

Distribution of Selected Elements in Surficial Marine Sediments of the Northern Gulf of Mexico Continental Shelf and Slope

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Distribution of Selected Elements in Surficial Marine Sediments of the Northern Gulf of Mexico Continental Shelf and Slope

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G E O L O G I C A L S U R V E Y P R O F E S S I O N A L P A P E R 8 1 4

*A study of the distribution of elements
in two continental shelf environments
of different depositional character*



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ILLUSTRATIONS

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- PLATE 1. Map showing the generalized distribution of surficial marine sediments on the continental shelf and slope of the northern Gulf of Mexico.
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2. Barium, boron, calcium, chromium, cobalt, and copper.
 3. Iron, lanthanum, lead, magnesium, manganese, and nickel.
 4. Scandium, strontium, titanium, vanadium, yttrium, and zirconium.
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upper limit value is prefaced by "G" signifying "greater than"; concentrations below the limit of determination are noted by "N" (not detected). If the spectrophotometer detects the presence of an element, but the analytical line is too faint for an accurate estimate of elemental concentration, the elemental values are reported as "L", which denotes that the element is present but in concentrations less than the lower limit of determination.

METHODS OF DATA ANALYSIS

The values obtained from the analyses for each element were plotted on charts and contoured. From these charts, maps were constructed with patterns representing the field between contour intervals. The contour interval for each map was chosen subjectively to show the regional variations. The patterns represent a subjective smoothing to avoid clutter in the areas of high sample density. Only those elements which were detected in more than 50 percent of the samples have been mapped.

For comparative purposes, the shelf was divided into three segments: (1) the northwestern shelf and upper slope west of the Mississippi River Delta and north of lat 28° N., (2) the northeastern shelf and slope east of the Mississippi River Delta and north of lat 28° N., and (3) the south Florida shelf and slope from lat 28° N. to the Florida Keys. Latitude 28° was chosen as the southern limit of the northwestern region to exclude Rio Grande sediments. The sediments in the northwestern shelf are primarily noncarbonate clastics, whereas the sediments in the south Florida area are wholly in a carbonate environment. The northeastern area represents the transition zone between the noncarbonate and carbonate areas. Statistical summarization of the elemental composition of each of the three areas allows chemical comparison and differentiation based on sediment type to be made.

The data were computer summarized by a program which yielded a listing of the data, the maximum and minimum values, a histogram plot, the frequency distribution, and a statistical summary which included the geometric mean and geometric deviation. Before these computations were performed, all G (greater than) values were removed from the data by assigning these values to the next higher geometric class midpoints. This type of manipulation was necessary for calcium, manganese, strontium, and zirconium. Justification for this procedure comes from the analysis of the data and known chemical distributions.

The geometric mean and geometric deviation are antilogs of the arithmetic mean and standard deviation of the logarithms of the analytical values. If samples had elemental concentrations less than the lower limit of detection, the geometric mean and deviations were estimated by a censored-distribution method (Cohen, 1959). The geometric mean is a more consistent measure of the central tendency of a frequency distribution than the arithmetic mean and thus is an estimate of the typical or most common concentration of an element. The geometric means and deviations are given in table 2.

The arithmetic means of the analytical data were computed from the estimated geometric means and deviations by using the method described by Miesch (1967), which is based on the techniques presented by Cohen (1959) and Sichel (1952). The arithmetic means listed in table 3 are estimates of geochemical abundance (Miesch, 1967) and are directly comparable to the arithmetic means (geochemical averages) reported in the literature (Shacklette and others, 1971).

Correlation coefficients—those statistical parameters which "measure" the reliability of one variable in predicting another—were calculated on the logs of the analytical values. The computer program¹ used for these calculations ignores data in which one or more values are qualified. Therefore, the correlation coefficient for some element pairs is based on less than the total number of samples. For these pairs, the data are derived from censored distributions and should be considered as an index of association (A. T. Miesch, written commun., 1971). However, if only a few values are qualified in a large data set, the calculated correlation coefficient may be used for statistical evaluation. The correlation coefficients for the elements in each area are given in table 4.

