THE SHELL CHEMISTRY OF SOME RECENT AND PLEISTOCENE MOLLUSKS AND ITS ENVIRONMENTAL SIGNIFICANCE

Thesis by

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ABSTRACT

In Part I Florida Bay is used as a model to describe some influences of environment on chemical variations of shell material. Geographic isolation and high evaporation in the Bay coupled with the influx of fresh water enriched in O^{18} produce a gradient of increasing H_2O^{18} going into the Bay. Dilution of Bay water by Ca rich fresh water lowers the Sr/Ca ratio in the Bay.

The gradient of H_2O^{18} in the water is clearly reflected in a similar gradient in the carbonate oxygen of mollusk shells. The effect of temperature on the carbonate isotopic composition is shown to be inadequate to explain the variations. Sr/Ca ratios of the shells vary but show no simple relationship to environment. A gradient of decreasing C^{13} in shells going into the Bay is attributed to the equilibration of CO_2 derived by oxidation of organic debris with the carbonate of the water.

Analyses of mollusks from sediment cores show that the present environmental framework of Florida Bay has existed for the last 3700 years. Analysis of the fine-grained sediment of the Bay suggests that part of it is washed in from the mainland.

In Part II fossil mollusks from the Pleistocene Caloosahatchee formation are analyzed. The O^{18}/O^{16} ratios coupled with geological and faunal data indicate an environmental framework strikingly similar to the Florida Bay model. A land mass immediately west of the outcrop area is postulated for most of Caloosahatchee time. The carbon isotope and strontium data reveal little environmental information.

ACKNOWLEDGEMENTS

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Part I

The Shell Chemistry of some Recent Mollusks from Florida Bay, Florida and its Relationship to Environment

INTRODUCTION

The application of geochemical techniques to the problems of paleoecology has become a fruitful line of paleontological research in recent years. The pioneer work of Bøggild (1) Clark and Wheeler (2) and Vinogradov (3) on the structure, mineralogy and trace element chemistry of carbonate shell materials has been extended by recent workers to provide new data on many taxonomic groups and to enlarge our understanding of the processes which determine chemical and structural modifications in shell materials.

Bøggild (1) described in great detail the mineralogical and microstructual variations of carbonate skeletons from a variety of mollusks. He concluded that these factors are genetically fixed in a given species and are of possible taxonomic value. Lowenstam (4) demonstrated that in mollusks and serpulid worms the mineralogical composition is not fixed and that species which precipitate both aragonite and calcite can have varying amounts of the two polymorphs depending on the temperature of shell growth.

Clark and Wheeler (2) recognized a relationship between magnesium content and both mineralogy and temperature in brachiopods and echinoderms. Bøggild, from this data, postulated three types of shell materials: low magnesium calcite, high magnesium calcite and low magnesium aragonite. Chave (5) made a comprehensive study of the magnesium content of the skeletons of a large number of carbonate secreting organisms covering all major taxonomic groups and concluded that the three factors governing magnesium replacement of calcium are mineralogy, temperature and phylogenetic level. Of the three, mineralogy appears to be the most important as Mg is not accommodated in the aragonite lattice.

Noll (6) showed that aragonite takes up strontium more readily than calcite and Lowenstam (7) suggested a strontium-temperature relationship operating indirectly through temperature-induced variations in aragonite composition. More recently Lowenstam (8) has found a direct strontium-temperature relationship in calcitic brachiopods.

In 1951 Urey and his co-workers (9) introduced the oxygen isotope paleothermometer as an entirely new and independent technique for determining the temperature of shell deposition. It is based on the exchange reaction:

$$(1.)\quad H_2O^{16} + 1/3CO_3^{18} \rightleftharpoons H_2O^{18} + 1/3CO_3^{16}$$

wherein the equilibrium is shifted to the right with increasing temperature. In organisms that select carbonate ions at random from sea water the $1/3CO_3^{18}/1/3CO_3^{16}$ ratio in the shell will be a measure of the temperature of the water. The technique has been applied with great success to Recent (10) and fossil (9) shell materials.

All of the techniques outlined above concentrate on the relationships between shell composition and temperature. Another aspect of environment which might be expected to influence shell composition is the chemistry of the water in which the shell has grown. Though salinity ranks with temperature in importance as a defining parameter of the ecology of an organism it has received much less attention in biogeochemical investigations.

Lowenstam (11) mentioned a possible "salinity effect" on the calcite-aragonite composition of some of his specimens from the Baltic Sea. The aragonite percentage appeared too high in some *Mytilis edulis* shells considering the temperature at which they grew. The salinity ranged from 3-34‰ in the areas of collection suggesting that salinity had a direct or indirect influence.

Odum (12) has shown experimentally that the Sr/Ca ratio of a shell is directly proportional to the Sr/Ca ratio of the water in which the shell is precipitated with proportionality factors varying from 0.1 to 1.0. The Sr/Ca ratio of fresh water is generally much lower than that of sea water (13). In theory, one could detect a salinity gradient by noting a decrease in the Sr/Ca ratio of shells grown in water which has been more and more diluted by fresh water.

Turekian (14) has suggested that salinity may have a direct effect on the strontium uptake of marine organisms. His argument is based on variations in the Sr/Ca ratio of fossils from the Florena shale which, he feels, cannot be explained by any other mechanism and must be related to salinity variations proposed by Imbrie (15) from other paleoecologic data. Odum (16) has criticized Turekian's conclusion on the basis that the very small quantities of strontium found in the fossils suggest diagenetic replacement of the carbonate has taken place.

Lowenstam (17) has recently found that Mg replacement of Ca may also be affected by salinity variations.

Jeffreys, et al (18) and Clayton and Degens (19) have found fresh water and marine deposits characterized by differences in the C^{13}/C^{12} ratio of the carbonate fraction in rock samples of varying ages. In both cases the grouping of the samples into fresh water and marine was on the basis of other geochemical or paleontological data.

It was recognized in the beginning of the oxygen isotope paleotemperature studies that variation in water chemistry can seriously affect the CO_3^{18}/CO_3^{16} ratio of carbonate shells and lead to errors in calculated temperature (9). From equation 1 it can be seen that though the $1/3CO_3^{18}/1/3CO_3^{16}$ratio will vary with temperature the actual value of the ratio at a given temperature will depend on the O^{18}/O^{16} ratio in the whole system. Because there is about 10,000 times as much water oxygen as carbonate oxygen in sea water the water will determine the basic O^{18}/O^{16} ratio on which the temperature variations will be impressed. The vapor pressure of H_2O^{16} is higher than that of H_2O^{18}. From Raoults law it follows that water vapor in equilibrium with liquid water will be enriched in H_2O^{16}. If H_2O^{16} enriched vapor is continuously removed by evaporation the remaining liquid will be enriched in H_2O^{18}. In the case of sea water this will be accompanied by an increase in salinity. By the same token, if the H_2O^{16} enriched vapor is precipitated as rain and added in large quantities to sea water there will be a decrease in the H_2O^{18}/H_2O^{16} ratio accompanied by a decrease in salinity.

For Recent shells a sample of the water in which the shell grew can be analyzed for H_2O^{18}/H_2O^{16} and a correction applied to the temperature determined from the CO_3^{18}/CO_3^{16} ratio (20). For fossil shells the water is not available and the H_2O^{18}/H_2O^{16} ratio must be assumed (9).

To determine what variations in H_2O^{18}/H_2O^{16} might be expected in nature Epstein and Mayada (21) made a comprehensive survey of the oxygen isotope composition of natural waters. They confirmed the relationship between H_2O^{18}/H_2O^{16} ratio and salinity and, in addition, showed that at the present time the oceans as a whole are enriched in H_2O^{18} because of a fractional distillation mechanism which causes the permanent snow and ice at the poles to be greatly enriched in H_2O^{16}.

The effect of high salinity on the oxygen isotope chemistry of carbonate skeletons was shown by Lowenstam and Epstein (22) on materials collected in the Bahama Islands.

The purpose of this study is to examine the relationship of water chemistry to the oxygen and carbon isotope and magnesium and strontium compositions of Recent mollusks and to determine to what degree such relationships reflect the climate and geography of the area of collection.

Florida Bay at the southern tip of the Florida peninsula was chosen as a model for this study. It is a shallow body of water of considerable geographic extent and has only limited exchange with open ocean water. A combination of geographic and climatic factors act to produce strong salinity gradients in the Bay during certain periods of the year. It is by means of these gradients that the influences of salinity on shell chemistry are measured. Because the Bay is shallow temperatures are quite uniform at all locations at any given time. This uniformity minimizes the possibility of confusing temperature and salinity effects.

Five weeks were spent in the field during August, 1958 collecting shell samples, water samples, and a few sediment cores. Additional samples were obtained in the absence of the writer as described below. The methods of collection, separation, and preparation for analysis are described in appendix A.

Selected shells were analyzed for oxygen and carbon isotope composition, strontium and magnesium content and mineralogy. Selected water samples were analyzed for salinity, strontium and magnesium composition and oxygen isotope composition. The techniques of analysis are described in appendix A. The locations of the sample collections are shown in fig. 2.

PHYSICAL SETTING

The state of Florida occupies only a portion of the surface of a large peninsular platform, the Floridan Plateau, which is roughly outlined by the 100 fathom bathymetric contour line (fig. 1). The Floridan Plateau is about 350 miles long and 200 to 300 miles wide and trends roughly north-south. Southeast of the Plateau there are four isolated platforms rising out of the Atlantic Ocean: Cay Sal Bank, the Great and Little Bahama Banks and the island of Cuba. These platforms are separated from the Floridan Plateau by a deep narrow trough, the Straits of Florida, which serves as a channel for the northward flowing Florida Current. South of Cape Hatteras the Florida Current becomes the Gulfstream.

The area to be discussed here is at the southeastern end of the Floridan Plateau. It includes a small portion of the Florida mainland, Florida Bay, the Florida Keys and the Florida reef tract (fig. 2).

Florida Mainland - The portion of the Florida mainland included in this study is the southernmost extension of the Florida Everglades. The area consists entirely of brackish water coastal swamps. The typical vegetation of sawgrass swamps and hardwood hammocks found in the interior of the Everglades is replaced along the coast by dense growths of black and red mangrove. Indeed, much of the coastline is merely a continuous thicket of mangrove growing in very shallow submerged mud flats. Along natural and man made channels the mangrove swamps extend as far as three miles in from the coast.

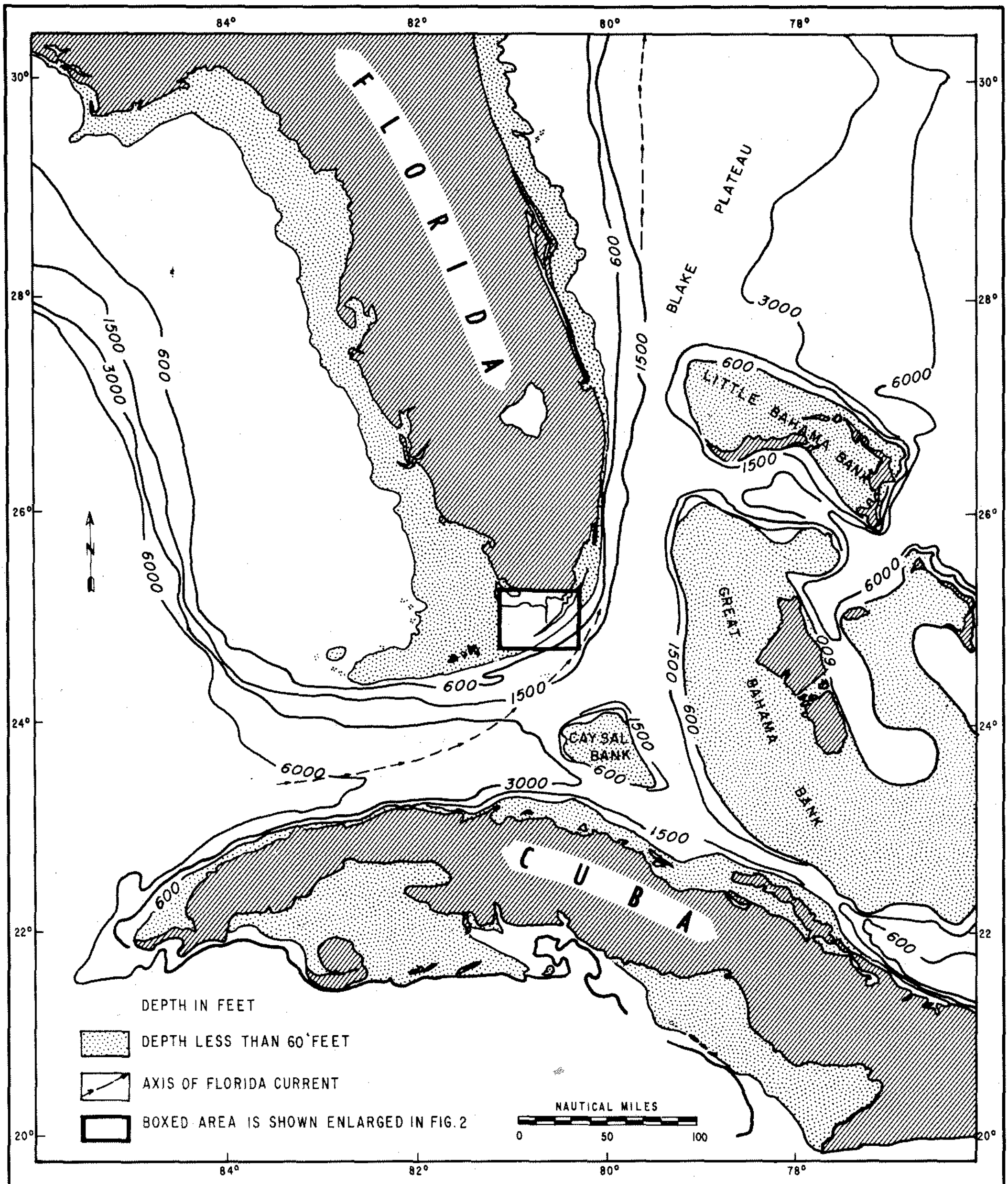

FIG 1. BATHYMETRY OF FLORIDA, CUBA AND THE BAHAMAS

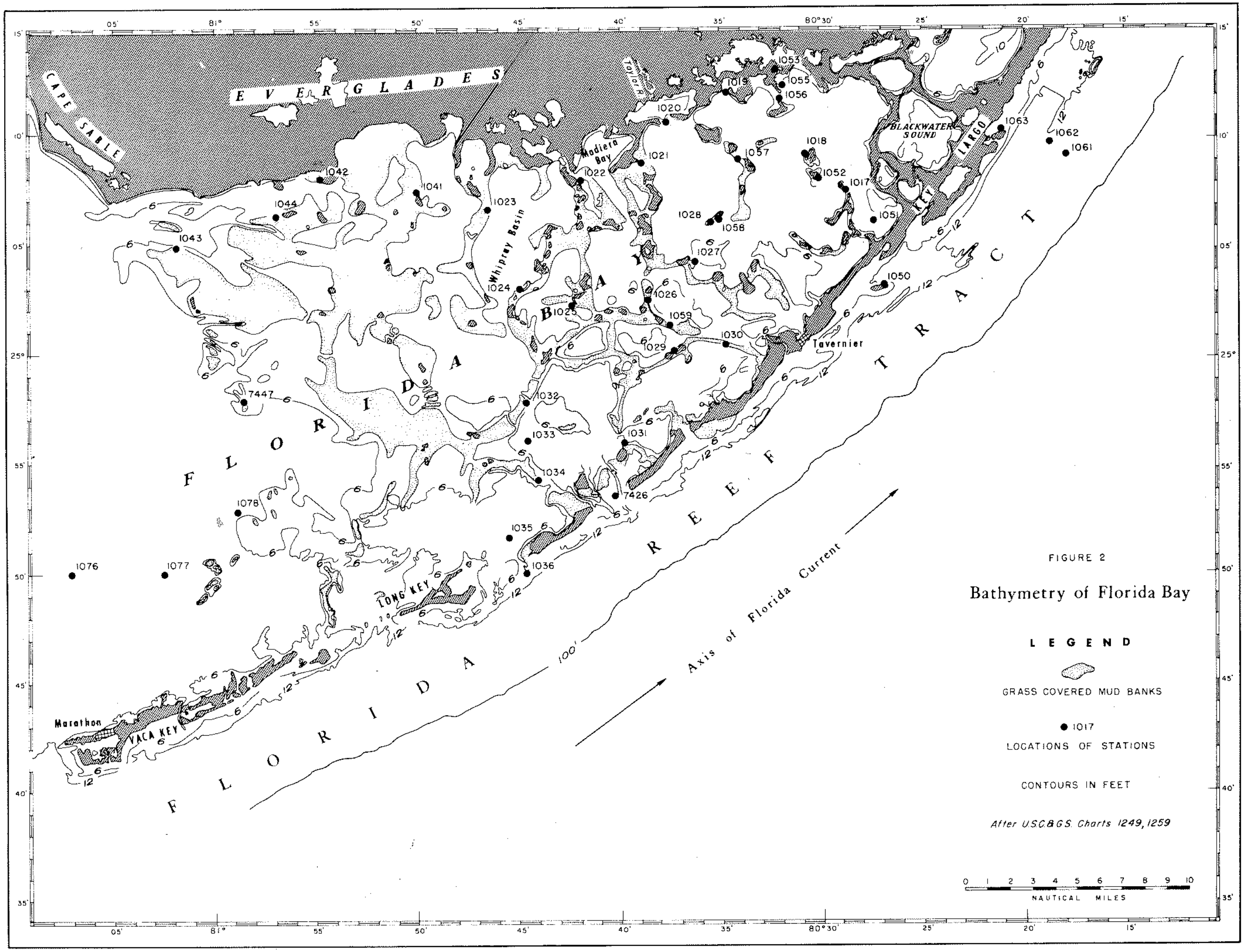

FIGURE 2

Bathymetry of Florida Bay

LEGEND

GRASS COVERED MUD BANKS

● 1017 LOCATIONS OF STATIONS

CONTOURS IN FEET

After USC&GS. Charts 1249, 1259

The mangrove is rooted in a richly organic, fine-grained, poorly sorted lime mud. The mud rests on a flat rock floor that slopes to the west. The depth from sea level to rock increases from one and a half feet at Madeira Bay to greater than 12 feet at Cape Sable.

The irregular growth of mangrove has resulted in a very complex shoreline. Open bays, semi-enclosed bays, and completely enclosed lakes and ponds are found along the entire length of the coast and well up into the mainland. The depth of water in these depressions varies with the Florida Bay water level and seasonal rainfall. The average depth is of the order of one to two feet.

Florida Bay - Florida Bay is a triangular-shaped body of water bounded on the north by the irregular coast line of the Florida mainland, on the southeast by the Florida Keys, and on the west by the open Gulf of Mexico. The Bay has a maximum depth of about ten feet along its western boundary. The bottom here is rocky and is a continuation of the bedrock surface that underlies the mainland. As along the mainland the flat bedrock surface underlying the Bay slopes toward the west.

The bathymetry of Florida Bay is complicated by grass-covered mud banks and bars which rest on the rock floor and rise to within a few inches of the water surface. Along the western end of the Bay the banks are very broad and occupy 50% or more of the surface area. In the eastern part of the Bay the banks are narrow elongate bars, joined to form large semi-isolated bodies of deeper water. These are called "lakes" by local inhabitants. They average six feet in depth and are covered along the bottom by only a thin veneer of sediment usually no more than eight inches thick.

Scattered irregularly over the tops of the mud banks are mangrove islands. The smaller islands are only mangrove thickets, usually covered with water. The larger islands consist of a rim of mangrove surrounding a raised mud flat which may be as much as a foot above Bay level. The interiors of the larger islands are usually dry or covered with rainfilled depressions and are flooded by sea water only during severe storms.

The accumulation of the Florida Bay mud into bars and banks is believed to result from trapping of sediment by thick baffle-like carpets of marine grasses (23). The islands are thought to form by the accumulation of mud above sea level in the tangle of roots formed by mangrove (24). Ecologically the banks and islands are very important because they have a profound influence on water circulation in the bay and provide a specialized habitat for many organisms.

Florida Keys - The Florida Keys are a string of rocky islands extending in a curved line south and west of Miami for a distance of some 200 miles. The largest island - Key Largo - is approximately 30 miles long. The remaining islands are much smaller and are separated from one another by channels through which Florida Bay water exchanges with water from the Florida Straits.

The maximum altitude in the Florida Keys is 25 feet at northern Key Largo. The remaining Keys are ten feet or less above sea level. Though well above the normal high tides, many of the Keys are known to have been flooded during the 1935 hurricane.

The rock unit that forms the northern keys, the Key Largo formation, is a Pleistocene reef limestone with well-developed intergranular and vuggy porosity. The islands, therefore, do not act as a completely impermeable barrier between the Bay and the reef tract and a certain amount of exchange between the reef tract water and Bay water occurs through them.

Florida Reef Tract - The term Florida reef tract as used here designates the shallow shelf extending some three to four miles seaward from the Keys and down to a depth of 300 feet. The reef tract can be divided into three linear zones: a sloping fore reef, an intermittent barrier reef and a semi-protected back reef zone. The reef tract has been described in detail by Ginsburg (25). In addition to contrasting the features of the reef tract with those of Florida Bay he was able to distinguish the environmental zones within the reef tract on the basis of sediment grain size and the nature and relative abundances of contributors to the skeletal carbonate fraction of the bottom sediment. He attributes the ecological zoning to the existence of the intermittent reef which creates its own specialized environment along the edge of the shelf and, at the same time, serves as a barrier to free water circulation in the back reef area.

The depth of the rock floor in the back reef area is of the order of 25 feet. In the vicinity of local patch reefs the water is much shallower and some of the larger coral knolls come within a few feet of the surface.

The barrier reef, where actively growing, forms a definite ridge along the shelf edge which rises to and, in some cases, above mean low tide.

The fore reef slopes steeply from the barrier reef toward the Straits of Florida with a slope of from 60 to 120 feet per mile. The bottom is usually rocky with sediment in holes and pockets.

In summary the south Florida area can be divided into three physiographic entities: a low coastal swamp, a shallow semi-isolated bay and a narrow open shelf.

CLIMATE

South Florida is at approximately 25° North Latitude, but because it is surrounded on three sides by water, two of which are traversed by the warm Florida current, the climate is milder than would normally be expected at this latitude. James John Audubon, from his observation of bird life, considered it tropical and in 1838 the area was "officially" recognized as tropical by the U. S. Congress after studying data on temperature and plant life collected by Dr. Henry Perrine (26). In most climatic atlases the climate is referred to as humid sub-tropical.

Air Temperature - The average annual temperature at Miami is 24°C while at Key West it is 25°C. The temperature range over the year is from 14° to 28°C at Miami and 21° to 31°C at Key West. Abrupt lowering of the temperature can occur when cold fronts invade the peninsula as far as South Florida. Miami has recorded below freezing temperatures during a few of these rare northers. On the Florida Keys the lowest recorded temperature is 5°C (27).

Wind - Both direction and intensity of winds vary seasonally in the South Florida area. The intensity in monthly average velocity is shown in fig. 3. There is a distinct peak in March, April and May. Summer winds are generally from the east and southeast and normal winter winds from the east and northeast. Strong winds associated with storms and cold fronts usually come out of the north and northwest.

Precipitation - Rainfall in South Florida is seasonal with two peak periods - a small peak in May and June and a major peak in September

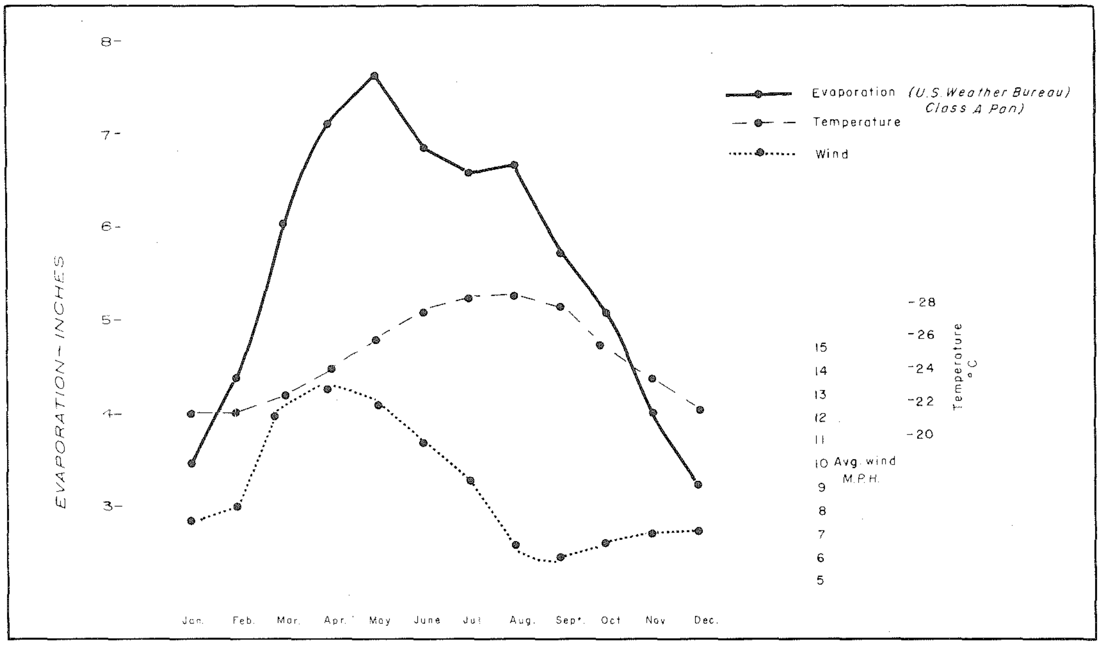

Figure 3. - Temperature, wind, and evaporation in south Florida

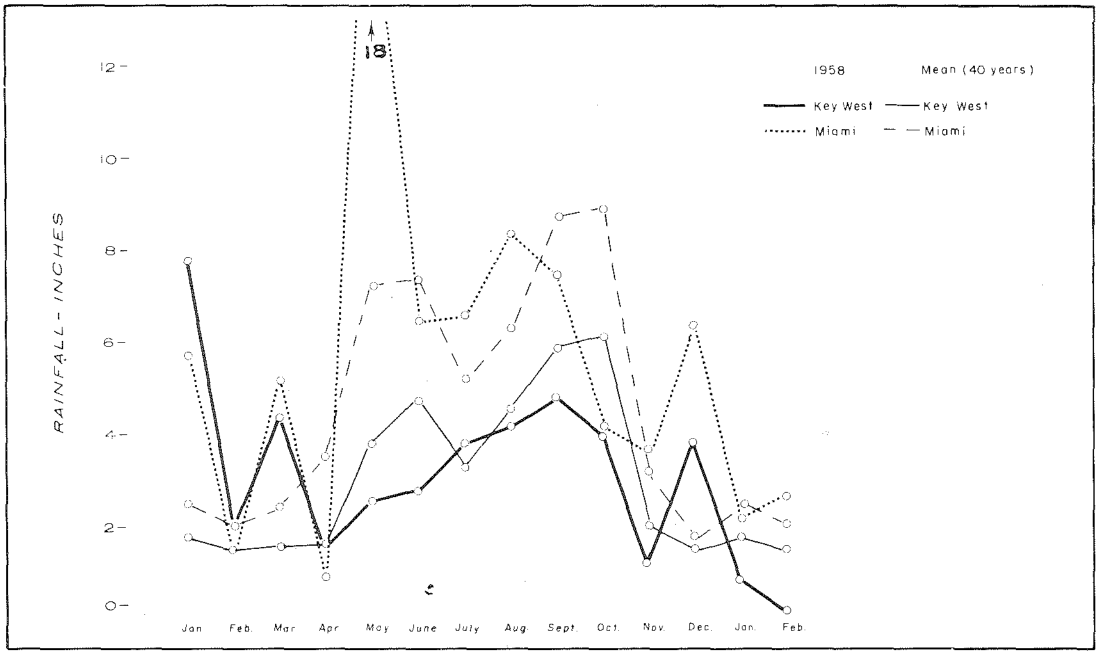

Figure 4. - yearly rainfall in south Florida

and October. The months of June, July and August are moderately wet and the dry season occurs during the winter months from November to April (see fig. 4). The average precipitation regimens of Miami and Key West parallel each other through the seasons with Key West values always somewhat dryer. The yearly average rainfall at Miami is about 55 inches while at Key West it is about 39 inches. The values given above are based on 40 year averages and the regimen for any particular year can deviate quite markedly from them. Because much of the data presented below are sensitive to particular conditions prior to the time of collection of samples the rainfall history for the period 1958-59 is compared to the 40 year average in fig. 4.

Evaporation - In a shallow semi-enclosed basin such as Florida Bay evaporation is an important contributing factor to variations in the chemistry of the water. Unfortunately, there is no precise technique available for the direct measurement of water loss through evaporation. Evaporation pans have been used by the U. S. Weather Bureau in the Miami area to estimate such losses and the data over an eight year period are shown in fig. 3.

Evaporation is sensitive to increasing temperature which raises the vapor pressure of the water and wind movement which flushes out and carries off moisture laden air (28). The temperature maximum in the Miami area occurs in July, August and September while maximum wind movement occurs in May. The combined effect results in an evaporation peak in May during high wind movement and rising temperature and a secondary peak in August due mainly to high temperature. The evaporation minimum occurs in December and January. The period of maximum rainfall corresponds with the period of maximum evaporation so that the contrast between wet and dry seasons is lessened. Evaporation rises sharply in February and March while rainfall remains at a low level, suggesting that February and March are the dryest months on a net basis.

HYDROGRAPHY

Tides and Circulation - Along the reef tract semi-diurnal tides contribute greatly to the exchange of water between the reef and the Straits of Florida. The tide range varies along the length of the reef tract. Near Miami the mean range is 2.4 feet and the spring range 2.9 feet. One hundred miles to the southwest the mean range is 2.2 feet and the spring range 2.6 feet. A continuous supply of fresh sea water is assured by the Florida Current and an intermittent counter current which flows southward very close to the reef. Additional circulation is provided by wind currents in the surface water.

In Florida Bay the semi-diurnal tides are attenuated to a mean of about 0.5 feet along the western margin of the Bay. Even then the effect dies out within two or three miles of the edge because of the presence of the mud banks. Small semi-diurnal tides can be measured on the Bay side of the Florida Keys indicating limited exchange through the porous rock barrier.

In general, the only effective tides in the Bay are those caused by wind. Persistent strong winds from the north or west pile up the water against the confining barriers of the mainland or the Keys. An easterly wind can blow water out of the Bay into the Gulf. The writer has observed the effect of a prolonged winter storm on the water level in the northern part of the Bay. For a period of two days persistent northerly winds of 20 - 30 miles per hour exposed large areas of mud banks which are normally covered by six inches to one foot of water.

Because the semi-diurnal tides are ineffective wind tides are probably the only effective force causing mixing of the Bay water.
Water Temperature - Seasonal water temperature variations along the reef tract based on monthly averages over a twenty-two year period are shown in fig. 5a. The data are from Vaughn (29). The temperature of the reef tract water appears to be sensitive to seasonal air temperature variations. The volume of water is large and there is constant exchange with water of the Straits of Florida, hence even large air temperature drops of short duration such as occur during winter storms produce negligible changes in water temperature (29). The observations were made at the Carysfort Reef lighthouse at the edge of the shelf. Recent observations by Smith, et al (30) suggests that the back reef area exhibits greater variation and a slightly higher mean temperature.

Temperature data on Florida Bay water are much less abundant. Ginsburg (25) gives a range of 19°C - 38°C from 40 observations but suggests that temperature as low as 15°C might occur during the winter. Bi-monthly observations made in the eastern part of the Bay from December 1956 to April 1958 were furnished to the writer by the Shell Oil Co. These represent the most comprehensive data available and are plotted in fig. 5b. The value plotted represents the mean of observations for a single day. The large range of values is due to heating by the sun from morning to evening on the shallow banks and gives some idea of the short term temperature sensitivity of shallow water.

A comparison of Bay water and reef tract water temperatures with seasonal air temperatures indicates that air temperature is the

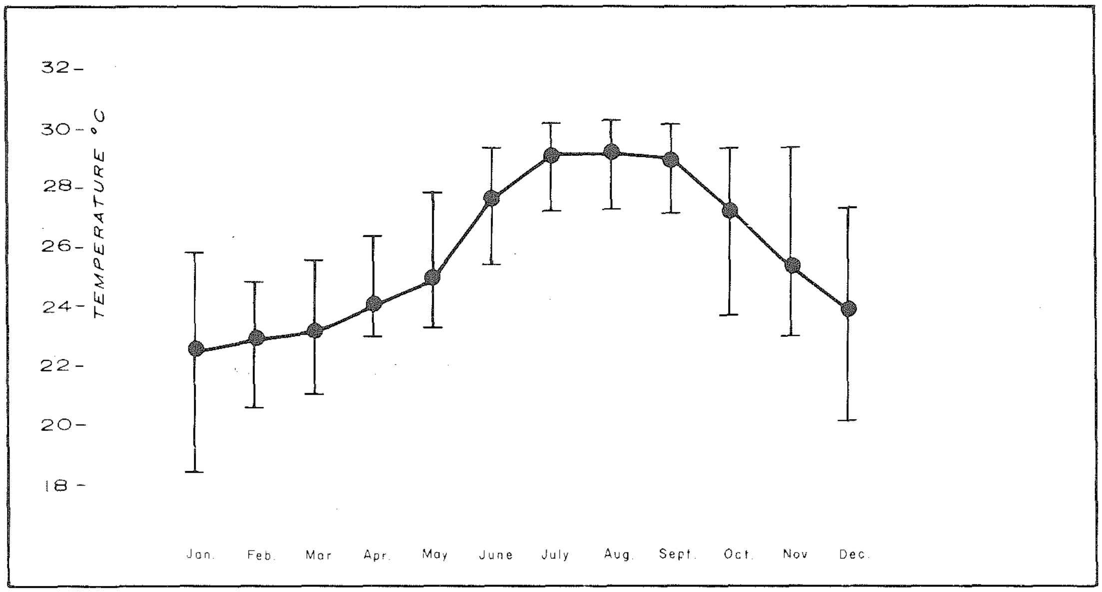

Figure 5a. - Water temperatures at Carysfort Reef

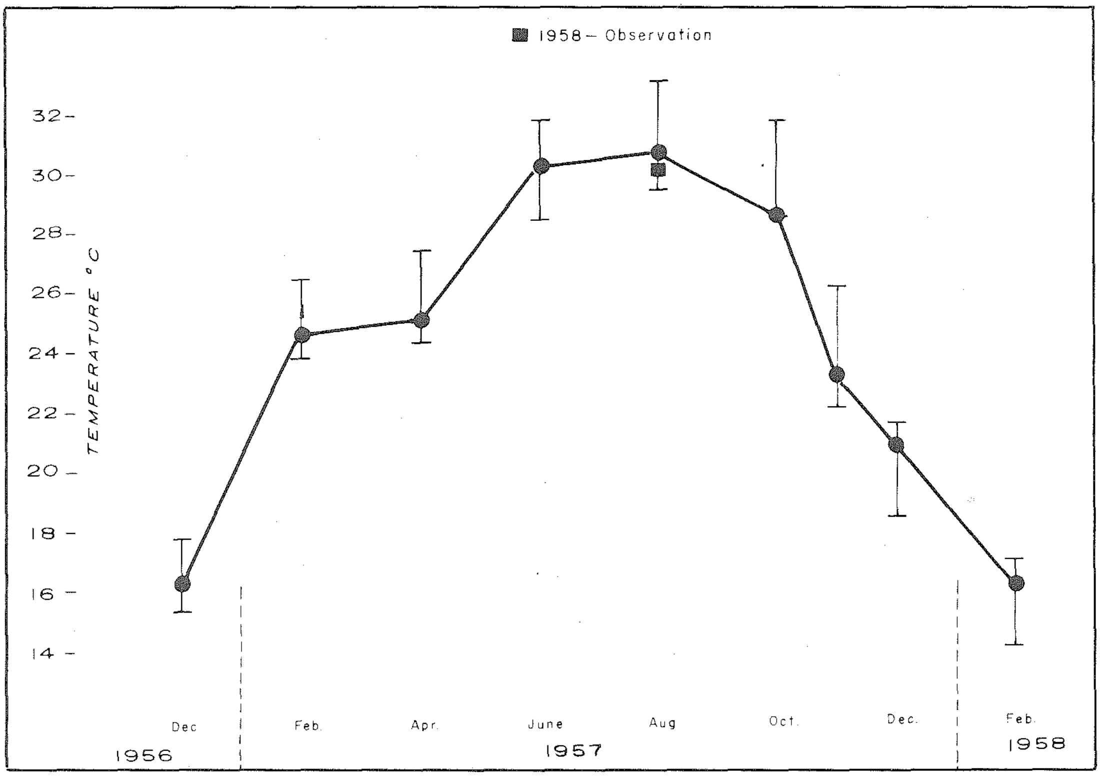

Figure 5b. - Water temperatures in Florida Bay

controlling factor in determining the water temperature of both areas. The mean temperatures of the Bay water (25.6°C) and of the reef tract water (25.8°C) are essentially the same although the amplitude is greater in the Bay (10°C - 31°C) than on the reef tract (22.5°C - 29.0°C).

