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A GEOCHEMICAL RECONNAISSANCE
OF PUERTO RICAN BEACH SANDS

BY

LOUIS MEINECKE III, 1944-

A THESIS

Presented to the Faculty of the Graduate School of the

UNIVERSITY OF MISSOURI-ROLLA

In Partial Fulfillment of the Requirements for the Degree

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Approved by

Lt J. B. Boltz (Advisor) Sheldon Kerry Grant

O. K. Manuel

226949

ABSTRACT

Twenty-four beach sand samples from the island of Puerto Rico were collected in 1964 by Dr. Ernst Bolter as part of a radiometric survey conducted by him. These samples were given to the author in 1969 for chemical analysis.

The purpose of this investigation was to conduct a geochemical reconnaissance study of the beach sands in order to determine the geochemical background and possible anomalies. This information could aid in offshore mineral exploration and source area determination.

This thesis presents the results of a quantitative chemical analysis for copper, lead, zinc, iron, manganese, aluminum, sodium, potassium, calcium, magnesium, and strontium in a silicate matrix by atomic absorption.

X-ray fluorescence was used as a semi-quantitative method to determine strontium, zirconium, and titanium in the heavy mineral fraction. X-ray diffraction was used in conjunction with fluorescence to determine the mineralogical matrices of the samples needed for the calculations.

A mineralogical analysis of the beach sands was also performed.

ACKNOWLEDGEMENT

I would like to express my gratitude to several people for the help that I received for this study: to Dr. Ernst Bolter who collected the samples and supervised the research, to Dr. S. K. Grant for his help with the X-ray and mineralogical analyses, and to Dr. O.K. Manuel for his helpful criticisms of the text.

My most sincere thanks also to my wife, Mary Jean, for her patience and the many hours she spent typing this paper.

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I. INTRODUCTION

A. Purpose and Scope of Investigation

During the weathering of rock, essentially three geochemical fractions are produced. One fraction consists of material in solution that is transported by streams to the ocean in dissolved form. The second fraction consists of material, which after dissolution, has been precipitated again in the form of new sedimentary minerals such as clay minerals or oxides. The third fraction is represented by the resistant, unweathered minerals which may sometimes be transported for a long distance.

As a result, beach sands associated with the stream drainage basins should reflect, at least in part, a depositional site for the resistant, unweathered fraction. The purpose of this investigation, therefore, is to determine the composition of this fraction, primarily to establish chemical background values for the beach sands. A knowledge of the geochemical background values for beach sands would aid in offshore exploration and be useful for the source area determination.

B. Location

1. Geographic Location

Puerto Rico is one of the islands of the West Indies, separating the Atlantic Ocean from the Caribbean Sea.

Puerto Rico is situated at $65^{\circ} 30'$ W longitude to $67^{\circ} 30'$ W

longitude and $17^{\circ} 55'$ N latitude to $18^{\circ} 30'$ N latitude.

2. Sample Location

The 24 beach sand samples were collected from beaches along approximately one-half of the coastline on the eastern, northern, and western parts of the island. Figure 1 shows the two areas of the island that were sampled. The sample numbers and locations are given in Table 1 and shown in Figures 2 and 3.

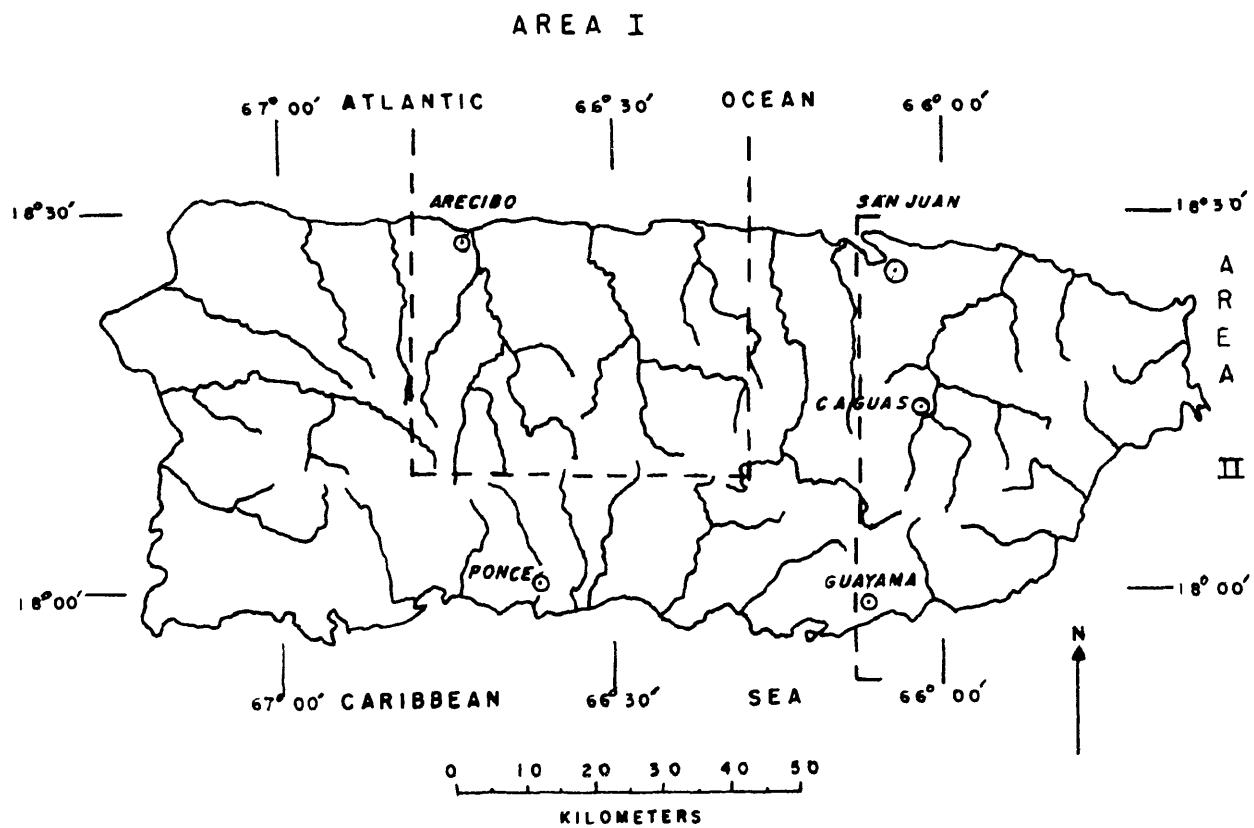


Fig. 1. Map of Puerto Rico Showing Sampled Areas
(after Briggs, 1964)

Table 1. Sample Locations and Major Rock Types of the Source Area

SAMPLE	QUADRANGLE	LOCATION	AGE*	ROCK TYPES*
216	Guayama	Beach sand, Road Number 3 southeast of Providencia near the Rio Chico	Tertiary-Cretaceous	Granodiorite and quartz diorite
220	Punta Tuna	Beach, very coarse sand and pebbles, Road Number 3 south of Escuela Segunda Unidad, near Quebrada Campo Libre, Florida	Tertiary-Cretaceous	similar to Sample Number 216
221	Punta Tuna	Beach, Road Number 3 halfway between Quebrada Manglillo and Cabo Mala Pascua	Tertiary-Cretaceous	similar to Sample Number 216
223	Punta Tuna	Beach, fine sand, Road Number 3 east of Cabo Mala Pascua	Cretaceous	similar to Sample Number 216 with some volcanics: lava, tuff, breccias, conglomerates with some limestone lenses
224	Punta Tuna	Beach, Road Number 3 extreme southwest corner of Municipio de Maunabo	Tertiary-Cretaceous	similar to Sample Number 216

Table 1. (Continued)

SAMPLE	QUADRANGLE	LOCATION	AGE*	ROCK TYPES*
225A	Punta Tuna	Road Number 760 halfway between the mouth of the Rio Maunabo and Puerto Maunabo. (Composite sample)	Tertiary-Cretaceous	Granodiorite and quartz diorite
225B	Punta Tuna	Road Number 760 halfway between the mouth of the Rio Maunabo and Puerto Maunabo (upper 2 cm is black sand)	Tertiary-Cretaceous	similar to Sample Number 225A
226	Punta Tuna	First small valley 500 m northeast of lighthouse at Punta Tuna	Tertiary-Cretaceous	similar to Sample Number 225A
229	Punta Guayanés	Beach, Road Number 901, 300 m south of Punta Quebrada Honda, at the mouth of a small stream (upper 6-7 cm is black sand)	Tertiary-Cretaceous	similar to Sample Number 225A

Table 1. (Continued)

SAMPLE	QUADRANGLE	LOCATION	AGE*	ROCK TYPES*
230	Punta Guayanés	Beach halfway between the mouth of the Rio Guayanés and Playa de Guayanés, northeast of Escuela Eugenio Maria de Hostos	Tertiary-Cretaceous	Granodiorite and quartz diorite
231	Punta Guayanés	At the edge of the water at the mouth of the Rio Humacao (does not agree with map)	Tertiary-Cretaceous	similar to Sample Number 230
233	Punta Guayanés	At former mouth of the Rio Humacao (as shown on map)	Tertiary-Cretaceous	similar to Sample Number 230
234	Humacao	At mouth of small stream	Cretaceous	Volcanics: lava, tuff, breccias, conglomerates with some limestone lenses
237	Naguabo	Beach, on the north bank of the Rio Anton Ruiz near the mouth of the river	Cretaceous	similar to Sample Number 234

Table 1. (Continued)

SAMPLE	QUADRANGLE	LOCATION	AGE*	ROCK TYPES*
238	Naguabo	Beach, on the north bank of the Rio Blanco near the mouth	Cretaceous	Volcanics: lava tuff, breccias, conglomerates with some limestone lenses; small granodioritic-dioritic intrusive at the head of the Rio Blanco
239	Naguabo	Beach, Road Number 3 in the village of Playa de Naguabo	Cretaceous	Volcanics: lava tuff, breccias, conglomerates with some limestone lenses
240	Fajardo	Beach, halfway between two swamps on Road Number 3 and Bahia Demajagua	Cretaceous	similar to Sample Number 239
241	Fajardo	Beach, fine, dark gray sand, 30 m northwest of Club Nautice de Puerto Real, in Playa de Fajardo	Cretaceous	similar to Sample Number 239

Table 1. (Continued)

SAMPLE	QUADRANGLE	LOCATION	AGE*	ROCK TYPES*
242	Fajardo	Road Number 987, halfway between Laguna Aguas Prietas and the southwestern end of Laguna Grande, 20 m from the building called "The Seven Seas"	Cretaceous	Volcanics: lava, tuff, breccias, conglomerates with some limestone lenses
243	Fajardo	Beach, southwest of Punta Embarcadero 100 m west of bathhouse on public beach	Cretaceous	similar to Sample Number 242
244	Carolina	Beach, on the south bank of the Rio Grande de Loiza near the mouth, north of the swamp which is northeast of Loiza Aldea	Cretaceous	similar to Sample Number 242
245	Carolina	Beach, near Boca de Cangrejos, north of Aeropuerto Internacional	Cretaceous	similar to Sample Number 242

Table 1. (Continued)

SAMPLE	QUADRANGLE	LOCATION	AGE*	ROCK TYPES*
42	Barceloneta	Beach, 400 yards west of the mouth of the Rio Grande de Manati, at end of Road Number 684 near La Boca	Tertiary and Cretaceous	primarily limestone with some dolomite and marl. Near the headwaters of the Rio Grande de Manati are some lavas and tuffs
45	Barceloneta	North of Charca La Tembladera, 100 m from the Atlantic Ocean near Road Number 681	Tertiary and Cretaceous	similar to Sample Number 42; also large granodioritic-dioritic intrusive near the headwaters of the Rio Grande de Arecibo

* (after Briggs, 1964)

