STUDIES OF TRACE ELEMENTS

IN

SEDIMENTS

By

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ABSTRACT

Studies of Trace Elements in Sediments
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By means of spectrographic analysis 96 samples of marine sediments were analyzed quantitatively for V, Ti, Zr, Co, Ni, Sc, Cr, and La, and semiquantitatively for Ba and Sr. Ca has been estimated by visual comparison of spectrographic plates, and several Fe values have also been determined in the same way. Geographically 40 of these samples are from the Pacific Ocean basin, one of which is a manganese nodule, 21 from the Gulf of Mexico, 11 from Atchafalaya Bay, La., 8 from American Devonian to Miocene sedimentary rocks, 4 from the Mississippi Delta, 3 from the San Diego trough, 3 from off Grand Isle, La., 3 from Lake Pontchartrain, La., 1 from Bay Rambour, La., 1 from Laguna Madre off the Texas coast, and 1 from the Guadalupe River, Texas. The afore-mentioned elements were sought using $PdCl_2$ as an internal standard, after the method developed by Ahrens (1950) and his co-workers. Samples were run in duplicate, and standard deviations varied from 5 to 14 percent. Working curves, from which final values were obtained, were constructed with the use of standard granite, G1, and the standard diabase, W1, as standards. See Fairbairn and others (1951). An experiment was carried out to determine the effect of matrix change, involving $CaCO_3$, on the spectral line intensities of the quantitatively analyzed elements. The distribution of each of the elements is discussed separately, and particular emphasis is given to oceanic "red clay", in which many elements are enriched. A general discussion is given to mineralogy of the sediments, cation exchange in its bearing on this thesis, and a brief recount of the two hypotheses of origin of oceanic "red clay". An application of the findings of this thesis to aid in the choice of the more likely hypothesis is made.

Thesis Supervisor: Louis H. Ahrens
Title: Associate Professor of Geology

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First and foremost to be acknowledged is Professor Louis H. Ahrens, who made the writer more aware of geochemistry and spectrochemistry, suggested the present problem, and guided the writer through it.

Marine sediments from Atchafalaya Bay, Bay Rambour, Lake Pontchartrain and south of Grand Isle, La., as well as a Laguna Madre sample from Texas are from various American Petroleum Institute projects which have been carried out under the supervision of Professor Walter L. Whitehead at the Massachusetts Institute of Technology. Seven composite samples of Cretaceous to Miocene sedimentary rocks, prepared at M.I.T., and one Devonian shale also were obtained from API project 43C through the courtesy of Professor Whitehead.

Drs. R. R. Revelle and M. N. Bramlette of the Scripps Institution of Oceanography kindly supplied the writer with 31 samples from the Pacific Ocean. Indebtedness is also acknowledged to Dr. Charles Welby, former student at M.I.T., for samples from the Gulf of Mexico, the Mississippi Delta, the Guadalupe River, Texas, the San Diego trough and 9 samples from the Pacific Ocean, and indirectly to Mr. H. C. Stetson of Harvard University and Professor F. P. Shepard, Drs. M. N. Bramlette and F. P. Phleger of Scripps Institution of Oceanography, who made these samples available to Dr. Welby.

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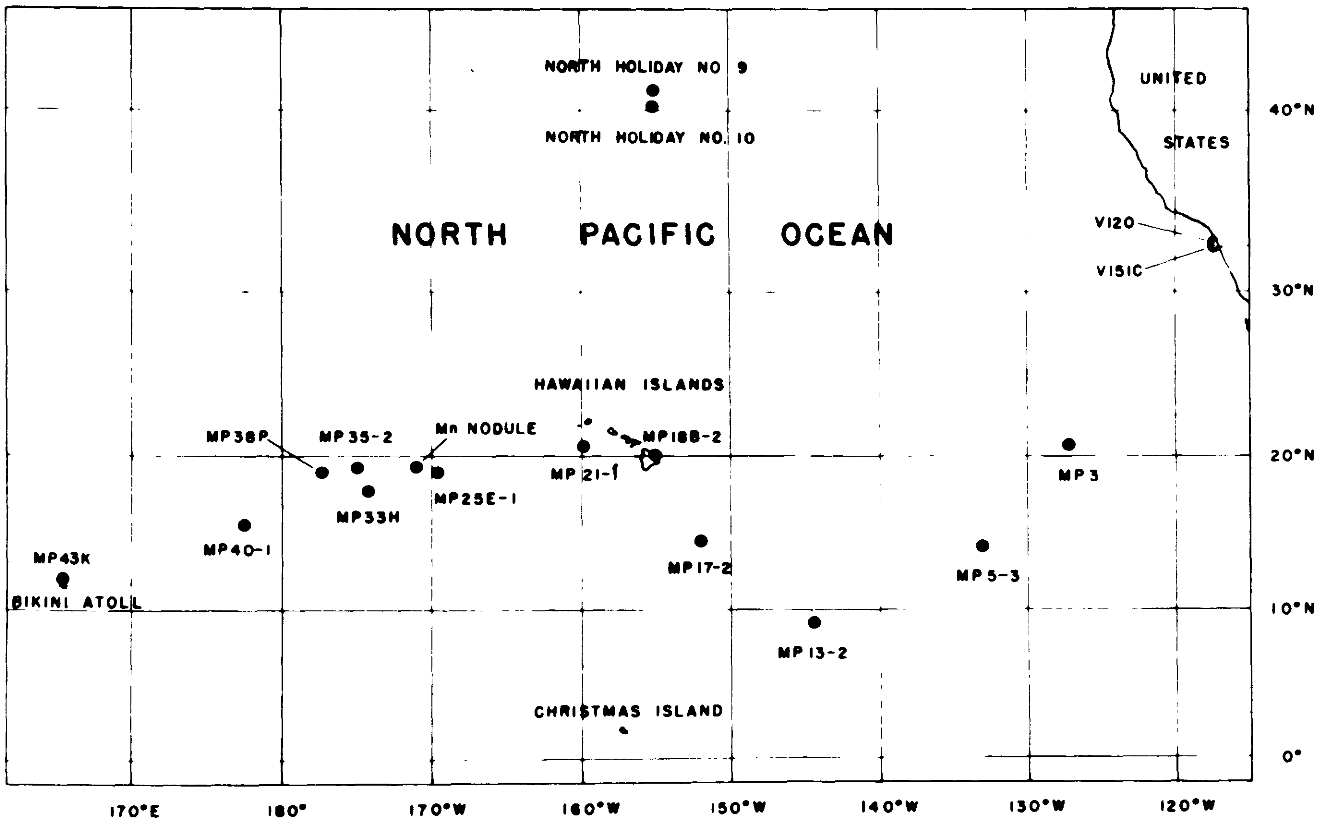
INTRODUCTION

Of what use is a list of minor element analyses of marine sediments? In the following pages use will be made of such analyses to effect a better understanding of marine sediments, especially pelagic deposits. Students of the geochemistry of igneous rocks have seen the importance which attaches to a study of minor elements in a suite of differentiated rocks, such as the well-worked Skaergaard intrusion of Greenland. See Wager and Mitchell (1951). Similarly, it is believed that the minor elements are also sensitive indicators of geologic events in sediments.

The object of the present study is to learn something of the distribution of such elements as Ti, Zr, Ba, Sr, Sc, La and the ferrides in sediments, particularly pelagic, and in addition, to learn why these elements are so distributed. With the aid of 96 samples the facts of distribution have, at least, been surveyed, but the second, and much more difficult part of the problem, concerning the whys of distribution can only be deduced hypothetically from the available facts, due to the very fine grained nature of the sediments.

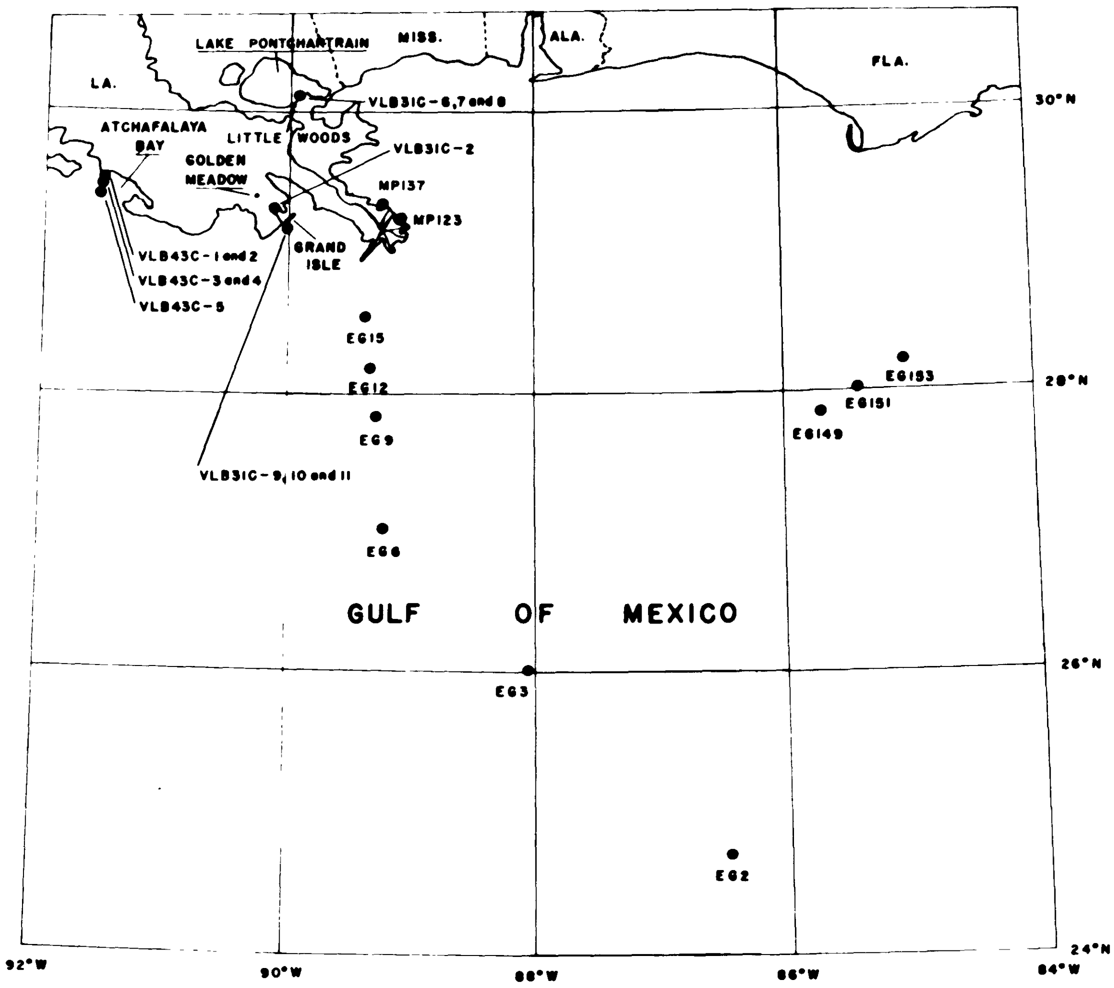
The original motive of the present study was to find out whether Zr showed evidence of being enriched in pelagic sediments. It had been reported by Revelle (1944) that such was the case in the Pacific basin. At the same time, with the use of $PdCl_2$ as an internal standard, it was possible to analyze the pelagic sediments for several other minor elements. In view of the scarcity of such analyses in the literature this is desirable.

Maps 1 and 2 show the locations of the various cores.



MAP I - LOCATION OF CORES

SCALE IN STATUTE MILES



MAP 2 - LOCATION OF CORES

CHAPTER 1

ANALYSIS

1. EQUIPMENT

A. The Spectrograph

The spectrograph used in this investigation was the 21-foot Wadsworth (stigmatic) mounted grating instrument in the Cabot Spectrographic Laboratory of the Massachusetts Institute of Technology. The grating contained 30,000 lines per inch, and the ruling was done in 1935 at Johns Hopkins University by R. W. Wood and W. Perry on speculum metal. Only 3 $\frac{1}{2}$ inches of the 6-inch grating have been used in the present work, the rest having been shielded with black paper because of a defective surface.

The dispersion is approximately 2.5 A/mm, and the resolving power is better than 40,000 in all wavelength regions. More correctly, the plate factor, or reciprocal dispersion, is 2.5 A/mm. Resolving power is defined as the wavelength divided by the wavelength difference of two closely-spaced but resolvable lines. There is a resolution of at least 0.074 A at 3100 A.

Power supply for the arc was 230 volts D.C.

B. The Photometer

The Hilger Microphotometer H.451 and the Hilger Galvo Scale Projector H 671 were used.

2. STANDARDS

The quantitative results are based on working curves derived from the arcing of standard granite, G 1, and standard diabase, W 1, worked on by Fairbairn and others (1951). Chiefly to aid in comparison working curves derived from synthetic standards were also prepared.

Synthetic standards were made in the following manner. First, a synthetic base of 55 percent SiO_2, 30 percent Al_2O_3 and 15 percent Na_2CO_3 was mixed in a mechanical agate mortar for one hour, and sintered for 12 hours at $900^{\circ}C$. The silica was derived from Herkimer diamonds (quartz crystals of unusual purity), and the alumina and sodium carbonate were C.P. reagents. Using the method of Nachtrieb (1950, p. 140) small residual values of 0.0007 percent ZrO_2, 0.001 percent TiO_2, 0.0004 percent NiO and approximately 0.0001 percent Cr_2O_3 were found in the base, which are negligible. See Figure 1.

Second, a mixture of oxides was prepared, containing 30.15 mg. each of Sc_2O_3, NiO, Co_2O_3, V_2O_5, Nd_2O_3, Ce_2O_3, La_2O_3, Cr_2O_3, SrO and Y_2O_3, 301.5 mg. each of BaO and ZrO_2, and 603.0 mg. of TiO_2, all of which was mixed for one hour and ten minutes in a mechanical agate mortar. This totaled 1,507.5 mg. 1/10 of which was mixed with 849.25 mg. of the synthetic base in the mechanical agate mortar for thirty-five minutes. This first oxide-base mixture contained, therefore, 6.03 percent TiO_2, 3.015 percent ZrO_2 and BaO, and 0.302 percent of each of the remaining oxides. By dilution with synthetic base, 8 more mixtures were made in such a way that the concentration of each oxide varied by the $\sqrt{0.1}$.

The resulting oxide concentrations ranged from a high of 6.03 percent TiO_2 to a low of 0.00003 percent NiO. The oxide concentrations for the nine standards are given in Table 1.

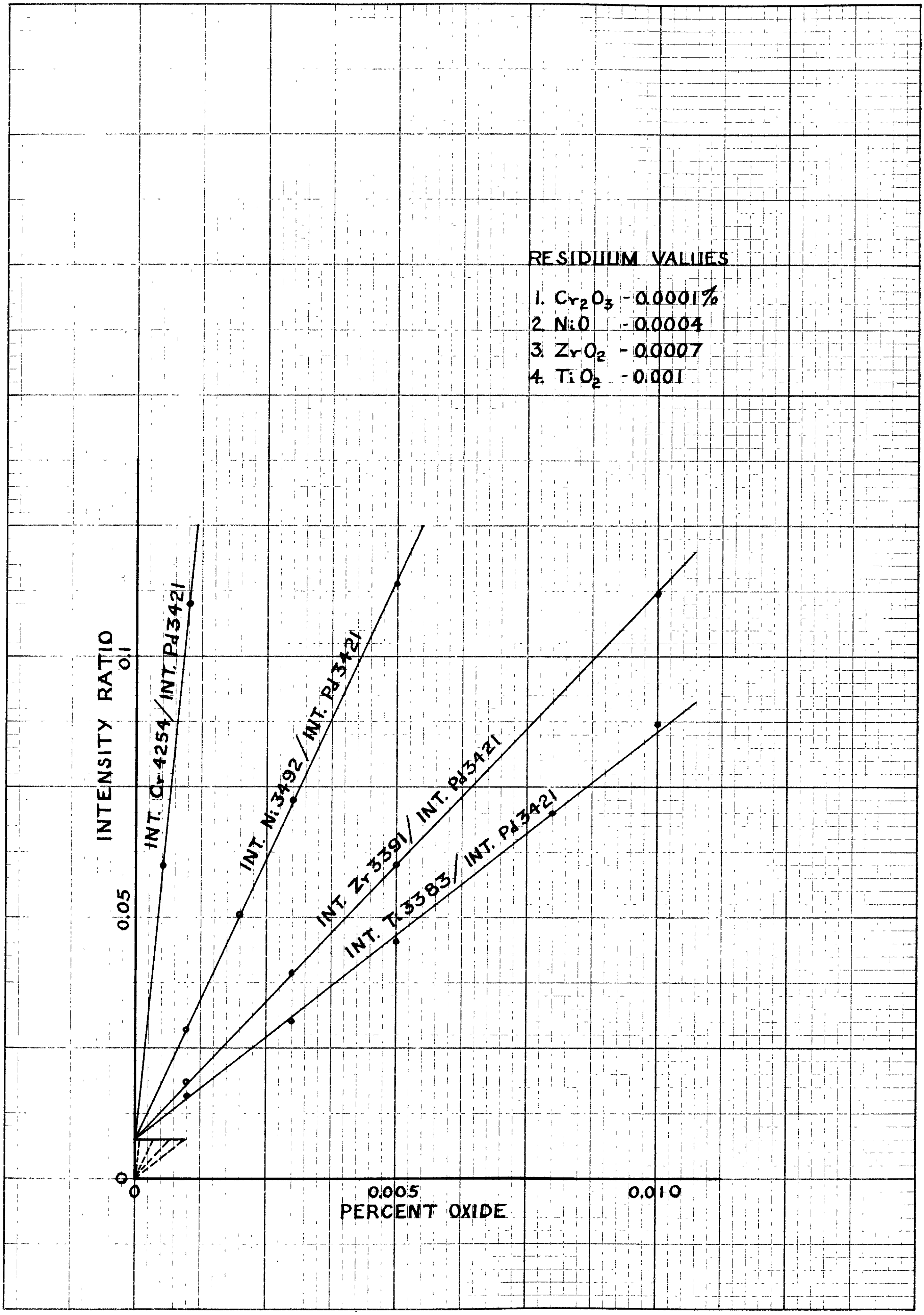


FIGURE I - RESIDUUM CURVES OF IMPURITIES IN SYNTHETIC BASE

Table 1

Oxide Concentrations in Standards

Standard	% TiO_2	% ZrO_2 and BaO	% of Each of the Remaining Oxides
1	6.03	3.015	0.3015
2	1.905	0.953	0.0953
3	0.603	0.301	0.0301
4	0.1905	0.095	0.0095
5	0.0603	0.030	0.0030
6	0.0190	0.0095	0.00095
7	0.00603	0.003	0.0003
8	0.0019	0.00095	0.000095
9	0.0006	0.0003	0.00003

Variable amounts of oxides were used because of the unequal distribution in rocks of the elements sought. Titania is so abundant that it is usually determined as a major constituent in a rock using wet chemical methods.

Previous work in the Cabot Spectrographic Laboratory by Ahrens (1950) and his co-workers determined the choice of an internal standard. $PdCl_2$ had been found satisfactory for the determination of involatile elements, such as Zr, Ti, Sc, Ni, Co, etc. Mrs. Gorfinkle, spectrographer in the Cabot Spectrographic Laboratory from 1947 to 1950, had been using a 0.125 percent $PdCl_2$ internal standard, but noted that at this concentration Pd lines were too strong. The present work, therefore, was carried out with the use of a lower $PdCl_2$ internal standard, namely 0.0800 percent. The mixing ratio of carbon to $PdCl_2$ was 40 to 0.04765, which resulted in 0.1190 percent $PdCl_2$. Mixing

0.1 gram of a powdered unknown with the internal standard mixture produced 0.0800 percent $PdCl_2$.

In the preparation of the internal standard all of the $PdCl_2$ (0.04765 gram) was mixed with one gram of carbon (powdered, from "special grade" electrodes) in the mechanical agate mortar for one hour, after which time 39 more grams of carbon were added. Rolling this mixture on paper for one hour and rolling it again in a bottle for half an hour completed its preparation. The homogeneity of the internal standard was then tested by taking three samples of it from different parts of its volume, mixing them with sample VLB31C-7, and arcing the three samples. Intensity ratios of Zr to Pd varied by an average of only 5 percent, which was considered tolerable.

Each of the nine standards was then mixed with the internal standard mixture.

Samples of standard granite, G 1, and standard diabase, W 1, were arced in order to compare recommended values (L. H. Ahrens, oral communication, June 1953) for V, Zr, Ni, Co, Ti, Sc, Cr, and La in these standard rocks with the values obtained from working curves constructed from synthetic standards. The latter values differ, but not too greatly, from the recommended values of these elements in the standard rocks.

Table 2 lists the two sets of values.

Table 2

Comparison of Oxides in G 1 and W 1

	G 1			W 1		
Oxide	Recommended Value (percent)	E. J. Young Analyst (percent)	Factor	Recommended Value (percent)	E. J. Young Analyst (percent)	Factor
V_2O_5	0.0036	0.0043	+1.19	0.043	0.055	+1.28
ZrO_2	0.027	0.043	+1.59	0.012	0.021	+1.75
TiO_2	0.3	0.30	1.00	1.1	1.10	1.00
NiO	nd*	0.0005	-	0.0115	0.0145	+1.26
Co_2O_3	0.0004	0.00065	+1.62	0.0051	0.0080	+1.57
Sc_2O_3	0.00045	0.00058	+1.29	0.0057	0.0097	+1.70
Cr_2O_3	0.003	0.003	1.00	0.019	0.019	1.00
La_2O_3	0.0235	0.0187	-0.80	0.0038	0.0031	-0.82

* no determination

Since the recommended values result from the efforts of at least five spectrographers, it was decided that the quantitative results of the present work should be based on working curves derived from the arcing of the standard rocks, rather than from synthetic standards.

3. SAMPLE PREPARATION

In general, sample preparation involved no great difficulty as the samples were unconsolidated or poorly consolidated sediments of clay and silt, and being homogeneous, sampling errors were considered to be negligible. All of the samples were small, weighing approximately one gram. Pre-heating of samples and accounting of loss on ignition (L.O.I.) was time consuming, but necessary in view of the clayey nature of the sediments. Failure to pre-heat would cause a sample to sputter and pop out of its electrode, or at best, to burn unevenly. This was due to structural water locked in clay minerals and other volatile products, such as CO_2, which expand violently when exposed to the high temperature in an arc. The procedure adopted in sample preparation was the following.

1. Approximately half a gram of sample was ground to a powder in an agate mortar.
2. The sample was heated to 110°C. for two hours and weighed.
3. The sample was heated to red heat (about 1000°C.) in a crucible over a bunsen flame for five minutes and weighed.
4. A mixture of 0.1 gram of sample with 0.2015 gram of internal standard was made in a mechanical agate mortar for 15 minutes.
5. An abrasive cleanser was used to clean the mortar between samples.

With the above procedure the percentage of element determined refers to the sample after it has been ignited. Between the 110° stage and the ignition stage it has lost structural water locked in clay and other minerals, volatiles from organic matter, and CO_2 resulting from the decomposition of carbonates. Possibly small amounts of the alkali metals may be lost. To obtain the percentage of element or oxide in the 110° dried sample, the percentage of weight loss due to ignition, or L.O.I., must be multiplied by the percentage of element in the ignited sample, and the product then subtracted from the percentage of element in the ignited sample.

4. DETAILS OF SPECTROCHEMICAL PROCEDURE

Potential drop across the arc was 50 volts, and the current was 7 amperes. Anode excitation was employed, i.e., the electrode containing the sample was the anode.

"Special Grade" carbon electrodes of 3/16 inch outer diameter, 1/8 inch inner diameter and 1/4 inch internal length were used.

Slit length was 12 millimeters and slit width 0.03 millimeter. A step sector with a 2:1 ratio and 7 steps was used. Six spectra were exposed on each plate.

Burns were started at 3 amperes and continued for 5 seconds, at which time the current was increased to 7 amperes. This procedure was adopted in order to prevent initial sputtering and loss of sample due to the sudden high temperature of the arc. Burns were taken to "completion", i.e., to a point where voltage increased suddenly from approximately 50 volts to 75 or 80 volts. Light intensity from the arc increased at the same time. Completion usually took approximately four minutes. Even after so-called completion, re-arcing of the same electrodes showed residual amounts of Zr and Ti. However, this is not a serious problem with the internal standard method. The alternative of longer arcing produces plates with excessive background.

An innovation in the present research has been the use of a shield placed before the plate-holder, which was useful in minimizing background fog accompanying long arcings of four minutes. The shield was made of plywood, in which there was a slot as long as the plate-holder and 14 millimeters wide. The width was chosen to admit the beam from a 12-millimeter long slit, which permitted the use of eight steps of a step sector.

Kodak 103-0 plates were used throughout the work. Two plates were placed in the plate-holder and the plate-holder was centered at 3800A. One plate covered the wavelength region from 3140 A to 3740 A, and the other from 3980 A to 4630 A. Plates were developed immediately after exposure in Kodak D-19 developer for 4 1/2 minutes at 20°C. The same batch of developer was used twice, i.e., for four plates. Fixing was done in Kodak acid fixer for 20 minutes at 20°C., and plates were washed in running water for one hour, sponged, and left to dry.

5. SPECTRAL LINES USED

The following spectral lines were used in the quantitative analysis of V, Ti, Zr, Co, Ni, Sc, Cr, and La, and the semiquantitative determination of Ba, Sr, Ca, and in some cases Fe.

Element	Spectral lines in Angstrom units
V	3185.396
Ti	3387.837 3383.761
Zr	3391.975
Pd	3421.24
Co	3453.505
Ni	3492.956
Sc	4246.829
Cr	4254.346
La	4333.734
Ba	4554.042
Sr	4607.331
Ca	4578.56 4581.40 4585.87
Fe	4250.790 4250.130

6. PHOTOMETRY, CALIBRATION CURVES AND WORKING CURVES

Using the Hilger microphotometer H.451, clear plate deflection, Do, was set at 50, and desirable spectral line deflections, d, were from 15 to 3. Background deflection was also noted on each side of a spectral line, and its corresponding background intensity was subtracted from spectral line intensity.

The standard way of drawing a characteristic or response curve is to plot $Do/_d$ values for two or three steps of a spectral line as the ordinate on log-log paper. Intensities are then read at the point where this curve intersects the $Do/_d = 10$ (arbitrary) line with the aid of a reversed log intensity scale. See Ahrens (1950, p. 123).

A method used by Dr. H. P. Eugster, Swiss guest of the Massachusetts Institute of Technology during 1951-52, saved much labor. The response curve was first established for each spectral line. The response curve for any one spectral line was not found to vary from plate to plate noticeably, although the response curves from V 3185 to La 4333 were found to change 3°. Thus the response curve for V 3185 was 58° and for La 4333 it was 61°. After establishment of the response curve, it was drawn anywhere on log-log paper, and a vertical line was drawn through it at the point of intersection of the response curve and the $Do/_d = 10$ line. A sliding log intensity scale was then used which obviated the need for drawing of response curves for every $Do/_d$ value.

An illustration of a response curve for Pd 3421 on 103-0 plates, and a particular case wherein an intensity is found is given in Figure 2.

The working curve is drawn on log-log paper with the intensity ratio of the analyzed element to the internal standard as ordinate and the concentration of the analyzed element as abscissa.

Working curves based on arcings of the standard rocks, G 1 and W 1, are given for eight oxides in Figures 3-5. Figure 6 illustrates an additional working curve for ZrO_2, which has been constructed from synthetic standards.

7. PRECISION (REPRODUCIBILITY)

Standard deviations have been calculated for each of the elements analyzed quantitatively according to the formula, $S = \pm\sqrt{\frac{\Sigma d^2}{n-1}}$.