Salinity - Salinity analyses of reef tract waters show very little variation. Fluctuations of less than 2.0‰ were reported by Dole and Chambers (31) and Smith, et al (30). The mean value of these analyses, 36.1‰ is close to the values reported by Vaughn (29) from surface waters of the Straits of Florida. The most significant variations were those reported by Dole and Chambers from Fowey Rocks off Miami. Sudden drops of as much as 1.5‰ were correlated with heavy rainfall on the mainland. The brackish water was apparently discharged through the opening in Biscayne Bay, a large shallow lagoon which receives most of the run-off from the Miami area. Lowered salinity was detected as much as five miles south of Fowey Rocks, although the difference was very slight.

In contrast to the reef tract, the water of Florida Bay has wide fluctuations in salinity. Davis (24) was the first to describe these variations and to relate them to the rainfall pattern. The mean values of two sets of twenty samples, one set taken during an unusually dry year and the other set during an unusually wet year differed by 12‰, 39‰ and 26.7‰ respectively.

Recently, Ginsburg (25) has shown that during the rainy season of 1953 a wedge of very low salinity water pushed into the eastern Bay from the mainland. Using the 30‰ isohaline he found that the low salinity water continued to advance during the dry season of December, and a retreat back to the mainland was only detected in June of 1954. Ginsburg explains this apparent anomaly by pointing out that studies on sea level variation by Marmer (32) indicate that at Key West a period of high sea level occurs from August to December with a peak in October. The same high sea level operating in the Bay would tend to hold back fresh water drainage from the mainland during the rainy season, releasing it only when sea level returned to normal in December. This would account for reduced salinity farther south in the Bay during the dry months. An examination of Ginsburg's map suggests an additional complication. Though the 30‰ isohaline had advanced south in December, the 15‰ isohaline which was present in October had disappeared. Thus, water to the north became more saline while water to the south became less saline indicating that mixing must have taken place.

For the present study a complete set of water samples was collected by the writer during August, 1958 and another set collected during late January and early February, 1959 by Capt. Herb Alley. A few additional samples collected in November, 1958 were obtained from rangers of the Everglades National Park. The recorded values are shown in table I Appendix B and isohaline lines are plotted in figs. 6, 7, 8.

In August a clearly defined salinity gradient existed over the Bay. Values ranged from 12‰ near the mainland to 38‰ near the southwestern boundary. At the same time salinity values along the reef tract were around 36‰.

The data for November are insufficient to define any pattern over the entire Bay but it can be noted that the gradient was much

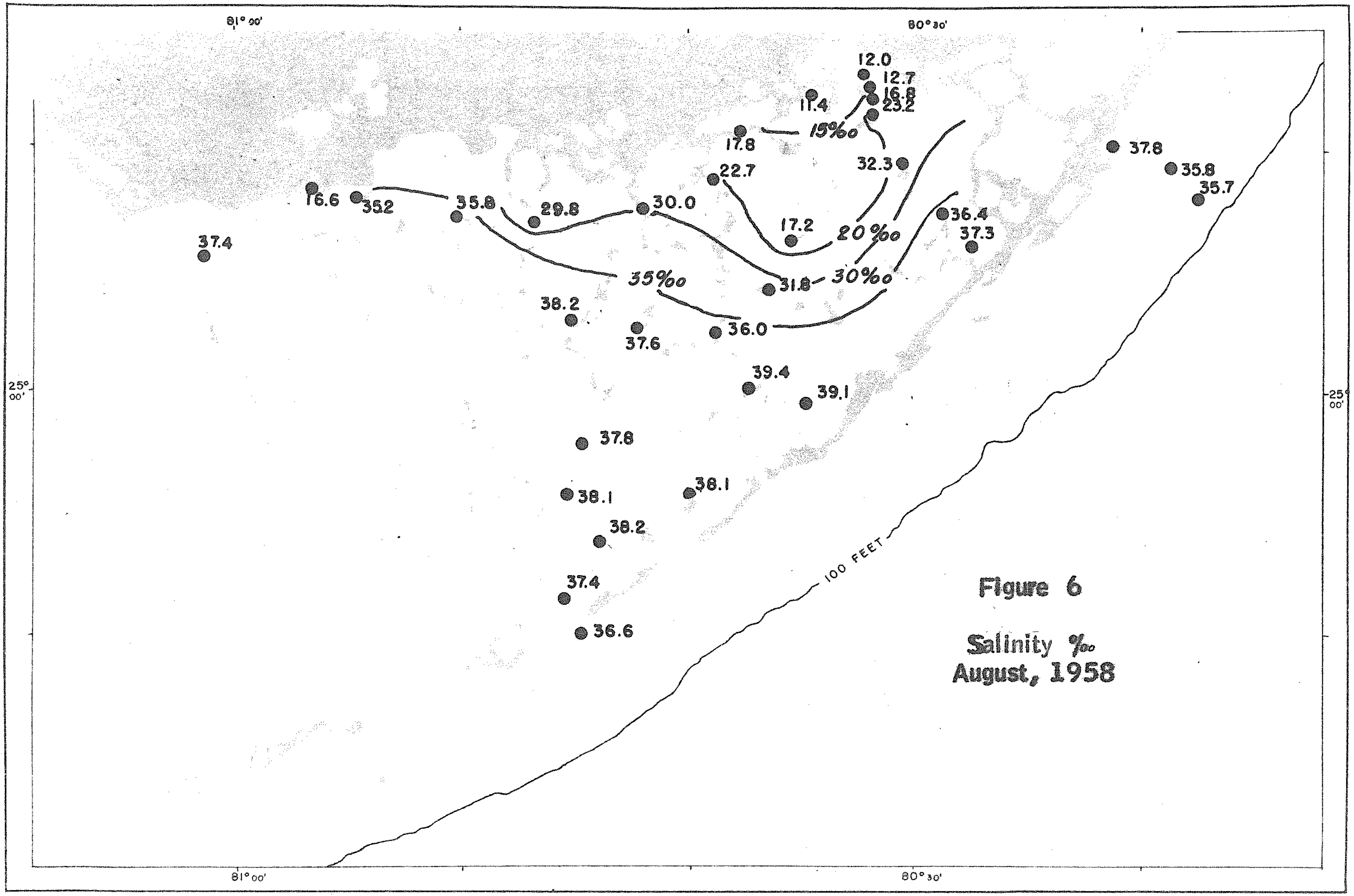

Figure 6

Salinity ‰
August, 1958

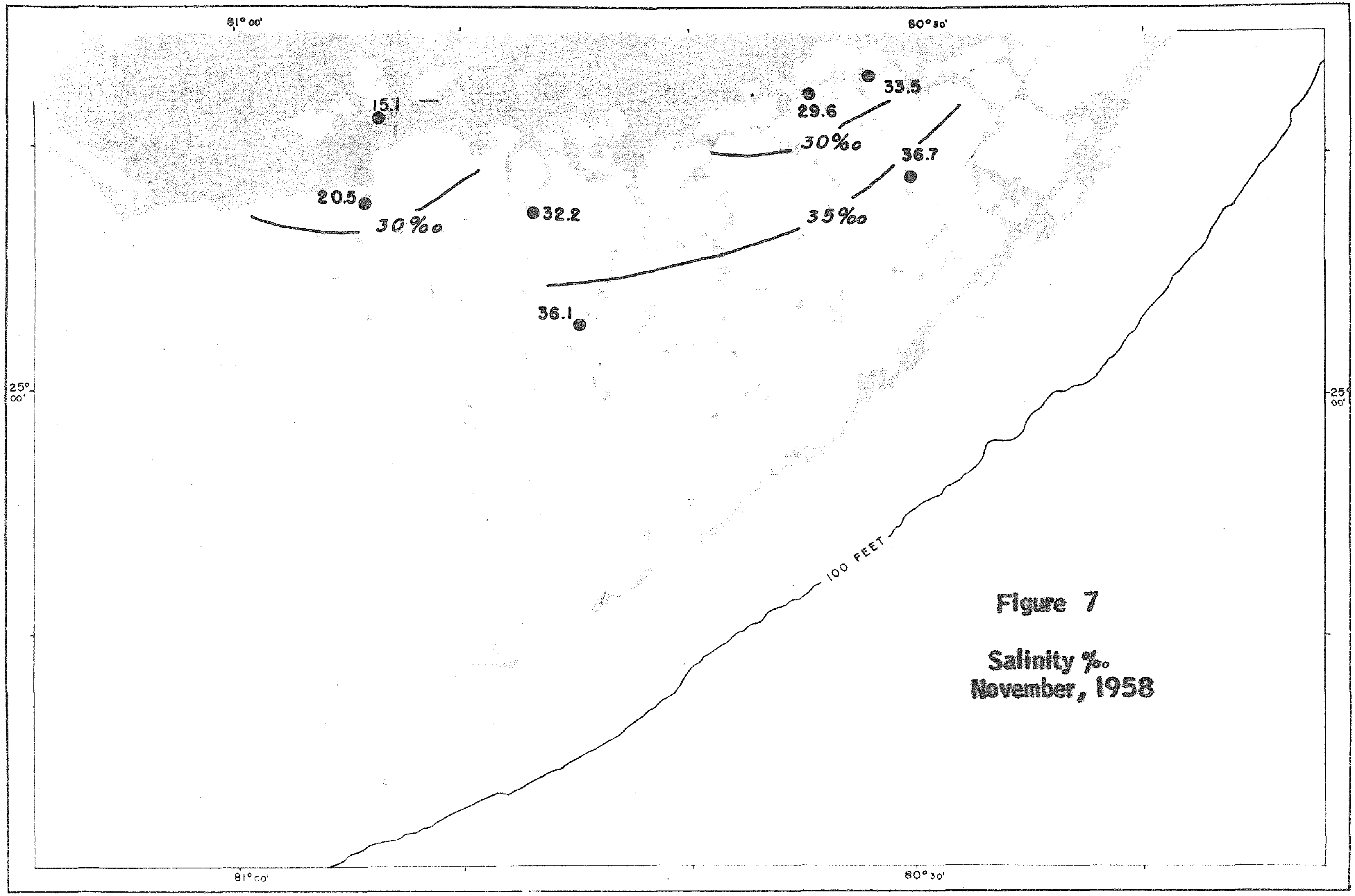

Figure 7

Salinity ‰
November, 1958

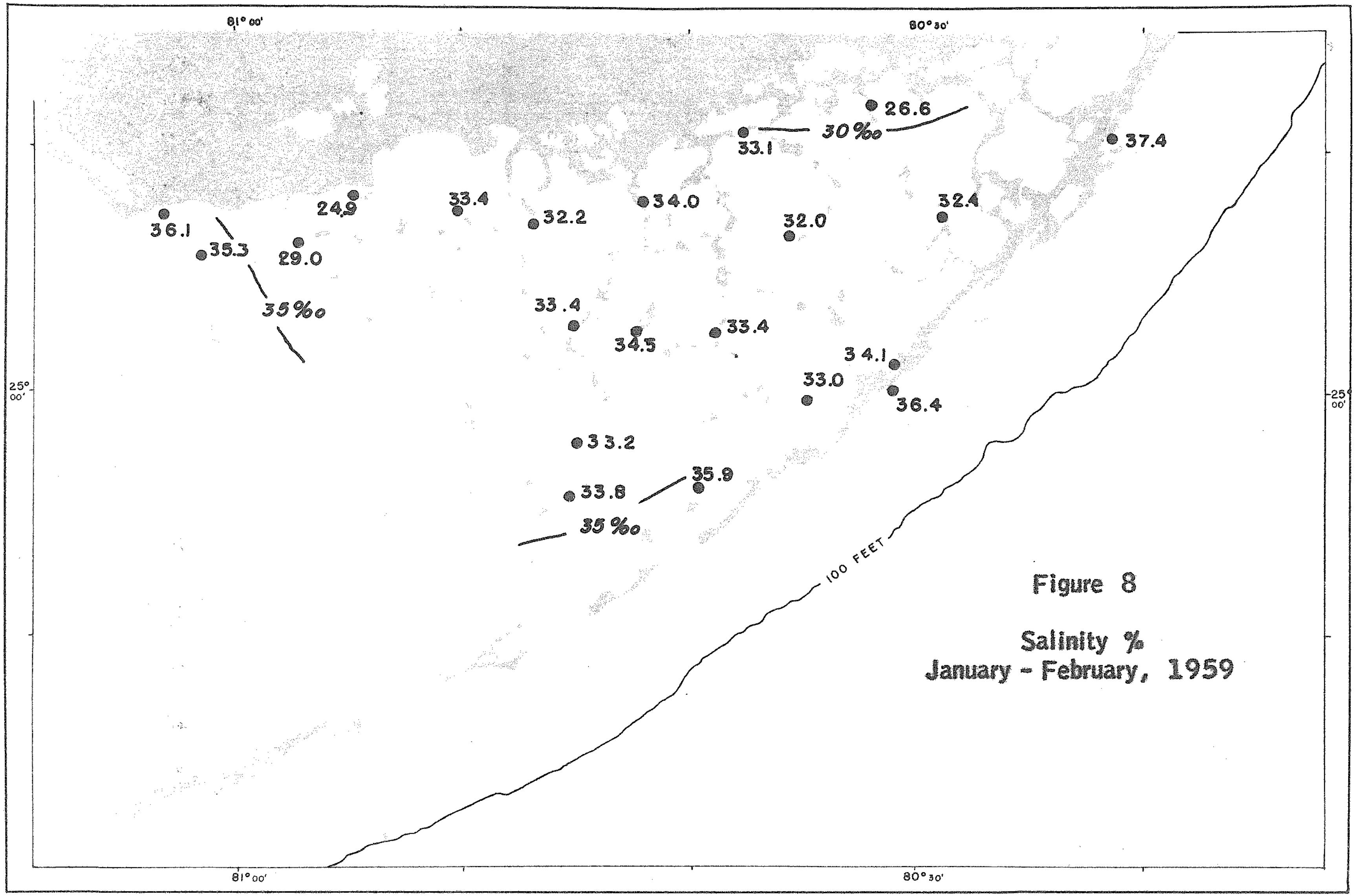

Figure 8

Salinity ‰
January - February, 1959

attenuated and the lowest salinity recorded near the mainland was 30‰.

By January and February the sharp salinity gradient shown for August had been reduced to a range of about 9‰ over the entire Bay. Over the central part of the Bay the variation was less than 3‰. The average salinity in the Bay was 33‰ at this time while along the reef tract it remained near 36‰.

These data are generally in agreement with those of Ginsburg (25) for the year 1953-1954. A wedge of brackish water advancing into the Bay during the later months of the rainy season is apparently incorporated into the remaining Bay water by mixing during the winter and early spring.

The effect of seasonal high sea levels on salinity patterns suggested by Ginsburg is also supported by these data. The low salinity wedge found in August near the mainland was replaced in November by water of higher salinity. If this increase were due only to the low rainfall of November coupled with normal evaporation, then salinities in the central part of the Bay would be significantly higher than those of August from the same location. The recorded values show a small change in the direction of lowered salinity. On the other hand, a period of high sea level in the western Bay could cause the low salinity wedge to retreat back into the mainland swamps with very little effect on the salinities in the central part of the Bay. The release of this brackish water during normal sea levels in January and February would account for the generally lowered salinity over the Bay as a whole at that time.

For the period from February to August the only data available are those of Ginsburg for June, 1954 which show a general increase in salinity for the central part of the Bay. This is in agreement with the average climatic data which show a period of very low rainfall and high evaporation in March and April.

There are other factors besides rainfall, evaporation, and seasonal sea level variations which affect salinity patterns in Florida Bay but their influence is much more difficult to support with data. Exchange of Florida Bay water with reef tract and Gulf of Mexico water and internal circulation within the Bay are probably sluggish under normal circumstances but can be greatly accelerated during strong storm winds. The net effect on salinity patterns would depend on the direction and strength of the winds and the duration of the storm. These data, correlated with salinity variations, are not available.

The data presented above from the years 1953-54 and 1958-59 probably reflect the range of salinity variation that could be expected during "normal" years, i.e., years during which the climatic pattern follows closely that of the long term average. Radical variations in salinity can occur during periods of abnormal climate. In 1956 the total rainfall for the year at Tavernier, Florida at south Key Largo was 26 inches while a normal year would yield 50 inches of rain. Salinities measured in northeast Florida Bay ranged as high as 50‰ in 1957 (33) even during the height of the rainy season in August. It appears that the deficiency of rain for the previous year had to accumulate in the mainland swamps before the characteristic brackish water wedge could advance into the Bay.

Because of the limited amount of data and the complexity of variations in Florida Bay salinity, it is only possible to suggest tentative relationships between salinity patterns and hydrographic and climatic factors. The following are interpreted as those relationships which obtain under "average" climatic conditions:

1. During the high rainfall season run-off from the mainland can produce a distinct gradient of decreasing salinity toward the mainland.
2. The areal extent of the gradient is dependent on the sea level in the Bay, the amount of mixing and the balance between evaporation and addition of fresh water.
3. The timing of the factors mentioned in 2 is such that there is a delay in the addition of run-off water from the mainland to the Bay.

Combining the above processes with information on the long term averages of climatic factors it is possible to propose an "average" or "normal" seasonal history of Florida Bay water.

During the months from June to August a head of fresh water due to high rainfall is built up on the mainland and forces its way into the Bay as a brackish water wedge. At the same time evaporation is at its highest and water in the central and western areas of the Bay can become hypersaline. During September, October and November there is still high rainfall but a period of high sea level in the Bay forces the wedge back into the mainland with only a minor amount of mixing. From December to March sea level returns to normal and the mainland fresh water is released into the Bay and mixed. Mixing is probably assisted by the shift of prevailing winds from the east and southeast to north and northeast. During April and May high evaporation and low rainfall result in a general increase in salinity over the Bay.

FAUNA AND FLORA

The fauna of Florida Bay consists in the main of tropical and subtropical species with a few forms that extend into temperate waters. Mollusks, foraminfera and ostracods make up the bulk of the skeletal organisms, in that order of abundance, with relatively low contributions from worms, corals and echinoderms. *Thallasia testudinum*, a marine grass, is the most important floral element in the Bay. Carbonate secreting green algae belonging to the Genera *Penicillis*, *Udotea*, *Rhipocephalus* and *Halimeda* are locally conspicuous but do not make a significant contribution to the Bay assemblege except perhaps in the form of fine-grained sediment as described by Lowenstam and Epstein (22).

The reef tract fauna and flora contrast sharply with that of the Bay (25). In the back reef the green alga *Halimeda* predominates with noticeable contributions from corals and red coralline algae. Mollusks and foraminifera are present in relatively small numbers. On the barrier reef corals and coralline algae predominate with lesser contributions from *Halimeda*, mollusks and forams. The fore-reef is characterized by abundant forams with lesser amounts of coral, coralline algae and mollusks.

The standing crop of living macro-organisms in Florida Bay is very low. The live-dead ratio of the mollusk shells collected varied from 0 to 25 per 1,000. These figures actually represent the ratio of living infauna to total fauna collected. However, a paucity of living individuals in the epifauna was also noted during the period of collection. *Chione cancellata* was the most common form collected alive, followed by *Tellina* spp. and *Anomalocardia cuneimeris*.

Because of the scarcity of living mollusks it was necessary to use specimens from the death assemblage to obtain adequate coverage over the Bay. This has the disadvantage of introducing uncertainty into correlations between the chemical composition of the shell and the water chemistry at the time of collection. On the other hand, the use of specimens from the death assemblage tends to integrate the analytical results over a greater period of time and provides a model which is more representative of fossil occurrences.

For the present study collections of mollusk shells were made by washing the sediment on a pair of nested screens of 3/16" and 3/64" mesh. All collections except 1061 and 1062 were made from mud bank surfaces in 10 to 18 inches of water. 1061 and 1062 were collected from the bottom of the back reef area in 18 feet of water. No attempt was made to take standard size samples because of local inhomogeneities in the distribution of shells. Instead sediment was washed until a sufficient amount of material was obtained. The preservation and storage of samples is described in appendix A.

For the purpose of investigating ecological zonations of the molluscan fauna selected samples (see fig. 14) were sorted according to species and counted. Only whole undamaged valves were counted to avoid the problem of making arbitrary distinctions between "good, damaged specimens" and shell fragments.

It was found that two genera, Cerithium and Tellina, and ten species, Modulus modulus, Bulla occidentalis, Prunum apicium, Tegula fasciata and Calliostoma euglyptum of the gastropods and Anomalocardia cuneimeris, Brachidontes exustus, Laevicardium mortoni, Chione cancellata, and Cardita floridana of the pelecypods comprise 75% - 95% of the molluscan fauna at almost every station. A few genera such as Crepidula, Lucina, Batillaria and others are abundant at one or two stations but are grouped here as miscellaneous. No attempt was made to identify all of the mollusks. A partial faunal list is given in appendix B.

The counts for pelecypods and gastropods were separately summed and equated to 100%. The data are given in table II, appendix B and cumulative bar graphs for each station are shown in figs. 9, 10, 11 and 12. The graphs should be regarded with caution as they contain many sources of bias. The counts represent only the molluscan fauna greater than 3/16" in effective sieve size. Some species, such as Pinctata radiata, have very delicate shells and, though abundant in the living fauna, do not appear in the graphs because they occur only as fragments in the sediment. The construction of the graphs themselves has an inherent flaw. By equating to 100% the count for any one species is no longer an independent number but is dependent on the values of other species in the sample. For instance, in fig. 11, traverse II the decline of A. cuneimeris from 50% to 2% of the pelecypod fauna may represent a real decrease in the rate of production of this species. The concurrent increase of Chione cancellata from 2% to 10%,