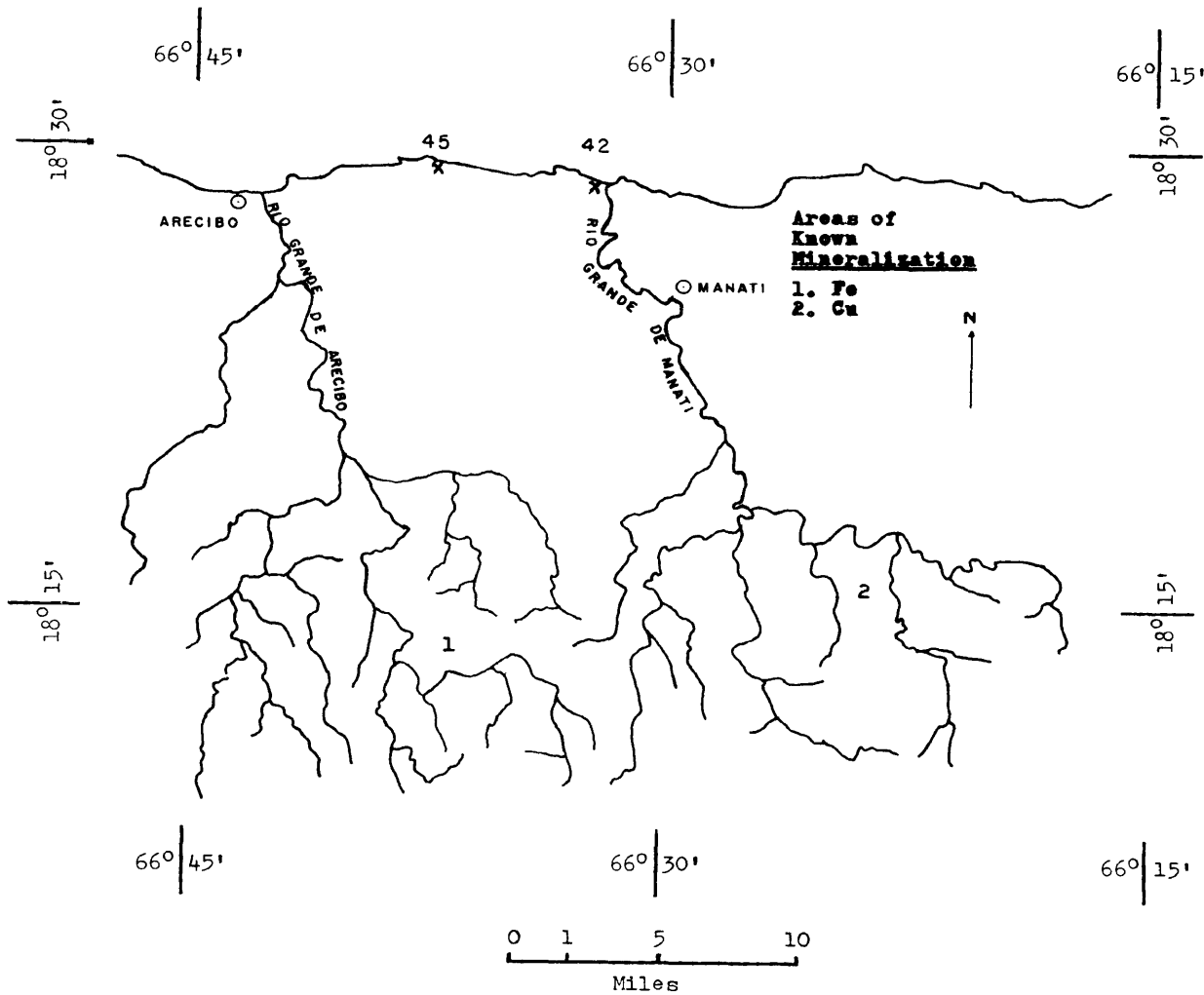


Fig. 2. Map Showing Location of Samples in Area I
(Base Map after Rand McNally, 1964)

II. PREVIOUS WORK

A. General Geology of Puerto Rico

Meyerhoff (1931) presented the most comprehensive treatment of the geology of Puerto Rico to that date. His work was the culmination of 18 years of work by about 20 scientists. The emphasis was placed primarily on the geologic history of the island as well as on the physiographic features.

Recent investigations have done much to clarify the geologic record of the island. Some of the investigations of a general nature are cited below. Kaye (1957) described the structural geology of the sedimentary and volcanic "older complex" which ranges in age from late Cretaceous to late Paleocene or early Eocene and the nonvolcanic middle Tertiary sequence which ranges in age from late Oligocene to late Miocene. Kaye (1956) examined the boundary between the lower Tertiary and the upper Cretaceous on the island. Berryhill, et. al. (1960), described the stratigraphy, sedimentation, and structure of the late Cretaceous rocks in the eastern segment of the island. These and other investigations have culminated in the work by Briggs (1964) assisted by other scientists of the United States Geological Survey, to produce a detailed, provisional geologic map of Puerto Rico. A library search indicated that at the present over 20 geologic maps covering about one-third of the island have been published.

Puerto Rico can be considered to be a somewhat mountainous island, having mountains with altitudes as high as 4400 feet. These mountains extend longitudinally from east coast to west coast. The rocks exposed on the island range in age from lower Cretaceous to Miocene. Heidenreich and Reynolds (1959, p. 4) state that these mountains are composed of "highly folded, faulted, altered, and metamorphosed volcanics, pyroclastics, tuffs, andesites, and sedimentary rocks, such as siltstones, sandstones, and limestones. The oldest rocks are the lower Cretaceous lavas, breccias, tuffs, and intermixed sandstones and siltstones. These volcanics are overlain unconformably in South-Central Puerto Rico by Tertiary, primarily calcareous limestones with interbedded marl, chalk, dolomite, sandstones, shales, and conglomeratic lenses. The Cretaceous and Tertiary rocks were intruded, possibly during Eocene time, by the dioritic San Lorenzo batholith which ranges in composition from gabbro to granodiorite with some quartz diorite and granodiorite stocks to the west.

Around the perimeter of the island are various Miocene to Recent sand, clay, and volcanic-rock-fragment sand deposits mapped as alluvial, landslide, blanket, compound dunes, beach and dune, or swamp and marsh deposits.

Near the sampled area the dominant rock units are the lower Cretaceous lava, lava breccia, tuff, and tuffaceous breccia and the upper Cretaceous unit composed of

tuffaceous sandstone, siltstone, breccia, and conglomerate, lava, and tuff. Also in this area is the Tertiary San Lorenzo batholith.

Three sedimentary formations are exposed inland from the location of samples 42 and 45. These are the Oligocene Lares Limestone, the Miocene Aguada Limestone, and the Aymamon Limestone.

B. Beach Sand Investigations

Investigators have primarily been concerned with the physical characteristics and the heavy mineral assemblages of beach sands.

Kholief, et. al. (1969), investigated sand deposits in the Nile Delta, nearby terraces, and dunes for mechanical and shape analysis, roundness of quartz grains, grain size, and heavy minerals. Jones (1971) made a textural analysis of grain size and sorting, comparing 120 bay samples with 15 beach sand samples taken from the Cardigan Bay, Wales area. Krumbein and Sloss (1963) described a study of beach environment by Miller and Ziegler in which they used trend analysis to study particle size distribution and sorting in the shallow water to foreshore region. Rogers and Adams (1959) studied heavy mineral assemblages and grain size of samples taken from front and back-bar beaches near Galveston, Texas, to determine grain size distribution curves.

Heavy mineral investigations of beach sands have also been published. Hatch, et. al. (1938), described heavy mineral concentrations found at various beaches throughout the world. Pomerancblum (1966) studied heavy mineral assemblages of samples taken from the coast of Israel to determine the source of the sand. Guillou and Glass (1957) made a reconnaissance study of Puerto Rican beach sands in search of economic heavy minerals. In addition, they performed a semi-quantitative spectrographic analysis on some of the sand samples. Pryor and Hester (1969) used beach sand samples and X-ray diffraction to produce "diffraction fingerprints" of heavy mineral groups as a rapid method for provenance and correlation studies. Stone and Siegel (1969) correlated heavy mineral assemblages from continental shelf sediments off the South Carolina coast with previously published data on beach and dune deposits, and coastal plain sediments. Wakeley (1970) used mineral composition and grain size to distinguish a unique beach sand at Rodeo Cove, California.

Other than the above mentioned semi-quantitative spectrographic analysis of Guillou and Glass (1957) very few geochemical investigations of beach sands have been performed.

Mahdavi (1964) determined thorium, uranium, and potassium concentrations of Atlantic and Gulf coast beach sands using a gamma-ray spectrometer. Haglund, et. al. (1969), compared the uranium concentrations of recent carbonate

beach sands with the Pleistocene "analogs" in Bermuda and Israel.

Bolter (1965) determined the gamma-ray radioactivity of the beach sands, investigated in the present study, in the field with a portable gamma-ray spectrometer. He subsequently determined, in the laboratory, the concentrations for uranium, thorium, and potassium oxide in the total sample. These data are listed in Table 2.

Table 2. Beach Sand Radiometric Survey (Bolter 1965)

SAMPLE	FIELD DETERMINATION (cpm)	LABORATORY RESULTS		
		U (ppm)	Th (ppm)	K ₂ O (%)
216	17 x 100	0.60	0.70	0.24
220	17 x 100	0.30	0.16	1.21
221	29 x 100	0.33	0.32	1.61
223	33 x 100	0.50	0.80	1.43
224	28 x 100	0.32	1.22	2.66
225A	38 x 100	3.95	4.83	0.71
225B		4.52	5.18	0.08
226	17 x 100	0.50	0.60	0.56
229	47 x 100	0.80	1.60	0.81
230	55 x 100	3.50	6.09	0.94
231	53 x 100			
233	51 x 100	2.62	5.08	1.98
234	46 x 100	0.64	0.99	2.87
237	28 x 100	1.22	1.83	0.86
238	18 x 100	0.30	0.30	0.95
239	18 x 100	0.73	0.65	0.58
240	13 x 100	0.15	0.20	0.40
241	34 x 100	0.51	0.50	0.60
242	8 x 100	< 0.10	0.16	0.04
243	17 x 100	0.10	0.17	0.10
244	37 x 100	1.90	1.30	2.17
245	21 x 100	1.36	1.82	1.17
42	32 - 39 x 100	0.85	0.50	1.43
45	28 x 100	0.90	0.70	1.25

III. SAMPLES

A. Sample Collection

Twenty-four beach sand samples, taken from along approximately one-half of the coastline of Puerto Rico, were collected in 1964 by Dr. Ernst Bolter as part of a radiometric survey conducted by him. Approximately one kg, from the top 20 cm, was taken from each location shown in Figures 2 and 3.

B. Sample Preparation

1. Heavy Liquid Separation Procedure

All 24 samples, weighing approximately one kg each, were quartered prior to the heavy liquid separation of the light from the heavier minerals.

The method used is a modification of a method suggested by Krumbein and Pettijohn (1938) employing Bromoform, of specific gravity 2.85, as the heavy liquid.

The Bromoform was poured into large (500-2000 ml), separatory funnels. Approximately 50-100 g of sand was then poured into the funnel. The amount of sand used in each funnel was dependent upon the size of the funnel and the concentration of heavy minerals. The sand in the Bromoform was stirred and allowed to stand for several hours to enable the heavy minerals to settle. The heavy minerals were then drawn out by opening the pinch-cock, allowing the heavy minerals to be caught on filter paper placed in a small funnel. The filter paper with the

heavy grains was then dried and the grains were weighed to determine the percentage of heavy minerals in the sample that was separated. The light mineral fraction was then collected by filtering the remaining fraction of the Bromoform.

The total amount of the sample separated was computed by adding together the weights of the two fractions. The percentage of heavy and light minerals was computed from the total weight values obtained and is shown in Table 3.

The light and heavy fractions were ground separately in a Spex Matic Ball Mill to approximately 100 mesh size to aid in dissolution.

2. Solution Procedures

The solution procedure used has been modified somewhat from a procedure for the analysis of silicate rocks published by Belt (1967) and also used by Al-Shaieb (1969, 1972).

One gram of the powdered light fraction was used; depending upon the amount of material available, 1.0 g, 0.5 g, and 0.3 g of the powdered heavy fraction was used.

To the powdered rock in a 30 ml Teflon beaker was added two ml of water, 20 ml of 48 per cent HF, and 10 ml of concentrated HNO_3 . The solution was allowed to stand overnight. Then two ml of 70 per cent HClO_4 were added and fumed until no more white fumes came off. The inside of the beaker was washed with one ml of water and taken

Table 3. Weight (in grams) of Separated Fractions

SAMPLE	TOTAL WEIGHT	HEAVY FRACT	LIGHT FRACT	%HEAVY MIN'LS	%LIGHT MIN'LS
216	48.6220	14.4824	34.1396	29.79	70.21
220	138.3812	9.1702	129.2110	6.63	93.37
221	106.0744	14.7155	91.3589	13.87	86.13
223	60.8612	16.7413	44.1199	27.51	72.49
224	105.0247	13.1592	91.8655	12.53	87.47
225A	81.9461	69.2041	12.7420	84.45	15.55
225B	937.6320	916.7579	20.8741	97.77	2.23
226	114.0892	11.0715	103.0177	9.70	90.30
229	48.8421	15.3073	33.5348	31.34	68.66
230	35.1018	16.9540	18.1478	48.30	51.70
231	60.9747	16.6775	44.2972	27.35	72.65
233	36.1337	13.5055	22.6282	37.38	62.62
234	271.2243	13.6938	257.5305	5.05	94.95
237	35.1905	15.2283	19.9622	43.27	56.73
238	79.2075	11.7330	67.4745	14.81	85.19
239	119.7936	14.7697	105.0239	12.33	87.67
240	206.3144	15.2919	191.0255	7.41	92.59
241	190.5916	14.9294	175.6622	7.83	92.17
242	436.1258	1.4326	434.6932	.33	99.67
243	602.0475	1.8674	600.1801	.31	99.69
244	113.1869	9.4291	103.7578	8.33	91.67
245	149.6523	17.2460	132.4063	11.52	88.48
42	34.9297	18.5375	16.3922	53.07	46.93
45	207.6645	11.2868	196.3777	5.44	94.56

to dryness. The temperature of the beaker was raised slightly, and five ml of concentrated HNO_3 were added. The beaker was covered by a Teflon watch glass and allowed to boil. When all material was dissolved, 10 ml of water was slowly added while boiling. The solution was boiled until clear and transferred to a 50 ml volumetric flask. The solution was cooled, brought to volume, then transferred to polyethelene bottles for storage.