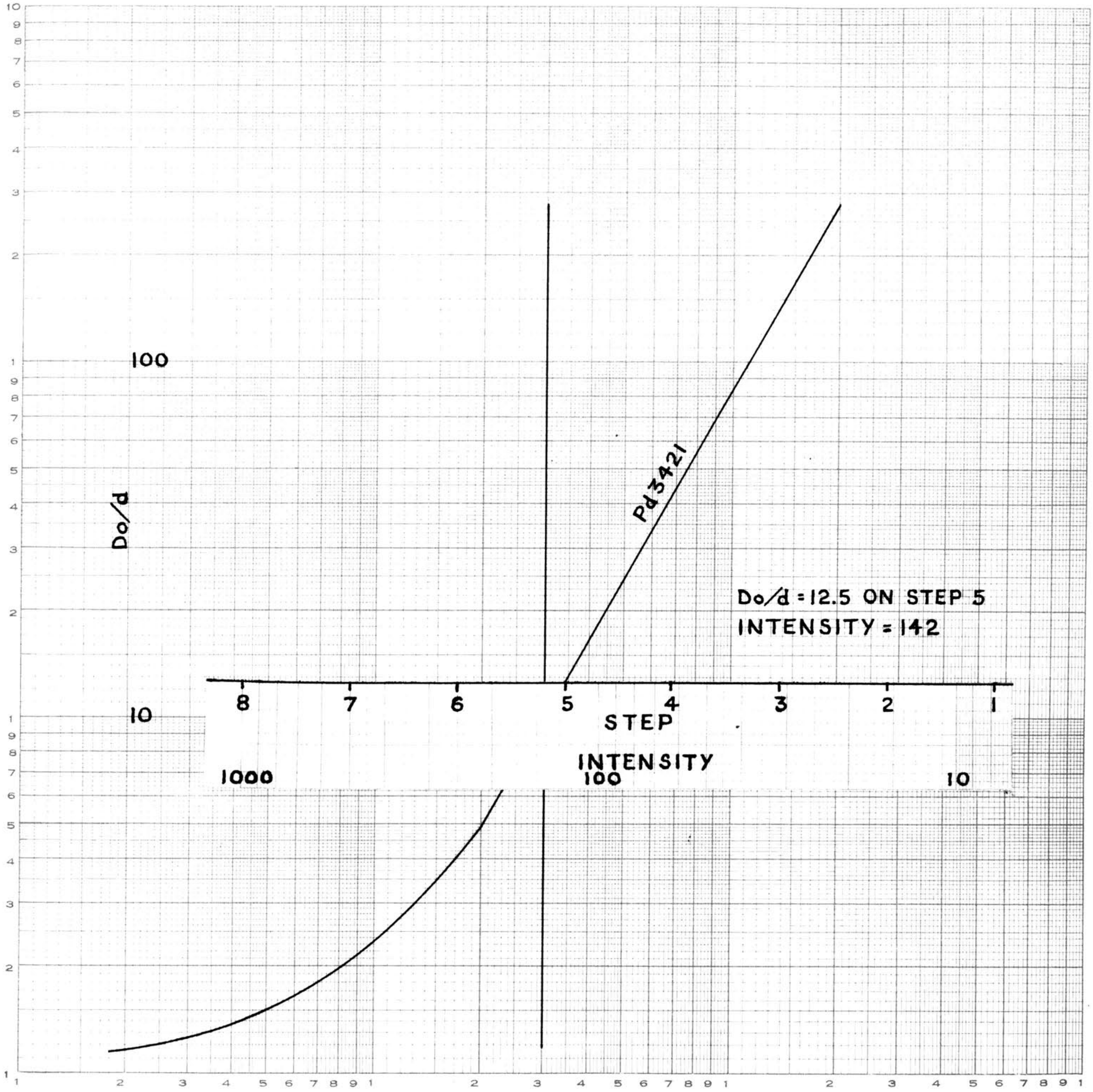


FIGURE 2 - CALIBRATION CURVE AND METHOD OF FINDING INTENSITY

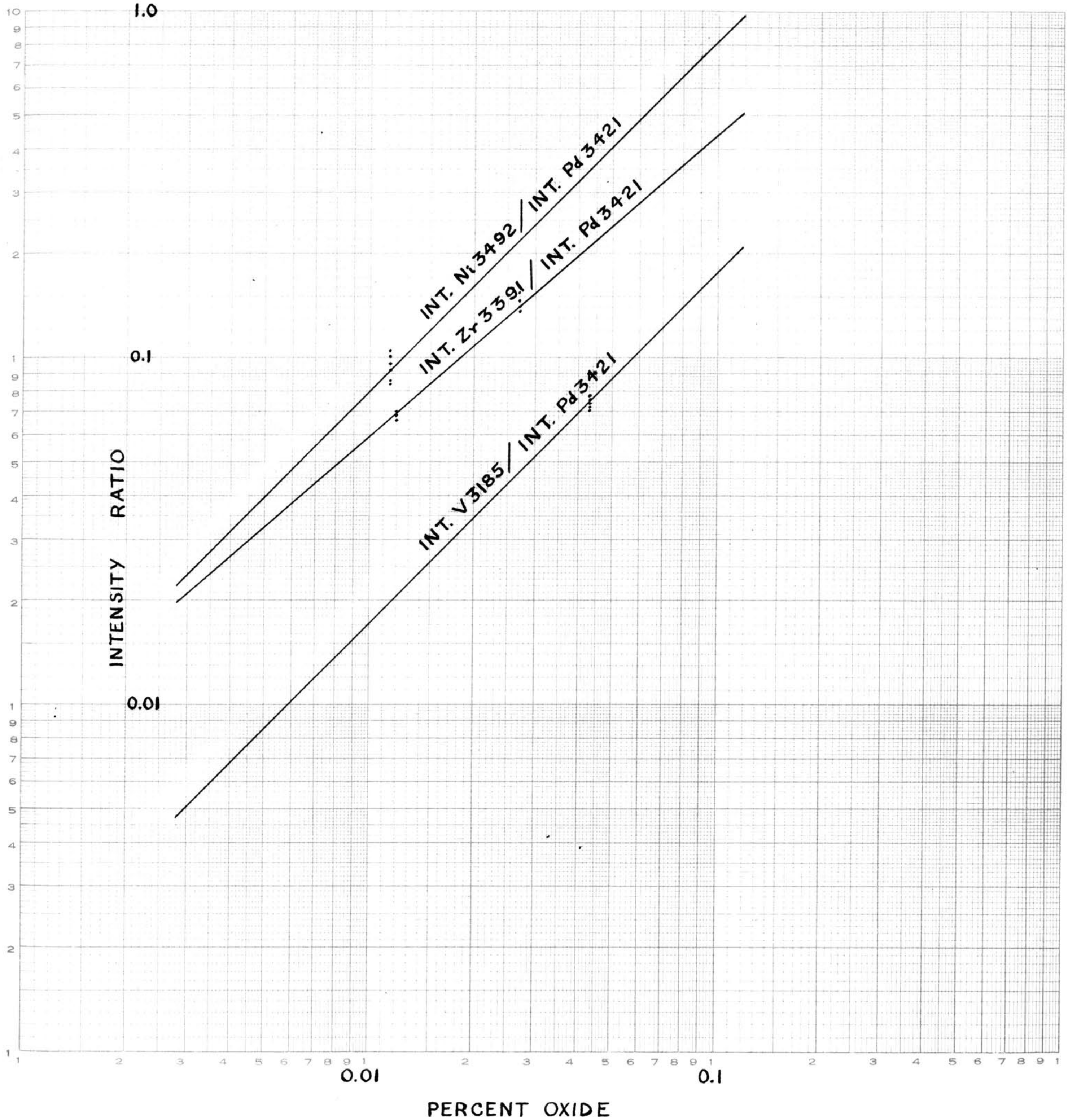


FIGURE 3 - WORKING CURVES FOR NiO ZrO_2 AND V_2O_5 BASED ON STANDARD GRANITE AND STANDARD DIABASE

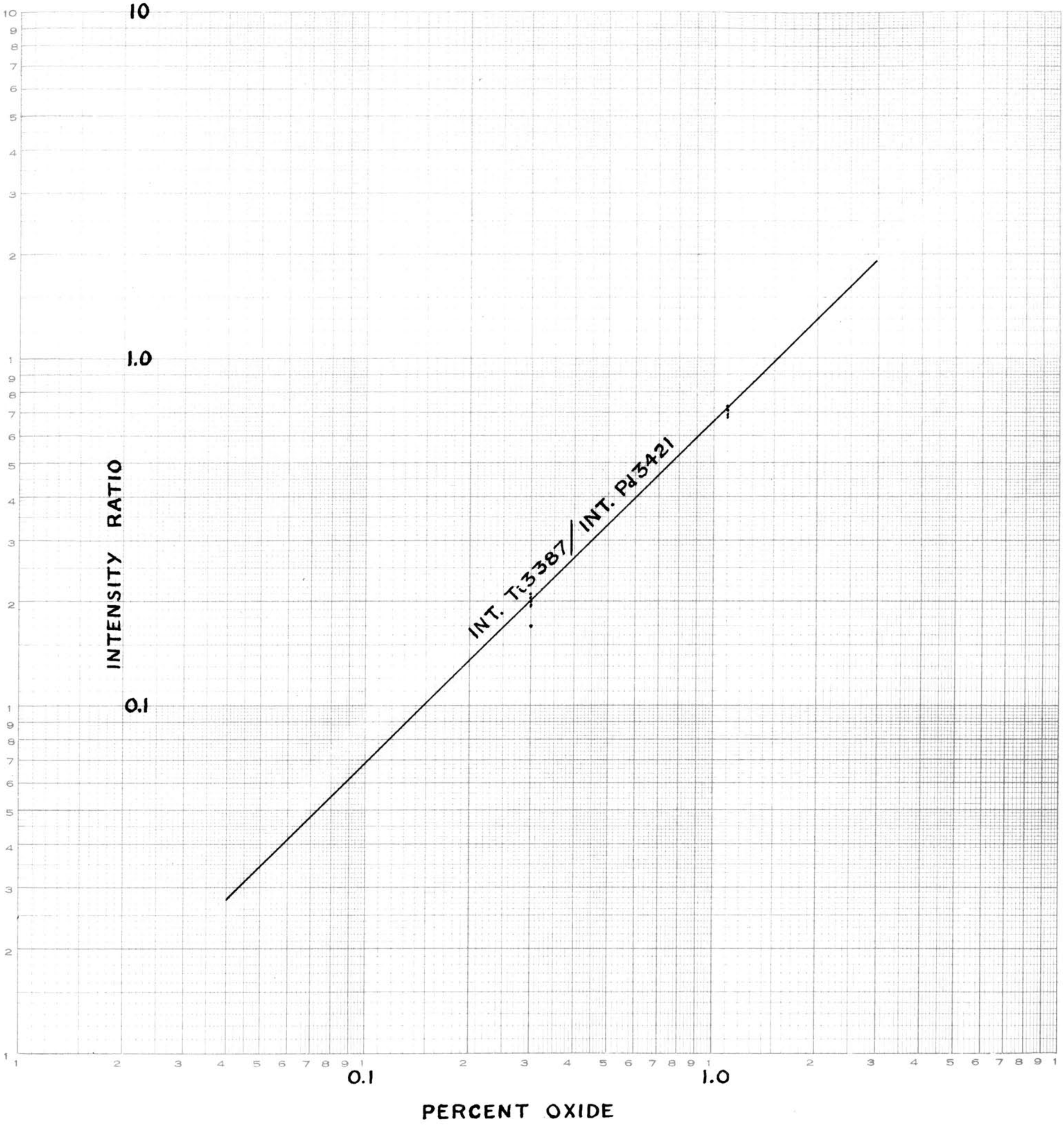


FIGURE 4 - WORKING CURVE FOR TiO_2
BASED ON STANDARD GRANITE AND STANDARD DIABASE

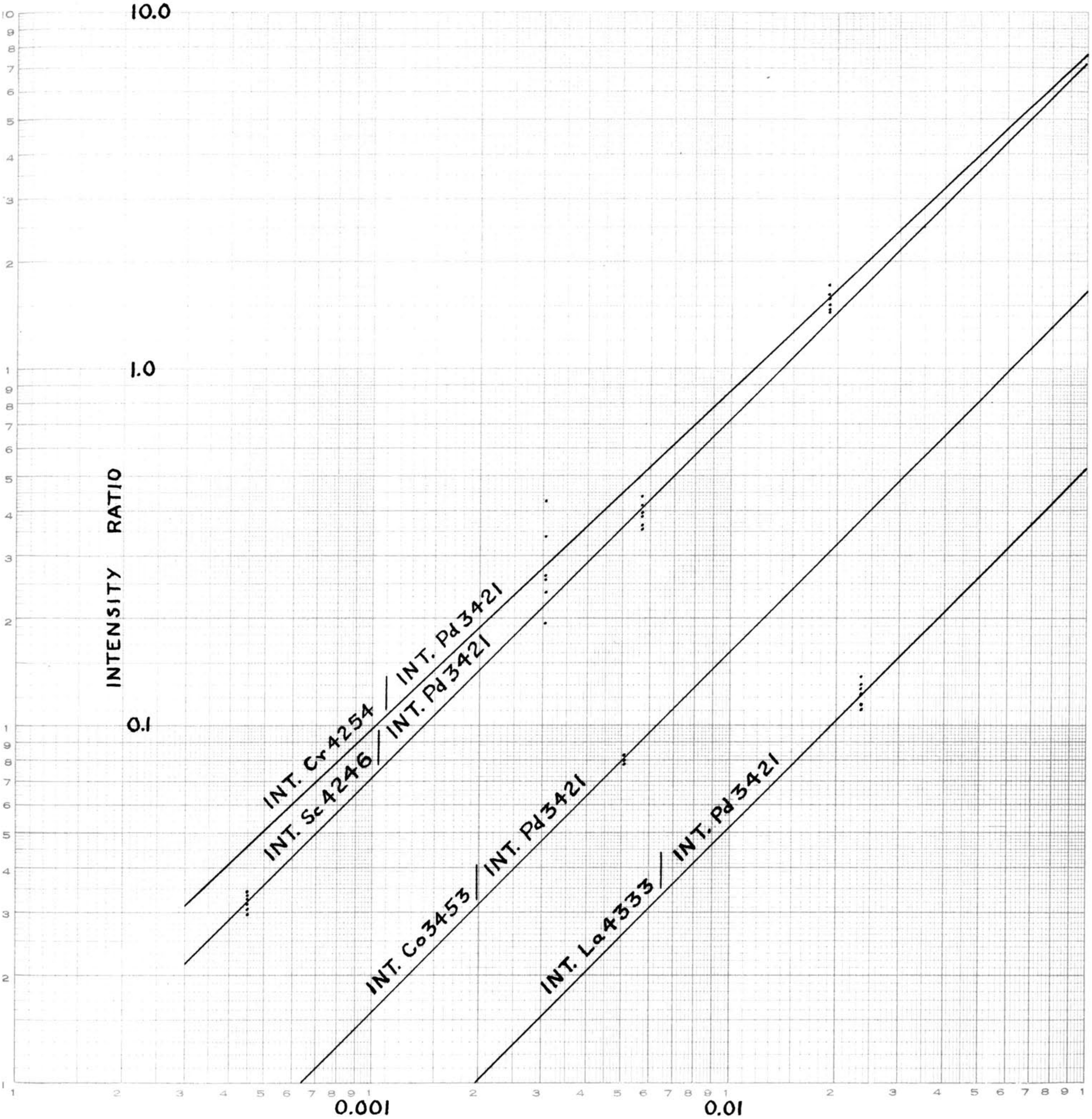


FIGURE 5 - WORKING CURVES FOR Cr_2O_3 Sc_2O_3 Co_2O_3 AND La_2O_3 BASED ON STANDARD GRANITE AND STANDARD DIABASE

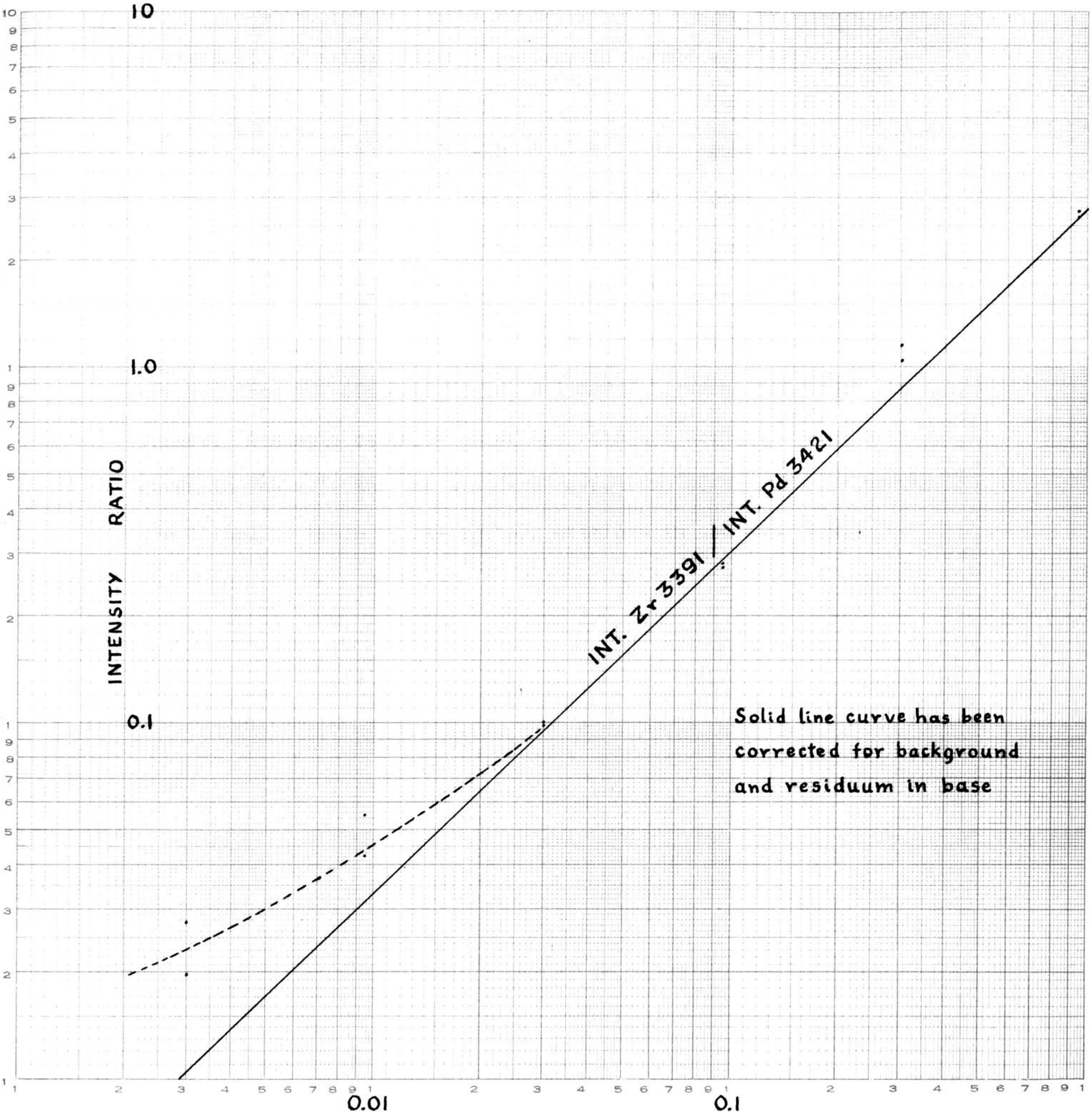


FIGURE 6 - WORKING CURVE FOR ZrO_2 BASED ON SYNTHETIC STANDARDS

As each sample was arced twice and the average value taken, the standard deviation for two determinations is $S/_{2}\sqrt{2}$.

Using the arbitrary classification scheme of Ahrens (1950) a standard deviation within 3 percent is termed excellent

from 3-5 " " " very good
" 5-10 " " " good
" 10-20 " " " fair
" 20-40 " " " poor
and > 40 " " " very poor.

Sample EG9-B was arced 10 times and the working curves derived from the standard rocks, G 1 and W 1, were used to obtain values. A sample calculation of the standard deviation of NiO is given in Table 3, and the standard deviations of the other elements are listed in Table 4, having been obtained in the same way.

Table 3

Calculation of Standard Deviation of NiO

Analysis No.	% NiO	% Deviation	(% Deviation)^2
1	0.0074	+21.3	455.
2	0.0078	+27.9	780.
3	0.0064	+ 4.9	24.
4	0.0057	- 6.6	43.5
5	0.0054	-11.5	132.
6	0.0058	- 4.9	24.
7	0.0060	- 1.6	2.6
8	0.0051	-16.4	269.
9	0.0058	- 4.9	24.
10	0.0054	-11.5	132.
	$10\overline{).0608}$	$10\overline{)111.5}$	1886.1
	Aver. = .0061	Aver. Dev. = ±11.2	

$$S = \pm\sqrt{\frac{\Sigma d^2}{n-1}}$$

$$S = \pm\sqrt{\frac{1886}{9}} = 14.5\%$$

For two determinations standard deviation = $S/2\sqrt{2}$ = $14.5/_2\sqrt{2}$ = 10.3%.

Reproducibility is fair.

The following conditions should hold:

1. 67 percent of all determinations, taken in duplicate and averaged, should fall within ± 10.3% of the mean value.
2. 95 percent of all determinations, taken in duplicate and averaged, should fall within ± 20.6% of the mean value.

Table 4

List of Standard Deviations given for two Determinations

Oxide	Standard Deviation in %	
V_2O_5	± 8.5%	Reproducibility is good.
TiO_2	± 5.9	" " good.
ZrO_2	±14.0	" " fair.
Co_2O_3	± 5.0	" " good.
Sc_2O_3	± 9.0	" " good.
Cr_2O_3	±10.5	" " fair.
La_2O_3	± 8.0	" " good.

Thus in summation, five of the oxides have good reproducibility, and three are fair.

Ba and Sr were estimated by visual comparison of standard plates, which were based on standards whose concentrations varied by the $\sqrt{0.1}$.

The standard granite, G 1, contains 1.42 percent CaO; W 1, the standard diabase, contains 10.95 percent CaO; and a G 1-W 1 mixture should contain 6.19 percent CaO. With the use of standard plates, the quantity of CaO in the samples was estimated. Determination of carbonate by acid leaching of a few of the globigerina oozes whose CO_3^{--} was practically all combined with Ca^{++}, gave standards which were useful in estimating the CaO content of Ca-rich samples. The values of CaO for the 96 samples are, therefore, approximate.

The few Fe_2O_3 values given are approximate also, having been estimated from comparison with standard plates containing spectral lines of G 1 which has 2.0 percent Fe_2O_3, W 1 which has 11.2 percent Fe_2O_3, and a G 1-W-1 mixture containing 6.6 percent Fe_2O_3.

8. SPECTRAL LINE ENHANCEMENT

It is well known that spectral line intensity is influenced by the nature of the matrix of the sample being analyzed. In the case of cathode excitation, Scott (1945) reports larger percentage errors at lower concentrations than at higher concentrations. Thus for V 3185 A he finds an error of + 215 percent at 0.003 percent V, and only + 41 percent at 0.1 percent V. Fast and Nielson (1947) report that alkali metals and alkaline earths have a large enhancing effect on the intensity of Sr spectral lines in the A. C. arc.

Not having any information on spectral line intensity change due to matrix change in the case of anode excitation in the D. C. arc, an experiment was set up to indicate how important matrix changes were. Citric acid was chosen as the leaching agent. As it was important to know the leaching effect, if any, of citric acid on the elements in question, sample VLB43C-4c from Atchafalaya Bay, La., was chosen because of its low CaO content of approximately 2 percent. Table 5 shows the effect of a saturated solution of citric acid on VLB43C-4c, which was leached overnight. Values were obtained from the standard rocks working curves.

Table 5

Effect of Citric Acid Leaching on Sample VLB43C-4c

Oxides	Unleached VLB43C-4c (percent)	VLB43C-4c, leached with citric acid (percent)	Percentage change
V_2O_5	0.021	0.018	-14.0
TiO_2	0.70	0.70	0
ZrO_2	0.037	0.032	-13.5
Co_2O_3	0.0014	0.0014	0
NiO	0.0055	0.0051	- 7.0
Sc_2O_3	0.0020	0.0019	- 5.0
Cr_2O_3	0.0090	0.0072	-20.0
La_2O_3	0.0091	0.0077	-15.0

From the results it appears that V, Cr, and La may be partly leached. The change in values for the other elements are within the limits of reproducibility.

In order to determine the extent to which spectral line intensity is enhanced by $CaCO_3$-rich samples, sample EG2-A was chosen because of its high CaO content (over 30 percent). Leaching with citric acid showed a 60 percent $CaCO_3$ loss. Three duplicate arcings were needed in this case; one of the unleached sample, the second of the leached sample, and the third of the leached sample plus an added amount of pure $CaCO_3$ equivalent to the amount lost by leaching. Table 6 records the experiment.

Table 6

Enhancement of Spectral Lines due to $CaCO_3$

Oxides	Unleached EG2-A (percent)	EG2-A, leached with citric acid (percent)	Percentage change	Leached EG2-A plus $CaCO_3$ (percent)
V_2O_5	0.017	0.008	-53.0	0.012
TiO_2	0.35	0.27	-23.0	0.24
ZrO_2	0.0076	0.010	+32.0	0.0078
Co_2O_3	0.0008	0.0005	-37.5	0.0048
NiO	0.0035	0.0019	-45.7	0.0018
Sc_2O_3	0.0008	0.00074	- 7.5	0.00085
Cr_2O_3	0.0070	0.0033	-53.0	0.0058
La_2O_3	0.0035	0.0030	-14.0	0.0026

From the foregoing results it appears that V, Co, Ni, and Cr have their spectral lines appreciably intensified by large amounts of $CaCO_3$. The reason for the opposite effect on Zr is that a rich $CaCO_3$ burn keeps the temperature too low for complete volatilization of the Zr. When $CaCO_3$ was added to the leached sample in order to compensate for the original $CaCO_3$ loss, it failed to intensify the lines of Ti, Co, Ni, and La for unknown reasons.

Fortunately most of the samples analyzed did not have large $CaCO_3$ contents. The few samples that were rich in $CaCO_3$ were not used in the calculation of average values.

CHAPTER 2

ANALYTICAL RESULTS

Atchafalaya Bay, Louisiana: 11 samples: gray silty clays.

Sample no.	Se-quence no.	Location	Water depth in ft.	Depth in core (in.)	Percent												
					V$_2$O$_5$	TiO$_2$	ZrO$_2$	NiO	Co$_2$O$_3$	Sc$_2$O$_3$	Cr$_2$O$_3$	La$_2$O$_3$	BaO	SrO	CaO	Fe$_2$O$_3$	LOI
VLB43C-1a	10	Lat. 29°31'00" N. Long. 91°31'10" W.	8	21	0.014	0.56	0.034	0.003	0.0009	0.0011	0.008	0.006	0.1	0.08	20-30	--	15
VLB43C-1b	6	...do.............	8	33	.016	.64	.037	.004	.0010	.0011	.007	.010	.2	.04	2	2	4
VLB43C-2a	8	...do.............	8	143	.016	.69	.034	.004	.0011	.0014	.009	.009	.2	.03	2	--	5
VLB43C-2b	7	...do.............	8	155	.021	.78	.048	.006	.0014	.0020	.011	.013	.2	.03	1	7	7
VLB43C-2c	3	...do.............	8	168	.031	.70	.022	.009	.0016	.0030	.016	.013	.2	.03	1	5	12
VLB43C-3b	9	Lat. 29°25'30" N. Long. 91°31'39" W.	8 3/4	23	.014	.59	.047	.004	.0013	.0012	.008	.008	.2	.03	5	5	6
VLB43C-3c	1	...do.............	8 3/4	40	.028	.76	.023	.006	.0017	.0021	.013	.012	.1	.03	1	--	11
VLB43C-4a	4	...do.............	8 3/4	99	.027	.70	.067	.006	.0019	.0030	.017	.018	.2	.05	5	--	8
VLB43C-4c	5	...do.............	8 3/4	123	.020	.70	.034	.006	.0015	.0017	.009	.009	.2	.04	2	7	7
VLB43C-5a	2	Lat. 29°22'45" N. Long. 91°31'50" W.	7 1/4	3	.026	.73	.037	.008	.0023	.0029	.013	.014	.2	.03	1	--	11
VLB43C-5b	11	...do.............	7 1/4	20	.015	.57	.038	.003	.0013	.0011	.008	.009	.2	.03	4	5	5
Average values for Atchafalaya Bay samples, excluding Ca-rich VLB43C-1a					.021	.69	.040	.006	.0015	.0020	.010	.012	.2	.03	2		8

Bay Rambour, Louisiana: 1 sample: gray silty clay.

VLB31C-2	12	10 miles SE of Golden Meadow; 1800' W. of the E line and 300' N of the S line of Sec. 26, T 20 S - R 23 E.	6	22	0.020	0.64	0.033	0.006	0.0016	0.0014	0.009	0.009	0.2	0.03	1	--	8

South of Grand Isle, Louisiana: 3 samples: gray silty clays.

VLB31C-9	13	Lat. 29°08' N. Long. 90°02' W.	39	0	0.018	0.65	0.041	0.004	0.0014	0.0014	0.009	0.011	0.1	0.03	3	--	7
VLB31C-10	17	...do.............	39	13	.022	.72	.022	.005	.0015	.0018	.010	.009	.1	.03	3	5	9
VLB31C-11	18	...do.............	39	33	.023	.73	.022	.005	.0016	.0021	.013	.011	.2	.03	2	--	8
Average values for Grand Isle samples					.021	.70	.028	.005	.0015	.0018	.010	.010	.1	.03	3		8

Notes: See Chapter 1, Section 7, for precision of results.
See Chapter 1, Section 8, for validity of results for Ca-rich samples.
See Maps in the Introduction for location of samples.
nm = not measurable
nd = not detectable
-- = not determined.

Lake Pontchartrain, Louisiana: 3 samples: gray silty sands.

Sample no.	Sequence no.	Location	Water depth (ft.)	Depth in core (in.)	Percent												
					V_2O_5	TiO_2	ZrO_2	NiO	Co_2O_3	Sc_2O_3	Cr_2O_3	La_2O_3	BaO	SrO	CaO	Fe_2O_3	LOI
VLB31C-6	14	6.3 mi. NE of Little Woods, and 3000' NW of the lake shore	8	0	0.007	0.64	0.194	0.001	0.0005	0.0007	0.010	0.011	0.1	0.03	1 or less	--	2
VLB31C-7	15	...do..............	8	12	.007	.55	.187	.001	.0005	.0008	.008	.008	.2	.03	1 or less	--	3
VLB31C-8	16	...do..............		24	.008	.63	.187	.002	.0008	.0007	.006	.009	.2	.03	1 or less	2	3
Average values for Lake Pontchartrain samples					.007	.61	.189	.001	.0006	.0007	.008	.009	.2	.03	1 or less		3

Laguna Madre, Texas: 1 sample: gray silty clay.

B2-1	19		--	6-24	0.011	0.29	0.012	0.002	0.0005	0.0007	0.005	0.005	0.05	0.16	20-30	1	18

Sedimentary Rocks: 8 samples

Selma chalk, composite	20	Upper Cretaceous, Southeastern U. S.			0.030	0.67	0.022	0.008	0.0017	0.0020	0.011	0.009	0.2	0.05	10	3	12
Antrim shale	21	Upper Devonian, Michigan			.024	.74	.037	.014	.0028	.0021	.013	.014	.05	.01	1	3	20
Austin chalk, composite	22	Upper Cretaceous, Texas			.017	.50	.018	.003	.0007	.0008	.008	.007	.1	.08	20-30	--	23
Tuscaloosa sandstone, composite	23	Upper Cretaceous, Southeastern U. S.			.024	.86	.049	.007	.0019	.0024	.012	.015	.2	.03	5	5	10
Woodbine sandstone, composite	24	Upper Cretaceous, South central U. S.			.017	.73	.129	.004	.0015	.0020	.010	.018	.2	.02	2	2	6
Eagleford shale, composite	25	Upper Cretaceous, South central U. S.			.017	.89	.088	.005	.0014	.0017	.009	.015	.1	.06	10-20	--	7
Lower Eutaw (clayey sand), composite	26	Upper Cretaceous, Southeastern U. S.			.026	.72	.031	.006	.0014	.0017	.010	.009	.2	.08	20-30	8	12
Playa del Rey shale, composite	27	Miocene, California			.043	.54	.012	.017	.0010	.0014	.021	.005	.1	.08	20-30	--	15

Gulf of Mexico: 21 samples: EG2-A, EG3-A, EG6-A, EG149-A, EG151-A and EG153-A are globigerina oozes; the rest are gray clays.

EG2-A	28	Lat. 24°45.5' N. Long. 86°27' W.	11,200	0-1	0.017	0.35	0.007	0.004	0.0009	0.0006	0.007	0.004	0.1	0.40	>30	--	28
EG2-B	29	...do...............	do	29	.026	.65	.015	.007	.0017	.0022	.014	.011	.2	.03	5	9.5	12
EG2-C	30	...do...............	do	59	.028	.70	.023	.007	.0020	.0025	.016	.015	.3	.03	5	9.	11
EG3-A	31	Lat. 26°01' N. Long. 88°03' W.	>6,000	0-1	.012	.37	.014	.004	.0011	.0007	.006	.004	.15	.23	>30	--	24
EG3-B	32	...do...............	do	29	.024	.62	.019	.006	.0021	.0018	.013	.010	.2	.09	20-30	--	16
EG3-C	33	...do...............	do	59	.033	.67	.022	.007	.0022	.0026	.015	.011	.2	.03	5	7.5	12
EG6-A	34	Lat. 26°58.5' N. Long. 89°12' W.	8,100	0.5-1.5	.017	.31	.009	.003	.0008	.0006	.005	.004	.1	.23	>30	--	27

Gulf of Mexico, continued

Sample no.	Sequence no.	Location	Water depth (ft.)	Depth in core (in.)	Percent												
					V_2O_5	TiO_2	ZrO_2	NiO	Co_2O_3	Sc_2O_3	Cr_2O_3	La_2O_3	BaO	SrO	CaO	Fe_2O_3	LOI
EG6-B	35	Lat. 26°58.5' N. Long. 89°12' W.	8,100	29	0.020	0.64	0.016	0.009	0.0025	0.0022	0.013	0.011	0.1	0.03	10-20	--	11
EG6-C	36	...do...........	do	59	.028	.74	.024	.008	.0023	.0022	.012	.011	.2	.03	5	5.5	11
EG9-A	37	Lat. 27°51' N. Long. 89°15' W.	4,500	0-1	.025	.61	.021	.008	.0015	.0019	.011	.010	.2	.09	20-30	5	13
EG9-B	38	...do...........	do	28	.025	.64	.023	.006	.0014	.0020	.011	.011	.1	.03	3	--	9
EG9-C	39	...do...........	do	58	.026	.68	.032	.006	.0016	.0019	.010	.010	.1	.02	2	3	9
EG12-A	40	Lat. 28°18' N. Long. 89°20' W.	2,400	0-1	.026	.62	.021	.007	.0016	.0019	.011	.012	.1	.04	9	--	13
EG12-B	41	...do...........	do	30	.027	.65	.021	.007	.0017	.0018	.010	.008	.1	.03	6	--	11
EG12-C	42	...do...........	do	59	.025	.56	.015	.006	.0013	.0019	.012	.008	.2	.09	10-20	4	15
EG15-A	43	Lat. 28°33.5' N. Long. 89°22' W.	978	0.5-1.5	.024	.60	.020	.006	.0014	.0019	.011	.009	.2	.03	9	--	13
EG15-B	44	...do...........	do	30	.024	.60	.019	.006	.0013	.0026	.016	.010	.2	.09	10	7	16
EG15-C	45	...do...........	do	59	.030	.52	.015	.007	.0015	.0021	.014	.008	.2	.09	7	7.5	13
EG149-A	46	Lat. 27°51' N. Long. 85°44' W.	3,000	0-1.5	.019	.19	.005	.006	.0010	.0013	.007	.003	.14	.20	>30	1.4	31
EG151-A	47	Lat. 28°01.5' N. Long. 85°22' W.	1,200	3-4	.016	.11	.003	.002	.0005	.0005	.005	nm	.05	.30	>30	--	27
EG153-A	48	Lat. 28°11.5' N. Long. 85°02' W.	480	2.5-3.	.016	.06	.002	.002	nm	nm	.005	nm	.01	.28	>30	--	29
Average values for all Gulf of Mexico samples excluding those with > 10 percent CaO.					.027	.64	.021	.007	.0017	.0021	.013	.011	.2	.04	6		12

Guadalupe River: 1 sample: gray clay.