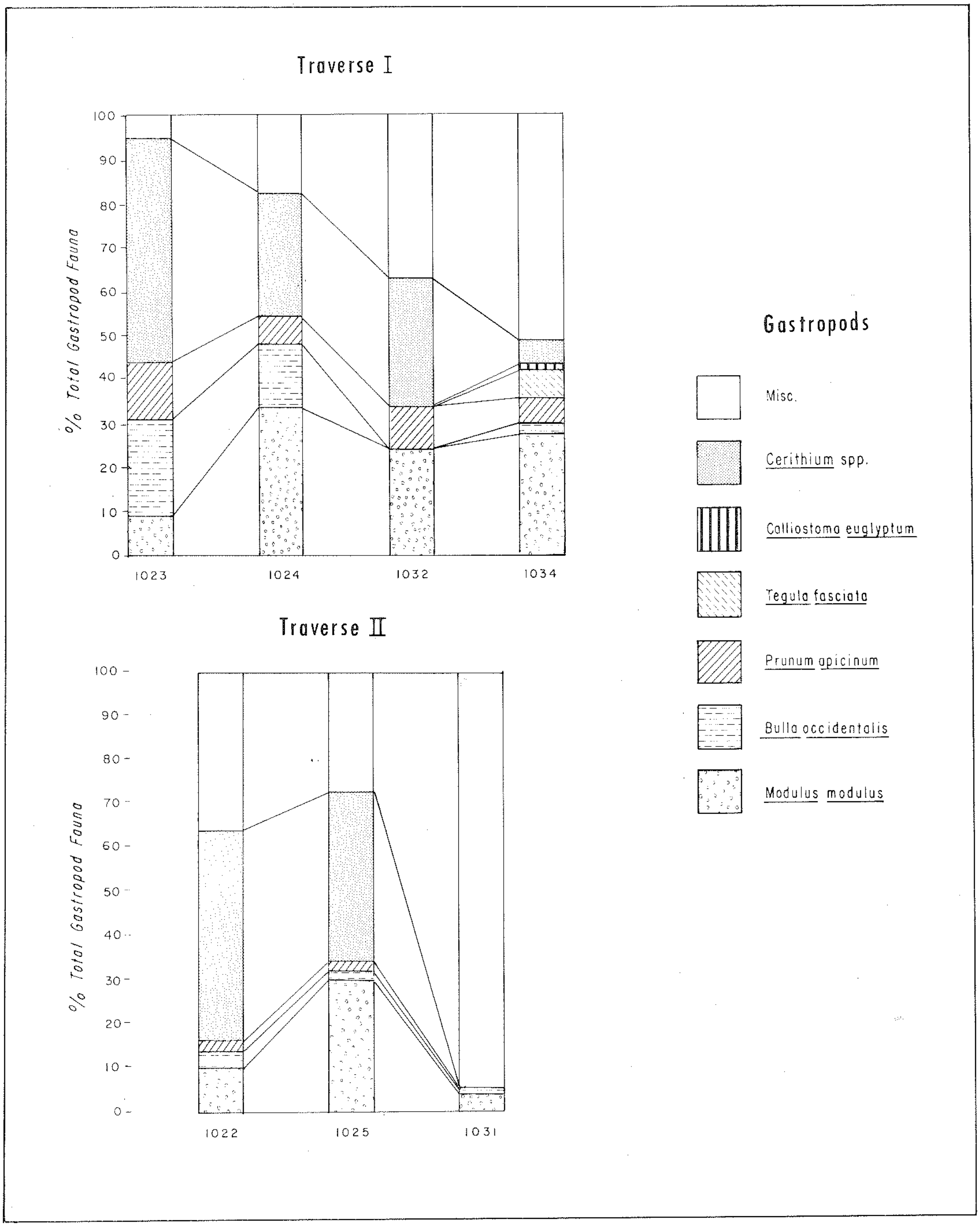

Figure 9. - Relative percent of gastropod species

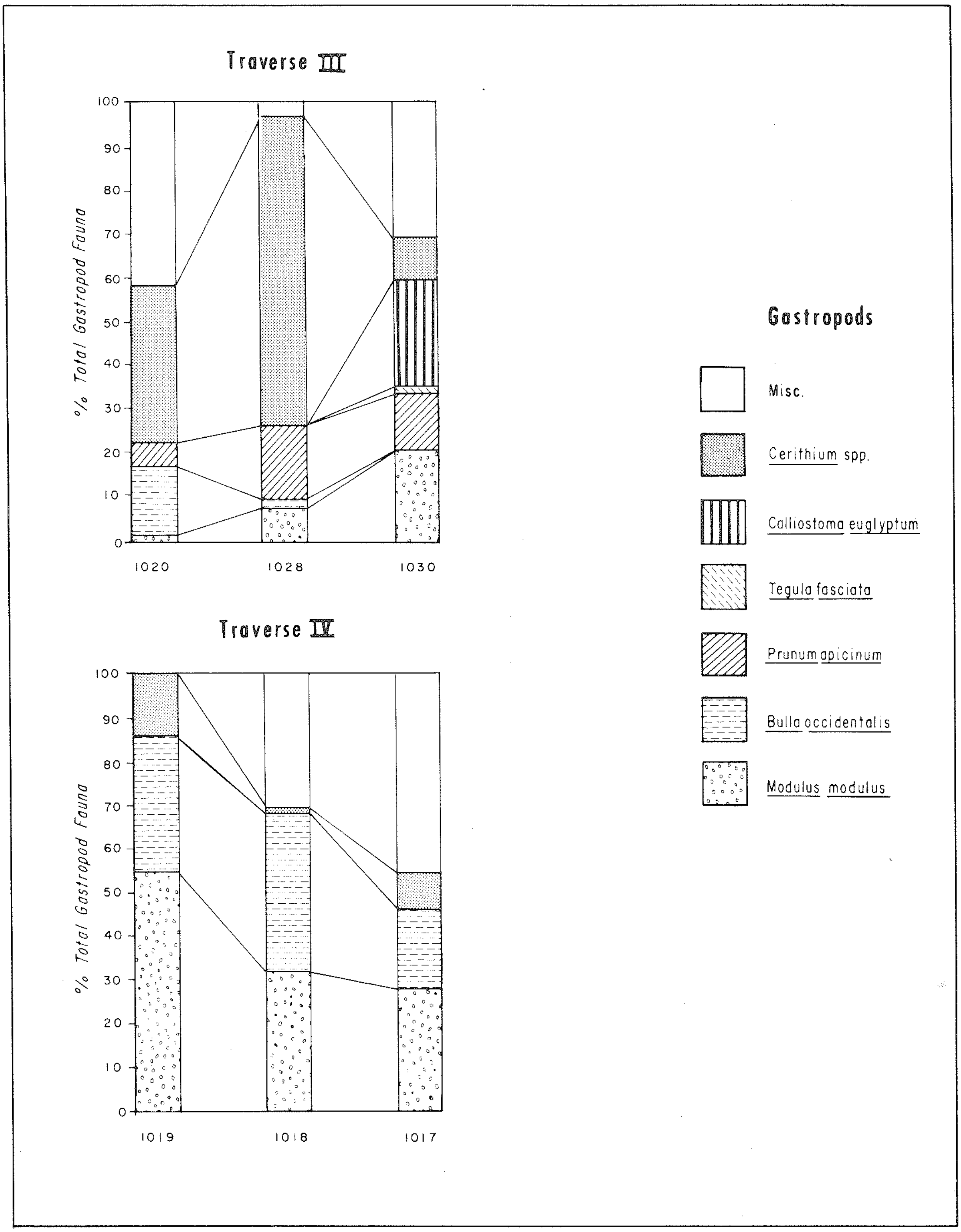

Figure 10. - Relative percent of gastropod species

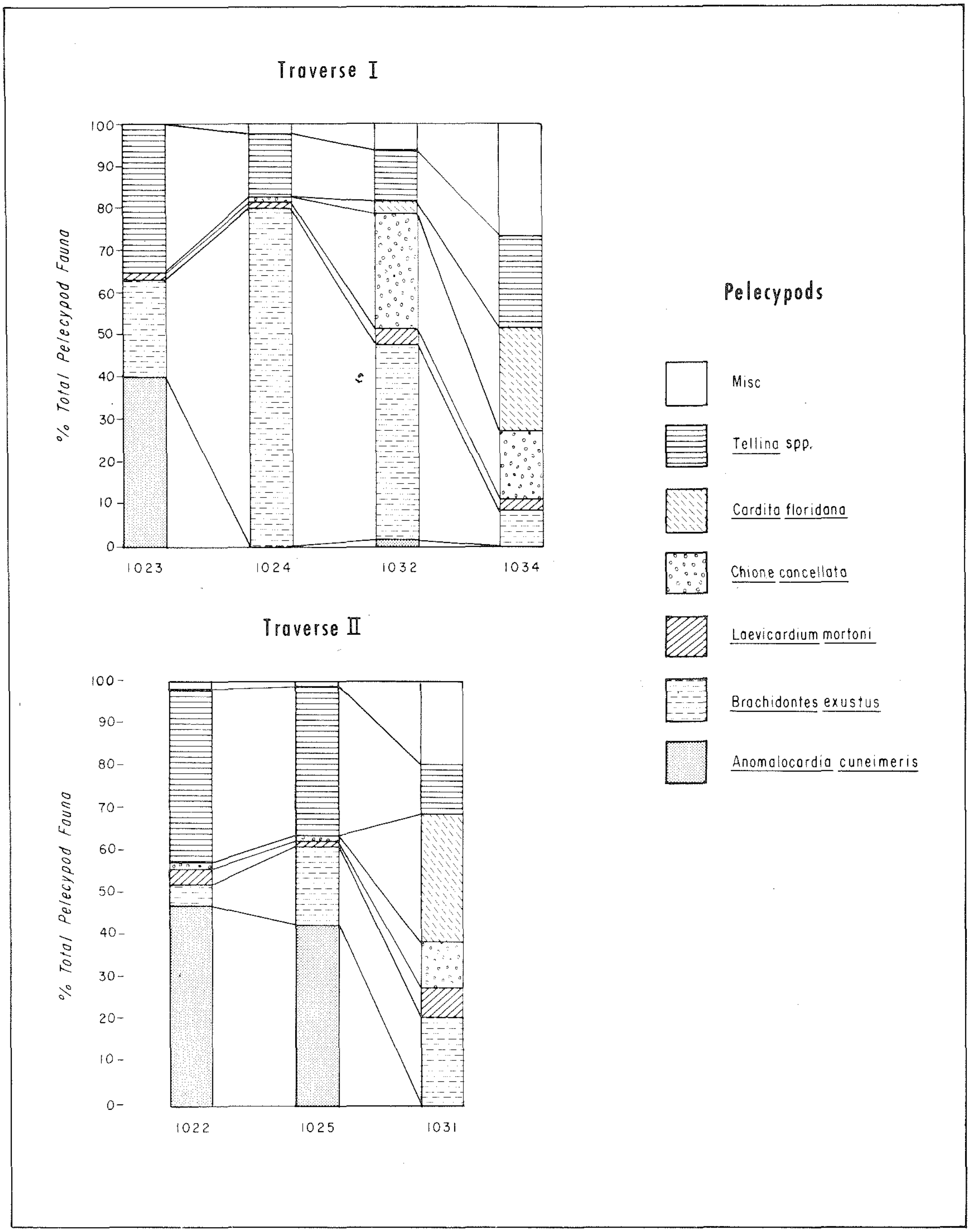

Figure 11.- Relative percent of pelecypod species

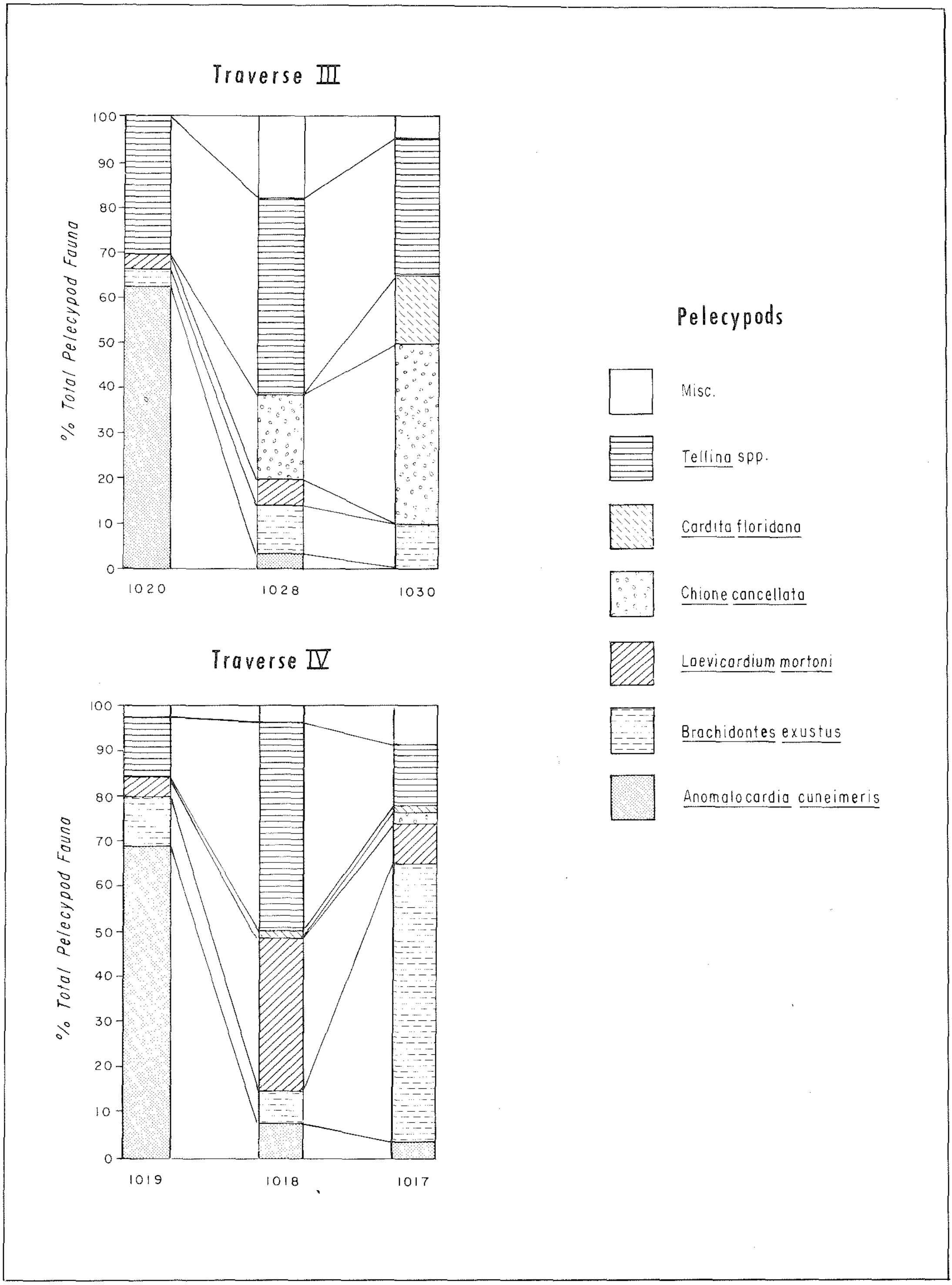

Figure 12. - Relative percent of pelecypod species

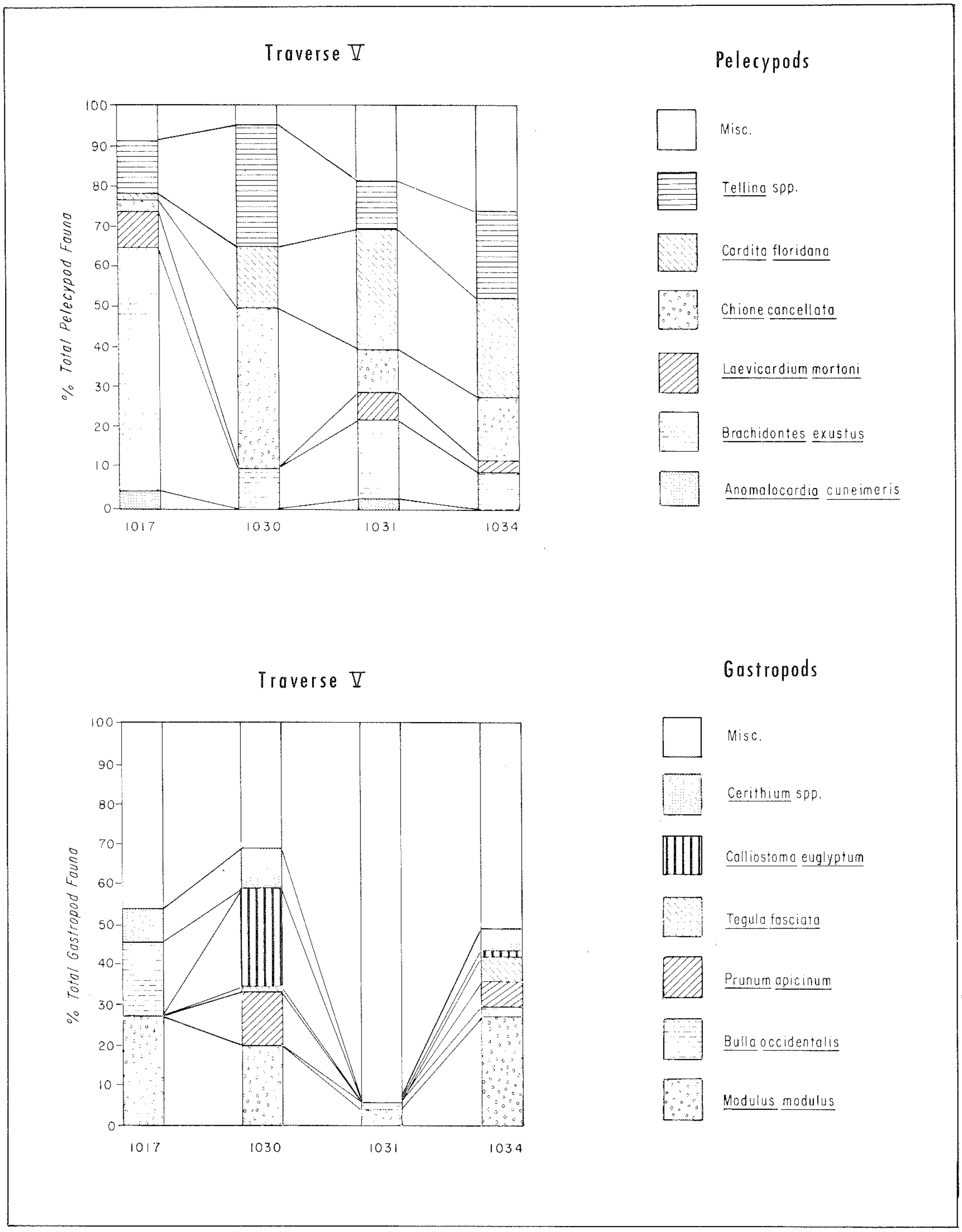

Figure 13. - Relative percent of gastropod and pelecypod species

on the other hand, probably reflects to a great extent a filling of the void left by A. cuneimeris rather than an actual production rate increase. Except perhaps for large percentage variations or the appearance or disappearance of a given species the graphs should be viewed in terms of variations in the entire faunal assemblage rather than in the behavior of individual species.

The character of the Bay fauna appears to be controlled primarily by salinity. Though salinities in parts of the Bay can reach 38‰ during normal periods of high evaporation and values as high as 50‰ have been recorded in the Bay interior during droughts, salinities over the Bay as a whole tend to be lower than average sea water. Ladd (34) used the term polyhaline to describe similar salinity conditions in bays along the Texas coast. The term is widely used by Europeans to denote brackish waters which range from 16 - 30‰ salinity. Florida Bay overlaps slightly on both ends of this range so the term can only be applied in a gross way.

Agreement between the faunal assemblage of Texas polyhaline bays and Florida Bay is quite good. Table 1 lists the five species which are common molluscan elements in both areas with their distributions in the Texas bays. Clearly, at least this part of the Florida Bay assemblage belongs in the polyhaline range of the salinity spectrum. The two Florida Bay species listed by Parker from the Mississippi Delta area (35) also agree with this salinity interpretation.

Within the Bay there appear to be consistent trends in each of the north-south traverses. From north to south there is a distinct

Table 1

Distribution of common Florida Bay species in Texas polyhaline bays

R = rare F = few A = abundant

Station	Facies	Salinity	*Anomalocardia cuneimeris*	*Chione cancellata*	*Laevicardium mortoni*	*Brachidontes recurvus*	*Modulus modulus*	*Cardita floridana*
29	Interreef	9 - 20%				R		
30								
31								
32								
33								
34								
35			A	A		F	A	F
36								
37				F	F			R
38	Polyhaline Bay	15 - 30% occasionally higher				A		
39					R	A		
40						A		
41						A		
42						R		
43				F		F		
44						R		
45								
46				A	A	A		
47								
48				A	R	F		
49			F		R	F	R	
50			A	F	A		A	A
51			A	F	A			
52			A	F	R		A	A
53			A	A	F	F	A	A
55	Passes	27 - 32%				R		
56					F	F		F
57			F			A	F	
58			R		R	R		F
59						F		
60								
61						F		
62								
63	Gulf	36%						
64				A				
65								
66								
67								
68								
69								

decrease in the relative contributions of *Anomalocardia cuneimeris*, *Bulla occidentalis*, and *Cerithium* spp. The decreases are compensated by increases in the relative contributions of *Chione cancellata*, *Cardita floridana*, *Tegula fasciata*, *Calliostoma euglyptum*, and by a general increase in the number of species found. *Modulus modulus*, *Prunum apicinum*, *Laevicardium mortoni*, *Tellina* and *Brachidontes exustus* are found in fair abundance in almost every collection but generally make their greatest contributions in the central part of the Bay. From this data it is possible to propose an ecological zonation for the Bay: a northern zone, an interior zone and a marginal zone. The boundaries of the zones are not distinct lines but are transitional. A summary of the zonation is given in table 2 and the approximate boundaries are shown in fig. 14.

The distribution of ecologic zones corresponds roughly to the salinity gradient pattern developed during the summer months in the Bay (see fig. 6). The correspondence does not prove a cause and effect relationship. However, there is other evidence supporting the hypothesis that salinity exerts the primary ecologic control. Gunter (36) has shown that in going from waters of normal salinity to brackish waters there is a progressive decrease in the number of species found. The species that survive the gradient are, in almost all cases, those members of the higher salinity population which have a greater range of salinity tolerance. Rarely is there an introduction of new species from the fresh water end of the spectrum. This is certainly the case in Florida Bay where there is a progressive "weeding out" of intolerant

Table 2

Stations and characteristic species of Florida Bay ecologic zones

	Northern Zone	Interior Zone	Marginal Zone
Traverse I	1023	1024, 1032	1034
Traverse II	1022	1025	1031
Traverse III	1020	1028	1030
Traverse IV	1019	1017, 1018	
Characteristic species	*Anomalocardia cuneimeris*	*Brachidontes exustus* *Chione cancellata*	*Cardita floridana* *Tegula fasciata*

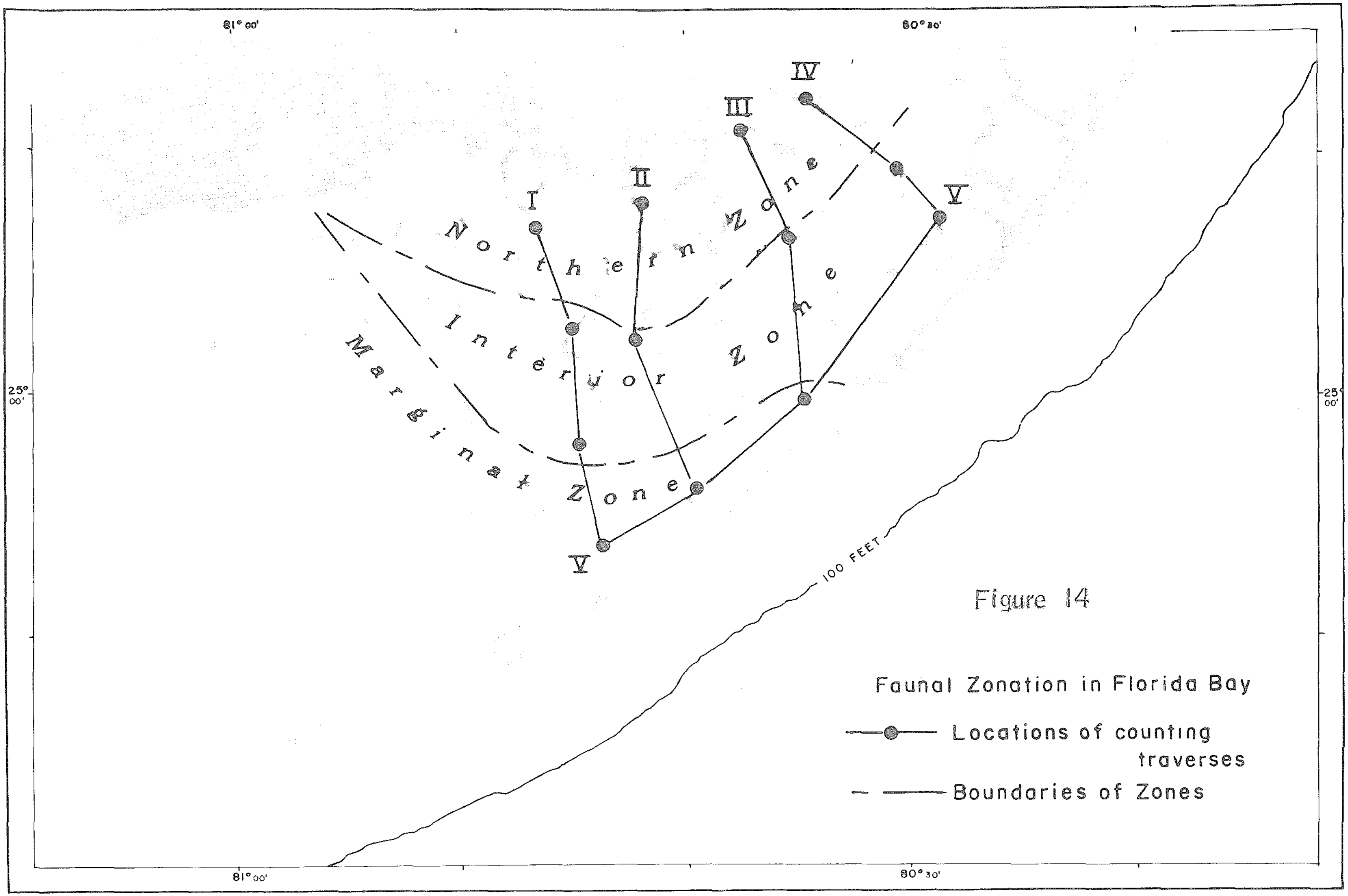

Figure 14

Faunal Zonation in Florida Bay

species toward the mainland. It is impossible to tell whether the "weeding out" is the sole mechanism causing the great increase in the relative contribution of such species as A. cuneimeris or whether some positive factor of the northern zone actually promotes an increased production rate of the species. To answer this question directly would require information on the total production rates of mollusks at various stations in the Bay.

Size is another factor which has been considered a measure of salinity variation (37). There are three possible mechanisms which might operate to produce the correlation:

1. Extreme salinities may slow the growth rate.
2. Variations in salinity may exceed growth thresholds and result in annual periods of no growth.
3. On a statistical basis the probability of exceeding the living tolerance level of a species is greater in areas of large salinity variations, hence long lived individuals would be rare.

Table 3 lists the size of the largest individuals of a number of species as a function of geographic location. The largest specimens are found at locations where there is a large contribution of the species to the assemblage.

In addition to the well-developed north-south zonation there is an east-west gradient in the faunal composition of the death assemblage. It can be seen in fig. 13 where the cumulative bar graphs for the southern-most station in each north-south traverse are arranged in

Table 3

Maximum dimension of largest individual of species in millimeters and relative percent of species in the assemblage

	Anomalocardia cuneimeris		*Chione cancellata*		*Bulla occidentalis*	
	Size mm	%	Size mm	%	Size mm	%
Traverse I						
1023	13	38	--	0	14	21
1024	--	0	15	2	15	12
1032	7	2	21	25	--	0
1034	--	0	26	15	8	5
Traverse II						
1022	20	44	26	2	13	4
1025	13	39	22	2	13	3
1031	8	1	22	9	11	2
Traverse III						
1020	12	62	--	0	17	15
1028	10	5	10	18	7	3
1030	--	0	22	38	--	0
Traverse IV						
1019	11	68	--	0	15	28
1018	9	8	--	0	14	34
1017	8	4	5	3	13	17

an east-west direction. It can also be seen by comparing the traverses themselves. The north-south zonation in each traverse becomes less definitive as one goes east. The east-west gradient is probably related to restricted exchange in the eastern part of the Bay.

Though salinity variations appear to exert the primary ecologic control in Florida Bay there are other environmental factors which can influence the distribution of mollusks. Allen (38) studied the distribution of living mollusks in Florida Bay as a function of water depth and type of bottom. In addition to major differences between the fauna of the mud bank surface and that of deeper adjacent "lakes" he found other variations along the mud bank surface itself. Table 4 summarizes his findings.

Ginsburg noted these differences and suggested that large local variations would tend to mask any large scale geographic variations that might exist.

In summary, it is clear that though there are large local variations in the faunal composition of Florida Bay, there is an overriding zonation of the fauna related to proximity to the mainland. Northern, interior and marginal zones can be roughly delineated on the basis of the total molluscan composition in each zone. Many lines of indirect evidence point to a gradient of increasing salinity from north to south as the controlling factor in the zonation. Direct evidence based on live collections is not available.

Table 4

Molluscan Fauna from Banks in Florida Bay

Water Depth	Character of Area	Average Number[1] of: Live Mollusks	Genera	Dominant
(Inches)				
½-5	Broad marl flat; fairly hard bottom; scattered grass	1,220	6	Cerithium minimum
1-2½	Narrow marl flats with soft bottom; no grass	68	6	Modulus modulus
2-2½	Broad marly flat; soft bottom; no grass	258	4	Cerithium minimum
2½-6	Broad marl flat; fairly hard bottom; scattered grass	150	9	Modulus modulus
3-5	Semi-enclosed slough; soft bottom	1,072	5	Anomalocardia cuneimeris
4½-5½	Broad marl flat; fairly hard bottom; no grass	129	8	Cerithium minimum
4½-5½	Broad marl flat; fairly hard bottom; sparse grass	88	6	Cerithium muscarum
5-7	Broad marl flat; fairly hard bottom; scattered grass	227	5	Pinctada radiata
(Feet)				
2	Edge of shoal; heavy grass on bottom	83	7	Pinctada radiata
3	Edge of shoal; heavy grass on bottom	76	1	Pinctada radiata
6	Open bay; marly bottom with sparse grass	75	1	Pinctada radiata
6½	Open bay; marly bottom; no grass	0	0	

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[1] The samples were standardized as to the size of area dredged.

WATER CHEMISTRY

The data on salinity presented above show that Florida Bay water contains varying proportions of water from four different sources: 1) Reef tract water, 2) Gulf of Mexico water, 3) Run-off water from the Everglades coastal swamps, 4) Rainwater falling directly into the Bay.

The chemistry of any given sample of Florida Bay water will depend on the composition of the original source waters, the relative amount of each source component in the mixture, and on climatic, geographic, and biologic effects imposed on the mixture.

Strontium, Magnesium and Calcium Composition

Six samples of Florida Bay water were analyzed for strontium, magnesium and calcium composition. The techniques are described in Appendix A and the results are given in table 5. The precision of the strontium data is ± 8% and of the calcium and magnesium data ± 1%.

Odum (13) investigated the distribution of strontium in natural waters and found considerable disagreement among early published values for the strontium content of average sea water. He settled on 8.1 mgm/L as the preferred value which is in agreement with recent values given by Chow and Thompson (39) and Bowen (40). Using the accepted value of 400 mgm Ca/L the atom Sr/1000 atoms Ca ratio of sea water is 9.3. The accepted value for the magnesium content of sea water is about 1250 mgm/L which yields a ratio of 5.20 atoms Mg/ atom Ca.

Table 5

Strontium, magnesium, and calcium content of Florida Bay water.

	A-1050	N-1044	F-1056	F-1024	N-1018	A-78
Date of collection	Aug, 58	Nov, 58	Feb, 59	Feb, 59	Nov, 58	Aug, 57
Salinity gm/Kgm	35.7	20.0	25.6	32.7	35.9	53.8
$\frac{\text{atoms Sr} \times 1000}{\text{atoms Cl}}$	.209	.197	.210	.207	.203	.192
$\frac{\text{atoms Ca} \times 1000}{\text{atoms Cl}}$	19.4	21.8	20.9	19.9	19.7	18.6
$\frac{\text{atoms Mg} \times 1000}{\text{atoms Cl}}$	97.0	95.2	96.0	96.2	96.8	95.4
$\frac{\text{atoms Sr}}{\text{1000 atoms Ca}}$	10.7	9.1	10.0	10.4	10.3	10.3
$\frac{\text{atoms Sr}}{\text{1000 atoms Ca}}$	5.0	4.3	4.6	4.8	4.9	5.1
Sr mgm/L	10.0	5.4	7.3	9.2	9.8	14.0
Ca mgm/L	426	274	334	406	438	625
Mg mgm/L	1280	717	922	1180	1290	1920

Sample A-1050 was collected in the back reef area but is probably representative of values that would be found along the reef tract and in the Gulf of Mexico. The Mg/Ca ratio for this sample is close to values found in open ocean waters. The Sr/Ca ratio is significantly higher than the preferred value given by Odum for ocean water. The disagreement may only reflect a systematic difference in the method of analysis. On the other hand, the difference may be real. Most calcium carbonate secreting organisms tend to exclude strontium from their skeletons. The high rate of carbonate precipitation on the Florida shelf as compared to the open ocean could result in a relative enrichment of strontium in the shelf waters. The process is discussed in more detail in a later section.

Everglades fresh water was not analyzed. Parker, et al (27) showed that fresh surface waters from the Miami area have a ratio of about 0.2 atoms Mg/ atom Ca. Odum (13) found a ratio of 1 to 3 atoms Sr/1000 atoms Ca in river and lake waters of central Florida. Though neither of these sets of values can be directly applied to Everglades swamp water they do indicate that fresh waters draining limestone terrains tend to have much lower Sr/Ca and Mg/Ca ratios than sea water.

In fig. 15 the ionic ratios of the six samples are plotted as a function of salinity. The plots of Sr/Ca and Mg/Ca ratios show a significant decrease with decreasing salinity. The ratios did not change when salinity increased to values greater than that of the reef tract and Gulf waters. This is consistent with an interpretation of dilution of reef tract water by fresh water having low Sr/Ca and Mg/Ca

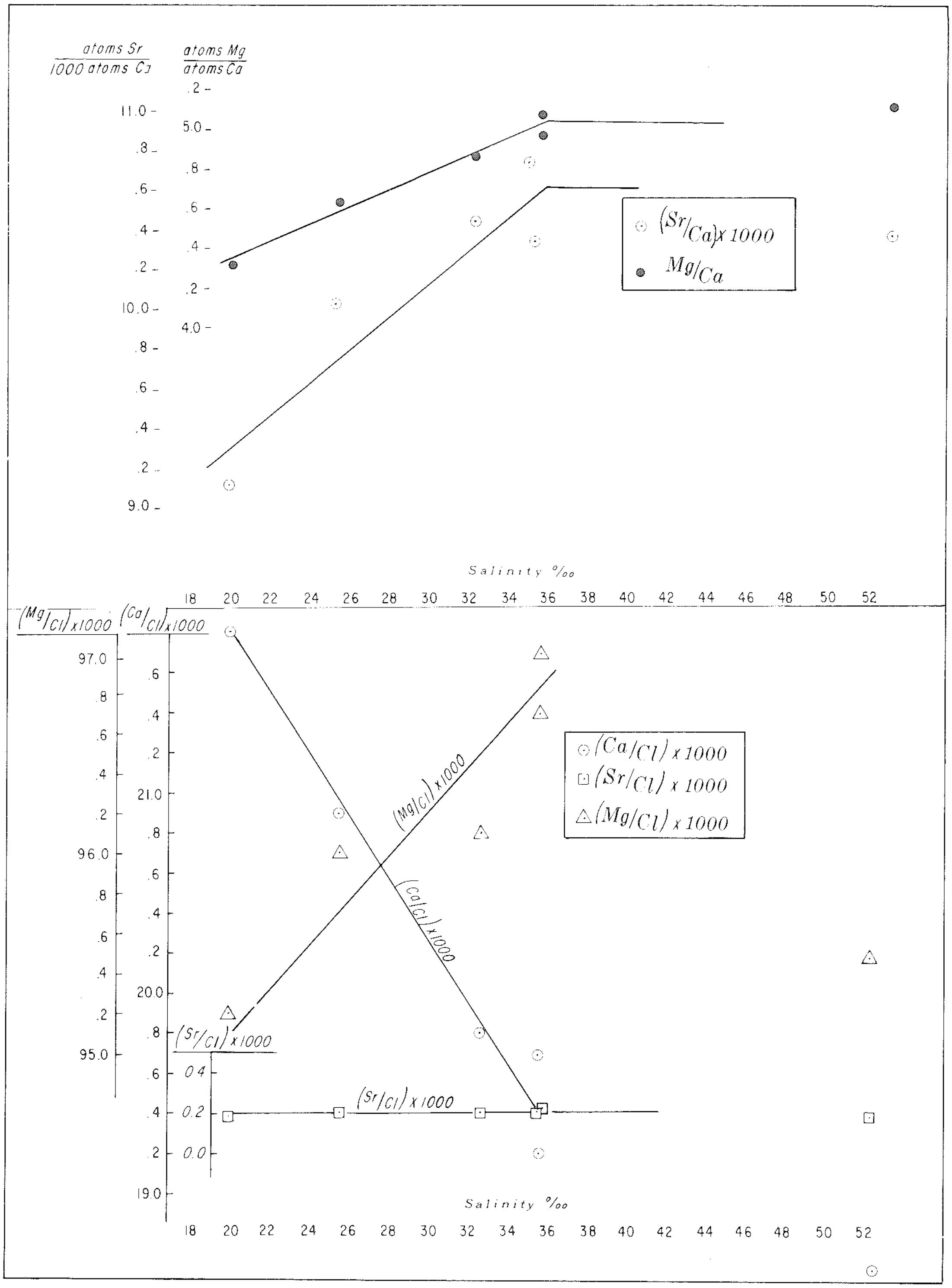


Figure 15. - Sr, Mg, and Ca compostion of Florida Bay and reef tract waters

ratios and simple evaporation of reef tract waters to produce higher salinities but no change in the ionic ratios.

The interpretation is confirmed by the plots of Ca/Cl, Sr/Cl and Mg/Cl ratios. Dilution with fresh water does not affect the Sr/Cl ratio but it increases the Ca/Cl ratio by a large amount and decreases the Mg/Cl ratio. It appears that the high calcium content of the fresh water diluent is the most effective factor causing low Sr/Ca and Mg/Ca ratios in the Bay waters that were analyzed.

A-78 is a high salinity sample collected by the Shell Oil Co. near station 1023 in August, 1957 following the drought of 1956. Though the Sr/Ca and Mg/Ca ratios do not appear to have been affected by the increase in salinity both the Ca/Cl and Mg/Cl ratios are significantly lower than the values found in the reef tract water sample. This suggests that the water was depleted in calcium and magnesium ions during this period of isolation from open sea water and from dilution by fresh coastal waters. Biological precipitation of calcium carbonate may have been responsible for the depletions but it is difficult to rationalize the large amount of magnesium removed with the known low Mg/Ca ratios of shell materials.

Oxygen Isotope Composition

The oxygen isotope composition of a given sample of Florida Bay water is a product of the mixing of waters from the four sources mentioned above plus the superimposed effects of evaporation.

All major variations in the isotopic composition of the surface waters of the earth are caused by distillation processes. Epstein and Mayada (21) made experimental determinations of the equilibrium fractionation between H_2O(liquid) and H_2O(gas). They found the H_2O^{18}/H_2O^{16} ratio in the vapor to be 0.8% (8.0‰) less than the H_2O^{18}/H_2O^{16} ratio in the liquid. In nature the same fractionation occurs when water is evaporated from the oceans. The "light" vapor (depleted in H_2O^{18}) is carried inland and condensed as rain or snow. Most of the light water is returned to the sea by rivers but a portion is retained in lakes, groundwater, snow fields, and glaciers. These fresh waters do not have an H_2O^{18}/H_2O^{16} ratio which is consistently 8‰ lighter than ocean water. Instead, there are wide variations in isotopic composition of samples collected from various parts of the fresh water reservoir. To explain this, Epstein and Mayada (21) proposed the following mechanism of fractional distillation:

The first water to condense from a cloud will be in equilibrium with the original vapor and therefore will have the same isotopic composition as the ocean water from which it was evaporated. The removal of this heavy water as rain will deplete the remaining vapor in H_2O^{18}. As more rain forms each increment of water will condense from progressively lighter vapor and will have a progressively lighter isotopic composition. Vapor carried to high latitudes or high altitudes will become very much depleted as more and more water is lost until the last large increment of vapor is frozen out as snow. Snow and ice have H_2O^{18}/H_2O^{16} ratios as much as 25‰ lower than ocean waters (41).

The removal of light water enriches the oceans in H_2O^{18}. The ocean reservoir is so large, however, that the removal of the present reservoir of fresh water from the oceans has raised the H_2O^{18}/H_2O^{16} ratio by an average of only 1 ‰ (21). A body of marine water which is not in good exchange with the oceans can be enriched to much higher concentrations of H_2O^{18} by evaporation.

For the present study a group of water samples were analyzed for H_2O^{18}/H_2O^{16}. The analyses were performed on CO_2 gas equilibrated with the water as described in Appendix A. A large but constant fractionation accompanies the equilibration so that the measured values are related to the true H_2O^{18}/H_2O^{16} ratios by a constant. The results are given in terms of δ which is defined as follows:

$$\delta = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000$$

where: R_{sample} = O^{18}/O^{16} ratio of the sample CO_2 gas

R_{standard} = O^{18}/O^{16} ratio of a standard CO_2 gas (PDBI)

δ is the per mil difference between the sample and the Chicago PDBI standard gas (1‰ = 0.1%). Using the same techniques and standard Epstein and Mayada found mean sea water to have a δ of 0.0. The values presented here can be considered as per mil deviations from mean sea water. The precision is ± 0.1‰. A complete discussion of techniques and standards can be found in Appendix A.

The results of analyses are given in table I, Appendix B. The areal distribution of values for different times of the year are shown in figs. 16, 17 and 18 and δO^{18} vs. salinity for all sea water samples is plotted in fig. 19.