IV. ANALYTICAL METHOD

A. Atomic Absorption Analysis

1. Reagents

All reagents used were analytical grade chemicals. A five per cent Lanthanum solution was made by dissolving 58.67 g of Lanthanum oxide in 250 ml of concentrated HCl and diluting it with distilled water to one liter.

Water used to make the solutions was obtained from the demineralized water in the University's reactor pool. It was further distilled by using a Barnstead Water Distiller to insure purity.

2. Sample Dilutions

a. Heavy Fraction

The original aqueous solution was used for the analysis of lead, copper, zinc, potassium, and sodium. For some elements, dilution was necessary.

Dilutions were made by taking a one ml aliquot of the sample solution and adding specified amounts of distilled water. A dilution of one ml in 75 ml was required for manganese and iron. Some of the samples to be analyzed for iron needed additional dilution of one ml in 25 ml. The same one ml in 75 ml dilution was used for magnesium and calcium. An additional dilution of one ml in 25 ml was required for some samples to bring them within the working range. A one ml in 20 ml dilution was necessary for strontium, while aluminum required a one

ml in 26.2 ml dilution.

Final solutions analyzed for calcium, magnesium, strontium, and aluminum were made to contain one per cent Lanthanum to suppress interference.

b. Light Fraction

The original aqueous solution was used for the analysis of lead, copper, zinc, manganese, iron, potassium, and sodium.

The original solution was diluted one ml in 50 ml for calcium and magnesium. An additional dilution of one ml in 10 ml was required for some samples analyzed for magnesium. A one ml in 25 ml dilution was required for strontium analysis. A one ml in 26.2 ml was required for aluminum analysis.

Final solutions analyzed for calcium, magnesium, strontium, and aluminum were made to contain one per cent Lanthanum in order to suppress interference.

3. Standards

Fisher Scientific Company Atomic Absorption Standards, 1000 ppm was used to make copper, lead, zinc, iron, manganese, strontium, and magnesium standards.

The sodium and potassium standards were made from reagent grade chloride salts. Chemically-pure aluminum wire was used to make a 1000 ppm aluminum standard. Reagent grade calcium carbonate was used for the calcium standard.

A 100 ppm copper, lead, and zinc commercial stock solution was diluted to concentrations of .25, .50, 1.0, 1.5, 2.0, 3.0, 4.0, and 5.0 ppm and used for both fractions. The 1000 ppm iron stock solution was diluted to 10, 20, 100, 300, and 500 ppm for the light mineral samples and to 2, 5, 7, 10, 12, 15, and 20 ppm for the heavy mineral samples. The 1000 ppm manganese stock solution was diluted to 1, 2, 5, 10, and 30 ppm for the light samples and to .5, 1.0, 1.5, 2.0, 5.0, and 7.0 ppm for the heavy samples. The 1000 ppm aluminum stock solution was diluted to 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, and 150 ppm for both the light and heavy samples. The 1000 ppm sodium stock solution was diluted to 50, 100, 200, 300, 400, and 500 ppm for the analysis of the light and heavy samples. The 1000 ppm potassium stock solution was diluted to 5, 9, 10, 15, 20, 30, 40, 50, 60, 70, 80, 90, and 100 ppm for the heavy and for a few of the light samples. The dilution range was extended to 200, 400, and 600 ppm for most of the light samples. The 1000 ppm magnesium stock solution was diluted to 0.5, 0.8, 1.0, 1.5, 2.0, 3.5, 5.0, 7.0, 10.0, 15.0, and 20.0 ppm for both fractions. The 1000 ppm calcium stock solution was diluted to 0.1, 0.2, 0.5, 1.0, 1.5, 2.0, 3.5, 5.0, and 7.0 ppm for the heavy samples. The dilution range was extended to 10, 15, 20, and 30 ppm for the light samples. The 1000 ppm strontium stock solution was diluted to 0.05, 0.10, 0.20,

0.50, 0.80, 1.00, and 1.50 ppm for the heavy samples. The dilution range was extended to 2.0, 3.0, and 5.0 ppm for the light samples.

A sufficient amount of the five per cent Lanthanum solution was added to the final dilutions of the calcium, magnesium, strontium, and aluminum standards for a one per cent concentration of Lanthanum in each standard.

The acid content of the samples was carefully matched in the standards.

4. Instrumentation

A Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer equipped with a Perkin-Elmer Recorder Readout Accessory Model DCR-1 and a Texas Instrument Servo-riter II Strip-Chart Recorder were used for the analysis of copper, lead, zinc, iron, manganese, magnesium, aluminum, strontium, calcium, and sodium. The availability of lamps in the lab determined the elements to be analyzed. All the lamps used were of the single element, hollow-cathode design except the calcium-magnesium lamp which was a multi-element, hollow-cathode lamp. A triple-slot burner was used with an air-acetylene flame. A nitrous oxide burner was used with a nitrous oxide-acetylene flame for the analysis of aluminum. The Deuterium Arc Accessory was used for the lead analysis. The instrument settings used were the same as those given in the Perkin-Elmer handbook (1964). Secondary analytical lines,

however, were used for the sodium (3303 \AA) and the potassium (4044 \AA) analysis. The burner was turned 90° for the zinc heavy fraction, the manganese light fraction, the iron light fraction, and the magnesium heavy and light fraction analyses.

5. Chemical Interferences

Nitric acid content of the samples was adjusted to the acid concentrations in the standards.

a. Determination of Copper, Lead, and Zinc

It was decided to test the effect of 1000, 2400, and 6000 ppm in solution of calcium, sodium, and potassium upon copper, lead, and zinc. The range was chosen because it reflects the values previously obtained from calcium, sodium, and potassium determinations. Each of the ten volumetric flasks which were used contained 1 ppm of the copper, lead, and zinc solution. Three of the flasks contained 1000, 2400, and 6000 ppm of calcium; likewise for sodium and potassium. The remaining flask, containing only the stock solution, served as the standard. An air-acetylene flame with a triple-slot burner and instrument settings given in the Perkin-Elmer handbook were used. Samples were recorded at scale expansions of 3x and 10x on the chart recorder. No significant enhancement or depression was shown for calcium, sodium, or potassium on copper or zinc. Sodium and potassium also had no effect

on lead. Due to the high calcium content, however, the effect of calcium on lead at a scale expansion of 10x showed a 14%, 18%, and 33% enhancement, respectively. The enhancement effect was eliminated by the use of the Deuterium Arc Accessory.

b. Determination of Iron and Manganese

According to Belt (1967) and others, no interferences have been reported as long as the standards contained the same acid concentrations as in the samples.

c. Determination of Calcium, Magnesium, and Strontium

The Perkin-Elmer handbook, Belt (1967), Medlin, et. al. (1969), Langmyhr and Paus (1968), Trent and Slavin (1964), Billings and Adams (1964), and many others advocated the addition of one per cent Lanthanum solution to samples and standards to suppress the interference of the silicate, alumina, and phosphate anions.

d. Determination of Sodium and Potassium

It was decided to test the effect of sodium and potassium upon each other. Six standards were made to contain 50 ppm sodium, 100 ppm potassium; 100 ppm sodium, 200 ppm potassium; 200 ppm sodium, 400 ppm potassium; 300 ppm sodium, 600 ppm potassium; 400 ppm sodium, 800 ppm potassium; and 500 ppm sodium, 1000 ppm potassium. This

analytical range was chosen because it best reflected the chemical and mineralogical nature of the samples. Six standards in the same range were then made containing no potassium, and six were made containing no sodium. An air-acetylene flame with a triple-slot burner was used. Instrument settings were the secondary 3303^o Å line of sodium and a 1x scale expansion. Potassium showed no significant enhancement or depression effects upon the sodium.

The secondary 4044^o Å line with a scale expansion of 3x was used to analyze for potassium. Under these conditions, sodium showed no significant enhancement or depression effects upon the potassium.

e. Determination of Aluminum

Van Loon (1968), using a HF-H₂SO₄-HCl dissolution technique for the determination of aluminum in high silica materials, recommended the addition of one per cent Lanthanum in acid solutions. For the analysis of silicates, Medlin et. al. (1969), employing a LiBO₂ fusion technique and HNO₃ as the dissolving solution, analyzed aluminum, silicon, calcium, magnesium, iron, and manganese in the same dilute solution containing one per cent Lanthanum. They reported no difficulty in the determinations of aluminum; therefore, one per cent Lanthanum was added to samples and standards analyzed for aluminum.

B. X-Ray Analysis

1. X-Ray Fluorescence Analysis

An X-ray fluorescence method was used to determine strontium, titanium, and zirconium in the heavy fraction only. The semi-quantitative method used was suggested by Dr. S. Kerry Grant, Department of Geology and Geophysics of the University of Missouri-Rolla.

Approximately 0.5 g of each ground heavy mineral fraction sample was placed in a three piece cap-plug assembly. The open top was covered by a thin film of Mylar plastic to prevent loss of the sample; however, the film still allowed the X-rays to penetrate the sample. A General Electric X-Ray XRD/S 5 was operated at 40 Kv, 20 ma, and from 14° to 90° on the spectrometer scale for the analyses. A lithium fluoride crystal and scintillation counter were mounted on the spectrometer. A permanent record was made by the automatic chart ratemeter. Ilmenite and zirconium oxide standards were made similar to the samples. The strontium atomic absorption value of sample number 240, heavy mineral fraction, was also used as a standard. This sample contains the greatest amount of strontium.

2. X-Ray Diffraction Analysis

The same instrument was then used for diffraction. The samples were mounted on glass slides, analyzed at 35 Kv, 15 ma, and from 10° to 80° on the diffractometer scale.

The primary mineral matrix was identified from the peaks recorded on the chart. The matrices found were: magnetite, amphibole, and epidote.

3. Method for Calculating Concentration

The method and basic equation used for computing the concentrations of strontium, zirconium, and titanium in the samples is given by Liebhofsky, et. al. (1960), as:

$$I_E^S = \frac{W_E^S I_E^E a^E}{a^S} \quad (A)$$

where,

I_E^S = intensity of the element in the sample

W_E^S = weight fraction of the element in the sample

I_E^E = intensity of the pure element

a^E = absorption of the pure element

a^S = absorption of the sample matrix

The absorption of the sample, a^S , is calculated from:

$$a^S = 1.155 \mu_{1_{total}} + 2.00 \mu_{2_{total}} \quad (B)$$

where $\mu_{1_{total}}$ and $\mu_{2_{total}}$ are the mass absorption

coefficients of the incident wavelength and the characteristic wavelength respectively. $\mu_{1_{total}}$ and $\mu_{2_{total}}$ may be

calculated as exemplified by equations (C) and (D), representing the calculation of titanium in amphibole using the main absorbing chemical constituents silicon, aluminum, iron, and sodium.

$$\mu_{1_{\text{total}}} = \mu_{1_{\text{Si}}} (W_{\text{Si}}) + \mu_{1_{\text{Al}}} (W_{\text{Al}}) + \mu_{1_{\text{Fe}}} (W_{\text{Fe}}) + \mu_{1_{\text{Na}}} (W_{\text{Na}}) \quad (\text{C})$$

$$\mu_{2_{\text{total}}} = \mu_{2_{\text{Si}}} (W_{\text{Si}}) + \mu_{2_{\text{Al}}} (W_{\text{Al}}) + \mu_{2_{\text{Fe}}} (W_{\text{Fe}}) + \mu_{2_{\text{Na}}} (W_{\text{Na}}) \quad (\text{D})$$

where,

W_{Si} = weight fraction in per cent
of Si in the mineral

Thus, equation (A) is simplified to solve for the weight fraction of a particular element in one matrix. For example,

$$W_{\text{Ti}}^{\text{S}} = I^{\text{S}} \times K$$

where,

W_{Ti}^{S} = weight fraction expressed as ppm or per cent of Ti in any particular sample

I_{E}^{S} = intensity in counts per second read from the Ti peak on the chart for that sample

K = a calculated number that is constant for Ti in a particular matrix

V. MINERALOGY

Guillou and Glass (1957) made a reconnaissance study of the beach sands of Puerto Rico in which they sampled beach sands from 43 sampling stations, representing approximately 95 per cent of the coastline of the island.

According to their study, they found that magnetite is the most abundant heavy mineral and that it occurs on all shores of the island. Ilmenite, associated with magnetite, is present also. Chromite occurs only on the west coast near Mayaguez. Sphene is a widely distributed minor constituent and zircon is rare.

The "heavy mineral" samples of the author's study were separated magnetically for ease of identification, first with a hand magnet, and then the balance of each sample was passed through a Frantz Isodynamic Magnetic Separator according to the method of Muller (1967) after Hess (1959). Each one of the magnetically separated "heavy mineral" groups as well as the "light mineral" fraction of each sample was then studied microscopically to determine the individual minerals that were present.