GR7PB	89	Guadalupe River bridge crossing of Highway 35, Aransas Co., Texas	Surface mud		0.012	0.54	0.028	0.003	0.0012	0.0016	0.008	0.009	0.1	0.03	10	--	15

Mississippi River Delta: 4 samples: gray clays.

MP137-51ABL	93	Lat. 29°20'40" N. Long. 89°14'05" W.	--	0	0.021	0.71	0.024	0.006	0.0015	0.0028	0.014	0.013	0.1	0.02	1	--	8
MP137-51ABL	94	...do.............	--	51	.023	.69	.020	.006	.0016	.0024	.012	.011	.1	.03	1	--	9
MP123-51ABL	95	Lat. 29°14'45" N. Long. 89°03'53" W.	--	0	.023	.76	.027	.007	.0016	.0026	.013	.014	.1	.03	1	7.5	9
MP123-51ABL	96	...do.............	--	51	.019	.73	.033	.005	.0014	.0025	.013	.013	.1	.03	1	5	7
Average values for Mississippi River Delta samples					.022	.72	.026	.006	.0015	.0026	.013	.013	.1	.03	1		8

San Diego trough: 3 samples: dark green clays.

Sample no.	Sequence no.	Location	Water depth (ft.)	Depth in core (in.)	Percent												
					V_2O_5	TiO_2	ZrO_2	NiO	Co_2O_3	Sc_2O_3	Cr_2O_3	La_2O_3	BaO	SrO	CaO	Fe_2O_3	LOI
CORE V120	90	Lat. 32°40.6' N. Long. 117°35.5 W.	3,612	4-12	0.023	0.69	0.013	0.007	0.0016	0.0033	0.017	0.007	0.2	0.09	7	--	14
CORE V120	91	...do............	do	32	.021	.67	.012	.008	.0014	.0024	.015	.004	.2	.17	11	--	16
CORE V151C	92	Lat. 32°30.4' N. Long. 117°35' W.	3,900	4-12	.022	.65	.014	.008	.0015	.0029	.017	.005	.2	.09	10	--	15
Average values for San Diego trough samples					.022	.67	.013	.008	.0015	.0029	.016	.005	.2	.12	9	--	15
The following 40 samples are from the Pacific Ocean floor.																	
Siliceous oozes: 3 cores, 9 samples: buff clays.																	
North Holiday core no. 9	49	Lat. 41° N. Long. 155° W.	17,520	2 1/2 - 3 1/2	0.025	0.78	0.024	0.013	0.0050	0.0045	0.018	0.012	0.9	0.02	1	--	8
...do.....	50	...do..........	do	22 - 33	.026	.72	.022	.013	.0046	.0050	.016	.011	.9	.02	1	--	8
...do.....	51	...do..........	do	46-48	.028	.81	.023	.013	.0055	.0046	.015	.012	.9	.02	1	--	8
...do.....	52	...do..........	do	68-69	.028	.79	.022	.014	.0062	.0047	.015	.011	.9	.02	1	8	7
Average values for North Holiday core no. 9					.027	.77	.023	.013	.0054	.0047	.016	.012	.9	.02	1		8
North Holiday core no. 10	78	Lat. 40°14' N. Long. 159°5.2' W.	16,500	0	.027	.70	.020	.014	.0049	.0056	.022	.014	.9	.05	1	--	8
...do.....	79	...do............	do	43	.024	.73	.020	.011	.0050	.0040	.012	.008	1.8	.05	2	--	8
Average values for North Holiday core no. 10					.026	.72	.020	.013	.0050	.0048	.017	.011	1.4	.05	1.5		8
MP13-2	72	Lat. 9°08.7' N. Long. 144°25.9' W.	16,500	3-4	.023	.67	.022	.012	.0040	.0048	.012	.014	.9	.05	1.3	--	12
...do.....	73	...do.............	do	20 - 21 1/2	.020	.62	.021	.015	.0091	.0065	.014	.021	.9	.05	1.3	--	11
...do.....	74	...do.............	do	35 1/2 - 38	.020	.63	.022	.014	.0083	.0066	.015	.023	.9	.05	1.3		11
Average values for MP13-2					.021	.64	.022	.014	.0071	.0060	.014	.019	.9	.05	1.3		11
Average values for 9 samples of siliceous ooze					.025	.72	.022	.013	.0058	.0051	.015	.014	1.0	.04	1.2		9
"Red clays": 5 cores, 20 samples: buff to dark brown clays.																	
MP43K	53	Near Bikini	13,800	4	0.034	0.81	0.024	0.028	0.0122	0.0052	0.019	0.032	0.9	0.09	4.5	9	8
...do.....	54	...do..........	do	20	.024	.81	.021	.032	.0128	.0042	.015	.028	2.7	.09	3	--	8
Average values for MP43K					.029	.81	.023	.030	.0126	.0047	.017	.030	1.8	.09	3.8		8
MP38P	55	Lat. 19°03' N. Long. 177°20' W.	15,450	1 - 1 1/2	.026	.76	.022	.023	.0079	.0058	.016	.022	.3	.05	3	--	8
...do.....	56	...do..........	do	20	.020	.50	.018	.088	.0251	.0074	.006	.072	.2	.09	7	7	9

"Red clays", continued

Sample no.	Sequence no.	Location	Water depth in ft.	Depth in core (in.)	Percent V_2O_5	TiO_2	ZrO_2	NiO	Co_3O_4	Sc_2O_3	Cr_2O_3	La_2O_3	BaO	SrO	CaO	Fe_2O_3	LOI
MP38P	57	Lat. 19°03' N. Long. 117°20' W.	15,450	22	0.025	0.80	0.021	0.022	0.0074	0.0032	0.014	0.019	0.4	0.05	1	--	7
Average values for MP38P					.024	.69	.020	.044	.0134	.0048	.012	.038	.3	.06	4		8
MP35-2	58	Lat. 19°21' N. Long. 174°58' W.	15,900	1-2	.031	.82	.022	.025	.0105	.0034	.016	.017	.2	.05	1	--	7
...do.....	59	...do...........	do	21-24	.033	.84	.022	.022	.0091	.0040	.018	.018	.2	.05	1	--	7
...do.....	60	...do...........	do	50-53	.031	.89	.024	.028	.0106	.0035	.017	.019	.2	.05	2	--	7
...do.....	61	...do...........	do	76.5-79.5	.032	.96	.028	.028	.0251	.0057	.016	.042	.1	.09	4.5	--	7
...do.....	62	...do...........	do	110-113	.031	.95	.024	.050	.0229	.0050	.018	.036	.1	.09	4.5	--	8
...do.....	63	...do...........	do	137.5-143	.026	.80	.025	.059	.0295	.0050	.009	.046	.2	.09	4.5	--	8
Average values for MP35-2					.031	.88	.024	.035	.0179	.0044	.016	.030	.2	.07	2.9		7
MP3	64	Lat. 20°51' N. Long. 127°15.7' W.	14,347	21-23	.032	.45	.027	.023	.0109	.0035	.004	.034	.9	.05	2	--	9
...do.....	65	...do.............	do	66.5-69	.020	.36	.020	.019	.0074	.0030	.004	.021	.9	.05	1	--	10
...do.....	66	...do.............	do	112-116	.023	.44	.026	.021	.0096	.0032	.004	.027	1.8	.09	4.5	--	9
...do.....	67	...do.............	do	144-166	.015	.57	.025	.027	.0124	.0040	.006	.029	.9	.09	4.5	7.5	8
...do.....	68	...do.............	do	189-192	.015	.55	.026	.034	.0128	.0037	.007	.019	1.8	.09	4.5	--	8
...do.....	69	...do.............	do	222-225	.018	.63	.025	.040	.0150	.0036	.007	.023	2.7	.09	3	--	8
...do.....	70	...do.............	do	257-260	.028	.74	.022	.042	.0159	.0040	.013	.020	1.9	.10	3.3	--	7
...do.....	71	...do.............	do	293-297	.029	.78	.021	.027	.0108	.0040	.018	.016	.9	.05	1	--	8
Average values for MP3					.023	.57	.024	.029	.0119	.0036	.008	.024	1.5	.08	3		8
MP5-3	81	Lat. 14°22.1' N. Long. 133°07' W.	16,020	2-3	.023	.59	.018	.023	.0084	.0044	.012	.017	.9	.05	2	--	10
Average values for 20 samples of "red clay"					.026	.70	.023	.033	.0138	.0044	.012	.026	.9	.07	3.1		8

Volcanic muds: 3 cores, 7 samples: gray to buff to light brown clays: MP17-2 and MP21-1 are partly volcanic and partly terrigenous.

MP18B-2	75	Lat. 20°02.2' N. Long. 155°11.4' W.	1,122	2 1/2-3	0.067	2.52	0.021	0.020	0.0055	0.0057	0.079	0.004	0.03	0.18	12	12	10
...do.....	76	...do.............	do	13 - 13 1/2	.039	1.63	.015	.020	.0040	.0038	.064	.005	.03	.27	14	--	13

Volcanic muds, continued

Sample no.	Sequence no.	Location	Water depth (ft.)	Depth in core (in.)	Percent												
					V_2O_5	TiO_2	ZrO_2	NiO	Co_3O_4	Sc_2O_3	Cr_2O_3	La_2O_3	BaO	SrO	CaO	Fe_2O_3	LOI
MP18B-2	77	Lat. 20°02.2' N. Long. 155°11.4' W.	1,122	22-23	0.035	2.26	0.021	0.022	0.0036	0.0035	0.087	0.006	0.03	0.18	12	--	11
Average values for MP18B-2					.034	2.14	.019	.021	.0050	.0050	.077	.005	.03	.21	13		11
MP17-2	82	Lat. 14°38' N. Long. 151°38' W.	18,450	11-14	.025	1.03	.015	.024	.0079	.0036	.032	.008	.1	.05	5.4	8.5	9
...do.....	83	...do...........	do	34-38	.038	1.30	.012	.034	.0059	.0050	.087	.003	.03	.08	8.6	--	5
...do.....	84	...do...........	do	38 3/4-41 1/2	.027	.82	.011	.025	.0104	.0055	.029	.017	.1	.05	3	7.5	8
Average values for MP17-2					.030	1.05	.013	.028	.0081	.0047	.049	.009	.08	.06	6		7
MP21-1	80	Lat. 20°43' N. Long. 159°57' W.	14,880	47	.039	1.46	.022	.018	.0072	.0043	.036	.011	.3	.05	4.5	--	9

Calcareous oozes: 3 cores, 3 samples: white to very light buff clays

MP33E	85	Lat. 17°30' N. Long. 174°15' W.	5,640	5 1/2-8 1/2	0.017	0.06	0.001	nd	nm	0.0005	0.014	nm	0.1	0.7	>30	1	28
MP25E-1	86	Lat. 19°05' N. Long. 169°40' W.	5,400	15-17	.017	.01	nm	nd	nm	.0005	nm	nm	.06	.37	>30	<1	24
MP40-1	87	Lat. 15°35' N. Long. 177°30' E.	13,392	25-29	nm	nm	nm	nd	nm	nm	nm	nm	.01	.08	>30	<1	22

Manganese nodule: 1 sample: 1 1/2 X 1 X 3/4 inches

MP26A-3	88	Lat. 19°25' N. Long. 171° W.	4,500	0	0.093	1.65	0.070	0.402	0.3380	0.0014	0.004	0.057	0.05	0.25	6.8	>20	15
Average values for 10 pelagic cores, excluding basaltic MP18B-2 and the calcareous oozes					.027	.82	.021	.025	.0097	.0046	.020	.020	.8	.06	3		8
Average values for 33 pelagic samples, excluding those from MP18B-2 and the calcareous oozes					.026	.76	.022	.027	.0109	.0045	.017	.022	.84	.06	2.9		9

CHAPTER 3

DISCUSSION

1. STRONTIUM

It is a well-known fact that Sr accompanies Ca, both in the igneous and the sedimentary environment. Many analyses of Ca-rich rocks bear this out. When the Sr/Ca ratio is considered, however, instead of being more or less equal from basic to acid igneous rocks, it is higher in acid rocks and especially in potash feldspars. Several values taken from Noll (1934) illustrate the phenomenon.

Rock or mineral	SrO (percent)	Sr/Ca·100
Gabbro, Germany, average	0.02	0.09
Plagioclase, Egersund	0.1	0.5
Granite, Germany, average	0.02	0.9
Orthoclase, Grua	0.07	8.0
Sanadine, Drachenfelz	0.48	56.0

It seems, therefore, that Sr^{++} substitutes quite readily for K^+ in the potash feldspar structure. Concerning ionic size, Sr^{++}, whose ionic radius is 1.12 A*, can replace K^+, whose ionic radius is 1.33 A, but charge-wise and size-wise, Sr^{++} should replace Ca^{++}, whose ionic radius is 0.99 A, much more easily. At any rate, in igneous rock there is a mechanism for Sr enrichment other than substitution for Ca, and in subsequent data, evidence is presented for still another method of Sr enrichment in sedimentary rocks.

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*Pauling-type radii based on 6-fold coordination are used throughout this work. See Ahrens (1952).

The following are pertinent analyses taken from the literature. The last one (6) is from this work.

Sample and Source	SrO (percent)	SrO/CaO·100
1. Composite of 51 samples of "red clay". Cited by Clarke (1924)	0.056	2.9
2. Composite of 52 samples of "terriginous clays," consisting of four "green muds" and 48 "blue muds." Cited by Clarke (1924)	0.03	1.5
3. Shales, composite, Noll (1934)	0.02	1.7
4. Limestones, Noll (1934)	0.05-0.09	0.04-0.077
5. "Red clay," average, Hevesy and Würstlin (1934)	0.007	-
6. Average of five "red clay" cores, Young, analyst	0.07	2.3

The "red clay" value of 0.007 percent SrO by Hevesy and Würstlin seems to be too low. As shown in Figure 7, the Pacific cores, with the exception of basaltic MP18B-2 and the calcareous oozes, average 0.06 percent SrO. The five "red clay" cores average 0.07 percent SrO. These percentages differ but slightly from the 0.056 percent SrO for "red clay" cited by Clarke (1924). The San Diego trough samples contain 0.12 percent SrO, which seems high, but their correspondingly high CaO content, 9 percent, is partially responsible for this. Basaltic core MP18B-2 is rich in SrO, 0.21 percent, but its CaO content is also high, 13 percent. Manganese nodule MP26A-3 contains 0.25 percent SrO. Clarke (1924) gives the SrO content of a similar oceanic manganese nodule as 0.11 percent.

Comparison of Sr values is of increased interest when the SrO/CaO·100 ratio is considered. The following tabulation is from the

NOTES: Samples with 20 percent or more CaO have not been used to form averages.

Pacific Ocean cores and samples do not include MP18B-2.

Numbers in parentheses indicate number of samples or cores contributing to average.

Samples from Atchafalaya Bay, La., South of Grand Isle, La., and Bay Rambour, La. are silty clays.

Samples from Mississippi Delta, Guadalupe River, Texas, Gulf of Mexico and San Diego trough are clays.

Samples from Lake Pontchartrain, La. are silty sands.

Preceding notes apply to following 9 distribution Figures also.

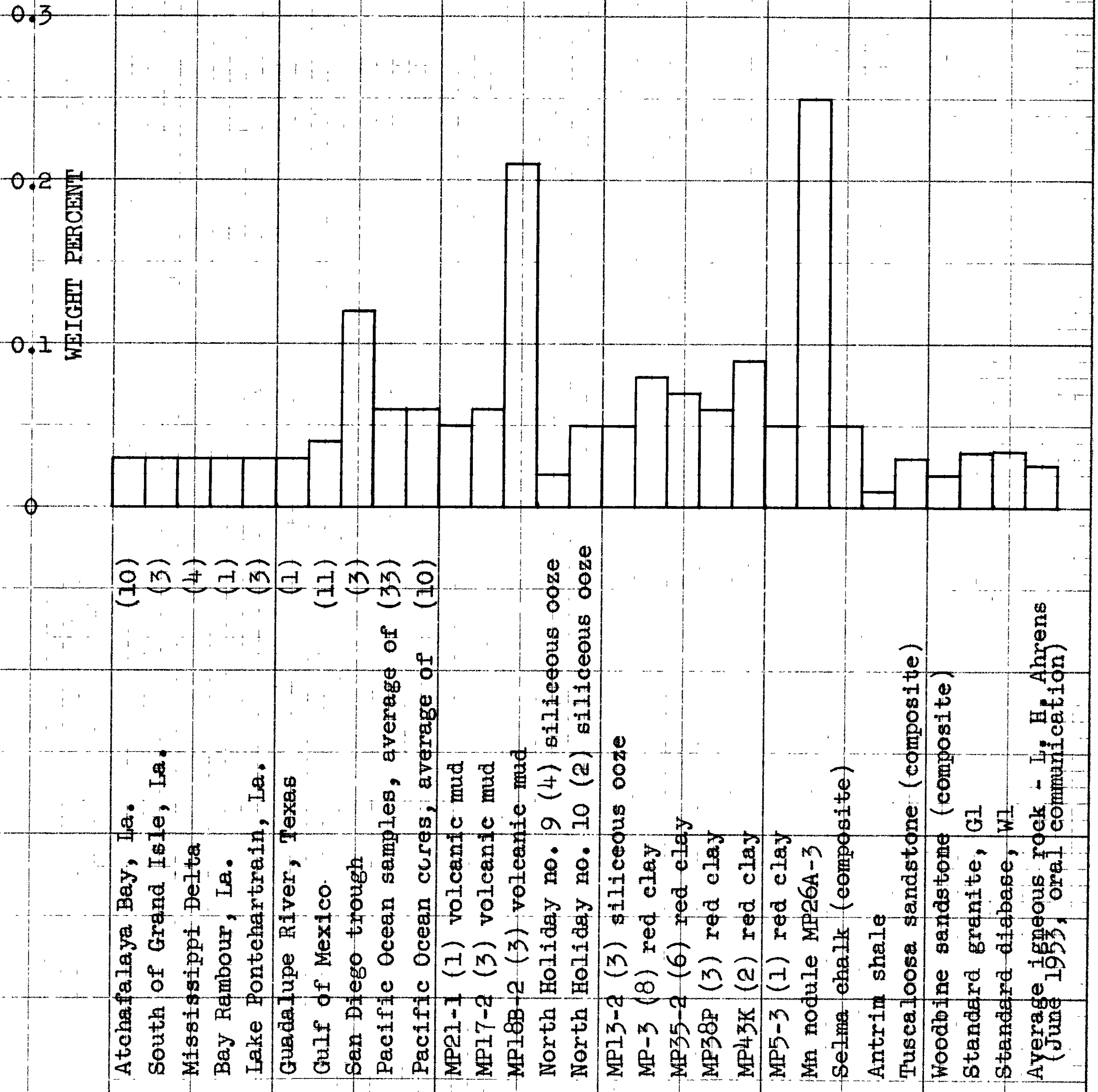

FIGURE 7.--DISTRIBUTION OF SrO

present work, except in the case of sea water.

Sample	SrO (percent)	CaO (percent)	SrO/CaO·100
10 Pacific cores, average	0.06	3.0	2.0
5 "red clay" cores, average	0.07	3.1	2.3
3 siliceous ooze cores, average	0.04	1.3	3.1
MP18B-2, average	0.21	13.0	1.6
Manganese nodule	0.25	7	3.6
San Diego trough, average	0.12	9	1.3
Mississippi Delta, average	0.03	1	3.0
Selma chalk	0.05	10	0.5
Antrim shale	0.01	1	1.0
Woodbine sandstone	0.02	2.0	1.0
G 1, standard granite	0.033	1.42	2.3
W 1, standard diabase	0.034	10.95	0.3
Sea water	0.0015	0.056	2.7

In the foregoing tabulation, W 1 has the least SrO content with respect to CaO. The Selma chalk is similar in this respect also. High SrO/CaO ratios of the manganese nodule, Pacific samples in general, the Mississippi Delta, and MP18B-2 suggest that a mechanism other than Sr^{++} substitution for Ca^{++} is in operation. Basaltic MP18B-2 has a ratio five times as great as W 1, the standard diabase. Two possibilities present themselves. Either Sr is present as finely dispersed celestite, $SrSO_4$, as Noll (1934) suspected, or else Sr has been adsorbed on clays and zeolites. Harvey (1945) notes that sea water is not saturated with respect to $SrCO_3$, but nothing is said of $SrSO_4$. The

$SrO/CaO \cdot 100$ ratio for sea water is approximately the same as that for the hydrolyzate sediments. If adsorption were of great importance, it would be suspected that the ratio for the hydrolyzate sediments would be greater than that of sea water because of the tendency of Sr^{++} to replace Ca^{++} in clays and zeolites by means of cation exchange.

The enrichment of the heavier elements of the alkali and alkaline earth metals in hydrolyzates is shown in Table 7.

Table 7

Data taken from Rankama and Sahama (1950), unless otherwise noted

Element	Percentage in sea water	Percentage in shale	Percentage in shale divided by percentage in sea water
Li	0.00001	0.0046	460.
Na	1.056	0.97	0.92
K	0.038	2.7	71.
Rb	0.00002	0.028, Canney (1951)	1400.
Cs	~ 0.0000002	0.00075, Canney (1951)	3750.
Mg	0.127	1.48	11.6
Ca	0.04	2.23	55.7
Sr	0.0013	0.017, Noll (1934)	13.1
Ba	0.000005	0.134, near-shore clayey sediments, present work	26,800.

The above table indicates that in shales the alkali metals are increasingly enriched from Na to Cs. Li is strongly enriched in shales also, and this upsets the trend established for the alkali metals, but it is a special case, largely unexplained. There is also enrichment of the alkaline earth metals with increasing atomic weight, with the exception of Ca, whose case is complicated by its extraction from sea water to form limestone tests for marine organisms, in addition to its direct precipitation under certain conditions. Nevertheless, there is a real enrichment in shales of the larger and heavier cations, as opposed to the smaller and lighter cations of the alkali and alkaline earth metals. Discussion of this point is given in Chapter 5.

The Group II elements in Table 7 form some increasingly insoluble compounds as atomic weight increases. For that reason, much of the enrichment indicated in Table 7 is due to insolubility effect. Possibly a better means of demonstrating enrichment would be to use the ratio of the amount of element in shales to the amount in the average igneous rock. In Table 8 this is done for Group I and Group II elements.

Table 8

Data taken from Ahrens (June 1953, oral communication), unless otherwise noted

Element	Percentage in average igneous rock	Percentage in shale divided by percentage in average igneous rock
Li	0.0022	2.1
Na	2.83 Rankama and Sahama (1950)	0.34
K	2.7	1.0
Rb	0.040	0.7
Cs	0.0005	1.5

Table 8 (continued)

Data taken from Ahrens (June 1953, oral communication), unless otherwise noted

Element	Percentage in average igneous rock		Percentage in shale divided by percentage in average igneous rock
Mg	2.09	Rankama and Sahama (1950)	0.71
Ca	3.63	Rankama and Sahama (1950)	0.61
Sr	0.022		0.77
Ba	0.10		1.34

In general, Group I elements become progressively enriched in shales as atomic weight increases. Li and K act anomalously. Group II elements also demonstrate the same trend. Ca acts anomalously for reasons mentioned before.

In conclusion, although precipitation of $SrSO_4$ on the sea floor is not discounted, adsorption of Sr^{++} on submarine clays and zeolites is thought to be probable.

2. BARIUM

In igneous rocks, Ba^{++}, whose ionic radius is 1.34 A, follows K^+, ionic radius 1.33 A, despite the valence difference. K is enriched in acid igneous rocks, and consequently, Ba is also enriched therein. In sedimentary rocks Ba is enriched in shales, which is a reflection of its tendency to be adsorbed on clay colloids, and Table 8 shows that Ba exceeds Sr in this tendency.

To aid in the discussion, a list of barium analyses from the literature follows. Analyses 1 through 5 are from Engelhardt (1936), 6 through 8 from Clarke (1924), 9 from Sahama (1945), and 10 to 12 from Grim, Dietz, and Bradley (1949).

	Rock	BaO (percent)
1.	"Red clay" from the Meteor Expedition, average of three station, Cape Verde Basin; depth approximately 6000 meters.	0.022
2.	"Gray mud", Meteor station 98	0.065
3.	"Gray mud", Meteor station 111	0.032
4.	14 German granites, composite	0.042
5.	14 German gabbros, composite	0.0045
6.	Composite of 51 samples of "red clay"	0.20
7.	Composite of 52 samples of "terriginous clays"	0.06
8.	Oceanic manganese nodule	0.67
9.	Rapakivi granite	0.10
10.	"Red clay", Pacific Ocean, Latitude 30°41'N, Longitude 121°46'W; depth 13,386 ft.; depth in core 87-89 inches.	0.79
11.	"Red clay", from southwest of Ensenado, Lower California; depth 9840 ft.; depth in core 8-11 inches.	0.37
12.	Sediment from mouth of Gulf of California	0.15

In addition, Caspari (1910), who studied "red clay" from the Atlantic, Pacific, and Indian Oceans, found BaO to vary from trace amounts to 1.16 percent. Bradley and others (1940) found appreciable amounts of barium in six samples from North Atlantic Ocean deep-sea cores. Revelle (1944) noted the unequal distribution of Ba in the Pacific basin sediments.

The distribution of BaO in the samples analyzed in this work is shown graphically in Figure 8. A few values are tabulated

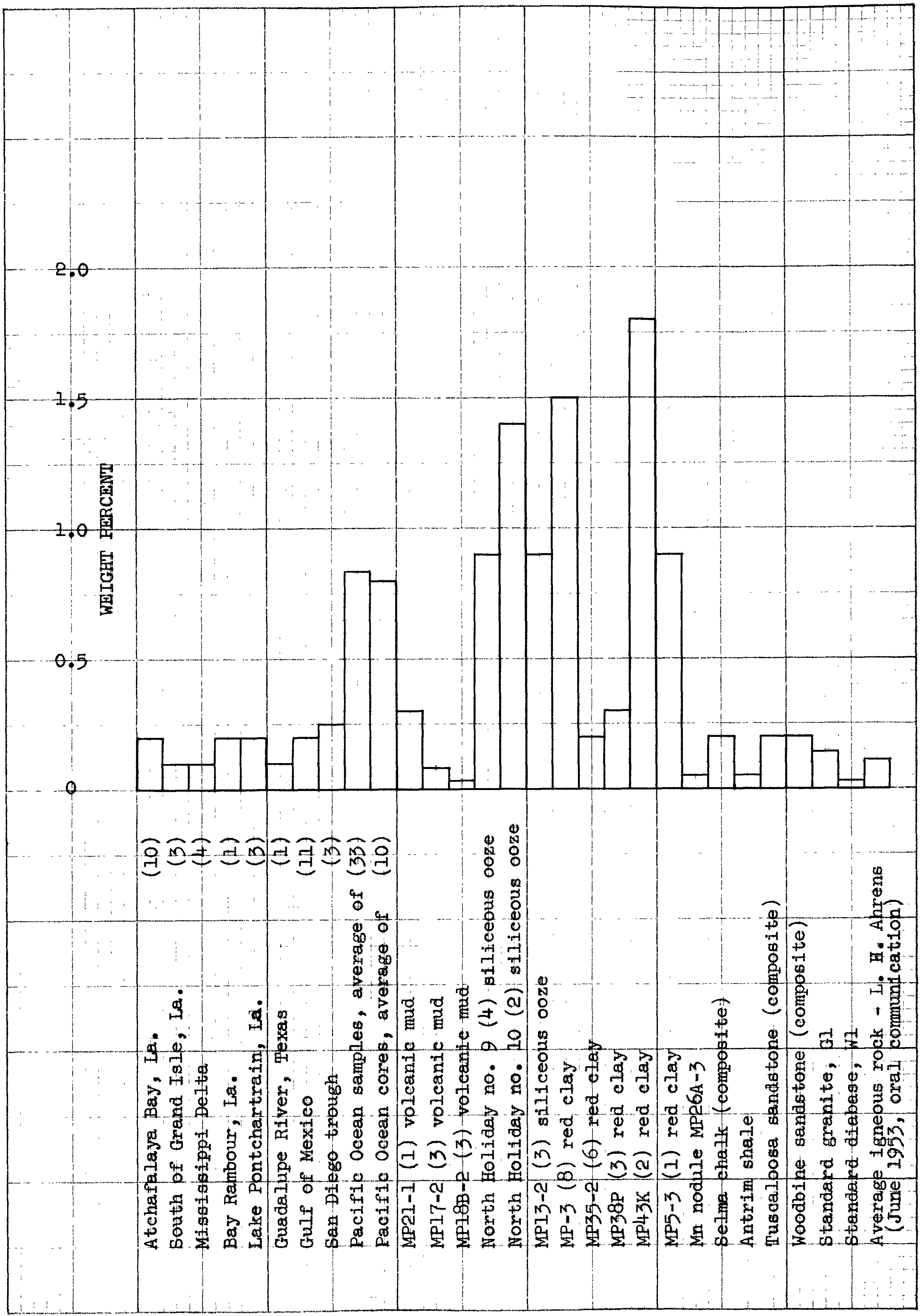

FIGURE 8.--DISTRIBUTION OF BaO

in the text to aid in comparison with preceding analyses.

Rock	BaO (percent)
G 1, standard granite	0.145
W 1, standard diabase	0.030
Pacific cores, average (excluding basaltic MP18B-2 and calcareous oozes)	0.80
MP43K, a "red clay"	1.8
MP3, a "red clay"	1.5
MP35-2, a "red clay"	0.20
North Holiday core no. 10, a siliceous ooze	1.4
MP18B-2, a volcanic mud	0.03
Manganese nodule	0.05
Gulf of Mexico samples, average (excluding samples with greater than 10% CaO)	0.20
Mississippi Delta, average	0.10

One of the first differences to be noted in the two preceding tabulations, is that Engelhardt's values (1-5) are the lowest reported. The average BaO content of the Pacific cores analyzed in this work is four times that reported by Clarke, and forty times that reported by Engelhardt. Regarding granite analyses, Engelhardt's value is lower than that of Sahama which is in turn lower than that of the G 1 value.

Although Engelhardt's values are surely too low, it may be assumed that they are proportionally low and are in correct relation to each other. He noted that his oceanic "red clay" values were lower than the values obtained at the mouth of the Rio de la Plata and near the South Shetland Islands, and postulated that barium carried into the ocean by rivers was quickly adsorbed by the copious quantities of clay in suspension in the shelf zone. The barium was deposited with the clay as the clay particles flocculated and precipitated. He thinks that, as a consequence, most of the barium never reaches the open sea.

Other analyses in the preceding tabulations, however, indicate the existence of Ba-rich oceanic sediments thousands of miles from land. The most puzzling part of the Ba enrichment in deep sea cores, however, is not the unusually high Ba values found, but the very unequal distribution of Ba on the sea floor. Reference to Figure 8 indicates that two of the volcanic cores, MP18B-2 and MP17-2, contain less than 0.10 percent BaO. What is more significant, however, is that two of the "red clay" cores, MP38P and MP35-2, contain comparatively small amounts of BaO, 0.30 and 0.20 percent, respectively. Of the six deep-sea cores with 0.90 percent or more BaO, three are "red clays" and three are siliceous oozes.

A few BaO/SrO ratios indicate, in another way, the differences among the above sediments.

Sample	BaO/SrO
North Holiday core no. 9, average	45.
MP43K, average	20.
MP38P, average	5.
MP35-2, average	2.9
MP18B-2, average	0.1
Atchafalaya Bay, average	6.7
Mississippi Delta, average	3.3

Regarding this ratio, near-shore sediments, such as those from Atchafalaya Bay or the Mississippi Delta, appear to be similar to those "red clay" deposits which are relatively poor in Ba content.

In spite of barium's ability to replace Mg, Ca and Sr in clays and zeolites (see Chapter 5), it is incorrect to seize upon cation exchange as the principal mechanism for the enrichment of Ba in some deep sea deposits. If cation exchange were the answer, one should not expect such variability of Ba content among the "red clays".