RESULTS

The results of this investigation are presented in a series of maps depicting regional elemental patterns (pls. 2-4). The data are also summarized in tables 2-4, which list the geometric means and geometric deviations, the arithmetic means, and correlation coefficients.

Of the 30 elements for which analyses were performed, 18 had sufficient concentrations to be detected in more than 50 percent of the samples; these data are shown on plates 2-4. Five of the remaining

¹ Selner, G. I., 1968, Correlation analysis. Program No. D0101: U.S. Geol. Survey, Computer Center Division, Denver, Colo.

ELEMENTS, MARINE SEDIMENTS, NORTHERN GULF OF MEXICO

TABLE 2.—Geometric means and geometric deviations of elements in the surficial marine sediments on the continental shelf and slope in the northern Gulf of Mexico

[Geometric means reported in parts per million; N , number of samples analyzed; N.E., not enough samples had detectable amounts of the element to allow for calculation of measure and deviation]

Element	Northwestern shelf and slope ($N=795$)		Northeastern shelf and slope ($N=206$)		South Florida shelf and slope ($N=148$)		Total number of samples analyzed ¹ ($N=1,304$)	
	Geometric mean	Geometric deviation	Geometric mean	Geometric deviation	Geometric mean	Geometric deviation	Geometric mean	Geometric deviation
	Ba	480	1.56	84	3.56	69	2.84	295
B	55	1.86	47	1.77	26	1.89	48	1.91
Ca	15,800	3.33	125,600	2.47	286,000	1.21	40,700	5.03
Co	8	1.41	7	1.44	2	3.27	8	1.43
Cr	47	2.05	31	2.89	26	1.88	40	2.18
Cu	10	1.70	9	1.85	N.E.	N.E.	10	1.81
Fe	15,100	2.09	12,100	3.33	3,710	3.74	10,300	2.99
La	32	1.79	18	2.63	6	2.65	25	2.04
Mg	7,400	1.98	12,500	2.62	24,100	1.37	10,200	2.39
Mn	401	1.75	217	4.96	95	4.34	230	3.36
Ni	19	2.07	16	2.48	5	3.52	17	2.21
Pb	24	1.77	23	1.99	N.E.	N.E.	24	1.87
Sc	9	1.54	8	1.51	.6	4.56	9	1.55
Sr	198	1.98	1,060	2.17	3,580	1.85	500	4.21
Ti	2,800	1.81	820	2.97	296	2.68	1,200	3.16
V	73	2.01	36	2.47	19	2.29	48	2.52
Y	21	1.51	18	1.53	9	2.19	20	1.54
Zr	309	2.36	55	2.63	11	2.26	121	4.72

¹ Includes 155 samples from west of De Soto Canyon and north of lat 28° N.

12 elements were found in some samples as follows: Beryllium, in 44.5 percent of the samples, ranging from 1 to 10 ppm; molybdenum, in 7.6 percent of the samples, ranging from 5 to 15 ppm; niobium, in 34.7 percent of the samples, ranging from 10 to 30 ppm; tin, in 4.3 percent of the samples, ranging from 10 to 500 ppm; and zinc, in 0.2 percent of the samples, ranging from 300 to 1,500 ppm. The remaining seven elements were looked for in all samples but were not detected. These elements and

their lower limit of detection (in parts per million) are as follows: Antimony, 100; arsenic, 200; bismuth, 10; cadmium, 20; gold, 10; silver, 0.5 and tungsten, 50.