Since the primary intention of the present investigation was directed towards the chemical composition of beach sands, no definite mineralogical percentages were determined either by grain counting or by being based upon the weight percentage of each mineral present. A definite and generally uniform mineral assemblage can be observed in the 24 samples studied, however. Magnetite

is present in varying amounts in all the samples, and is especially abundant in samples 225A, 225B, 229, and 230. Ilmenite and amphiboles are also present in all the samples. Hornblende is the most common amphibole occurring in all the samples. Other amphiboles present in some samples are tremolite and actinolite. Zircon, garnet, chlorite, apatite, and epidote are present in small quantities in 80 per cent of the samples. Staurolite and rutile grains are present in about 75 per cent of the samples, while tourmaline and cassiterite grains occur in small quantities in approximately 50 per cent of the samples. Twenty-five per cent of the samples contain minute quantities of beryl and spinel. A few grains of biotite and muscovite occur in less than five samples. Only a few grains of limonite, pyrite, and pyrrhotite can be found in the following samples: 220, 240, and 245, respectively. Aragonitic shell fragments occur as a minor constituent in all the samples.

All of the "light mineral" samples consist predominantly of quartz. Plagioclase is the prevalent feldspar. Calcareous shell fragments are common in all the samples. Phlogopite occurs in most of the samples as a minor accessory mineral.

Table 4 shows the occurrence of heavy minerals in each sample.

Table 4. Distribution of Heavy Minerals in the Sampled Beach Sands

	Hornblende	Magnetite	Ilmenite	Olivine	Garnet	Chlorite	Epidote	Hypersthene	Tremolite	Actinolite	Tourmaline	Staurolite	Diopside	Apatite	Zircon	Cassiterite	Rutile	Beryl	Limonite	Phlogopite	Biotite	Muscovite	Spinel	Pyrite	Pyrrhotite
216	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X							
220	X	X	X	X	X	X	X		X	X		X	X		X		X		X	X					
221	X	X	X	X	X	X		X	X	X	X		X	X	X	X									
223	X	X	X	X	X	X		X	X	X	X		X	X	X	X	X								
224	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X								
225A	X	X	X	X			X		X	X		X			X	X	X				X				
225B	X	X	X	X			X	X	X		X	X	X	X	X	X	X				X		X		
226	X	X	X	X	X	X	X	X	X	X	X	X	X		X	X	X				X				
229	X	X	X	X	X			X	X		X		X	X	X	X	X						X		
230	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X						X		
231	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X							X	
233	X	X	X	X	X	X	X	X	X	X	X	X		X	X	X									

Table 4. (Continued)

	Hornblende	Magnetite	Ilmenite	Olivine	Garnet	Chlorite	Epidote	Hypersthene	Tremolite	Actinolite	Tourmaline	Staurolite	Diopside	Apatite	Zircon	Cassiterite	Rutile	Beryl	Limonite	Phlogopite	Biotite	Muscovite	Spinel	Pyrite	Pyrrhotite
234	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X					X				
237	X	X	X	X	X	X	X	X	X	X	X		X		X	X	X	X					X		
238	X	X	X	X	X	X	X	X	X	X	X	X		X	X	X	X	X							
239	X	X	X	X	X	X	X	X	X	X		X	X	X		X									
240	X	X	X	X		X	X	X	X	X			X	X	X		X							X	
241	X	X	X	X	X	X	X	X		X			X	X								X			
242	X	X	X	X	X	X	X	X					X	X											
243	X	X	X	X	X	X	X	X				X	X	X	X										
244	X	X	X	X	X	X	X	X	X	X		X	X	X	X		X						X		
245	X	X	X	X	X	X	X	X	X	X		X	X	X	X	X	X	X							X
42	X	X	X	X	X	X	X	X	X	X		X	X	X	X	X	X	X							
45	X	X	X	X	X	X	X	X	X	X		X	X	X		X	X	X							

VI. RESULTS AND DISCUSSION OF RESULTS

A. Results of Analysis

1. Results of Atomic Absorption Analysis

As was previously mentioned, copper, lead, zinc, iron, manganese, sodium, potassium, manganese, calcium, and aluminum were analyzed in the heavy and light mineral fractions by atomic absorption spectrophotometry. The results of the light mineral fraction analyses are presented in Table 5. The results of the heavy mineral fraction analyses are presented in Table 6.

Although lead was analyzed in both the light and heavy mineral fractions, no reliable lead values are given due to the extremely low lead concentration. In more than half of the heavy mineral fraction and three-fourths of the light mineral fraction, the concentration was less than 20 ppm. Apparently anomalous values in the heavy mineral fraction are sample 223 (85 ppm), sample 239 (40 ppm), and sample 242 (130 ppm). Apparently anomalous values in the light mineral fraction are sample 230 (43 ppm), sample 238 (65 ppm), and sample 243 (63 ppm).

2. Results of X-Ray Fluorescence Analysis

The results of the X-ray fluorescence analysis are given in Table 7. There is close agreement between the X-ray and atomic absorption values of strontium for all three matrices. The titanium ($\text{Ti}_{K\alpha}^{2.75 \text{ \AA}}$) X-ray values

Table 5. Results of Light Mineral Fraction Analysis by Atomic Absorption

SAMPLE	Cu (ppm)	Zn (ppm)	Mn (ppm)	Sr (ppm)	Fe (%)	Al (%)	Mg (%)	Na (%)	K (%)	Ca (%)
216	7.5	18.0	225.0	750.0	.90	2.49	.53	1.40	.18	7.25
220	13.0	25.0	288.0	813.0	1.23	5.11	.60	2.38	1.00	3.75
221	9.0	15.0	143.0	375.0	.73	5.70	.24	2.28	1.30	1.28
223	31.0	17.5	200.0	250.0	1.03	4.45	.21	1.85	1.23	.90
224	12.5	15.5	212.0	250.0	.96	4.85	.23	2.08	1.45	.90
225A	12.0	15.5	220.0	363.0	1.15	4.32	.30	1.75	.95	1.75
225B	12.0	17.5	200.0	475.0	1.05	4.85	.35	2.08	.98	2.38
226	6.5	10.0	200.0	1638.0	.63	2.62	1.43	1.43	.41	14.50
229	8.0	8.5	200.0	688.0	.73	4.32	.54	1.90	.88	4.45
230	10.0	12.5	212.0	813.0	.78	4.85	.35	1.80	1.68	3.63
231	14.5	13.5	200.0	363.0	.75	4.59	.13	1.68	1.83	.83
233	10.5	15.0	200.0	363.0	.83	4.45	.15	1.58	1.80	.88

Table 5. (Continued)

SAMPLE	Cu (ppm)	Zn (ppm)	Mn (ppm)	Sr (ppm)	Fe (%)	Al (%)	Mg (%)	Na (%)	K (%)	Ca (%)
234	8.0	17.5	220.0	438.0	.75	4.45	.16	1.68	2.10	1.00
237	11.5	20.0	225.0	375.0	1.05	4.19	.31	1.63	1.03	1.50
238	12.5	18.0	275.0	475.0	1.23	3.93	.30	1.58	.75	1.75
239	18.5	52.5	375.0	2188.0	1.53	4.06	.75	2.28	.48	11.25
240	18.5	17.5	175.0	563.0	.93	1.64	.31	1.03	.31	3.13
241	31.0	49.5	275.0	313.0	2.00	3.28	.43	1.50	.44	1.45
242	6.5	12.0	108.0	3413.0	.31	.30	2.00	.48	.04	27.50
243	14.5	10.5	278.0	2625.0	.46	.43	2.50	1.03	.07	24.50
244	11.0	15.0	212.0	363.0	.90	4.59	.30	1.65	1.73	1.43
245	7.5	10.0	138.0	875.0	.40	1.51	.95	.70	.70	8.25
42	44.5	49.5	837.0	406.0	3.22	7.07	1.43	2.40	1.73	2.58
45	17.5	24.0	350.0	1438.0	1.58	3.28	2.25	1.23	.66	15.75

Table 6. Results of Heavy Mineral Fraction Analysis by Atomic Absorption

SAMPLE	Cu (ppm)	Zn (ppm)	Sr (ppm)	Mn (%)	Fe (%)	Al (%)	Mg (%)	Na (%)	K (%)	Ca (%)
216	25.0	100.0	680.0	.38	10.88	8.65	1.35	.65	.14	14.06
220	33.0	120.0	480.0	.19	6.00	9.37	1.43	1.05	.15	10.78
221	32.0	180.0	330.0	.39	20.63	5.83	3.83	1.03	.31	9.84
223	45.5	180.0	420.0	.33	13.13	6.68	3.68	1.03	.33	10.78
224	28.0	107.5	435.0	.31	11.25	6.68	3.60	1.13	.42	9.84
225A	23.0	290.0	220.0	.72	41.25	3.67	2.02	.33	.17	6.56
225B	21.0	375.0	40.0	.81	56.25	.66	.45	.22	.05	1.22
226	62.0	70.0	880.0	.23	9.38	8.65	2.70	1.18	.25	12.66
229	21.0	175.0	140.0	.30	63.00	1.30	.42	.24	.05	2.63
230	41.0	200.0	70.0	.56	50.63	1.13	1.72	.27	.13	3.51
231	28.5	132.5	370.0	.41	27.19	4.59	2.81	.45	.25	8.91
233	44.2	166.7	266.7	.46	37.50	5.02	2.00	.45	.26	6.25

Table 6. (Continued)

SAMPLE	Cu (ppm)	Zn (ppm)	Sr (ppm)	Mn (%)	Fe (%)	Al (%)	Mg (%)	Na (%)	K (%)	Ca (%)
234	24.5	132.5	620.0	.38	11.25	7.60	3.90	.13	.38	11.72
237	19.0	125.0	300.0	.44	11.70	6.03	5.55	.67	.23	12.19
238	18.5	112.5	380.0	.36	13.13	5.96	5.33	.88	.22	11.25
239	45.0	128.3	1379.4	.27	10.69	8.21	1.80	.71	.19	16.03
240	44.9	51.0	1713.6	.19	6.20	10.16	.77	.56	.22	14.34
241	59.4	110.0	1166.0	.24	7.43	9.22	1.56	.55	.20	14.44
242	115.0	300.0	1020.0	.25	11.33	3.01	3.30	.40	.10	20.63
243	33.1	114.0	1003.2	.28	6.75	3.14	4.28	.57	.13	60.92
244	35.0	125.0	500.0	.35	12.30	7.07	3.15	.75	.30	10.31
245	36.7	108.3	766.7	.41	11.25	8.73	1.75	.58	.21	14.06
42	30.1	127.5	336.6	.19	19.13	3.88	4.97	.41	.15	13.87
45	29.1	65.0	894.4	.14	6.16	5.04	4.06	.83	.38	13.65

Table 7. Results of X-Ray Fluorescence Analysis

SAMPLE	MINERAL MATRIX	Sr (ppm)	Zr (ppm)	Ti (%)
216	magnetite	518	1780	.93
220	epidote	436	151	.43
221	magnetite	275	1610	.72
223	amphibole	418	210	.46
224	amphibole	613	190	.37
225A	magnetite	101	5390	3.23
225B	magnetite	23	7890	4.58
226	epidote	813	261	.57
229	magnetite	115	2420	.65
230	magnetite	92	3959	1.29
231	amphibole	267	360	2.14
233	amphibole	252	509	1.44
234	amphibole	634	169	1.43
237	amphibole	490	706	.76
238	amphibole	375	149	.41
239	epidote	1351	370	.71
240	epidote	1711	nd.*	.40
241	epidote	995	nd.	.71
242	epidote	1101	nd.	.28
243	epidote	805	nd.	.43
244	amphibole	577	nd.	.80
245	epidote	623	930	1.56
42	magnetite	321	562	.95
45	amphibole	1464	nd.	.32

*nd.: Zr peak not determinable

given should be reasonably accurate even though titanium is not as sensitive as the other elements, since its peak occurs in the large Angstrom region. Zirconium ($Zr_{K\alpha} .78 \overset{\circ}{\text{A}}$) X-ray values, like strontium ($Sr_{K\alpha} .87 \overset{\circ}{\text{A}}$), should be accurate. The intensity in counts per second of the zirconium peak which affects the concentration has been corrected, however, to compensate for the nearness of the zirconium ($Zr_{K\beta_1} .78588 \overset{\circ}{\text{A}}$) to the strontium ($Sr_{K\beta_1} .78288 \overset{\circ}{\text{A}}$) peak.

3. Precision of Analysis

A comparison of the strontium values as determined by X-ray fluorescence and atomic absorption analysis was previously mentioned.

Al-Shaieb (1969, 1972) used the silicate dissolution technique of Belt (1967) and atomic absorption for the analysis of granodiorite and other types of rock. His calculated average per cent of the coefficient of variation for the elements analyzed appears in Table 8. Essentially similar analytic conditions were used under the supervision of Dr. Al-Shaieb for this present investigation.

B. Discussion of Results

The 24 beach sand samples can be divided into three sample groups. These groups are based upon the nature of

Table 8. Precision of Analysis (after Al-Shaieb 1972)

ELEMENT	AVERAGE PER CENT COEFFICIENT OF VARIATION
Cu	3.5
Pb	6.2
Zn	1.5
Mn	2.4
Na	10.0
K	4.3
Ca	4.8
Mg	6.5
Fe	4.0
Al	5.0

the source rock that has been subjected to weathering processes within the drainage basins of rivers or streams. Group I, consisting of samples 216-233, is from Area II as shown in Figure 3. The beach sands in this group are derived primarily from the granodioritic San Lorenzo batholith. Group II beach sand samples, 234 to 245 also from Area II, are derived primarily from Cretaceous volcanics. Group III, consisting of samples 42 and 45, is from Area I as shown in Figure 2. These two samples are derived primarily from Tertiary limestones.

