Spring 1990

A Comparison of Metals in Several Ahermatypic Corals and Surficial Sediments: Mobile Pinnacles and Hoffa Reef, Northcentral Gulf of Mexico

Kathryn M. Conko
Old Dominion University

Recommended Citation

Conko, Kathryn M.. "A Comparison of Metals in Several Ahermatypic Corals and Surficial Sediments: Mobile Pinnacles and Hoffa Reef, Northcentral Gulf of Mexico" (1990). Master of Science (MS), Thesis, Ocean & Earth Sciences, Old Dominion University, DOI: 10.25777/pfvr-7j05
https://digitalcommons.odu.edu/oeas_etds/107

A COMPARISON OF METALS IN SEVERAL AHERMATYPIC CORALS AND SURFICIAL SEDIMENTS: MOBILE PINNACLES AND HOFFA REEF, NORTHCENTRAL GULF OF MEXICO

Kathryn M. Conko
B. S. May 1984,
California University of Pennsylvania

A Thesis Submitted to the Faculty of
Old Dominion University in Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

GEOLOGY

OLD DOMINION UNIVERSITY
May, 1990

Approved by:

Joseph H. Rule (Director)

Dennis A. Darby

Ronald C. Circé

ABSTRACT

A COMPARISON OF METALS IN SEVERAL AHERMATYPIC CORALS AND SURFICIAL SEDIMENTS: MOBILE PINNACLES AND HOFFA REEF, NORTHCENTRAL GULF OF MEXICO

Kathryn M. Conko
Old Dominion University, 1990
Director: Dr. Joseph H. Rule

Metal concentrations in marine sediment and carbonate secreting invertebrates are representative of surrounding environmental chemistry. Aluminum, Ba, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Sr, and Zn were measured in both carbonate and terrigenous phases of the <63 μm fraction sediment samples from two locations in the northcentral Gulf of Mexico. Each location has a separate source of sediment based on the ratios of clay minerals. The ratios of Metal/Fe_{sed} to Metal/Fe_{crust} indicate that Al, Ba, Cu, Cr, Mg, Mn, and Ni are all slightly depleted in these sediments relative to crustal abundances. Chemical variations in the environment are indicated based on discriminant function analyses showing that Pb, Mn, Sr, Ca and Mg concentrations differ between locations.

Ahermatypic coral (106 specimens) from five genera collected from the study sites were analyzed for Cd, Cu, Cr, Pb, Zn, Mn, Sr, Ba, Fe, Ca and Mg. Ratios of Metal/Ca_{coral} to

Metal/Ca$_{seawater}$ suggest an enrichment of Al, Fe, Mn, and Pb and a depletion of Mg, Cu, and Zn in the coral skeleton relative to seawater. The elements Al, Ba, Ca, Cd, Cu, Mg, Pb and Sr varied between some genera implying a genetic effect. Two elements, Al and Ba also vary in concentration in corals between either location; this variation is interpreted as an environmental influence. The ratio of Metal/Ca$_{coral}$ to Metal/Ca$_{sediment}$ shows that all elements except Sr are significantly depleted in the coral with respect to the sediment. Strontium values are approximately equal to one implying an equilibrium with the sediment, coral, and seawater relative to Ca.

DEDICATION

To my parents,
Eleanor and Stephen Conko, Jr.
for all their love, support and understanding.

ACKNOWLEDGEMENTS

I would like to thank my thesis committee: Joseph H. Rule, Dennis A. Darby, and Ronald C. Circé (USGS), for their patience, assistance and advice throughout my research and the preparation of this thesis. Their help is sincerely appreciated.

A debt of gratitude is owed to many people. A special thanks to Stephen Cairns (NMNH) for his help in identifying the corals. Thanks also to Carl F. Koch for his helpful discussions on cluster analysis and to Michael W. Bennett for his assistance on the maps. A very special thanks to Michael J. Ehret not only for his invaluable assistance performing the statistical analysis but for his helpful technical suggestions.

Most of all I would like to thank my parents, Eleanor and Stephen Conko, and my sister and brothers for their unfailing support and encouragement throughout this entire endeavor. Thanks also to the many friends and various aunts, uncles and cousins who could always be counted on to feed and encourage a starving grad student.

TABLE OF CONTENTS

page

Chapter

LIST OF TABLES

LIST OF FIGURES

Chapter I

INTRODUCTION

GENERAL REMARKS

Much of what is known about the geochemistry of past environments is inferred from the study of fossil carbonate skeletons (Goreau, 1977). Research on planktonic organisms, especially foraminifera, have found many unique relationships between calcite test chemistry and that of the open ocean water (Delaney et. al., 1985; Boyle, 1986).

Other studies have focused on the geochemistry of benthic organisms, for example, molluscs, foraminifera and reef corals, to determine their geochemical relationships with the surrounding environment (Turekian and Armstrong, 1960; Dodge and Gilbert, 1984). The primary applications of coral chemical data are: paleoecological interpretation, carbonate sediment chemistry, and the investigation of geochemical cycles and history of seawater chemistry (Dodd, 1967). The key to understanding and predicting metal transport and accumulation lies in the ability to identify and quantify the metal associations in the sediment and the reactions that occur between the sediment, water and the biota (Horowitz, 1985).

Although hermatypic coral (reef-builders) are quite spectacular in mass and of ecological and economic importance, their distribution is controlled by environmental factors. Hermatypic corals have a symbiotic relationship with photosynthetic zooxanthellae algae which restricts them to the photic zone and warm waters (18° C). Ahermatypic corals lack photosynthetic algae and can live in deeper, colder water, and therefore are less restricted by environmental conditions. Thus, ahermatypic corals are candidates for environmental chemical analysis if their response to the chemical environment can be understood.

OBJECTIVES

The distribution patterns of select elements from the two separate study locations in the Gulf of Mexico can be used to trace the history of metals in this environment. It can also be used to interpret the geochemical environment of this area of the Gulf, and by extension, other areas.

"The composition of any environment or object is determined by a partial balance between material transport process and the chemical reactions in and around it" (Aller, 1982). The carbonate skeletons of corals can be used as environmental indicators, past and present, once it is determined that individuals are representative of their geochemical environment. Due to this geochemical sensitivity, for certain environmental data from a single coral analysis may give more information than a composite of sediment at a given site.

The objectives of this study are:

1. To describe the distribution of metals found in the surficial sediment from sites at the Mississippi Canyon and the Mobile Pinnacles in the northcentral Gulf of Mexico.
2. To document the metal concentrations of five genera of ahermatypic corals.
3. To determine if the accumulation of metals in the ahermatypic corals is influenced by genetic or by environmental factors.
4. To quantify the geochemical relationships between the ahermatypic corals and terrigenous sediment.

Due to the nature of this study, it was necessary to make one presumption. Although no validation is possible, it must be assumed that all of the coral and the sediment at each of the sites are Recent. Care was taken to analyze individual coral specimens that were relatively free of encrustations and borings, indications of prolonged post-mortem exposure. Thus it can be reasonably assumed that the relative ages of the corals are Recent.

To achieve the previous objectives three null hypotheses were formulated:

1. There is no difference in the metal concentrations of sediment from the two different locations.
2. There is no difference in the metal concentrations

of the skeleton in different coral genera.

3. There is no difference in the metal concentrations of the corals regardless of location.

Chapter II

STUDY AREA

GENERAL GEOLOGY

The Gulf of Mexico is a small ocean basin that covers an area of approximately 1.6 million km^2. The northern Gulf can be divided into three geographic regions: Eastern, Central, and Western. The Louisiana-Mississippi-Alabama continental shelf and slope as well as the Mississippi Canyon are part of the northcentral Gulf of Mexico. Late Quaternary sedimentation in this region is primarily derived from the Mississippi and Mobile Rivers. This sediment is predominately sandy-mud and locally produced skeletal material (Rezak, et. al., 1985).

The continental interior of the United States is drained by the Mississippi River and is a major source of clastic sediments to the northcentral section of the Gulf of Mexico. This sediment deposition covers the entire shelf and spreads far onto the abyssal plain. The geology of the northern Gulf has been extensively studied due to the large potential of petroleum resources. Shepard (1937), was the first to report numerous large "domes and ridges" along the 160 meter contour line in the north-western Gulf. He mapped approximately thirty submarine domes between the Mississippi Canyon area (89° 30'W, 28° 39'N) and the Flower Garden Banks (94° 00'W, 27° 50'N). At present more than eighty such banks have been mapped and described on the shelf and shelf-edge of the northern Gulf of Mexico. These banks form a discontinuous belt along the geographic boundary of the continental shelf and slope (Poppe and Circé, 1983). The geology of these banks have been the object of investigations for the past fifty years (Shepard, 1937; Ludwick and Walton, 1957; Matthews, 1963; Poag, 1972; Poppe and Circé, 1983; Rezak, et. al., 1985; and Circé and Tunnell, 1987).

Two locations in the northern Gulf of Mexico have been chosen for study: (A) the Mississippi Canyon area, and (B) the Mobile Pinnacles area (Figure 1). These two areas include several carbonate-capped banks located on an ancient shore line when the sea level was 140 to 160 meters lower than present (Ballard and Uchupi, 1970). Molluscan assemblages at these two areas (R. C. Circé, personal communication) suggests that the biological controls, for example, temperature and salinity are currently similar to past conditions.

MISSISSIPPI CANYON AREA

The Mississippi Canyon (Figure 2) is an area of hard rock, calcareous capped banks located about 50 km southwest of the Mississippi Delta. Although these banks are sometimes called "reefs" they are not true coral reefs.

FIGURE 1. Location of Study Locations: (A) Hoffa Reef; Mississippi Canyon Area; (B) Mobile Pinnacles Area, Northcentral Gulf of Mexico.

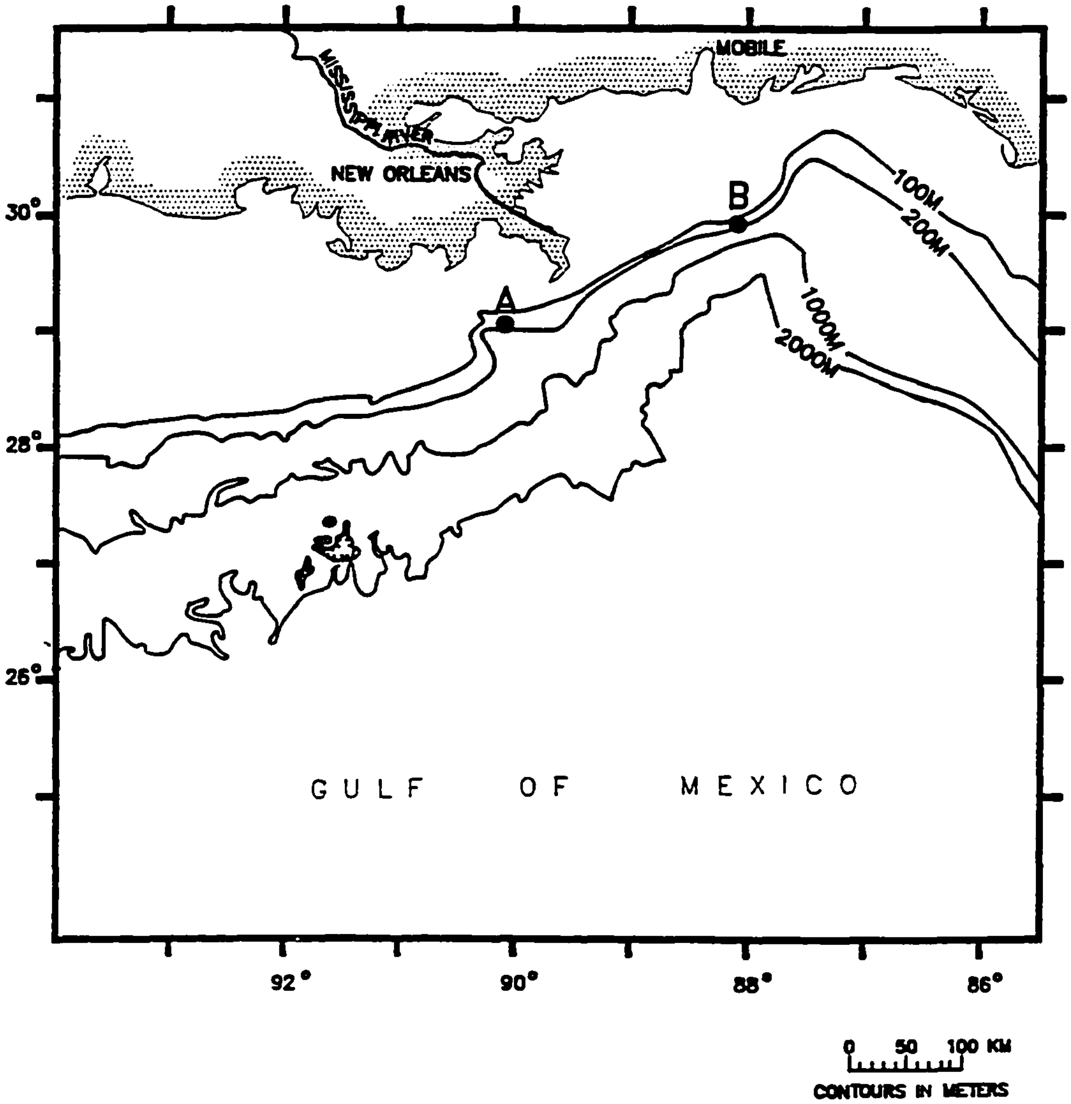
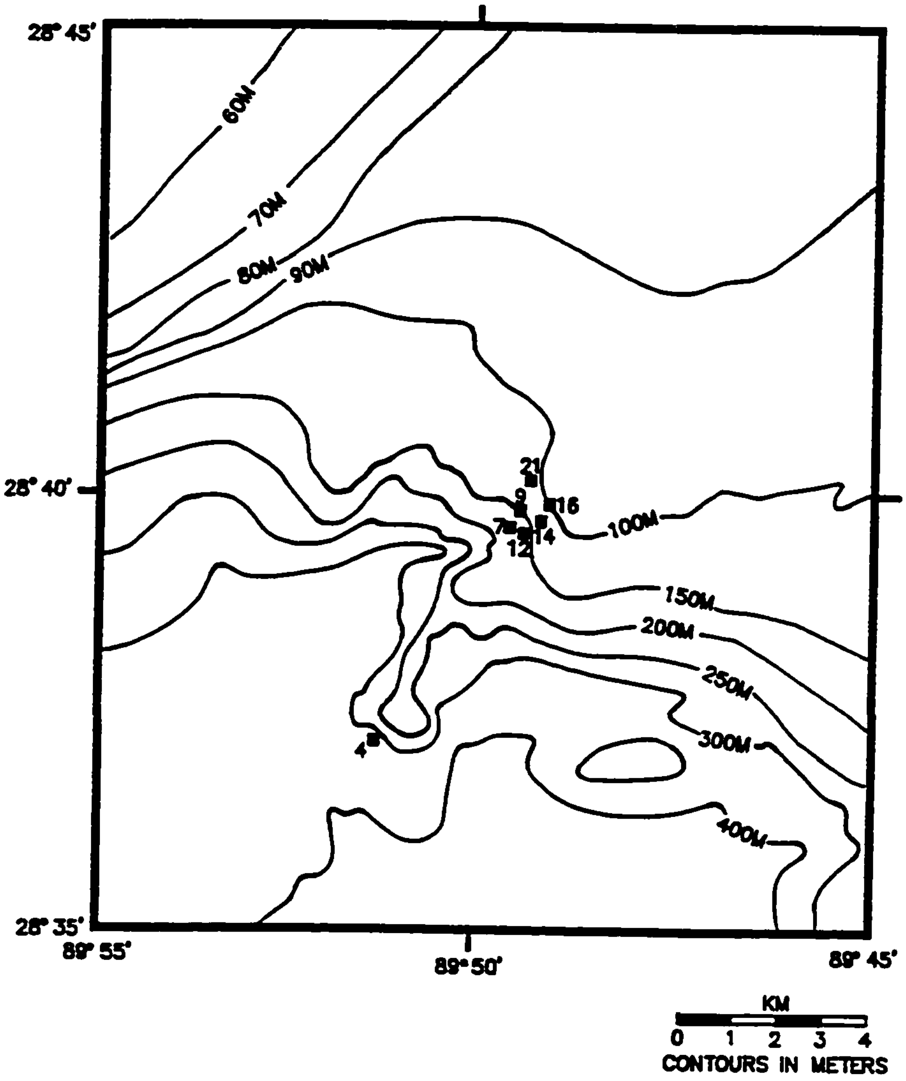

MOBILE
MISSISSIPPI RIVER
NEW ORLEANS
B
A
100M
200M
1000M
2000M
30°
28°
26°
GULF OF MEXICO
92°
90°
88°
86°
0 50 100 KM
CONTOURS IN METERS

FIGURE 2. Location of Sites at Mississippi Canyon Area. Latitude and Longitude listed in Appendix A.