DISCUSSION AND CONCLUSIONS

Examination of the maps accompanying this report (pls. 2-4) reveals certain regional variations in the concentrations of the elements. Because of operative bias in the analytical method, mapped patterns

TABLE 3.—Average element content in surficial marine sediments of the Gulf shelf and average element content reported for major sedimentary units

[Data in parts per million; each average represents arithmetic mean; X indicates that only order of magnitude estimate could be made]

Element	Gulf shelf marine sediment, this report				Worldwide elemental averages of major sedimentary units								
					Horn and Adams (1966)			Turekian and Wedepohl (1961)					
	North-western shelf	North-eastern shelf	South Florida shelf	Total samples ¹	Car-bon-ate	Shale	Sand stone	Mobile belt sedi-ments ²	Car-bon-ate	Shale	Sand-stone	Deep-sea car-bon-ate	Deep-sea clay
Ba	509	140	66	341	35	263	199	233	10	580	X	190	2,300
B	64	56	31	57	12	79	25	56	20	100	35	55	230
Ca	31,760	182,140	286,000	151,320	272,000	22,200	22,200	26,900	302,300	22,100	39,100	312,400	29,000
Co	8	5	3	6	.2	8	.5	5	.1	19	.3	7	74
Cr	64	48	32	52	7	427	121	295	11	90	35	11	90
Cu	11	7	X	9	4	47	15	34	4	45	X	30	250
Fe	18,910	25,290	8,920	18,450	8,660	39,600	21,000	31,100	3,800	47,200	9,800	9,000	65,000
La	37	30	9	32	6	25	11	18	X	92	30	10	115
Mg	8,920	19,420	24,680	14,920	45,500	16,600	8,760	13,900	47,000	15,000	7,000	4,000	21,000
Mn	442	740	257	519	385	300	10	188	1,100	850	X	1,000	6,700
Ni	23	21	10	21	13	33	3	21	20	68	2	30	225
Pb	25	21	X	21	6	20	7	15	9	20	7	9	80
Sc	9	6	2	7	1	11	1	7	1	13	1	2	19
Sr	273	1,436	4,264	1,300	544	242	24	168	610	300	20	2,000	180
Ti	2,730	1,400	470	2,410	389	4,520	2,100	3,430	400	4,600	1,500	770	4,600
V	91	54	25	77	13	102	21	68	20	130	20	20	120
Y	22	17	12	18	6	12	2	8	30	26	40	42	90
Zr	431	89	15	375	18	144	206	160	19	160	220	20	150

¹ Includes samples from west of De Soto Canyon and north of lat 28° N.

² Mobile belt sediments are defined as 59 percent shale, 36 percent sandstone, 2 percent carbonate, and 3 percent evaporites.

DISCUSSION AND CONCLUSIONS

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TABLE 4.—Bielement correlation coefficients based on analyses of surficial marine sediments on the northern continental shelf and slope of the Gulf of Mexico

[Coefficients (r) are given in the upper right; numbers of samples (n) upon which coefficients are based are given in the lower left]