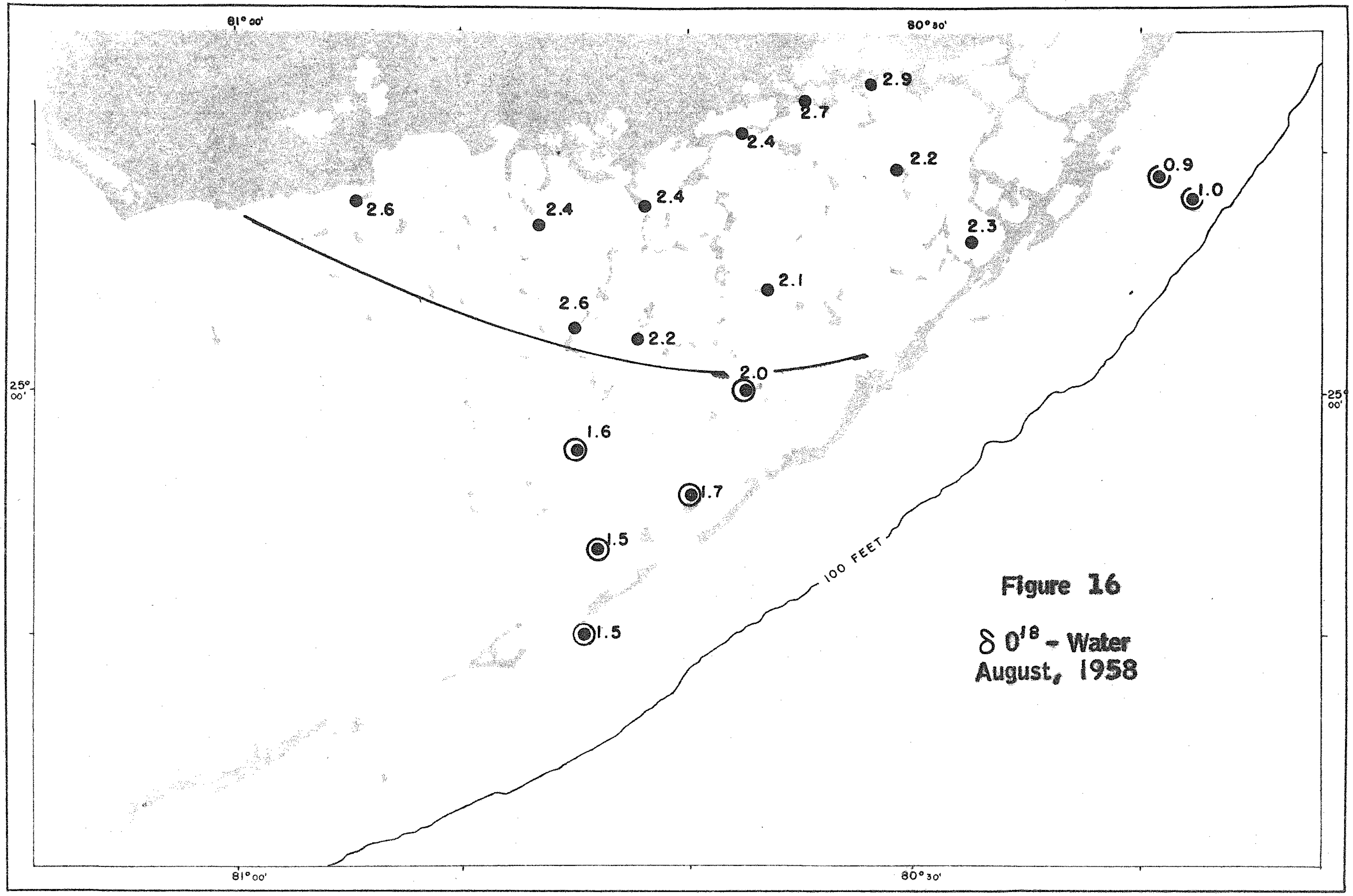


Figure 16

δ O^{18} - Water
August, 1958

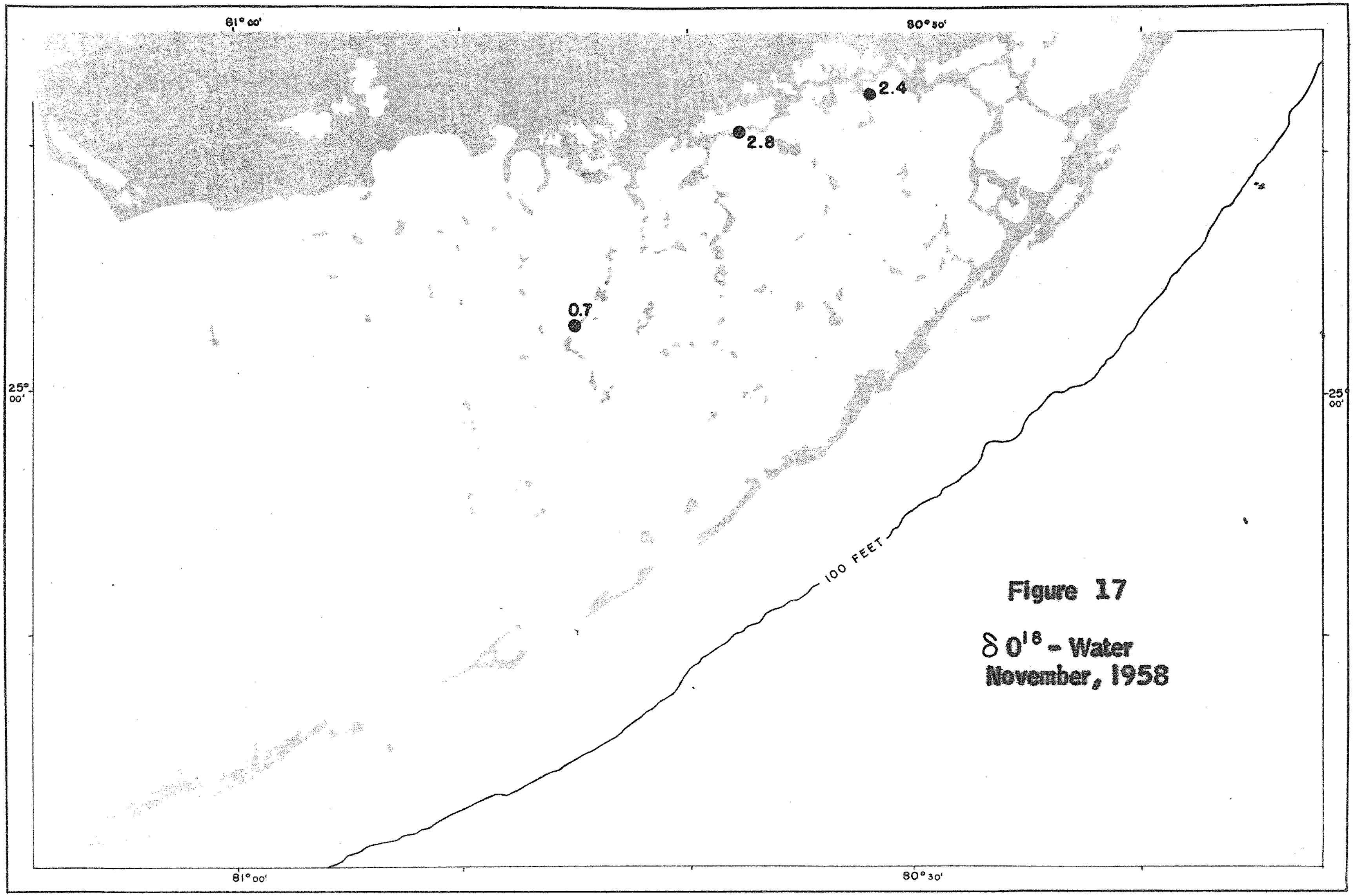


Figure 17

δO^{18} - Water
November, 1958

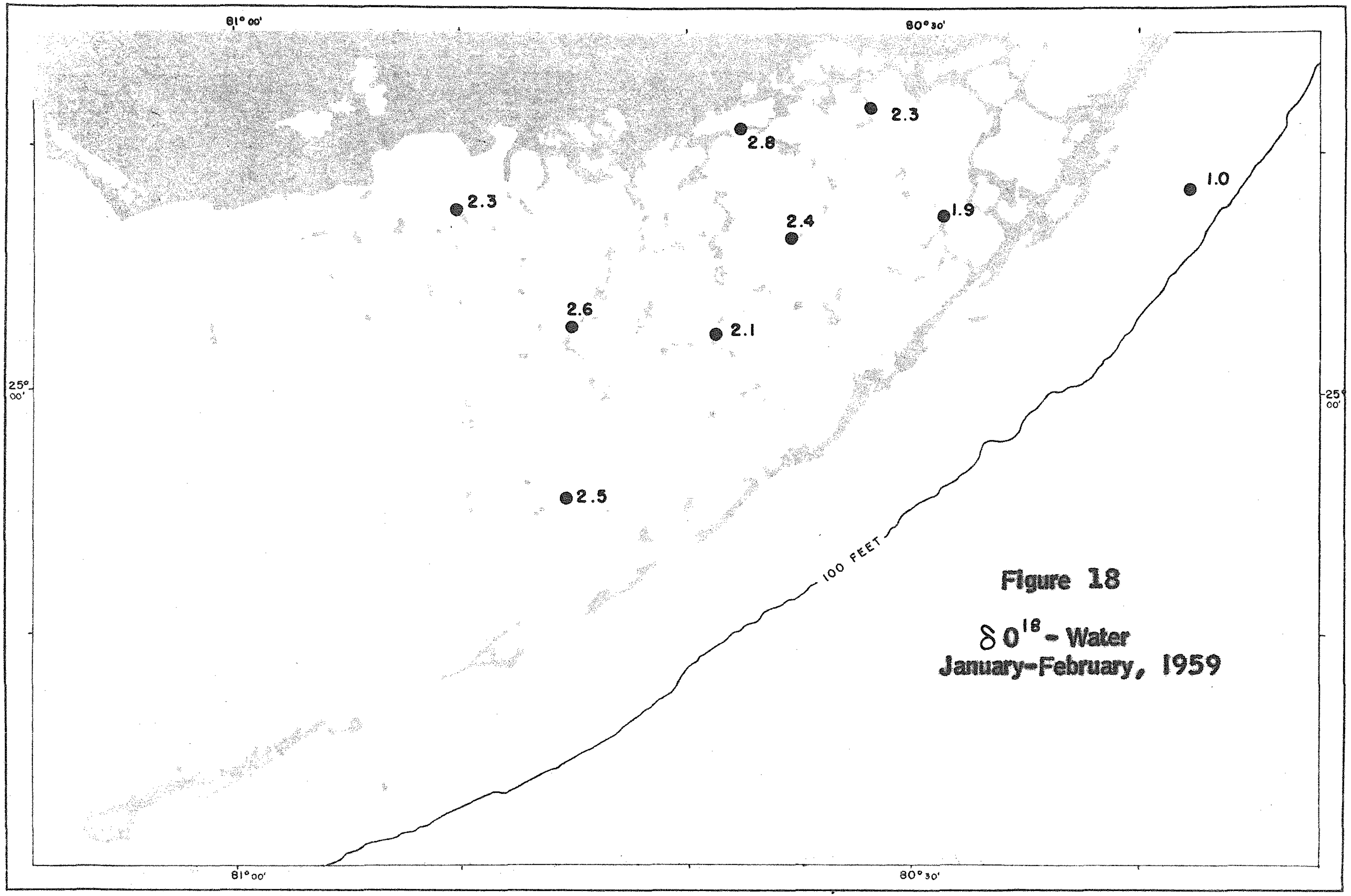


Figure 18

δO^{18} - Water
January-February, 1959

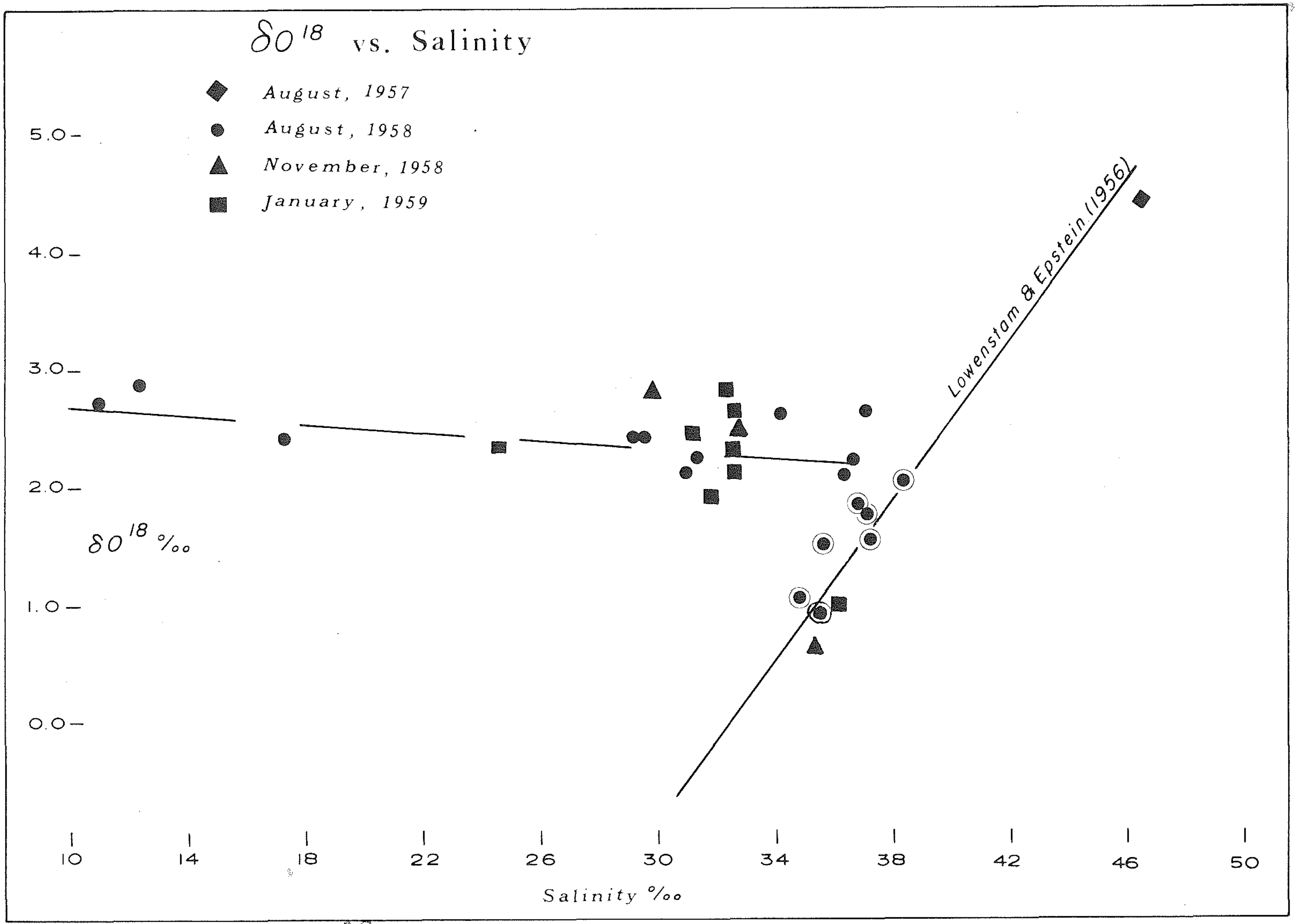


Figure 19. - δO^{18} vs. salinity for Florida Bay and reef tract waters

Two analyses of reef tract water (1061) collected in August and January have identical values of 1.0‰ . This agrees with open water values found by Lowenstam and Epstein (22) from the Bahamas and probably represents a good value for surface ocean waters in this region.

A sample of Gulf of Mexico water (1078) collected in August, 1959 from north of Long Key (δ = 1.4) is slightly higher than the reef tract value. The sample may have been mixed with some heavy Florida Bay water or it may represent a greater enrichment of the Gulf shelf waters which are partially blocked from open exchange with ocean waters.

Only two samples of rain water were analyzed. These were collected in August, 1959 about 10 miles north of Florida Bay in the Everglades. The rain fell from local squall clouds which formed in the late morning from clear skies at an altitude of about 1000 feet. Sample 1080 (δ = -0.2) was caught directly from water running off a car roof during the rain. Sample 1081 (δ = 0.7) was collected from a rain puddle in the road which had formed during an earlier shower that same day. The high δ values for the rain water suggest that both samples originated in the early stages of condensation of the cloud. If Florida Bay water was the source of the vapor then the vapor itself may have been unusually enriched prior to condensation as the Bay water (see below) can have δ values as high as 2.5% .

Fresh water from the coastal swamps was not collected. The closest samples to the swamps are A-1019 and A-1054 which have salinities of 11.2‰ and 12.5‰ and δ values of 2.7‰ and 2.9‰ respectively. These values, when compared to the reef tract salinity and isotopic composition, indicate that the coastal fresh waters have an unusually high δ value. Epstein and Mayada (21) were the first to note this peculiar character of the Everglades swamp water. They found salinity values of 29.6‰ and 28.3‰ and δ equal to 3.5% and 4.5% respectively for two water samples collected from shallow lakes about five miles north of the mainland coast. They attributed the composition to a mixing of normal sea water with an evaporated residue of fresh water enriched in H_2O^{18} to a δ value of 24‰ . Such extreme enrichments are consistent with known hydrologic data. Rainwater falling in the Everglades was shown to originate from the first stages of condensation of rain clouds so enrichment processes start on fresh water with a δ value close to that of mean ocean water. The swamps are very shallow, exposing a large surface area for a given volume and allowing a rapid warming of the water. Both of these factors encourage evaporation. Langbein (44) has estimated that 80% of the rain water falling in the Everglades is re-evaporated before it can be incorporated into the ground water or discharged into the drainage system. A large amount of this vapor is probably retained in the area by recycling in local rains but the portion that escapes is enriched in H_2O^{16} relative to the swamp water and over a long period the swamp waters are enriched in H_2O^{18}.

The effects of mixing and evaporation in the Bay can be seen clearly in map figs. 16, 17 and 18 and in the plot of δO^{18} vs. salinity. During August, 1958 water originating from the reef tract and Gulf of Mexico was progressively evaporated and enriched in H_2O^{18} going into the Bay. These are the circled samples in figs. 16 and 19. It is interesting to note that the relationship of δO^{18} to salinity agrees very well with that found by Lowenstam and Epstein (22) from Bahaman waters. The initial waters in both cases had a δO^{18} and salinity characteristic of the region and the process was one of simple progressive evaporation. A sample of very high salinity water collected in August, 1957 falls along the same δO^{18} vs. salinity trend supporting the conclusion that highly evaporated reef tract or Gulf of Mexico water can penetrate the inner areas of the Bay in the absence of the low salinity wedge.

The remaining samples for August show the effects of mixing of Everglades run-off water with evaporated reef tract and Gulf waters. In fig. 19 an extrapolation of δO^{18} vs. salinity back to 0 ‰ salinity would intersect the δO^{18} ordinate at about $\delta = 3.0‰$. As this is a heavier δ value than even the most highly enriched sea water sample in the Bay the influx of fresh water tends to augment the gradient of increasing δO^{18} toward the mainland. In the upper parts of the Bay the gradient of δO^{18} has the same shape and extent as the brackish water wedge described in an earlier section.

The November, 1958 samples are too few in number to permit a meaningful interpretation of the isotopic composition of Bay water at that time. The two samples collected near the coast (N-1020, N-1054) have high δ values similar to August samples from the same locations but the salinities are much higher. The low salinity water from coastal swamps appears to have left the area by some means other than evaporation. The one sample from the center of the Bay has a δO^{18}-salinity relationship similar to that of the open Gulf or reef tract waters. The data are consistent with the suggested migration of open water into the Bay during a high sea level period.

The mixing of Bay water noted in the salinity data for January and February, 1959 is also evident in the oxygen isotope compositions. The range of values over the Bay is 0.7‰ as compared to the 1.4‰ range found in August. The gradient of increasing δO^{18} toward the mainland is replaced by more or less randomly distributed values. The mean value for both August and January-February samples is 2.3‰ .

The spread of the oxygen isotope values, though small, is larger than would be expected considering the narrow spread of salinity values. Sample 1055 which had the lowest salinity for January (26.2‰) might be expected to have the highest δ values as it contains the greatest amount of fresh water. The measured value was relatively low (δ = 2.3‰). Clearly, the mixing of evaporated sea water and coastal fresh water was not the only source of isotopic variation in the Bay waters during January, 1959. What these other sources of variation were is difficult to suggest from the limited amount of data available. The unseasonably high rainfall recorded in December, 1958 (see fig. 3) may have brought in large amounts of unusually light fresh water especially if the rain were associated with a cold front and represented late stages of condensation of the vapor. This would account for some of the lower δ values in the diluted Bay water. The spread of δ values over the

Bay points up the influence of the complicated bathymetry of Florida Bay in controlling local water circulation.

Clearly, the few data presented here cannot give a complete picture of the variations in oxygen isotope chemistry of Florida Bay water. The major variations, however, appear to be controlled by a few simple processes which can be summarized as follows:

1) The shallowness of Florida Bay and its poor exchange with reef tract and Gulf waters tend to promote and maintain radical variations in the isotopic chemistry of the water.

2) Evaporation of Florida Bay water causes an enrichment in H_2O^{18} which becomes more pronounced as the water becomes more isolated toward the mainland.

3) Fresh water in the Everglades coastal swamps is also enriched in H_2O^{18} by evaporation to even greater values than the Bay water.

4) The mixing of the coastal swamp water with evaporated Bay water during the rainy season tends to produce a well-developed gradient of increasing δO^{18} toward the mainland.

5) Mixing within the Bay or unusual weather conditions can upset the δO^{18} gradient but the O^{18} values remain relatively high in the Bay compared to open water.

6) Reef tract and Gulf waters can penetrate far into the Bay for brief periods in response to high sea levels

or for extended periods in the absence of fresh water influx.

SHELL CHEMISTRY

Strontium and magnesium composition and oxygen and carbon isotope composition were determined on selected specimens of eight of the common species of Florida Bay mollusks. *Anomalocardia cuneimeris* and *Bulla occidentalis* were chosen as representative of the northern ecologic zone and *Tegula fasciata* and *Cardita floridana* as representative of the marginal ecologic zone. *Chione cancellata*, *Brachidontes exustus*, *Modulus modulus* and *Prunum apicinum* are distributed over the entire Bay but are relatively more abundant in the interior zone.

Only whole valves or groups of whole valves were selected for analysis. The specimens were thoroughly cleaned as described in appendix A and checked for contamination under a binocular microscope. Analyses were performed on powders made from the entire shell sample.

Strontium and Magnesium Composition

Strontium and magnesium were determined by copper spark emission spectrograph technique as outlined in appendix A. The precision of analysis is ± 10% of the amount present. The results are given in table III, appendix B and the areal distributions of strontium values for the different species are given in figs. 20 to 27.

The magnesium concentration of all of the specimens examined was very low. No analysis yielded more than 0.5 atoms Mg/1000 atoms Ca. In this range of values the precision of the technique falls off very rapidly and differences of 0.1 to 0.3 atoms Mg/1000 atoms Ca which were found are not considered significant.