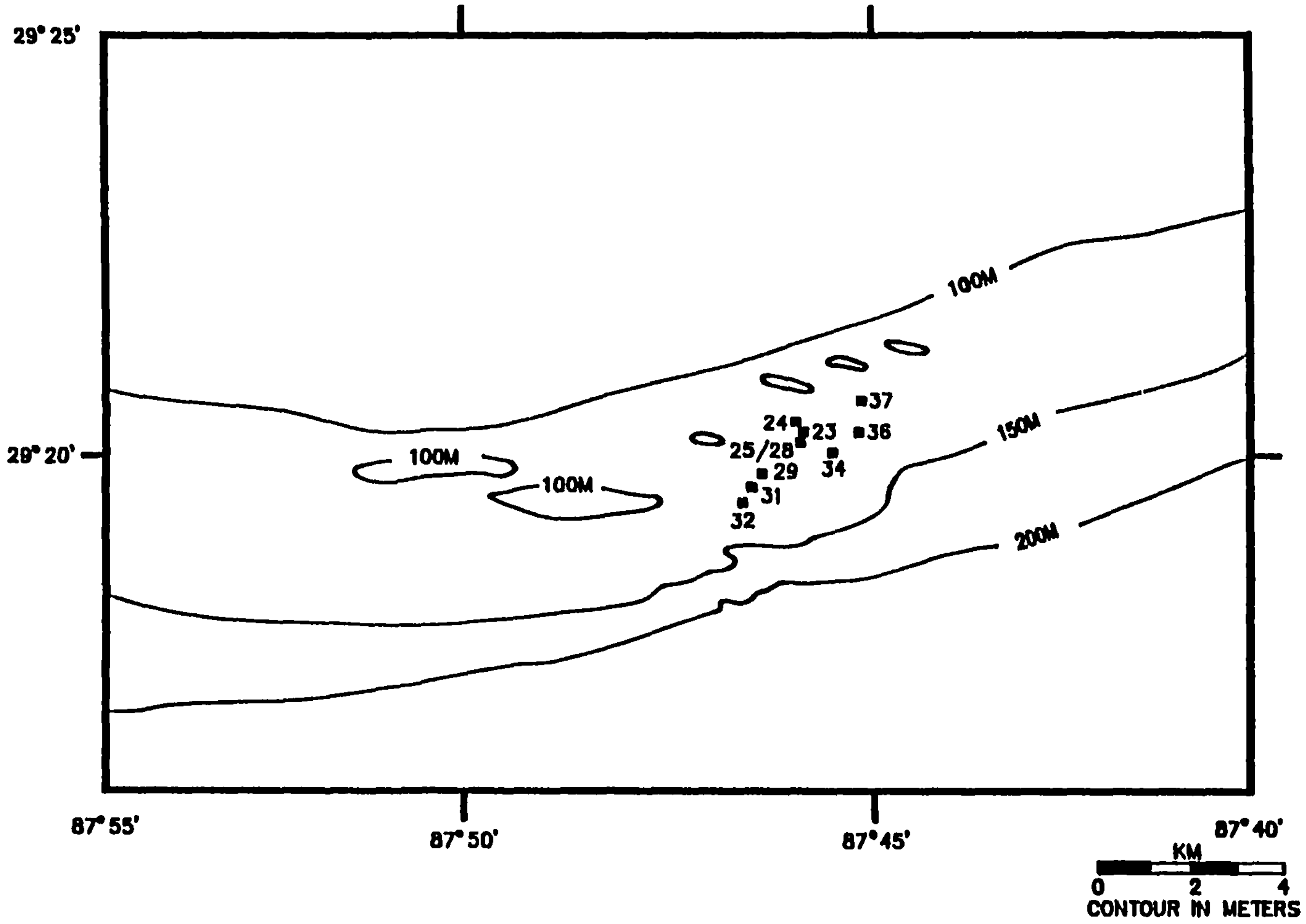

28° 45'
28° 40'
28° 35'
89° 55'
89° 50'
89° 45'
60M
70M
80M
90M
100M
150M
200M
250M
300M
400M
21
9
16
7
14
12
4
KM
0 1 2 3 4
CONTOURS IN METERS

High-resolution seismic data suggests that the banks were formed by a combination of diapiric activity and erosion during the late Pleistocene when the Mississippi Canyon was formed. The banks are composed of two major facies: a dolostone substrate, and a macrofaunal component of carbonate secreting organisms (Poppe and Circé, 1983). The hard bottom consists of ahermatypic coral (solitary coral polyps), coquina, and dolostone outcrops (Poppe and Circé, 1983). Greater than 50% of the sediment is terrigenous, predominately from the Mississippi River.

MOBILE PINNACLES AREA

The Mobile Pinnacles (Figure 3) are a series of two large and four smaller hard banks, south of Mobile, Alabama, on the continental shelf-edge. They were first described by Ludwick and Walton (1957) as true bioherms. They are now thought to be the expressions of a pro-deltaic build-up of sediment from an ancient river system capped by a coral "reef". Approximately half of the sediment on the pinnacles is of terrigenous origin.

FIGURE 3. Location of Sites Mobile Pinnacles Area.
Latitude and Longitude listed in Appendix A.


29° 25'
29° 20'
87° 55'
87° 50'
87° 45'
87° 40'
100M
150M
200M
100M
100M
■37
■36
24■
■23
25/28■
■29
■31
■32
■34
KM
0
2
4
CONTOUR IN METERS

Chapter III

PREVIOUS INVESTIGATIONS

SEDIMENT

The sediment from the study sites contains essentially two distinct fractions: (1) a carbonate phase of shell fragments, mollusc and coral and; (2) a detrital fraction. The grain size analysis (Table 1) shows the relative amount of clays are higher in the Canyon area and the carbonate material being higher at the Pinnacle sites.

Elements in solution may become incorporated into the sediment by: adsorption on colloidal material, chemical precipitation, or biological accumulation. Various factors can affect the sediments ability to concentrate an element: grain size, surface area, cation exchange capacity, and phase associations (for example; sulfides, carbonates, organic matter). Phase association is not a thermodynamic term, it implies association with categories of sediment. In studies of the processes of elemental deposition and accumulation it is important to distinguish the non-detrital fraction of a metal from that which is structurally bound in the detrital minerals (Gad and LeRiche, 1966). The concentration of metals in certain fractions

Table 1. Partial Grain Size Analysis of Sediment from Study Sites at the Mississippi Canyon Area and the Mobile Pinnacles Area.*

SAMPLE ID	>63 µm WT %	SILT WT %	CLAY WT %	%$CaCO_3$ IN >63 µm FRACTION	
GS-4	1.96	54.26	44.72	24.52	C
GS-7	2.44	54.88	42.68	90.15	A
GS-9	77.48	13.31	9.21	75.26	N
GS-12	51.38	27.35	21.07	29.98	Y
GS-14	39.59	27.27	33.14	30.02	O
GS-16	39.25	28.20	32.55	12.38	N
GS-21	14.29	34.94	50.77	9.41	
GS-23	81.04	13.38	5.58	96.62	
GS-24	75.07	16.43	8.50	95.95	P
GS-25	62.22	23.82	13.96	97.35	I
GS-28	71.33	18.34	10.33	98.16	N
GS-29	72.81	14.68	12.51	99.12	N
GS-31	83.37	10.33	6.30	98.69	A
GS-32	68.26	19.33	12.41	98.60	C
GS-34	67.68	19.91	12.41	98.69	L
GS-36	74.03	18.72	7.25	98.50	E
GS-37	70.92	18.43	10.66	98.63	S

* from the U. S. Geological Survey, Woods Hole, Massachusetts.

reflect the unique geochemistry of an area.

Sediments from the Texas-West Louisiana coast and east of the Mississippi River were found to have generally lower metal concentrations than those from the area directly west of the river in a trace metal study of the Mississippi Delta region (Trefry and Presley, 1976a). They also reported metal pollution (Pb and Cd) along the continental shelf of the north-western Gulf of Mexico. However, the samples with higher concentrations were taken in the immediate sediment transport pathway of the Mississippi River.

Core samples from the Mississippi Delta recorded a 60% increase of Pb and a 100% increase of Cd for sediment less than 25-30 years old (Trefry and Presley, 1976b). This anomaly was not noticed for Pb and Cd farther from the mouth of the Mississippi River, and was not recorded for other elements (Fe, Mn, Zn, Cu, Co, Ni) anywhere in their study area. Suspended particulates transport >90% of the Mississippi River metal load. When compared to river particulates, delta sediments show a 20-40% reduction of Mn, Cu, Co, Ni and Zn concentrations (Trefry, 1977).

Holmes, (1976) measured several elements in cores from the central Gulf of Mexico (Table 2). The values for Cd were less than 20 ppm for all of the samples analyzed. Zinc was less than 200 ppm in 99% of the samples. "The distribution of the geochemical properties of the sediment are in direct response to the sediment regime of the shelf"

Table 2 Average Element Concentrations of Sediment, central Gulf of Mexico. (Holmes, 1976).

	Ba	**Cu**	**Mn**	**Ni**	**Pb**	**Sr**	**Ca**	**Mg**	**Fe**
ppm	291	20	892	36	7	1050	6.91%	1.53%	2.2%

(Holmes 1982). Metals that have been used to discern the movement of the sediment (off the Texas continental shelf) include Ba, a major element in drilling mud, that tags sediment movement from areas of hydrocarbon exploration. Lead, anthropogenically introduced from urban areas, tags sediment derived from metropolitan complexes. Manganese, because of diagenic mobilization, is concentrated in areas of slow sediment accumulation (Holmes, 1982).

CORALS

The Order Scleractinia is divided into two groups: reef builders (hermatypic) and non-reef builders (ahermatypic). Scleractinians are a major source of carbonate sedimentation to the oceans, and all have an aragonitic skeleton. The calcium carbonate skeleton of corals are precipitated from the ocean water by the flowing reaction:

$$Ca(HCO_3)_2 \text{ ---> } CaCO_3 + H_2CO_3.$$

Corals have been used as environmental indicators because of their widespread geological and geographic range and because they are quite sensitive to their chemical environment (Shen and Boyle, 1988). This environmental sensitivity of the carbonate skeleton is reflected in the elements that replace the Ca ion in the crystal structure. The orthorhombic structure of aragonite favors substitution for the calcium by ions with radii greater than that of Ca, for example, Sr, Ba and Pb. Thus, the skeleton is a physical remnant of the chemical nature of the organism's environment.

Paleoecological interpretations have been based on the elemental concentrations of fossils and sediments. Most studies have concentrated on group I and II elements that will readily substitute for Ca in the calcite or aragonite skeleton, Sr (Turekian, 1955; Schneider, and Smith 1982), Mg (Chillingar, 1962; Lowenstam, 1961; Weber, 1974), and Ba (Turekian and Armstrong, 1960; Lea, et. al., 1989). Other studies have focused on transitional elements, Cd (Shen and Boyle, 1988), Cu (Linn, et. al., 1990), and Pb (Dodge and Gilbert, 1984, Shen and Boyle, 1987). Recent studies have focused on the response of reef coral to the chemistry of the surface water. Elemental concentrations change with depth, so deeper living ahermatypic corals may not be influenced by the changes at the surface.

The paleoenvironment of an area may be determined by examining the ratios of certain elements in fossil skeletons. Chester (1965), used the chemical sensitivity of corals to differentiate reef from non-reef facies in carbonate rocks and found that Ni, Ba, and Sr could be used as facies indicators.

In a study of the effectiveness of Ag, Co, and U to interpret the history of this element in past oceans, (Veeh and Turekian, 1968) Co was found in a much lower concentration in the coral carbonate than in the open ocean. This was interpreted as a discrimination against Co by the coral. Also noted were slight differences in the Co concentrations between species from the same location.

It has been suggested that the physiology of the organism is responsible for the accumulation of certain minor elements in the coral skeleton. More phylogenetically advanced taxa have higher Sr and lower Mg values (Dodd, 1967). In fact, the preferential accumulation of Sr by some coral, in areas of abundant growth, has been reported to cause a depression of the Sr/Ca ratio in the surrounding seawater.

Species specific controls on Sr and U accumulation was also recorded in a study of modern corals (Thompson and Livingston, 1970). Although large differences within each group were not found, the concentration of Sr was slightly higher in ahermatypic species than hermatypics. The uptake of Sr and U was independant of water temperature, but related to the coral growth rates and metabolic processes.

Livingston and Thompson (1971) analyzed both hermatypic and ahermatypic scleractinian corals to determine the distribution of elements between the carbonate skeleton and the residual phase. They found that Sr, Ba, Cu, and Zn were present in the skeleton and that the ratios of Sr and Ba to Ca in the coral skeleton were the same as in the seawater. Variations in the Sr concentration were found between different species from the same locale, but larger differences were noticed between hermatypic and ahermatypic species. Zinc was generally discriminated against by the coral, except in a few ahermatypic species.

Livingston and Thompson (1971) also quantified the elements in the residual phase of the coral. They found that Fe, Mn, Co, Ni, and Pb were present in both the skeletal and residual phases. They also noted that the nature of the residual material in the coral skeleton reflects the nature of the sediment environment.

Trace metals will not precipitate in the same ratio to Ca as in the seawater due to a thermodynamic disequilibrium that exists between biogenic carbonate and seawater with respect to metal concentrations (St. John, 1974). In contrast to an inorganic system, which is in equilibrium with the surrounding seawater, Ca and Sr must first pass through the coral's polypal tissue to become incorporated into the skeletal carbonate, and is unlikely that an equilibrium would exist.

The uptake of Mg by corals from seawater has been linked to "taxonomic affinity, suggesting that physiologic controls dominate" (Weber, 1974). In a paleoenvironmental analysis of corals using Sr, Mg, and Na, Swart (1981) attributes differences of metal concentrations to temperature related metabolic functions. These temperature changes could effect the growth rate which may affect the uptake of Sr or a temperature change might result in the redistribution of molecular species of Ca and Sr in the seawater.

Apparent taxonomic deviations in minor element concentrations of reef coral were also found for Mg, Sr, and U (Cross and Cross, 1983), these variations were also attributed to "taxa-specific skeletogenesis." Also noted were concentration changes during diagenesis that might limit the usefulness of these elements for paleoenvironmental interpretation.

Recently, more sensitive analytical methods have expanded the application of trace elements to interpret past ocean chemistry. These methods allow the study of very small accurately dated portions of a coral. Several studies have been done on massive, annually banded hermatypic scleractinian corals. By analyzing individual growth rings a complete history of industrial Pb pollution in the oceans has been documented (Dodge and Gilbert, 1984; Shen and

Boyle, 1987).

The uptake of Cd by corals has been used to trace the history of upwelling and industrial fallout (Shen and Boyle, 1988). "Chemical studies of corals provide records of modern and ancient surface ocean conditions" (Shen and Boyle, 1988). A preferential uptake of Pb over Ca was recognized in this study. Of the elements analyzed only Pb and Cd exhibit temporal variability that could be associated with industrialization and or natural perturbations in ocean circulation such as upwelling.

The ratio of Ba/Ca in the coral skeleton has been used to track historical sea surface temperatures (Lea, et. al., 1989). The substitution of Ba for Ca in the coral skeleton is expected to be proportional to the ratio of Ba/Ca in seawater, which increases as seawater temperatures decreases. The Mn/Ca and Cd/Ca ratios have been used as indicators of the El Nino Southern Oscillation (ENSO) events (Linn, et. al, 1990). There was a suppression of Cd/Ca and higher Mn/Ca during the El Nino events.

The metals in coral carbonate skeletons have been proven to reflect the chemistry of their environment. They have been used to interpret temperature and salinity changes, as well as, to examine anthropogenetic influences, and to determine the history of seawater chemistry and ocean circulation.

Chapter IV

METHODS

SAMPLING PROCEDURES

A total of seventeen sample sites were examined: 7 from the Mississippi Canyon area, and 10 from the Mobile Pinnacles. The samples from the study areas were supplied by the United States Geological Survey (USGS), Woods Hole, Massachusetts. Samples from the Mississippi Canyon Area and Mobile Pinnacles were collected using a 0.01 m^3 Van Veen grab sampler in October, 1983. The samples were stored in 10 liter plastic tubs, sealed and archived at the USGS warehouse in Woods Hole, Mass. They were sub-sampled in the spring of 1987 and transported to Old Dominion University.

SEDIMENT

The geochemical analysis of the surficial sediment required two steps of preparation: (1) wet sieving with a 63μm screen to separate the coarse from the fine fraction; and, (2) partial sequential extraction to separate the carbonate from the non-carbonate (terrigenous) phase. The <63μm fraction was used because it had been established that metals tend to adsorb onto the finer particles (Horowitz, 1985). This step insured that trace elements would not be diluted in sediments with higher sand content. The carbonate phase was extracted from the fine (<63 um) fraction using 100 ml of 25% v/v acetic acid (Hirst and Nicholls, 1958). Sediment samples of approximately 5.00 grams were placed in 250 ml Erlenmeyer flasks with glass "caps". They were leached for 12 hours in a water bath at 60° C. The residue from this extraction was filtered using acid-rinsed, dried and weighed 0.45μm cellulose nitrate filter discs. The 470 mm diameter filter discs were supported by a 540 mm filter funnel with a 450 mm teflon coated ring placed on top. The residue was rinsed several times with deionized water, dried and weighed to calculate percent carbonate.

The residue was digested in 300 ml tall form beakers using the procedure for total metals in sediment, method 3050 (Environmental Protection Agency, 1986). Forty ml of 50% redistilled nitric acid was added to each sample, the beakers covered with watch glasses, and the samples allowed to soak for 12 hours before digesting. The samples were then heated to 95° C and allowed to reflux for about 15 minutes without boiling. An additional 10 ml of nitric acid was added and the sample refluxed for 30 minutes, this step was repeated to ensure complete oxidation.

The solution was evaporated to approximately 5 ml without boiling. After the sample had cooled, 5 ml of deionized water and 8 ml of 30% H_2O_2 were added and heated again for an additional 20 minutes. After cooling, the digestate was filtered and diluted to 50 ml with deionized water.

To determine the relative amounts of minerals present in the sediment at each location, an X-Ray Diffraction (XRD) analysis was done. Eight samples, four from each location were randomly chosen for mineral identification. The XRD was performed on a finely crushed portion of the < 63 μm fraction of the sediment.

CORALS

The second part of the study involved the analysis the coral skeletons for Al, Ba, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Pb, Sr, Zn. Individual coral specimens were selected from the bulk sediment samples. Only identifyable specimens were used. The corals were then identified to the genus level (Cairns, 1977). The five genera of corals selected from these two study areas are: (1) *Madracis*, (2) *Madrepora*, (3) *Oculina*, (4) *Paracyathus*, and (5) *Balanophyllia*.

The individual specimens (Table 3) were cleaned for analysis using a modified procedure described by Shen and Boyle (1988). The corals were washed several times with deionized water, followed by several washes in redistilled 0.2 N HNO_3. They were coarsely crushed, and rinsed several more times in deionized water, followed by 2 more rinses

TABLE 3. Coral Taxonomy and the Number of Indivudals of each Genus from Each Sample Site.

- Suborder Astrocoeniina
  - Family Pocilloporidae
    - *Madracis*
- Suborder Faviina
  - Family Oculinidae
    - *Madrepora*
    - *Oculina*
- Suborder Caryophylliina
  - Family Caryophylliidae
    - *Paracyanthus*
- Suborder Dendrophylliina
  - Family Dendrophylliidae
    - *Balanophyllia*

	Madracis	*Madrepora*	*Oculina*	*Paracyathus*	*Balanophyllia*
GS-9	12	4	6	4	4
GS-12	8	4	18	2	*
GS-14	5	*	6	*	*
GS-16	*	*	1	*	*
GS-21	*	*	4	1	*
GS-24	*	1	*	*	*
GS-25	2	2	*	1	*
GS-28	5	2	1	3	3
GS-29	*	*	*	1	*
GS-30	*	*	*	1	*
GS-31	1	*	*	*	*
GS-34	3	3	*	2	*
TOTAL	36	12	36	15	7

* No specimens of this genus found in this sample.

with 0.2 N HNO_3 and 3 additional rinses with deionized water. Each wash included a 60 - 90 second placement in a sonicating bath to help remove any attached material.