$n \backslash r$	Ba	B	Ca	Co	Cr	Cu	Fe	La	Mg	Mn	Ni	Pb	Sc	Sr	Ti	V	Y	Zr	
Northwestern shelf and slope north of lat 28° N. (795 samples in this region)																			
Ba -----	785	0.31	-0.22	0.28	0.32	0.09	0.45	0.42	0.21	0.23	0.35	0.16	0.10	-0.28	0.57	0.30	0.22	0.10	
B -----	785	---	-0.18	.67	.37	.09	.70	.17	.57	.43	.66	.49	.46	-0.25	.62	.63	.22	.37	
Ca -----	795	785	---	-0.02	.18	-0.05	-0.04	.11	.28	.10	.01	-0.14	.15	.85	-0.09	-0.09	.25	-0.32	
Co -----	692	692	692	---	.51	.19	.74	.26	.63	.49	.70	.58	.57	-0.07	.56	.73	.43	-0.12	
Cr -----	787	777	787	690	---	.03	.63	.22	.68	.40	.66	.47	.68	.03	.55	.70	.56	-.08	
Cu -----	717	712	717	635	710	---	.03	.14	.05	.24	.08	.31	.24	-0.12	.18	.14	.15	.01	
Fe -----	795	785	795	692	787	717	---	.37	.79	.62	.77	.66	.63	-0.11	.71	.81	.45	.01	
La -----	696	696	696	626	695	630	696	---	.33	.25	.31	.29	.31	.15	.31	.16	.38	-0.05	
Mg -----	795	785	795	692	676	717	795	696	---	.61	.75	.64	.74	.23	.51	.71	.56	-0.25	
Mn -----	795	785	795	692	787	717	795	696	795	---	.52	.52	.57	.09	.44	.55	.45	-0.11	
Ni -----	760	756	760	692	768	698	760	671	760	760	---	.65	.77	-0.03	.56	.81	.44	-.23	
Pb -----	664	569	694	500	664	610	664	643	664	664	644	---	.62	-0.16	.42	.66	.34	-0.23	
Sc -----	678	675	678	628	678	634	678	646	678	678	665	624	---	.06	.48	.77	.52	-0.42	
Sr -----	795	785	795	692	787	717	795	696	795	795	760	664	678	---	.29	-0.18	.16	-0.40	
Ti -----	795	785	795	692	787	717	795	696	795	760	664	678	795	---	.67	.45	.37	-.05	
V -----	779	770	779	689	776	704	779	694	779	779	749	664	678	779	779	---	.53	-.05	
Y -----	764	755	764	680	768	694	764	693	764	764	734	660	676	764	760	---	-.04	-.04	
Zr -----	795	785	795	692	787	717	795	696	795	760	664	678	795	795	779	764	---	---	---
Northeastern shelf and slope north of lat 28° N. (206 samples in this region)																			
Ba -----	196	0.74	-0.01	0.56	0.64	0.69	0.59	0.47	0.28	0.76	0.82	0.77	0.74	-0.29	0.86	0.73	0.55	0.55	
B -----	196	---	.15	.27	.66	.56	.69	.26	.39	.74	.70	.65	.62	-0.08	.75	.78	.54	.42	
Ca -----	196	206	---	-0.15	.26	.01	.34	---	.15	.76	.32	.27	-0.16	-0.03	.86	-0.03	.27	.16	-0.29
Co -----	93	94	94	---	.27	.58	.42	.40	.17	.43	.52	.52	.65	-0.26	.43	.38	.11	.23	
Cr -----	175	184	184	94	---	.39	.81	.10	.58	.77	.80	.60	.56	.01	.58	.85	.58	.21	
Cu -----	117	118	118	85	107	---	.50	.28	.34	.65	.69	.61	.70	-0.16	.46	.60	.40	.09	
Fe -----	194	203	203	93	183	117	---	.37	.71	.83	.75	.67	.71	.12	.57	.84	.49	.17	
La -----	102	104	104	83	104	83	103	---	.03	.16	.16	.54	.39	-0.25	.45	.04	.03	.32	
Mg -----	196	206	206	94	184	118	203	104	---	.56	.51	.32	.39	.65	.16	.58	.30	-.21	
Mn -----	196	206	206	94	184	118	203	104	206	---	.86	.67	.61	.05	.70	.89	.54	.22	
Ni -----	148	151	151	94	143	101	150	100	151	151	151	151	151	151	151	151	151	151	
Pb -----	128	129	129	88	129	97	129	91	129	129	118	118	118	118	118	118	118	118	
Sc -----	96	96	96	86	96	91	96	88	96	96	96	95	95	95	95	95	95	95	
Sr -----	196	206	206	94	184	118	203	104	206	206	151	129	96	206	206	206	206	206	
Ti -----	196	206	206	94	184	118	203	104	206	206	151	129	96	206	206	206	206	206	
V -----	193	203	203	94	184	117	201	104	203	203	151	129	96	206	206	206	206	206	
Y -----	157	162	162	92	162	102	162	101	162	162	133	126	96	162	162	162	162	162	
Zr -----	196	206	206	94	184	118	203	104	206	206	151	129	96	206	206	206	206	206	
South Florida shelf and slope from lat 28° N. to the Florida Keys (148 samples in this region)																			
Ba -----	60	0.60	-0.61	0.69	0.62	0.58	0.78	0.51	-0.28	0.73	0.78	0.47	0.82	-0.67	0.81	0.68	0.50	0.64	
B -----	66	---	-0.55	.74	.48	.38	.28	.15	.02	.28	.54	.20	.88	-0.22	.64	.55	.12	.56	
Ca -----	67	146	---	-0.72	-0.43	-.35	-.46	-.55	.22	-.38	-.52	-.13	-.77	.51	-0.59	-.67	-.33	-.60	
Co -----	31	33	34	---	.78	.21	.71	-.16	.05	.33	.67	.05	.66	-.73	.63	.71	.37	.65	
Cr -----	67	145	147	34	---	.44	.65	.50	.02	.38	.60	.18	.67	-.34	.65	.62	.48	.60	
Cu -----	40	42	42	28	42	---	.49	.52	-.01	.53	.61	.67	.87	-.39	.59	.47	.17	.54	
Fe -----	67	138	139	34	139	42	---	.75	-.27	.75	.81	.46	.85	-.75	.71	.79	.69	.47	
La -----	12	23	23	12	23	12	23	---	-.43	.68	.39	.38	.95	-.74	.69	.68	.49	.71	
Mg -----	67	146	148	34	147	42	139	23	---	-.29	.42	-.01	.10	.44	-.18	-.34	-.13	-.19	
Mn -----	67	146	148	34	147	42	139	23	148	---	.83	.49	.44	-.75	.73	.73	.56	.41	
Ni -----	60	83	84	34	84	40	84	12	84	84	84	84	84	84	84	84	84	84	
Pb -----	32	41	41	26	41	29	41	12	41	41	37	37	37	70	18	.18	.39	.22	
Sc -----	18	20	20	18	20	18	20	12	20	20	18	16	16	61	20	144	144	.61	
Sr -----	67	146	148	34	147	42	135	21	144	144	144	144	144	144	144	144	144	144	
Ti -----	67	142	144	34	143	42	139	23	148	148	148	148	148	148	148	148	148	148	
V -----	67	136	138	34	138	42	133	23	138	138	138	138	138	138	138	138	138	138	
Y -----	60	79	80	34	80	41	80	20	80	80	66	34	20	20	80	80	80	80	
Zr -----	67	146	148	34	147	42	139	23	148	148	148	148	148	148	148	148	148	148	