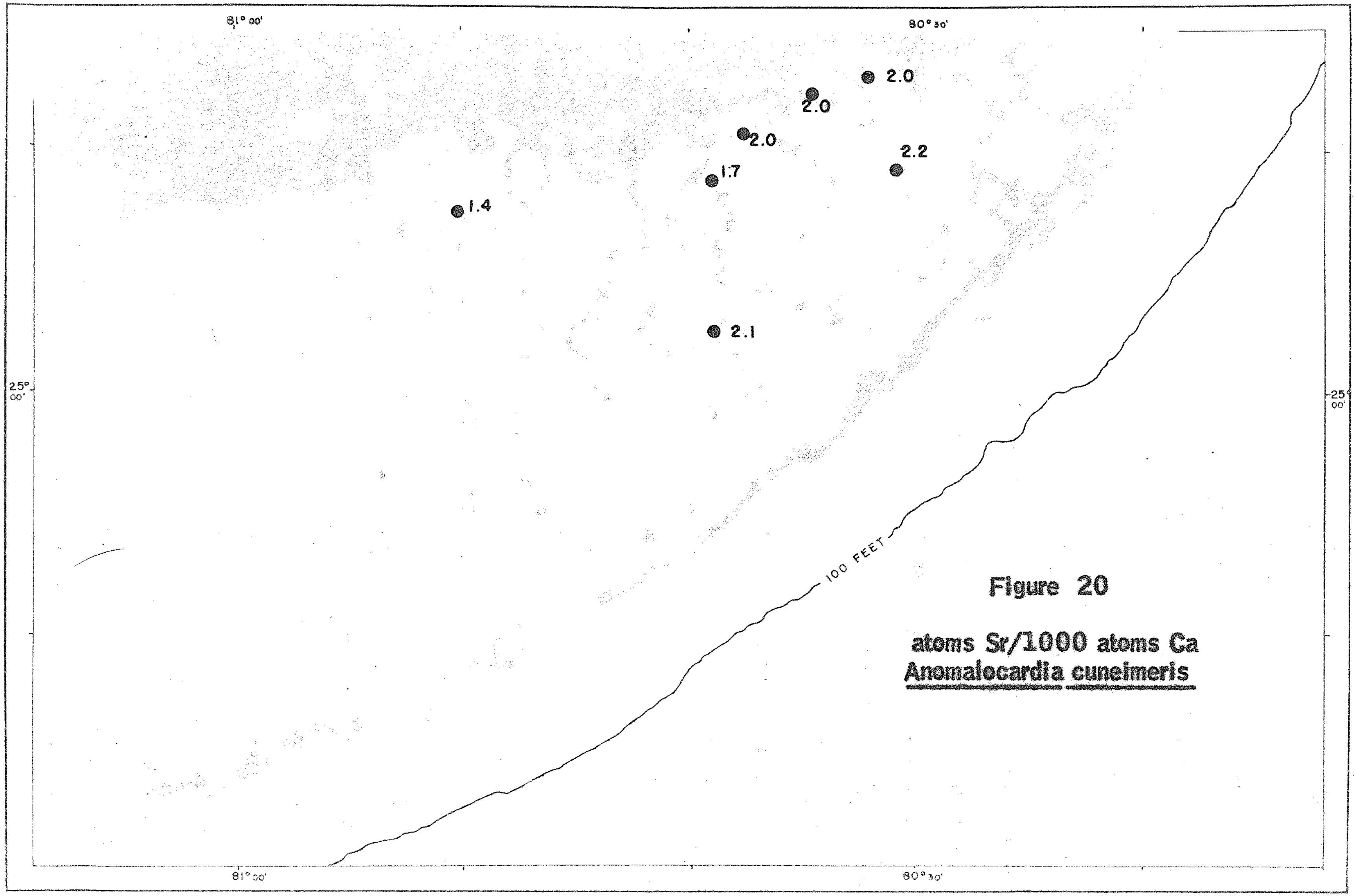


Figure 20

atoms Sr/1000 atoms Ca
Anomalocardia cuneimeris

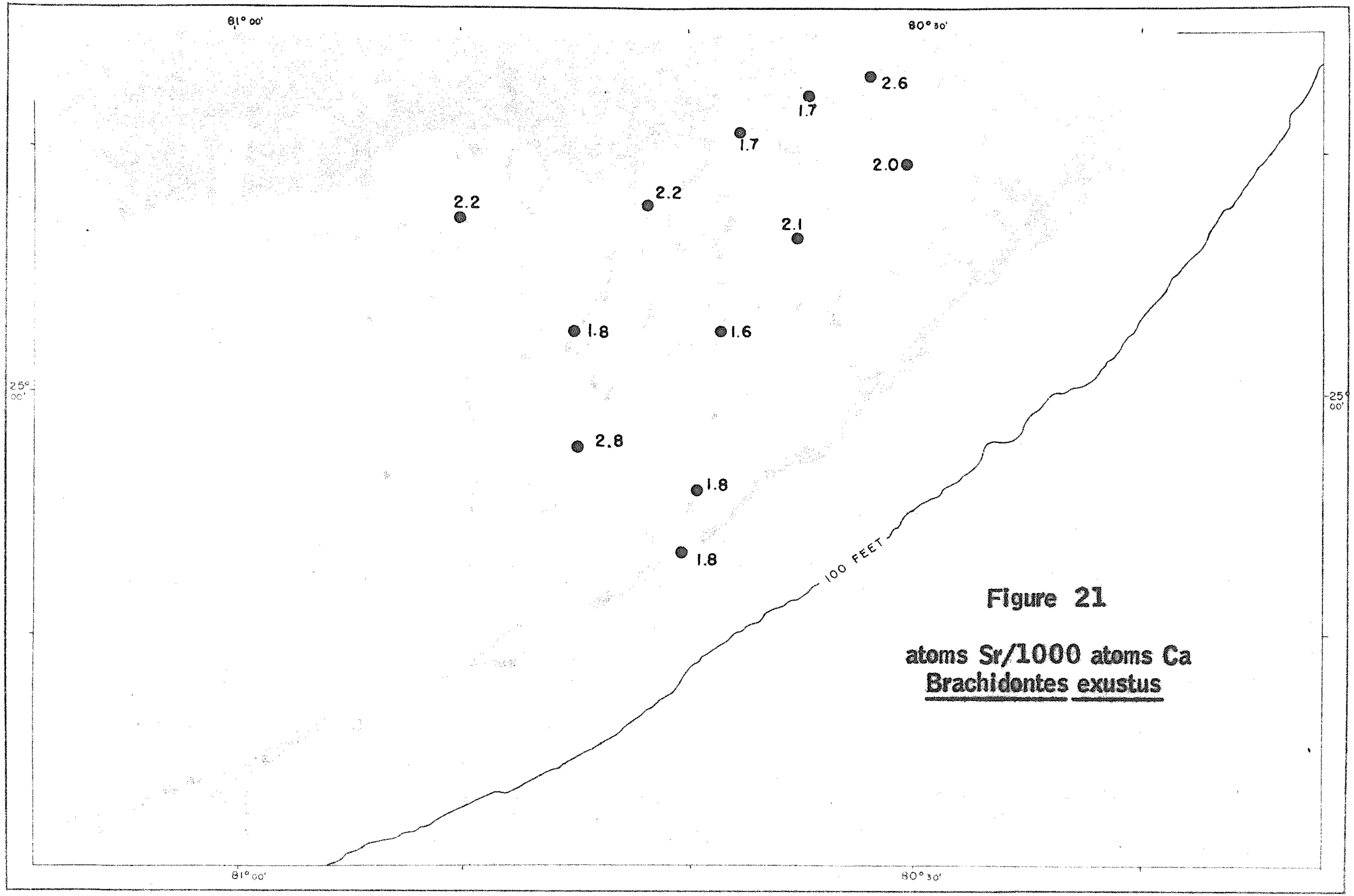


Figure 21

atoms Sr/1000 atoms Ca
<u>Brachidontes exustus</u>

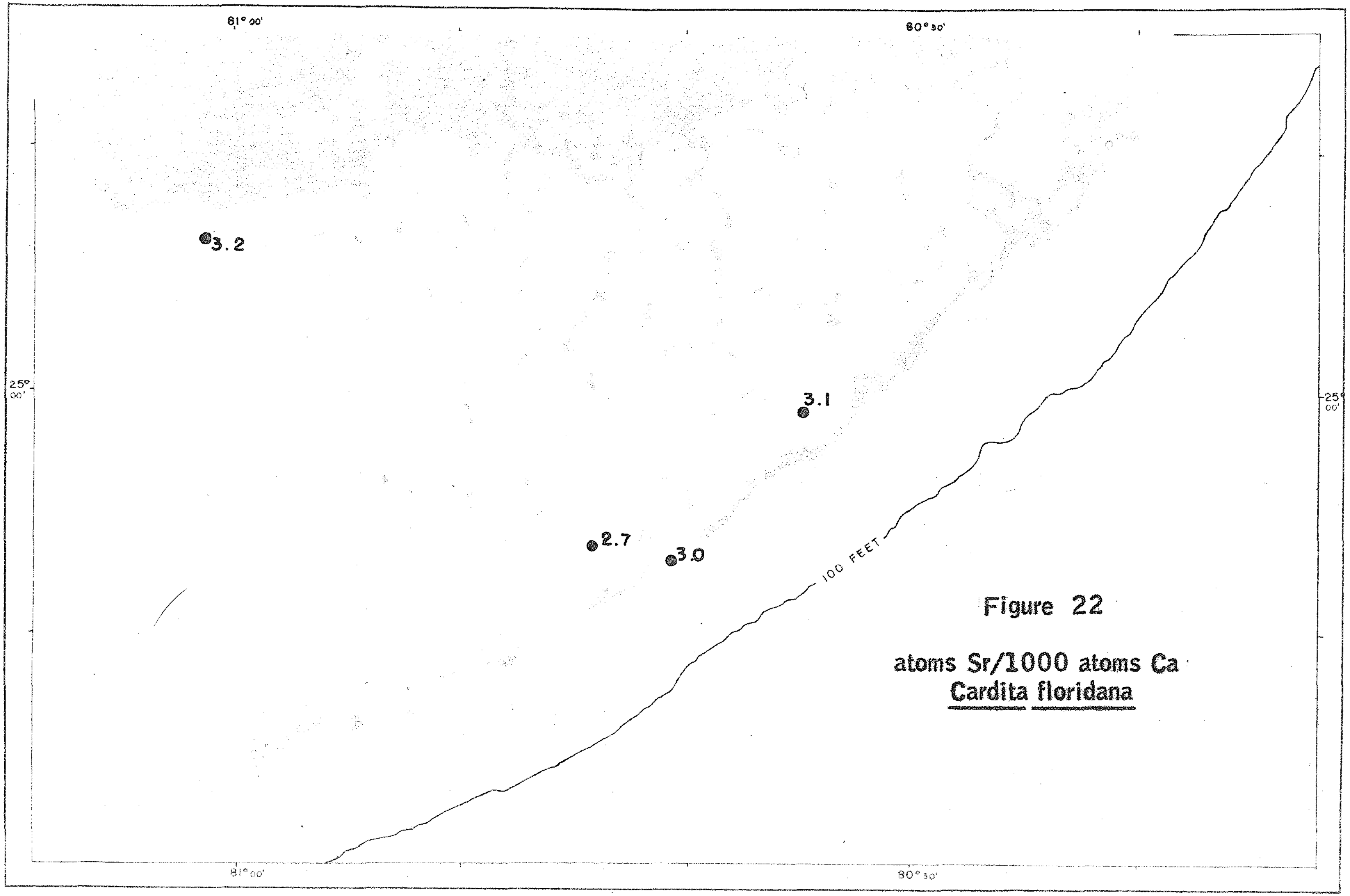


Figure 22

atoms Sr/1000 atoms Ca
Cardita floridana

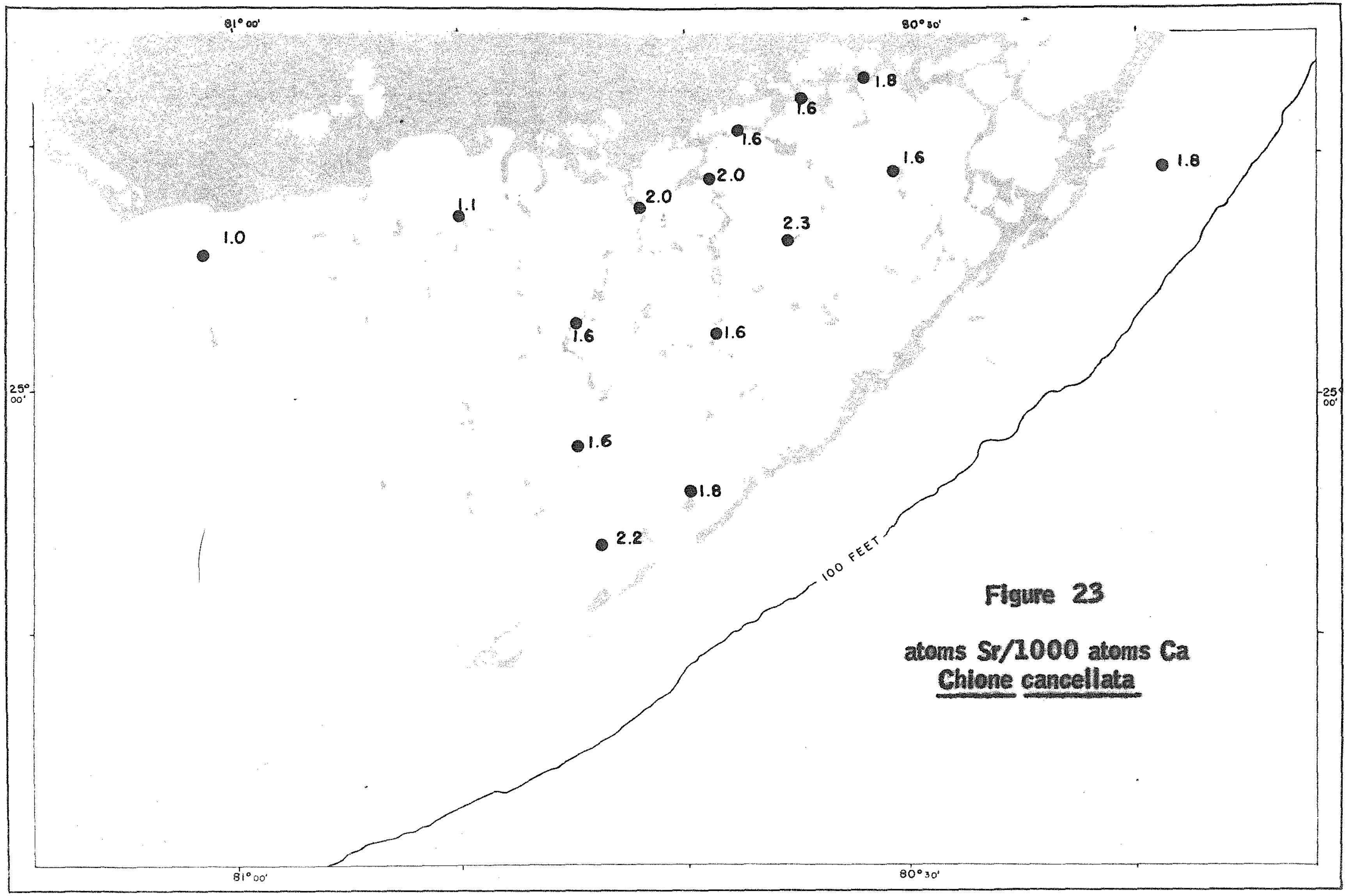


Figure 23

atoms Sr/1000 atoms Ca
Chione cancellata

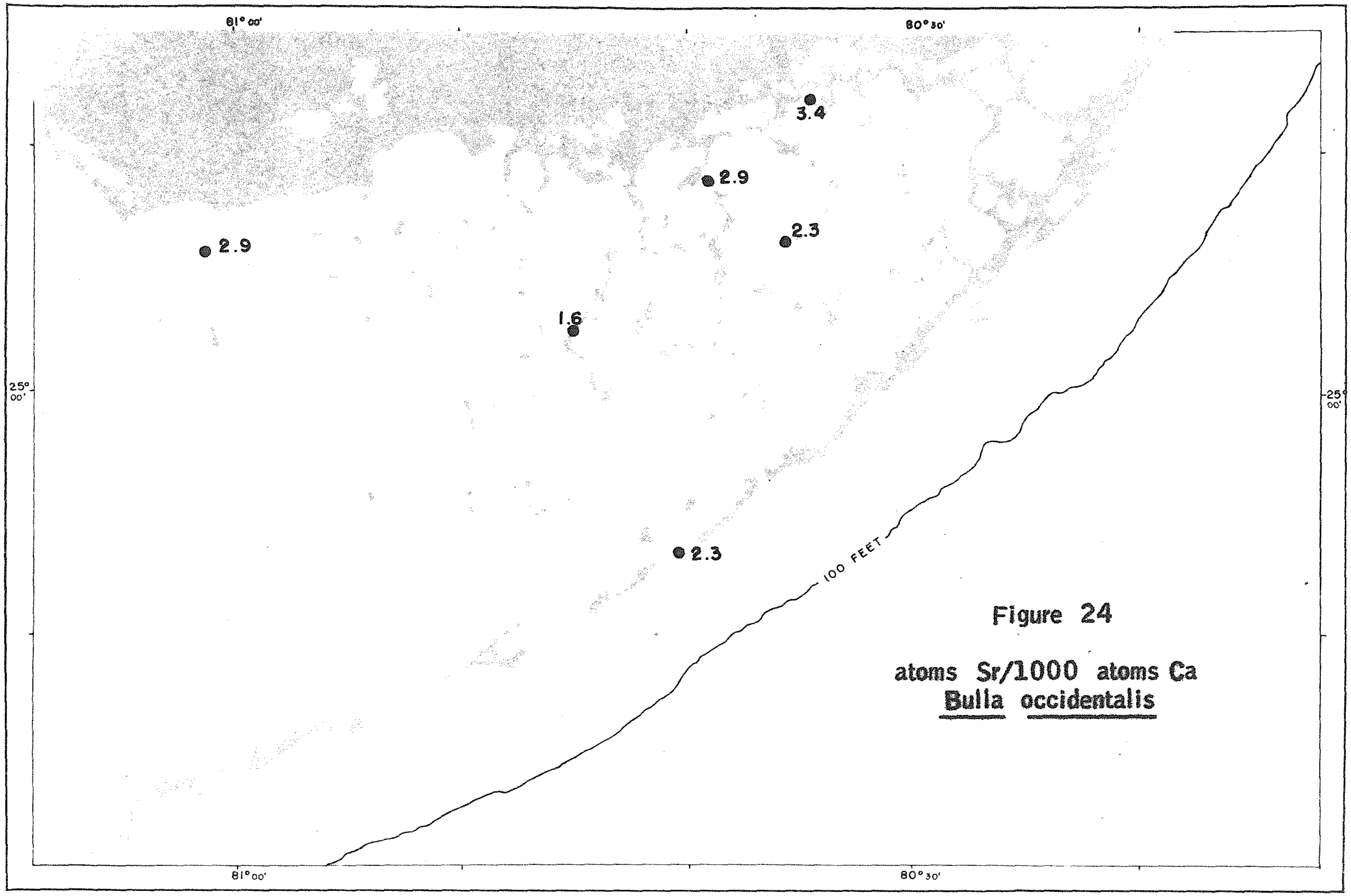


Figure 24

atoms Sr/1000 atoms Ca
Bulla occidentalis

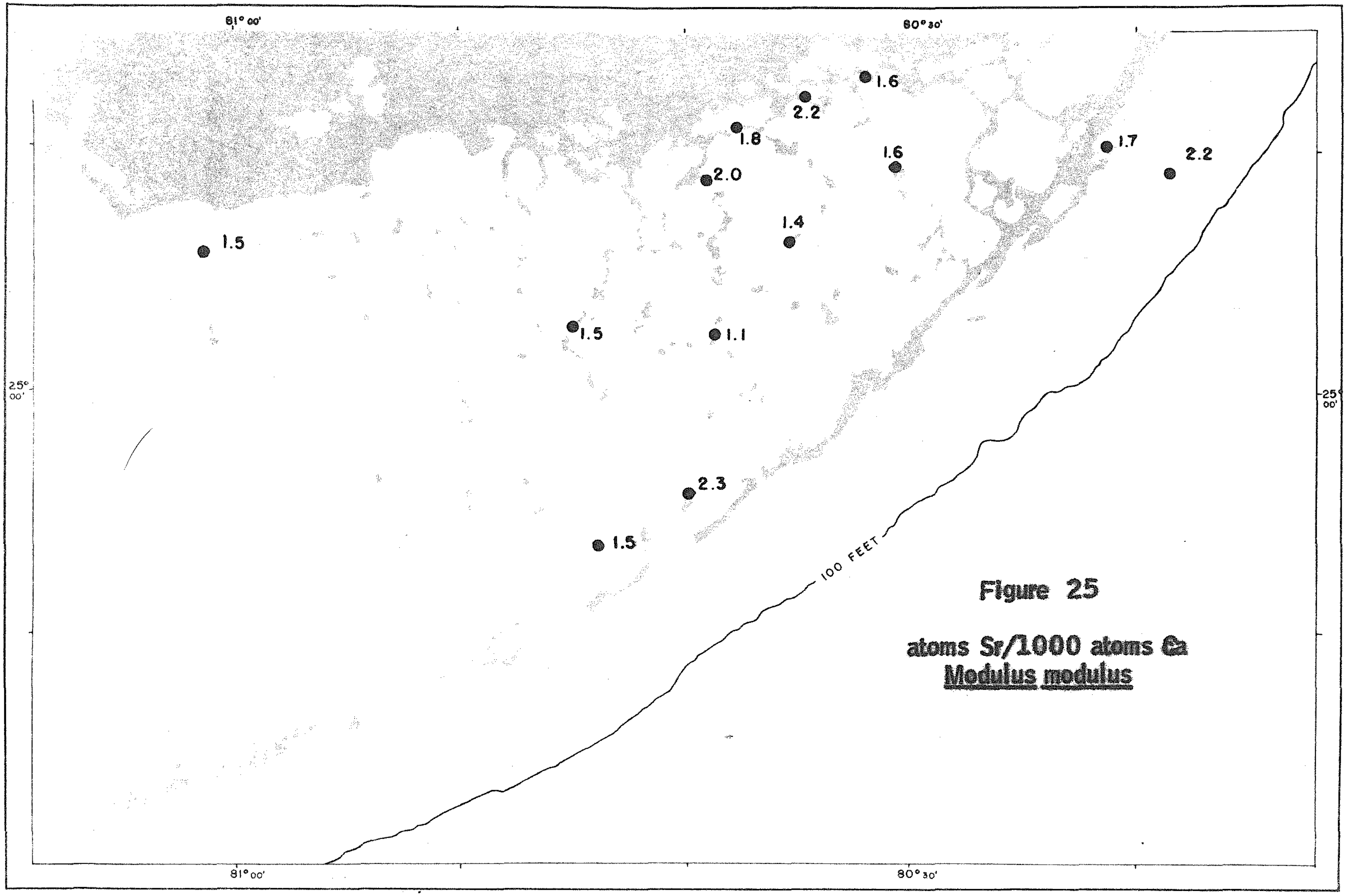


Figure 25

atoms Sr/1000 atoms Ca
<u>Modulus modulus</u>

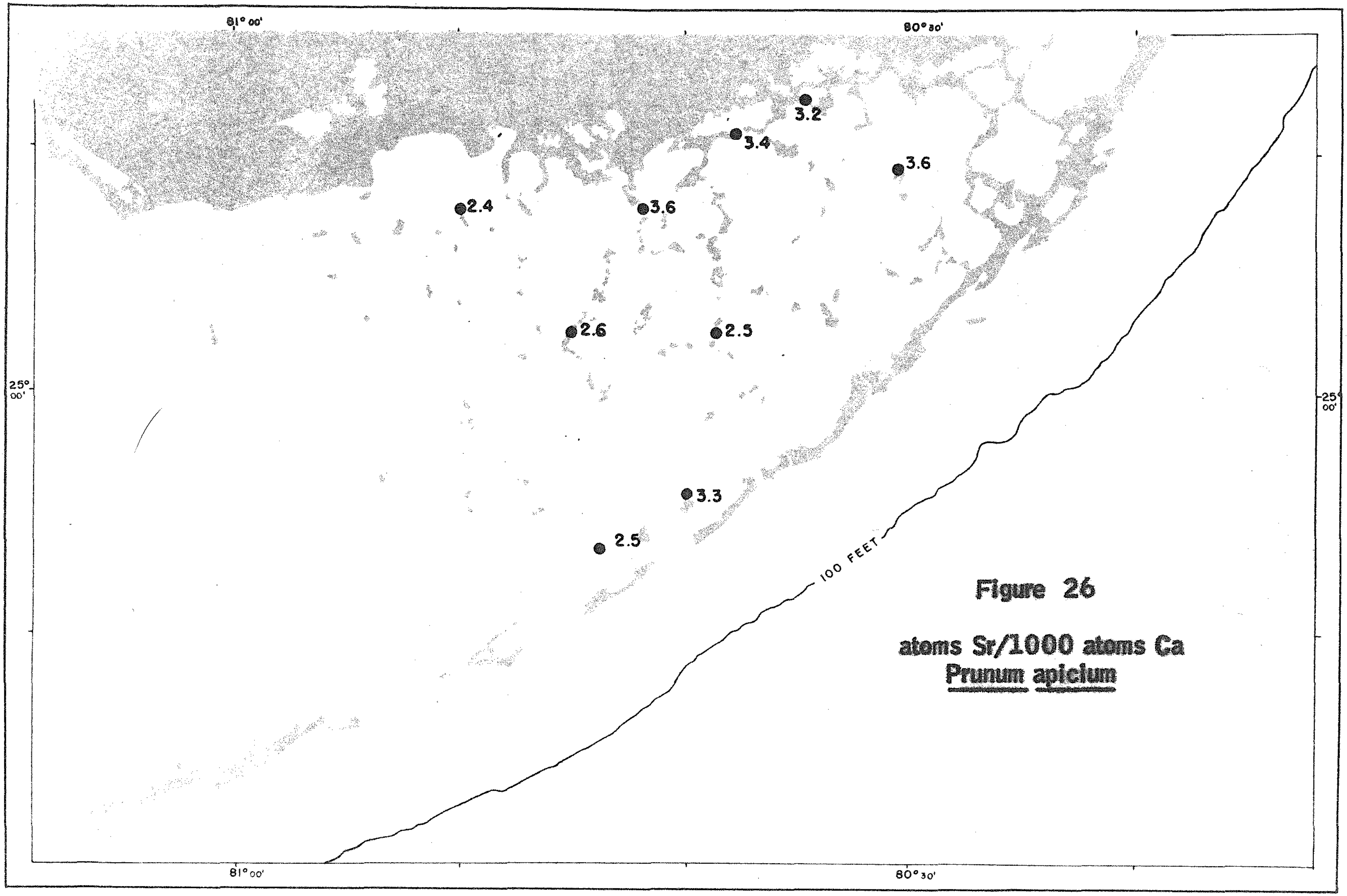


Figure 26

atoms Sr/1000 atoms Ca
<u>Prunum apicium</u>

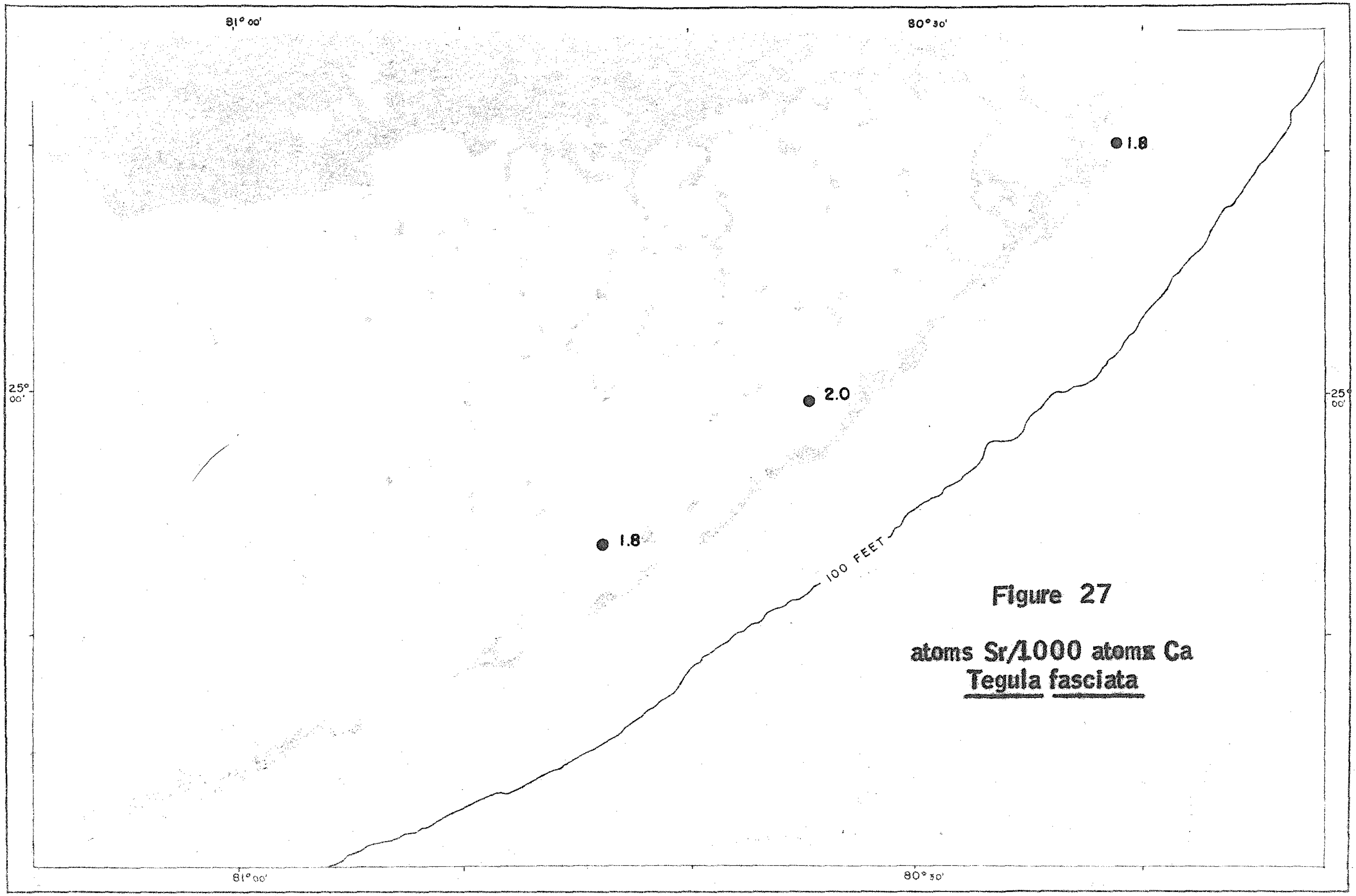


Figure 27

atoms Sr/1000 atomx Ca
Tegula fasciata

The low values are consistent with those found by other workers (5, 7). Magnesium is not easily accommodated in the aragonite lattice and all of the mollusks analyzed are 90% or more aragonite.

Strontium can replace calcium to some extent in the aragonite lattice. The mollusks yielded from 0.08 to 0.31 % strontium. With a precision of ± 10% for the analysis these differences are considered significant.

According to Odum (12) the Sr/Ca ratio of calcium carbonate shell material is proportional to the Sr/Ca ratio of the water in which the shell is grown. The proportionality factor varies from 1.2 for some coelenterates and algae to 0.16 for some serpulid worms and foraminifera.

The average strontium content of 14 aragonite mollusks studied by Odum is 2.44 atoms Sr/1000 atoms Ca. Thompson and Chow (39) found an average of 1.68 for similar material. Odum calculated proportionality factors from his data which averaged 0.27.

The data from the present study confirm, in general, the earlier work. The Sr/Ca ratio of all specimens averages 2.1 atoms Sr/1000 atoms Ca. Differences between species are large; for example, Cardita floridana and Prunum apicinum average 3.0 while Chione cancellata and Modulus modulus average 1.7 atoms Sr/1000 atoms Ca.

Large variations were also found among individuals of the same species collected from different localities. The range of variation is as follows:

Pelecypods	Range (atoms Sr/1000 atoms Ca)	Difference (atoms Sr/1000 atoms Ca)
Anomalocardia cuneimeris	1.4 -2.2	0.8
Chione cancellata	1.0 -2.3	1.3
Cardita floridana	2.7 -3.2	0.5
Brachidontes exustus	1.6 -2.8	1.2
Gastropods		
Prunum apicinum	2.4 -3.6	1.2
Modulus modulus	1.1 -2.3	1.2
Tegula fasciata	1.8 -2.0	0.2
Bulla occidentalis	1.6 -3.4	1.8

Cardita floridana and Tegula fasciata, species which are limited to the marginal ecologic zone, show much less variation than the central Bay species. This is consistent with a more constant water chemistry along the western margin of the Bay. The wide range of variation found among different specimens of the same species within Florida Bay suggests that the variations found in the Sr/Ca ratio of Florida Bay water are reflected in the Sr/Ca ratio of shell materials precipitated in the Bay. The water data showed that the major cause of variation in the Sr/Ca ratio is the large amount of calcium in fresh water which tends to dilute the strontium of the marine water. If this were the only cause of Sr/Ca ratio variations in the water one might expect to find a gradient of decreasing Sr/Ca ratio in shells which grew closer to the mainland. No such gradient is apparent in the Sr/Ca ratios of any of the species studied. The areal distributions of values are erratic (figs. 20 to 27). In some species, such as Prunum apicinum and Brachidontes exustus, the high Sr/Ca ratios are found near the mainland.

Such erratic variations can be explained in two ways: 1) the mollusks are not maintaining a constant fractionation factor between the sea water and the shell material, or 2) there are other sources of variation in the Sr/Ca ratio of the sea water.

The experiments which led Odum to suggest that the fractionation factor between sea water and shell material is constant for a given species were performed in sea water of normal salinity in which only the Sr/Ca ratio had been changed (12). The mechanism which causes the mollusk to exclude strontium is part of the total metabolic activity of the organism. Pearse and Gunter (37) cite a number of cases where the stress of hyper- or hyposalinity conditions caused the disruption of normal metabolism in aquatic organisms. The large variations in salinity measured in the Bay and the small size of the mollusks suggest that much of the life span of an individual mollusk is spent under marginal salinity conditions which could promote erratic variations in the Sr/Ca ratio of the shell.

The exclusion of strontium in shell building is a characteristic of all of the major sediment producing organisms in the Bay. Each increment of biologically precipitated calcium carbonate produced tends to enrich the water in strontium relative to calcium. In Florida Bay, in order to raise the Sr/Ca ratio of the water to 13 atoms Sr/1000 atoms Ca which would account for some of the unusually high values in the shells, it would be necessary to precipitate 200 mgms of $CaCO_3$ per liter of average Bay water. This is equivalent to 50 mgms/cm^2 or a layer 0.02 mm thick. From dated peat layers found in the mud banks and a calculation of the total volume of sediment in the Bay it appears that the net rate of accumulation of sediment cannot be slower than 0.2 mm. per year. As will be shown in a later section at least half of this sediment must have been precipitated from Bay water. At normal rates of sediment production there could be significant enrichments of the Bay water in strontium.

Any combination of the three mechanisms mentioned above could produce the large variations in the Sr/Ca ratio of shell materials and it is not surprising that the distribution of values is so erratic.

Oxygen Isotope Composition

As outlined in the introduction the oxygen isotope composition of calcium carbonate precipitated in equilibrium with sea water varies with the temperature and the H_2O^{18}/H_2O^{16} ratio of the water. Urey (43) calculated the temperature dependence using spectroscopic data. He found the ratio:

$$\frac{1/3\ CO_3^{18}/1/3CO_3^{16}}{H_2O^{18}/H_2O^{16}} = K(T)$$

to have a value of 1.0137 at 25°C and to vary with 1/T at a rate of 0.0002/°C. McCrea (45) determined the same ratio from mollusks grown at fixed temperatures in water of known isotopic composition. His data confirmed the calculations of Urey and further demonstrated that the mollusks precipitated their shells in equilibrium with the water. Epstein, et al (20) repeated McCrea's experiments over a wide range of temperatures and established an empiric temperature scale based on measured O^{18}/O^{16} ratios of CO_2 gas prepared by standard procedures (see appendix A) from calcium carbonate and water:

$$t°C = 16.5 - 4.3(\delta_c - \delta_w) + 0.14(\delta_c - \delta_w)^2$$

δ_c = O^{18}/O^{16} ratio of calcium carbonate relative to PDBI.

δ_w = O^{18}/O^{16} ratio of water relative to PDBI.

This relationship shows that a difference of 1‰ in the δ values is equivalent to a temperature difference of about 5°C.

Recently a number of papers have appeared which stress the influence of the H_2O^{18}/H_2O^{16} ratio on water-carbonate systems as a means of studying equilibrium processes in geological materials. The work of Lowenstam and Epstein (22) is particularly applicable to the work presented here. They found an increase in δO^{18} with increasing salinity in water samples collected from a high salinity wedge west of Andros Island on the Great Bahama Bank (see fig. 19). Applying the δO^{18} water correction to the δO^{18} of calcium carbonate precipitated on the Bank they were able to distinguish between equilibrium and non-equilibrium sediment producers and thus draw conclusions on the origin of the Bank sediments. Without the corrections their data on carbonates showed a distinct increase in δO^{18} in the areas of high salinity.

For the present study selected mollusks from Florida Bay and the reef tract were analyzed for oxygen isotope composition. The technique is described in Appendix A. The precision of analysis is ± 0.1‰. The results are listed in table IV, Appendix B and the areal distribution of values for each species is shown in figs. 28 to 35.