The skeletons (less than 1.200 grams dry weight) were dissolved with three mls 15.4 M HNO_3 heated until near dryness and brought to volume (25 ml) with deionized water.

ANALYSIS

The sediment extracts were analyzed by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) (ARL model 3410) for the following elements: Al, Ba, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Sr, and Zn. The coral extracts were analyzed by ICP-AES for Al, Ba, Ca, Fe, Mg, Mn, Sr, and Zn and by graphite furnace Atomic Absorption Spectroscopy (AAS) (Perkin-Elmer model 5100Z with Zeeman background correction) for Cd, Cr, Cu, and Pb. Each AAS analysis was based on duplicate injections and used L'vov platforms.

Two blanks were prepared for the sediment extraction and continued through the digestion, a third blank was prepared exclusively for the digestion. The corals were digested in five batches, each batch included two blanks. The blanks were used to evaluate the purity of the reagents, as well as, to verify a contaminate free procedure. Ten percent of the sediment samples and fifteen percent of the coral samples were randomly chosen to be extracted and analyzed in duplicate. The replicate samples were done to resolve any error in the procedure or sample handling.

The replicates for the coral analysis were done in one of two ways. Either the coral was broken into two pieces before the crushing and cleaning procedure or the coral was crushed and cleaned before splitting.

In order to determine the accuracy of the graphite furnace analysis ten percent of the coral extracts were spiked (pre-injection) with known amounts of Cd, Cr, Cu, or Pb. Due to the complex nature of the extract matrix, 80 - 120 percent recoveries were accepted. If the analysis did not yield a spike recovery within this range, procedure modification was attempted until an acceptable spike was determined.

The accuracy of the calibration curves for AAS as well as the ICP analysis of Al, Cd, Cr, Cu, Pb, Ni and Zn were confirmed by using a U. S. Environmental Protection Agency (EPA) quality control sample (avialable from the EPA Cincinnati, Ohio). The WP-284 concentration #2 was prepared as instructed by the EPA, and analyzed as a sample during all sediment and coral analyses. All values were within the 95% confidence interval that is determined by the EPA.

DATA INTERPRETATION

Elemental ratios are one of the most informative ways to interpret chemical relationships of sediment, biota, and seawater (Dodd, 1967). Although the following proportions are calculated similarly, each are used for a different interpretation, thus are labeled and described separately.

The Distribution Coefficient (DC) will be defined here (Equation 1) as the ratio of the solution and solid proportions of a minor or trace metal (M) to the major element (Ca) for which it is presumed to be substituting. This ratio can quantify the elemental relationships of a solid to the chemistry of the solution from which it formed (Delaney, 1983; Linn, et. al., 1990). The Distribution Coefficients are calculated using the standard seawater values by Goldberg (1965) that are listed in Table 4.

Equation 1

$$DC = \frac{(M/Ca)\ \text{coral}}{(M/Ca)\ \text{seawater}}$$

If the coral has precipitated a metal in direct proportion to the concentration of that metal relative to Ca in seawater, then DC will equal unity (1.0). If DC is greater than one the coral is accumulating the metal preferentially over Ca. If DC is less than one, the coral is discriminating against this metal relative to Ca.

The Partition Coefficient (PC) (Equation 2) is an attempt to quantify (distinguish) the chemical "pathway" of the incorporation of a metal into either the skeletal or the sediment phase.

Equation 2

$$PC = \frac{(M/Ca)\ \text{coral}}{(M/Ca)\ \text{sediment}}$$

The Partition Coefficient indicates where an element is more likely to be concentrated. When PC is greater than one, the metal is concentrated in the coral skeleton; if PC is less than one, the metal is concentrated in the sediment.

The Enrichment Factor (EF) (Equation 3) is a proportion of the ratios of an element to a reference metal in the sediment and in the earth's crust (Table 4).

Equation 3

$$EF = \frac{(M/Fe)\ \text{sediment}}{(M/Fe)\ \text{crustal abundance}}$$

It is calculated using Fe as the reference metal and the crustal abundances from Turekian and Wedepohl (1961). Iron was chosen to use as a reference metal because it correlates with grain size, carbonates, organic material, etc. but it is unlikely to be anthropogenically increased. Also, previous studies in the Gulf of Mexico have used Fe as the reference metal (Trefry and Presley, 1976a).

Although it is recommended that the enrichment factor be calculated when evaluating the pollution status of the sediment (Rule, 1986), a high enrichment factor may or may not indicate contamination. It is used primarily to provide a reference for comparison from site to site and as a base line for future studies.

Table 4. Standard values for: Seawater (Goldberg, 1965) and Crustal Abundance (Turekian and Wedepohl, 1961) Concentrations in parts per million.

	Seawater	**Crust**
Al	1	81000
Ba	20	500
Ca	410000	41000
Cd	0.1	0.15
Cr	0.5	100
Cu	3	50
Fe	3	54000
Mg	1300000	23000
Mn	2	1000
Ni	7	75
Pb	0.03	12.5
Sr	8000	375
Zn	10	70

An appropriate multivariate technique can simplify the interpretation of a large data matrix. It is also helpful to use a technique that is able to graphically represent the influence of elemental concentrations on individual coral specimens. The cluster analysis technique groups similar samples. If the corals cluster into their taxonomic hierarchy this will indicate that the accumulation of the elements reflect genetic differences. If the corals cluster by their geographic area the environmental conditions will be presumed to have produced the metal accumulation.

Principle Component Analysis (PCA) is an additional technique that describes the differences or variations in a data set. It is a descriptive method that is useful to identify the variables most responsible for differences in the data. The principle components are eigenvalues or vectors of a covariance or correlation matrix. Observations in the data are scored using elements of the eigenvectors that are called "loadings" (Davis, 1973). The principle component scores are plotted to determine grouping in the original data matrix.

A Discriminate Function Analysis (DFA) distinguishes specified groups using the variables that maximize separation between the groups. Functions are based on the data set, then the DFA attempts to reclassify all of the data. A multivariate analysis of variance (MANOVA) followed the DFA to determine the significance of the "loadings".

Chapter V

RESULTS AND DISCUSSION

SEDIMENT

The most obvious difference in the sediment from the two locations is the amount of carbonate in the < 63 μm fraction (Table 5). The samples from the Canyon area contained less carbonate than samples from the Pinnacles. In most cases, the total concentration of each metal (Table 6) is similar between the two locations for Al, Ba, Cr, Cu, Mg, Ni and Zn. However four metals (Ca, Fe, Pb, Sr) have different concentrations between the two areas.

Elements most commonly associated with Fe (Al, Cu, Cr and Ni) had the highest concentration in the terrigenous phase (Table 7). The carbonate elements, Ca and Sr, had concentrations that were more elevated in the carbonate phase. Several exceptions especially in the Pinnacles area were noted. Magnesium and Ba, which are elements more chemically associated with Ca, had increased levels in the terrigenous fraction. Manganese area was found to be two to three times higher in the carbonate phase in the sediments from the Canyon. Lead, except in a few sites where slightly higher values are found, had a fairly uniform concentration between the two phases. The metal values for total sediment are generally lower than the expected based on previous

Table 5. Percent Carbonate from Sediment Digestion from the Mississippi Canyon Area and Mobile Pinnacles Area. (Dry Weight in grams)

Sample	**Pre-extract**	**Carbonate**	**Terr**	**%Carb**	**%Terr**	
4b	4.003	0.33	3.671	8.29	91.71	
4b	4.980	0.46	4.519	9.26	90.74	C
7	4.988	0.47	4.515	9.48	90.52	A
9	4.647	0.91	3.735	19.63	80.37	N
12	4.994	0.44	4.556	8.77	91.23	Y
14a	5.089	0.41	4.676	8.12	92.88	O
14b	5.091	0.37	4.718	7.33	92.67	N
16	5.049	1.50	3.548	29.73	70.27	
21	4.308	0.76	3.507	18.59	81.41	
23	4.962	2.58	2.383	51.98	48.02	
24	5.033	1.95	3.085	38.70	61.30	P
25	5.051	1.60	3.455	31.60	68.40	I
28	5.088	1.90	3.184	37.42	62.58	N
29a	5.146	1.78	3.366	34.46	65.54	N
29b	4.972	1.70	3.271	34.21	66.79	A
30	4.960	1.88	3.085	37.80	62.20	C
31a	5.005	2.00	3.003	40.00	60.00	L
31b	4.994	1.94	3.051	38.91	61.09	E
32	5.054	1.16	3.895	22.93	77.07	S
34	5.003	1.28	3.721	25.62	74.38	
36	4.991	1.17	3.820	23.46	76.54	
37	4.979	1.31	3.672	26.25	73.75	

Table 6. Total Element Means (X) and Standard Deviations (S) for sediment samples at each study location. (Concentration in mg/kg).

	CANYON		PINNACLE	
	X	**S**	**X**	**S**
CU	17	5.8	14	4.1
CR	22	2.7	23	2.6
NI	13	1.9	12	1.3
PB	17	7.6	7	1.7
ZN	64	13.5	61	9.3
MN	340	126	129	13
SR	43	27	118	44
BA	64	30	56	14
FE	32650	15244	22000	1934
AL	23600	4512	24409	3241
CA	6050	2202	11518	3185
MG	4783	256	4254	273

Table 7. Means (X) and Standard Deviations (S) for elements in the Carbonate and Terrigenous Phases.

	CARBONATE PHASE				**TERRIGENOUS PHASE**			
	CANYON		**PINNACLES**		**CANYON**		**PINNACLES**	
	X	**S**	**X**	**S**	**X**	**S**	**X**	**S**
Cu	3.6	2.8	0.4	0.2	17.9	6.9	21.1	6.8
Cr	2.1	0.9	1.2	0.5	28.0	4.1	35.2	3.5
Ni	7.4	2.8	2.4	0.9	14.6	1.9	17.4	1.7
Zn	28.0	6.1	6.6	2.6	70.7	13.8	84.3	15.2
Pb	11.3	3.5	4.8	1.6	17.9	8.0	7.7	2.4
Mn	591	148	105	35	302	108	143	14.4
Sr	93	63	232	83	27.4	12.4	63.8	13.0
Ba	14.5	6.5	4.0	2.5	67.1	32.9	82.1	11.3
Fe	5311	2705	360	125	40000	13964	33846	3532
Al	217	80	86	41	28670	3535	37690	3200
Ca	1080	3090	24520	2920	2866	854	4492	1365
Mg	4660	661	1820	526	5066	466	5577	715

studies in the Gulf of Mexico (Holmes, 1973). Only Pb, Zn, and Fe values are similar to those reported. Cadmium concentrations for all sediment extracts were below the detection limit of 0.14 mg/kg.

The Enrichment Factor (Appendix B) was calculated using the total sediment data. Several elements Mn, Ba, Cu, Cr, Mg, Al, and Ni were slightly less than one. The low Enrichment Factor for Ba was surprising due to the extensive petroleum exploration in this region. Barium is a major component of drilling muds and was expected to be present in higher concentrations in these sediments. It is possible that the significant reduction of petroleum exploration prior to the collection of the sediment samples in the early 1980's contributed to the low Ba values.

The Pb and Zn Enrichment Factors were approximately equal to one, indicating no obvious anthropogenic influences in either of these two locations. At one site, GS-12, the Enrichment Factors were consistently greater than one for all of these elements. The inconsistent EF for this sample is due to the unusually low concentration of Fe at this location.

Clay mineral ratios in the samples indicate two different sources control the sediment accumulation. The silt/clay fraction of the sediment was analyzed for mineral content by X-ray diffraction. The ratios for the sediments were compared to the rivers responsible for sediment contribution to these areas (Table 8). Sediment in the

Table 8. Comparison of Clay Ratios between sediments at the Canyon and Pinnacles area to previously reported sediment ratios from the Mississippi and Mobile Rivers (Griffin, 1962).

	Illite	**Smectite**	**Kaolinite**
Canyon[1]	32%	32%	35%
Pinnacles[1]	9%	45%	45%
Miss. River[2]	20-30%	60-80%	10-20%
Mobile River[2]	0-5%	40-50%	40-50%

1 this study 2 Griffin, 1962

Canyon area was found to be derived in part from the Mississippi River and the Pinnacles are influenced by the Mobile River.

The cluster analyses of the total metals of the sediment show that the sites grouped geographically (Appendix E-1). The elemental concentrations of the sediment were significantly different between locations, as shown in the cluster dendrograms as well as the Principle Component Analysis (Appendix F-1). Principle component (PC) 1 accounted for 56% of the variation between samples and grouped the Canyon sites by a higher concentration of Fe and Mg in the carbonate phase. Whereas the Pinnacles sites were characterized by higher Sr in the terrigenous phase. Principle Components 2 and 3 (accounting for 12% and 7% respectively) did not differentiate between sample locations, indicating similar concentration of the elements Ba, Ca, Cu, Mn, Pb and Zn.

A Principle Component Analysis (Appendix F-2) that used the total elemental concentration also separated the Canyon from the Pinnacles along PC1. This component accounted for 41% of the variability between sites, and is most dependant on Mg, Pb and Mn (with higher amounts of each in the Canyon Area than the Pinnacles). Principle components 2 and 3 again did not show any separation of locations. Elements with similar distributions in the sediment are Al, Ba, Cu, Cr, and Zn.

An additional PCA, using only the terrigenous fraction of the sediments, (Appendix F-1) separated the locations along PC1 which accounted for 49% of the variation. Principle Component 1 is loaded heavily on Cr, Ni, and Sr with the Pinnacles having higher concentrations of each of these metals.

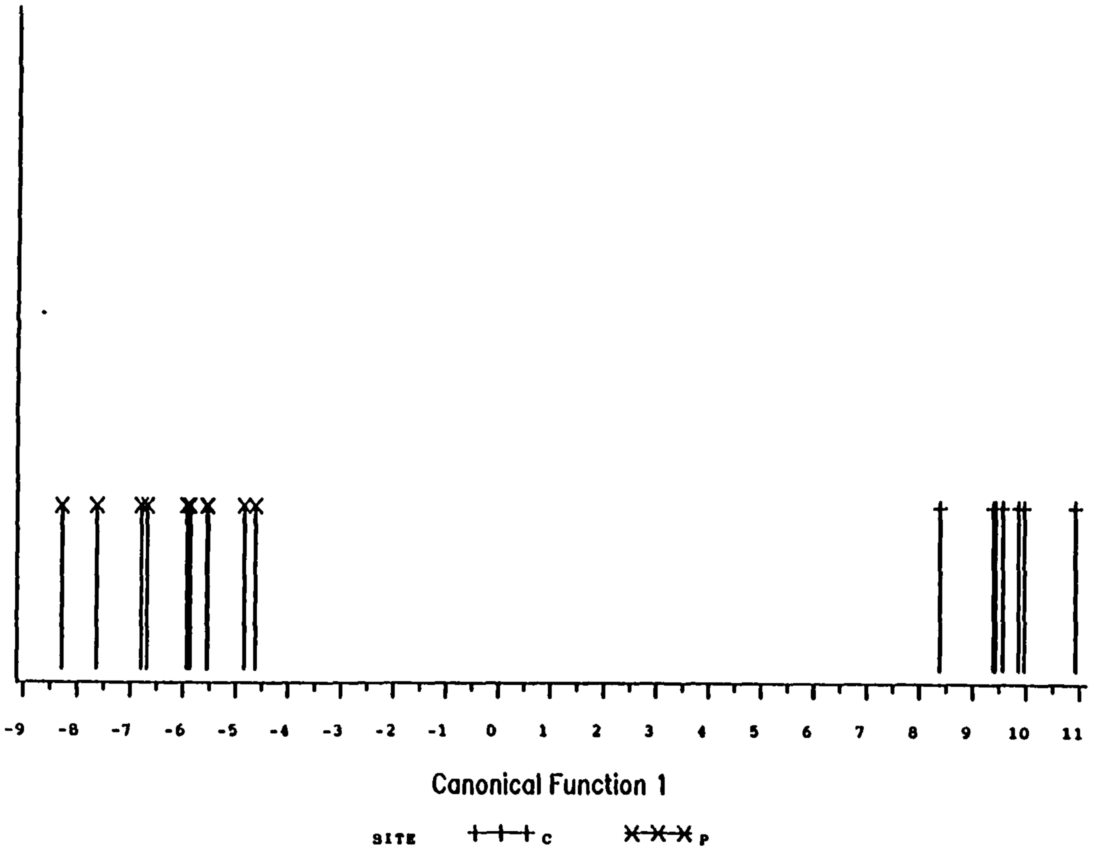
Discriminate Function Analysis (Figure 4) successfully separated and reclassified 100% of each of the sample location into the groups based on the original locations. The most important elements in the separation based upon the MANOVA (probability .99) are Pb, Mn, Sr, Ca, Mg and Fe.

The Canyon and Pinnacles each seem to have certain elemental signatures that were shared by all of the sites in the same geographic location. However, only the concentrations of a few elements were responsible for the

FIGURE 4. Needle plot, using Discriminate Function Analysis, showing the separation of the two locations: (C) Mississippi Canyon Area; and (P) Mobile Pinnacles Area. Values based on total metal concentrations in the sediment.

DISCRIMINANT FUNCTION ANALYSIS

SEDIMENT DATA



variations. Iron, Mg, Sr and Ni were most distinguishable between study areas. Barium, Ca, Cu, Al, and Zinc were the most similar. As expected, due to different sources of sediment, these two locations did not have similar metal concentrations.

CORALS

Corals do not absorb metals directly from the sediment. They either precipitate metals in solution directly out of the seawater or incorporate particles of foreign material from suspended sediment. In either case the total digestion procedure for the corals is sufficient to free metals bound in any phase of the coral except for quartz or other resistant minerals that may have become part of the skeleton.