When the areal distribution of Ba is considered, the region from Longitude 150°W to Longitude 180°, and roughly along the 20°N parallel, is found to be comparatively low in Ba. (See Map 1 in the Introduction.) Even the manganese nodule, which comes from this region, is extraordinarily low in BaO, containing 0.05 percent. Clarke (1924) and Engelhardt (1936) cited 0.67 and 0.10 percent BaO, respectively, for manganese nodules, and it must be remembered that Engelhardt's values are too low. The cores which are rich in Ba are found in the periphery of the region outlined above, and are the six aforementioned cores with 0.90 percent BaO, or more.

Revelle (1944) reported concentrations of Ba in the northeast and southeast Pacific Ocean. Probably much more work on the areal distribution of Ba in the Pacific basin will be necessary for an understanding of its distribution pattern. Possibly ocean currents and physical properties of the ocean, such as temperature and salinity, play an important role in this pattern.

It was suspected that much of the barium in oceanic sediments might be due to tiny barite concretions or nodules. To check this possibility, sample MP3 from 222 to 225 inches in the core, which contained 2.7 percent BaO, was analyzed in the Norelco X-ray spectrometer, and also examined under the microscope. No indications of barite were found with either method. This, however, is not proof that small quantities are absent.

In conclusion, the two problems, one of the distribution, and the other of the mode of occurrence of Ba, remain unsolved. However, it is thought, after consideration of the available facts, especially barium's unequal distribution on the sea floor, that the distribution problem is linked with physical oceanography, and that the mode of occurrence is primarily as a separate mineral phase (possibly very finely precipitated sulfate or carbonate), and subordinately as adsorbed Ba^{++}.

3. TITANIUM

There are many analyses of sediments which list titanium content, since titanium is usually determined with other major chemical constituents. Titanium is listed by Rankama and Sahama (1950) as being present in sea water, but the quantity is not measured due to its scarcity.

There are no great discrepancies between TiO_2 values for marine "red clay" deposits reported in this work and other works. Clarke (1924) reported 0.98 percent TiO_2 for a composite of 51 samples of "red clay", which is in reasonable agreement with the average value of 0.82 percent TiO_2 in deep-sea cores found in this work. He reported a higher value of 1.27 percent TiO_2 for a composite of 52 samples of "terrigenous clays".

Koczy (1950) gave 0.79 percent TiO_2 for the eastern part and 0.61 percent TiO_2 for the western part of the equatorial Atlantic Ocean, from Meteor records. Correns (1937) noted that titania decreased with particle size in deep-sea clays. Thus in a "red clay" from station 305, which had been separated into various size fractions, the 5.5 to 1.0 micron size range contained 1.02 percent TiO_2, and the fraction less than 0.1 micron only contained 0.55 percent TiO_2. The difference in the titania content of the two fractions is due to the fact that less Ti minerals, such as rutile and ilmenite, occur in the finer sizes.

Edgington and Byers (1942) reported similar titania analyses. At a depth of 338 meters, on the ocean floor, off Ocean City, Md., 0.61 percent to 0.70 percent TiO_2 was reported from a 200-centimeter core. In the same report 0.20 to 0.57 percent TiO_2 was reported in the globigerina oozes on the Atlantic floor in a string of cores from the Newfoundland Banks to the Irish coast. These rather low values are due to the large quantities of globigerina ooze in the samples. An exception to these low readings was found in samples 10-A4 and 10-A6, which contained 0.90 to 1.35 percent TiO_2. The $CaCO_3$ content of these two samples was correspondingly low, and the Fe content correspondingly high. On the floor of the Caribbean Sea, in the Bartlett Deep, titania was reported from 0.31 to 0.64 percent in samples rich in globigerina ooze.

Grim, Dietz, and Bradley (1949) reported a Pacific core from a depth of 13,386 feet, and at Longitude 121°46'W, and Latitude 30°41'N, which contained 0.73 to 1.10 percent TiO_2. The part of the sample less than 0.1 micron in size, at 67 to 69 inches in the core, contained 0.73 percent TiO_2, and the fraction 1.0 to 0.1 micron in size contained 1.10 percent titania. These findings agree with those of Correns, mentioned earlier.

Revelle (1944) found the titania content of Pacific "red clays" to vary from 0.47 to 0.85 percent. In globigerina oozes titania varied from trace to 0.45 percent, the amount varying inversely with $CaCO_3$. Radiolarian and diatomaceous oozes averaged about 0.50 percent TiO_2.

Landergren (1948a) reported an average of only 0.33 percent TiO_2 from three cores from the Tyrrhenian Sea. The sediment consisted of volcanic and terrigenous muds.

Schneiderhohn and others (1949), in an investigation of trace metals in German sedimentary rocks, found that Tertiary lignite sands and clays contained up to 1.0 percent Ti, and that Ti content was directly proportional to clay content. Throughout the geologic column Ti showed enrichment in shales as compared to sandstone and limestone.

Consideration of Figure 9 reveals the similarity of titania content of most of the samples analyzed. Only slight differences are noted in the recent bay, gulf, lake, and ocean sediments and older sediments. Basaltic MP18B-2 contains over 2.0 percent titania, and MP21-1 and MP17-2, which also contain basaltic material to a lesser extent, contain over 1.0 percent titania. The manganese nodule is also relatively rich in TiO_2 (over 1.5 percent). Clarke (1924) reported 0.72 percent titania for a similar nodule.

As would be expected, the several calcareous oozes analyzed are very poor in titania (trace to 0.06 percent).

Titania does not appreciably change with depth in any core, with the exception of MP3, the longest core of "red clay". At 66.5 to 69 inches in the core there is a minimum of 0.36 percent titania, and a maximum of 0.78 percent titania at the bottom of the core at 293 to 297 inches.

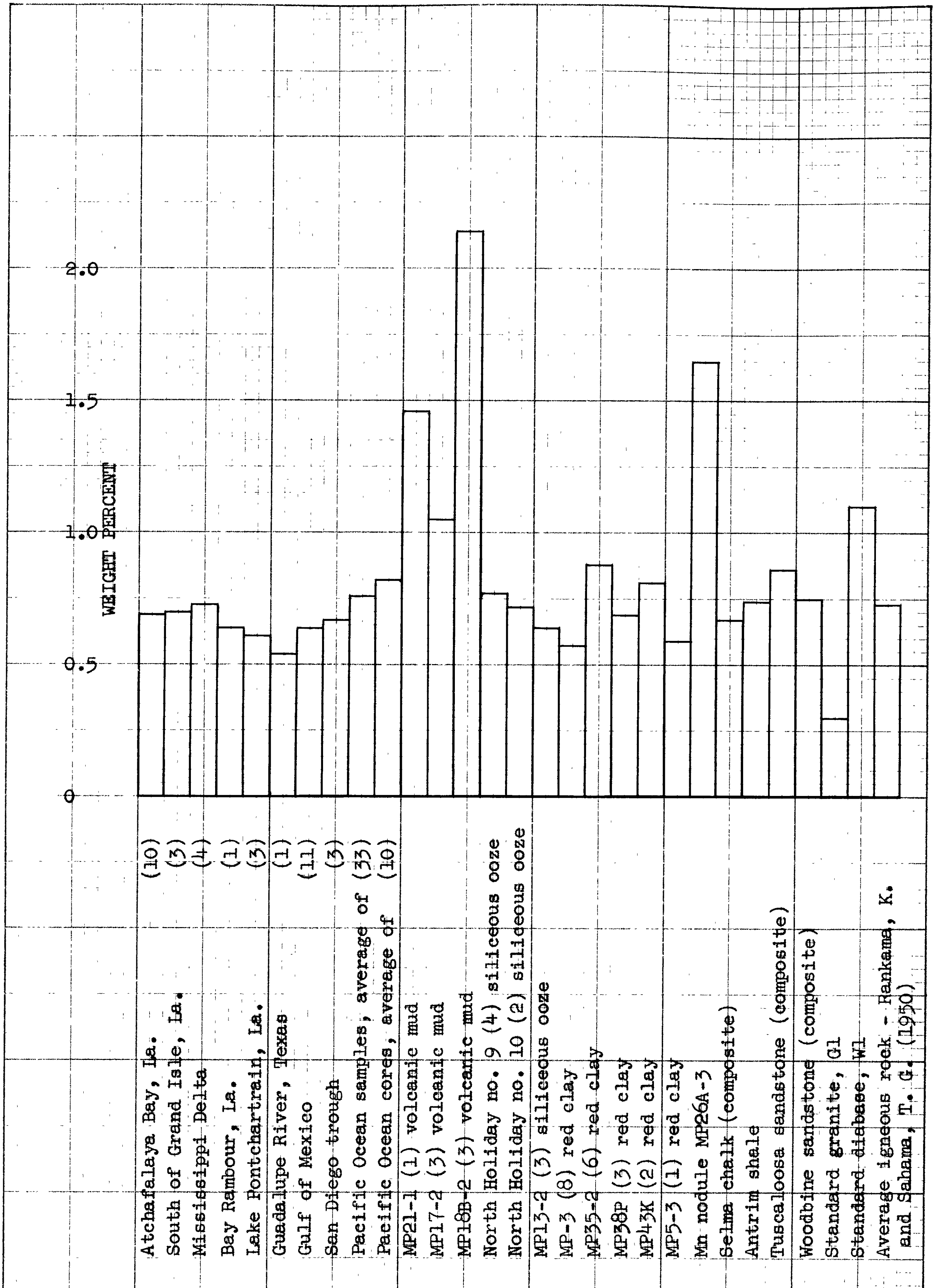

FIGURE 9.--DISTRIBUTION OF TiO_2

Some interesting relations are obtained with a consideration of titania/zirconia ratios. A few are listed here.

Sample	TiO_2/ZrO_2
G 1	11
W 1	92
Average igneous rock*	36.5
MP18B-2, volcanic mud	113
MP17-2, volcanic mud	81
MP21-1, volcanic mud	66
MP43K, "red clay"	35
MP3, "red clay"	24
Gulf of Mexico, average	30
Atchafalaya Bay, average	17
Lake Pontchartrain, average	3

The high ratio of MP18B-2 reveals its basaltic nature, and MP17-2 and MP21-1 exhibit a more dilute basaltic character. All of the average ratios of the "red clay" cores and the siliceous ooze cores fall between 24 and 37, straying little from the average igneous rock ratio of 36.5. This is a significant fact, and will be used in Chapter 6, to arrive at a decision regarding the origin of "red clay". The low ratios of the Lake Pontchartrain samples are a reflection of their sandy, zircon-rich nature.

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*TiO_2 = 0.73 percent, Rankama and Sahama (1950); ZrO_2 = 0.020 percent, Ahrens (June 1953, oral communication).

A frequency distribution histogram* of TiO_2 for 95 samples is given in Figure 10. The small mode at 0.34 to 0.37 percent TiO_2 is due to the sediments rich in globigerina ooze. The part of the histogram from 0.73 to 0.98 percent TiO_2 is mostly accounted for by the deep-sea sediments.

4. ZIRCONIUM

The paucity of Zr determinations in sediments is a reflection of the difficulties inherent in wet chemical methods of analysis for trace amounts of Zr. Recently, Grimaldi and White (1953) developed a precise and accurate method for determination of trace amounts of Zr.

The results of Hevesy and Würstlin (1934) for zirconia in deep-sea "red clays" are in accord with those obtained in this work. Their analyses were made with the X-ray spectrograph. See Hevesy (1932). They presented two analyses of "red clays" from the Challenger Expedition, both of which contained 0.019 percent ZrO_2, and also reported 0.020 percent zirconia for shales. In the present work, the average value for all the deep-sea cores (excluding basaltic MP18B-2 and calcareous oozes), most of which are "red clays", is 0.021 percent zirconia. It is also interesting to note that Hevesy and Würstlin (1934) reported a mixture of various igneous rocks to contain 0.022 percent zirconia, which agrees well with the 0.020 percent zirconia which Ahrens (June 1953, oral communication) ascribes to an average igneous rock.

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*Only samples which afforded valid analyses were used. For example, samples rich in globigerina ooze were not used in the Cr_2O_3 histogram, because $CaCO_3$ intensifies Cr spectral lines. Various logarithmic bases were used depending on the spread of values.

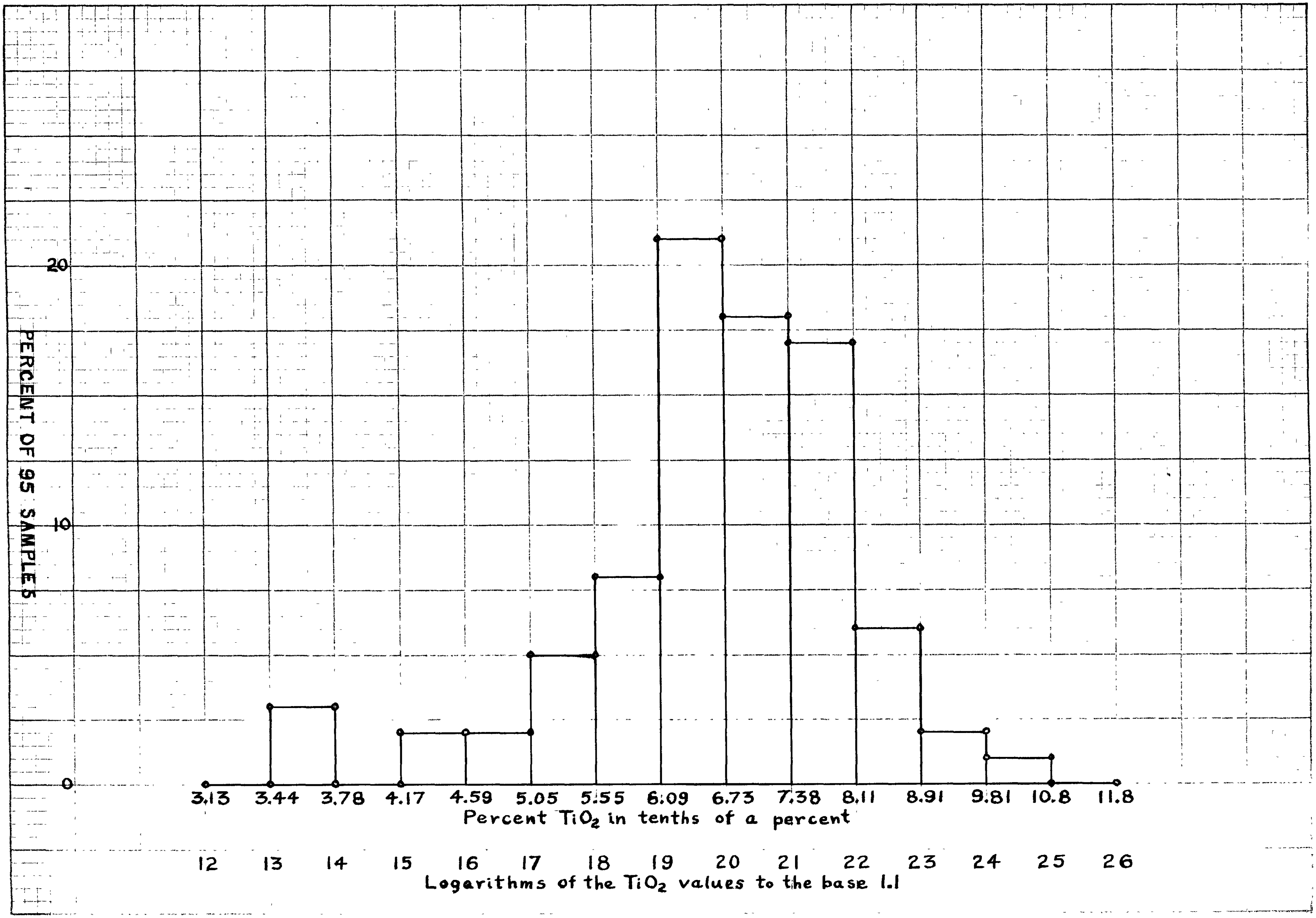

FIGURE 10 - FREQUENCY DISTRIBUTION OF TiO_2

Using the method of Grimaldi and White (1953), Glen Edgington, chemist of the Geochemistry and Petrology Branch of the U. S. Geological Survey, kindly analyzed two of the "red clay" samples, MP5-3 and MP35-2 (depth in core 76.5 to 79.5 inches), and also the standard granite, G 1, and the standard diabase, W 1, in order to check the writer's spectroscopic analyses. The comparisons are all within a factor of 2.

Sample	Percentage ZrO_2			
	Chemical analysis (Edgington)	Spectroscopic analysis (Young)		Recommended value Ahrens (June 1953 oral communication)
		Based on Gl and Wl	Based on synthetic standards	
MP5-3	0.034, 0.031	0.018	0.029	--
MP35-2	0.024, 0.039, 0.039	0.028	0.045	--
G 1	0.038	--	0.043	0.027
W 1	0.024	--	0.021	0.012

Unusually high zirconia contents of "red clays" and oceanic sediments, in general, have been reported by Revelle (1944). The analyses were done by the Sharp-Schurtz Co. using wet chemical methods, and since the Zr occurs in definitely minor amounts, these analyses are suspect. To choose one analysis at random, will illustrate the unlikelyhood of the result. Sample 25, a globigerina ooze, taken in the Pacific Ocean at Longitude 91°52'W, Latitude 34°35'S, depth 3610 meters, was stated to have 42.7 percent CaO, 32.75 percent CO_2, 0.04 percent TiO_2 and 0.08 percent ZrO_2. Assuming that all of the CO_2 was contained in $CaCO_3$, the total amount of $CaCO_3$ is calculated to be 74.45 percent. Thus in a globigerina ooze three quarters of which was $CaCO_3$, there was reported

0.08 percent zirconia. This extraordinary figure is greater than the G 1 value, and greater by a factor of four than most of the "red clays" examined in the present work, and greater by a factor of 10, or more, than most of the globigerina oozes analyzed herein.

The titania/zirconia ratio; discussed at the end of the preceding section on titanium, lends further support for rejection of Revelle's zirconia analyses. In the same sample discussed above, the TiO_2/ZrO_2 ratio is 0.5, whereas almost all titania/zirconia ratios of sediments analyzed in the present work are between 10 and 100, and the lowest deep-sea core ratio was over 15. In Revelle's (1944) report, zirconia percentages in "red clay" varied from trace to 0.24 percent, the average being about 0.12 percent. Titania averaged about 0.80 percent. The average titania/zirconia ratio of 6.7 from these figures appears to be too low to be valid for "red clay".

Figure 11 illustrates the uniformity of zirconia content in "red clay", siliceous ooze, and even volcanic sediments. The river, bay, and near-shore deposits, in general, contain more zirconia than the deep-sea deposits, which would be expected since detrital zircon is more common near shore than in abyssal sediments. The Lake Pontchartrain samples, and the Woodbine sandstone are apparently rich in zircon. Figure 12 gives the frequency distribution pattern of ZrO_2, and the many modes are due to the more or less sandy nature of the sediments. The principal mode at approximately 0.022 percent zirconia is due mainly to the deep-sea sediments.

The problem of the mode of occurrence of Zr in "red clay" remains open, although the finding of trace amounts of zircon in "red clay"

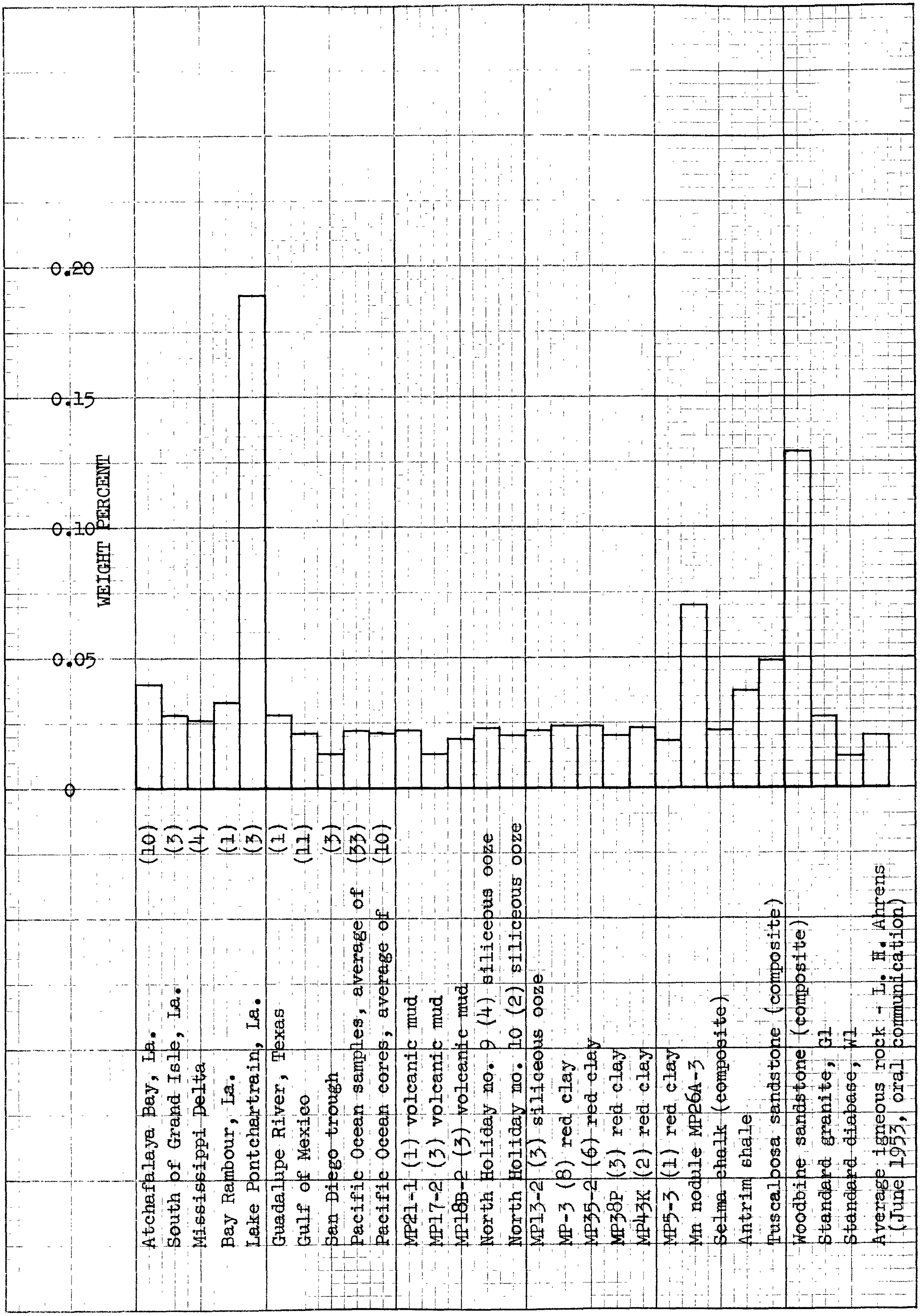

FIGURE 11.--DISTRIBUTION OF ZrO_2

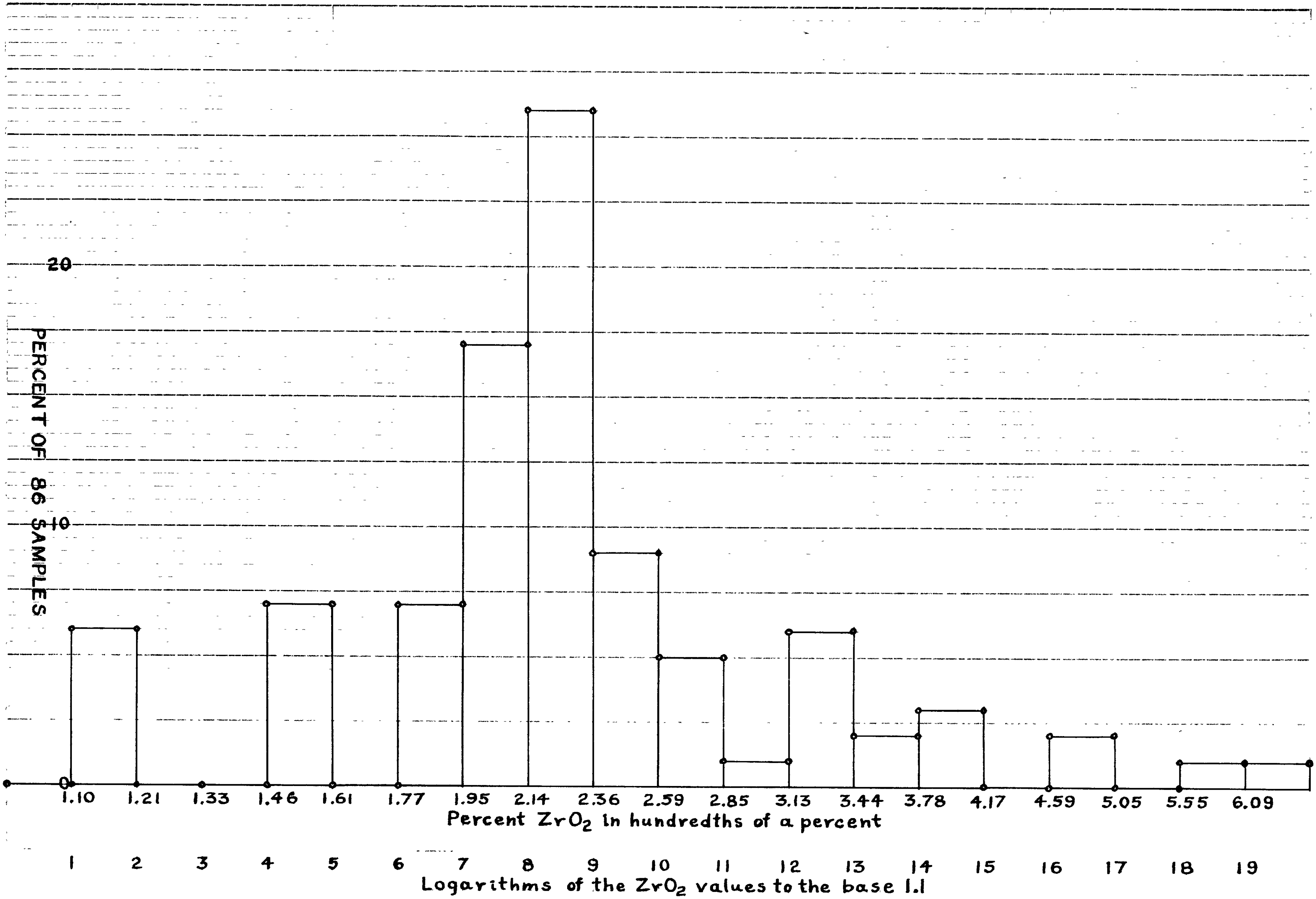

FIGURE 12 - FREQUENCY DISTRIBUTION OF ZrO_2

by Correns (1937), Neeb (1943) and others leads one to suspect that the bulk of zirconium occurs as zircon. Both titanyl and zirconyl ions may be adsorbed by suitable hosts, but with the extreme paucity of Zr and Ti in sea water it is difficult to attach any quantitative importance to this process.

$$TiO(OH)_2 \rightarrow TiO^{++} + 2(OH)^-$$
$$ZrO(OH)_2 \rightarrow ZrO^{++} + 2(OH)^-$$

Rankama and Sahama (1950) list Zr as being present in marine organisms.

The fact that zirconia contents of "red clay" and the average igneous rock are essentially the same leads to the conclusion that Zr on the sea floor is the result of terrigenous contribution by means of wind primarily and water secondarily. Since "red clay" areas are regions of slow sedimentation, even what would be modest increments of wind-blown sediments in near-shore deposits, would figure importantly on the sea bottom. Dust fogs, dust storms, and volcanic dust appear to be minor agents of deposition of sediments on land because their deposits are quickly dispersed by wind or water. Landing in the ocean, however, they are captured so to speak, and their ultimate fate is deposition on the sea floor.

5. NICKEL

Of the elements considered in this study, Ni and Co are the two most enriched in deep-sea deposits, and especially in "red clays". The average NiO content of 20 "red clay" samples is 0.033 percent, which agrees reasonably with the 0.039 percent combined NiO + CoO, which Clarke (1924, p. 518) reported for a composite of 51 samples of "red clay". It is noticeably short of the 0.056 percent NiO reported by Pettersson and Rotschi (1952) for an average of 77 samples.

Concerning the Clarke values in general, however, incongruity is evidenced since an inordinately high value of 0.063 percent for combined NiO-CoO was reported for a composite of 52 "terrigenous clays."

A selected tabulation of pertinent NiO and Co_2O_3 analyses from the literature follows.

Rock	NiO (percent)	Co_2O_3 (percent)
Sandstones, three determinations; Wells (1943)	0.0013	--
Limestones, Västergötland, Sweden; Lundegårdh (1946), quoted in Rankama and Sahama (1950, p. 685)	0.0004- 0.0013	$<$ 0.00004- 0.0003
Mississippi Delta silt, composite of 235 samples; Clarke (1924, p. 509)	0.017	--
Shales, Västergötland, Sweden; Lundegårdh (1946)	0.0191	0.0084
Volcanic and terrigenous mud, Tyrrhenian Sea; Landergren (1948a)	0.0050	0.0038

Schneiderhöhn and others (1949) found the Kulmische Alaunschiefer (alum shale or slate) and Kieselschiefer (siliceous schist ?) in Westphalia of Unterkarbon age (Mississippian) to be especially rich in Ni, containing up to 0.2 percent. A connection with Devonian diabase in the surrounding area was suspected, however.

An examination of Figure 13 reveals that the bay, gulf, and Mississippi Delta sediments contain an almost constant 0.006 percent NiO which is approximately one quarter of the NiO content of the deep-sea core average. The low average value of 0.001 percent NiO for the Lake Pontchartrain samples is attributed to their sandy character which is proven by their low L.O.I. of 2 to 3 percent, compared with the L.O.I. of 8 to 10 percent, which is usual for more clayey sediments.

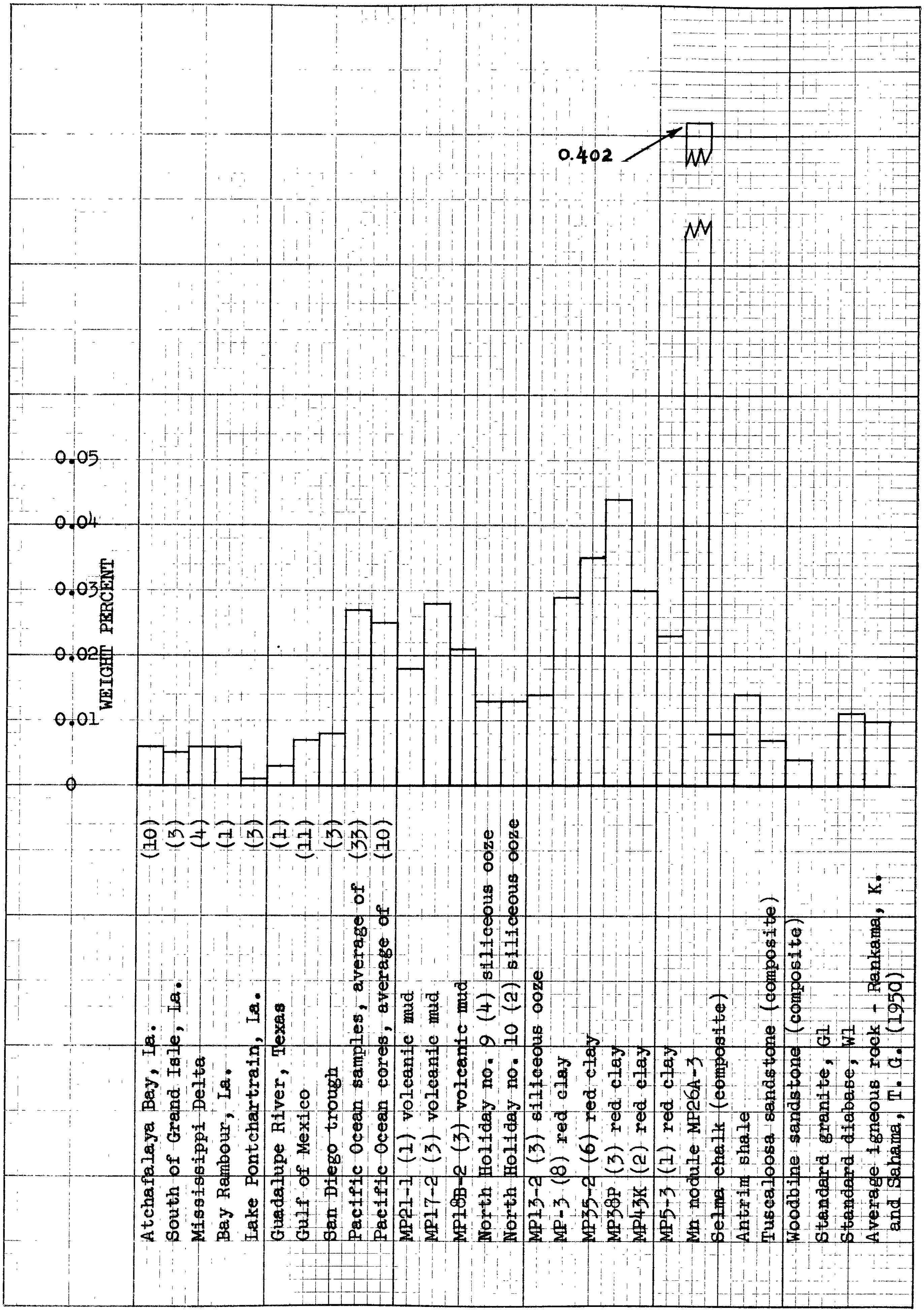

FIGURE 13.--DISTRIBUTION OF NiO

The three siliceous oozes, North Holiday cores 9 and 10, and MP13-2 contain only half as much NiO as the average deep sea core, but twice as much NiO as the near-shore sediments. It is assumed that the siliceous oozes accumulate faster than "red clays", with consequent dilution of Ni content.