The analyses of samples 42 and 45 for iron, titanium, copper, zinc, manganese, zirconium, magnesium, calcium, and strontium are similar to the semi-quantitative spectrographic analyses by Guillou and Glass (1957) of samples taken from part of the northwestern coastline of the island.

Even though Group I contains only 12 samples and Group II contains only 10 samples, certain trends and apparent anomalous values are evident. Tables 9 and 10 present the range, median values, mode (the value occurring with the greatest frequency), and the estimated background for the elements analyzed in the heavy mineral fraction.

It is apparent that for the value of the estimated background to be statistically valid, more samples would have to be collected from each area. Nevertheless, the

Table 9. Statistical Data of Group I, Samples 216-233
Heavy Mineral Fraction

ELEMENT	RANGE (ppm)		MEDIAN (ppm)	ESTIMATED BACKGROUND	MODE (ppm)
	LOW	HIGH			
Cu	21	62	33	30	20- 30
Zn	70	375	174	180	100- 180
Zr	151	7890	2086	1000	151-1000
Sr	40	880	361	400	401- 500

ELEMENT	RANGE (%)		MEDIAN (%)	ESTIMATED BACKGROUND	MODE (%)
	LOW	HIGH			
Fe	6.00	63.00	28.92	21.00	11.00-20.00
Mn	.19	.81	.42	.40	.31- .40
Al	.66	9.37	5.19	5.20	5.01- 7.00
Mg	.42	3.83	2.17	2.00	1.01- 2.00
Na	.22	1.18	.67	.45	.22- .50
K	.05	.42	.21	.20	.11- .20
Ca	1.22	14.06	8.09	10.00	9.00-11.00
Ti	.37	4.58	1.40	1.40	.37- 1.00

Table 10. Statistical Data of Group II, Samples 234-245
Heavy Mineral Fraction

ELEMENT	RANGE (ppm)		MEDIAN (ppm)	ESTIMATED BACKGROUND	MODE (ppm)
	LOW	HIGH			
Cu	18.5	115.0	43.11	45	31- 40
Zn	51.0	300.0	130.66	135	121-130
Zr	149.0	930.0	480.75	706	0-100
Sr	300.0	1713.6	884.89	800	300-500

ELEMENT	RANGE (%)		MEDIAN (%)	ESTIMATED BACKGROUND	MODE (%)
	LOW	HIGH			
Fe	6.20	13.13	10.203	13.13	11.01-12.00
Mn	.19	.44	.317	.44	.21- .30
Al	3.01	10.16	6.913	8.00	7.01- 9.00
Mg	.77	5.55	3.139	3.50	0- 2.00
Na	.13	.88	.58	.60	.51- .60
K	.10	.38	.218	.25	.21- .30
Ca	11.25	60.92	18.58	16.03	14.01-15.00
Ti	.28	1.56	.75	.80	.61- .80

samples analyzed serve the purpose of a preliminary geochemical reconnaissance study in that the geochemical trend and apparently anomalous values for each element are indicated for Groups I and II. Further investigations could, of course, center around the high values determined by this investigation.

Figures 4, 5, and 6 show the distribution of iron and manganese, titanium and zirconium, and copper and zinc in the heavy mineral fraction of the Group I samples, 216-233. Iron, manganese, titanium, and zirconium correlate well with each other, from sample to sample, and generally with the percentage of heavy minerals in each sample, Figure 7. Zinc correlates somewhat with iron, manganese, titanium, and zirconium. Copper seems to vary independently of the other elements, except in samples 229, 230, 231, and 233, where the trend is similar to zinc, manganese, and zirconium. Figure 8 illustrates that even though uranium and thorium were analyzed in the total sample rather than in the heavy mineral fraction, they correlate well with iron, manganese, titanium, and zirconium, and fairly well with zinc from sample to sample.

Figures 9, 10, and 11 show the distribution of iron and manganese, titanium and zirconium, copper and zinc in the heavy mineral fraction of the Group II samples. These elements do not correlate as well with each other or with the percentage of heavy minerals, from sample to sample, as