Prior to analysis each individual coral specimen was graded (1-5) for "freshness" to track the condition of the specimen through analysis. Freshness was defined as the relative amount of wear, stain, encrustations or boreings. No correlation could be found between samples considered to be more worn or stained with higher or lower amounts of any element.

There were two different methods of creating replicates for the coral analysis. Only slight differences were observed between the two methods. Coral samples that were split after cleaning had metal values closer to the mean of the whole sample.

The elemental concentrations for *Madracis* are comparable to other reported levels for this genera (Table 9), although Sr, Cu, and Cr values are slightly lower and the Fe and Mn are higher. Metal studies of the other genera have not yet been published.

The Distribution Coefficient (Appendix B) was calculated with the mean of each genera at each site and uses standard seawater values. Krinsley (1960) determined that the ratios of the substitution ions to Ca were controlled by three factors: (1) preferential accumulation over calcium in direct proportion to the amount in the aqueous medium at a given time; (2) in response to a physiochemical factor such as temperature or salinity; and (3) in one species, due to a genetic effect.

The Distribution Coefficients (Appendix B) for Al, Fe, Mn and Pb are much greater than one, indicating an enrichment of each of these metals over seawater. These ratios also vary erratically, and show no correlation with genera, location, or grade of "freshness". The average Sr and Ba ratios are approximately equal to one demonstrating an equilibrium with the seawater. These ratios are in agreement with previous studies by Livingston and Thompson (1971) and Linn, et. al. (1990).

There is a slight depletion of Cu (DC = 0.26), and Zn

Table 9. Comparison of elemental values for <u>Madracis</u>.

	Milliman 1974	**Livingston and Thompson 1971**	**This Study**	
			Mean	Range
Ca	37.5 - 41 %	37.5 - 40.5%	37.6	32.6 - 42.7%
Sr	0.83 - 0.88%	0.827 - 0.856%	0.71	0.24 - 0.97%
Fe	5 - 95 ppm	<5 - 95 & 750 ppm	224 ppm	1 - 4330 ppm
Mn	2 - 5 "	<2 - 9	12.5 "	0 - 166 "
Ba	11 - 38 "	11 - 38	12 "	8.8 - 34.5 "
Cu	2 - 5 "	<2 - 5	0.98 "	0.06 - 3.52 "
Zn	<2	<2 - 28	3.1 "	<0.1 - 19.0 "
Cr	trace - 23	not reported	1.7 "	<0.1 - 24.0 "

(DC = 0.39) and a significant reduction in Mg (DC = 0.0007) relative to seawater. This is interpreted as a discrimination of these elements by the coral. Hermatypic corals from the Pacific Ocean are also reported to have low Distribution Coefficients of Cu (DC = 0.3) (Linn, et. al., 1990).

The Distribution Coefficient of Cd in the corals indicate a great deal of variability among genera. The two solitary corals *Paracyanthus* and *Balanophyllia* are consistently greater than one. The other three corals show a slight depletion of Cd. This generic difference is evident for other metals as well. At all sites *Madracis* have Sr/Ca ratios of coral to seawater at or greater than one and the Ba ratios for *Oculina* are all greater than one. Apparent taxonomic distribution of certain elements is attributed to small variations in the protein matrices between genera which serve as the nuclei for the individual aragonite crystals (Harriss and Almy, 1964; Mitterer, 1978). Kieth and Weber (1965) suggest that taxonomic differentiation of elements reflect the genetic selectivity for suspended and dissolved particles during feeding.

The Mn measurements reported here are highly variable and are usually greater than one. The higher Mn values could not be correlated with either genera or study location. Linn et. al. (1990) reported Distribution Coefficients of Mn in modern corals to be approximately equal to one, although older corals from the years 1600 - 1725 have higher Mn. It is possible that a post-mortem accumulation of Mn is causing this irregularity.

The cluster dendrogram (Appendix E-2) of all corals at all sites shows that most of the *Oculina* cluster in a small distinct group indicating that *Oculina* is different from the rest of the corals. Of all of the genera examined in this study, *Oculina* is the only eurythermic genera, able to tolerate a much wider range of temperatures and thus live over a larger gradient of latitudes. This biophysical difference could explain its greater chemical diversity from the other corals. *Madracis* and *Madrepora* also group together, indicating that these two genera are chemically similar.

A second cluster (Appendix E-3) of the corals form the Canyon area, separates and groups *Oculina* together. Many of the *Madracis and* Madrepora *are also grouped and are distinct from the other genera*. Most of the genera at the Pinnacles (Appendix E-4) also group together. Cluster analysis (Appendix E-5) of all of the corals at site GS-9 show that *Madracis* and *Madrepora* cluster together indicating that *Madracis* and *Madrepora* are chemically similar even though not closely related taxonomically.

The PCA of all coral samples (Appendix F-1) show only small differences between genera. The first and second principle components (accounting for 29% and 17% of the variation, respectively) separates *Balanophyllia* slightly along PC1 based on higher Fe, Pb and Al concentrations. PC3 accounts for only 12% of the variation and indicates some chemical differences between *Oculina* (higher in Mn and Ba) and the other genera.

A second PCA using only the corals from the Canyon also show *Oculina* to be chemically different although no variation was seen along PC1 or PC2. The *Madracis* and *Madrepora* group separate based upon higher Cu concentrations. A third PCA at the Pinnacles suggests that *Madracis* has lower Ba, Zn and Mg than the other genera.

Separate cluster analyses (Appendix E-3,4) and PCAs (Appendix F-3) on each location demonstrated that the corals tend to group according to the taxonomic hierarchy. This indicates that a genetic related process is controlling the uptake and accumulation of some metals. *Oculina* accumulates more Mn and Ba, wheras *Balanophyllia* has higher concentrations of Fe, Pb, Al. *Madracis* and *Madrepora* seem to have similar functions that control metal uptake.

A Discriminate Function Analysis (Appendix G) of the corals was able to verify the grouping and separation of some of the genera seen in both the cluster and the PCA. The DFA on all of the corals at both sites (Appendix G-1) correctly reclassified 71% of the *Balanophyllia*, 92% of the *Madracis*, 86% of the *Oculina*, but only 25% of the *Madrepora*, and 27% of the *Paracyanthus* as to their correct genera based on their metal composition.

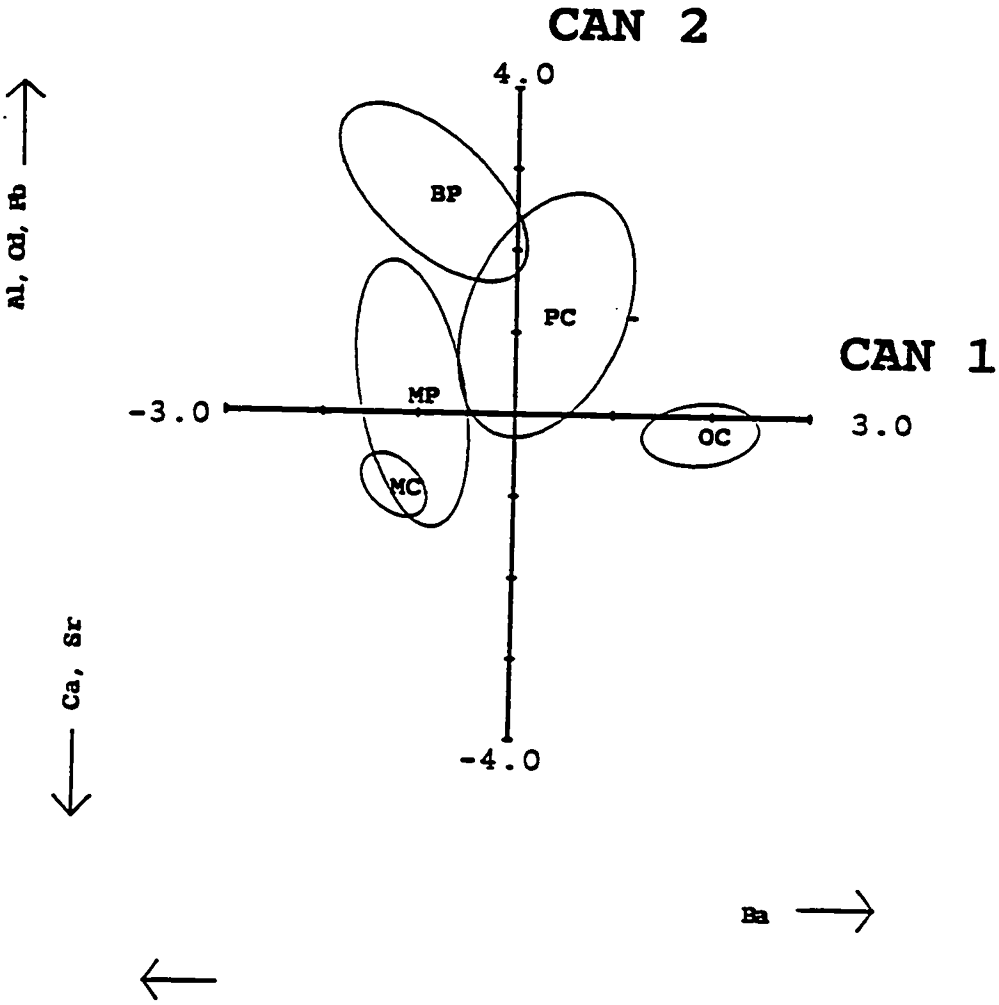
Fifty percent of the *Madrepora* grouped with the *Madracis* and 33% of the *Paracyanthus* grouped with the *Madracis*. This indicates that although *Balanophyllia*, *Madracis*, and *Oculina* have unique elemental concentrations, *Madrepora* and *Paracyanthus* do not. The similarity of *Madrepora* and *Madracis* seen in the cluster and PCA is confirmed. The genera separated based upon differences in Ba (along Canonical function 1) and Pb, Cd, Al, Sr, and Ca (along Canonical function 2) (Figure 5).

Discriminate Function Analyses were also conducted on the corals elemental content at each of the locations (Appendix G-2). At the Canyon site, 50% of the *Balanophyllia*, 88% of the *Madracis*, and 86% of the *Oculina* were correctly reclassified into there original groups. The elements influencing the separation between corals at the Canyon are Ba, Pb, Cd, Al, Sr, and Ca.

At the Pinnacles 100% of the *Balanophyllia* and 100% of the *Madracis* were reclassified into their original groups. Only 88% of the *Madrepora* and 88% of the *Paracyanthus* were also correctly grouped by DFA. There is only one *Oculina* at the Pinnacles so it was not included in the PCA. Only Canonical function 1 is significant at the Pinnacles area.

The Discriminate Function Analyses confirm that a genetic function is responsible, at least in part, for controlling the uptake and accumulation of the metals Ba,

FIGURE 5. Confidence Elipses: Discriminate Function Analysis shows the separation and grouping of the five different genera of corals (BP) *Balanophilia* (PC) *Paracyanthus* (MP) *Madrepora* (MC) *Madracis* (OC) *Oculina*.


CAN 2
4.0
Al, Cd, Rb
BP
PC
CAN 1
-3.0
MP
3.0
OC
MC
Ca, Sr
-4.0
Ba

Pb, Al, Sr, Mn, Zn, Mg. *Oculina* has the most unique elemental concentrations.

A fourth DFA was done on the corals to differentiate any location influenced variations. Because the number of genera at either location were not similar, the concentrations needed to be "centered" on the means of the genera in order to correctly determine any location affects. This centering is a mathematic calculation that subtracts the individual values from the mean of each genera ate each site. This is done to remove any genera affects so that differences between the two sites can be examined. Two elements showed a slight difference in the corals depending on the locations. The corals at the Canyon area have higher amounts of Ba, whereas the corals from the Pinnacles were characterized by higher levels of Al.

SEDIMENT/CORAL RELATIONSHIP

Metals exist in a number of forms in the aquatic environment, for example; free ions, inorganic complexes, or adsorbed on or incorporated into particulates. Corals can accumulate metals into their carbonate skeleton either of two ways. If the metal is in solution, it can become incorporated into the carbonate crystal, most likely as a replacement for Ca^{+2}, but also as a crystal inclusion. If the metal is not in solution but rather a part of a larger molecule (organic or inorganic) or a clay or silt particle, it can become attached to the coral or imbedded into the matrix but not part of the carbonate crystal. The sediment influences the chemistry of the water and thus the coral by either contribution to the suspended material or by the exchange of dissolved metals between the sediment and the overlying water.

The relative ability of an organism to concentrate a metal is dependant on many environmental factors; exposure time, salinity, temperature, life cycle, physiology, feeding habits and the physiochemical form of the metal (Fowler, 1982). It is difficult to determine the chemical relationship between sediment and the corals, especially when no in situ seawater data is present. However, the corals are probably influenced by the surrounding sediment, either by incorporation of the suspended material or by dissolved ions present in the seawater/sediment exchange.

The geochemical relationship between the corals and the sediment are quantified by the Partition Coefficient (Appendix B). For every element except Sr there is a substantial enrichment in the sediment. However, the Sr ratios are about equal to one, demonstrating an equilibrium between the corals and the sediment for this element. The Distribution Coefficient of Sr in the coral to seawater shows a similar ratio between the coral and seawater. This could indicate that an equilibrium exists between the sediment and seawater as well.

Chapter VI

SUMMARY

This study documents the distribution of Al, Ba, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Sr, and Zn in the in the surficial sediment from two separate locations in the northcentral Gulf of Mexico. It also discusses the distribution of these metals in the carbonate skeleton of five different genera of ahermatypic corals present at these locations. Comparison of the metal concentrations in the corals to the surrounding sediments can resolve where metals accumulate in a natural system.

Metal concentrations can be used to differentiate sediment samples from two locations in the Gulf of Mexico. Several statistical methods were employed to determine the elements most responsible for differentiation between locations. Based upon Principle Component Analysis and Discriminate Function Analysis; Pb, Mn, Sr, Ca, and Mg are the elements with the most variability between the two locations.

In the terrigenous fraction of the sediment, Cr, Ni and Sr account for 49% of the differences between locations. Although both locations have similar biological and geographical environments, it is evident that there are chemical differences as reflected in the sediment. These variations are most probably due to different sources of the sediment.

The variation in chemical environment is also evident in the metal concentrations of the coral skeletons. One-hundred and six individuals of five genera were analyzed for twelve elements, the corals were distinguished by discriminate analysis according to location based on Ba, and Al, indicating that there is an environmental influence on the coral chemistry. It is interesting to note that although the concentrations of Ba and Al in the corals were different between the two locations, there was little variations of these two elements in the sediments. It is possible that the corals could be more sensitive to slight changes in the seawater concentration of Ba and Al, or these elements could be in a form more easily accepted by the coral.

Oculina is the most different of the genera. Cluster analysis and PCA suggest that this coral has a unique chemical signature regardless of location. The other four genera can be divided into two separate groups based upon their metal concentrations. The first group includes *Madracis* and *Madrepora*, the second group consists of *Paracyathus* and *Balanophyllia*. These groups are unique because all four genera belong to different sub-orders.

Chapter VII

CONCLUSIONS

The distribution of metal concentrations in the sediments from the two location in the northcentral Gulf of Mexico indicate that the Mississippi Canyon Area is significantly different from the Mobile Pinnacles Area. Although these two locations have similar physical and biological parameters, this study shows that their chemical environments were not the same. The mineral concentrations and percentages of carbonate material differ demonstrating separate sources of sediment. The two different source areas almost certainly influence the chemical differences that were found. The elements most significant in the variations are Fe, Mg, Sr, and Ni. These metals are quite possibly influenced by deposition of river sediments.

The correlation of metals in the five genera of ahermatypic corals show that metal concentrations vary in different genera. The coral *Oculina* is statistically different in elemental concentration from the other four genera tested. *Madrepora* and *Madracis,* although not as close taxonomically as other corals, have similar metal values. The two solitary corals *Paracyathus* and *Balanophyllia* are chemically similar to each other, but are significantly different in metal composition from the other three colonial corals.

There is also a slight variation regardless of genera in the metal content of the corals due to location. The corals present in the Mississippi Canyon Area have higher amounts of Ba, and lower concentrations of Al, when compared to the same corals at the Mobile Pinnacles Area. This may be attributed to a physical environmental factor (temperature or salinity), but is more likely due to higher amounts of the metal in an available form that was not represented in the sediment.

It is possible to interpret environmental data using the elemental ratios in the carbonate skeletons of coral. The results of this study indicate that the metal chemistry of ahermatypic corals can parallel current work on hermatypic (reef) corals. In fact, due to the less restrictive habitats of ahermatypic corals, the collection of environmental data need not be limited to warm, shallow waters.

Future work should concentrate on accumulating base-line data on many types of ahermatypic corals. The chemistry of the seawater surrounding the corals in question should also be monitored for environmental data. The elemental concentrations of the residual material after digestion should also be monitored to determine if it is similar to the digested sediment.

REFERENCES

Aller, R.C., 1982. The Effect of Macrobenthos on Chemical Properties of Marine Sediment and Overlying Water, in McCall, P.L. and Tevesy M.J.S (eds), Animal-Sediment Relations; Plenum Press, N.Y. p. 53-96.

Ballard, R. D. and Uchupi, E., 1970. Morphology and Quaternary History of the Continental Shelf of the Gulf Coast of the United States. Bulletin of Marine Science, 20(3); 547-559.

Boyle, E. A., 1986. Paired Carbon Isotopes and Cadmium Data from Benthic Foraminifera: Implications for Changes in Oceanic Phosphorous, Oceanic Circulation, and Atmospheric Carbon Dioxide. Geochimica et Cosmochimica Acta, 50; 265-276.

Cairns, S. D., 1977. Stony Corals: I Caryophylliina and Dendrophylliina (Anthozoa: Scleractinia). Memoirs of the Hourglass Cruises, vol. 3, part 4. Florida Department of Natural Resources, St. Petersburg, Florida.

Chester, R., 1965. Geochemical Criteria for Differentiating Reef from Non-Reef Facies in Carbonate Rocks. Bulletin of the American Association of Petroleum Geology, 49(3); 258-276.

Chillingar, G. V., 1962. Dependance on Temperature of Ca/Mg Ratio of Skeletal Structures of Organisms and Direct Chemical Precipitates out of Sea Water. Bulletin of the Southern California Academy of Sciences, 61(1); 45-60.