The rather high content of NiO in the manganese nodule, MP26A-3, of 0.402 percent is apparently not unusual. Clarke (1924, p. 136) reported 1.96 percent NiO for a similar nodule, and Murray and Renard (1891) reported 0.40 percent NiO for a North Pacific nodule from 2740 fathoms, and 1.82 percent NiO for a South Pacific nodule from 2350 fathoms.

There seems to be much in favor of the hypothesis of nickel enrichment in deep-sea cores through the agency of cosmic contribution outlined by Pettersson and Rotschi (1952). "Red clay" MP38P exhibits large variability in Ni content. At 20 inches in the core, NiO content is 0.088 percent, and at 1 to 1 1/2 inches and at 22 inches there is 0.023 and 0.022 percent NiO, respectively. Variability in Ni content to such a large degree has been found only in the "red clays" and is easily explained by layers <u>more</u> or <u>less</u> rich in meteoritic matter. It must be noted, however, that the part of the preceding core which is richest in Ni is also richest in La_2O_3, containing 0.072 percent. This fact remains unexplained. Basaltic MP18B-2, taken close to the Island of Hawaii, contains 0.021 percent NiO which is considerably less than the average for "red clays" (0.033 percent) but twice as much as W 1. This is an illustration of the fact that proximity to a volcanic source does not insure highest nickel content for a marine sediment. In fact, if cosmic contribution is important in deep-sea deposits, one would expect to find the highest

Ni content in the slowest accumulating sediments, such as the "red clays", rather than in volcanic sediments which accumulate much faster.

Figure 14 gives the frequency distribution pattern of the NiO values. Modes at 0.003 and 0.004 percent are due to sandy sediments. The large mode at 0.007 percent represents most of the near-shore samples, whereas the one at 0.013 percent represents the siliceous deep-sea sediments. The rather large mode at ~ 0.025 percent stems from most of the deep-sea sediments.

Pettersson and Rotschi (1952) arrived at their "red clay" average of 0.056 percent NiO by means of colorimetric determinations on 77 samples. They reported a maximum reading of 0.10 percent NiO, which is not much greater than that of 0.088 percent NiO obtained in the present work. The two authors also analyzed for Fe and Mn, and found that in general there was no correlation between the three elements, with the exception of all three forming corresponding minimum values in several cores. A diagram of a radiolarian-rich core, 83B, illustrated a general correlation, however.

Four possible sources for the rather large quantities of Ni found in "red clay" were considered by Pettersson and Rotschi.

1. Terrestrial sources
2. Sea water
3. Submarine volcanic activity
4. Cosmic additions

The chief argument against terrestrial sources is that such additions are not rich enough in Ni to produce Ni-rich deposits. The average igneous rock contains only 0.010 percent NiO according to Rankama and Sahama (1950, p. 39). Sea water has only a minute quantity of Ni in it [0.0001 to 0.0005

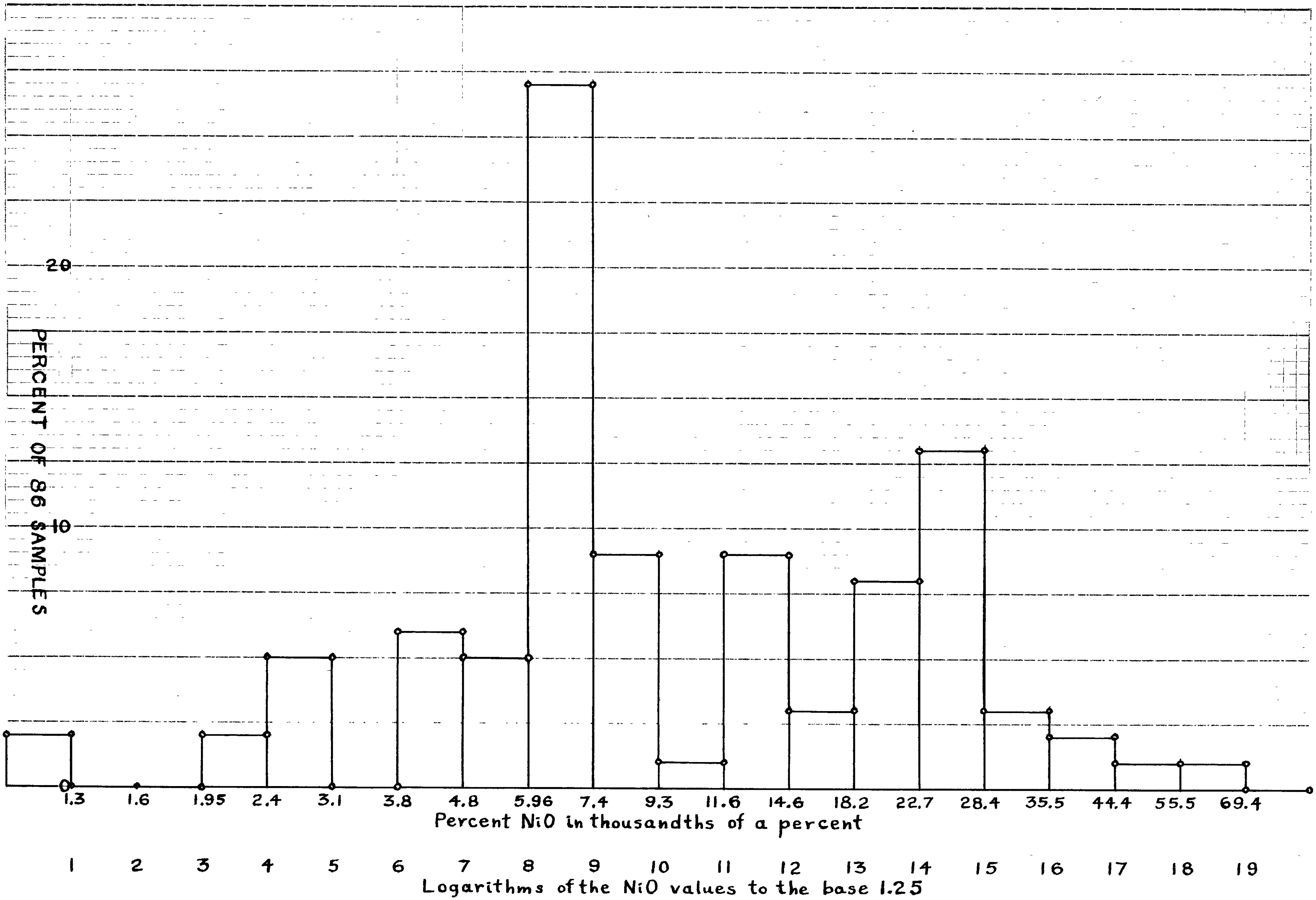

FIGURE 14 - FREQUENCY DISTRIBUTION OF NiO

g/ton or 0.00000001 to 0.00000005 percent, Rankama and Sahama (1950, p. 290)] , and although it is possible that some Ni may be adsorbed, it strains credulity to think that such enrichment should occur with so little Ni available. Submarine volcanic activity, including lava flows and ash falls, meets with the same obstacle that terrestrial sources encounter, namely, that the source rock has too low a Ni tenor. In conjunction with this idea, Dr. Landergren analyzed several submarine and supramarine basalts spectrographically, and obtained an average of 0.014 percent NiO for 10 basaltic specimens. To be sure, ultrabasic rocks would contribute a richer store of Ni, but they are not so commonly effusive as basalts.

Since Ni and Co are enriched greatly in "red clay", and since meteoritic matter is especially rich in these elements, one is led quite naturally to suppose that significant cosmic additions take place on the sea floor. V. M. Goldschmidt, quoted in Rankama and Sahama (1950, p. 678), gave the Co and Ni contents of the nickel-iron of meteorites as 0.57 and 8.49 percent, respectively.

Using calculations based on an average Ni content of 0.040 percent in their core 69, and a sedimentation rate of 0.04 mm per 1000 years (from radium analyses), Pettersson and Rotschi (1952) arrived at a total contribution of cosmic matter to the earth of 2 million tons per year, assuming a Ni content of 2 percent for cosmic dust.

Believing that their rate of sedimentation, 0.04 mm per 1000 years, or 0.004 cm per 1000 years, was entirely too slow, the writer has recalculated, using 0.1 cm per 1000 years or 1 mm per 1000 years, as the rate of sedimentation.* W. H. Twenhofel, quoted in Trask (1939, p. 410), estimated that 0.35 cm of inorganic material is deposited in abyssal sediments in 1000 years. W. Schott, in the Trask symposium (1939, p. 411), gave the smallest rate of sedimentation in "red clay" in the equatorial Atlantic Ocean as less than 0.5 cm per 1000 years.

The initial information in the paper of Pettersson and Rotschi (1952) is that an air-dried sample of "red clay" contains 0.040 percent Ni, and that the fresh sediment has a S.G. of 1.5, and contains 65 percent sea water. Therefore, 1 cc of fresh sediment weighs 1.5 g, but only approximately 1/3 of its volume consists of sediment, which weighs 0.83 g.

The calculation is as follows: Let G = the specific gravity of the sediment (dry); then $1/3\ G + 2/3 \times 1 = 1.5$, and $G = 2.5$. Therefore, 1 cc of the dry sediment weighs 2.5 g, and 1/3 cc weighs 0.83 g. When multiplied by 0.04 percent Ni, the sediment yields 332×10^{-6} g of Ni, which is contained in 1 cc. Multiplying this latter figure by the rate of sedimentation of 0.1 cm per 1000 years, yields 3.32×10^{-5} g of Ni, which is the amount accumulated on a square centimeter of bottom surface. The area of the surface of the earth is approximately 5×10^{18} cm^2, from Birch, Schairer and Spicer, quoted in Rankama and Sahama (1950, p. 798). Assuming that all of the Ni is of cosmic origin, the total accumulation to the earth in 1000 years will be $3.32 \times 10^{-5} \times 5 \times 10^{18}$ g = 1.6×10^{14} g or 1.6×10^{8} metric tons. In one year this amounts to 1.6×10^{5} tons. Following Pettersson and Rotschi (1952), by ascribing

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*Pettersson (1953) arrived at a sedimentation rate of 1 mm per 1000 years.

an average nickel content of 2 percent to cosmic dust, the total contribution of extraterrestrial matter is then $1.6 \times 10^5 \times 50 = 8{,}000{,}000$ tons per year.

This latter figure may be reduced to 3,600,000 tons per year if the starting average value of 0.026 percent Ni in "red clay" is used, which was obtained in the present work, and if terrestrial Ni on the sea floor is assumed to be 0.008 percent, which is the amount of Ni in an average igneous rock, Rankama and Sahama (1950, p. 39). The calculation is

$$\frac{0.026 - 0.008}{0.040} \times 8 \times 10^6 = 3.6 \times 10^6.$$

Although only 1,800 tons of cosmic matter are accounted for from meteor counts, according to Dr. F. Watson, quoted in Pettersson and Rotschi (1952, p. 89), the role of micrometeorites, a few microns or less, appears to be highly significant. According to Whipple (1950) (1951), micrometeorites may escape being heated to incandescence by aerial friction, and their total mass may be 10,000 times greater than that of visible meteors. Further corroboration was given by E. J. Öpik, who, in a private communication to the writers, stated that the total quantity of cosmic dust accumulated by the earth approaches the value obtained by them in their calculation.

Further evidence which suggests a cosmic origin for at least part of the Ni and Co found on the sea floor, is found in "cosmic spherules", so-called by John Murray (1891), who found them to be more numerous in the central Pacific than elsewhere. They were brought up by dredging and trawling, and although some were Fe or Ni-Fe, others were chondritic. If only the metallic ones had been found, it could be argued that they represented bits of iron blown out of a steamer smokestack. The association of the chondrites with the metallic bits, however, seems to offer convincing evidence of their cosmic origin.

The metallic "cosmic spherules" described and figured by Murray were generally smaller than 0.2 mm in diameter, usually round, had a surface entirely covered with a brilliant black coating with all the properties of magnetic iron oxide, and often had cup-like depressions clearly marked. Once broken open, they revealed white or gray metallic centers, some of which could be Cu-plated, indicating native iron, and others which could not be Cu-plated, indicating Ni and Co alloys of Fe, which hinder Cu-plating.

The chondrites were yellowish brown with a bronze-like luster, generally about 0.5 mm in diameter, and their surfaces were grooved by thin lamellae which had a "leafy radial" structure. None of them occurred as perfect spheres like the metallic ones. They contained magnetic Fe inclusions and were called bronzite, a variety of hypersthene, by Murray.

Correns (1937) reported two cosmic pellets from the equatorial Atlantic Ocean, one having a diameter of 0.38 mm, the other of 0.27 mm. One was strongly drawn to a magnet, the other weakly. Cosmic pellets were looked for by the writer, but not found. Samples were usually only a few grams or less, however.

Almost all of the NiO/Co_2O_3 ratios of the deep-sea cores, and near-shore samples fall between 2 and 4. The average of the deep-sea cores is 2.6, while the average for the near-shore cores* is 3.8, indicating more enrichment of Co with respect to Ni in the deep-sea cores

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*The near-shore cores include those from Atchafalaya Bay, La., Gulf of Mexico, the Mississippi Delta, south of Grand Isle, La., and Bay Rambour, La.

than in the near-shore cores. The manganese nodule ratio is only 1.2, illustrating its unusually high Co content with respect to Ni, while the composite of the Playa del Rey shale is 17, indicating Ni enrichment, which is no doubt due to its organic content. Southwick (1951) has shown Ni to be present in crude oil in an oil-soluble complex of the porphyrin type.

The average Cr_2O_3/NiO ratio of the "red clay" cores is 0.39, that of the near-shore cores, 1.84. Again, Ni enrichment in "red clay" is shown, in this case, with respect to Cr. Basaltic cores MP18B-2, MP17-2, and MP21-1, denote their difference from "red clay", which is essentially devoid of volcanic detritus, by their respective ratios of 3.7, 1.75, and 2.0. The manganese nodule has the very low ratio of 0.01.

6. COBALT

The value of 0.0084 for Co_2O_3 in shale from Västergötland, Sweden by Lundegårdh (1946), quoted in Rankama and Sahama (1950, p. 685), seems to be very high. The highest value for Co_2O_3 in shales in the present work is 0.0028 percent, found in the Antrim shale. Co_2O_3 content of the near-shore cores is practically constant at an average of 0.0015 percent, and the sandy samples from Lake Pontchartrain were lower at 0.0006 percent.

From Figure 15, the most striking relation shown is that the Co_2O_3 content of the deep-sea cores is, on the average, 6.5 times that of near-shore sediments. In the case of NiO, the corresponding enrichment factor was 4. Four of the "red clay" cores, MP43K, MP38P, MP35-2, and MP3, contain an average of 0.0139 percent Co_2O_3, which is 9 times

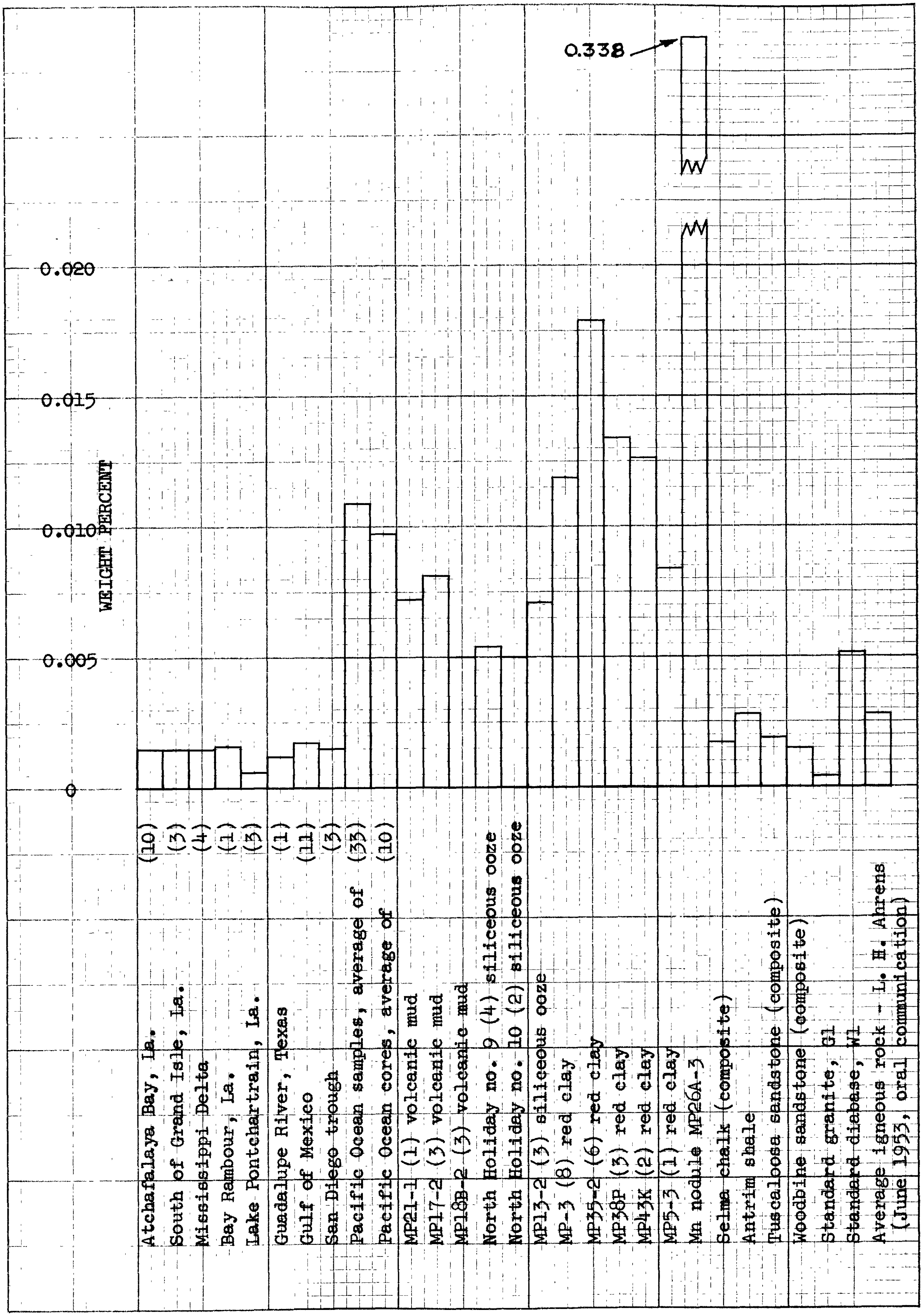

FIGURE 15.--DISTRIBUTION OF Co_2O_3

the content of Co_2O_3 of the near-shore cores. The "red clays" are even richer in Co_2O_3 than the three basaltic cores MP18B2, MP17-2, and MP21-1 by a factor of 2, and also richer, by the same factor, than the three siliceous ooze cores, North Holiday cores 9 and 10, and MP13-2, that seem to have undergone faster sedimentation which, in effect, dilutes trace element content of certain elements.

The large quantity of Co_2O_3 in the manganese nodule, 0.338 percent, is not unusual. Murray and Renard (1891) reported a nodule from the North Pacific at 2740 fathoms, as containing 0.277 percent Co_2O_3, and Clarke (1924, p. 136) reported one as containing 0.62 percent Co_2O_3.

The great enrichment of Co in "red clay" needs explanation,* for if it is assumed that cosmic contributions are the main source of Ni and Co, a moment's reflection proves that cosmic additions alone would bolster the Ni content of a deep-sea deposit more than the Co content, since both metallic and silicate meteorites contain about ten times more Ni than Co. See Rankama and Sahama (1950, p. 678). For calculation of a hypothetical case 1000 g of dispersed Ni-Fe meteorites are assumed to have fallen into a metric ton of ocean-bottom sediment. From Rankama and Sahama's data 5.7 g of the meteoritic matter will be Co, and 84.9 g will be Ni. Assuming at least an amount of Co and Ni, in the original metric ton of sediment, equivalent to the amount in a metric ton of average igneous rocks, 20 g of Co must be added to 5.7 g, and 80 g

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*The possible role of macro and micro-organisms in extracting Co and other elements from sea water and thereby concentrating these elements in sediments has been suggested by Prof. R. R. Shrock (Dec. 1953, oral communication).

of Ni must be added to 84.9 g. Thus the ocean-bottom sediment will contain 25.7 g/ton or 0.0026 percent of Co and 164.9 g/ton or 0.0165 percent of Ni.

At first glance this appears to be a very serious obstacle to the hypothesis of cosmic contribution of matter to oceanic sediments, but there is still another important consideration, namely that of co-precipitation.

The deep-sea cores exhibit, in general, strongly oxidizing conditions with Eh usually between +400 to +500 MV, and pH readings generally between 7.1 and 7.6, Bramlette (May 12, 1952, written communication). These conditions should maintain Co in the +3 valence state, for in alkaline solution $Co^{II} \rightarrow Co^{III}$ at +170 MV. See Latimer (1952). Ni will certainly be in the +2 state in this environment, for in alkaline solution $Ni^{o} \rightarrow Ni^{II}$ at -660 MV,* and possibly even in the +4 state since $Ni^{II} \rightarrow Ni^{IV}$ at +490 MV.

The amount of Co in sea water is given as 0.0001 g/ton, or 10 billionths of a percent, and that of Ni as 0.0001 to 0.0005 g/ton. See Rankama and Sahama (1950, p. 290). Notwithstanding the fact that there may be slightly more Ni than Co in sea water, evidence that $Co(OH)_3$ co-precipitates with $Fe(OH)_3$ to a greater degree than does $Ni(OH)_2$ can be demonstrated in two ways.

The first demonstration involves a typical near-shore sample, VLB43C-2c, from Atchafalaya Bay, a typical "red clay" sample, MP43K at 4 inches in the core and the manganese nodule MP26A-3, whose Fe_2O_3 content is assumed to be similar to that of the manganese nodule reported

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*Positive signs indicate oxidizing conditions; negative signs reducing.

by Clarke (1924, p. 136), which contained 31.76 percent. With the standards available, MP26A-3 was estimated to contain more than 20 percent Fe_2O_3.

$$\frac{Co_2O_3}{Fe_2O_3} \text{ in the manganese nodule} = \frac{0.338}{31.76} = 0.0107$$

$$\frac{Co_2O_3}{Fe_2O_3} \text{ in VLB43C-2c} = \frac{0.0016}{5} = 0.00032$$

$$\frac{NiO}{Fe_2O_3} \text{ in the manganese nodule} = \frac{0.402}{31.76} = 0.013$$

$$\frac{NiO}{Fe_2O_3} \text{ in VLB43C-2c} = \frac{0.009}{5} = 0.0018$$

$$\frac{Co_2O_3}{Fe_2O_3} \text{ in MP43K at 4 inches in core} = \frac{0.0122}{9} = 0.00135$$

$$\frac{NiO}{Fe_2O_3} \text{ in MP43K at 4 inches in core} = \frac{0.028}{9} = 0.0031$$

Thus the Co_2O_3/Fe_2O_3 ratio in the manganese nodule is 33 times as great as the same ratio in the typical near-shore sediment, whereas the NiO/Fe_2O_3 ratio in the manganese nodule is only 7.2 times as great as the same ratio in the typical near-shore sediment. Similarly, the Co_2O_3/Fe_2O_3 ratio in the typical "red clay" is 4.2 times as great as the same ratio in the near-shore sediment, whereas the NiO/Fe_2O_3 ratio in the "red clay" is only 1.7 times as great as the same ratio in the near-shore sediment. In other words, Co shows more enrichment with respect to Fe in manganese nodules and red clay than does Ni.

Further evidence that $Co(OH)_3$ co-precipitates with $Fe(OH)_3$ to a greater degree than does $Ni(OH)_2$ can be seen in the results of Landergren (1948), quoted in Rankama and Sahama (1950, p. 685), who found more Co than Ni or an equal amount, in sedimentary iron ores and in a residual ore.

Rock	Co (percent)	Ni (percent)
Laterite - bauxite ore	0.0300	0.0180
Bog iron ores, Finland	0.0130	0.0040
Marine oolite-siliceous iron ores	0.0200	0.0200

The Co_2O_3/Sc_2O_3 ratio appears to be useful in distinguishing deep-sea deposits, and especially "red clays" from near-shore deposits. All of the deep-sea cores have ratios of 1 or greater, while the near-shore cores are usually less than 1. A few average ratios are given.

Sample	Co_2O_3/Sc_2O_3
Deep-sea cores, average	2.1
5 "red clay" cores, average	3.0
Near-shore cores, average	0.82
Manganese nodule	242.

Figure 16 records the frequency distribution pattern of the Co_2O_3 values. The small mode at 0.0005 percent is caused by the sandy near-shore samples, and the largest mode at approximately 0.0015 percent is the result of most of the near-shore samples. The mode at approximately 0.0055 percent represents the siliceous oozes and the volcanic sediments, and the broad mode from $\sim$ 0.0084 to $\sim$ 0.0094 percent represents most of the deep-sea samples. The small mode at $\sim$ 0.0250 percent stems from a few "red clay" samples unusually rich in Co.

7. VANADIUM

Vanadium is not especially enriched in the hydrolyzates (shales), including the "red clays", which contain approximately the same amount of

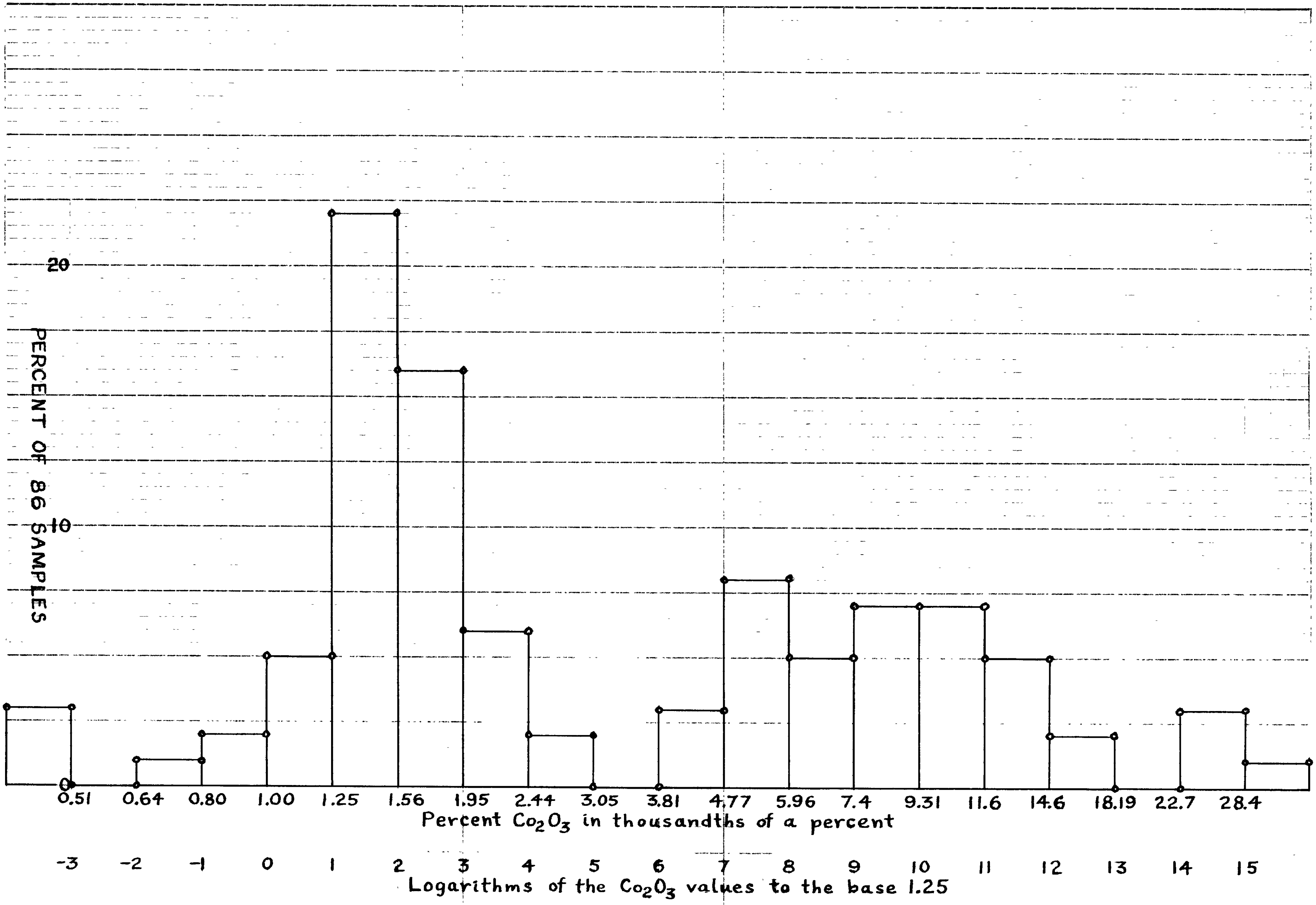

FIGURE 16 - FREQUENCY DISTRIBUTION OF Co_2O_3

V as the average igneous rock. The selected listing below indicates V to be especially enriched in oxidates, such as sedimentary iron ores and also in bioliths.

Rock	V_2O_5 (percent)
Sandstones, average, Jost (1932)	0.0036
Calcitic and dolomitic limestones, average, Jost (1932)	$<$ 0.0018
Clays and shales, average, Jost (1932)	0.0214
Volcanic and terrigenous mud, Tyrrhenian Sea, Landergren (1948a)	0.024
Bauxite, average, Jost (1932)	0.107
Oolitic and siliceous iron ores, average, Landergren (1948), quoted in Rankama and Sahama (1950, p. 601)	0.0892
Asphalt, average, Bader (1937)	0.962
Coal, average, Bader (1937)	0.161
Average igneous rock, Ahrens (June 1953, oral communication)	0.0214

The average quantity of V_2O_5 in "red clays" and in the average of the deep-sea samples, excluding basaltic MP18B-2 and the calcareous oozes, is 0.026 percent from the present work, which is less than the 0.042 percent V_2O_5 reported by Clarke (1924) in a composite of 51 "red clays".

Schneiderhöhn and others (1949) reported rather large quantities of V from Upper Silurian alum shales (Alaunschiefer) and siliceous shales (Kieselschiefer) in Thüringen and Saxony. Their average value for V in these rocks was 0.090 percent, and maximum values went up to 0.7 percent V. On weathered surfaces some of these rocks appeared bleached and rusty, but in general these did not show higher trace metal content than fresh types. These shales have been classified by Schneiderhöhn and his co-workers as Vollfaulschlammgesteinen (muds deposited under anaerobic conditions) of the Black Sea facies on the basis of petrographic and paleontologic criteria. Under such an H_2S-rich environment a steady metal precipitation is effected, giving rise to especially high contents of V and Mo.