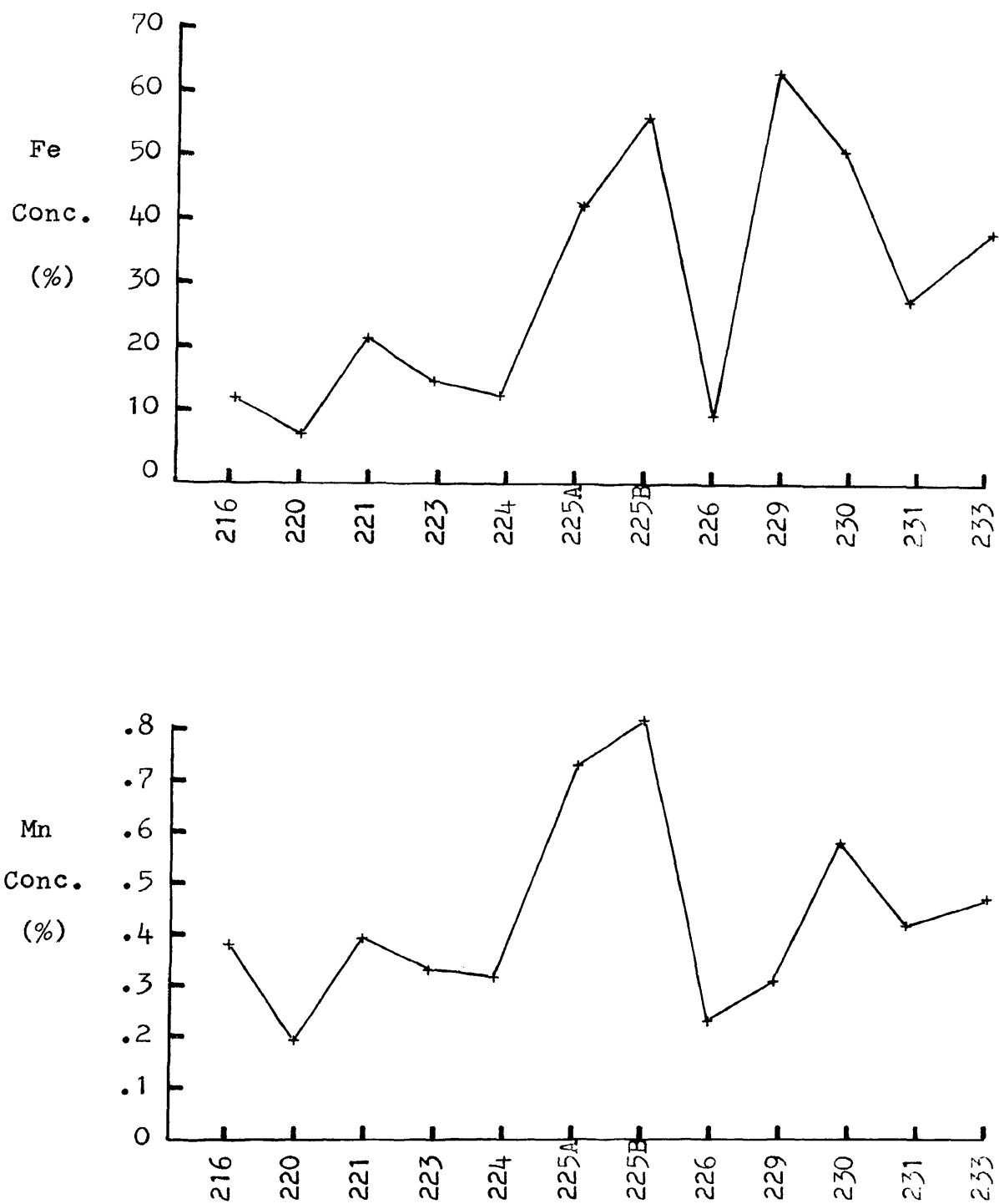


Fig. 4. Distribution of Fe and Mn, Group I, Heavy Mineral Fraction

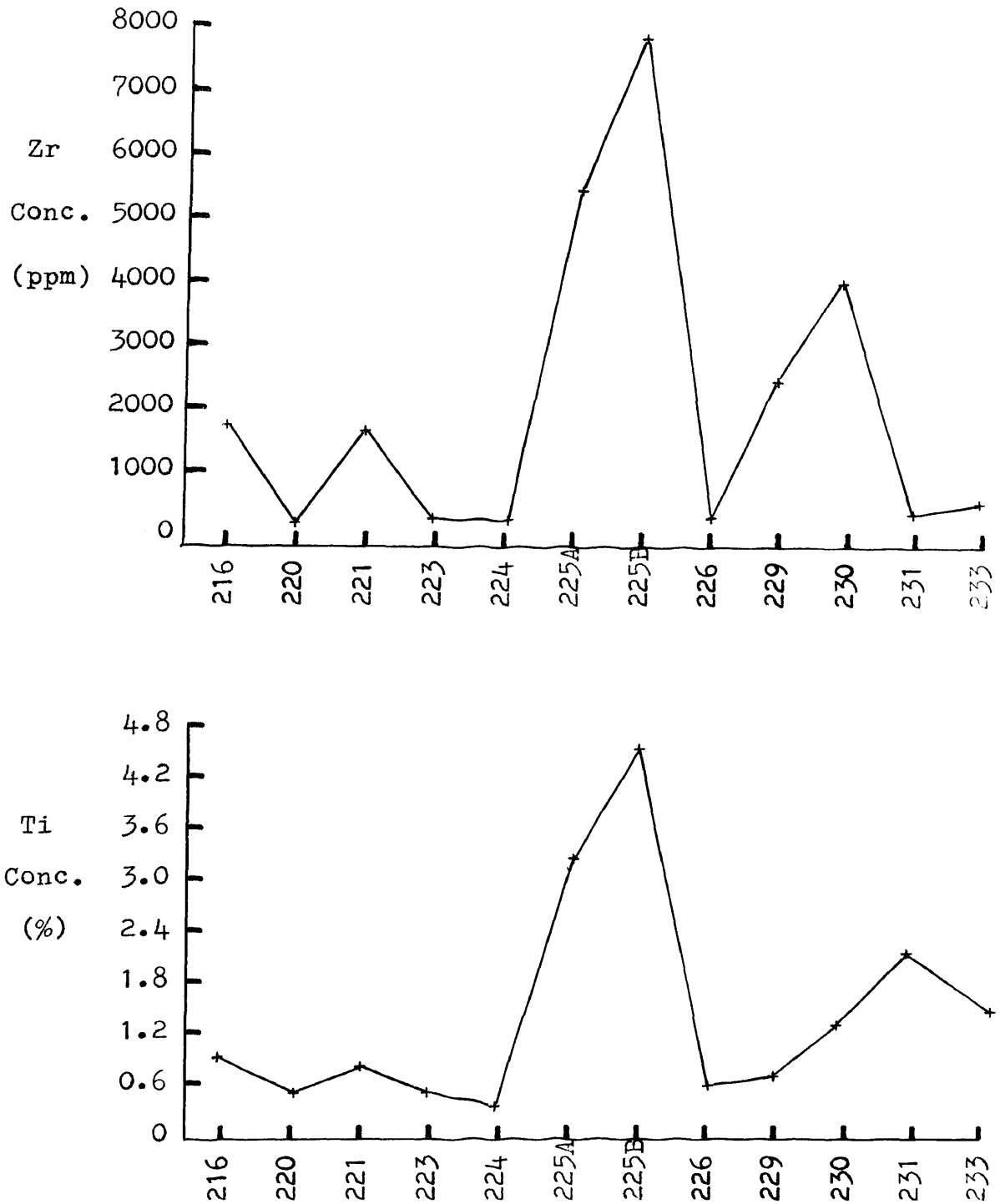


Fig. 5. Distribution of Zr and Ti, Group I, Heavy Mineral Fraction

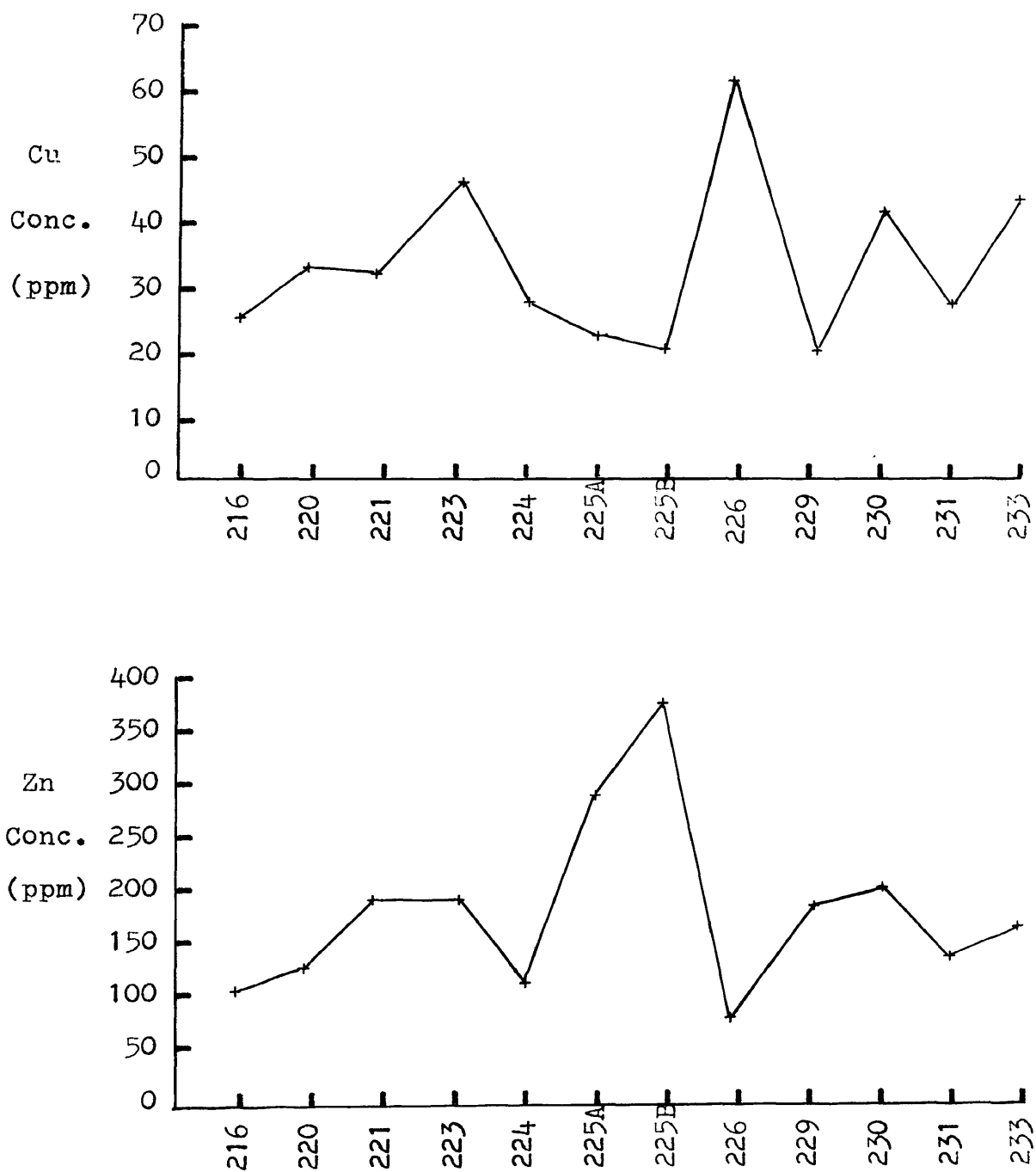


Fig. 6. Distribution of Cu and Zn, Group I, Heavy Mineral Fraction

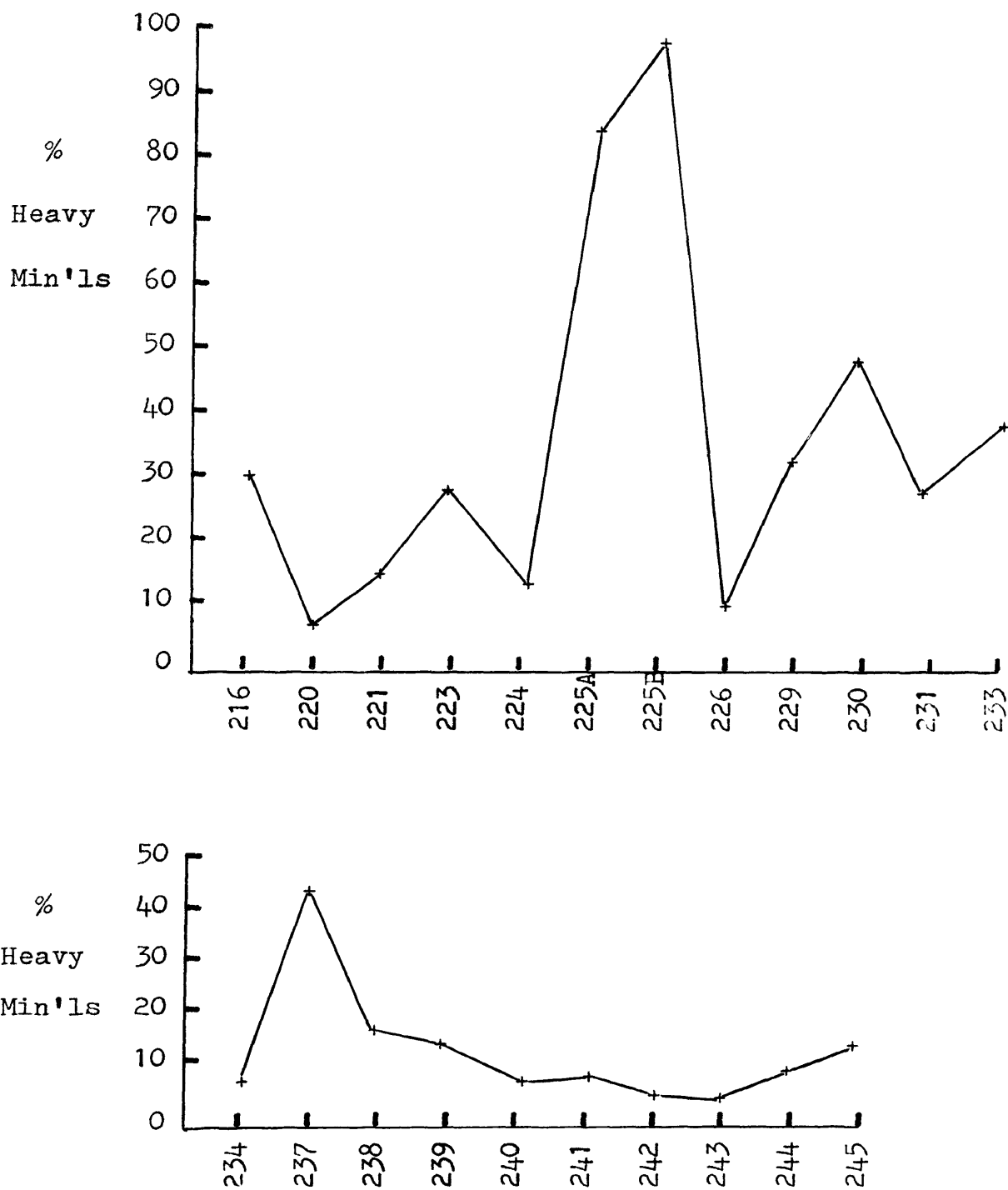


Fig. 7. Distribution of Percent Heavy Minerals in Groups I and II

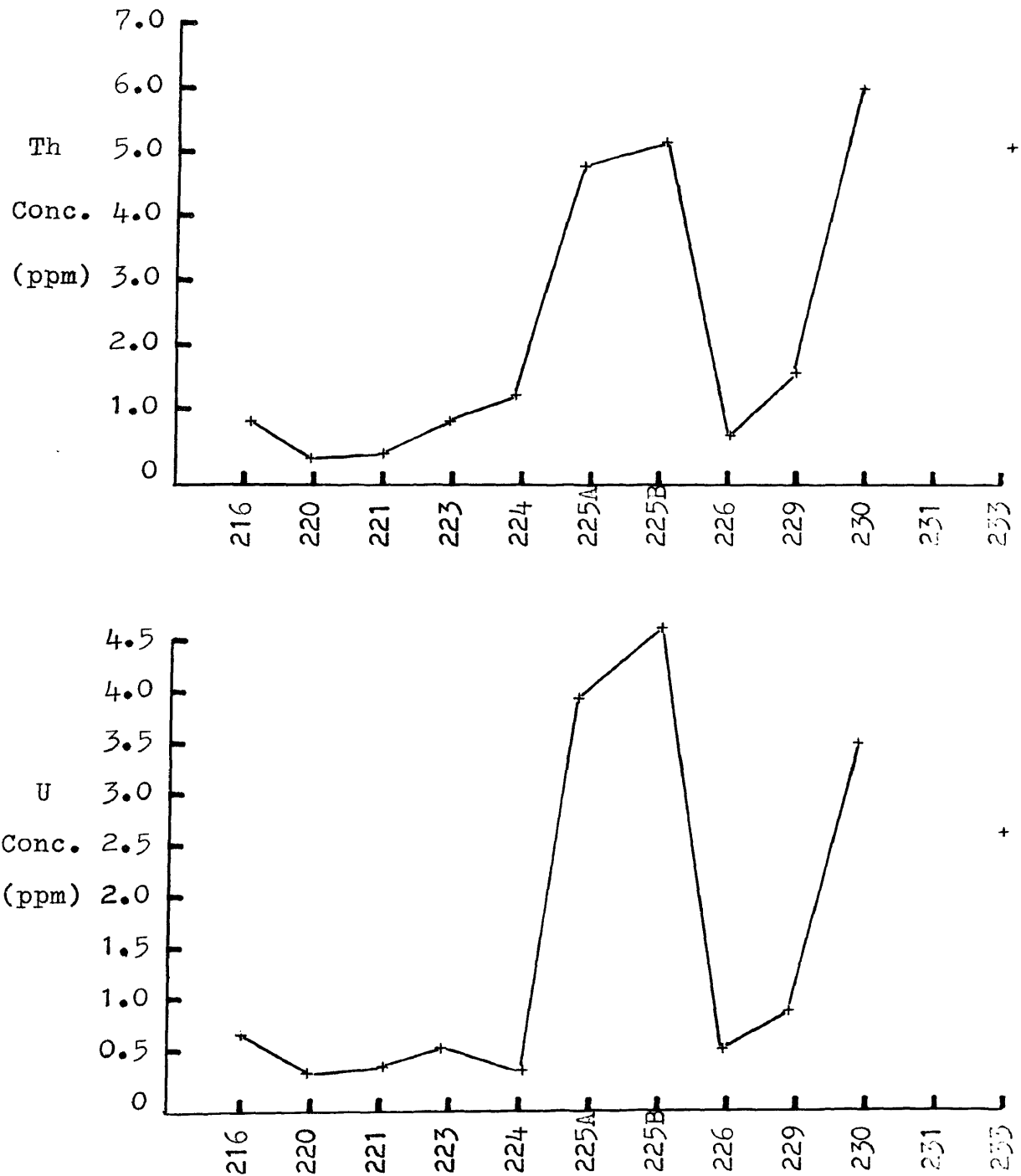


Fig. 8. Distribution of Th and U, Group I, Total Sample (after Bolter 1965)