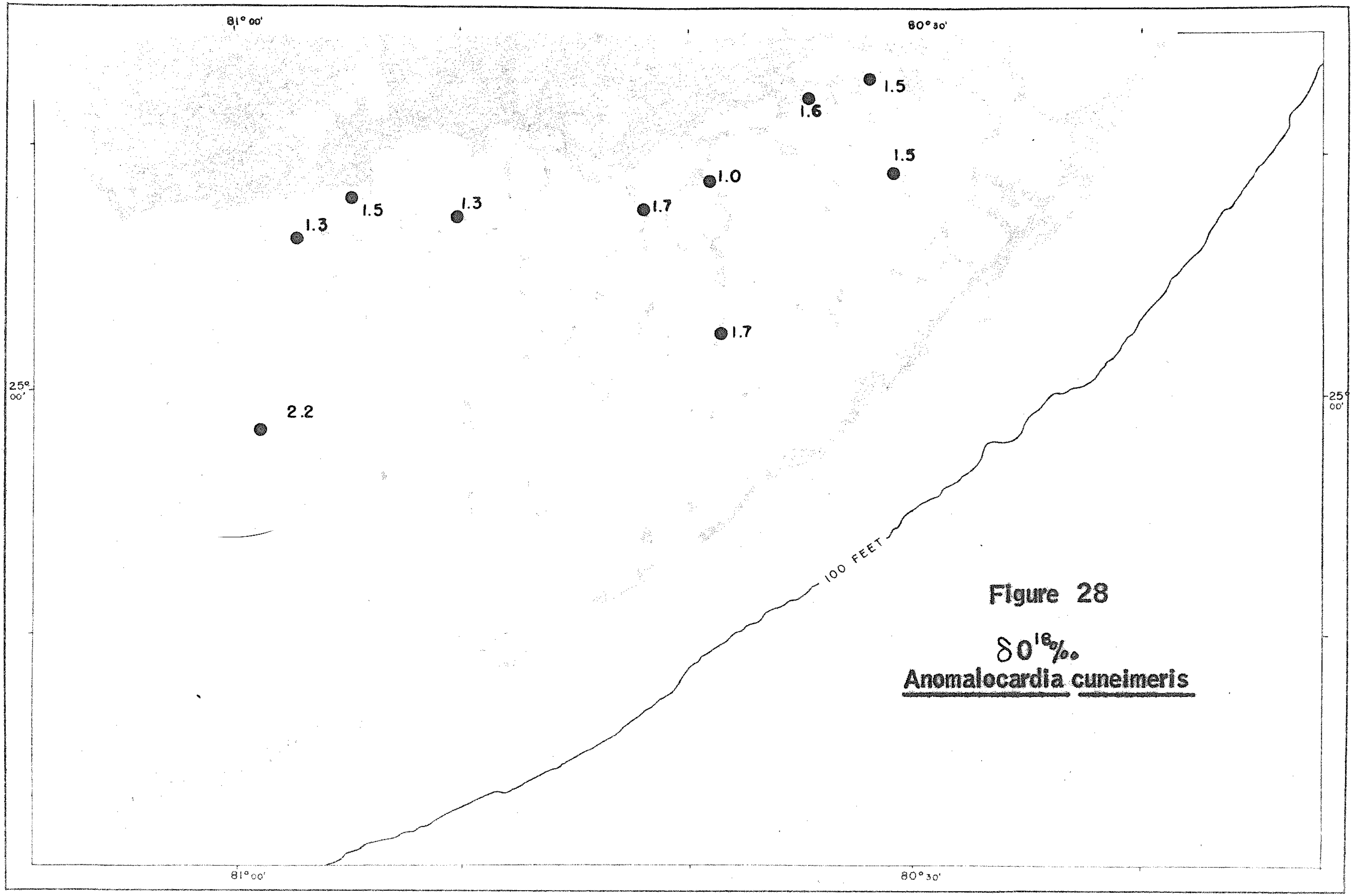


Figure 28

δO^{18}‰

Anomalocardia cuneimeris

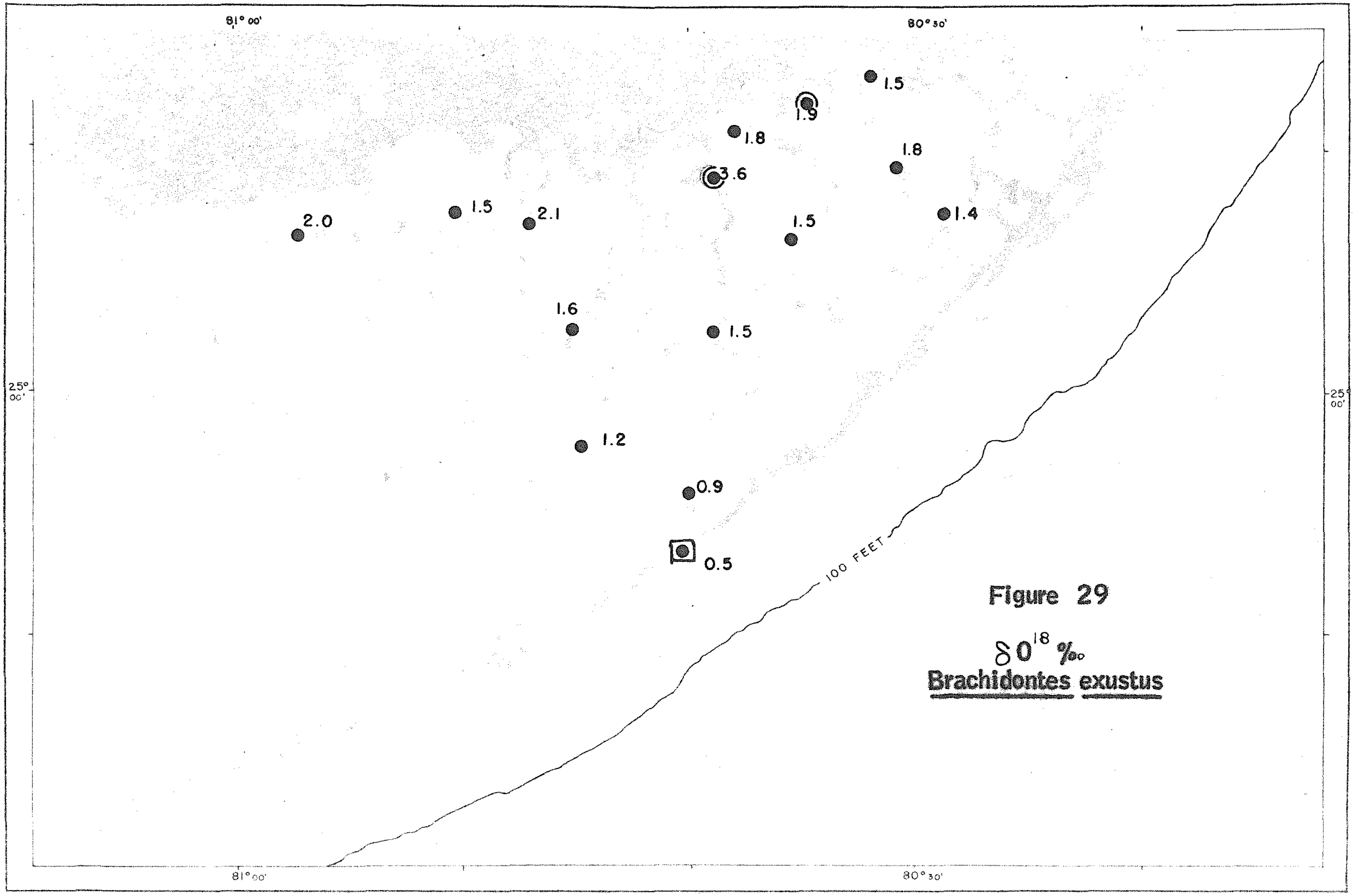


Figure 29

δO^{18} ‰

Brachidontes exustus

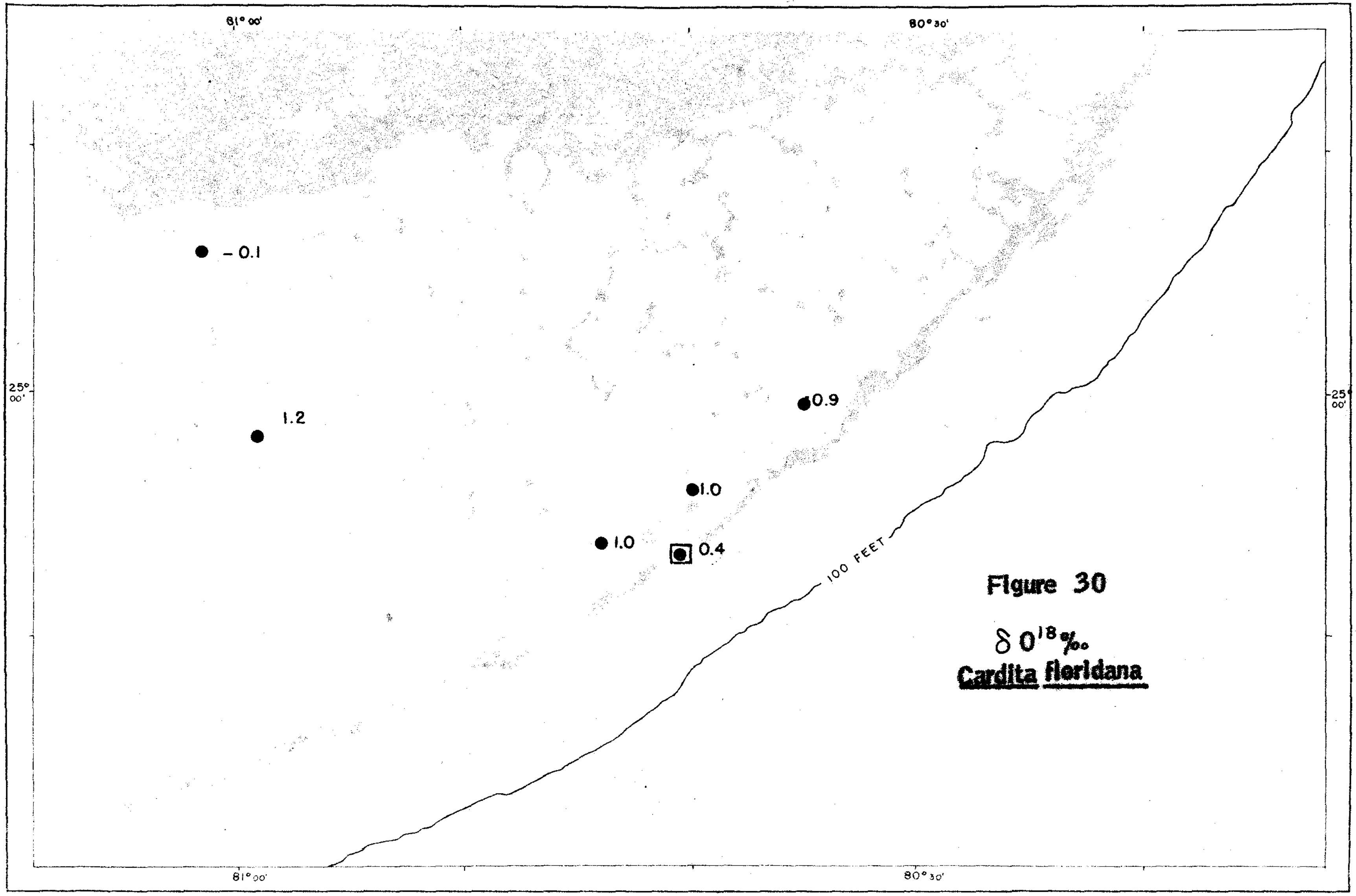


Figure 30

δO^{18}‰

Cardita floridana

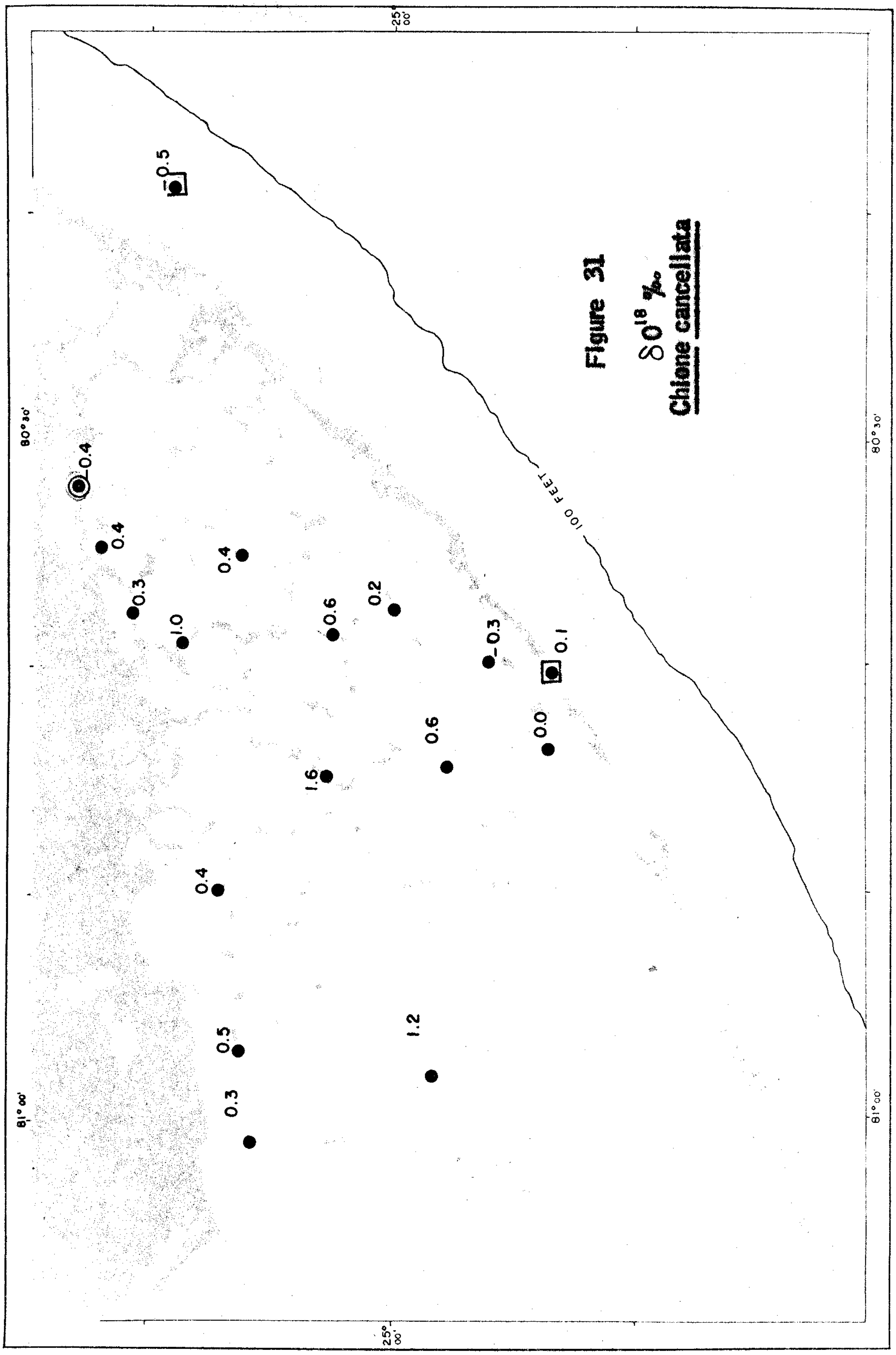


Figure 31
δO^{18} ‰
Chione cancellata

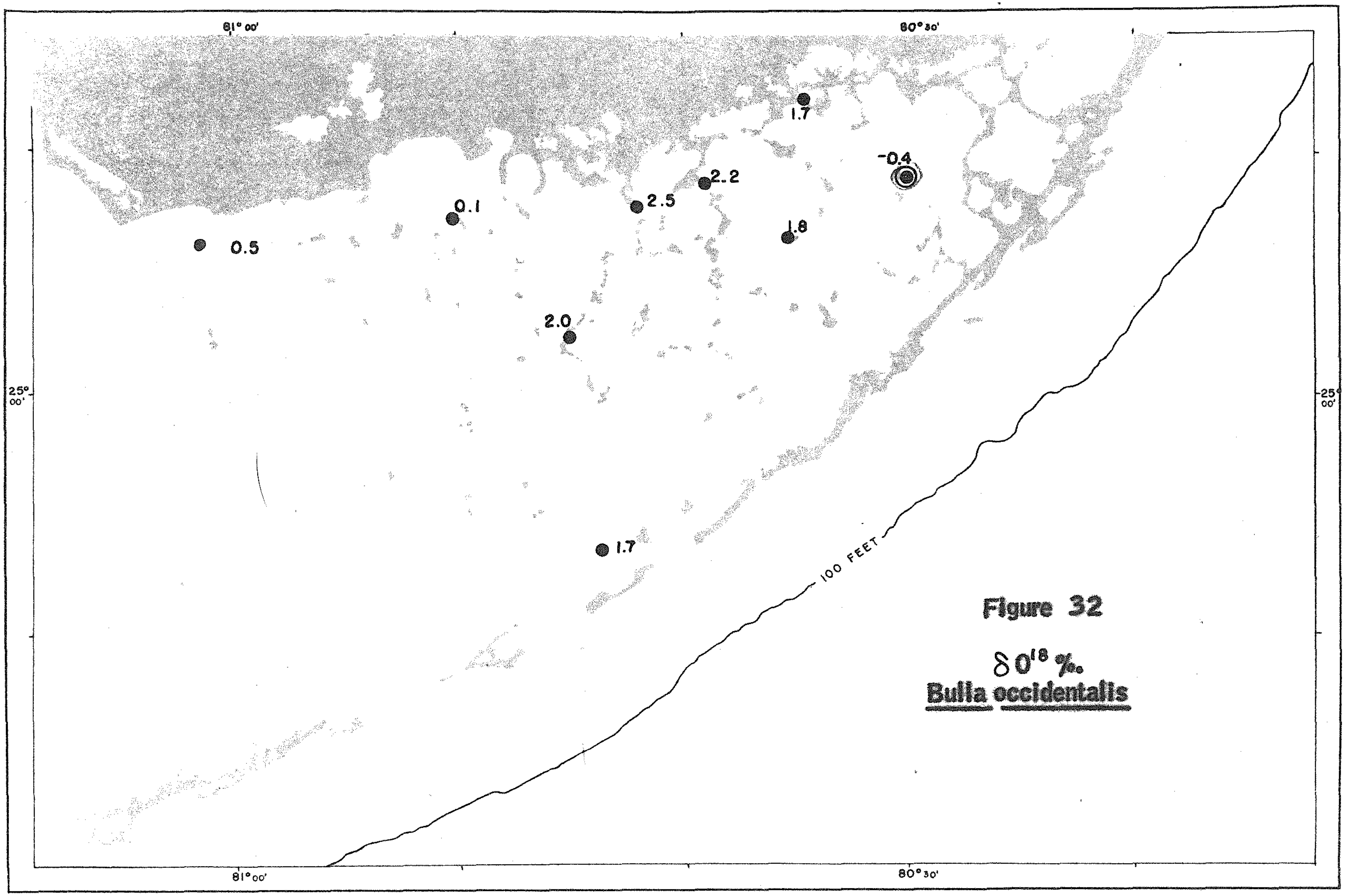


Figure 32

δO^{18} ‰

<u>Bulla occidentalis</u>

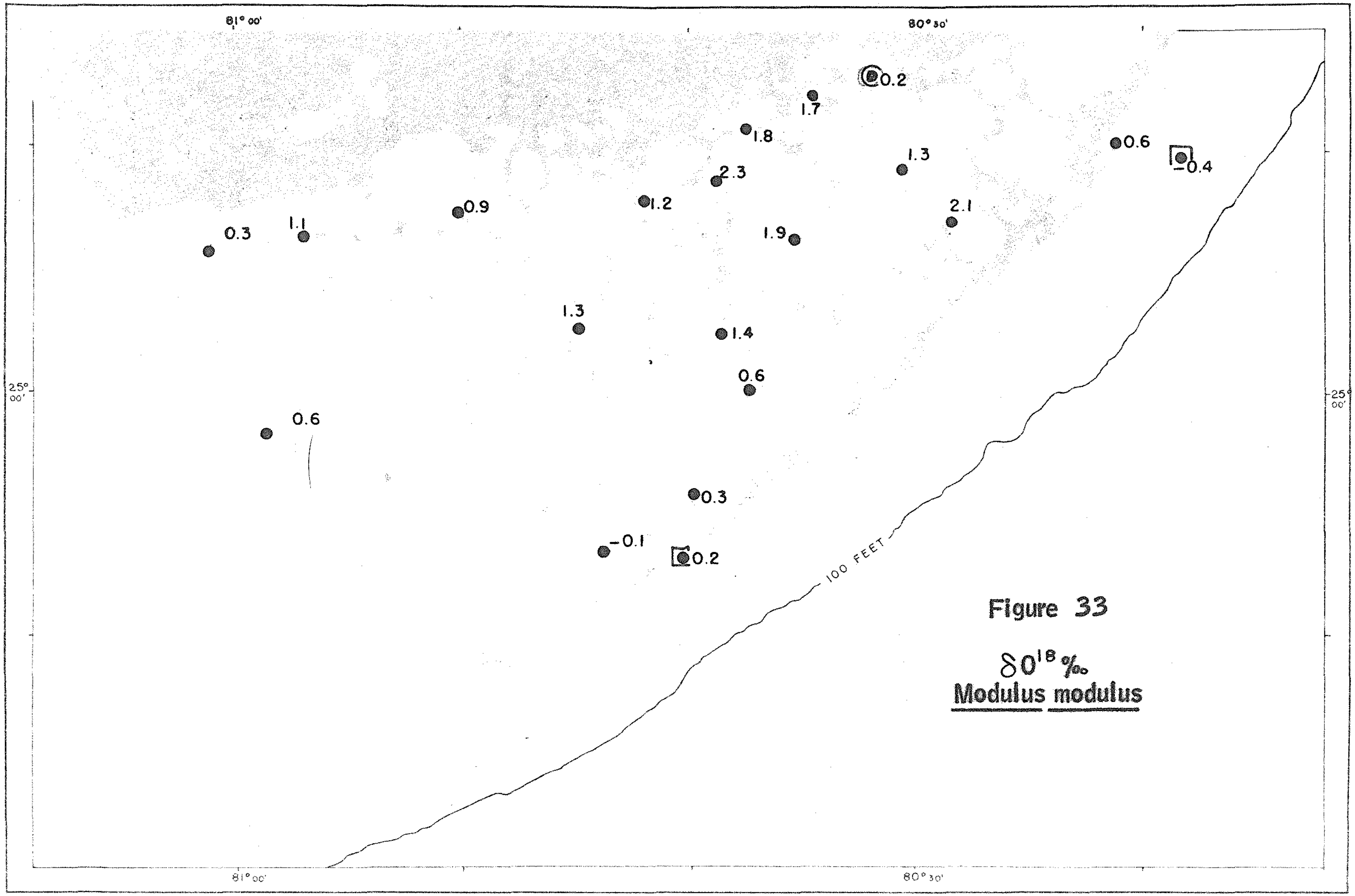


Figure 33

δO^{18} ‰
Modulus modulus

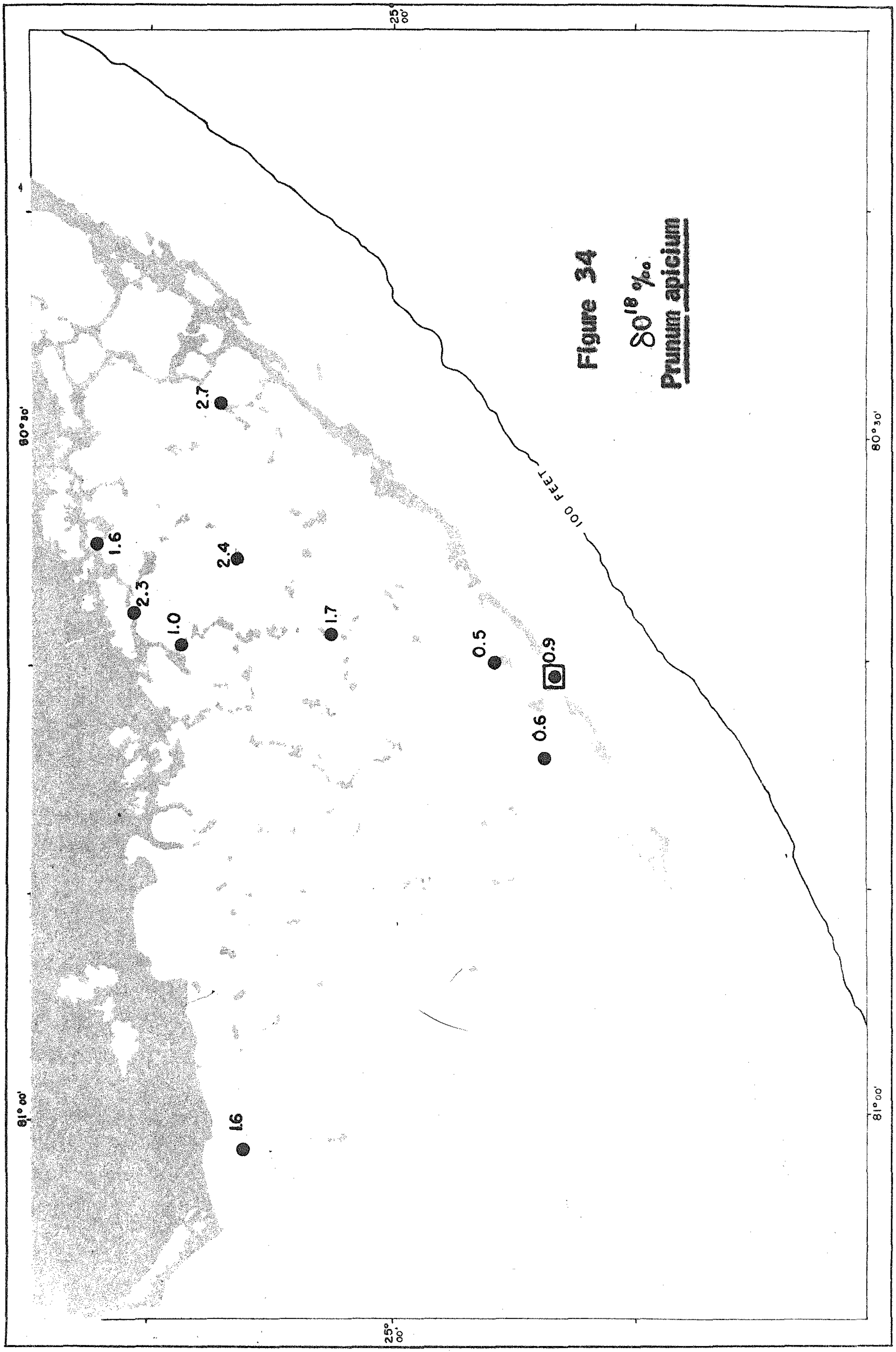


Figure 34

δO^{18} ‰

Prunum apicium

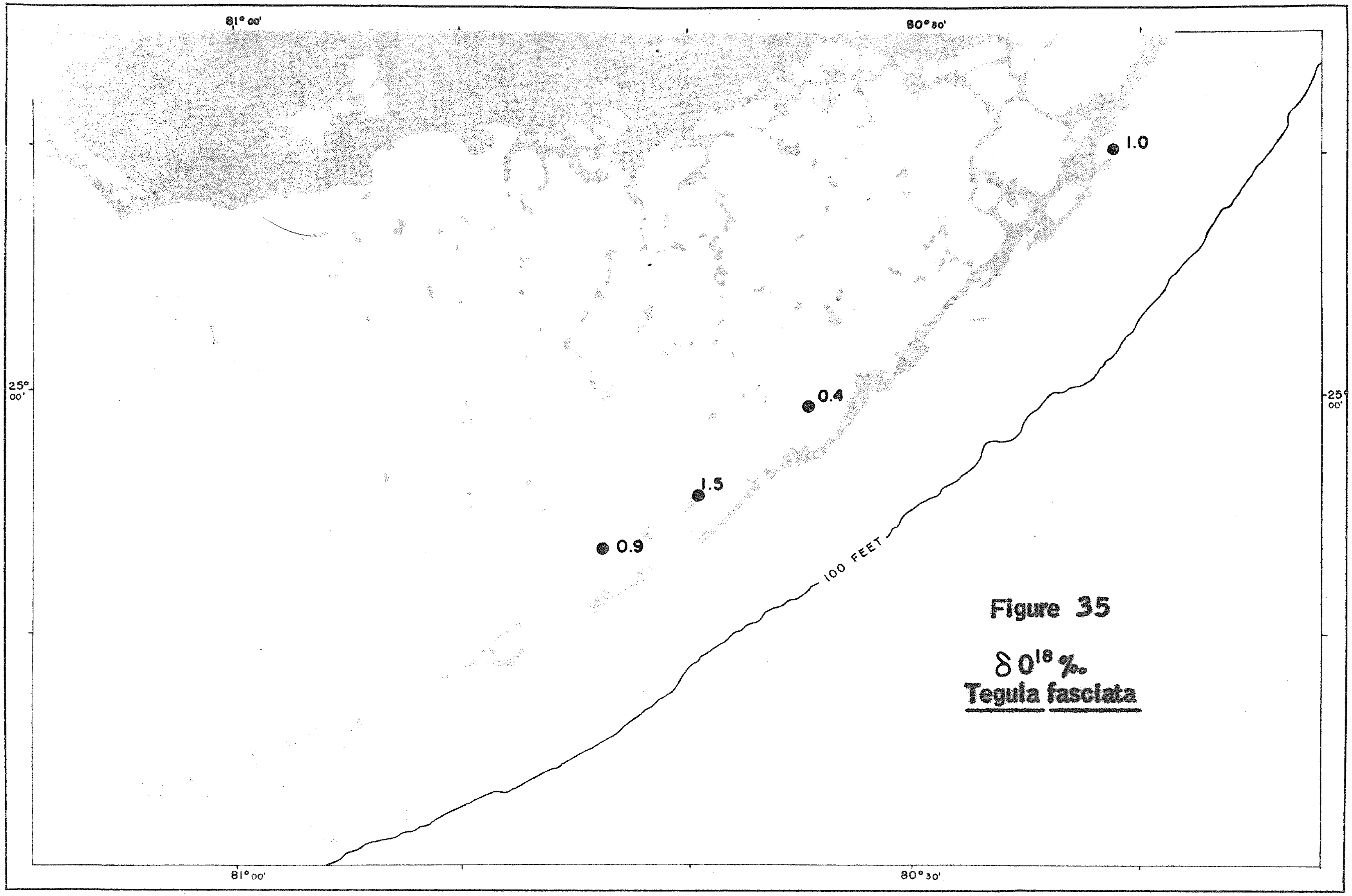


Figure 35

δO^{18} ‰

Tegula fasciata

A gradient of increasing δO^{18} going into the Bay can be seen in three of the four species that are distributed over the entire Bay - Chione cancellata, Modulus modulus, and Brachidontes exustus. The fourth species, Prunum apicinum, shows a sharp contrast between specimens from the northern and those from the southern margin of the Bay.

Tegula fasciata and Cardita floridana, species limited to the southern and western margins of the Bay, show less variation and tend to group around a value of 1.0‰.

Anomalocardia cuneimeris from the northern Bay shows little variation around a value of 1.5‰.

Species that are found both along the reef tract and in the Bay exhibit much higher δO^{18} values in the Bay.

The contrast between Florida Bay and reef tract ratios and the pattern of areal gradients within Florida Bay correlate very well with the distribution of δO^{18} values for the water samples collected in August, 1958. However, the fact that the patterns appear in the analyses of randomly selected shells suggests that this distribution of oxygen isotopes in the water is a persistent feature of the area. Temperature variations alone could not have produced the pattern. It would require a persistent temperature gradient of the order of 8°C between the northern and southern margins of the Bay to account for the δO^{18} values of a species such as Modulus modulus. The average yearly temperature gradient along the entire length of the west coast of Florida is less than 5°C.

Though temperature variations could not have produced the pattern of δO^{18} variations, temperature is still a factor in determining the isotopic composition of a given specimen and it is necessary to understand something of the contribution temperature to the δO^{18} values before they can be examined in detail. Only a few specimens were collected in areas along the reef tract which could be considered free from radical variations in water composition. Mean growth temperatures calculated for Modulus modulus and Chione cancellata collected at 1062 using a δ for water of 1.0 are 23.3°C and 22.8°C respectively. The values are about 2°C below the mean water temperature indicating the major part of the shell was grown in the winter. These were small specimens and probably do not represent the true growth temperature ranges for the species.

Calculations of mean growth temperatures for specimens collected in and around the Bay would require assumptions about the δO^{18} of the water during growth. Considering the wide range of values found in the few water samples analyzed such assumptions would be difficult to justify. An attempt was made to estimate the temperature influence by use of the plots shown in figs. 36 to 39. The plots are a graphical averaging of the carbonate and water data presented in terms of possible growth temperature ranges. The construction of the plots was as follows: The isotopic temperature equation was solved for three temperatures; 20°C, 25°C, and 30°C, yielding values for $\delta_c - \delta_w$. A plot was made of δ_c vs. δ_w for each of these temperatures. The carbonate and water data were

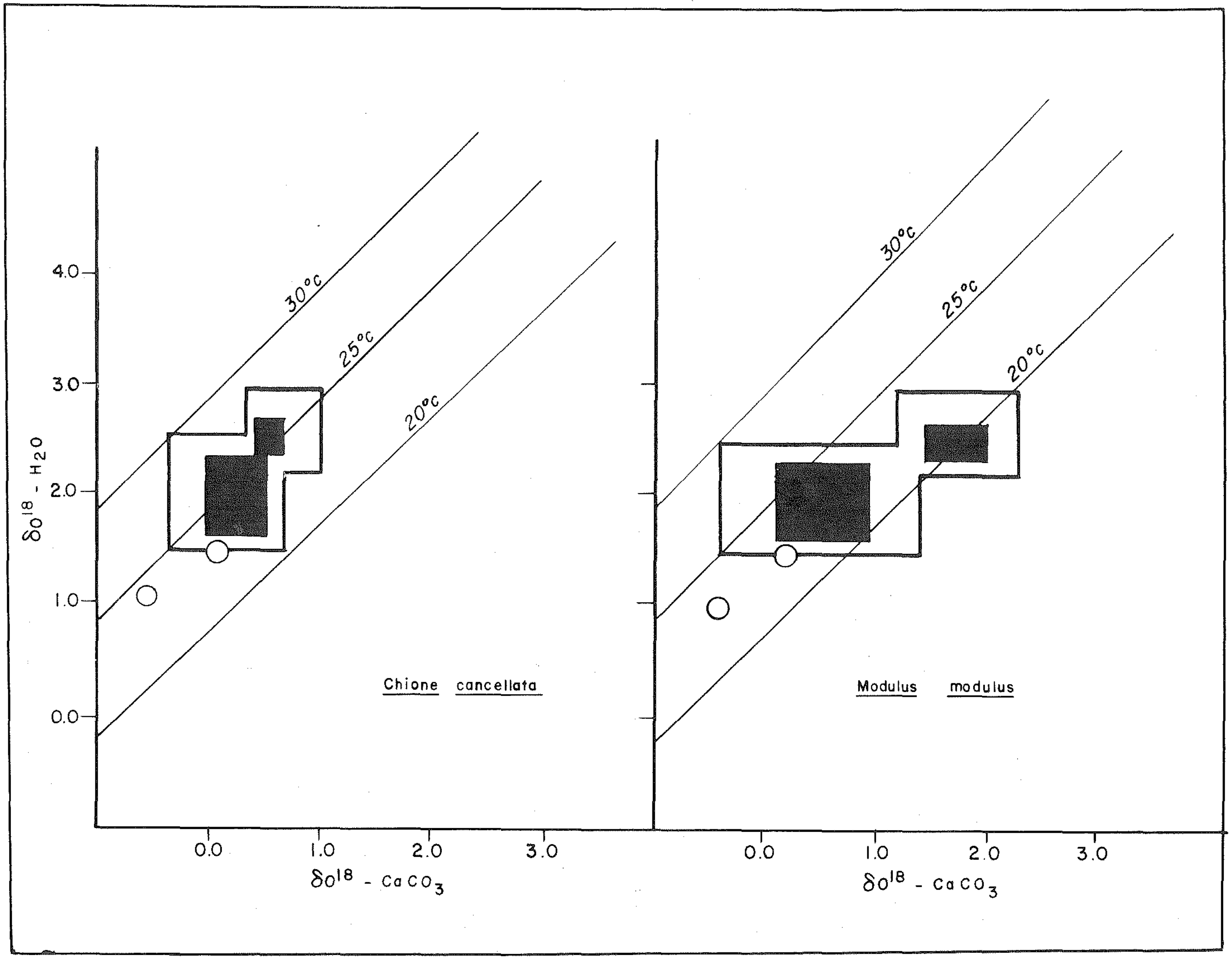


Figure 36. - Apparent isotopic temperature growth ranges of mollusks

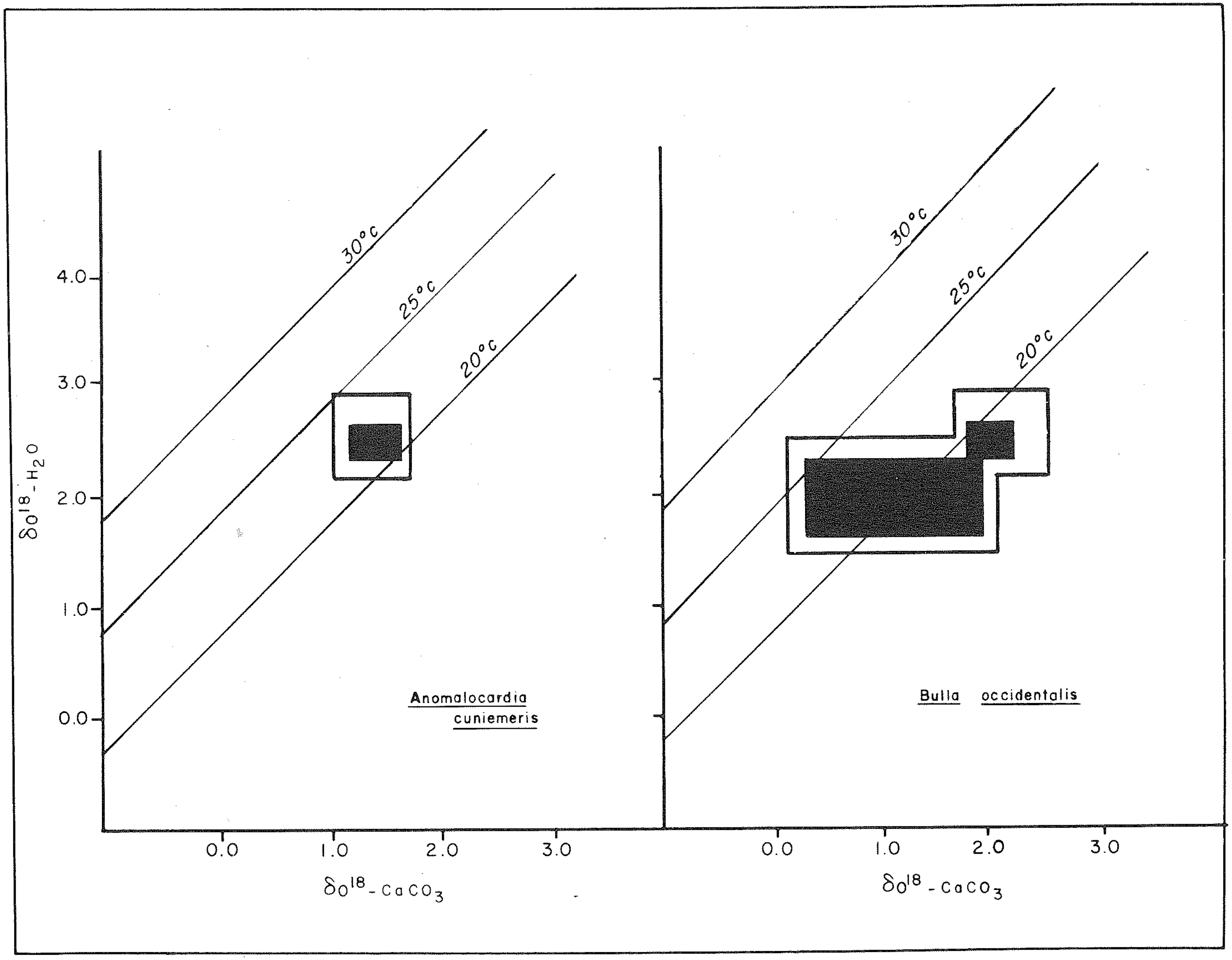


Figure 37. - Apparent isotopic temperature growth ranges of mollusks

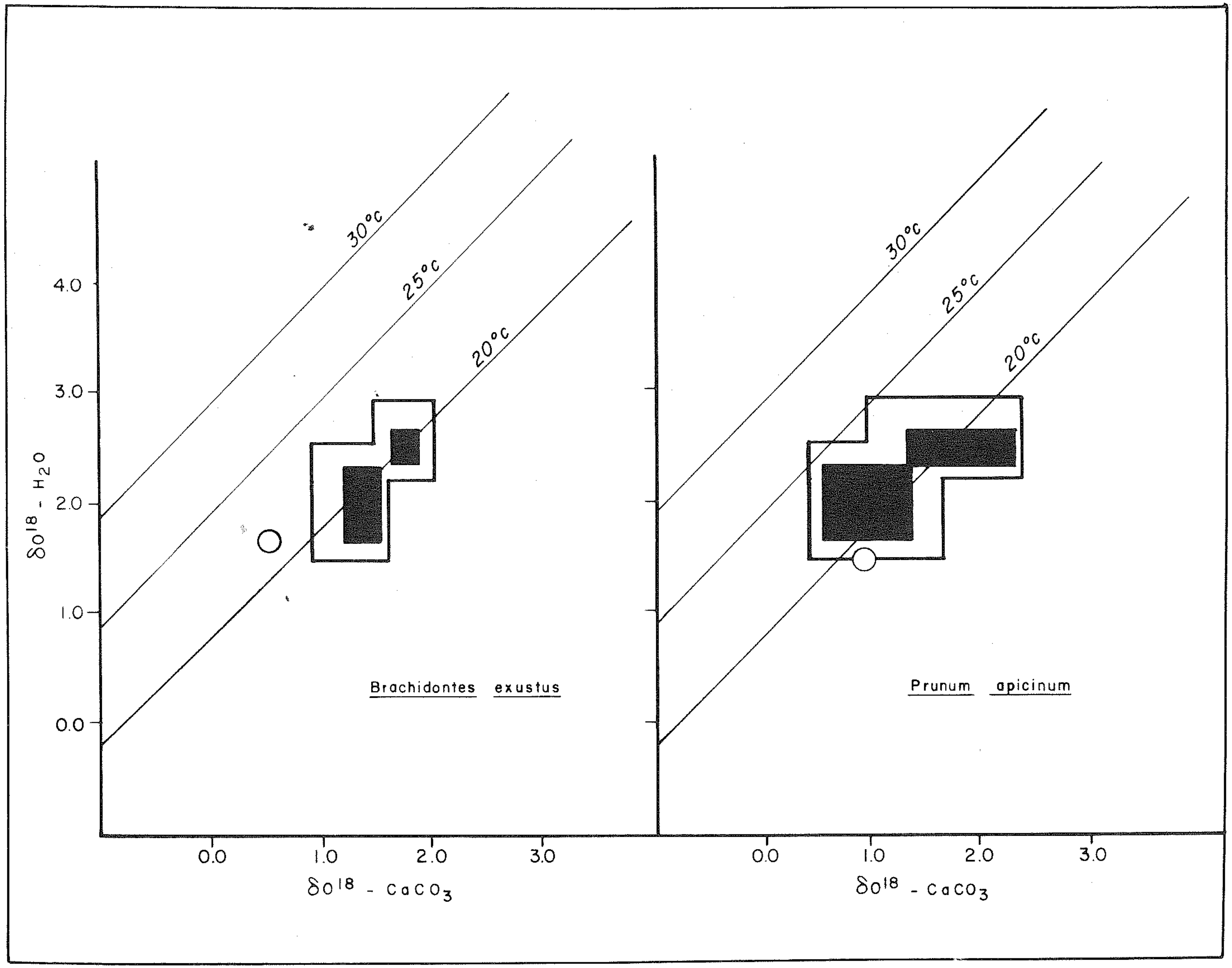


Figure 38. - Apparent isotopic temperature growth ranges of mollusks

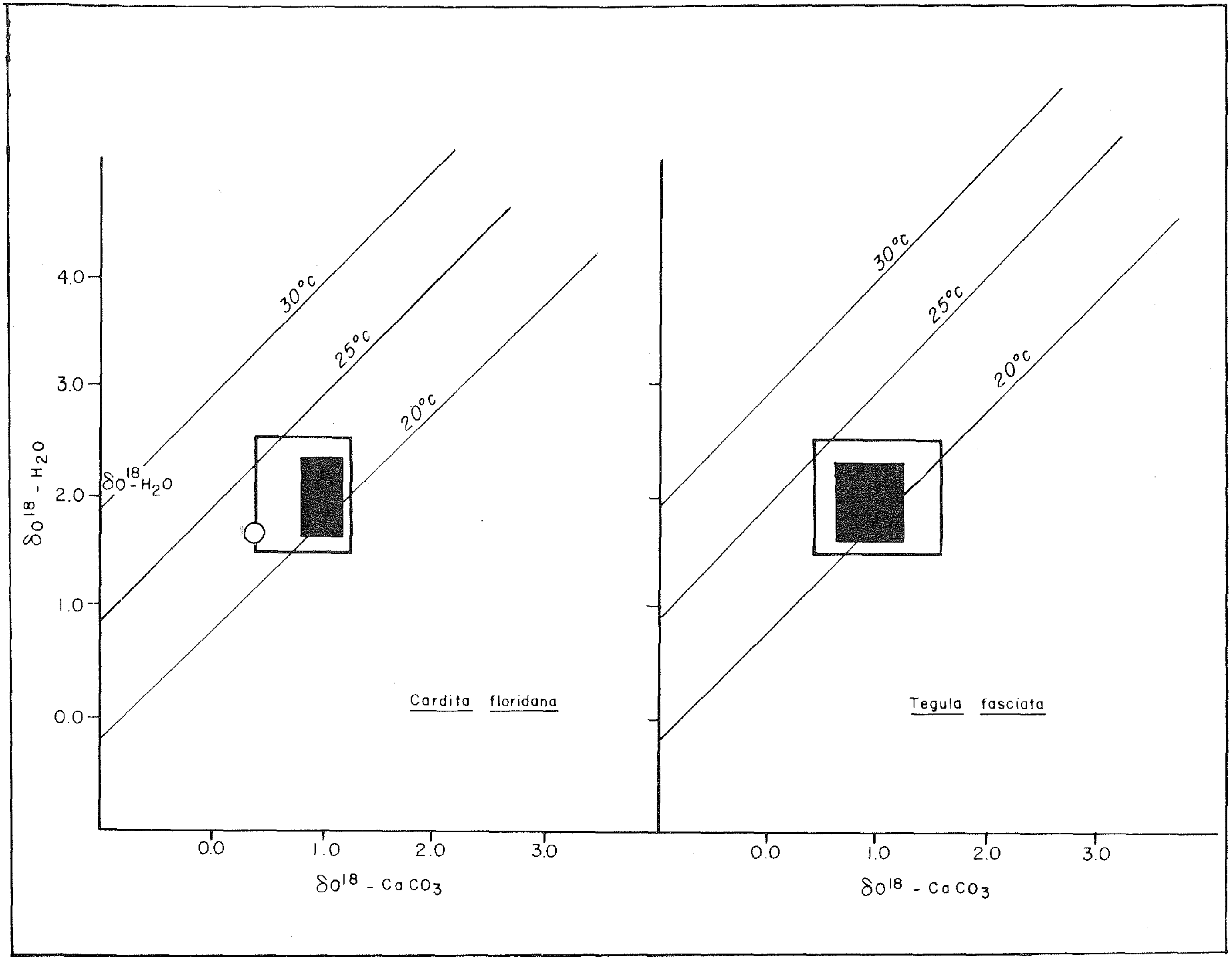


Figure 39. - Apparent isotopic temperature growth ranges of mollusks

divided into two geographic groups, separated by the line drawn in fig. 16. The line was selected on the basis of the water data for August, 1958 and represents the limit of mixing of Bay water with reef tract and Gulf water at that time. For each species, two blocks were constructed representing the two groups of samples. The height of a block represents the range of δO^{18} for all waters in that geographic group while the width of a block represents the range of δO^{18} values for the carbonate samples from that group. Shell samples which showed very obvious discrepancies or reversals in trend were not plotted. These samples are circled in figs. 28 to 35. Any temperature line that passes through a large block is a possible mean growth temperature for that species in water of the composition analyzed. The small solid blocks represent the average deviation from the mean of the water and carbonate values. The large circles are individual points from carbonate samples believed to be least influenced by extreme variations in water chemistry. These samples are squared in figs. 28 to 35.

Because of the limited sampling of water available it would be misleading to interpret mean growth temperatures from these plots. However, they do provide a rough temperature framework from which the carbonate values can be viewed.

Chione cancellata is the only species which exhibits an apparent mean growth temperature near the mean temperature of Florida Bay water (25°C). Modulus modulus, Cardita floridana, Tegula fasciata, and Anomalocardia cuneimeris show apparent temperatures which are significantly below the mean. Bulla occidentalis, Prunum apicinum, and Brachidontes exustus have apparent mean growth temperatures around 20°C - a temperature which obtains only during one or two months of the year in Florida Bay. It must be concluded that either the majority of the species analyzed add significant amounts of shell material only during a few cold months of the year or that the δO^{18} composition of Florida Bay water is generally somewhat higher than the values measured in 1958-1959.

Lowenstam and Epstein (10) determined the isotopic composition of a large number of molluscan species from Bermuda and found that some forms add shell during most of the year and record the mean temperature of the water while other forms are limited by a low temperature growth threshold and record only the higher water temperatures. None of their species appeared limited by a high temperature threshold. Bulla occidentalis, Prunum apicinum, and Brachidontes exustus have all been reported from tropical localities where water temperatures never fall below 23°C. (60, 61). It appears that the Florida Bay species are not limited by temperature thresholds but are only reflecting a generally higher δO^{18} composition of the water than was measured in 1958-1959.

The fact that there are consistent differences between different species from the same localities indicates that there are ecological factors other than water chemistry which tend to bias the record left in the isotopic composition of the shell. Chione cancellata, for instance, has consistently lower δ values than any of the other species analyzed. This could mean that it is limited by a low temperature growth threshold and that the apparent agreement with the mean temperature of the Bay water is only another reflection of the incomplete sampling of the water.

Temperature and water chemistry are just two of many possible limiting factors which make up the ecological niche of a species. Food supply, larval ecology, and type of bottom are other important ecological parameters which could relate indirectly to those factors of climate and geography that exert the primary control on the isotopic composition of the water. Anomalocardia cuneimeris, for instance, occurs in extremely large numbers of small specimens in a narrow band along the mainland coast. Ladd, et al (34) have reported what appeared to be "blooms" of this species in Bays along the Texas coast. Such occurrences suggest some sort of ecological trigger mechanism which permits the rapid reproduction of large numbers of short-lived individuals. The small range of δ values for the species suggests that the ecological limits as far as temperature and water chemistry are concerned are also narrowly defined.

A number of specimens have δO^{18} values which appear out of place in the areal gradient patterns. Some are exceptionally high such as Modulus modulus at 1021 ($\delta = 2.3$) and Brachidontes exustus at 1021 ($\delta = 3.6$). These must represent periods of exceptionally high δO^{18} of the water. In order to deposit shell with these high values in even the heaviest water of the 1958-1959 collection ($\delta = 2.9$) it would be necessary to have mean growth temperatures of 18°C and 13°C respectively.

If a mean growth temperature of 23°C is assumed for both species then the δO^{18} values of the water would be 3.3 and 4.5‰ respectively. Water enriched to this degree has been measured in a sample having a salinity of about 47‰ (see fig. 19) and in the heavy brackish swamp waters measured by Epstein and Mayada.

Shells with δ values which appear to be low when compared to surrounding samples are Chione cancellata and Modulus modulus at 1053 and Bulla occidentalis at 1018. The δ values for these specimens are -0.4, 0.2 and -0.4 respectively. If calculated back from a mean temperature of 23°C, the δ values of the water would be 0.8, 1.4 and 0.8‰ ; a mean temperature of 25°C would indicate water of 1.2, 1.8 and 1.2‰ composition.

The lowest measured δO^{18} for water in the northern part of the Bay was 2.2‰ . A radical lowering of the δ values in this part of the Bay could only occur by almost complete replacement of the water with water having a δO^{18} value near open sea water or by partial dilution of the Bay water with very light rain water. The first case might occur during a hurricane when high tides breech the low lying Keys. The second case would be unlikely to occur during locally produced showers which yield fairly heavy water but might occur with rain from a cold front which could contribute considerably lighter water.

An interesting local anomaly is at location 7447 along the west-central margin of the Bay. The specimens were furnished by the Shell Oil Co. Immediately to the west of this location (see fig. 2) is the open Gulf of Mexico. The station itself is on an isolated mud bank surrounded by deeper water. The four species analyzed all yielded δO^{18} values characteristic of the Bay interior and much heavier than similar open circulation localities to the north and south. A sample of water collected at 1078 in August, 1959 about 5 miles to the south in the open Gulf had a δO^{18} of 1.4 and a salinity of 35.5‰ normal values for the location. Clearly some local effect must be operative but lack of detailed information on the location precludes interpretation.

In summary, the large variations in the δO^{18} composition of Florida Bay and reef tract waters are reflected in similar variations in the δO^{18} composition of mollusks shells which grow there. The enriched Florida Bay waters cause consistently high δO^{18} ratios in Bay mollusks as compared to the same species living along the reef tract. The gradient of increasing δO^{18} toward the mainland found in Florida Bay water samples can also be seen in shells of molluscan species which are distributed over the entire Bay. In detail the influences of temperature and water chemistry are difficult to separate but the limitations of temperature growth ranges and the absence of temperature contrasts and gradients over the area at any given time suggest that isotopic variations in the water are the major cause of variations in the shells.

Carbon Isotope Composition

An analysis of the C^{13}/C^{12} ratio was made on each of the gas samples prepared for O^{18}/O^{16} analysis. Carbon isotope analyses were also made on some dilute acid insoluble residues of the fine-grained sediment and on pieces of red and black mangrove. The combustion technique for obtaining CO_2 from the organic materials is described in appendix A. The results of the carbon analyses are given in table III, appendix B and the areal distribution of values for the carbonate carbon of each species of mollusk are presented in figs. 41 to 48.