Reference to Figure 17 shows the general even distribution of V in the sediments analyzed. The samples from Lake Pontchartrain and the Guadalupe River are relatively poor in V, since they are sandier than the other near-shore sediments. The composite of the Playa del Rey shale contains 0.043 percent V_2O_5, which is approximately twice as much as the average of the other shales. This rather high value is due to its organic content, but since it contains 20 to 30 percent CaO, the intensity of the V spectral lines has been enhanced somewhat. See Chapter 1, Section 8.

Cores MP18B-2, MP21-1 and MP17-2 contain more V than the average deep-sea sample, which is a reflection of their basaltic constituents, which have a higher V content than acid rocks. The manganese nodule contains 0.093 percent V_2O_5. Clarke (1924, p. 136) has reported a similar nodule as containing 0.14 percent V_2O_5.

Figure 18 exhibits the almost lognormal pattern of the V_2O_5 frequency distribution histogram. Small modes at 0.007 percent and approximately 0.017 percent V_2O_5 are due to the sandier sediments, and the tailing out to 0.070 percent V_2O_5 is due to the deep-sea basaltic sediments.

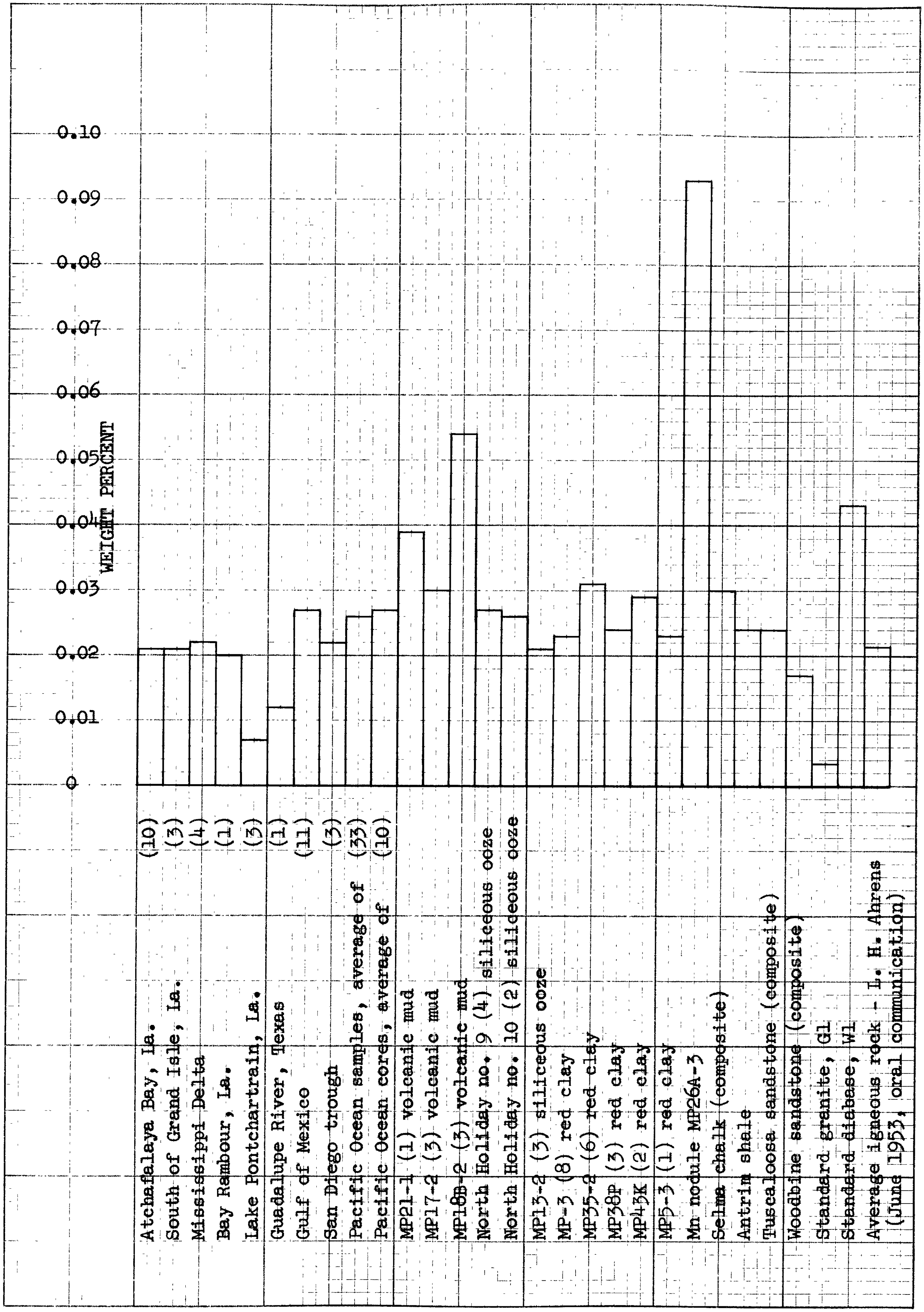

FIGURE 17.--DISTRIBUTION OF V_2O_5

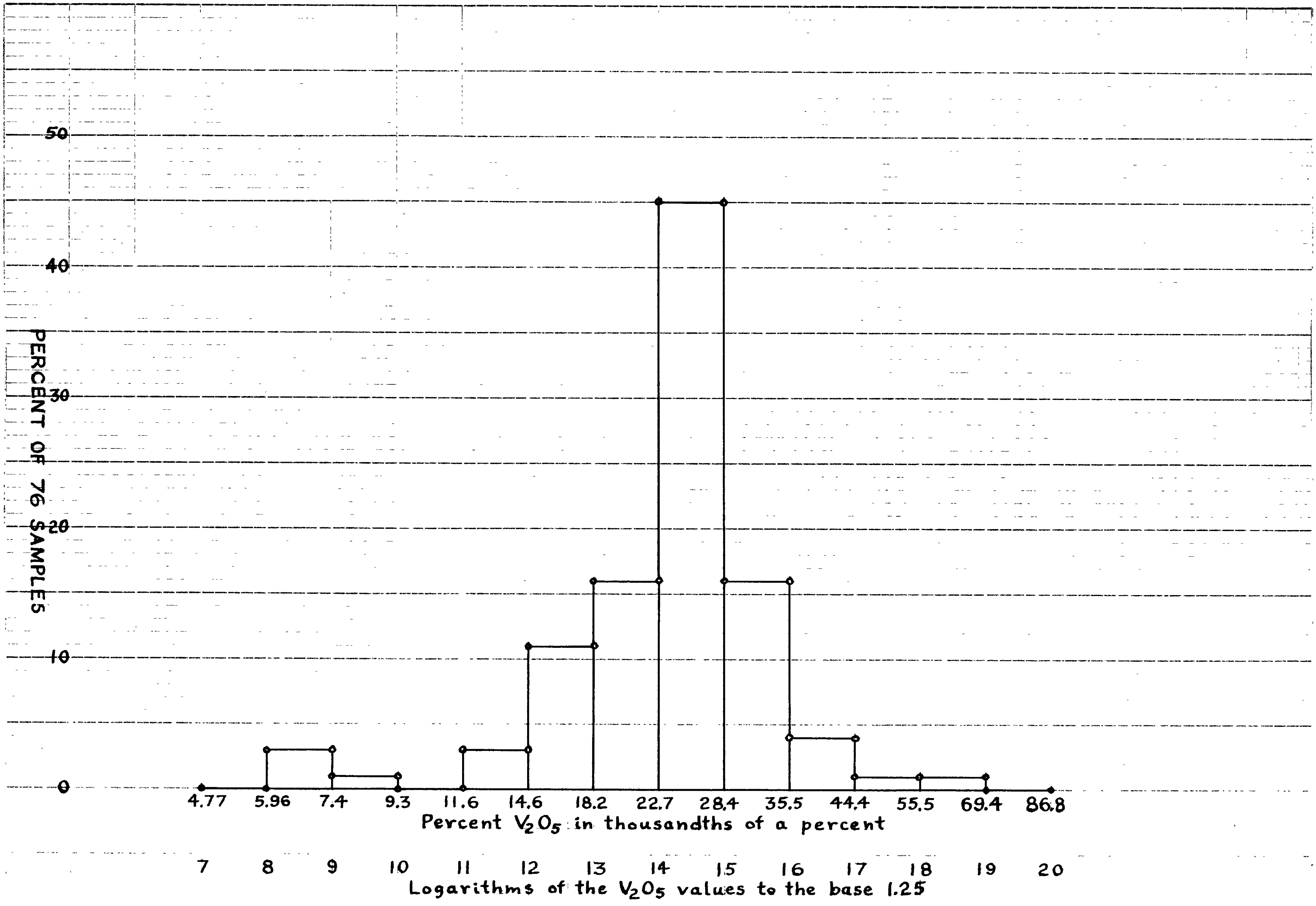

FIGURE 18 - FREQUENCY DISTRIBUTION OF V_2O_5

A list of various ratios is given to illustrate differences among the types of sediments analyzed.

Sample	V_2O_5/NiO	V_2O_5/Co_2O_3	V_2O_5/Cr_2O_3	V_2O_5/Sc_2O_3
Deep-sea cores, average	1.1	2.8	1.4	5.9
5 "red clay" cores, average	0.84	2.1	2.1	6.0
Near-shore cores, average	3.7	14.3	2.0	11.6
Basaltic MP18B-2	2.6	10.8	0.71	10.8
Manganese nodule MP26A-3	0.23	0.28	23.0	66.0

Of the preceding ratios V_2O_5/Cr_2O_3 shows the "red clays" and near-shore samples to be practically the same with respect to these two elements. On the other hand, the V_2O_5/NiO, V_2O_5/Co_2O_3 and V_2O_5/Sc_2O_3 ratios reflect the enrichment of Ni and Co, and to a lesser extent, Sc in the "red clays". Basaltic MP18B-2, because of its high Cr content, differs in the V_2O_5/Cr_2O_3 ratio from both near-shore and deep-sea sediments. In the other ratios, it resembles near-shore sediments.

Apparently vanadium's role in sediments is more complicated than the roles of the other elements studied. Thus Assarsson (1941) stated that vanadium content in Swedish alum shales is not proportional to the content of organic matter, as opposed to Jost's (1932) findings, which showed that vanadium content in bituminous sediments increases with bitumen content. Assarsson suggested that vanadium was probably combined with sulfur. But Bøgvad and Nielson (1945) found sulfides in alum shales totally devoid of V, besides finding no relation between V content of alum shales and their organic matter content. Bader (1937) attributed V-rich bioliths to the precipitation of V derived from weathering solutions as V_2S_5, and the subsequent formation of organic V complexes, particularly porphyrin complexes. Both V and Ni were shown to be present in an oil-soluble complex of the porphyrin type in crude oil by Southwick (1951).

The V content of sea water is 0.0003 g/ton or 30 billionths of a percent according to Rankama and Sahama (1950, p. 290). Vanadium should be present in sea water as VO_3^-, the vanadate anion, since $V^0 \rightarrow V^{+5}$ in alkaline solution at -1150MV (reducing environment) according to Latimer (1952). Being present in sea water as an anion VO_3^- would not be expected to be adsorbed by clays or zeolites nor to be co-precipitated with $Fe(OH)_3$.

In conclusion, since the V content of deep-sea cores is practically the same as that of the average igneous rock, it is thought that its content in deep-sea deposits originates from terrigenous sources in much the same way as that of Ti and Zr.

8. SCANDIUM

Little is known about the distribution of Sc in sediments. In fact, the work of Goldschmidt and Peters (1931) is the only one known by the writer to contain a quantitative analysis for Sc in sediments. Unfortunately, the values reported in that work seem to be too low. For example, samples of "red clay" from Challenger Expedition stations 244, 286, and 353, were listed as containing 0.0005, 0.0005, and 0.0010 percent Sc_2O_3, respectively, whereas the average of the deep-sea samples (most of which were "red clays") obtained in this investigation is 0.0045 percent Sc_2O_3.

That something is amiss in the values obtained by Goldschmidt and Peters (1931) is suggested by the fact that they also listed radiolarian ooze and globigerina ooze from Challenger Expedition stations 157 and 332, respectively, as containing 0.0005 percent Sc_2O_3. Since Sc was an element apparently little if at all affected by a rich $CaCO_3$ matrix (See Chapter 1, Section 8), it is justifiable to compare the Sc values for globigerina oozes obtained in the present investigation with those of Goldschmidt and Peters (1931). They are samples MP33H, MP25E-1 and MP40-1, of which the first two contain 0.0005 percent Sc_2O_3, and the third an immeasurably small amount. Thus a real difference (factor of 9 or greater) is reported herein between "red clay" and globigerina ooze in regard to Sc content, as would be expected due to the different mineralogy of the two types of sediments.

It might also be noted that Goldschmidt (1934, 1937) reported 0.003 percent Sc_2O_3 in gabbros, and Sahama (1945) reported 0.003 percent Sc_2O_3 in gabbros and dolerites from southern Lapland, as quoted in Rankama and Sahama (1950, p. 516), whereas the standard diabase, W 1, has a recommended value of 0.0057 percent Sc_2O_3, Ahrens (June 1953, oral communication). Similarly, the recommended Sc_2O_3 value for the standard granite, G 1, is 0.0005 percent, as compared with values of 0.0002 and 0.0001 percent for granites, also reported by Goldschmidt and Sahama, respectively. It is not known how G 1 and W 1 compare in minor element content with the gabbros and granites analyzed by Goldschmidt and Sahama, but indications are that the values of Goldschmidt and Sahama are too low.

From Figure 19 it is seen that the deep-sea samples, which are mainly "red clays", contain approximately 2 1/2 times as much Sc_2O_3 as the

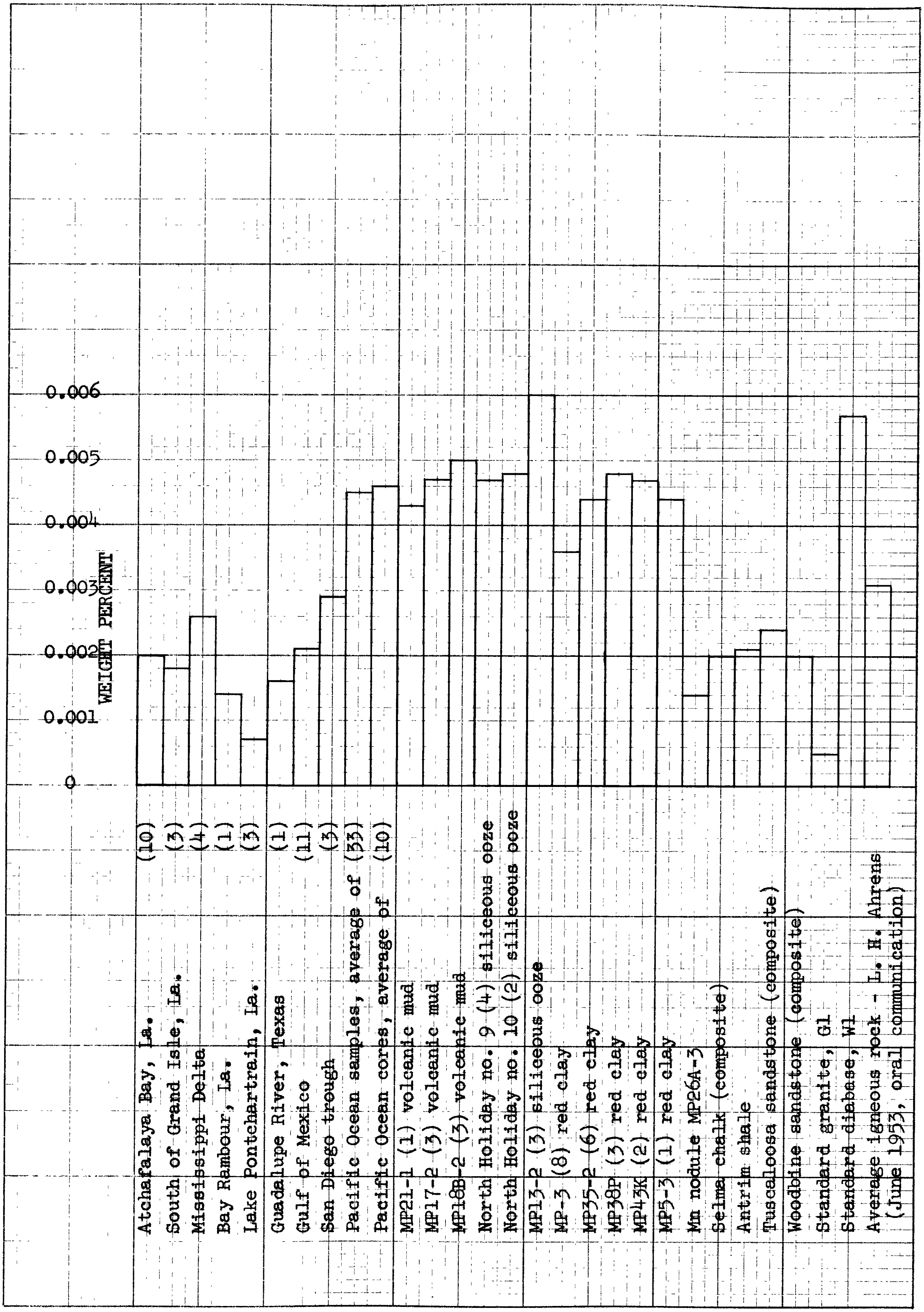

FIGURE 19.--DISTRIBUTION OF Sc_2O_3

average of the near-shore sediments, which is 0.002 percent. The average of the deep-sea samples is 0.0045 percent. The Lake Pontchartrain samples are decidedly lower with 0.0007 percent Sc_2O_3, which is a reflection of their sandy character. The geologically older shaly sandstones and sandy shales like the Antrim shale and the Tuscaloosa sandstone also conform to the average scandia content of 0.002 percent for near-shore recent sediments. All of the deep-sea cores are rather constant in their scandia content, except MP13-2, which averages 0.006 percent, and MP-3 which averages 0.0036 percent. The highest value for Sc_2O_3 in the deep-sea samples is 0.0074 percent, found in MP38P at 20 inches from the top of the core, and the lowest value is 0.003 percent, found in MP3 at 66.5 to 69 inches from the top of the core. As mentioned before, the scandia content of globigerina oozes can become too small to be measurable. Scandia does not show any appreciable enrichment in the Gulf of Mexico sediments compared to the other near-shore sediments, and further shows the diluting effect of globigerina ooze on scandia content. Manganese nodule MP26A-3 contains a rather small amount of scandia, 0.0014 percent. Goldschmidt and Peters (1931) listed a manganese nodule as containing 0.0005 percent scandia, but as mentioned before their values are too low. The fact that the sediments from the Mississippi Delta and the San Diego trough contain somewhat more scandia than the average of the near-shore sediments seems to imply a rather rich content of ferromagnesian minerals, like biotite and hornblende, in those sediments. This was verified from microscopic work.

Figure 20 shows the frequency distribution histogram of the samples. Small modes at 0.0005 and 0.0007 percent Sc_2O_3 are due to sandy sediments and globigerina oozes. The large mode at approximately

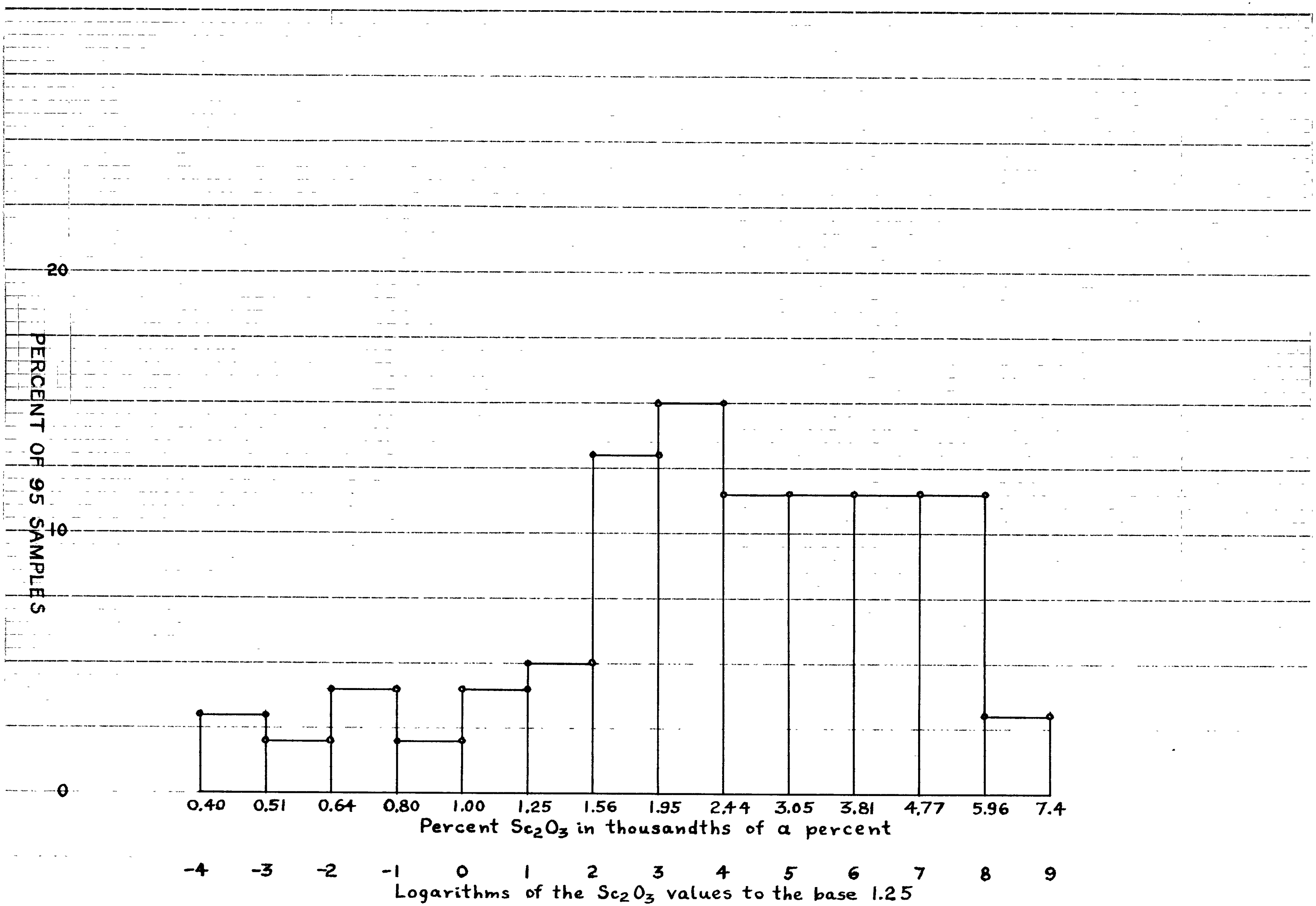

FIGURE 20 - FREQUENCY DISTRIBUTION OF Sc_2O_3

0.0022 percent scandia represents most of the near-shore sediments. It merges into the higher values of 0.0030 to 0.0059 percent scandia, which are found mostly in the deep-sea sediments.

Scandium with an ionic radius of 0.81 A for its +3 state is a common follower of Fe^{+2} (ionic radius 0.74 A) in biotite, hornblende, augite, etc., despite the charge difference in the two elements. Since the ferromagnesian content of W 1 is much larger than the ferromagnesian content of G 1, W 1 is much richer in scandia than G 1. This is borne out quantitatively as follows. Pyroxene, biotite, and opaque accessories are the minerals in which practically all of the scandium is found in W 1, and total 50.1 percent. Biotite and opaque accessories are the minerals in which practically all the scandium is found in G 1, and total 4 percent. See Fairbairn and others (1951, p. 61). G 1 contains 0.00029 percent Sc, and W 1 0.0037 percent Sc; recommended values, Ahrens (June 1953, oral communication). Thus W 1 contains $50.1/4 = 12.5$ times as many scandium host minerals as G 1, and W 1 contains $\frac{0.0037}{0.00029} = 12.8$ times as much scandium as G 1. The similarity of the factors, 12.5 and 12.8, testify to the correctness of the assumption that practically all the Sc is found in the minerals listed above in G 1 and W 1.

There is only a very minute amount of Sc in sea water. Rankama and Sahama (1950, p. 290) listed 0.00004 g/ton or 4 billionths of a percent of Sc in sea water. Table 9 shows the relative enrichment of Group III elements in shales.

Table 9

Data taken from Rankama and Sahama (1950), unless otherwise noted

Element A	Percentage in sea water B	Percentage in shales C	Percentage in igneous rocks D	$\frac{C}{B}$	$\frac{C}{D}$
Al	16 to 190 x 10^{-6}	8.19	8.13	43,100-512,000	1.01
Sc	4 x 10^{-9}	0.0013, near-shore clayey sediments, present work	0.002, Ahrens (June 1953, oral communication)	325,000	0.65
Y	3 x 10^{-8}	0.0028	0.0035, Ahrens (June 1953, oral communication)	93,000	0.8
La	3 x 10^{-8}	0.0094 near-shore clayey sediments, present work	0.0045, Ahrens (June 1953, oral communication)	283,333	2.09

In general, enrichment seems to increase with increasing atomic weight, especially in the ratio of percentage in shales to percentage in igneous rocks. The ratio of percentage in shales to percentage in sea water is probably not too meaningful because of insolubility effects. If three elements of the sixth Period, Cs, Ba, and La, are compared as regards their enrichment in shales, their respective ratios of percentage in shales to percentage in igneous rocks are 1.5, 1.34 and 2.09. From this it appears that La is enriched in shales more than Cs and Ba.

Goldschmidt and Peters (1931) reported 0.0100 percent Sc_2O_3 in limonitic iron ore from Würtemberg and, therefore, claimed that Sc is enriched in oxidates rather than hydrolysates. It is their idea that during the weathering cycle, Sc, which as a base is brought into solution more easily than $Al(OH)_3$, is co-precipitated with $Fe(OH)_3$, and correspondingly enriched in sedimentary iron ores.

In conclusion, if Sc content of deep-sea cores was entirely the result of terrigenous contributions, it should approximate that of the average igneous rock. But from Figure 19, deep-sea cores contain approximately 1 1/2 times as much scandia as the average igneous rock. It is thought that co-precipitation or possibly cation exchange are the causes of the enriched scandia content of deep-sea cores.

9 CHROMIUM

The geochemistry of chromium in igneous rocks resembles that of iron, although in the case of chromium, differences are much more pronounced between acid and basic rocks. Thus Goldschmidt (1937) gave the following average values for Cr in igneous rocks as quoted in Rankama and Sahama (1950, p. 621).

Rock	Percentage Cr
Peridotite (dunite)	0.34
Gabbro	0.034
Diorite	0.0068
Granite	0.0002

North American granites contain 0.004 percent Cr, according to Ahrens (June 1953, oral communication). Thus Goldschmidt's peridotite value is 85 times greater than Ahrens' granite value, or 1700 times greater than his own granite value, while a dunite or gabbro usually contains only 2 to 4 times as much Fe as a granite.

Some selected values of Cr_2O_3 in sediments from the literature are listed below.

	Sample	Source	Percentage Cr_2O_3
1.	1 oceanic "red clay", (Challenger Expedition)	Hevesy, Merkel, Würstlin (1934)	0.092
2.	"Red clay", composite of 51 samples	Clarke (1924)	0.012
3.	"Terrigenous clays", composite of 52 samples	Clarke (1924)	0.050
4.	Volcanic and terrigenous muds, Tyrrhenian Sea	Landergren (1948a)	0.0056
5.	300 slates and phyllites, Germany	Hevesy, Merkel, Würstlin (1934)	0.053
6.	Aluminum-rich schists, southern Lapland	Sahama (1945), quoted in Rankama and Sahama (1950, p. 623)	0.060 - 0.099
7.	Upper Silurian alum shales, Germany	Schneiderhöhn and others (1949)	0.007
8.	Phyllites, Stavanger area, Norway	O. Røer in Goldschmidt (1937), quoted in Rankama and Sahama (1950, p. 623)	0.020
9.	Oolitic siliceous marine iron ores	Landergren (1948), quoted in Rankama and Sahama (1950, p. 623)	0.035
10.	Limestone, average, Schwäbischen Schwarzjura	Schneiderhöhn and others (1949)	~0.0015

For comparison, average values of Cr_2O_3 found in the present work are listed.

	Percentage Cr_2O_3
Recent near-shore sediments	0.011
Average of eight predominantly shaly sediments from Devonian to Miocene formations; sequence Nos. 20 to 27	0.012

	Percentage Cr_2O_3
Average for all deep-sea cores, except MP18B-2, MP17-2, MP21-1, and calcareous oozes	0.014
MP18B-2, volcanic mud	0.077
MP17-2, volcanic mud	0.049
MP21-1, volcanic mud	0.036

Concerning shale and shale derivitives, the slates and phyllites of Hevesy, Merkel and Würstlin (1934), and the aluminum-rich schists of Sahama (1945) seem to be extraordinarily rich in Cr. On the other hand, the alum shale of Schneiderhöhn and others (1949), the phyllites of O. Røer, given in Goldschmidt (1937), and the recent near-shore sediments and other shale and shale-like sediments from the present work approximate each other, and are close to 0.0146 percent Cr_2O_3 given by Ahrens (June 1953, oral communication) for North American igneous rocks.

The "red clays" analyzed herein are also practically identical with the latter igneous rock value, and Clarke's figure for the "red clay" composite is also strikingly close, but the high value reported for terrigenous clay is suspect. Hevesy, Merkel, and Würstlin (1934) cited 0.092 percent Cr_2O_3 for an oceanic "red clay". It seems that error is present in their analyses, however, because they also reported approximately the same value for 94 granites, and especially because the average value of Cr in 23 ultrabasic rocks was reported as being only twice the value for the granites, which is completely invalid.

Were it not for the apparent mentioned error, it is conceivable that an oceanic sediment could contain that much Cr, but them it would erroneously be called a "red clay". Such oceanic sediments were analyzed in this work, and are the samples from cores MP18B-2, MP17-2, and MP21-1. Figure 21 shows how markedly they differ from the rest of the deep-sea sediments with regard to Cr. Core MP18B-2 is unquestionably basaltic in character, and cores MP17-2 and MP21-1 are less so. See Chapter 4.

Figure 22 gives the frequency distribution histogram for Cr_2O_3. Asymmetry on the low value side of the histogram is due to the sandy nature of some of the sediments. However, the small mode at 0.004 percent Cr_2O_3 is due to three samples from "red clay" core MP-3. Modes at 0.035 and 0.084 percent Cr_2O_3 are due to the basaltic deep-sea sediments.

Pacific basin basalts are obviously richer in chromium than terrestrial basalts, for core MP18B-2, which contains some fossil shells and some terrigenous material as diluents, still contains 2.4 times as much Cr_2O_3 as the average North American basalt, which contains 0.034 percent Cr_2O_3 according to Ahrens, (June 1953, oral communication).

The longest core, MP3, shows enrichment in Cr with depth in core. From 0.004 percent Cr_2O_3 at the surface, the Cr content increases 4 1/2 times to 0.018 percent Cr_2O_3 at 293-297 inches in the core. This could be an indication of more basaltic material at depth, but 0.018 percent Cr_2O_3 is only slightly larger than the average "red clay" content.

There is very little Cr in limestones as can be seen from the analysis of Schneiderhöhn, mentioned earlier, and from the immeasurable quantities in the globigerina oozes MP40-1 and MP25E-1. The 0.014

NOTE: The averages for Pacific Ocean cores and samples do not include the volcanic muds.