Circé, R. C., and Tunnell, J. W., 1987. Distribution of Shelf and Shelf-edge Banks in the northwestern Gulf of Mexico. (abst) 4th annual mid year meeting SEPM, 53(2); 587-594.

Cross, T. S., and Cross, B. W., 1983. U, Sr, and Mg in Holocene and Pleistocene Corals *A. palmata* and *M. annularis*. Journal of Sedimentary Petrology, 53(2); 587-594.

Davis, J. C., 1973. Statistics and Data Analysis in Geology. John Wiley and Sons, New York. pp. 550.

Delaney, M. L., 1983. Foraminiferal Trace Elements: Uptake, Diagenesis, and 100 M. Y. Paleochemical History. PhD Dissertation, Massachusetts Institute of Technology. pp. 253.

-----, Bé, A. W. H., and Boyle, E. A., 1985. Li, Sr, Mg, and Na in Foraminiferal Calcite Shells from Laboratory Culture, Sediment Traps, and Sediment Cores. Geochimica et Cosmochimica Acta, 49; 1327-1341.

Dodd, J. R., 1967. Magnesium and Strontium in Calcareous Skeletons : A Review. Journal of Palentology, 41; 1313-1329.

Dodge, R.E. and Gilbert, T. R., 1984. Chronology of Lead Pollution Contained in Banded Coral Skeletons. Marine Biology, 82; 9-13.

Environmental Protection Agency, 1986. Test Methods for Evaluating Solid Waste, Volume 1A: Laboratory Manual Physical/Chemical Methods. Office of Solid Waste and Emergency Response, Washington DC.

Fowler, S.W., 1982. Biological Transfer and Transport Processes in G. Kullenberg (ed), Pollution Transfer and Transport in the Sea, Vol 2; CRC Press, Boca Raton, Fl. p. 1-65.

Gad, M. A., and LeRiche, H. H., 1966. A Method for Separating the Detrital and Non-detrital Fractions of Trace Elements in Reduced Sediments. Geochimica et Cosmochimica Acta, 30; 841-846.

Goldberg, E. D., 1965. Minor Elements in Seawater, in J.P. Riley and G. Skirrow (eds), Chemical Oceanography V. 1; Academic Press, N.Y., 163-196.

Goreau, T. J., 1977. Seasonal Variations of Trace Metals and Stable Isotopes in Coral Skeletons: Physiological and Environmental Controls in Proceedings of the Third International Coral Reef Symposium, Miami, Florida. p. 425-430.

Griffin, G. M., 1962. Regional Clay-Mineral Facies--Products of Weathering Intensity and Current Distribution in the Northeastern Gulf of Mexico. Geological Society of America Bulletin, 73; 737-768.

Harriss, R. C., and Almy, C. C., Jr., 1964. A Preliminary Investigation into the Incorporation and Distribution of Minor Elements in the Skeletal Material of Scleractinian Corals. Bulletin Marine Science of the Gulf and Caribbean, 14(3); 418-423.

Hirst, D. M., and Nicholls, G. D., 1958. Techniques in Sedimentary Geochemistry. (1) Separation of the Detrital and Non-Detrital Fractions of Limestones. Journal of Sedimentary Petrology, 28; 461-468.

Holmes, C. W., 1973. Distribution of Selected Elements in the Surficial Marine Sediments of the Northern Gulf of Mexico Continental Shelf and Slope. United States Geological Survey Professional Paper 814.

Holmes, C. W., 1976. Distribution, Regional Variation, and Geochemical Coherence of Selected Elements in the Sediments of the Central Gulf of Mexico. United States Geological Survey Professional Paper 928.

-----, 1982. Geochemical Indices of Fine Sediment Transport, Northwest Gulf of Mexico. Journal of Sedimentary Petrology, 52(1); 307-321.

Horowitz, A. J., 1985. A Primer on Trace Metal Sediment Chemistry, United States Geology Survey Water-Supply Paper 2277. pp. 67.

Kieth, M. L., and Weber, J. N., 1965. Systematic Relationships between Carbon and Oxygen Isotopes in Carbonates Deposited by Modern Corals and Algae. Science, 150; 498-501.

Krinsley, D., 1960. Trace Elements in the Tests of Planktonic Foraminifera. Micropaleontology, 6; 297-300.

Lea, D. W., Shen, G. T., and Boyle, E. A., 1989. Coralline Barium Records Temporal Variability in Equatorial Pacific Upwelling. Nature, 340(3); 373-376.

Linn, L. J., Delaney, M. L., Druffel, E. R. M., 1990. Trace Metals in Contemporary and Seventeenth-Century Galapagos Coral: Records of Seasonal and Annual Variations. Geochimica et Cosmochimica Acta, 54; 387-394.

Livingston, H. D. and Thompson, G., 1971. Trace Element Concentrations in Some Modern Corals. Liminology and Oceanography, 16(5); 786-796.

Lowenstam, H. A., 1961. Mineralogy and O18/O16 Ratios, Sr and Mg Contents of Recent and Fossil Brachiopods and their Bearing on the History of the Oceans. Journal of Geology, 69(3); 241-260.

Ludwick, J. C. and Walton, W. R., 1957. Shelf-edge Calcareous Prominences in the Northeastern Gulf of Mexico. Bulletin of the American Association of Petroleum Geologists, 41; 2054-2101.

Matthews, R. K., 1963. Continuous Seismic Profiles of a Shelf-edge Bathymetric Prominence in Northern Gulf of Mexico. Transactions of the Gulf Coast Association of Geological Societies, 13; 49-58.

Milliman, J. D., 1974. Marine Carbonates. Springer-Verlag, New York. pp. 319.

Mitterer, R.M., 1978. Amino Acid Composition and Metal Binding Capability of the Skeletal Protein of Corals. Bulletin of Marine Science, 28(1): 173-180.

Poag, C. W., 1972. Shelf-edge Submarine Banks in the Gulf of Mexico: Paleoecology and Biostratigraphy. Transactions of the Gulf Coast Association of Geological Societies, 22; 267-287.

Poppe, L. J. and Circé, R. C., 1983. Hoffa Reef: a Shelf-edge Calcareous Prominence in the Northern Gulf of Mexico. United States Geological Survey Open File Report 83-745.

Rezak, R., Bright, T. J., and McGrail, D. W., 1985. Reefs and Banks of the Northwestern Gulf of Mexico. John Wiley and Sons, New York. pp. 259.

Rule, J. H., 1986. Assessment of Trace Element Geochemistry of Hampton Roads Harbor and Lower Chesapeake Bay Area Sediments. Environmental Geology Water Science, 8(4); 209-219.

St. John, B. E., 1974. Heavy Metals in the Skeletal Carbonate of Scleractinian Corals. Proceedings of the Second Internations Coral Reef Symposium 2. Great Barrier Reef Committee, Brisbane, 461-469.

Schneider, R. C., and Smith, S. V., 1982. Skeletal Sr Content and Density in *Porites* spp. in Relation to Environmental Factors. Marine Biology, 66;121-131.

Shen, G. T., and Boyle, E., 1987. Lead in Corals: Reconstruction of Historical Industrial Fluxes to the Surface Ocean. Earth and Planetary Science Letters, 82; 289-304.

----, and ----, 1988. Determination of Pb, Cd, and other Trace Metals in Annually-banded Corals. Chemical Geology, 67; 47-62.

Shepard, F. P., 1937. "Salt" Domes Related to Mississippi Submarine Trough. Bulletin of the American Association of Petroleum Geologists, 48; 1349-1362.

Swart, P. K., 1981. The Strontium, Magnesium and Sodium Composition of Recent Scleractinian Coral Skeletons as Standards for Paleoenvironmental Analysis. Palaeogeography, Paleoclimatology, and Paleoecology, 34; 115-136.

Thompson, G., and Livingston, H. D., 1970. Sr and U Concentraions in Aragonite Precipitated by Some Modern Corals. Earth and Planetary Science Letters, 8; 439 -442.

Trefry, J. H., and Presley, B. J., 1976a. Heavy Metals in Sediments from San Antonio Bay and the Northwestern Gulf of Mexico. Envoronmental Geology, 1; 283-294.

-----, and -----, 1976b. Heavy Metal Transport from the Mississippi River to the Gulf of Mexico in Windom, H. L., and Duce, R. A. (eds), Marine Pollution Transfer; Lexington Books, Lexington, MA, 39-76.

-----, 1977. The Transport of Heavy Metals by the Mississippi River and their Fate in the Gulf of Mexico, MS Thesis, Texas A & M University.

Turekian, K. K., 1955. Paleoecological Significance of the Sr-Ca Ratio in Fossils and Sediments. Bulletin of the Geological Society of America, 66; 155-158.

-----, and Armstrong, R. L., 1960. Mg, Sr, and Ba Concentrations and Calcite-Aragonite Ratios of Some Recent Molluscan Shells. Journal of Marine Research, 18(3); 133-151.

-----, and Wedepohl, K. H., 1961. Distribution of the Elements in some Major Units of the Earth's Crust. Bulletin of the Geological Society of America, 72; 175-192.

Veeh, H. H., and Turekian, K. K., 1968. Co, Ag, and U Concentrations of Reef Building Corals in the Pacific Ocean. Liminology and Oceanography, 13(2); 304-308.

Weber, J. N., 1974, Skeletal Chemistry of Scleractinian Reef Corals; Uptake of Mg form Seawater. American Journal of Science, 274; 84-93.

APPENDIX A

LATITUDES AND LONGITUDES FOR EACH SITE

Locations of Sample Sites
Latitude and longitude Determined by Loran-C

SAMPLE	STUDY SITE	Lat (N)	Long (W)	Depth (m)
4	Mid-Canyon Pinacle	28° 37.07'	89° 51.25'	200
7	Hoffa Reef	28° 39.61'	89° 49.56'	125
9	"	28° 39.76'	89° 49.42'	82
12	"	28° 39.55'	89° 49.42'	125
14	"	28° 39.56'	89° 49.28'	90
16	"	28° 39.75'	89° 49.05'	88
21	"	28° 40.18'	89° 49.44'	90
23	Mobile Pinacles	29° 20.29'	87° 45.87'	100
24	"	29° 20.36'	87° 45.99'	100
25	"	29° 20.26'	87° 45.92'	NR*
28	"	29° 20.26'	87° 45.92'	104
29	"	29° 19.84'	87° 46.41'	107
31	"	29° 19.70'	87° 46.55'	106
32	"	29° 19.54'	87° 46.65'	100
34	"	29° 20.07'	87° 45.57'	NR
36	"	29° 20.19'	87° 45.13'	NR
37	"	29° 20.64'	87° 45.17'	NR

*NR: depth not recorded

APPENDIX B

ELEMENTAL RATIOS

Enrichment Factor (M/Fe(sediment) to M/Fe(crust)).

ID/ SITE	Al	Ba	Cr	Cu	Mg	Mn	Ni	Pb	Sr	Zn
4 C	0.43	0.10	0.35	0.35	0.30	0.44	0.24	1.96	0.07	1.26
7 C	0.37	0.08	0.20	0.22	0.20	0.34	0.14	1.28	0.06	0.75
9 C	0.39	0.30	0.32	0.57	0.27	0.56	0.23	2.81	0.31	1.45
12 C	1.37	0.50	1.05	1.55	1.11	2.91	1.16	10.82	0.57	6.12
14 C	0.49	0.17	0.35	0.32	0.33	0.38	0.24	1.50	0.10	1.26
16 C	0.51	0.21	0.50	0.84	0.44	0.41	0.34	1.45	0.14	1.51
21 C	0.46	0.27	0.46	0.89	0.38	0.51	0.36	1.98	0.23	1.75
23 P	0.66	0.20	0.57	0.76	0.48	0.42	0.37	2.05	1.32	2.57
24 P	0.68	0.30	0.58	0.96	0.54	0.35	0.45	2.11	1.08	2.32
25 P	0.71	0.22	0.60	0.09	0.45	0.23	0.42	0.76	0.25	2.13
28 P	0.70	0.21	0.50	0.71	0.44	0.32	0.36	1.26	0.91	1.81
29 P	0.73	0.23	0.51	0.65	0.40	0.29	0.36	1.02	0.90	1.72
30 P	0.74	0.24	0.53	0.81	0.44	0.29	0.36	1.50	0.86	1.81
31 P	0.72	0.25	0.54	0.74	0.45	0.33	0.39	1.36	1.11	2.93
32 P	0.76	0.36	0.55	0.63	0.40	0.28	0.39	1.11	0.42	1.90
34 P	0.75	0.30	0.60	0.67	0.43	0.31	0.40	1.14	0.58	2.11
36 P	0.83	0.30	0.61	0.61	0.45	0.30	0.42	0.99	0.50	1.96
37 P	0.79	0.37	0.67	0.72	0.49	0.34	0.44	1.27	0.67	2.27

Distribution Coefficients (Me/Ca (Coral) to Me/Ca (seawater)

Site/ Coral	Al	Cd	Cr	Mn	Fe	Sr	Ba	Pb	Cu	Mg	Zn
09 BP	320	1.61	0.85	26	502	0.63	0.95	40	0.32	0.0009	0.72
09 MC	47	0.48	0.64	7	53	0.84	0.70	15	0.33	0.0006	0.14
09 MP	--	0.56	0.69	1	2	0.58	0.82	8	0.16	0.0005	0.00
09 OC	66	0.83	0.85	23	210	0.66	1.05	15	0.22	0.0009	0.43
09 PC	235	1.44	0.68	18	182	0.95	1.27	28	0.30	0.0017	0.55
10 MC	0	0.27	0.71	3	5	1.08	0.66	22	0.22	0.0005	0.31
12 MC	53	0.24	0.56	2	25	0.98	0.67	13	0.38	0.0005	0.18
12 OC	54	0.17	1.58	18	83	0.94	1.39	7	0.20	0.0007	0.17
12 PC	105	1.32	6.04	28	109	0.57	1.10	30	0.33	0.0021	0.25
13 MC	43	0.30	0.52	23	23	0.99	0.69	12	0.49	0.0005	0.68
13 OC	162	0.16	0.82	9	211	1.05	1.20	9	0.26	0.0006	0.07
14 MC	144	0.16	0.27	95	1391	0.95	1.33	27	0.07	0.0012	0.92
14 OC	77	0.30	0.45	8	181	0.88	1.40	6	0.16	0.0006	0.13
16 OC	54	0.06	0.22	4	24	1.01	1.47	3	0.40	0.0004	0.08
21 OC	11	0.49	0.87	2	30	0.65	1.77	2	0.20	0.0006	0.15
21 PC	5	0.91	0.04	4	11	0.56	0.61	8	0.45	0.0005	0.14
24 MP	--	0.41	0.32	1	37	0.91	0.85	14	0.13	0.0006	0.82
25 MC	109	0.34	26.47	1	49	1.01	0.64	14	0.55	0.0005	0.59
25 MP	120	0.31	0.23	1	17	0.78	0.88	12	0.10	0.0004	0.00
25 PC	468	0.89	0.55	5	126	0.75	0.85	30	0.14	0.0007	2.03
28 BP	625	1.36	1.42	9	268	0.75	0.78	39	0.24	0.0008	0.76
28 MC	186	0.38	3.25	2	91	1.03	0.59	16	0.35	0.0006	0.52
28 MP	132	0.38	1.04	0	48	0.88	0.64	20	0.13	0.0004	0.37
28 OC	--	1.14	0.60	3	14	0.50	0.74	2	0.12	0.0010	0.17
28 PC	168	0.43	0.42	4	74	0.80	0.72	13	0.12	0.0006	0.23
29 PC	160	0.62	2.09	2	122	0.58	0.68	6	0.06	0.0007	0.17
30 PC	223	1.03	1.20	23	77	1.02	1.00	42	0.52	0.0013	0.67
31 MC	121	0.57	0.96	1	114	0.90	0.72	40	0.39	0.0006	0.00
34 MC	156	0.61	1.50	4	53	0.95	0.60	9	0.19	0.0006	0.19
34 MP	860	1.38	1.51	55	929	0.64	0.62	54	0.30	0.0008	0.41
34 PC	16	1.03	0.07	1	3	0.55	0.73	3	0.13	0.0005	0.15

Partition Coefficient (M/Ca CORAL to M/Ca SEDIMENT)

SITE/ CORAL	MN	FE	SR	BA	PB	CU	MG	ZN	CR
9 BP	0.00152	0.000340	1.068	0.00160	0.000428	0.000428	0.002861	0.000896	0.000163
9 MC	0.00040	0.000036	1.415	0.00118	0.000166	0.000438	0.001945	0.000182	0.000122
9 MP	0.00005	0.000001	0.984	0.00138	0.000088	0.000221	0.001493	0.000011	0.000131
9 OC	0.00137	0.000142	1.122	0.00177	0.000165	0.000289	0.002916	0.000545	0.000163
9 PC	0.00106	0.000123	1.609	0.00213	0.000307	0.000401	0.005096	0.000687	0.000131
12 MC	0.00006	0.000045	1.691	0.00185	0.000107	0.000484	0.000982	0.000157	0.000091
12 OC	0.00047	0.000164	1.598	0.00383	0.000056	0.000276	0.001477	0.000144	0.000248
12 PC	0.00072	0.000215	0.977	0.00302	0.000228	0.000443	0.003944	0.000205	0.000948
14 MC	0.00197	0.000131	2.101	0.00162	0.000222	0.000637	0.001020	0.000726	0.000056
14 OC	0.00042	0.000088	1.940	0.00274	0.000091	0.000275	0.001010	0.000127	0.000060
16 OC	0.00029	0.000014	2.578	0.00279	0.000074	0.000337	0.000847	0.000089	0.000022
21 OC	0.00018	0.000021	1.321	0.00324	0.000037	0.000174	0.001521	0.000166	0.000113
21 PC	0.00029	0.000008	1.128	0.00113	0.000154	0.000382	0.001265	0.000155	0.000006
24 MP	0.00010	0.000046	1.369	0.00256	0.000495	0.000187	0.001835	0.001182	0.000062
25 MC	0.00023	0.000056	1.752	0.00230	0.000909	0.008298	0.001375	0.000824	0.004388
25 MP	0.00018	0.000020	1.358	0.00316	0.000750	0.001518	0.001088	0.000000	0.000039
25 PC	0.00092	0.000143	1.296	0.00306	0.001939	0.002183	0.001926	0.002799	0.000092
28 BP	0.00151	0.000265	1.061	0.00266	0.001886	0.000357	0.002433	0.001112	0.000258
28 MC	0.00028	0.000090	1.451	0.00203	0.000751	0.000523	0.001756	0.000760	0.000588
28 MP	0.00004	0.000048	1.244	0.00221	0.000961	0.000197	0.001238	0.000550	0.000188
28 OC	0.00045	0.000014	0.704	0.00252	0.000107	0.000179	0.002808	0.000253	0.000108
28 PC	0.00063	0.000073	1.131	0.00247	0.000631	0.000177	0.001907	0.000349	0.000077
29 PC	0.00015	0.000060	0.429	0.00108	0.000191	0.000051	0.001136	0.000135	0.000182
30 PC	0.00408	0.000076	1.483	0.00294	0.001579	0.000676	0.003628	0.000985	0.000198
31 MC	0.00010	0.000122	1.203	0.00224	0.001930	0.000644	0.001879	0.000000	0.000171
34 MC	0.00057	0.000053	1.495	0.00148	0.000469	0.000300	0.001699	0.000248	0.000227
34 MP	0.00844	0.000929	1.010	0.00152	0.002728	0.000476	0.002396	0.000532	0.000229
34 PC	0.00012	0.000003	0.864	0.00179	0.000142	0.000218	0.001501	0.000196	0.000011

APPENDIX C

SEDIMENT DATA

Sediment Data Total Element Concentrations; Based Upon %Carbonate Phase + %Terrigenous Phase.