The distribution of carbon isotopes in nature has attracted the interest of many investigators. A summary of the results of some of this work, along with the present results, is shown in fig. 40. The carbon isotope compositions of natural materials fall roughly into three groups: a low group consisting of terrestrial plants and petroleum, a high group consisting of carbon fixed in calcium carbonate and bicarbonate ions in the sea, and an intermediate group consisting of carbon found in marine organisms, organic residues of marine sediments and atmospheric CO_2. Not represented in the diagram are values for carbon associated with igneous and metamorphic processes.

Each of the materials listed has at some time exchanged directly or indirectly with atmospheric CO_2. The wide range of values (40‰ or 4.0%) reflects the large fractionation factors associated with the exchange mechanisms during fixation of the carbon.

The low values for terrestrial plant material result from a net fractionation in the process $CO_2 \longrightarrow$ carbohydrate. Whether it represents a physical sorting of CO_2 molecules during diffusion or fractionation during biochemical synthesis or both is not clear. The problem is discussed in detail by Craig (46). The extremely low values for petroleum are believed to result, in part, from the low C^{13} values

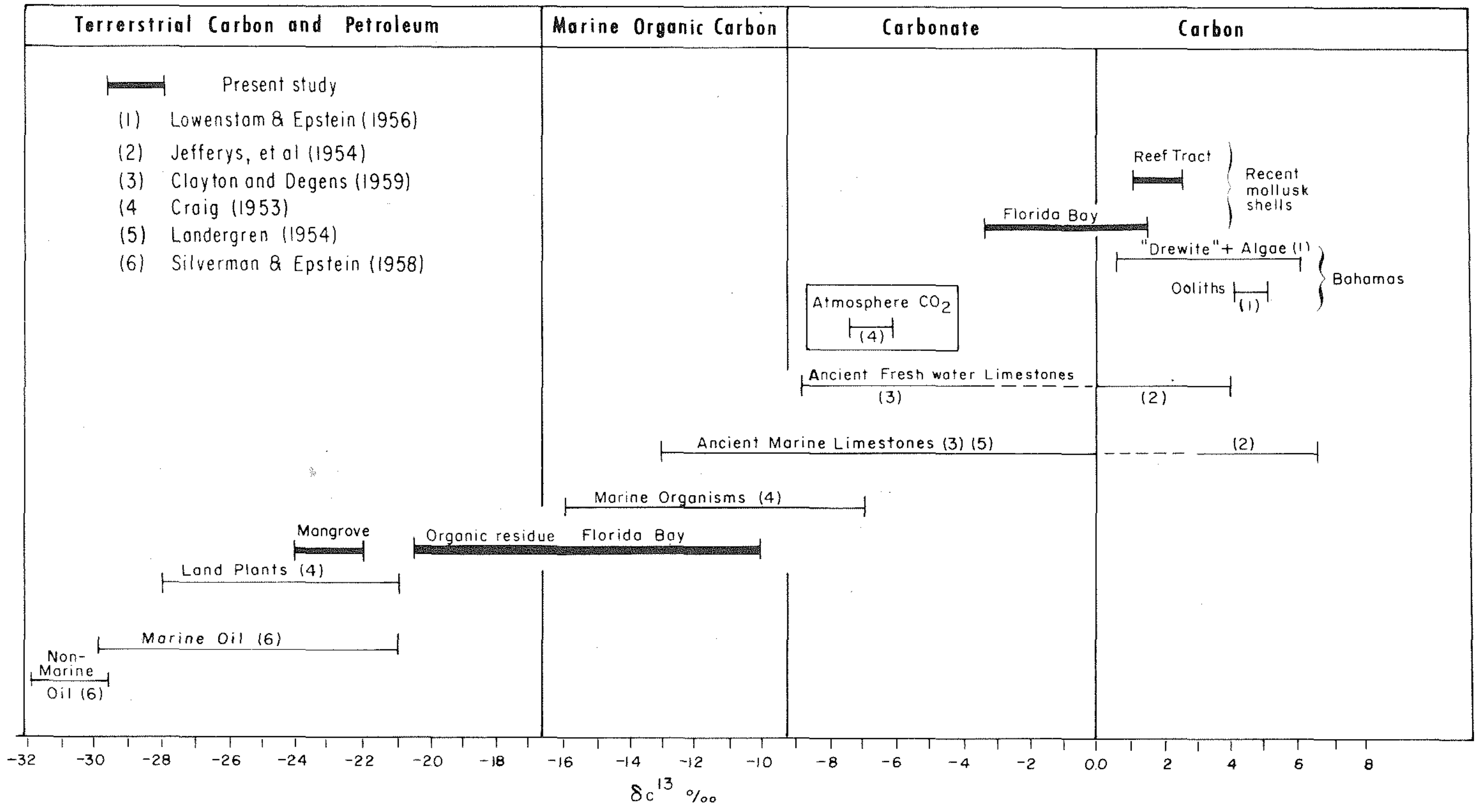


Figure 40 - Distribution of carbon isotopes in nature

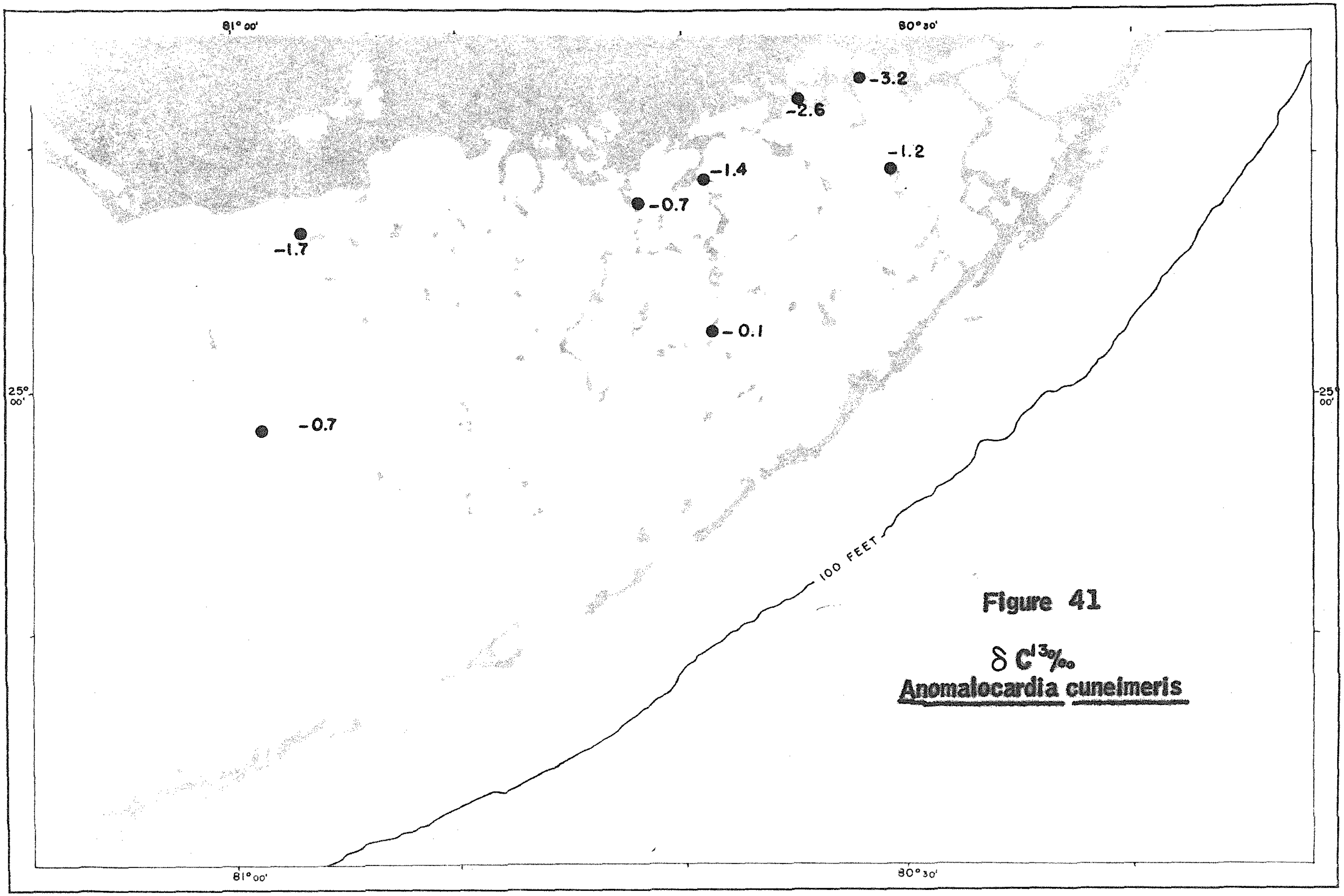


Figure 41

δC^{13}‰

<u>Anomalocardia cuneimeris</u>

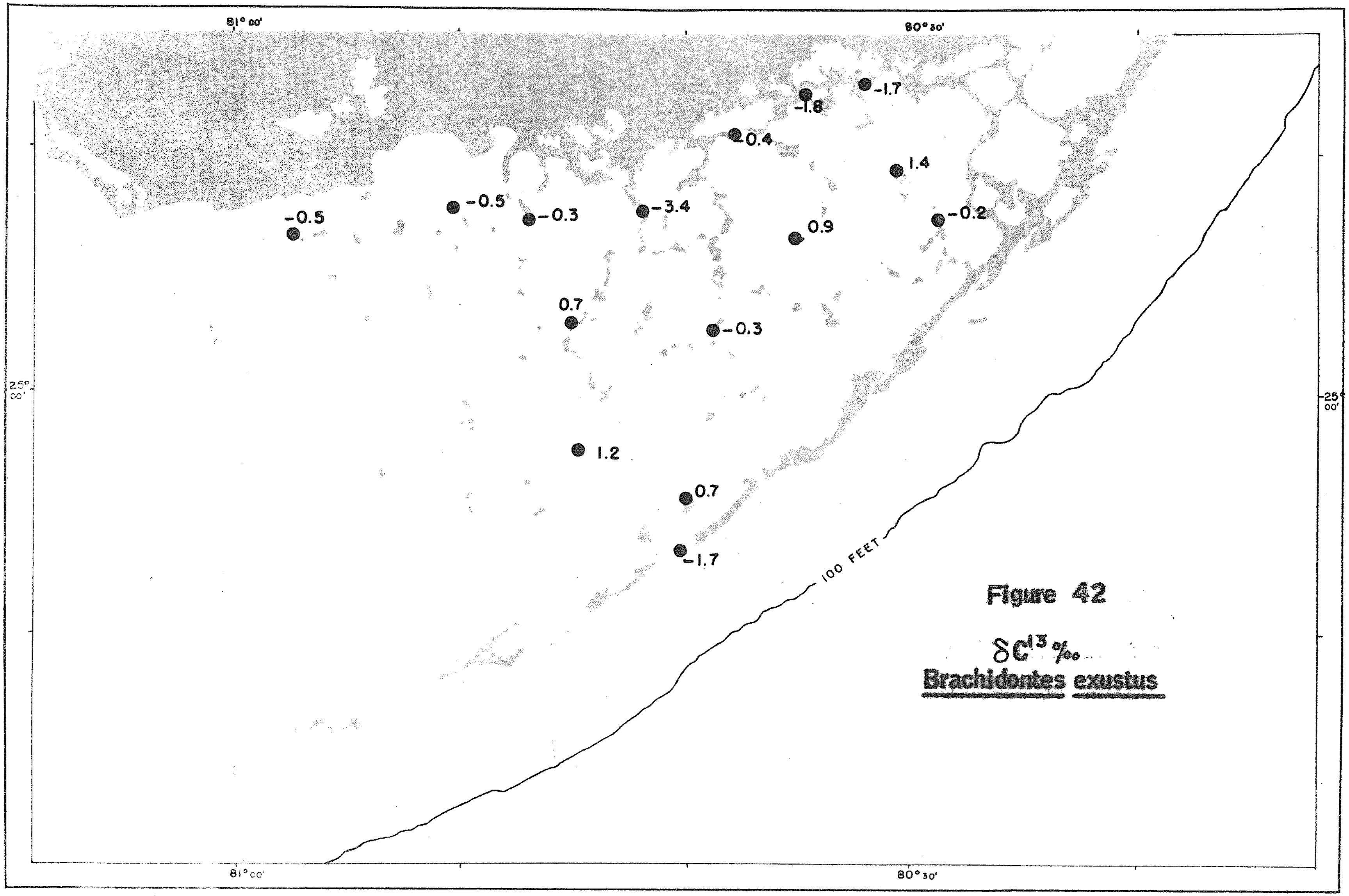


Figure 42

δC^{13} ‰

Brachidontes exustus

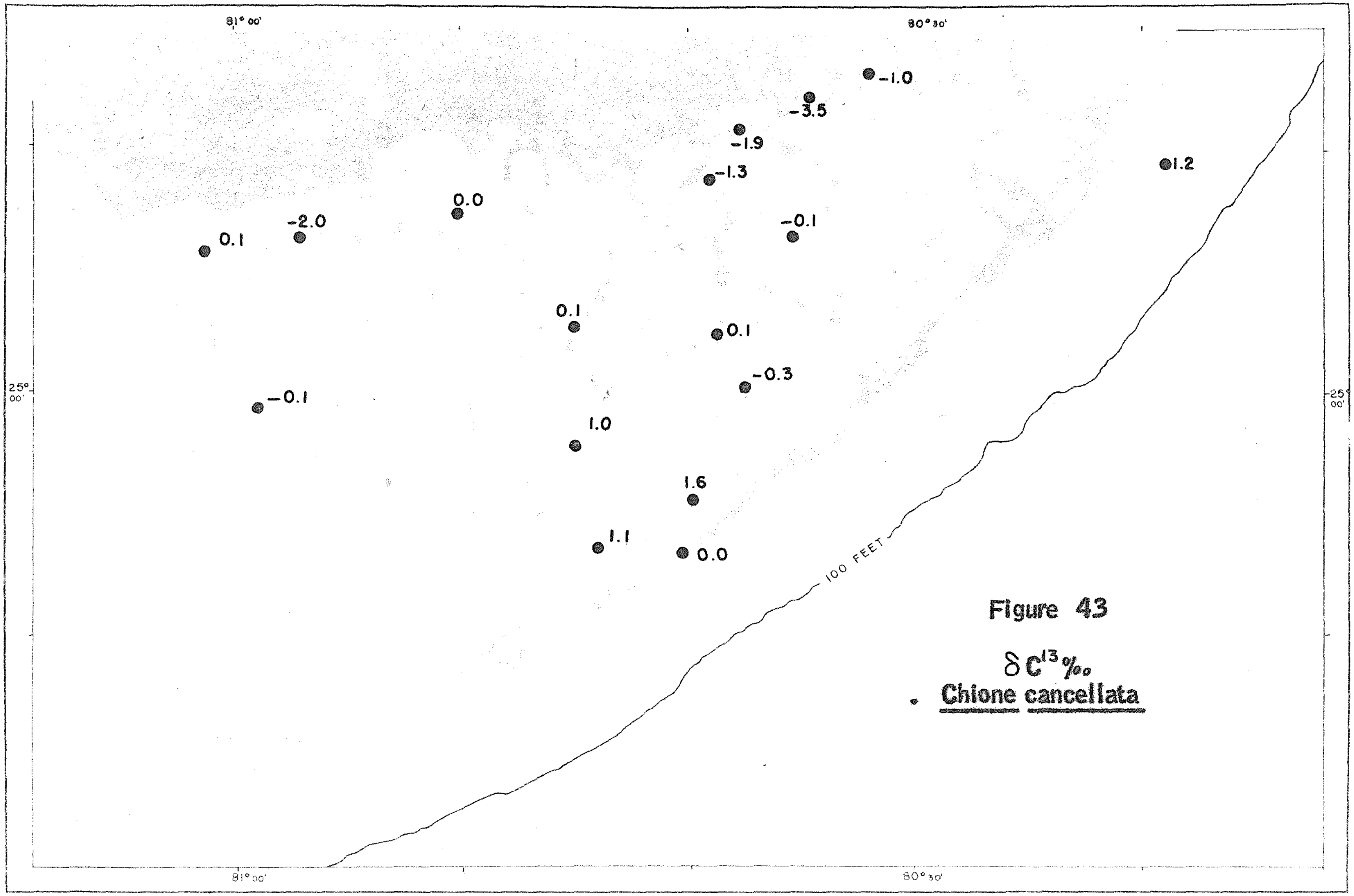


Figure 43

δC^{13}‰

• <u>Chione cancellata</u>

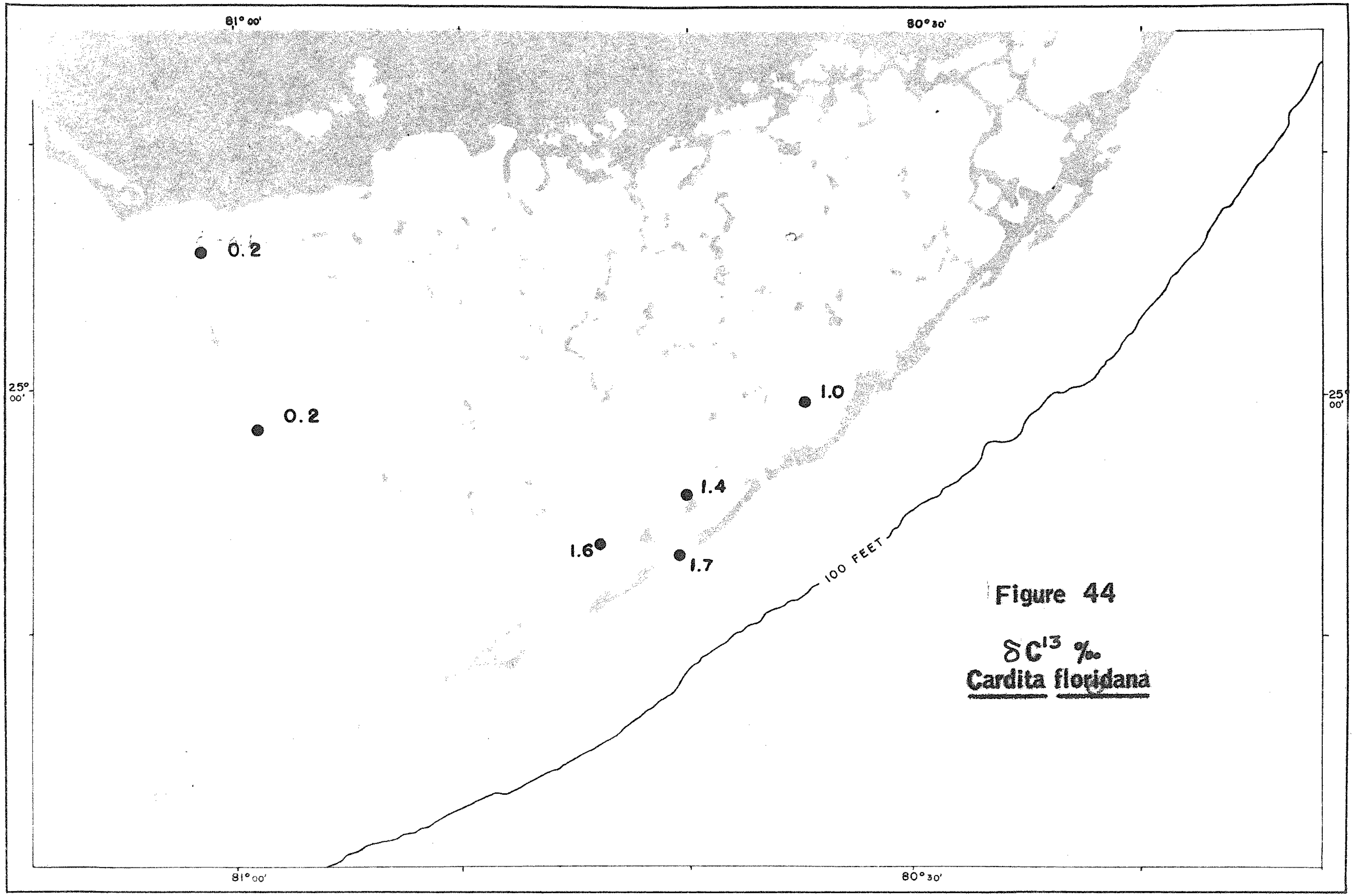


Figure 44

δC^{13} ‰
Cardita floridana

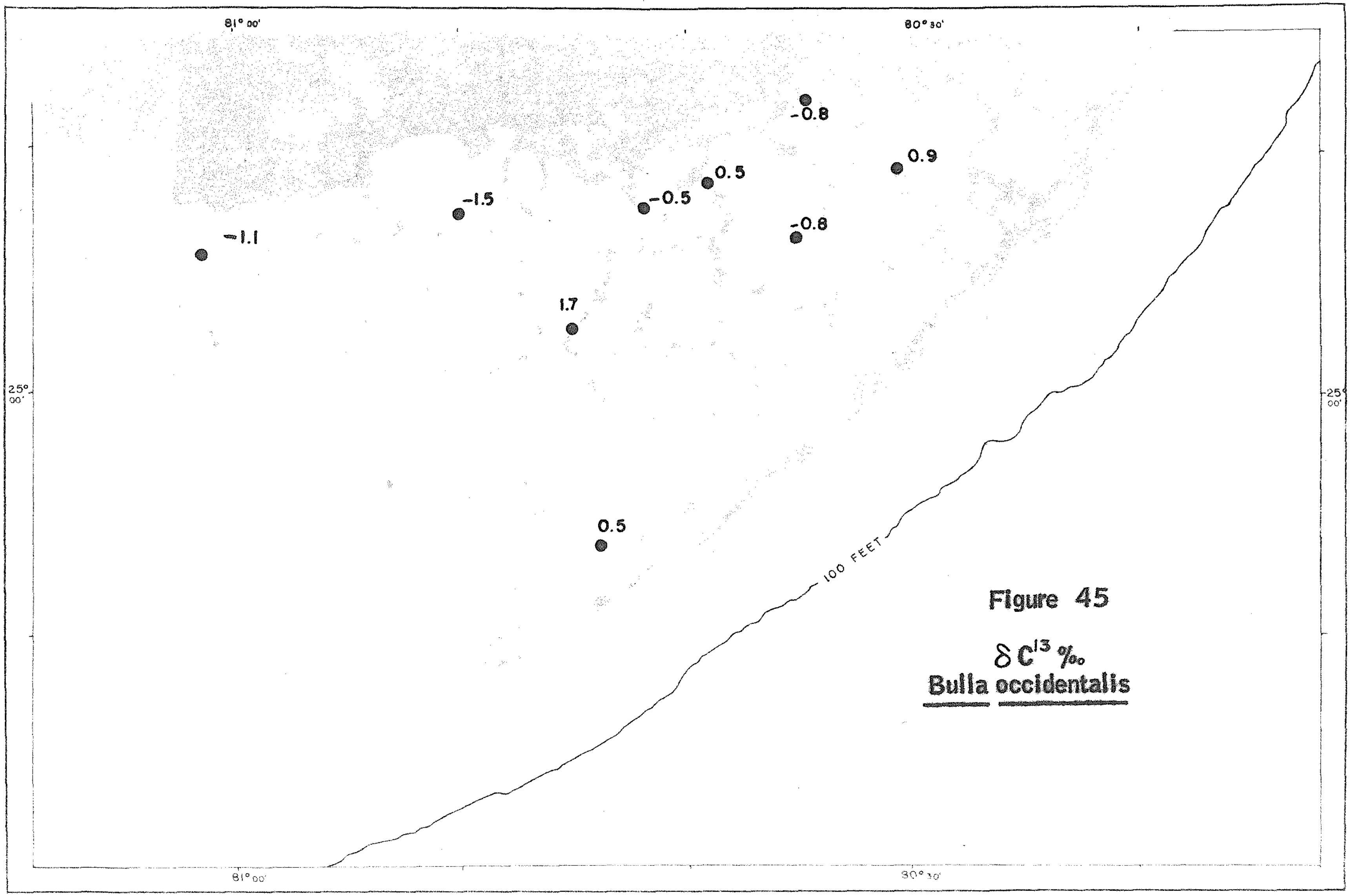


Figure 45

δC^{13} ‰
<u>Bulla occidentalis</u>

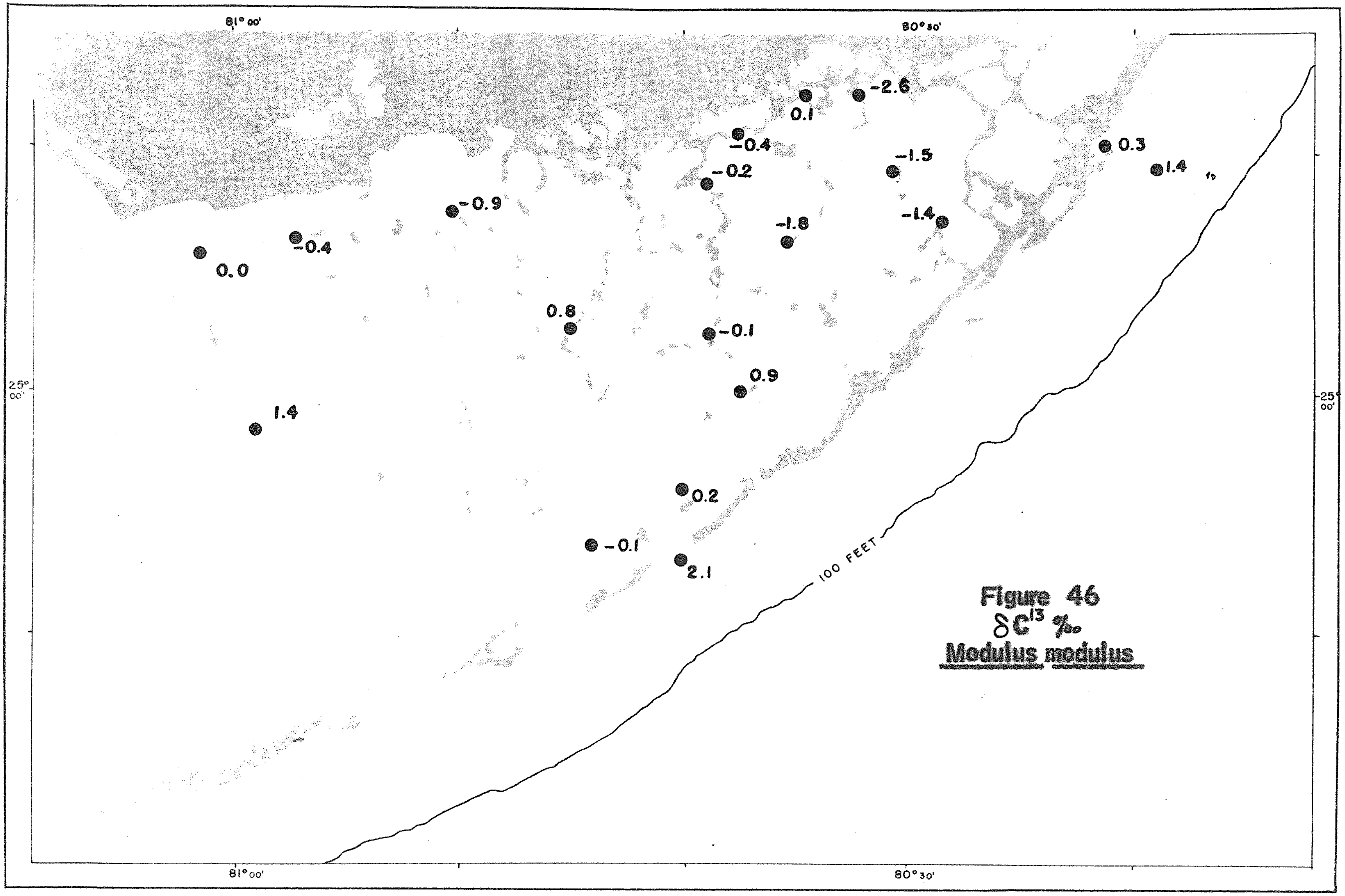


Figure 46
δC^{13} ‰
<u>Modulus modulus</u>

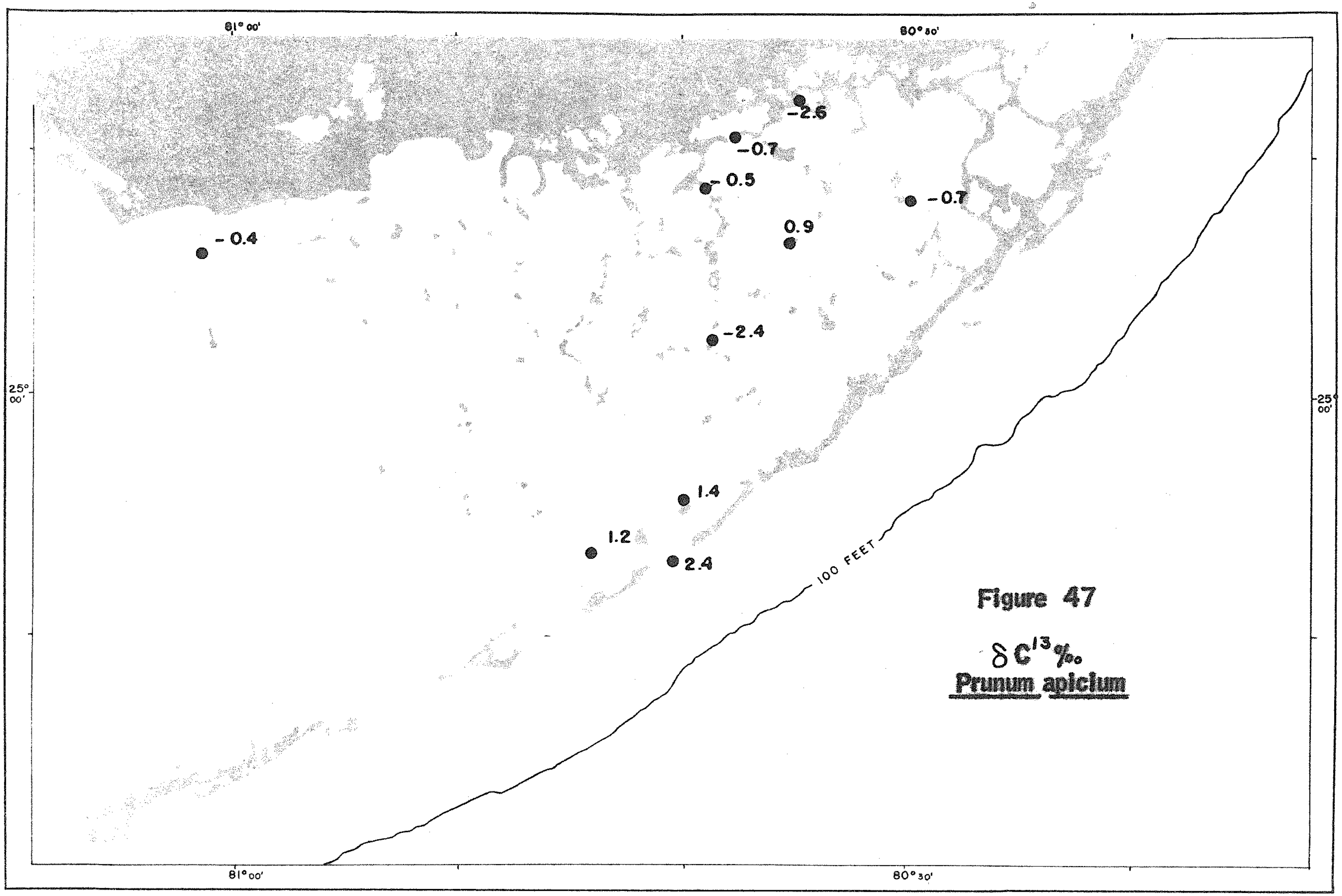


Figure 47

δC^{13} ‰

<u>Prunum apicium</u>

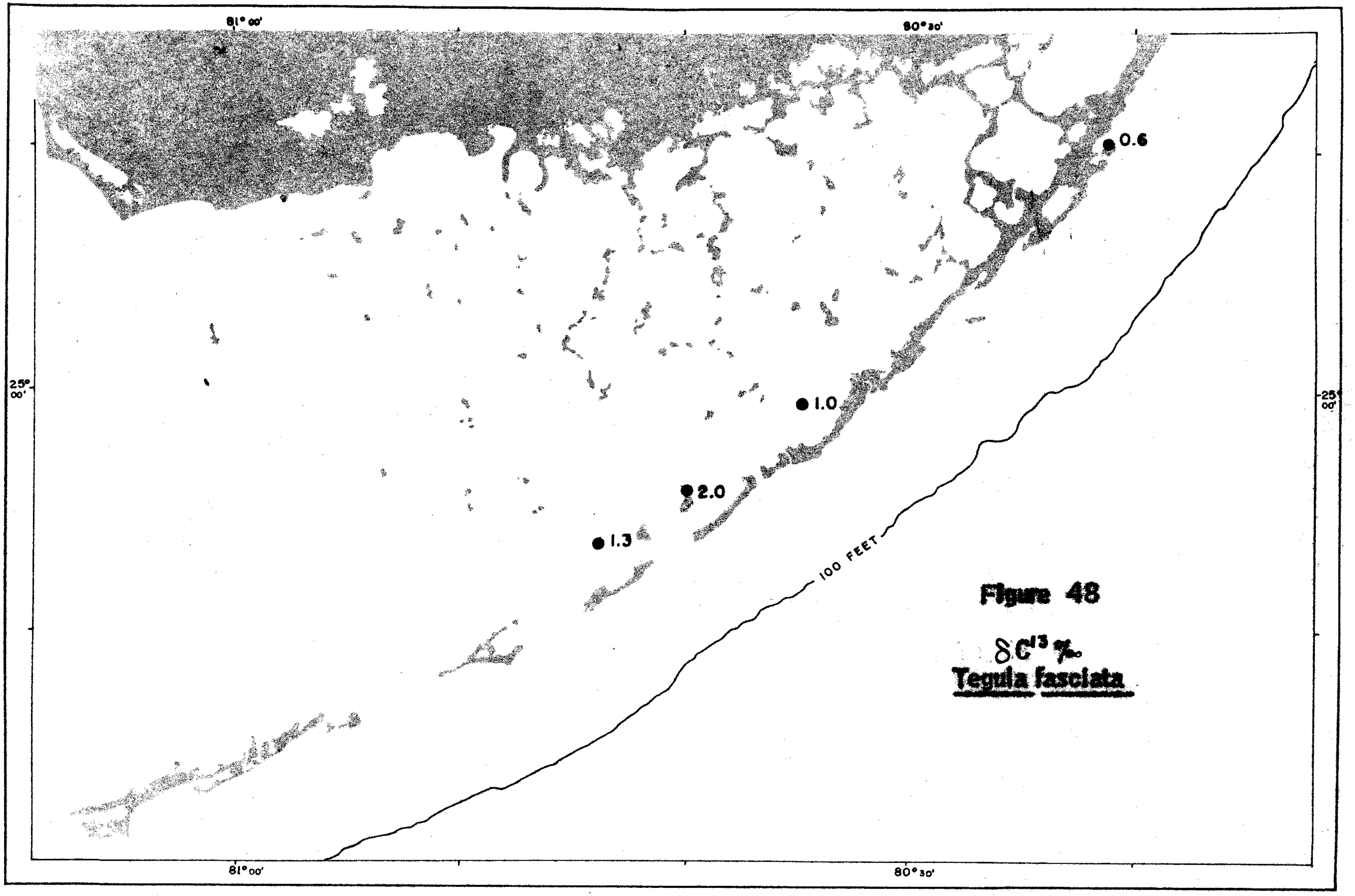


Figure 48

δC^{13} ‰
Tegula fasciata

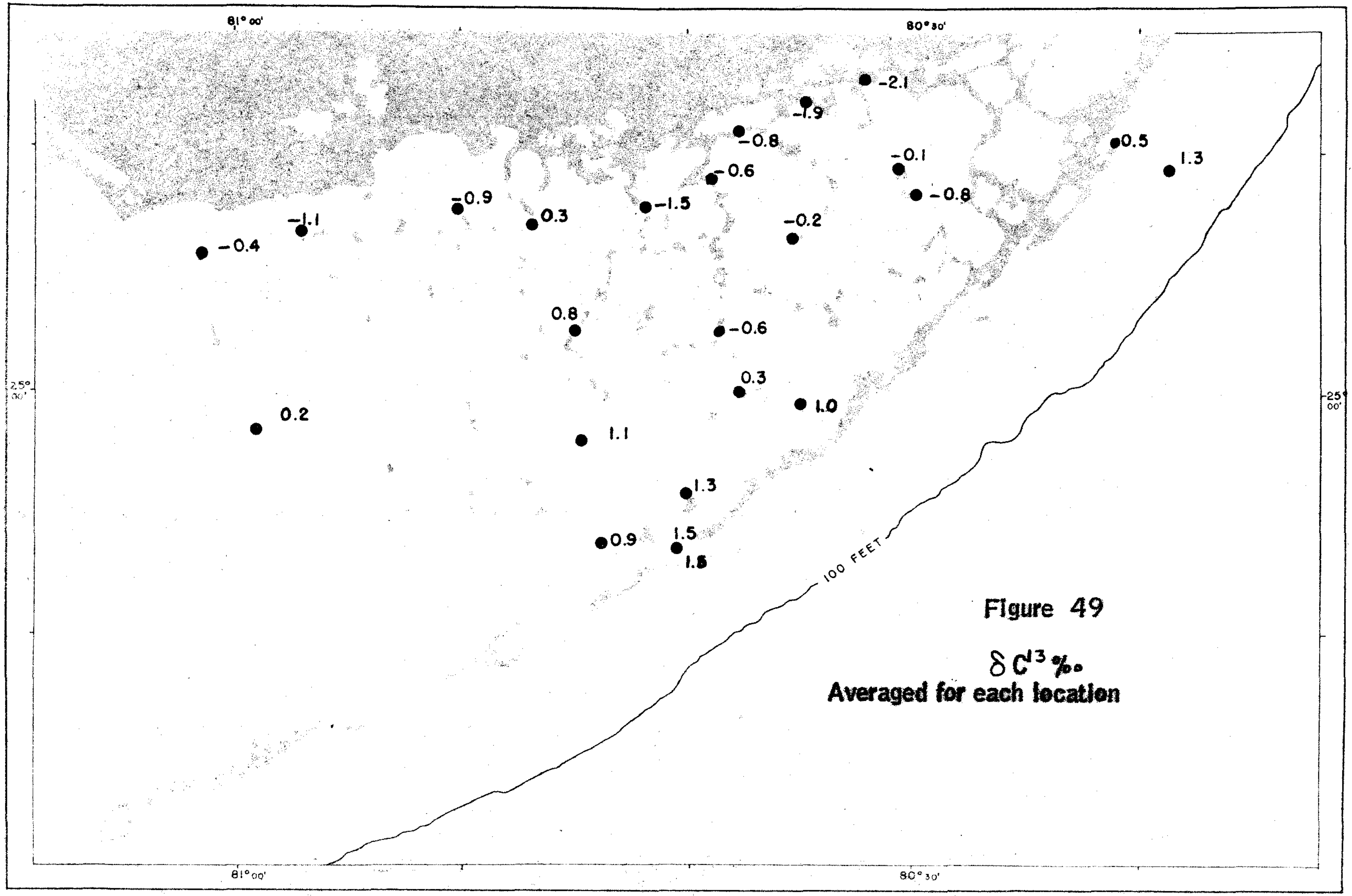


Figure 49

δC^{13} ‰
Averaged for each location

for source materials, i.e., marine and nonmarine organisms and in part a fractionation during the transformation of these materials into hydrocarbons (47).