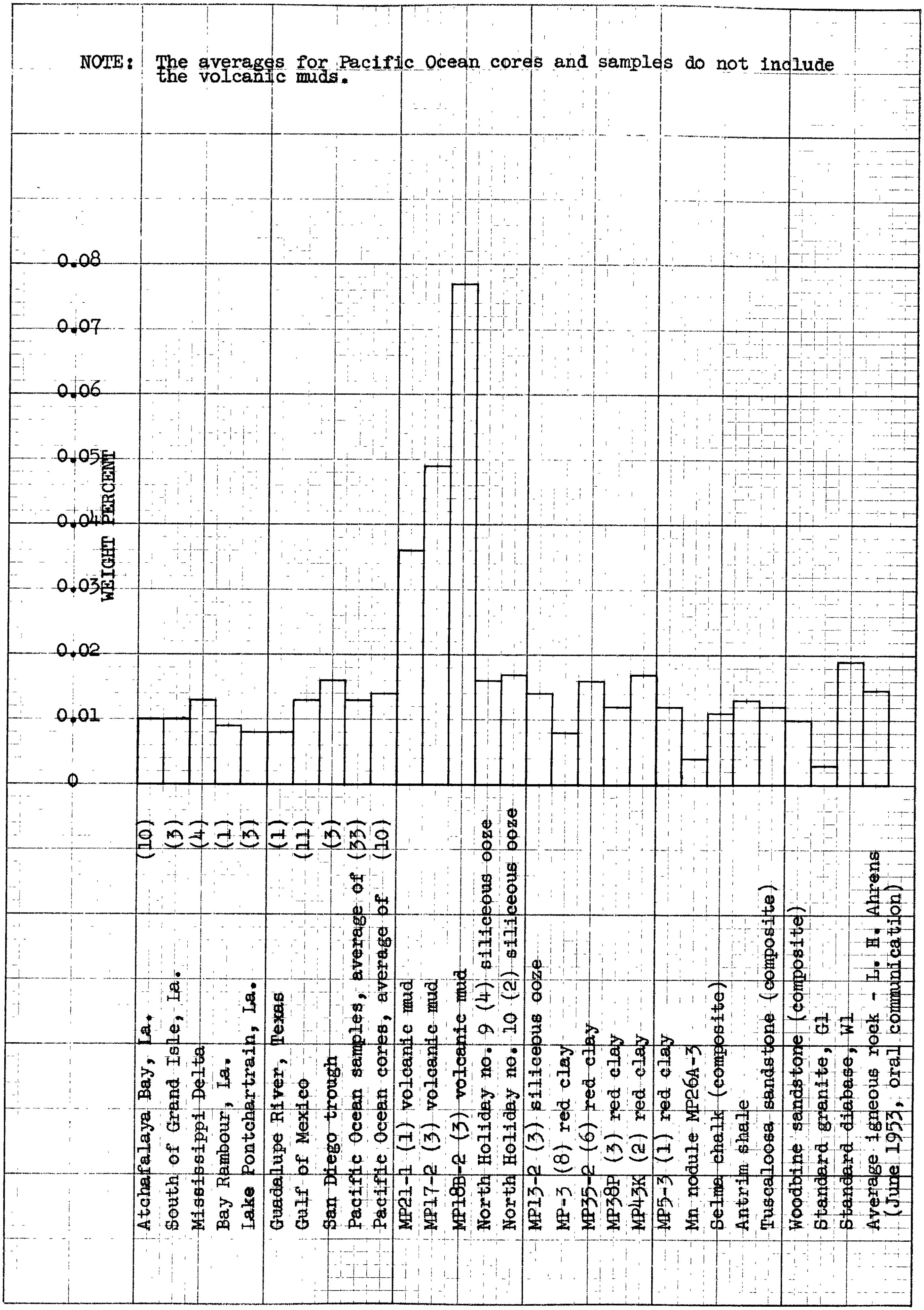

FIGURE 21.--DISTRIBUTION OF Cr_2O_3

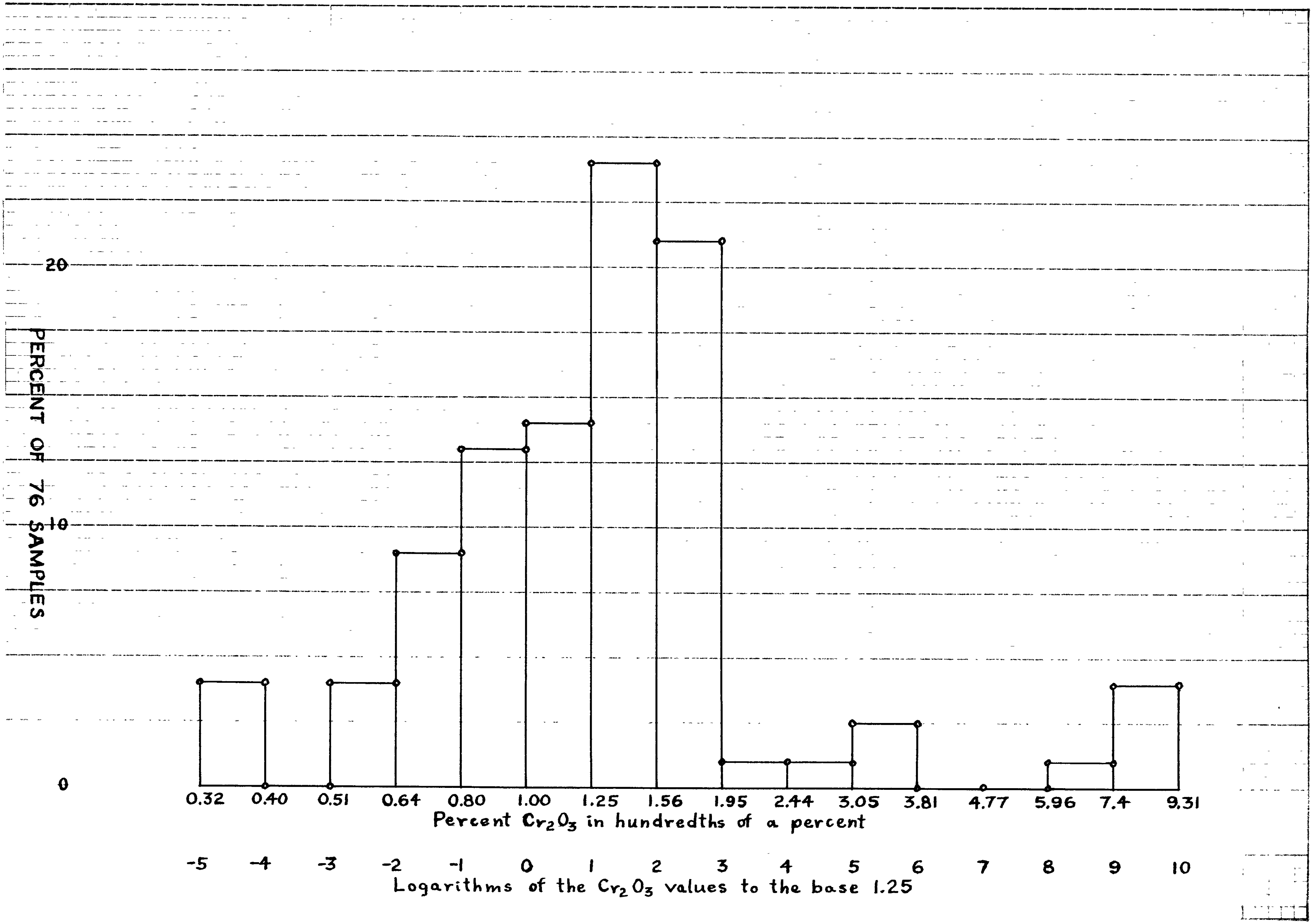

FIGURE 22 - FREQUENCY DISTRIBUTION OF Cr_2O_3

percent Cr_2O_3 reported for MP33H and the Cr analyses of the Gulf of Mexico globigerina oozes are all too high because of matrix conditions. See Chapter 1, Section 8. The manganese nodule, which contained only 0.004 percent Cr_2O_3 suggests that manganese nodules have no genetic connection with submarine basalts, which are relatively Cr-rich.

The ratio Cr_2O_3/Co_2O_3 is useful in emphasizing differences among sediments. For near-shore sediments the average ratio is 7.1, and for 5 "red clay" cores it is 1.04.

In conclusion, the fact that the average value for Cr_2O_3 in "red clays" approximates that of the average igneous rock seems to be good evidence that Cr in "red clays" originates from terrigenous sources. Chromium has not been detected in sea water although it is present in marine organisms. Rankama and Sahama (1950, p. 291). Practically Cr-free sea water prohibits enrichment of Cr in deep-sea sediments by means of cation exchange or co-precipitation. Probably one of the most important conclusions one can draw from relatively Cr-poor "red clay", is that "red clay" cannot result from the submarine weathering of volcanic rocks, as thought by Murray and Renard (1891), since submarine volcanic rocks are relatively Cr-rich.

10. LANTHANUM

Lanthanum is one of the most abundant rare earths, and is part of the cerium-earth subgroup of the rare earths, which forms the strongest bases, viz., La, Ce, Pr, Nd, (Pm), Sm, and Eu. The yttrium-earth subgroup contains the remainder of the rare earths, viz., Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y.

A selected list of lanthana analyses for igneous rocks from the literature follows.

Rock	Source	Percentage La_2O_3
Standard granite (G 1)	Ahrens (June 1953, oral communication)	0.0235
Granite	Goldschmidt (1937), quoted in Rankama and Sahama (1950, p. 528)	0.0051
Granites, southern Lapland	Calculated from Sahama (1945) by Rankama and Sahama (1950, p. 528)	0.0070
North American granites	Ahrens (June 1953, oral communication)	0.0074
Standard diabase (W 1)	Ahrens (June 1953, oral communication)	0.00375
Gabbro	Goldschmidt (1937), quoted in Rankama and Sahama (1950, p. 528)	0.0011
North American diabase	Ahrens (June 1953, oral communication)	0.00176
North American igneous rocks	Ahrens (June 1953, oral communication)	0.0053
Igneous rocks	Rankama and Sahama (1950, p. 39)	0.0021
Igneous rocks, Dutch East Indies	Van Tongern (1938), quoted in Rankama and Sahama (1950, p. 510)	0.00196

From the preceding list, G 1 and W 1 contain 3 to 4 times as much lanthana as other granites and diabase. This is significant because the values for lanthana obtained in the present work are based on G 1 and W 1 values.

Very little is known about the distribution of La in sediments. In fact, the only data found by the writer are those of Minami (1935), who gave the following percentages of La_2O_3 in a group of composite shales, determined by the method of chemical enrichment and X-ray spectrography. See Hevesy (1932).

	Percentage La_2O_3
Composite of European Paleozoic shales	0.0019
Composite of Japanese Paleozoic shales	0.0026
Composite of Japanese Mesozoic shales	0.0019

The average of the three composite shales is 0.0021 percent La_2O_3. From the present work the average of a Devonian shale, two Cretaceous shales, two Cretaceous shaly sandstones, and a Miocene shale is 0.013 percent La_2O_3. The average of the near-shore clayey sediments is 0.011 percent La_2O_3. Thus the value for lanthana in shales, arrived at in this work is 5 or 6 times greater than that found by Minami (1935).

The lanthanum cation owing to its comparatively large size of 1.14 A and +3 charge tends to become enriched in late crystallized products of differentiation, i.e., in granites and pegmatites, or acid rocks in general, occurring in such minerals as bastnaesite and monazite, and in lesser amounts, as a follower of Ca in apatite and sphene.

Regarding Figure 23, the uneven distribution of La_2O_3 in the deep-sea cores is noticed at once, as opposed to the similarity in scandia content of the same cores. The values range from a low of 0.005 percent La_2O_3 in basaltic MP18B-2 to a high of 0.038 percent La_2O_3 in MP38P, although the manganese nodule is even richer in lanthana, containing 0.057 percent. The highest lanthana value is 0.072 percent, found in core MP38P at 20 inches in the core. This, oddly enough, is also the sample with the highest NiO content, 0.088 percent. The San

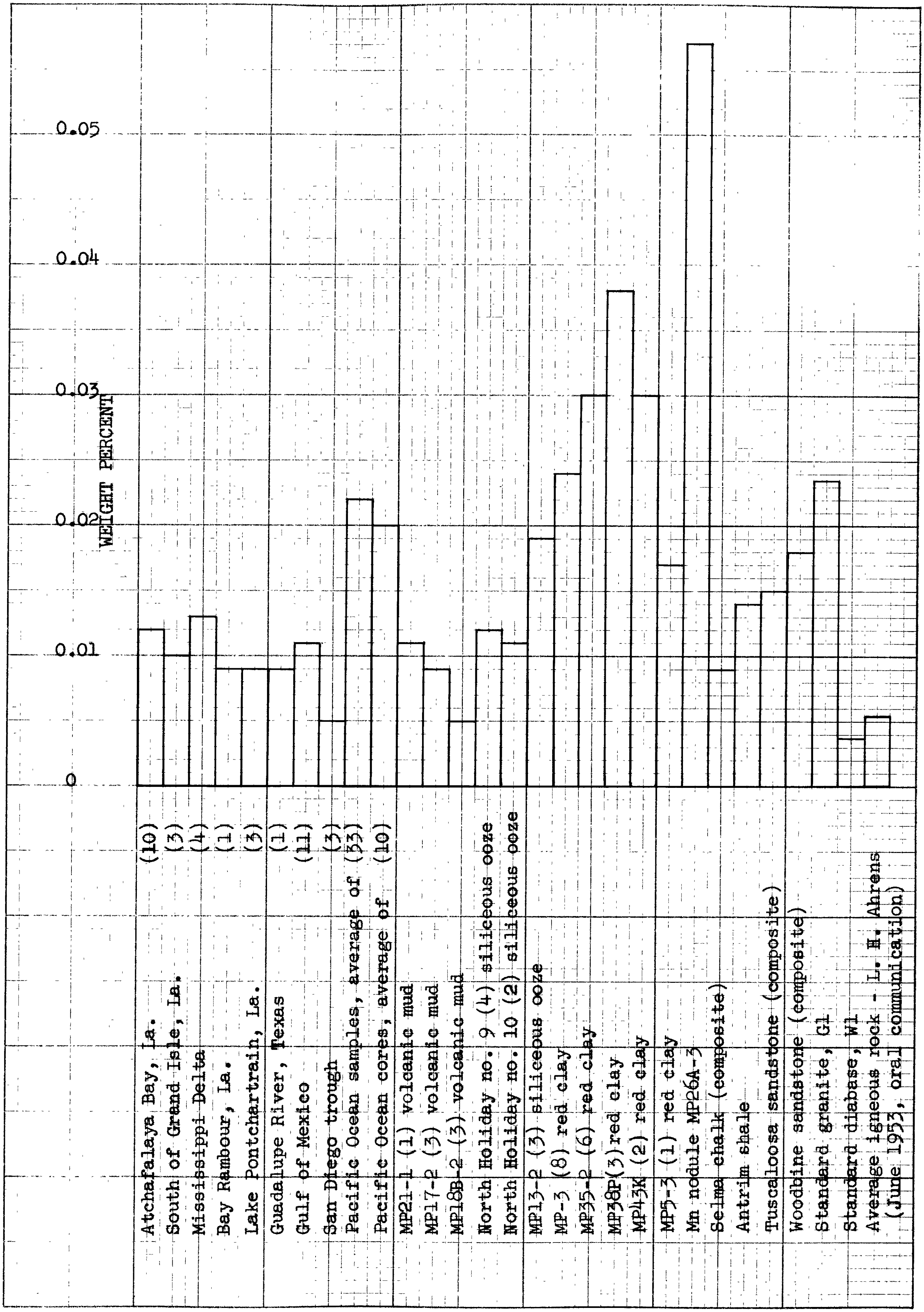

FIGURE 23.--DISTRIBUTION OF La_2O_3

Diego trough sediments contain only 0.005 percent La_2O_3. This is attributed to an abundance of basic rock minerals like biotite and hornblende in which there is very little lanthana.

Of the various types of deep-sea sediments, "red clays" contain the most lanthana with 0.028 percent, and the volcanic sediments and globigerina oozes contain the least. The siliceous oozes contain an average of 0.014 percent lanthana. The fact that lanthana is enriched threefold in "red clays" compared to near-shore sediments requires an explanation. Lanthanum occurs in sea water to the extent of 0.0003 g/ton or thirty billionths of a percent, Rankama and Sahama (1950, p. 290). Despite this small amount, La shows an enrichment in shales greater than that of even Ba and Cs. (pp. 27, 28 and 60). In addition, Boyd, Schubert, and Adamson (1947) have determined experimentally the following order of adsorption affinity: $La^{3+} > Y^{3+} \gg Ba^{2+} \gg Cs^{+} > Rb^{+} > K^{+} > Na^{+} > H^{+} > Li^{+}$. Thus to explain the surplus of lanthana in "red clays", which is over and above the amount found in the average igneous rock, cation exchange is invoked. In further support of cation exchange is the fact that the "red clay" samples contain a zeolite, probably phillipsite, which has a higher base-exchange capacity than clay minerals. See Chapters 4 and 5.

Figure 24 shows the frequency distribution histogram for La_2O_3. The small mode at 0.004 percent lanthana is due to globigerina oozes and the San Diego trough sediments in part. The large mode at 0.011 percent represents the near-shore sediments, and the tailing-out to higher values is caused by the deep-sea sediments.

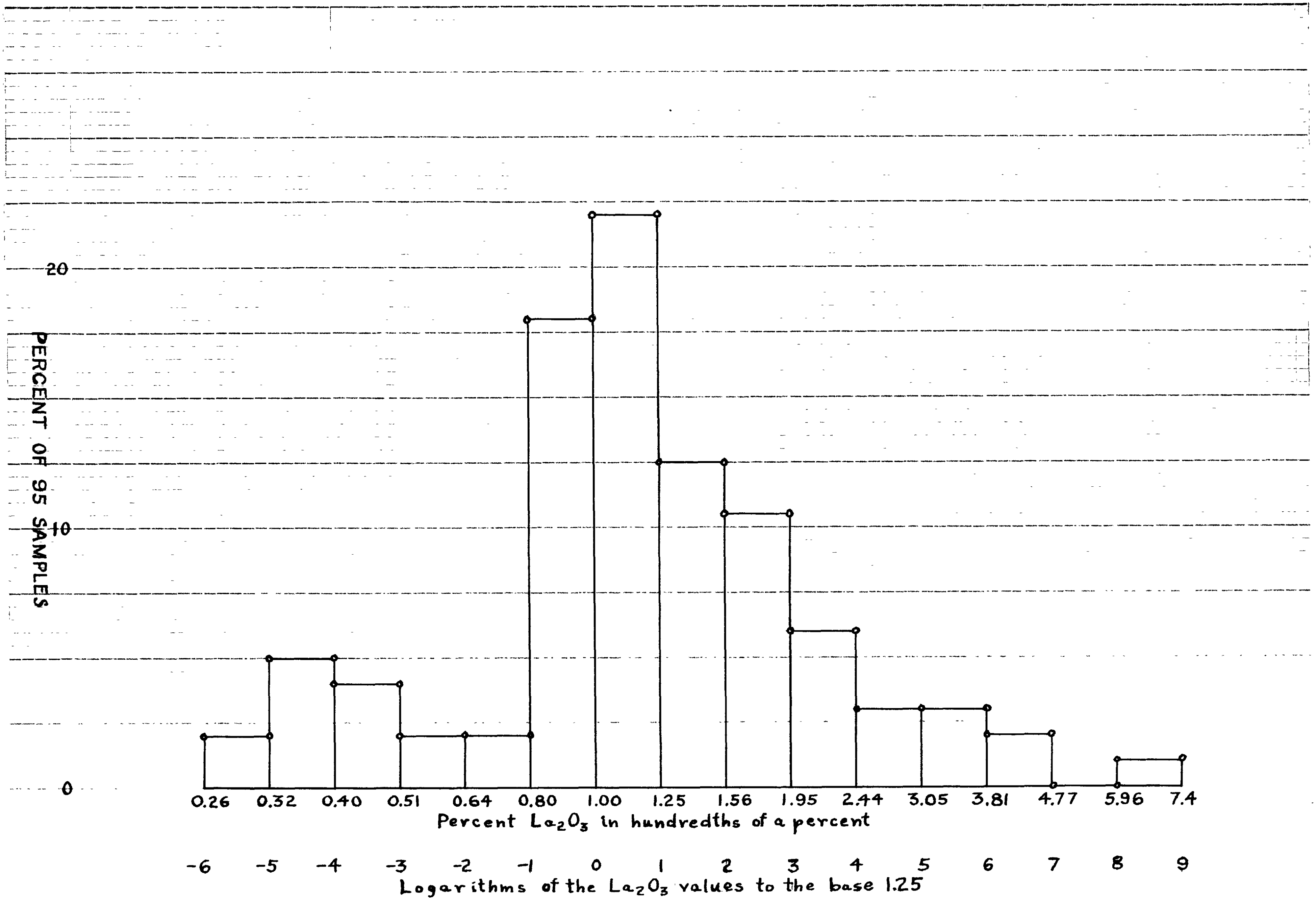

FIGURE 24 - FREQUENCY DISTRIBUTION OF La_2O_3

CHAPTER 4

MINERALOGY

Very little mineralogy was studied in the 96 samples analyzed because the fine-grained nature of deep-sea deposits makes the study of their mineralogy a project in itself, and insufficient time was available for such a project. It must be emphasized, however, that the crux of the problem is the relation of the mineralogy of the sediments to the trace-element content.

When oceanic "red clays" were first examined in the last century they were thought to be largely composed of amorphous material, but later work by many investigators has shown them to be mixtures of many minerals. On the basis of some microscopic and X-ray work, in addition to the trace-element study, it was possible to separate the deep-sea cores worked on in the present work into four types, although of course, these types can and do blend to form mixtures. The four end-member types are "red clay", siliceous ooze, volcanic mud, and globigerina ooze. The five cores of "red clay" and the globigerina oozes, when compared with the other types, are comparatively pure and typical of their type. The siliceous oozes are only dominantly siliceous, and the volcanic muds contain terrigenous material also, although core MP18B-2 is considerably purer than the other volcanic muds. The deep-sea cores and types are:

"Red clay" - MP43K, MP3, MP38P, MP35-2, and MP5-3
Siliceous ooze - North Holiday cores 9 and 10, and MP13-2
Volcanic mud - MP18B-2, MP17-2, and MP21-1
Globigerina ooze - MP33H, MP25E-1, and MP40-1.

A typical sample from the first three preceding types was differentiated microscopically, and short descriptions are listed.

"Red clay"-MP38P, depth in core 20 inches. Approximately half of the sample consists of a zeolite, and the other half consists of dark-brown mineral aggregates of very fine size, having a mean index of refraction of approximately 1.54. Under crossed nicols, many tiny points and spots of birefringent material could be seen in the aggregates. Very few mineral grains were large enough to be determined optically. The zeolite is usually well crystallized in lathlike form, and exhibits pointed or wedge-shaped terminations. One which was rolled on a slide in an index oil displayed a square cross section. The largest one seen was 0.26 mm long and 0.08 mm wide, and the smallest were at the limit of magnification of the microscope. Most of the zeolite crystals are less than 30 microns long and appear isotropic and colorless. Refractive indices vary from +1.48 to -1.51. The largest crystals are slightly birefringent (light-grey interference color at best), and many appear zoned. In one crystal under crossed nicols, symmetrical parts of the crystal extinguished simultaneously suggesting twinning. Some of the smaller crystals appear fresh, while others are clouded, corroded, and partially obscured by a coating of the dark-brown mineral aggregates. From the optical work and X-ray study, to be discussed, the mineral is evidently an authigenic zeolite, and indications are that it is phillipsite. Winchell (1951) gives the following formula for phillipsite, but doubts its validity ($mKCa_3Si_9Al_7O_{32}\cdot12H_2O$ + $nK_3CaSi_{11}Al_5O_{32}\cdot12H_2O$). Plate 1 shows a group of the zeolite crystals, the largest being $\sim$0.03 mm long, and the dark-brown aggregates immersed

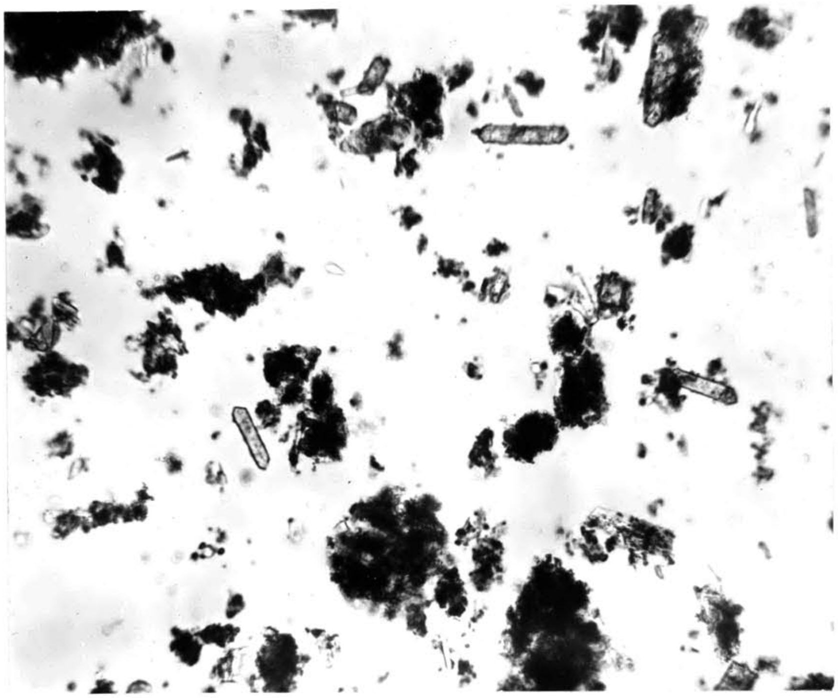

PLATE 1

Photomicrograph of "red clay" MP38P, depth in core 20 inches. Note zeolite crystals approximately 0.03 mm long and dark-brown aggregates. X325.

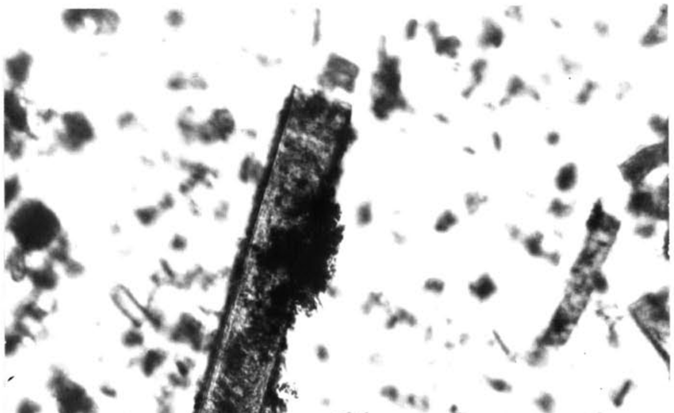

PLATE 2

Photomicrograph of zoned zeolite crystal from MP38P. Length of crystal 0.16 mm. X325.

in index oil 1.54. Pointed terminations of the lathlike crystals are shown. Plate 2 shows a zoned crystal of the zeolite, 0.16 mm long. One end is pointed, and the other is wedge-shaped. Plate 3 is an electron micrograph of MP3, 112 to 116 inches in the core.

Siliceous ooze - North Holiday no. 9, depth in core 22 inches. Approximately one third of the sample consists of diatoms and sponge spicules, and the other two thirds consists of brownish aggregates of very fine minerals which showed birefringence. The mean index of refraction of the aggregates is approximately 1.54. The diatoms are opaline and isotropic, and their refractive index is less than 1.45. As in MP38P, very few mineral grains were large enough to be determined optically.

Volcanic mud - MP18B-2, depth in core 22 to 23 inches. This sample differs from the two preceding ones, in that it contains a large assortment of minerals, most of which are optically determinable. There is an almost complete absence of dark-colored aggregates. Many fragments of basaltic glass, pale olive in color and isotropic or showing speckled birefringence, are present. Their index of refraction is greater than 1.54.

An X-ray spectrometer and recorder was used to learn more about the mineralogy of the deep-sea cores. Spectrograms of each of the three samples previously described are given in Figure 25. Information from the spectrograms is in terms of angles of 2θ for $K\alpha$ copper radiation (nickel filtered). The wavelength used was 1.5418 A, and samples were run at a speed of 1°/minute. The fact that the samples are mixtures, and not pure mineral separates makes possible the identification of only a few dominant minerals at best.

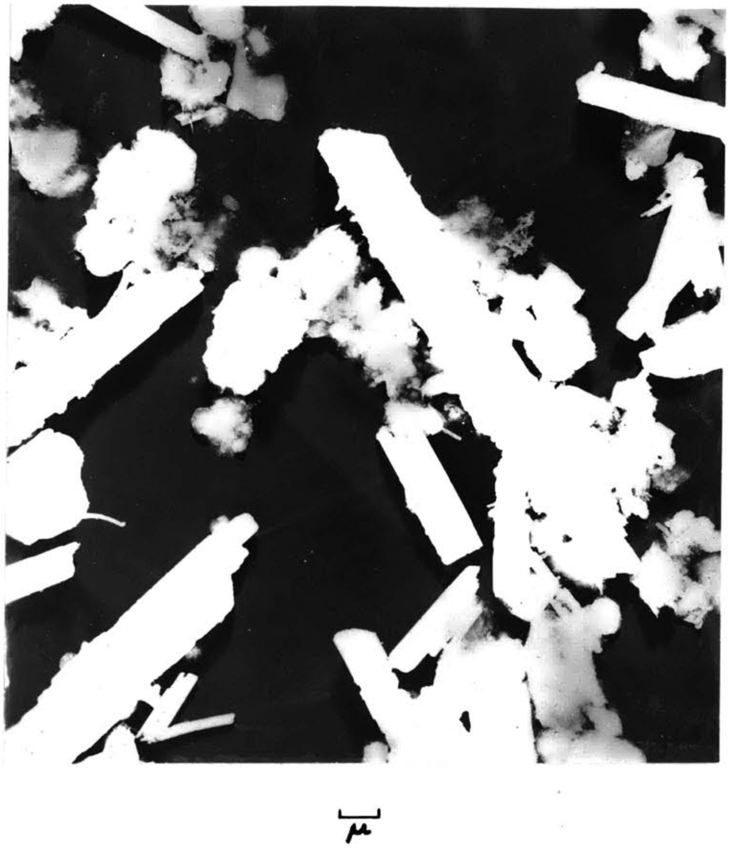

PLATE 3

Electron micrograph of "red clay" MP3, 112 to 116 inches in the core, showing zeolite crystals and clay-like aggregates. Nichrome shadowed at 35°. Micrograph taken by E. J. Dwornik and C. P. Davis, United States Geological Survey. X5200.