ID	L	Cu	Cr	Ni	Zn	Pb	Mn	Sr	Ba	Fe	Al	Ca	Mg
4	C	14	28	14.5	70	19.5	355	23	42	42800	28100	3800	5600
7	C	11	20	10.7	52	15.8	343	24	41	53300	30100	3700	4600
9	C	23	26	14.3	82	28.3	452	95	121	43400	25600	9500	5000
12	C	14	19	15.7	77	24.3	524	39	45	9700	20000	4400	4600
14	C	11	24	12.5	59	12.6	258	27	58	36100	26700	4600	5200
16	C	19	23	11.6	48	8.2	189	24	48	24400	18900	7100	4600
21	C	24	25	14.6	66	13.3	274	48	73	29000	20300	7000	4700
23	P	14	21	10.4	66	9.4	154	182	37	19800	19700	19400	4100
24	P	18	22	12.7	61	9.9	133	152	57	20200	20800	13700	4700
25	P	2	26	13.6	64	4.1	102	41	49	23100	24800	10600	4500
28	P	14	20	10.7	50	6.2	129	135	42	21200	22300	11400	4000
29	P	14	22	11.6	52	5.5	125	145	50	23200	25700	12200	4000
30	P	16	21	10.8	50	7.4	115	128	49	21200	23600	11100	4000
31	P	15	22	11.9	83	6.9	135	169	51	21800	23700	13100	4200
32	P	15	26	13.9	63	6.6	136	75	86	25500	29300	8000	4400
34	P	14	25	12.5	61	5.9	130	90	63	22300	25200	8900	4100
36	P	14	28	14.4	62	5.6	140	86	70	24400	30400	8900	4700
37	P	13	24	11.8	57	5.7	125	91	67	19300	23000	9400	4100

Sediment Data for Minor and Trace Elements; Carbonate Phase (I) and Terrigenous Phase (II).

	Cu		Cr		Ni		Zn		Pb		Mn		Sr		Ba	
	I	II	I	II	I	II	I	II	I	II	I	II	I	II	I	II
4a	2.4	15	2.7	31	9.4	15	36.4	78	14.5	20	670	320	62	20	13.3	45
4b	1.1	15	2.4	30	8.3	15	29.8	68	12.2	19	600	340	55	20	11.5	45
7	2.6	12	2.8	23	7.9	11	25.7	55	13.2	16	680	310	64	20	15.7	43
9	3.0	28	0.9	32	3.4	17	15.4	98	5.6	34	620	410	244	58	20.4	146
12	2.0	15	3.4	21	12.3	16	26.8	82	6.6	26	670	510	119	31	12.3	48
14a	2.4	12	2.0	26	6.6	13	31.5	63	11.7	13	604	230	64	23	21.5	61
14b	3.5	12	2.4	26	6.5	13	32.7	59	14.6	12	680	220	73	23	23.8	61
16	10.5	23	1.0	32	3.7	15	24.0	59	8.6	8	210	180	35	20	3.8	67
21	4.7	29	1.1	31	8.2	16	30.1	74	14.9	13	590	200	118	32	8.6	88
23	0.5	29	0.8	43	1.5	20	8.2	129	6.1	13	130	180	265	91	1.7	76
24	0.4	30	1.0	36	2.8	19	7.2	95	6.6	12	90	160	276	73	3.3	91
25	0.0	3	0.0	39	0.0	20	0.1	94	0.0	6	1	150	2	60	0.0	72
28	0.3	23	1.1	31	2.2	16	6.5	77	5.1	7	110	140	250	64	1.9	66
29a	0.3	20	1.1	31	2.8	15	6.3	72	5.3	5	110	130	301	62	4.2	74
29b	0.1	22	1.4	36	2.5	18	6.2	80	3.9	7	100	140	286	66	4.0	76
30	0.4	26	1.1	34	2.3	16	6.3	77	4.8	9	90	130	237	62	2.4	77
31a	0.4	22	1.0	33	2.8	16	5.4	75	4.8	7	120	140	310	76	2.8	78
31b	0.6	25	1.2	39	2.9	19	5.0	86	5.6	9	120	150	307	78	2.8	87
32	0.5	19	1.3	34	3.5	17	7.4	80	5.1	7	120	140	167	48	6.2	110
34	0.6	19	1.6	33	2.8	16	12.1	78	5.8	6	130	130	199	51	7.3	82
36	0.3	19	2.1	36	2.9	18	7.4	79	4.1	6	140	140	200	50	7.6	90
37	0.2	18	2.0	33	2.7	16	8.2	74	5.1	6	110	130	211	49	7.6	88

Sediment Data for Major Elements; Carbonate Phase (I) and Terrigenous Phase (II).

	Fe		Al		Ca		Mg	
	I	II	I	II	I	II	I	II
4a	6600	47000	300	31000	19700	2500	4800	5800
4b	5500	45000	240	30000	17800	2500	4200	5600
7	6300	58000	190	33000	18900	2200	4500	4600
9	1000	54000	150	32000	27300	5000	3500	5400
12	6200	10000	200	22000	21900	2700	4400	4600
14a	8000	38000	300	28000	20400	2600	5200	5200
14b	9000	39000	330	30000	23300	2400	5900	5100
16	1900	34000	120	27000	17700	2600	4700	4600
21	3300	35000	120	25000	22700	3300	4700	4700
23	290	41000	50	41000	31600	6200	1600	6800
24	250	33000	70	34000	26400	5600	1700	6600
25	4	34000	1	40000	22000	5300	200	6500
28	350	34000	70	36000	22500	4600	1900	5300
29a	420	36000	80	40000	27700	4300	1900	4900
29b	410	35000	80	39000	25900	500	1800	5400
30	360	34000	80	38000	21600	4600	1900	5300
31a	390	35000	70	37000	24700	5100	1900	5200
31b	400	37000	70	42000	24800	5400	1900	6300
32	470	33000	130	38000	20900	4200	2100	5100
34	470	30000	140	34000	22700	4100	2200	4800
36	460	32000	140	40000	23500	4300	2300	5500
37	400	26000	140	31000	24400	4200	2200	4800

APPENDIX D

CORAL DATA

(BP) *Balanophilia* (PC) *Paracyanthus*
(MP) *Madrepora* (MC) *Madracis* (OC) *Oculina*

Elemental Concentrations of Coral Samples.

ID	MN	FE	CA	SR	BA	CD	PB	CU	MG	ZN	AL	CR
BP09	58	3900	375000	5630	14.4	0.108	2.82	0.65	1299	11.5	577	0.76
BP09	7	192	331000	4400	14.8	0.132	0.12	0.49	735	6.7	160	0.10
BP09	81	727	357000	3610	19.1	0.164	0.69	1.45	1017	4.1	232	0.41
BP09	32	414	361000	3990	18.1	0.154	0.52	0.83	1349	2.6	143	0.22
BP28	20	721	366000	5710	13.2	0.066	1.68	0.73	1135	2.6	842	0.63
BP28	21	780	354800	6450	14.6	0.135	1.14	0.66	936	16.0	520	0.45
BP28	9	630	366000	3890	13.7	0.162	0.30	0.55	976	1.6	296	0.81
MC09	7	17	381800	6000	12.0	0.024	1.15	0.60	692	*	*	0.21
MC09	13	550	361000	9400	11.4	0.026	0.82	0.28	1490	3.9	106	0.10
MC09	5	126	417000	5910	13.4	0.028	0.54	0.42	575	3.4	38	0.07
MC09	8	80	336600	6560	12.5	0.043	0.52	0.43	625	*	*	0.05
MC09	11	255	392600	8560	13.6	0.016	0.15	0.81	705	2.0	101	0.33
MC09	65	268	402000	8120	14.2	0.019	0.77	3.52	745	1.4	34	0.25
MC09	7	151	359000	7810	13.4	0.023	0.30	1.53	725	0.8	56	0.07
MC09	4	48	369500	4120	13.1	0.030	0.18	0.42	843	0.3	46	0.15
MC09	4	1	343300	3790	12.6	0.101	0.23	0.45	758	0.8	33	0.29
MC09	11	30	352000	3960	11.9	0.086	0.14	1.07	767	*	*	1.51
MC09	4	61	362600	4410	13.0	0.085	0.12	0.50	706	1.5	5	0.30
MC09	5	144	373100	4420	12.4	0.042	0.08	0.91	722	1.7	93	0.16
MC10	5	12	354000	7520	11.4	0.023	0.58	0.57	604	2.7	*	0.31
MC12	7	198	460000	9210	17.1	0.028	0.35	1.06	818	*	171	0.38
MC12	4	94	354600	7220	12.6	0.020	0.30	0.60	632	*	60	0.26
MC12	3	68	409000	9120	13.7	0.021	1.33	1.82	608	2.3	*	0.38
MC12	4	43	427000	7800	13.1	0.020	0.16	1.24	636	0.2	*	0.10
MC12	4	55	403000	7950	12.4	0.024	0.15	1.24	642	0.3	64	0.08
MC12	7	43	398000	8440	12.7	0.021	0.28	0.89	704	8.7	70	0.14
MC12	3	16	366000	4300	11.2	0.033	0.09	1.12	664	0.9	*	0.61
MC13	4	62	369000	6270	12.1	0.025	0.27	0.30	682	4.5	32	0.06
MC13	1	13	402800	8560	14.3	0.054	0.39	2.99	570	14.0	*	0.57
MC13	166	41	405000	7680	12.5	0.019	0.25	0.82	786	0.5	71	0.10
MC13	6	146	388000	7960	13.8	0.019	0.49	1.56	612	7.0	61	0.28
MC14	163	3594	353000	6610	23.0	0.014	0.71	0.20	1382	8.0	123	0.12

*= ?

MC25	3	208	374000	7680	11.7	0.027	0.50	0.97	727	2.8	202	0.51
MC25	2	65	385000	7380	12.0	0.037	0.27	2.12	553	8.3	*	24.00
MC28	0	126	350000	6120	9.5	0.035	0.35	0.45	623	6.3	105	0.20
MC28	3	50	376700	8210	12.7	0.036	0.72	0.72	942	1.1	222	1.44
MC28	6	93	360000	7470	9.9	0.032	0.35	1.05	584	3.5	117	0.44
MC28	5	578	403000	7730	11.0	0.027	0.36	1.26	936	4.9	244	4.48
MC28	2	407	387600	8360	11.5	0.046	0.36	1.43	715	8.1	165	0.89
MC31	1	298	357000	6300	12.6	0.050	1.05	1.03	735	0.0	105	0.42
MC34	16	357	378000	7320	11.0	0.016	0.59	0.55	792	1.2	335	1.46
MC34	1	26	377900	8890	9.5	0.065	0.03	0.52	653	2.0	*	0.14
MC34	3	43	342000	4220	12.0	0.085	0.13	0.46	740	1.9	82	0.41
MP09	1	3	337200	5330	13.8	0.031	0.28	0.36	537	*	*	0.66
MP09	1	4	339400	2350	12.9	0.032	0.32	0.45	575	*	*	0.24
MP09	1	4	347000	3980	12.0	0.024	0.16	0.77	576	0.3	*	0.25
MP09	3	7	374000	4290	17.7	0.110	0.08	0.15	566	*	*	0.03
MP24	1	95	349000	6230	14.5	0.035	0.37	0.35	755	7.0	*	0.14
MP25	2	39	403000	5950	17.4	0.029	0.33	0.28	504	*	101	0.11
MP25	2	58	362000	5810	15.5	0.030	0.32	0.29	517	*	123	0.11
MP28	0	153	376000	6590	12.2	0.026	0.68	0.37	543	6.8	136	0.73
MP28	1	109	362400	6180	11.2	0.043	0.40	0.36	511	*	102	0.21
MP34	0	13	359000	6560	13.4	0.058	0.39	0.46	493	7.0	*	0.09
MP34	125	3430	343000	3070	9.0	0.120	1.81	0.96	1228	0.6	1080	0.96
MP34	150	3537	325000	3280	8.8	0.170	1.90	0.85	1160	2.8	1075	0.85
OC09	9	238	360000	5790	32.2	0.034	0.49	0.60	572	13.0	*	*
OC09	20	745	416700	8350	13.6	0.014	0.88	1.11	897	*	189	0.4
OC09	90	725	376600	3700	16.4	0.109	0.33	0.61	1900	3.3	59	0.5
OC09	114	1435	347000	3430	14.5	0.160	0.43	0.63	1990	4.6	56	0.6
OC09	15	217	382000	4160	24.2	0.040	0.12	0.25	860	0.8	52	0.7
OC09	4	92	366000	3830	15.2	0.096	0.27	0.45	861	2.2	6	*
OC12	5	112	377000	7000	27.0	0.016	0.33	1.05	700	3.2	54	10.1
OC12	3	83	382000	7500	25.8	0.018	0.29	0.98	750	3.6	*	0.6
OC12	25	86	366000	7780	25.1	0.008	0.09	0.46	894	1.0	29	*
OC12	11	302	384000	7940	25.3	0.005	0.14	0.82	796	1.2	27	*
OC12	73	368	382000	7700	26.3	0.004	0.13	0.81	1003	3.1	54	*
OC12	54	306	376000	8060	25.5	0.007	0.13	0.51	1593	1.8	64	0.2
OC12	44	233	387800	7880	26.2	0.004	0.10	0.93	1419	3.4	94	0.1

OC12	25	206	378000	7300	20.3	0.005	0.09	0.56	787	0.9	70	0.1
OC12	46	379	403800	7480	21.9	0.006	1.14	0.51	879	1.1	117	0.1
OC12	31	269	383300	8010	21.1	0.019	0.12	0.60	775	1.5	64	0.1
OC12	23	218	386000	7280	22.1	0.018	0.17	0.71	1055	1.3	85	0.1
OC12	98	615	372000	7940	20.4	0.021	0.23	0.56	1314	1.4	112	0.4
OC12	134	514	392500	8190	31.7	0.020	0.16	0.61	1302	1.7	105	0.4
OC12	18	169	412800	7660	33.0	0.033	0.23	0.54	806	0.6	*	*
OC12	16	225	405600	7560	31.4	0.029	0.23	0.46	792	2.9	26	*
OC12	4	42	376000	4080	29.6	0.018	0.07	0.17	931	0.7	10	0.1
OC12	3	31	375000	3660	27.2	0.038	0.03	0.14	755	0.4	*	*
OC12	3	32	352000	3450	29.6	0.028	0.03	0.16	793	0.2	*	*
OC13	16	587	379900	7860	22.4	0.015	0.24	0.75	767	0.7	150	0.3
OC14	22	1541	391800	8280	25.1	0.011	0.26	0.84	748	1.8	132	0.2
OC14	6	88	388700	7700	26.8	0.015	0.11	0.58	671	0.8	53	0.2
OC14	26	775	376000	8540	20.2	0.021	0.22	0.47	981	1.2	102	0.1
OC14	10	81	349000	3680	32.2	0.076	0.15	0.17	826	0.9	52	0.3
OC14	6	43	407000	4660	26.5	0.020	0.06	0.22	777	1.7	20	0.1
OC16	8	70	395000	7830	28.4	0.006	0.09	1.18	592	0.8	52	0.1
OC21	1	1	352400	4000	32.2	0.042	0.06	0.42	810	0.6	7	0.4
OC21	9	290	371000	3810	27.6	0.036	0.04	0.57	816	2.8	31	0.4
OC21	3	15	390000	6010	30.0	0.039	0.06	0.42	709	1.5	*	0.5
OC21	3	13	326000	4610	34.5	0.057	0.05	0.80	784	0.3	*	*
OC28	5	38	367800	3600	13.3	0.103	0.06	0.33	1190	1.5	*	0.2
PC09	12	114	400000	5950	32.7	0.067	0.48	0.81	844	0.0	37	*
PC09	23	1208	303100	5700	17.2	0.129	1.16	0.72	920	14.0	675	0.2
PC09	78	432	254000	3790	17.5	0.070	0.94	1.14	5061	1.6	56	0.7
PC09	4	41	390000	9710	16.3	0.207	0.23	0.36	589	2.5	5	*
PC12	91	549	352400	3890	19.7	0.186	1.17	0.68	4011	1.5	176	4.3
PC12	7	24	366000	4170	18.9	0.046	0.41	1.09	817	2.9	8	1.0
PC21	6	28	345000	3770	10.4	0.077	0.21	1.16	622	1.2	4	*
PC25	10	352	382700	5610	15.9	0.084	0.84	0.41	904	19.0	437	0.2
PC28	0	25	382100	6350	15.2	0.033	0.33	0.36	603	0.0	40	0.1
PC28	14	110	361000	5620	9.4	0.077	0.38	0.31	1140	3.1	79	0.2
PC28	7	457	350400	5230	14.2	0.007	0.34	0.30	660	3.3	330	0.1
PC29	3	319	356700	4080	12.0	0.054	0.17	0.16	870	1.5	139	0.9
PC30	44	216	382000	7640	18.8	0.096	1.18	1.46	1597	6.3	208	0.5