based on a single sample which varies by only one class from neighboring samples may be meaningless. However, individual values that differ by more than two classes from surrounding sample points are considered to be significant.

In general, the concentrations of most elements are highest in the silty and clayey sediments on the continental slope off south Texas, on the outer shelf and slope off central Louisiana, and in the lower reaches of the De Soto Canyon. Terrigenous material is presently being deposited in these regions (Curray, 1960; Ludwick, 1964). In the sediments on the central Texas shelf southeast of Galveston, and on the south Florida shelf, the amounts of trace and minor elements are comparatively low.

In the relict sediments of the shelf southeast of Galveston, subaerial weathering during the Pleistocene sea-level fluctuations has depleted the supply of trace and minor elements. Those elements which occur in chemically resistant minerals, however, show a relative enrichment in these sediments. For example, Holmes (1971) demonstrated that the zirconium enrichment in the sediments of this region marks relict strandlines. The calcium, strontium, and magnesium in a few samples from this area represent relict shelly sediments. These sediments are probably lagoonal material deposited at some epoch during the Pleistocene.

On the south Florida shelf, the sediments are predominantly carbonates. These formed primarily

from chemical species in sea water which is depleted in trace elements and reflect the chemistry of the sea water. As a result, carbonate sediments are similarly depleted in trace and minor elements with the exception of strontium and magnesium.

Superimposed on these regional patterns are several anomalous elemental concentrations. Iron and manganese are enriched in the sediments on the upper slope south of Galveston and on the central and lower sections of the De Soto Canyon. The vertical concentration patterns of iron and manganese in cores from these areas indicate that both elements have become concentrated at the surface, possibly the result of upward migration of these elements within the sediment column (unpub. data). In the De Soto Canyon region, the surficial sediments also contain greater amounts of barium, cobalt, copper, magnesium, and nickel than the surrounding sediments. Jenne (1968) has pointed out that the chemical complexes of iron and manganese which are free to migrate also act as chemical "sinks" for other elements. This may account for the high concentration of other elements in this region.

