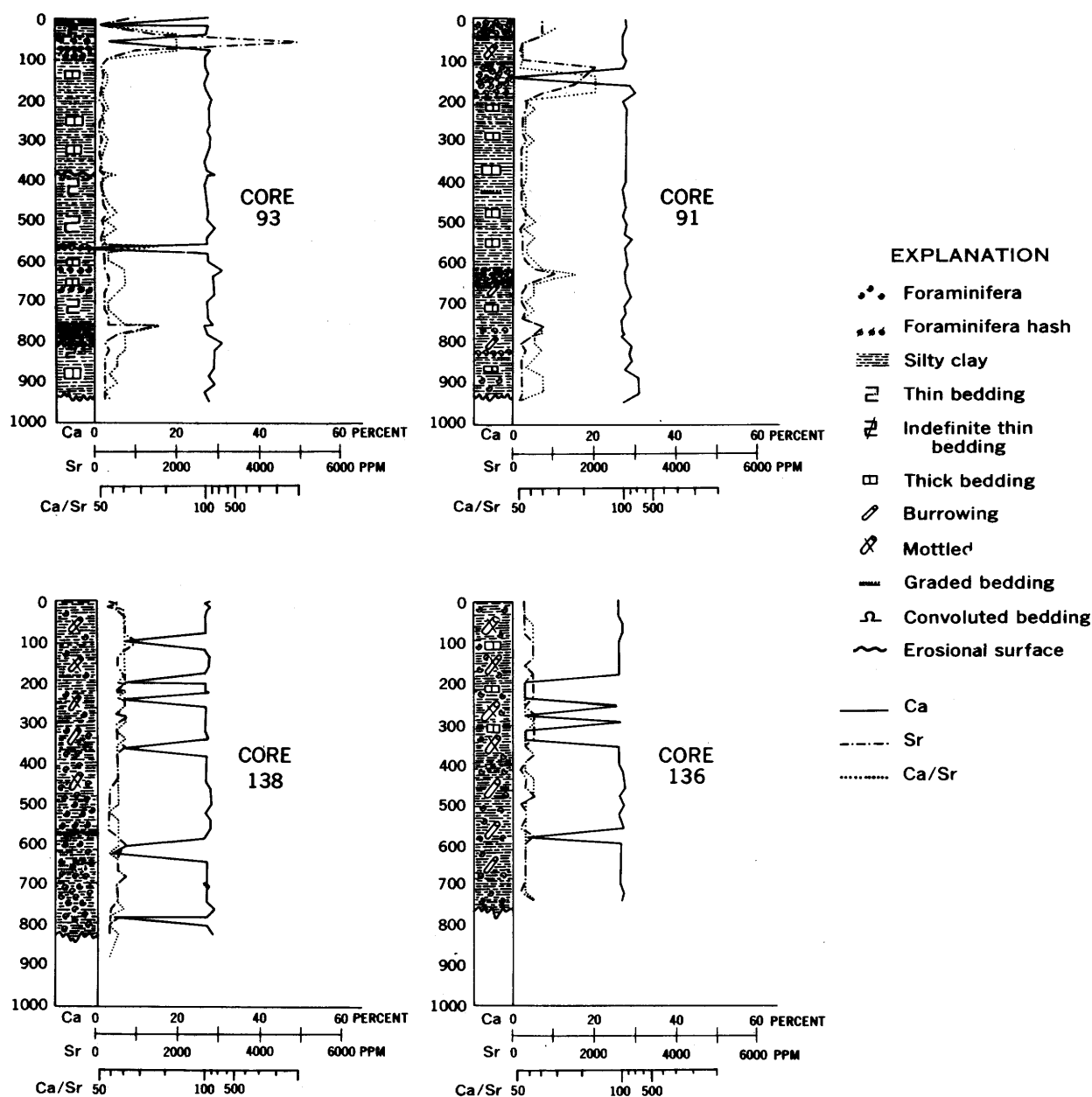
FIGURE 16.—Continued.

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