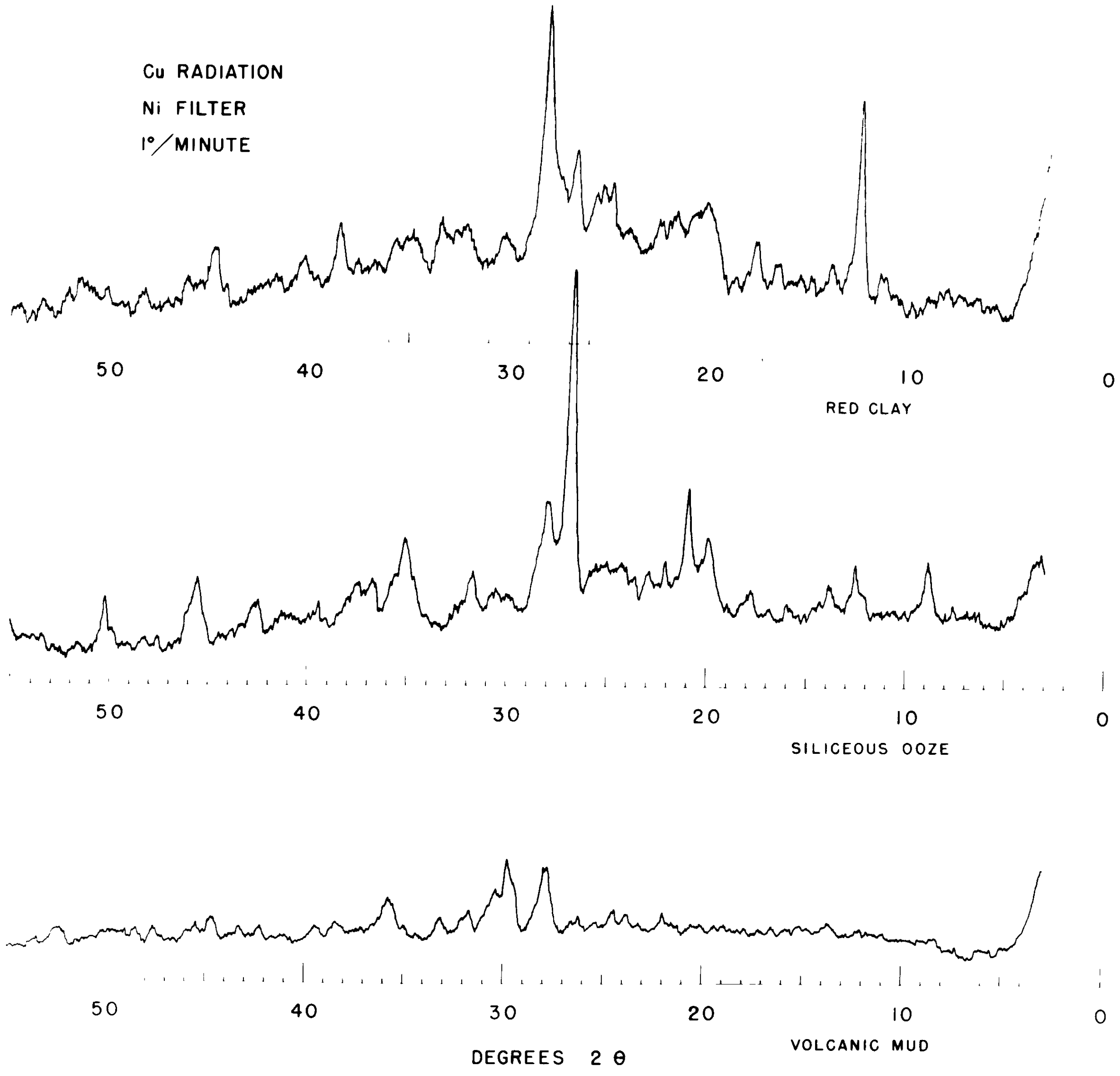

FIGURE 25 X-RAY SPECTROGRAMS OF PELAGIC SEDIMENTS

"Red clay - MP38P, depth in core 20 inches. The two outstanding peaks in the spectrogram of MP38P are at 2θ = 12.4° and 28.1°. These peaks could result from the zeolite phillipsite. At any rate, since the zeolite forms about 50 percent of the sample and is well crystallized, the largest peaks on the spectrogram should result from it. It must be admitted however, that X-ray data on phillipsite from the literature do not correspond too well with that obtained in this work. In view of the apparently variable composition of many zeolites there is no certainty regarding the identity of the zeolite found in MP38P. Revelle (1944) gave the following Bragg reflections in degrees 2θ for phillipsite from Carnegie sample 44 and from a crystal from Australia. For comparison, 2θ's from the files of the A.S.T.M. are given also. Only 2θ's for the strongest lines are given.

Phillipsite from Carnegie sample 44		Phillipsite from Melbourne, Australia		Phillipsite reported in the ASTM file	
2θ	Relative Intensity	2θ	Relative Intensity	2θ	Relative Intensity
12.3°	ms	12.3°	ms	11.58°	100
17.7	ms	17.7	ms	12.8	100
21.2	ms	21.2	ms	20.9	70
21.7	ms	21.7	ms	21.8	70
28.05	vs	27.97	vs	28.05	100
33.3	s	33.2	s	33.0	70

A peak of medium intensity at 2θ = 26.7° suggests a small amount of quartz. The peak at approximately 2θ = 20° probably results from a clay or clay minerals, and the medium peak at 2θ = 38.4° and the small peak at approximately 2θ = 25° could result from kaolinite. Ordinarily kaolinite exhibits a strong peak at 2θ = 12.4°, but in this case it would be overlapped by the phillipsite peak. No peaks at $2\theta = 6^{\circ}$ and 8.9° suggest the absence of montmorillonite and illite, respectively. It is possible, however, for much clay to be present and yet fail to produce a peak if the clay crystals are below a certain size. Particles of the order of 0.1 micron are of optimum utility. Smaller sizes reduce intensity and resolution. See Grim, Dietz, and Bradley (1949).

In summation, X-ray data indicate a large amount of zeolite which is probably phillipsite, a small amount of quartz, and a clay mineral, probably kaolinite. The other "red clay" cores gave roughly similar spectrograms, but their peaks at 12.4° and 28.1° were not as large as those of MP38P - 20 inches, which correlates well with the fact that the latter sample contained the most zeolite.

Siliceous ooze - North Holiday no. 9, depth in core 22 inches. The spectrogram of this sample is notably different from that of "red clay" MP38P in that the most intense peaks are those of quartz at $2\theta = 26.7^{\circ}$ and 20.9°. Peaks of medium intensity at $2\theta = 8.9^{\circ}$, 19.8°, $\sim 35^{\circ}$ and 45.6° suggest illite, although muscovite also contains peaks in the same positions. Peaks of medium intensity at 12.5° and 28.05° suggest the zeolite phillipsite, and feldspar appears to be present because of the peak at 27.9°. Kaolinite may be present also. Halite may be represented by a peak at 31.7°.

In summation, a sizable amount of quartz is indicated. Illite or muscovite is present, probably some kaolinite and phillipsite, feldspar, and halite. MP13-2 at a depth of 3 to 4 inches in the core, apparently contained less quartz, although approximately half of the sample consisted of opaline diatoms. The other peaks, which were similar to those of North Holiday no. 9, were reduced in intensity owing to the large quantity of diatoms in the sample.

Volcanic mud - MP18B-2, depth in core 22 to 23 inches. This sample presents an entirely different spectrogram from the "red clays" and siliceous oozes. It is essentially free of quartz and clay since there are no peaks at 26.7° and ~20°. From its basaltic character one would expect to find a calc-alkalic feldspar, a pyroxene, and possibly olivine among its dominant minerals. Labradorite has its strongest peaks at the following 2θ's, 27.7° to 27.9°, 35.5°, and 21.8° or 50.1°, which match the spectrogram of MP18B-2, except for the 50.1° position. The most intense peak on the spectrogram is at 29.8°, which could be caused by augite, diopside, or other pyroxenes. Augite and diopside also have strong peaks at 35.6°, which appears as a broad peak on the spectrogram. Two of the strongest peaks of olivine at 52.3° and 35.6° also appear on the spectrogram.

In summation MP18B-2 contains a plagioclase feldspar which is probably labradorite, a pyroxene, and possibly olivine. The other volcanic cores, MP17-2, and MP21-1, have similar spectrograms, although MP21-1 contains more quartz than the other two. A spectrogram of V120 from the San Diego trough at a depth of 32 inches in the core indicated the presence of quartz, feldspar, calcite, and possibly illite or muscovite, and a spectrogram of Mississippi Delta sample MP137-51ABL at a depth of 51 inches in the core indicated the presence of a large amount of quartz, feldspar, illite or muscovite and kaolinite.

As stated before, much mineralogic work has been done on the very fine grained oceanic "red clays". Murray and Renard (1891) in their incomparable Deep Sea Deposits volumes have described and figured phillipsite crystals (plate facing p. 816 in Vol. 1, 2nd part) as often fibro-radiated, with a diameter of about 0.5 mm. They also found twin-crossed crystals, in addition to lathlike ones with pointed terminations. Fibro-radiated crystals could not be found by the writer, but Bramlette (Oct. 1953, oral communication) mentioned seeing them.

Correns (1937) and his co-workers did an enormous amount of work -- mineralogic, chemical, size analytic and paleontologic -- on sediments from the equatorial Atlantic Ocean. From one of their "red clays" at station 305, Longitude 34°12.2'W and Latitude 12°3.2'N, and depth 6025 meters, they reported the following minerals and material determined microscopically: quartz, feldspar, hornblende, augite, biotite, silica tests, muscovite, ore, montmorillonite, glauconite, dolomite, tourmaline, zircon, titanite, and rutile. Regarding X-ray analysis, they claimed the clay fraction of the deep-sea sediments to be composed of a mixture of the following minerals in descending order of abundance: calcite, quartz, mica, halloysite, kaolinite, montmorillonite, feldspar, augite, and aragonite. It is difficult to understand the position of calcite in their list since it has not been detected by the writer except, of course, in globigerina ooze and perhaps in the volcanic sediments. Correns looked for phillipsite, but failed to find any. He listed the following as authigenic minerals on the sea floor: glauconite, limonite, manganese nodules, dolomite, siderite, breunnerite, and gypsum. He mentioned kaolinite as a possibility but admitted the possibility of six-sided perfect crystals being transported by water or wind.

The Snellius Expedition in the Dutch East Indies was the motive force behind another large mineralogic work on deep-sea deposits.

Kuenen (1942) and his co-worker Neeb (1943) reported on the mineralogy of 382 samples, which had been separated into 10 size fractions. Mineralogy similar to that of Correns (1937) was reported, phillipsite not having been identified. From X-ray analysis, quartz, muscovite, feldspar, kaolinite, and montmorillonite were reported. The size fractions 2-5 microns, 0.5-2 microns, and less than 0.5 microns were used in X-ray analysis, and they were able to show that kaolinite content remained about the same in all fractions, montmorillonite content increased with fineness of fraction, and quartz, muscovite, and feldspar contents declined with fineness of fraction.

Grim, Dietz, and Bradley (1949) used X-ray diffraction, differential thermal, optical, chemical, and electron microscopic methods in a study of the clay mineral composition of a number of Pacific deep-sea and near-shore sediments. They reported that all of the Pacific samples and those from the Gulf of California contained illite, montmorillonite, and kaolinite, generally in that order of abundance. The mineral terms were used as group names rather than specific mineral names. They also reported small amounts of quartz and probable feldspar in many samples.

CHAPTER 5

CATION EXCHANGE

It has been conjectured that cation exchange is one cause for the enrichment of many elements in deep-sea deposits. Because of insufficient time the writer has not done any experimental work on the subject. The literature, however, contains pertinent data which are used in the following discussion.

Cation exchange, or base exchange, is the process whereby an ion in solution is exchanged with one from a solid which is in contact with the solution. Equations to fit the cation exchange process have been proposed from various viewpoints such as adsorption of a gas on a solid, the law of mass action, and from kinetic reasoning, but there is no general agreement on which equation most satisfactorily expresses cation exchange relationships. Concerning this problem, Kelley (1948, p. 50) in writing of the constant k, used in various equations, stated that "the lack of constancy of k, will not be due to the inapplicability of the mass law owing to diffuse layer effects or to the nonchemical nature of cation exchange. It can be accounted for simply by the lack of uniformity of the exchange material in the experimental sample."

The history and theory of cation exchange are discussed thoroughly by Kelley (1948) and Nachod (1949).

Cation exchange capacity is usually measured in terms of milliequivalents per 100 grams and is a measure of the amount of cations, contained by a material, that are exchangeable for the cations of a neutral salt solution. As an illustration, 1 m.e. of K_2O = 0.047 g.

The relative replacing power of the different cations depends on the interplay of several factors enumerated by Kelley (1948, p. 65). These factors are: (1) the kind of material on which the exchangeable cation is held, (2) the degree of saturation with that cation, (3) the nature of the exchangeable cations associated with a given exchangeable cation, (4) the kind of liquid in which the exchange takes place. Other factors may possibly be involved also. These factors will be discussed to the extent that they affect the enrichment of various elements in deep-sea deposits.

(1) The kind of material on which the exchangeable cation is held. Under this factor there are good indications that cation exchange may be responsible, at least partially, for the trace-element enrichment in deep-sea deposits. Grim (1942) stated that in recent marine sediments illite is most abundant, kaolinite is less abundant, and montmorillonite is either absent or of very minor abundance. As far as can be told from X-ray studies in the present work, this seems to be borne out. Furthermore, Correns (1937) and Neeb (1943) indicate similar clay mineralogy, if their reported occurrence of muscovite as determined by X-ray analysis proves to be illite which has an X-ray pattern very similar to that of muscovite. The zeolite, phillipsite, and possibly others, are important quantitatively in much of the "red clay" of the Pacific basin.

For the clay minerals mentioned, Grim (1942) gave the following cation exchange capacities in m.e. per 100 grams.

Montmorillonite	60-100
Illite	20-40
Kaolinite	3-15

Zeolites have even higher cation exchange capacities. Revelle (1944) listed natrolite and stillbite as containing 221 and 312 m.e. per 100 grams, respectively.

Grim (1942) stated that 80 percent of the exchange positions of montmorillonite are on the basal-plane surfaces, and the remainder are on the edges of the flakes, but Kelley (1939), in Recent Marine Sediments, believed that cation exchange processes took place at flake edges where there were broken bonds. He further believed that as crystals of montmorillonite or bentonitic clay were usually smaller than those of kaolinite, relatively many more cell edges were exposed making for greater exchange capacity. It is known that finely ground kaolinite shows greater cation exchange capacity than coarse crystalline kaolinite. See Kelley and Jenny (1936).

Regardless of the theory, the fact remains that the clay minerals possess cation exchange properties. Revelle (1944) listed the cation exchange capacities of several deep-sea deposits. The highest ones, 53 and 58 m.e. per 100 grams, were of the less than 1.5 micron fractions of two "red clays". The importance of the fine fraction was evident because sample 77, which had the 58 m.e. capacity for its less than 1.5 micron fraction, had a capacity of only 34.3 m.e. as a whole sample.

In conclusion, most deep-sea deposits, and marine deposits in general, possess minerals which are noted for their cation exchange properties.

(2) <u>The degree of saturation with that cation</u>. Cited in Kelley's (1948) book is an experiment by Schachtschabel (1940), which

showed that Ca^{++} and Ba^{++} replaced NH_4^+ ion almost twice as much as K^+ ion did in dilute solution (0.0025 normality), whereas in more concentrated solutions of 0.04 normality, almost equal amounts of Ca^{++}, Ba^{++}, and K^+ replaced the NH_4^+. However, when Ba^{++} was made to replace Ca^{++} in a similar experiment, dilution of the Ba^{++} ion had very little effect on the amount of Ca replaced. In sea water, of course, the Ba^{++} ion is much more dilute than it was in the experiments. The most dilute solution, 0.0025N, used by Schachtschabel was equivalent to 0.015 percent Ba^{++} ion, whereas there is 0.000005 percent Ba^{++} in sea water according to Rankama and Sahama (1950, p. 290), making sea water 3000 times more dilute. With the trend established in Schachtschabel's experiment, however, there is good reason to suppose that even more dilution than that used by him would show the even greater activity of Ba^{++} and Ca^{++}, as opposed to K^+, in replacing a univalent cation. The preceding extrapolation assumes equal amounts of the various cations in solution, but such is not the case in sea water, which contains much more Ca and K than Ba in solution. What results would obtain under such conditions have not been determined experimentally, except in a limited way. Kelley and Liebig (1934) shook both soil and bentonitic clay with sea water, and found that rather large amounts of Mg and Na were adsorbed and smaller amounts of K. Ca decreased after the shaking, but both the soil and the clay were Ca-rich before the shaking.

Schubert, J. in the book "Ion Exchange" by Nachod (1949) found that tracer levels of very insoluble metals such as zirconium, columbium, and protoactinium may be highly adsorbed by organic cation exchangers. He, however, invoked physical surface adsorption rather than the usual cation exchange mechanism in this case. It is not known how this information relates to natural cation exchangers. At any rate, Zr does not seem to be enriched in deep-sea deposits.

(3) <u>The nature of the exchangeable cations associated with a given exchangeable cation</u>. Noll (1931), in writing of the geochemical role of adsorption, or cation exchange, stated that the adsorptivity of an ion increased with increasing charge, decreasing hydrated volume, increasing polarization, and increasing dipole nature. It might be noted, however, that increasing polarization, and, as a consequence, increasing dipole nature, are concomitants of increasing ionic volume.

Experimental results of Boyd, Schubert, and Adamson (1947), obtained with a metallic zeolite salt, gave the following order of adsorption affinity: $La^{+++} > Y^{+++} \gg Ba^{++} \gg Cs^{+} > Rb^{+} > K^{+} > Na^{+} > H^{+} > Li^{+}$. This series illustrates how adsorptivity of an ion increases with increasing charge and decreasing hydrated volume. In water solution, the larger Cs ion is much less hydrated than the smaller Li ion. Decreasing hydrated volume does not always mean increasing adsorptivity, however, because in a specific case Mg^{++} and Ca^{++} ions, which are more highly hydrated in aqueous solution than Li^{+} and Na^{+} ions, demonstrated the power to replace Ba^{++} ions from Ba-saturated chernozem soil much more than did those of Li^{+} and Na^{+}, according to Gedroiz (1919), quoted in Kelley (1948, p. 63). In other words, when cations of different charge are compared, correlation of hydrated radius with adsorptivity breaks down.

Boyd, Schubert, and Adamson (1947) also predicted the following series of decreasing adsorptivity among cations of +3 charge: La > Ce > Pr > Nd > Sm > Eu > Y > Sc > Al, which fits the scheme of adsorptivity varying inversely as hydrated volume, or directly as ionic (nonhydrated) volume, at least for ions of the same valence.

(4) <u>The kind of liquid in which the exchange takes place</u>. This factor has no concern here as sea water is the only liquid involved. In liquids other than water hydration of cations is not effected.

Aside from cation exchange there is the possibility that some enrichment of deep-sea deposits in elements like Co, Sc, and La may take place through the process of co-precipitation. Cooper (1937) calculated the redox potential of sea water as 0.43 to 0.75 volts (oxidizing condition). At this Eh, and at a pH of approximately 8, the ferric ion in sea water is removed by precipitation as fast as it is formed. In consequence, the tendency for ferrous ion to be oxidized is increased, and solutions of ferrous salts are very unstable. Cooper (1937) further stated that "It appears reasonable to extend these conceptions to the very small amounts of Fe in sea water." Rankama and Sahama (1950, p. 290) listed 0.02 to 0.002 g/ton of Fe in sea water.

Harvey (1937) noted a further complication concerning $Fe(OH)_3$, namely, that when it is formed in the presence of very small quantities of various emulsoids, it does not flocculate on adding to sea water, or flocculates less rapidly. Many molecules of $Fe(OH)_3$ are adsorbed on and "protected" (his quotes) by one molecule of emulsoid. He then stated that it was probable that $Fe(OH)_3$ in the sea was similarly adsorbed on emulsoids.

CHAPTER 6

HYPOTHESES OF ORIGIN OF "RED CLAY"

There have been two schools of thought on the origin of oceanic "red clay". The earlier one stems from the work of Murray and Renard (1891), in which they attributed "red clay" to the submarine weathering of volcanic glasses like pumice and volcanic ashes. They noted, however, admixtures, to varying degrees, of cosmic dust, sharks' teeth, bones of cetaceans, manganese nodules, and zeolites, which they believed to have been formed from the decomposition of volcanic rock fragments. The prevalence of volcanic debris in the abyssal Pacific and the vast deposits of "red clay" there also led Murray and Renard to their concept of submarine weathering. Murray cited occasions when great slabs of tufas were dredged, some showing distinct layers produced by showers of volcanic ashes. See Murray and Hjort (1912).

One of the chemical facts which disturbed Murray and Renard (1891), however, was the fact that there seemed to be too much silica in "red clay", which was attributed to siliceous tests. Later there will be a discussion of the fact that silt and clay-size particles of quartz can be transported far out over ocean basins by the wind.

Caspari (1910) analyzed about 13 "red clays" from the Atlantic, Pacific, and Indian Oceans for major constituents, and concurred with Murray's belief that they originated, in the main, from the degradation of acid and basic volcanic glasses.

Correns (1937) represents the opposing school of thought, which sees "red clay" as the slow accumulation of terrigenous material. He (1937a) also related globigerina ooze to "red clay" by stating that the residual product of dissolved globigerina ooze helps to form "red clay" deposits. According to him (1937), volcanic materials are more noticeable in "red clay" than in globigerina ooze or in the blue and green mud found nearer shore, because of the slower sedimentation in "red clay". Nevertheless, with the aid of the microscope he found traces of volcanic materials in globigerina ooze. Schott (1939) in Recent Marine Sediments, gave the average rates of deposition for blue mud, globigerina ooze, and "red clay" in the equatorial Atlantic Ocean as 1.78, 1.2, and less than 0.86 cm per 1000 years, respectively. Twenhofel (1929) gave 0.35 cm of inorganic constituents per 1000 years for "red clay", which agrees well with the figure obtained by Schott for "red clay" containing some foraminifera, which take up a relatively great volume compared to the mineral constituents of "red clay".

Correns (1937) offered the following bits of evidence to champion his hypothesis. He cited a piece of basalt having a glassy crust from 2000 meters depth at Latitude 1°56'S and Longitude 12°4.7'W, station 244a, which weighed 62.7 grams and seemed to be a roll or bulge of a lava flow, apparently quite young. The core of the piece was fresh, and the crust and the core differed chemically. The crust contained less silica, less Ca, less Mg, less Fe^{+2}, less Na, more H_2O+ and H_2O-, more K, more Mn, more Ti, and Al remained approximately the same. Chemical differences could have been caused by the reaction of the hot lava and the sea water according to Correns. The crust showed some signs of weathering, but possibly the young age of the basalt precluded great weathering. A geologically old piece of submarine basalt would be an interesting sample to analyze in this context.

Correns (1937) further remarked about the fresh character of feldspars, even at depth in a deep-sea core. He also noted that there were some clouded feldspars that showed beginning decomposition, but these could have brought into the sea from the land. And only on a few pieces of volcanic glass could there be found decomposition signs similar to that observed in the basalt crust.

From a physical and chemical standpoint, submarine weathering should not be very operative according to Correns (1937). Mechanical disintegration, which is continually taking place on land, is inoperative under deep water. Chemically, sea water is predominantly a weathering solution, being the receptacle for all the ions brought to it from land throughout geologic (oceanic) time, in contrast to the ion-poor solutions (fresh water) found on land.

The flocculation of a suspension not only depends on the concentration of salt in the sea, but also on the concentration of the suspended matter. The less concentrated the suspension, the more improbable it is that the particles will be brought together and flocculated. Correns (1937) is of the opinion that some rivers in some seasons, and others always, do not carry enough suspended matter to have it flocculate. This fine material can be dispersed widely by sea currents, and he claims that observations of turbidity in sea water support this view. The fine material forms the clayey component of "red clays" and is not different basically from near-shore sediments like blue mud and globigerina ooze, as shown by microscopic, X-ray, and chemical investigations.

Eolian contribution to deep-sea deposits must be considerable as indicated by the literature concerning air transport of sediments. Correns (1937) mentioned red-brown iron-stained quartz grains, typical of the Sahara, which were picked up in sea sediments from the Cape Verde Basin. Also Leinz, one of Correns' co-workers, showed that in the Guinea Basin zircon and rounded quartz were characteristic of land proximity. Great dustfalls are observed from time to time. The one at Madison, Wisconsin, on March 9, 1918, dropped 13.5 short tons per square mile, according to Winchell and Miller (1918), and the one of March 12, 1920, dropped twice that much. Same authors (1922). These great clouds of dust consisted mostly of feldspar and quartz, but hornblende, calcite, mica, magnetite, apatite, tourmaline, and zircon were also found. Dust fogs have occurred on the California coast with the prevailing west wind, and Clarence King, cited in Pumpelly (1879), suggested that they might be the finest residuum of the loess dust of an Asiatic dust storm. In the great Turkestan Basin thousands of feet of wind-deposited loess have been described by Pumpelly (1908). Udden (1894) has calculated that the capacity of the atmosphere to transport dust is 1000 times as great as the capacity of a large river like the Mississippi to transport sediment. Volcanic dust and ashes also account for a considerable part of the sediment in regions of slow sedimentation like the "red clay" area. Radczewski (1939) gives a short bibliography concerning eolian deposits in marine sediments. The few references given above were only to indicate the importance of the atmosphere as a transporting medium for sediments as far as marine deposits are concerned.

Sverdrup, Johnson and Fleming (1942, p. 990) listed the following factors as supporting the hypothesis of terrigenous origin for deep-sea deposits:

(1) There are no sharp changes in mineralogical composition or properties in passing from known terrigenous deposits to the pelagic deposits.

(2) There is no progressive change in the mineralogical constituents with depth in cores from pelagic deposits. If submarine weathering were active, changes with time should occur which would be reflected in the cores.

(3) The variety of fine-grained minerals indicates a number of sources as would be found in terrigenous debris.

(4) Fine-grained material, particularly in dilute suspension, is not necessarily flocculated by mixing with sea water, hence can be transported for great distances in the sea.

To these factors may be added two others which have emerged from the present work.

(1) The 20 "red clay" samples and 9 siliceous ooze samples analyzed in the present work are, without exception, too low in V, Ti, and especially Cr content to have been derived from the submarine weathering of oceanic basalts, which are Cr-rich. It must be mentioned, however, that the longest core of "red clay", MP3, showed an increase in Cr with depth. Nevertheless, the highest value which occurred at the bottom of the core, 293 to 297 inches, was only 0.018 percent

Cr_2O_3, which is still four times lower than the Cr_2O_3 content of basaltic core MP18B-2, and only slightly higher than the 0.0146 percent Cr_2O_3 assigned to the average igneous rock, according to Ahrens (June 1953, oral communication).

(2) The TiO_2/ZrO_2 ratios of the "red clays" and siliceous oozes suggest a terrigenous origin for these pelagic deposits, as their ratios are very similar to that of the average igneous rock (see p. 36). The utility of the ratio is, of course, the fact that basic rocks have high Ti and low Zr content, and acid rocks vice versa. Indeed, the basaltic cores have ratios 2 to 4 times greater than the "red clays". If "red clay" owed its origin to submarine weathering of volcanic rock, its TiO_2/ZrO_2 ratio should be correspondingly high, as Ti and Zr, owing to their insolubility, could hardly have been leached from the volcanic rocks by sea water. More corroboration is offered by the amounts of Ti, Zr, Cr, and V occurring in pelagic deposits, which approximate that of an average igneous rock. That fact is explainable by the terrigenous hypothesis, but not by the submarine weathering hypothesis.

CONCLUSIONS

Spectral lines of V, Co, Ni, and Cr are appreciably enhanced by the presence of large quantities of $CaCO_3$.

Conclusions concerning individual elements are listed. Where the term deep-sea cores is used, it is taken to mean mostly "red clay" with some siliceous ooze. Basaltic core MP18B-2 and the calcareous oozes are excluded.

1. SrO content of deep-sea cores is 0.06 percent, which is about twice that of near-shore sediments and twice that of the average igneous rock. Pelagic sediments with volcanic minerals are rich in Ca, and correspondingly rich in Sr.

2. BaO content of deep-sea cores is variable, although an areal pattern suggests itself. The greatest range of values occurs in the "red clays", the lowest sample containing 0.1 percent BaO, and the highest sample containing 2.7 percent BaO. The average BaO content of the deep-sea cores is 0.8 percent, which, although not too meaningful in view of the variability, is four times that of near-shore sediments and seven or eight times that of the average igneous rock.

3. Titania content is rather constant in the deep-sea cores and is similar to near-shore sediment content and average igneous rock content. Almost all values are between 0.60 and 0.85 percent TiO_2; however, deep-sea sediments with volcanic minerals contain more Ti.

4. The amount of zirconia in deep-sea cores is practically the same as that in the average igneous rock and in clayey near-shore sediments, namely, $\sim$ 0.020 percent.

5. NiO content of deep-sea cores is $\sim$ 0.025 percent, which is four times that of near-shore sediments and 2 1/2 times that of the

average igneous rock.

6. Co_2O_3 content of deep-sea cores is $\sim$ 0.0097 percent, which is 7 times that of near-shore sediments and 3 1/2 times that of the average igneous rock.

7. V_2O_5 content of deep-sea cores, of the average igneous rock, and of near-shore clayey sediments is virtually the same, most values falling in the range 0.020 to 0.026 percent. Deep-sea sediments with volcanic minerals show higher V content.

8. Sc_2O_3 content of deep-sea cores is $\sim$ 0.0046 percent, which is about twice that of near-shore sediments and 1 1/2 times that of the average igneous rock.

9. Cr_2O_3 content of "red clay" is $\sim$ 0.014 percent, which is the same as that of the average igneous rock and similar to that of near-shore sediments. When Cr_2O_3 content of pelagic sediments rises above 0.025 percent volcanic minerals are probably present.

10. La_2O_3 content of deep-sea cores is variable, but, on the average, it is $\sim$ 0.020 percent, which is twice that of near-shore sediments and four times that of the average igneous rock.

Enrichment of Ni and Co in pelagic cores may be the result of the accretion of meteoritic matter, at least in part. Co may co-precipitate with $Fe(OH)_3$ to a greater extent than Ni does, and may thereby be enriched relatively more than Ni. The enrichment of Ba, Sr, Sc, and La in deep-sea deposits may be, in part, the result of cation exchange. In addition, precipitation of $BaSO_4$ or $BaCO_3$ is suspected in the case of Ba. The extreme paucity of Ti, Zr and Cr in sea water prohibits their enrichment in "red clay". Vanadium, perhaps by formation of complex anions in sea water, is prevented from being enriched in "red clay".

From the fact that "red clay" is relatively poor in Ti, V, and particularly Cr, compared to volcanic muds, and from other considerations discussed in Chapter 6, it is believed that "red clay" originates, in the main, from terrigenous material finding its way to the sea bottom by means of wind and water.

SUGGESTIONS FOR FUTURE WORK

One of the most challenging problems which this thesis suggests is the correlation of mineralogy with trace element content. The fineness of grain of the deep-sea sediments, and the consequent difficulty of their quantitative mineralogic analysis makes the problem seem almost insuperable, but even a semiquantitative mineralogic analysis would aid correlation with trace element content. Heavy liquid separations, or other means of separation, might aid in proving or disproving the existence of barite or witherite in Ba-rich pelagic sediments.

Cation exchange studies should be made on pelagic sediments to determine the extent and nature of possible replacement. This would necessitate spectroscopic analysis before and after leaching of the sediment.

A most desirable sample to obtain and analyze would be a submarine piece of basalt, such as that worked on by Correns (1937), but preferably it should be of moderately old age (Mesozoic or older), so that the effects of submarine weathering on trace elements, if any, could be measured.

Finally, Sverdrup, Johnson, and Fleming (1942, p. 990), in writing about the clay-size material found in both near-shore and pelagic sediments, stated that "The detection of this finely divided material in the water and the determination of its distribution in the ocean waters will be the conclusive argument in deciding upon the source of the red clay and the nonorganic fraction of the pelagic oozes." Minor element determination of this finely divided matter would also aid in the quoted problem.

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The author was born on February 18, 1923 in Roselle, New Jersey. He was educated in Linden, New Jersey Public Schools and received his high school diploma in 1941. While attending evening sessions at Union Junior College in Cranford, New Jersey from September 1941 to December 1942, he worked variously as a chemical laboratory assistant, an electrical inspector of armatures and coils, and as an apprentice surveyor. From January 1943 to December 1945 the Army occupied the author's time. During this interim most of his time was spent in wire communications in the Infantry. A six-month period from September 1943 to March 1944 was spent at the Texas College of Arts and Industries in the Army Specialized Training Program. After termination of Army service a Batchelor of Science degree in Geology was obtained at Rutgers University in 1948. While at Rutgers he was a geology laboratory instructor from September 1947 to January 1948. In September of 1948 he began graduate work at the Massachusetts Institute of Technology and terminated work there in 1952. From 1948 to 1950 he was a research assistant to Prof. P. M. Hurley who was engaged in geologic age determinations. One summer was spent in western Newfoundland as a senior assistant geologist to the retired Rutgers University Prof. A. O. Hayes in a coal survey. Another summer was spent as a geologist in Nova Scotia on a water-supply problem which culminated in an S.M. thesis from M.I.T. in 1950. For two summers he worked for the Quebec Department of Mines, one in the Lake Timiskaming area with Prof. Pierre Mauffette of Ecole Polytechnique, Montreal, and the other near Lake Chibougamau with J. R. Smith of Princeton. From October 1952 to the present the author has been working with the United States Geological Survey on the Southeast Phosphate Project with Z. S. Altschuler. The author belongs to Sigma Xi and Phi Beta Kappa.