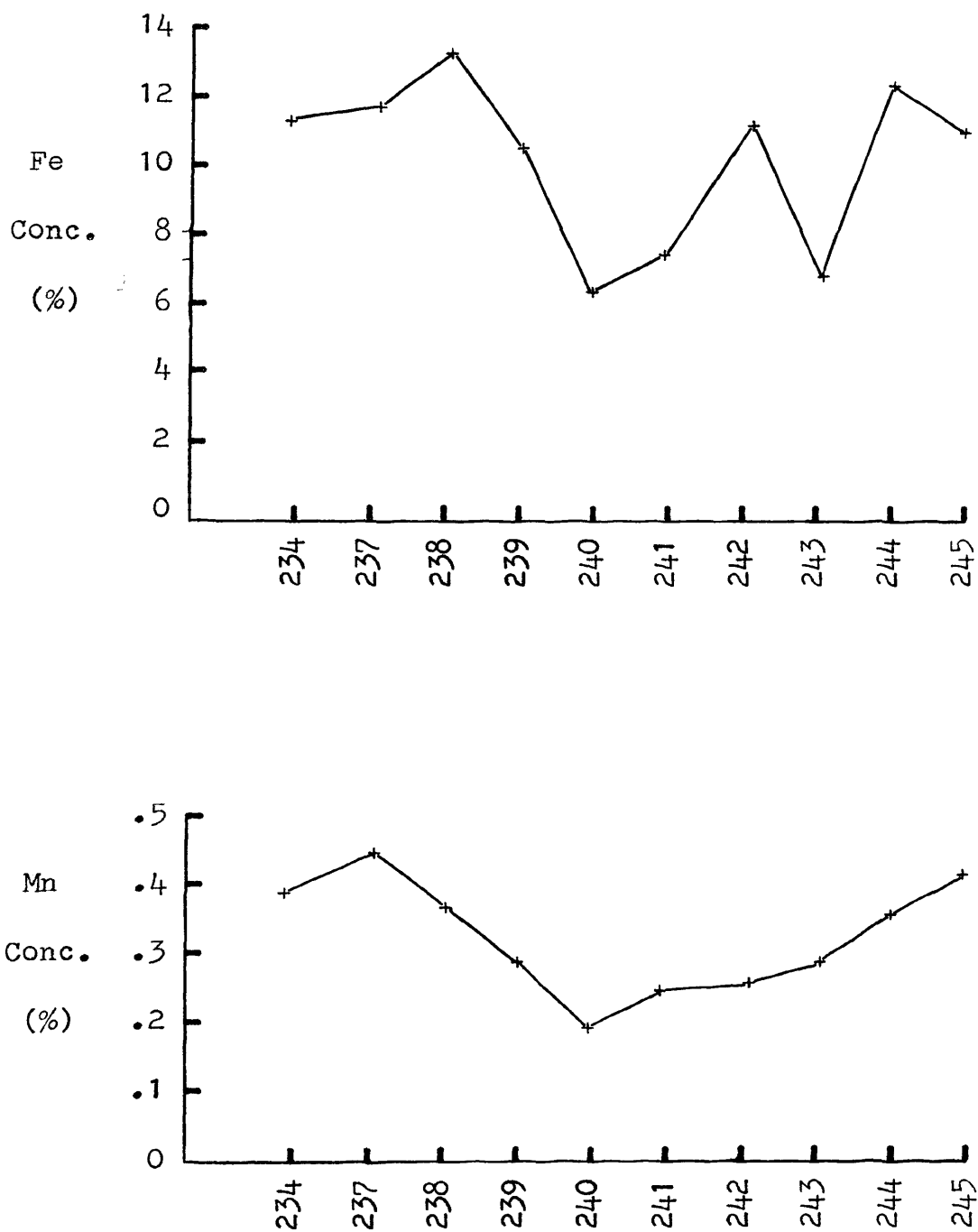


Fig. 9. Distribution of Fe and Mn, Group II, Heavy Mineral Fraction

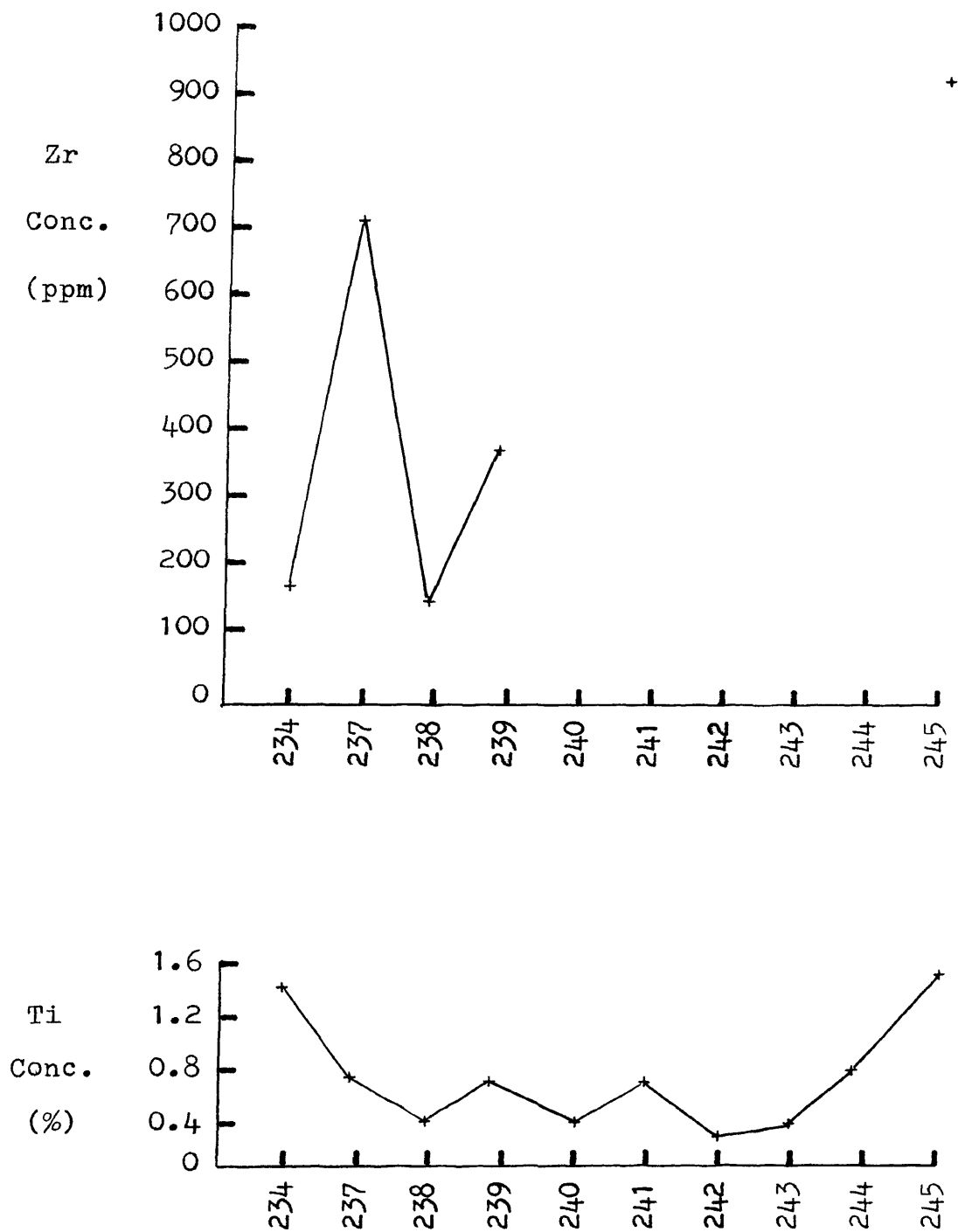


Fig. 10. Distribution of Zr and Ti, Group II, Heavy Mineral Fraction

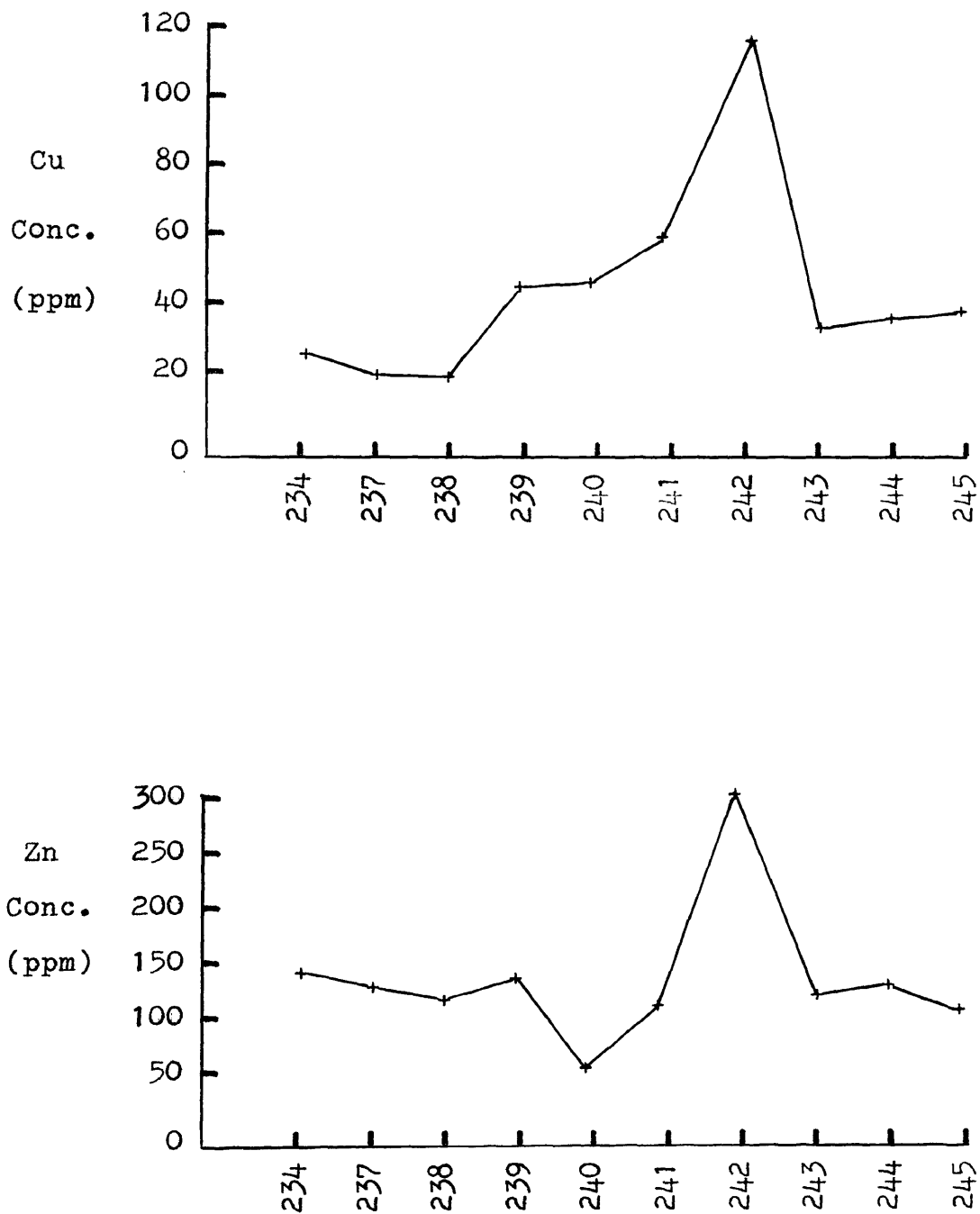


Fig. 11. Distribution of Cu and Zn, Group II, Heavy Mineral Fraction

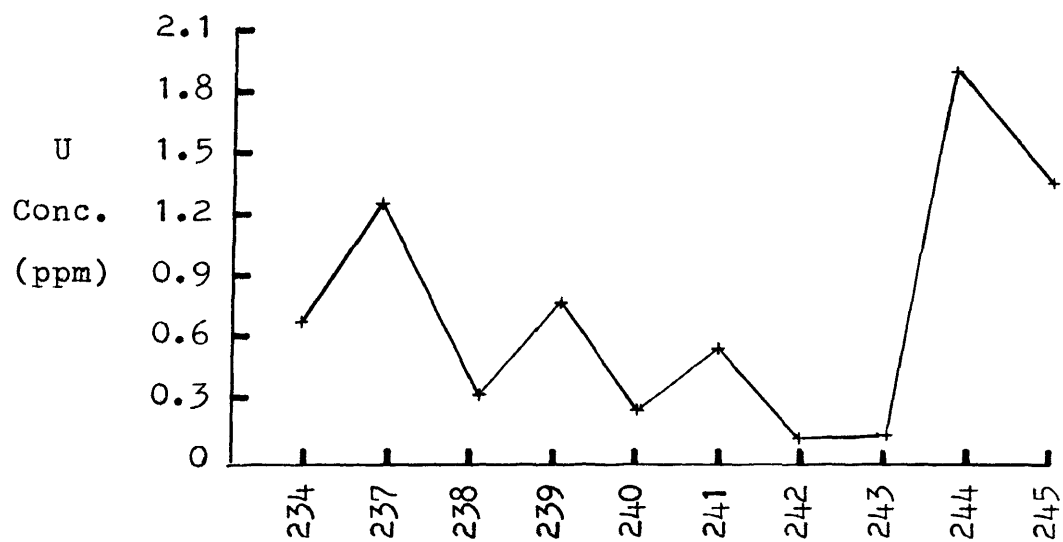
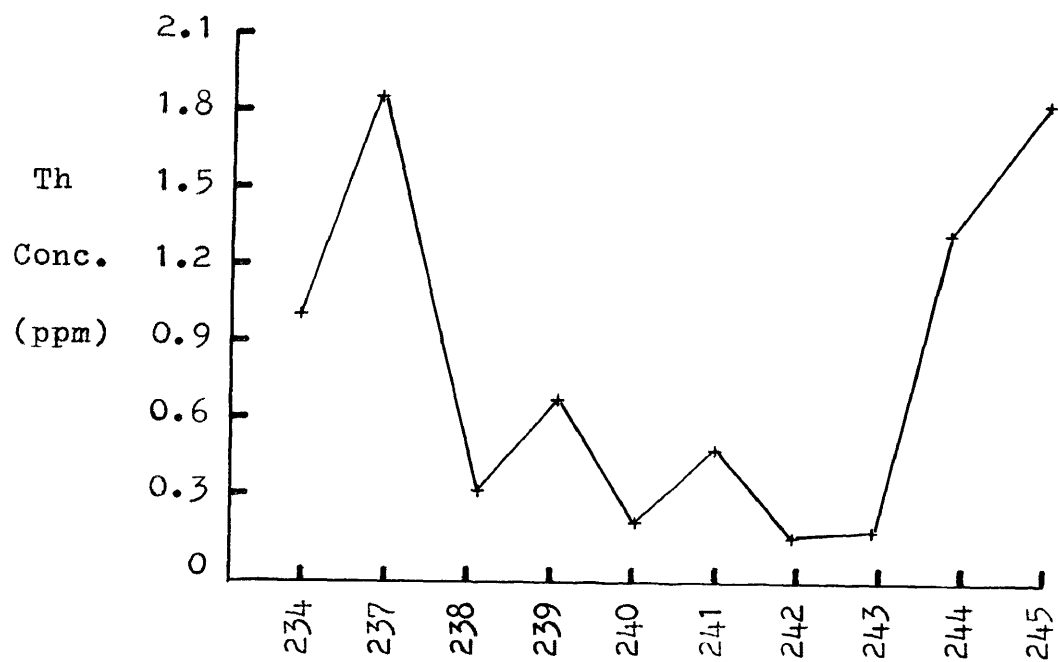


Fig. 12. Distribution of Th and U, Group II, Total Sample (after Bolter 1965)

was the case with the Group I samples. The trend of the copper concentration, from sample to sample, generally seems to vary independently of the other elements. This generally independent variation in the Group II samples is similar to the Group I samples. Uranium and thorium, Figure 12, correlate well with titanium and zirconium in samples 234 to 239.