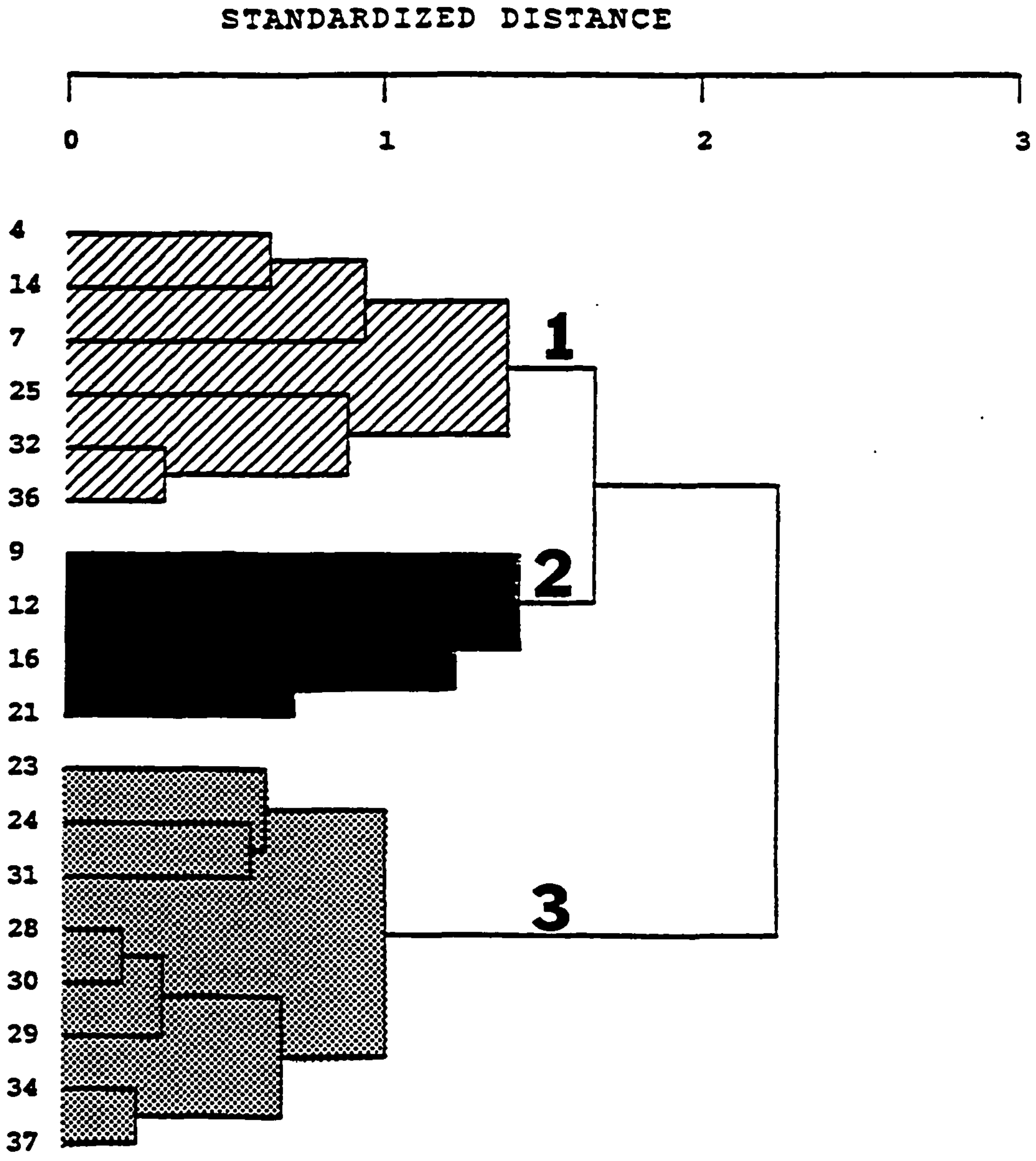
PC34	2	11	391000	4330	12.9	0.107	0.10	0.39	761	2.5	26	*
PC34	1	6	378000	3940	14.7	0.087	0.06	0.39	591	0.4	4	*

APPENDIX E

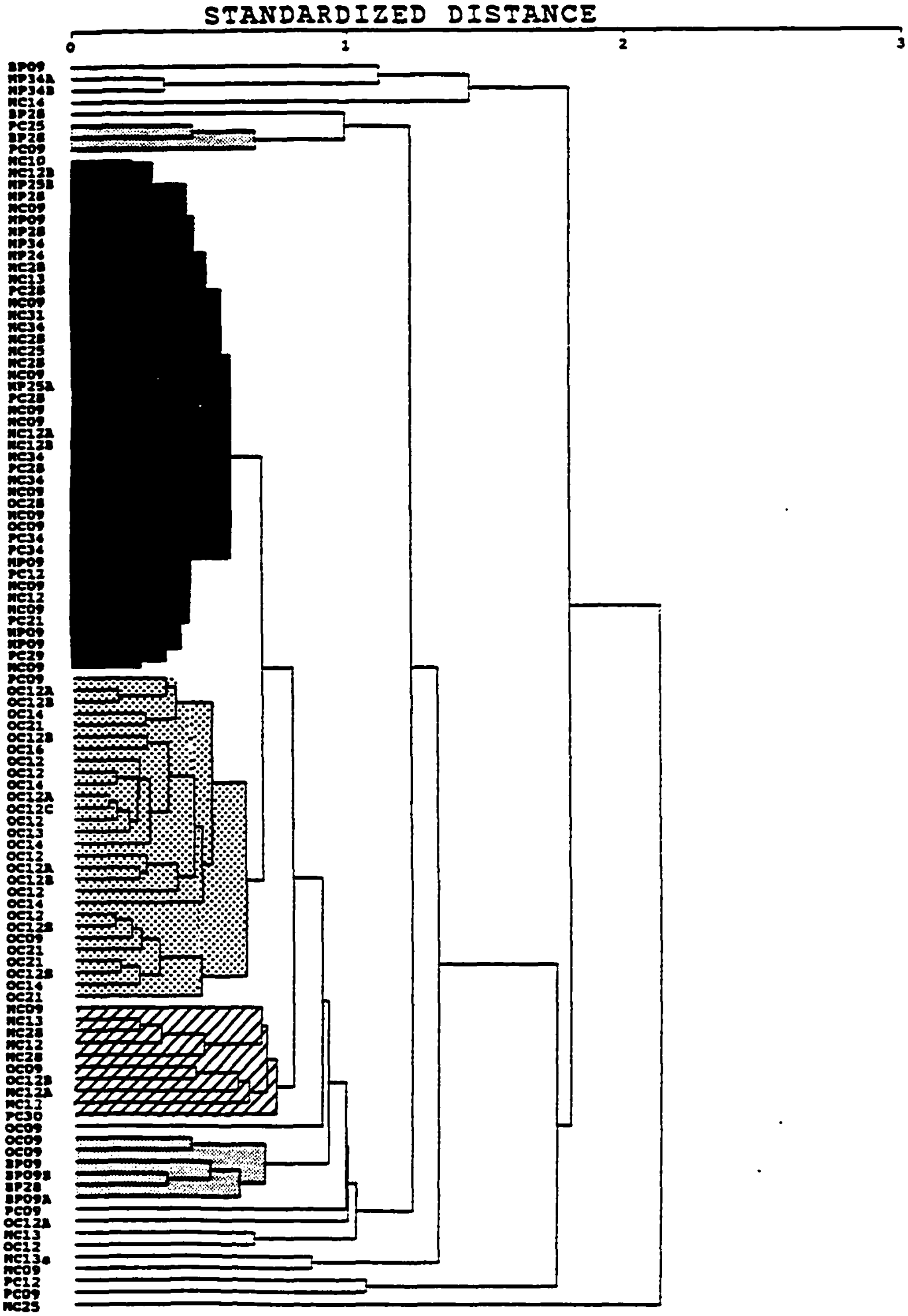
CLUSTER DENDROGRAMS

(BP) *Balanophilia* (PC) *Paracyanthus*
(MP) *Madrepora* (MC) *Madracis* (OC) *Oculina*

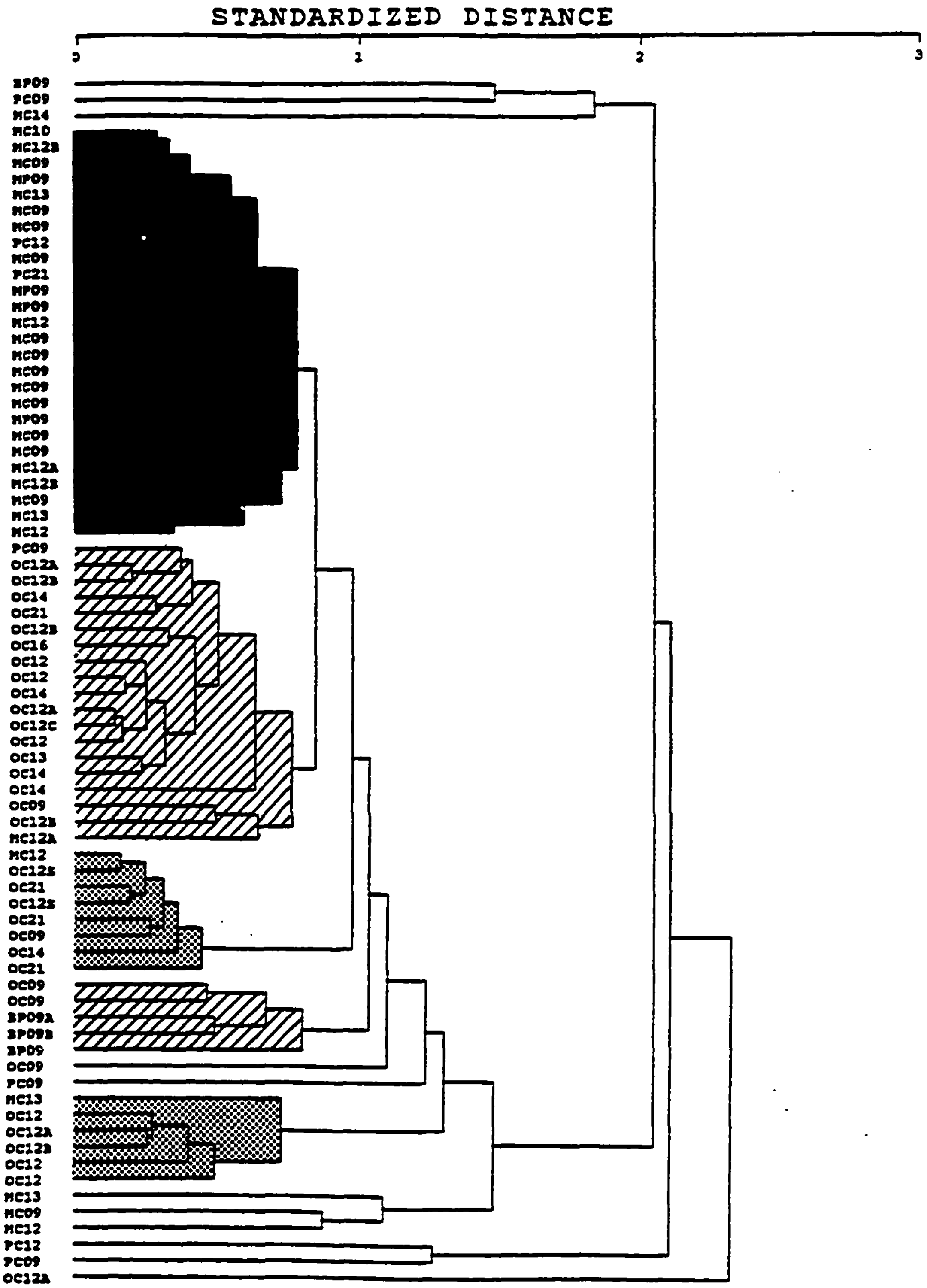
E-1. Cluster Analysis of Total Element Values for the Sediment Samples. Numbers represent sites.



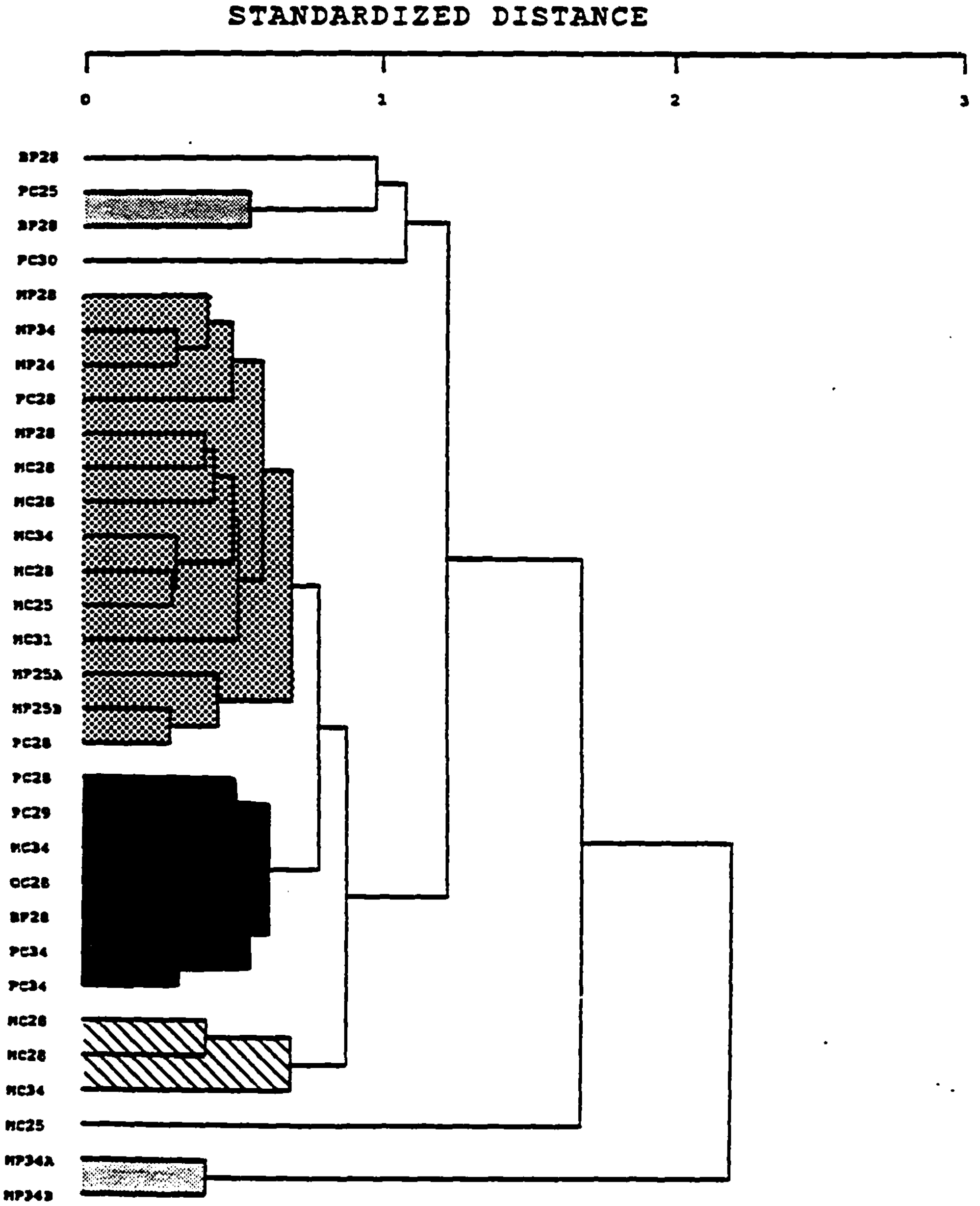
E-2. Cluster Analysis of Corals at all sites.



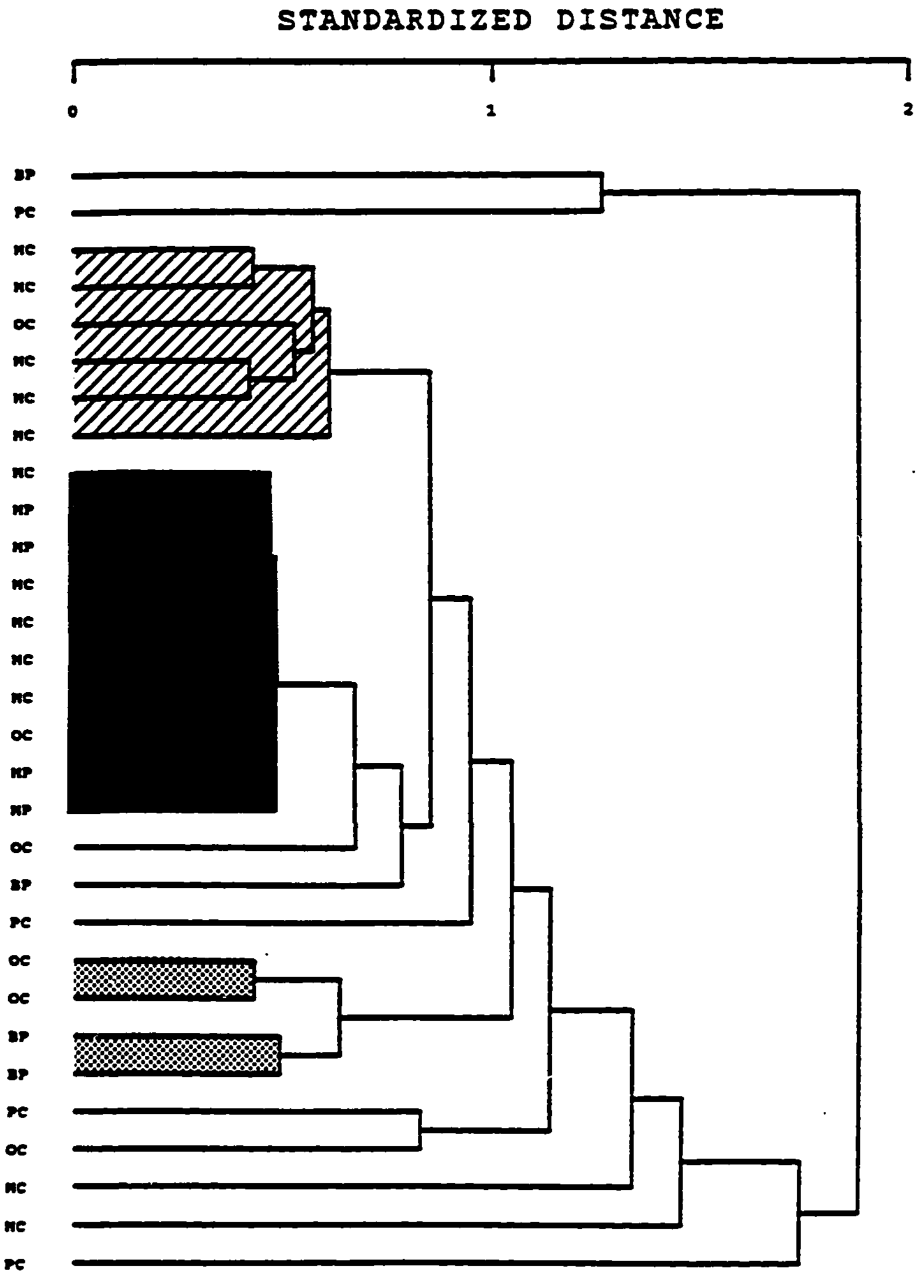
E-3. Cluster Analysis of Corals at the Canyon Area.