Along the upper slope south of Louisiana, the high calcium and strontium content of the sediments reflects the presence of the carbonate banks, for example, the Flower Gardens (Parker and Curran, 1956). A similar calcium and strontium anomaly on the upper reaches of the De Soto Canyon denotes the carbonate bank present on the rim of the canyon (Ludwick and Walton, 1957).

Sediment samples taken in the vicinity of bay and river mouths often have a high concentration of trace elements. Directly seaward of Galveston Bay, barium, copper, iron, lanthanum, and lead are relatively high. South of Mobile Bay, barium, copper, iron, lead, scandium, titanium, vanadium, and yttrium are anomalously high. West of the delta of the Mississippi, barium, boron, cobalt, copper, iron, lanthanum, nickel, lead, titanium, vanadium, and yttrium are concentrated relative to the surrounding sediment. Although it is difficult to determine the origin of these trace elements, their disposition suggests that they are deposited almost immediately after entering the marine environment. To determine which elements occur naturally and which are artificially introduced by man will require a more extensive investigation into the chemical nature and the distribution of these elements in the sediments, organisms, and waters of these areas.

On the south Florida shelf, the sediments surrounding the Dry Tortugas show a high content of boron, chromium, nickel, and strontium, attributed to the biologic activity in the region. The mechan-

isms resulting in these concentrations, however, must await more extensive laboratory and field analysis.

The data summarized in tables 2-4 show both differences and similarities of the regions. The geometric means (table 2) and the arithmetic means (table 3) show the general decrease in iron, lanthanum, manganese, titanium, vanadium, and zirconium from the terrigenous clastics of the northwestern shelf to the carbonates of the south Florida shelf. Boron, chromium, cobalt, copper, lead, nickel, scandium, and yttrium appear to be nearly equal in both the northwestern and northeastern shelf sediments. Calcium, strontium, and magnesium increase toward the more carbonate sediments of south Florida.

The average compositions for major sedimentary materials (table 3) have been reported by Horn and Adams (1966) and Turekian and Wedepohl (1961). As the sediments of the shelf are varied in type, regional comparison will yield little information. However, Horn and Adams (1966) modeled the chemical composition of a sedimentary class termed "mobile belt sediments." This class, modeled after the sediments in the North American Gulf of Mexico coastal plain, was defined as consisting of 59 percent shale, 36 percent sandstone, 2 percent carbonate, and 3 percent evaporites. Element-by-element comparison of the average abundances for each region with the element composition of the mobile belt sediments shows that barium, lanthanum, lead, and zirconium are significantly higher than average in the northwestern area. In the northeastern area, only lanthanum, lead, magnesium, manganese, and yttrium have an average abundance greater than the mobile belt sediments. The significance of most of these differences is not clear, but the large concentration of barium in the sediments of the northwestern Gulf may be attributed to the extensive use of barite in drilling mud for oil exploration in the Southwest during the last few decades.

Table 4 gives the calculated correlation coefficients. The purpose of this analysis is to quantify and evaluate correlations which may be intuitively apparent, as well as to focus attention on relationships that are not as clearly discernible. Although these relationships are not conclusive, they do yield evidence suggesting certain chemical and mineral relationships. For example, high correlation between iron, vanadium, nickel, chromium, lead, cobalt, manganese, and magnesium in the terrigenous clastic sediments of the northeastern and northwestern Gulf shelf suggests that these elements are associated with clay minerals. This relationship has been suggested by

Jenne (1968) and also has been shown to exist in the sediments of the Gulf of Paria, off Venezuela, by Hirst (1962).

The semiquantitative data on the distribution of minor and trace elements in the sediments on the northern shelf of the Gulf of Mexico have established a geochemical base for further studies. As the data presented in this report were based on the analysis of the bulk sample, no new precise knowledge was obtained concerning the marine chemistry of the metals. The statistical summarization and analyses of the data also do not yield the precise information needed to understand the marine geochemical cycle of the elements. However, the data are sufficiently detailed for future planning for such studies.

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