The uranium and thorium concentrations were recalculated on the basis of the concentration per one per cent heavy minerals, Figures 13 and 14. This method gives a clearer picture of the uranium and thorium concentration in each sample since the concentration is related to a constant value, one per cent heavy minerals in this case. Samples 242 and 243 have very high uranium concentrations, .30 and .32 ppm/1% heavy minerals, respectively. These same samples also have the highest thorium concentrations, .49 and .55 ppm/1% heavy minerals, respectively.

Mahdavi (1964) calculated a Th/U ratio of 2.5 to 3.0 and modes of 1 to 2 ppm thorium and .3 to .6 ppm uranium for the Atlantic and Gulf Coast beach sands.

According to the present investigation, the modes of the Group I samples are .16 to 1 ppm thorium and .31 to .50 ppm uranium. The modes of the Group II samples are .10 to .30 ppm thorium and .10 to .30 uranium. The mode of the Th/U ratio is .51 to 1.00 for all the beach sands in the present investigation. Twenty-three of the beach

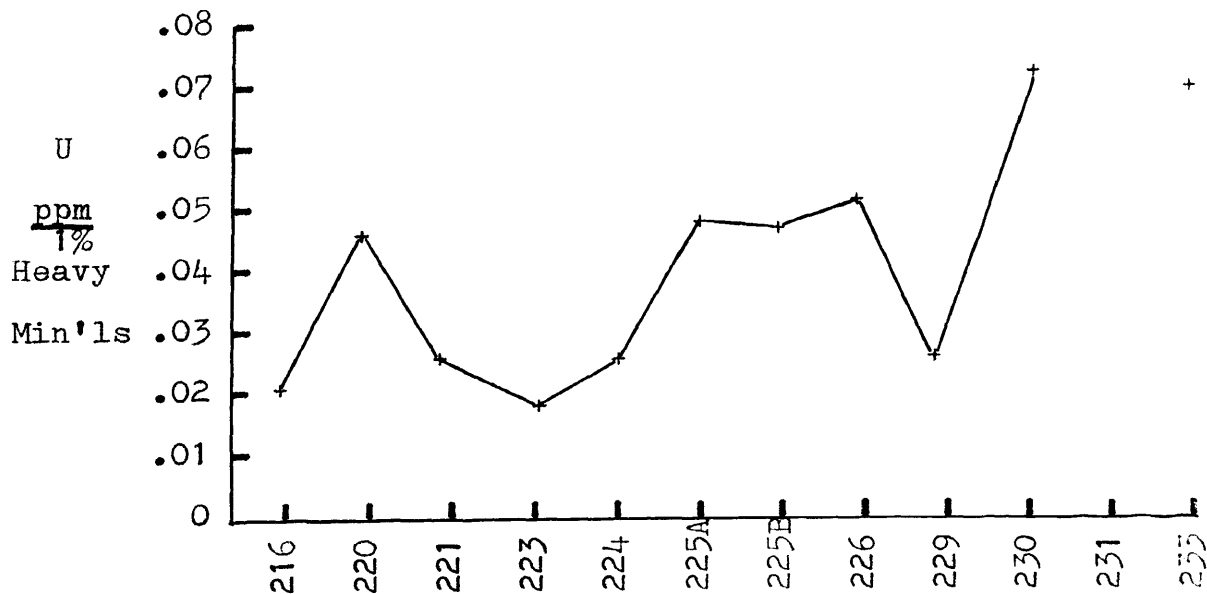
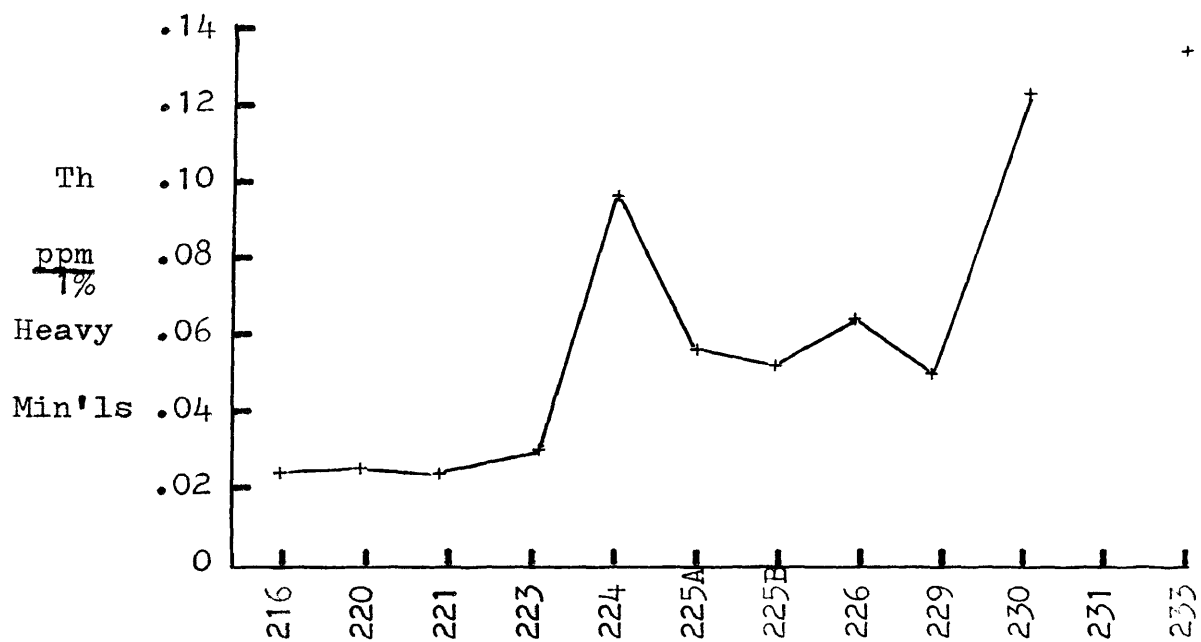


Fig. 13
Concentration of Th and U per One Per Cent Heavy Minerals,
Group I, (after Bolter 1965)

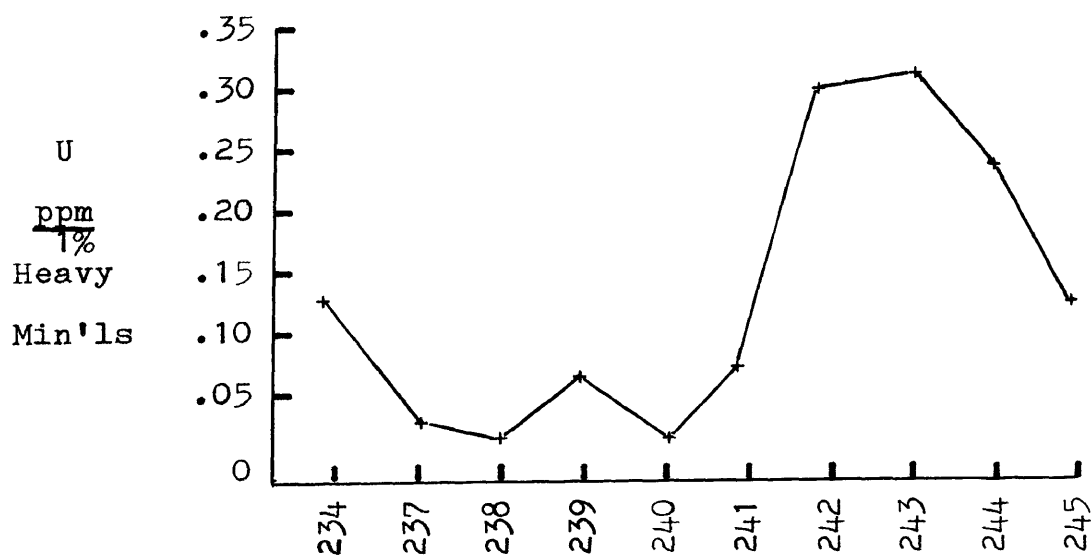
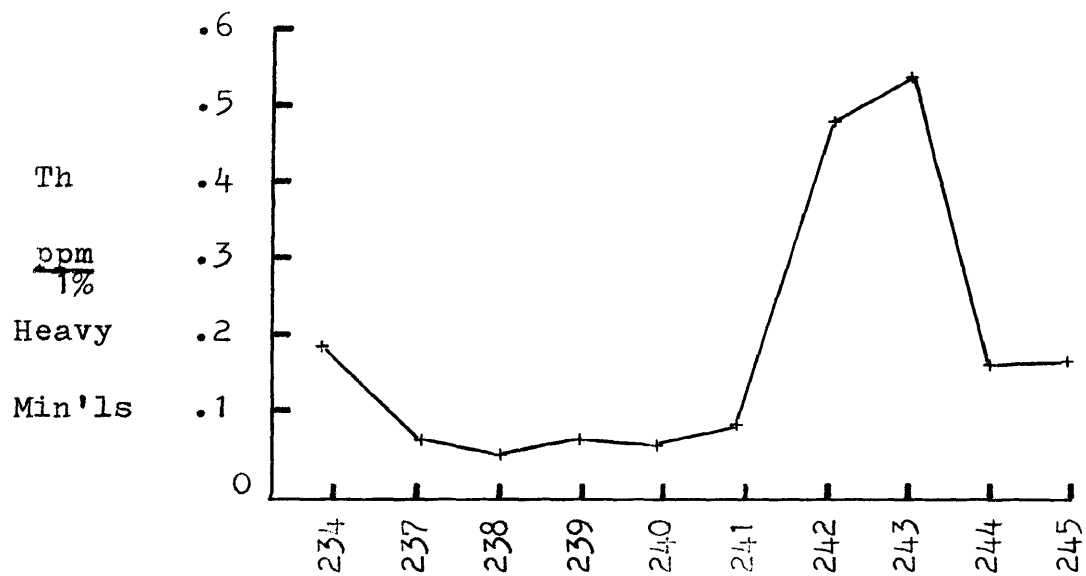


Fig. 14
Concentration of Th and U Per One Per Cent Heavy Minerals,
Group II, (after Bolter 1965)

sands, however, have a Th/U ratio of .51 to 2.00. These beach sands have a lower Th/U ratio than the Atlantic and Gulf Coast beach sands Mahdavi analyzed and are considerably lower than the crustal average Th/U ratio of 3.8.

Figures 2 and 3 show the locations of known mineralization. The elements analyzed do not show anomalously high values in the beach sands associated with the drainage basins of the mineralized areas.

VII. CONCLUSIONS

Very little is known about the geochemical characteristics of beach sands. The purpose of this investigation has been directed towards the chemical analysis of the sampled beach sands in order to see if any significant trends or anomalous values, primarily in the heavy mineral fraction, do exist. It is evident from this investigation that there is better correlation between the elements analyzed in the plutonic Group I sampled area than there is in the volcanic Group II sampled area. Apparently anomalous values of iron, manganese, copper, zinc, titanium, and zirconium are present in the Group I samples. Copper and zinc are the only two elements that have apparently anomalous values in the Group II samples.

It is worthwhile to note that the beach sands associated with the drainage basins of the known areas of mineralization do not show anomalously high values.

Other areas, however, have apparently anomalous values. This presents several possibilities. Either these locations possess physical characteristics which cause the accumulation of the element in placer-like deposits or there is an unknown area of mineralization, at least to this author, in the source area.

It is evident that, due to the limited number of samples that were taken, this investigation gives only a preliminary or partial picture of the geochemical make-up

of Puerto Rican beach sands.

Naturally, suggestions for further research concerns primarily sampling. More samples should be taken from each beach to guard against a biased sample, such as one that is taken from a placer-like deposit. More beaches should be sampled in areas of differing rock types, thereby enabling the investigator to distinguish the effects of variable lithologies on the geochemical trend from area to area.

Samples should be taken from offshore to determine the effects of longshore currents and wave action on the individual beaches.

Lastly, a comprehensive geochemical picture of each beach could be obtained if samples were also taken from within the drainage basin itself, thereby showing the source of the mineral.

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VITA

Louis Meinecke III was born December 18, 1944, in St. Louis, Missouri. He is the son of Mr. and Mrs. Louis Meinecke, Jr., of St. Louis.

He attended Buder Elementary and Southwest High School in St. Louis.

He received his undergraduate education from the University of Missouri-Columbia, Columbia, Missouri, and Drury College in Springfield, Missouri, from which he received his B. A. in geology in May, 1967.

He entered the University of Missouri-Rolla in Rolla, Missouri, in September, 1967.

Mr. Meinecke attended the U.M.R. graduate school from September, 1968 to June, 1970, at which time he fulfilled his military obligation with the United States Army. He received an honorable discharge in April, 1972.

He is married to the former Mary J. Hedworth and has two sons, Louis IV and Brian E.