E-4. Cluster Analysis of Corals at the Pinnacles Area.



E-5. Cluster Analysis of Corals at site GS-09, (Canyon Area).

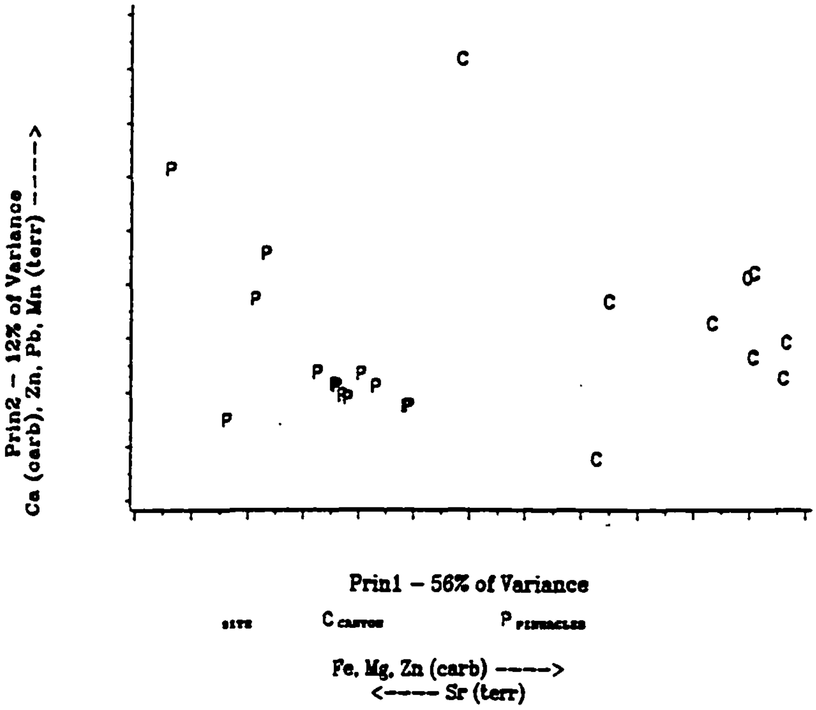


APPENDIX F

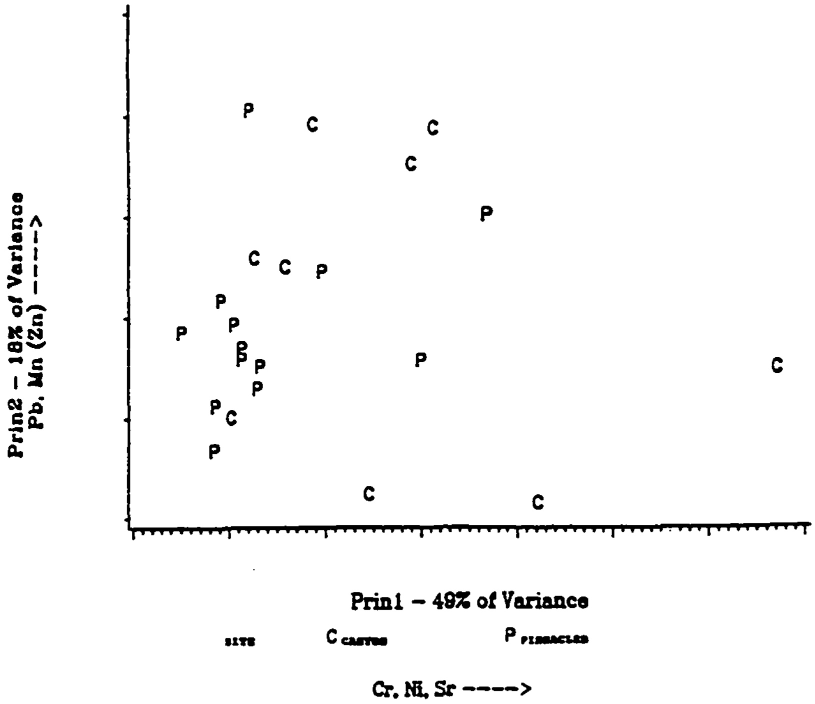
PRINCIPLE COMPONENT ANALYSES

(BP) *Balanophilia* (PC) *Paracyanthus*
(MP) *Madrepora* (MC) *Madracis* (OC) *Oculina*

F-1. SEDIMENT FRACTIONS SEPERATE

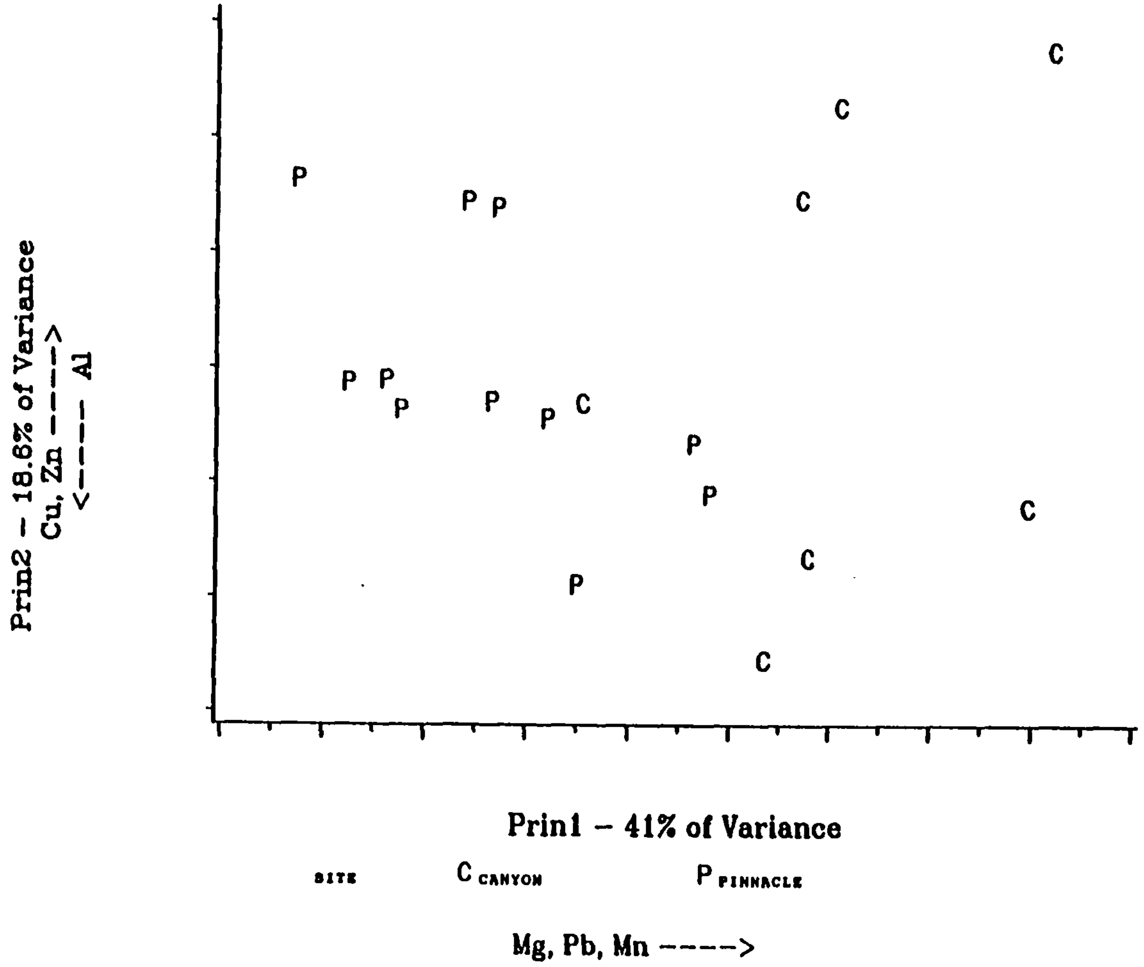


TERRIGENOUS FRACTION

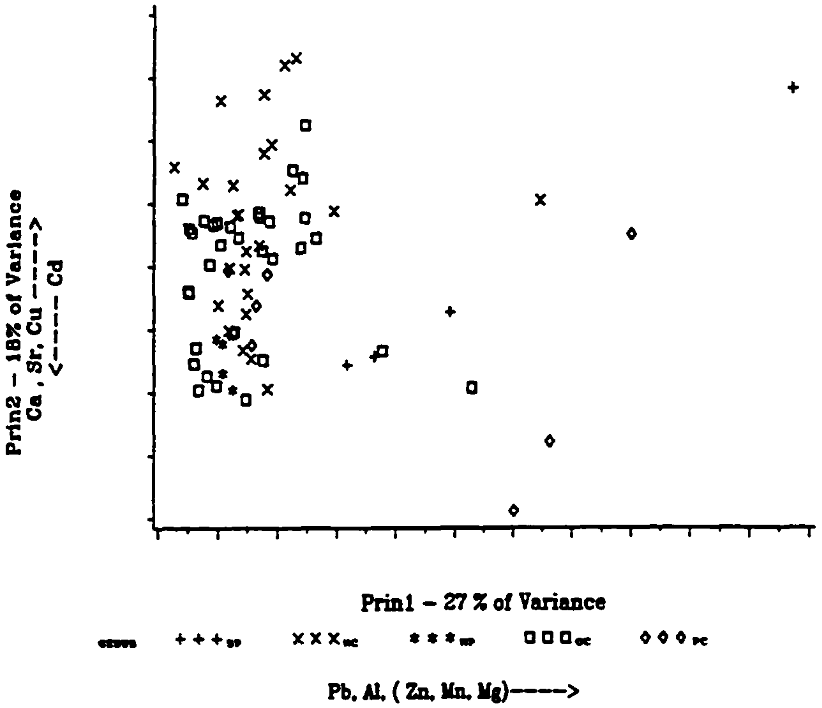


F-2.

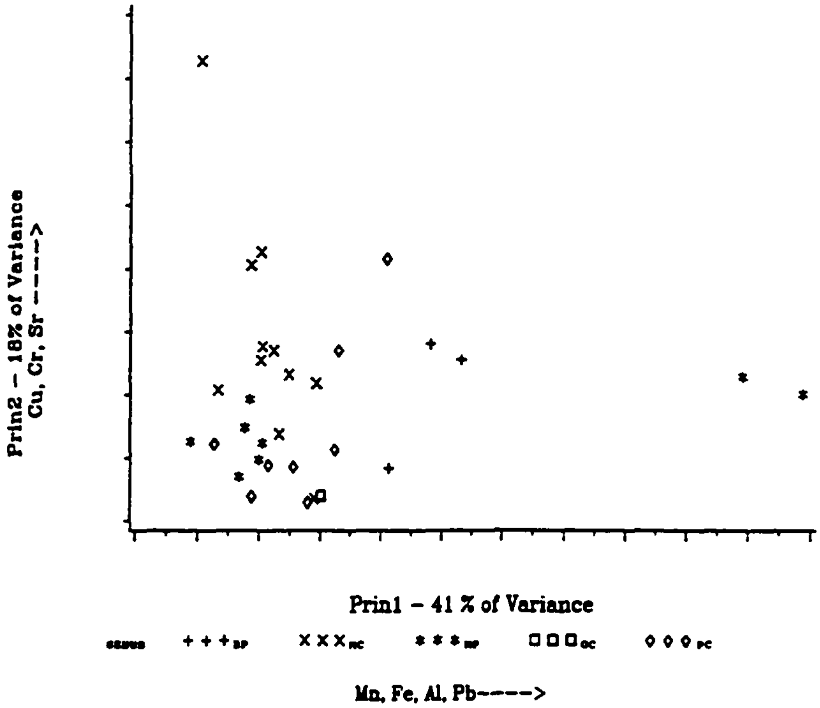
TOTAL SEDIMENT



F-3. CORALS AT THE CANYON AREA



CORALS AT THE PINNACLES AREA



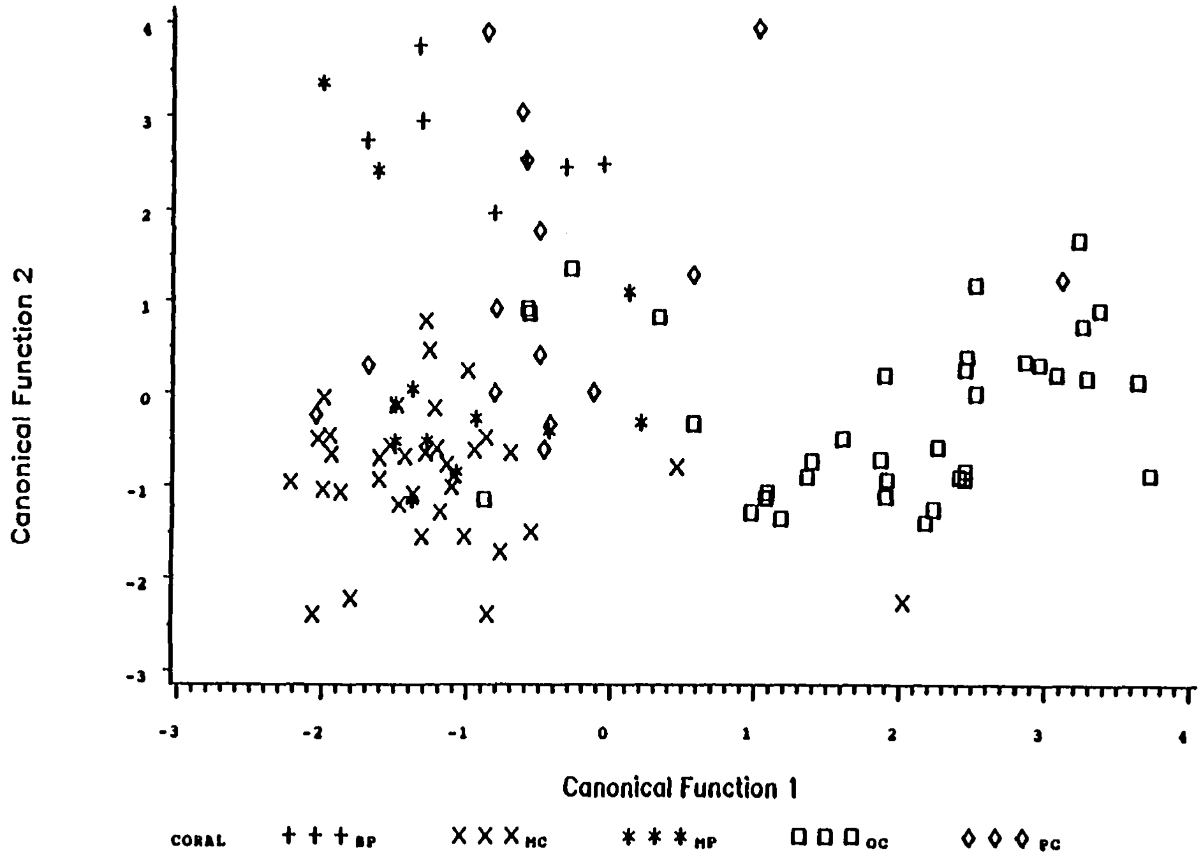
APPENDIX G

DISCRIMINATE FUNCTION ANALYSES

(BP) *Balanophilia* (PC) *Paracyanthus*
(MP) *Madrepora* (MC) *Madracis* (OC) *Oculina*

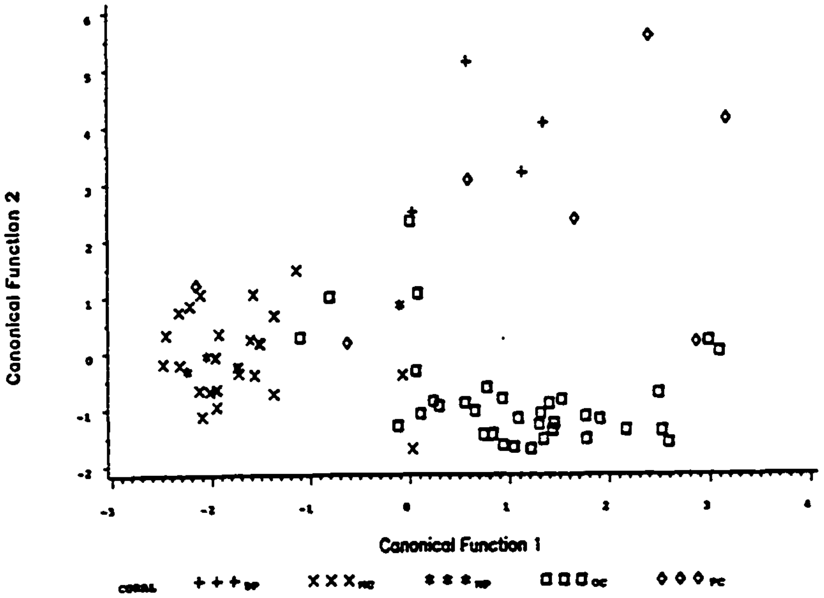
DISCRIMINANT FUNCTION ANALYSIS

CORALS DATA– OVER ALL SITES



DISCRIMINANT FUNCTION ANALYSIS

CORALS DATA– Canyon



DISCRIMINANT FUNCTION ANALYSIS

CORALS DATA– Pinnacles