The high values for carbonate materials come about by fractionation in the reaction:

$$\underset{\text{(gas)}}{C^{13}O_2} + \underset{\text{(solution)}}{C^{12}O_3} \rightleftharpoons \underset{\text{(gas)}}{C^{12}O_2} + \underset{\text{(solution)}}{C^{13}O_3}$$

which favors enrichment of the carbonate ion in C^{13}. Urey and Greiff (48) calculated the equilibrium constant from thermodynamic data for this reaction and found it to be 1.012 at 25°C. Craig (46) and Landergren (50) considered this value too high and calculated an apparent K on the basis of measured values for the isotopic ratio of atmospheric CO_2 and averaged marine limestones. Their value was 1.008. Both Craig and Landergren used a δC^{13} value near 0.0 for their average limestone composition and assumed that such limestones retained the isotopic composition that was originally in equilibrium with the atmosphere. Most Paleozoic and many Mesozoic and Tertiary limestones have been thoroughly recrystallized and cemented with secondary calcite. In most cases this recrystallization has been accompanied by exchange of oxygen isotopes with fresh water (51). Though Clayton and Degens (19) work indicates that there is some "memory" of the original high δC^{13} in recrystallized marine limestones, they are poor values to use in calculating equilibrium constants.

A better value for sea water - atmosphere equilibration - can be had from Recent carbonate deposits. The Bahaman ooliths described by Lowenstam and Epstein (22) are most probably formed by inorganic precipitation on shallow sand bars which are constantly agitated by tides, currents and waves. The bars are usually at the edge of a platform in good exchange with open ocean water. These are almost "laboratory conditions" for equilibrium studies. δC^{13} values for samples collected from all the important oolitic localities on the Bahama Bank fall within a range of 1.0‰ around a value of about 4.5‰ . Using this value and a value of -7.0‰ for atmospheric CO_2 (46) K calculates out to 1.011---very close to the theoretical value of Urey and Greiff.

If 4.5‰ is taken as the true equilibrium value for the exchange $CO_2(\text{air}) \rightleftharpoons CO_3(\text{solution})$, then the lower values exhibited by biologically precipitated carbonates must reflect: (1) a vital effect, (2) a condition of non-equilibrium or (3) equilibration with a source of CO_2 other than the atmosphere. As will be shown below the third appears to be the most probable cause for the major δC^{13} variations though (1) and (2) may still obtain to some small degree.

Landergren (50) was the first to systematically study the effects of locally produced CO_2 on the $CO_2 \rightleftharpoons CO_3 \rightleftharpoons CaCO_3$ equilibrium in sea water. His study, based on both limestones and deep sea sediment cores, showed that in all cases where the C^{13}/C^{12} ratio of a carbonate sample appears to be lower than the atmosphere ⟶ sea water equilibrium value evidence can be found indicating there was local production of CO_2 by oxidation of organic detritus. The partial equilibration of this "light" CO_2 with the carbonate of the water is recorded in the $CaCO_3$ of the rock or sediment. In the case of the rocks it is again not clear whether the equilibration represents the condition of deposition or later recrystallization.

Fig. 39 suggests that locally produced CO_2 has a similar influence on the shells analyzed in this study. All of the δC^{13} values fall below the equilibrium value of 4.5‰ proposed here and a large number of those from Florida Bay even lie below the equilibrium value of 0.0‰ used by Craig and Landergren. The sediments of the Bay are richly organic, dark grey muds with a strong odor of H_2S when freshly collected. In many areas there is a layer, seldom more than 2 inches thick, overlying the grey mud, which is tan to white indicating at least partial oxidation of the entrapped organic detritus.

An examination of the areal distribution of the δC^{13} values reveals a well defined gradient of decreasing δC^{13} approaching the mainland (figs. 41 - 48). The simplest explanation for this gradient would be that it reflects various degrees of mixing of reef tract water which is near the atmosphere-sea water equilibrium value with Florida Bay water that has equilibrated to a great extent with CO_2 produced locally from the oxidation of organic detritus. Williams and Barghorn (52) give values for the bicarbonate carbon isotopic composition of water from the reef tract and from Florida Bay. The numbers converted to the δ scale are 0.5 and - 10.0 ‰ respectively. There is evidence to show that the simple mixing explanation may be complicated by local factors. Craig (46) found a great variation in the δC^{13} of organic residues extracted from sediment collected around a single island - Long Key. He suggested that these variations reflect differences in the relative contribution of mangrove debris (δC^{13} = -23‰) and debris of dead marine organisms, mainly marine grass (δC^{13} averaging about -10‰). The variations in local organic carbon contribution over the Bay as a whole were investigated. The organic residues of three samples of mud were analyzed for δC^{13}. The samples are located as follows:

1053 -- Small lake completely surrounded by mangrove. Marine organic production slow as judged by lack of grass, algae and scarcity of shells.

1042 -- Grass covered mud bank just off shore of mangrove coast and near mangrove island.

1059 -- Center of grass covered mud bank about one mile from nearest island and about 10 miles from mangrove coast.

The results of the analyses are as follows:

	1053	1042	1059
δC^{13}	-20.5%	-15.0%	-9.8%

Clearly, there is a strong local influence on the carbon isotope composition of the organic detritus. To test whether these local variations of carbon composition have a significant effect on the δC^{13} of the shell carbonate a plot was made of the δC^{13} data grouped according to the proximity of the station to a source of mangrove detritus (fig. 50). Because of the nature of the sampling it is difficult to remove the effect of geography, and the trend that appears reflects to a great extent the same geographic gradient noted for individual species. However, there are some definite indications of local influences such as at 1042 and 1063 where δC^{13} is low but there is still opportunity for good exchange with open water. The averaged values for each station are shown in fig. 49.

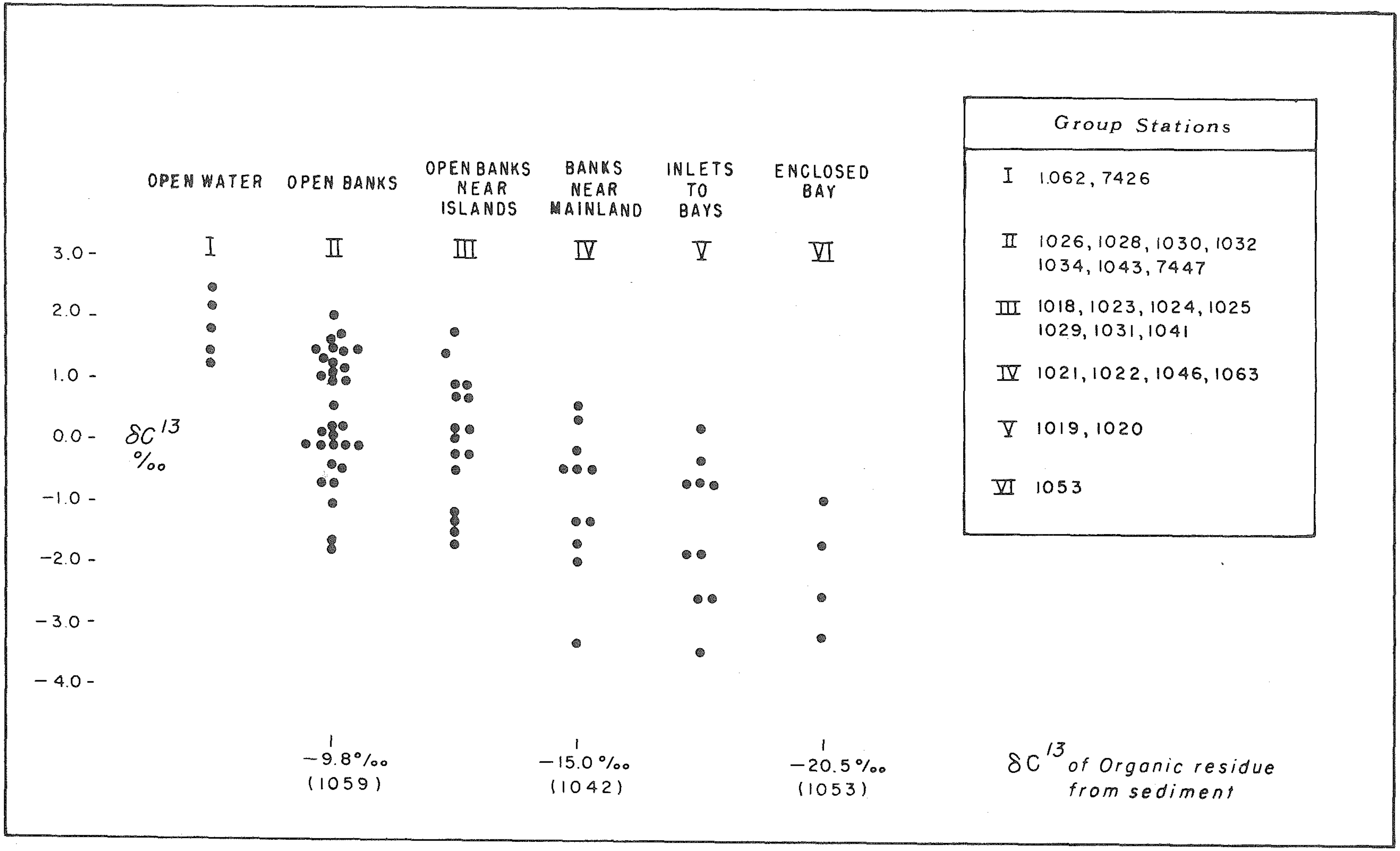


Figure 50. - Carbon isotope composition of Florida Bay and reef tract mollusks organic residue of Florida Bay sediment

The fact that all of the carbonate values, even those from the reef tract, are depressed below the proposed level for atmosphere ⟶ sea water equilibrium suggests that the process of partial equilibration with local CO_2 occurs wherever conditions of constant mixing do not obtain. The possibility that a vital effect is involved is not supported by the oxygen evidence which indicates that mollusks select carbonate ions at random from the water. Also a specimen of Salmancia sp. from an oolite bank analyzed by Lowenstam and Epstein (22) had a δC^{13} of 4.2 indicating equilibrium with the atmosphere while the same species collected from a more organic rich mud area had a δC^{13} of 2.6‰.

Slight variations in the δC^{13} of shell materials related to temperature and roughly equal to δO^{18} variations probably occur but these should average out over the year. Lack of equilibration near the site of precipitation because of the low concentration of bicarbonate ions in sea water will also contribute small variations to the δC^{13} composition of the shell.

Seasonal variations in the photosynthetic activity of marine grasses which die back each winter might serve as another source of short term variations in δC^{13} composition. Summer growth would tend to raise the δC^{13} of the water as C^{12} is concentrated in the plants. At the same time, however, the increased temperature would enrich bicarbonate ions in C^{12} and the processes would tend to cancel.

In summary, of all the processes that might produce variations in the C^{13}/C^{12} ratio of Florida Bay mollusk shells the most effective is the equilibration of locally produced CO_2 with the carbonate cycle in the water. The source of the CO_2 is the oxidation of organic detritus derived from mangrove and marine grass debris. The gradient of decreasing δC^{13} toward the mainland reflects mainly the decrease of exchange with open water but an increase in the relative contribution of mangrove over marine grass to the detritus may also influence the gradient.

SHELL MINERALOGY

A representative collection of the important molluscan species of Florida Bay was analyzed for calcite and aragonite. The technique used is that described by Lowenstam (4) and outlined in appendix A of this report.

Table 6 below lists the values of the initial survey. The results agree roughly with those of Bøggild (1) and Lowenstam (4). The pelecypods belonging to the order Eulamellibranchia are 100% aragonite while those belonging to the sub order Anisomyaria contain varying amounts of calcite. Brachidontes exustus contains traces of calcite in its temperate water occurrences but is 100% aragonite in warmer water areas (4). The gastropods contain small but detectable amounts of calcite or are 100% aragonite.

The precision of measurement is about ± 3% in the vicinity of 90% aragonite, so it was considered impractical to look for ecological variations in calcite composition in most of the species.

Additional aragonite-calcite determinations were made on a few forms and the results are given in table 7.

The Brachidontes exustus specimens were run to determine if marginal salinity conditions would induce the deposition of calcite in a manner analogous to marginal temperature conditions. The results were inconclusive. Two analyses yielded distinct peaks at the calcite 3.03 Å line but they were just in the detectable limit of the technique. B. exustus shells break down easily into very fine crystals

Table 6

Mineralogy of common Florida Bay mollusks

	% Aragonite
Class Pelecypoda	
Order Eulamellibranchia	
Sub order Heterodonta	
Chione cancellata	100
Cardita floridana	100
Laevicardium mortoni	100
Tellina alternata	100
Order Filibranchia	
Sub order Anisomyaria	
Brachidontes exustus	100
Pinctata radiata	88
Class Gastropoda	
Order Archaeogastropoda	
Calliostoma euglyptum	100
Tegula fasciata	97
Order Mesogastropoda	
Molulus molulus	93
Cerithium musearum	97
Prunum apicinum	97
Order Tectibranchia	
Bulla occidentalis	100

Table 7

% Aragonite of some Florida Bay mollusks by location

Sample	*Brachidontes exustus*	*Modulus modulus*	*Prunum apicinum*	*Pinctata radiata*
1018		92	97	97
1020	100	93		
1021		92		
1024	pos.trace	95		100
1026	100	94		100
1028	pos.trace	94		81
1034		91		96
1041	100		96	
1043		96		
1053		95		

and small amounts of calcite may have been produced during grinding.

The *Pinctata radiata* samples were obtained from shell fragments as no whole shells were found in the sediment. The wide range of values for these analyses placed some doubt on the samples and, after careful microscopic examination, it was concluded that most of the variation was due to cleaving and spalling off of aragonite layers of the shell fragments. If a good collection of live forms could be obtained the species might prove the best available for determining the influence of salinity on mineralogy.

The species which appeared to offer the best opportunity for studying calcite-aragonite variations was *Modulus modulus*. A series of analyses were made on samples from various localities. The areal distribution of values is shown in fig. 51. A range of values was found, the end members of which are considered significantly different. The distribution of the values, however, seems to be random and no systematic relationship to any ecological factors could be detected.

It appears that the ecological gradients which occur in Florida Bay either have no influence on the mineralogy of the mollusks studied or have an influence which is below the sensitivity of the technique.

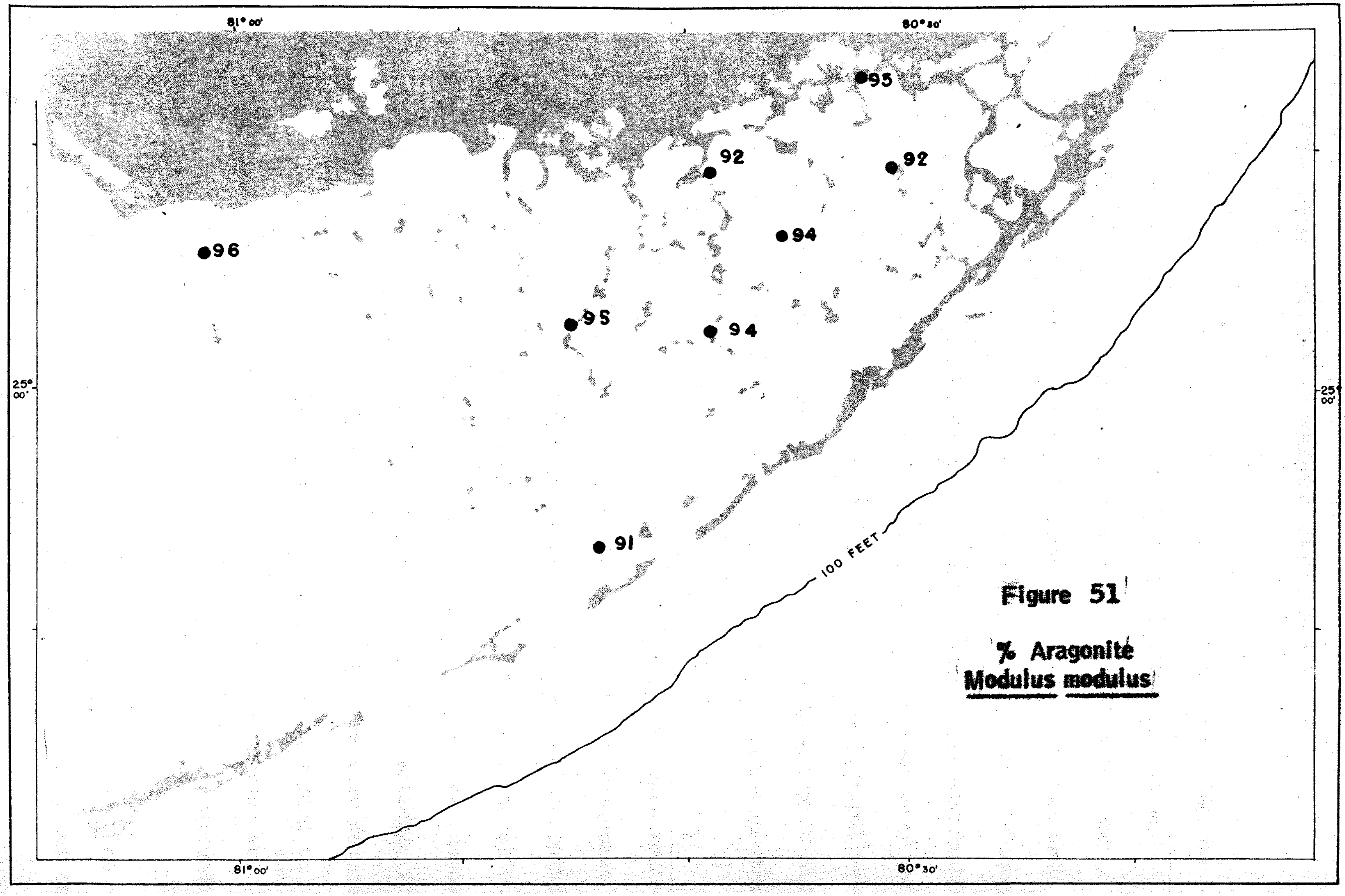


Figure 51

% Aragonite
Modulus modulus

THE SHELL CHEMISTRY OF MOLLUSKS FROM CORES

The data discussed in the preceding sections showing the influence of environment on shell chemistry hold only for those shells found in a thin layer of sediment over the surfaces of the mud banks and are only valid for conditions during perhaps the last few hundred years. The basin which constitutes Florida Bay is formed in rocks of Pleistocene age and has probably existed as a topographic feature for tens of thousands of years, although it may not have been filled with water during all of this time. It would be informative to study the history of the Bay as reflected in the chemistry of older shell materials as a check on the consistency of the conclusions drawn from the surface data.

During the course of the field work a group of short sediment cores were taken in the mud banks. The locations of the cores are shown in fig. 52. In the laboratory the cores were split lengthwise and carefully examined. Shell samples were removed from various depths in the core and analyzed for oxygen and carbon isotope composition. The selection of samples was limited to what was available in the core section, so the representation of species is greatly reduced compared to surface samples. Modulus modulus was the only form to appear consistently in the cores. The results of the analyses are presented diagramatically in fig. 53 and listed in table VI, appendix B.

The data on mollusks from the minus five foot level show a progressive enrichment in δO^{18} in the same direction and of about the

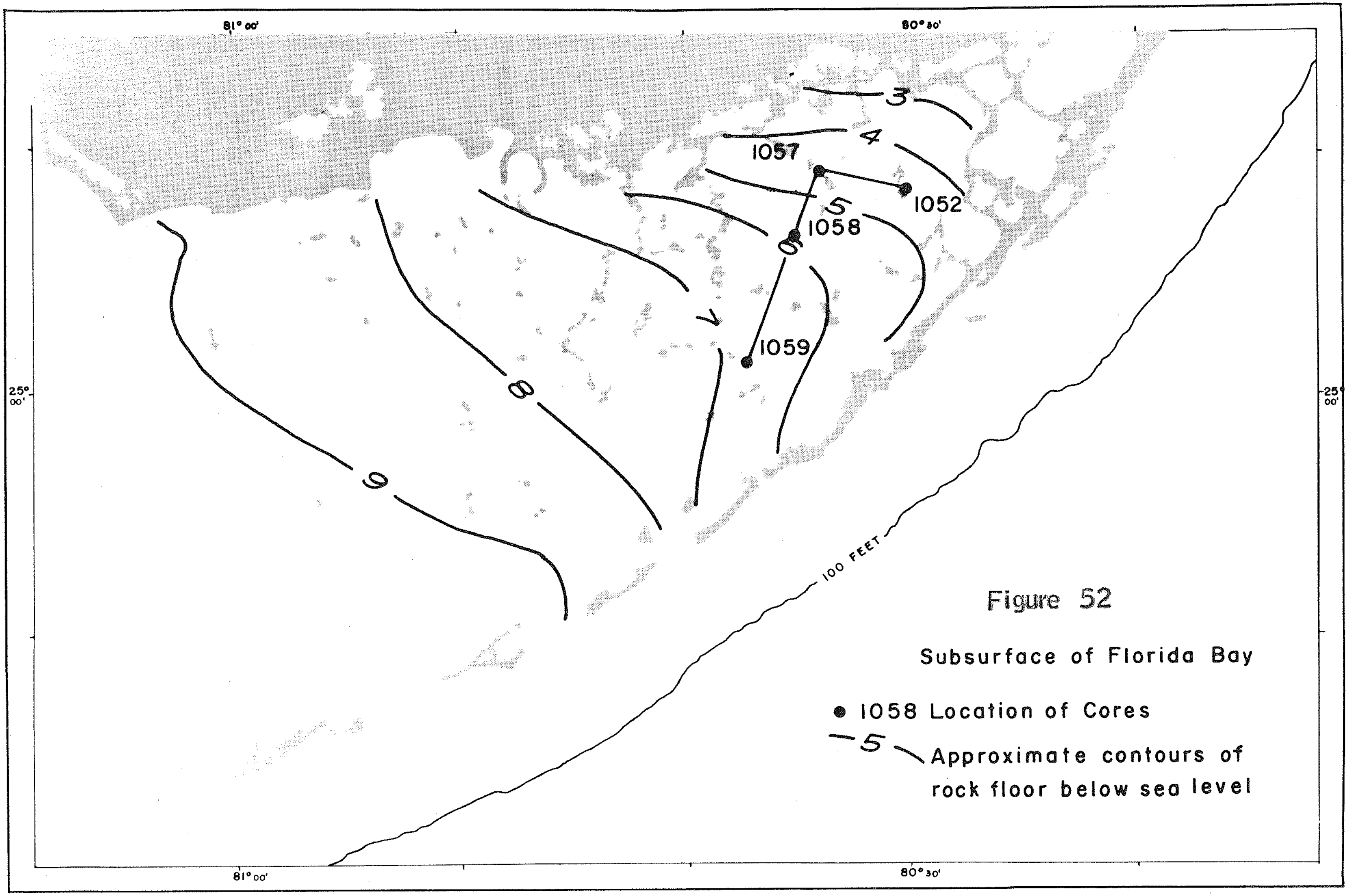


Figure 52

Subsurface of Florida Bay

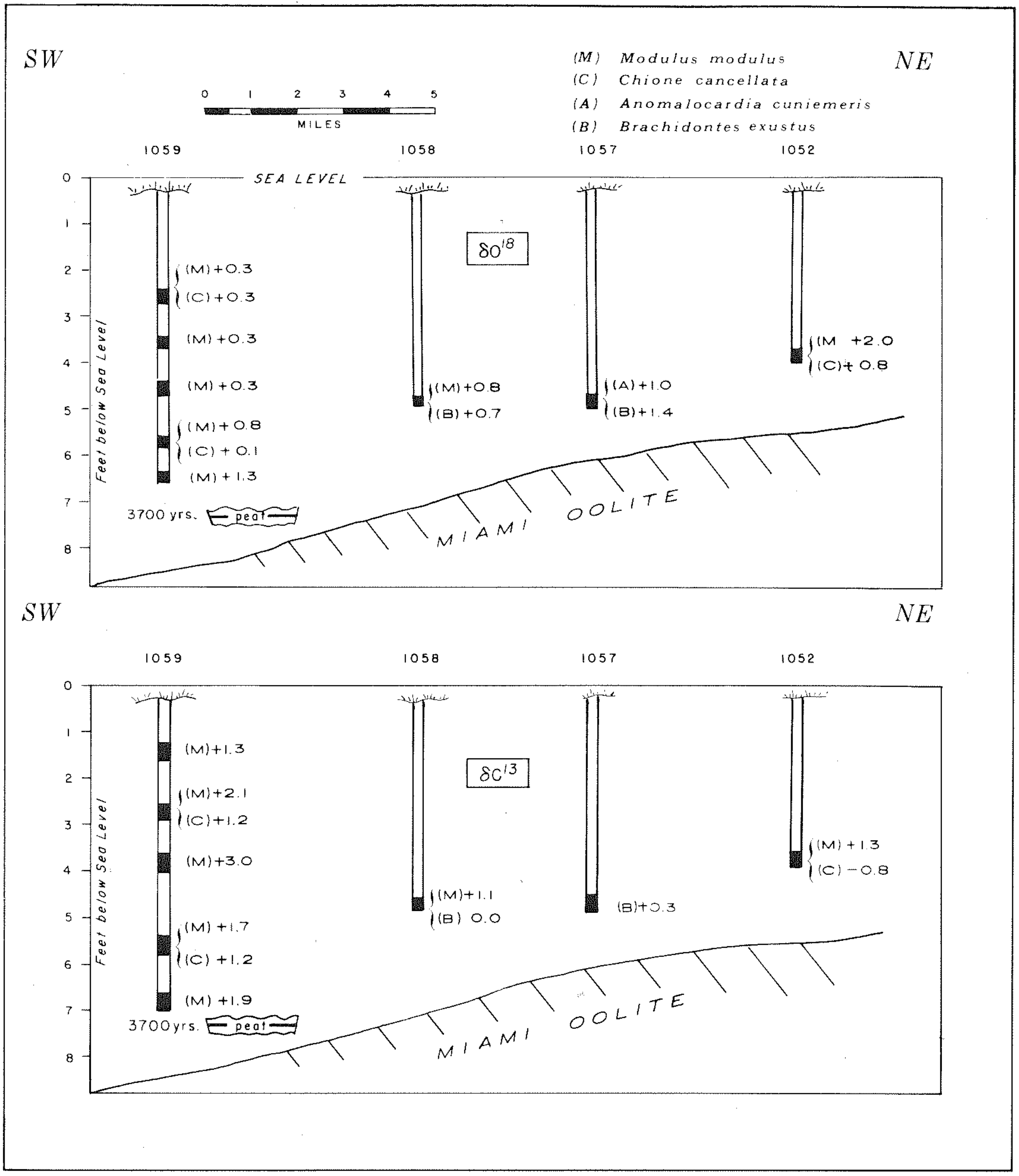


Figure 53. - δO^{18} and δC^{13} of mollusks from cores

same magnitude as is found in surface samples. This is in agreement with an interpretation of the sedimentary history of Florida Bay:

Peat layers have been found at levels of six to eight feet below the present mud bank surface near Crane Key about one mile southeast of 1059. These have been dated by radiocarbon analysis and give ages around 3700 years. Ginsburg (33) cites evidence to indicate that the peat layers were formed near sea level from piles of dead *Thalassia* which accumulated in very shallow water or on island shores and that the growth of the mud banks has more or less kept pace with a gradual relative rise of sea level. If this is the case, one would expect the same general environment of restricted circulation to have obtained through time as the shoreline slowly migrated up the sloping rock floor surface of the Bay. On the other hand, if the present mud banks had grown up from the bottom of the Bay in water near the present depth one would expect to find better circulation and exchange with reef tract and Gulf waters in the upper reaches of the Bay and "lighter" δO^{18} values in the shells from the cores.

Below the five feet level there are no data on the interior of the Bay. Rock floor contours (fig. 52) indicate that at this time the northern shoreline was probably at the position of the present shoreline but was a rocky shore instead of a coastal swamp. Evidence for the existence of such rocky shores can be found over most of the Bay. Laminated "algal crusts" are often found when pieces of the bedrock are brought up in core noses or from the bottoms of lakes.

Such crusts are presently found as a coating on the rocky seaward shores of the Florida Keys. Ginsburg (23) has described them in detail and concludes that they are formed by sediment binding blue-green algae. The sediment is introduced during periods of flooding of the normally dry shore rock, held by the mucilagenous algae and later cemented by some as yet unknown process.

From the five foot level downward the rocky shore was progressively closer to the present Bay margin. Rock floor contour data is very limited but it appears that significant reduction in the size of the Bay begins between the 4 and 6 foot level. In core 1059 there is a sudden increase in the δO^{18} composition of M. modulus at about the six foot level. This could reflect the proximity of the shoreline and greater addition of mainland drainage with high δO^{18}. The slope of the rock floor is only 0.5 feet per mile and one might expect shallow basins of fresh water analogous to the present Everglades swamp to have existed in local depressions with or without the assistance of mangrove rims and embayments. These basins would provide the necessary evaporating pans for δO^{18} enrichment.

Another factor which could promote the enrichment of the water in O^{18} is a decrease in the amount of exchange with reef tract water. At 1059 the best exchange at the present time probably occurs through Tavernier Creek at the south end of Key Largo and Snake Creek, the next channel to the south. These channels have a natural depth of around six to seven feet below present sea level. At a minus six foot sea level exchange of reef tract water with Bay water would be greatly reduced and the possibilities of enrichment in O^{18} by evaporation greatly increased.

The C^{13} values of carbonate carbon in shells from the cores are consistently higher than the values found in surface samples. There is only one core specimen with a value less than 0.0 while surface samples are characterized by rather high negative values. If the interpretation given in the preceding sections on carbon isotope chemistry is correct then it appears that locally produced CO_2 had somewhat less of an effect on the carbonate ion carbon in the past than it has at present. There are two possible explanations for this. Either a lesser quantity of locally produced CO_2 was equilibrated with the carbonate-water system or the isotopic composition of the CO_2 that was equilibrated had a δC^{13} somewhat heavier than found in the present day water.

The first condition could obtain as a result of better exchange with atmospheric CO_2. The water was shallower and of smaller volume and would tend to mix more quickly.

The second hypothesis was tested by analyzing the composition of organic detritus from three core samples. The results are given below:

Station	Depth	C^{13} Organic Residue
1058	47"-49"	-13.3%
1059	39"-41"	-11.0%
	61"-63"	-12.9%

The values are all within the range of marine organic carbon values and show only a slight influence from terrestrial carbon. The subsurface values at 1059 are lower than the surface value indicating a slightly greater contribution from land plants. Sample 1058, on the other hand, is only slightly more influenced by land carbon though it was much closer to the shoreline at the time it was deposited.

The data suggest that though there were contributions to the sediment carbon residue by land plants such contributions were much less than are presently being incorporated in the sediment. This is in agreement with what would be expected with a rising sea-level along a rocky shore. The present dense growth of mangrove along the mainland shore is probably due to the encroaching process described by Davis (24). The pioneer red mangrove send out shoots and roots which trap sediment and provide a base for the dense root clusters of the black mangrove moving up from behind. The mangrove, in effect, collect their own "soil" for encroaching growth into the Bay. The process requires a rather stable or perhaps slowly falling sea level to maintain the dense growth. With a rising sea level the tendency would be for the mangrove to retreat as it is successively drowned and one would expect only a narrow fringe of mangrove along the shore at any given time. The fact that the shoreline was rocky would also tend to hold down mangrove growth.

CHEMISTRY OF FINE-GRAINED SEDIMENT

Taken as a whole, the sediments of Florida Bay are very fine-grained. The shell materials analyzed and discussed above represent only a small portion of the total sediment and were they found in an ancient rock of similar origin would probably be described as "scattered fossils in a calcilutite matrix." Usually more than 60 weight % and often more than 80 weight % of the sediment are silt and clay-size (25). The origin of this fine-grained material is not known. Some small microfauna can be seen in the coarse silt-size and suspension slides reveal needle-like particles in the 5-10 micron size range. The bulk of the sediment consists of aggregates of unrecognizable particles.

Determinations of some of the chemical properties of the less than 62μ size fraction were made to see if more light could be shed on the origin of the fine sediments and to see if environmental gradients recognized in the shells are present in the sediment.

Table 8 gives the results of these analyses along with analyses of the possible sediment contributors. Mg in calcite refers to the replacement of Ca by Mg in the calcite lattice as described by Chave (5). The values were determined by displacement of the 3.03 Å calcite X-ray reflection peak. A fixed-count step-scanning method (see appendix A) was used in preference to the X-ray spectrometer to increase the resolution. Plots of the step-scanning are shown in fig. 54. In table 8 high Mg calcite refers to values of the order of 5% $MgCO_3$ while low Mg calcite refers to values less than 0.5% $MgCO_3$.

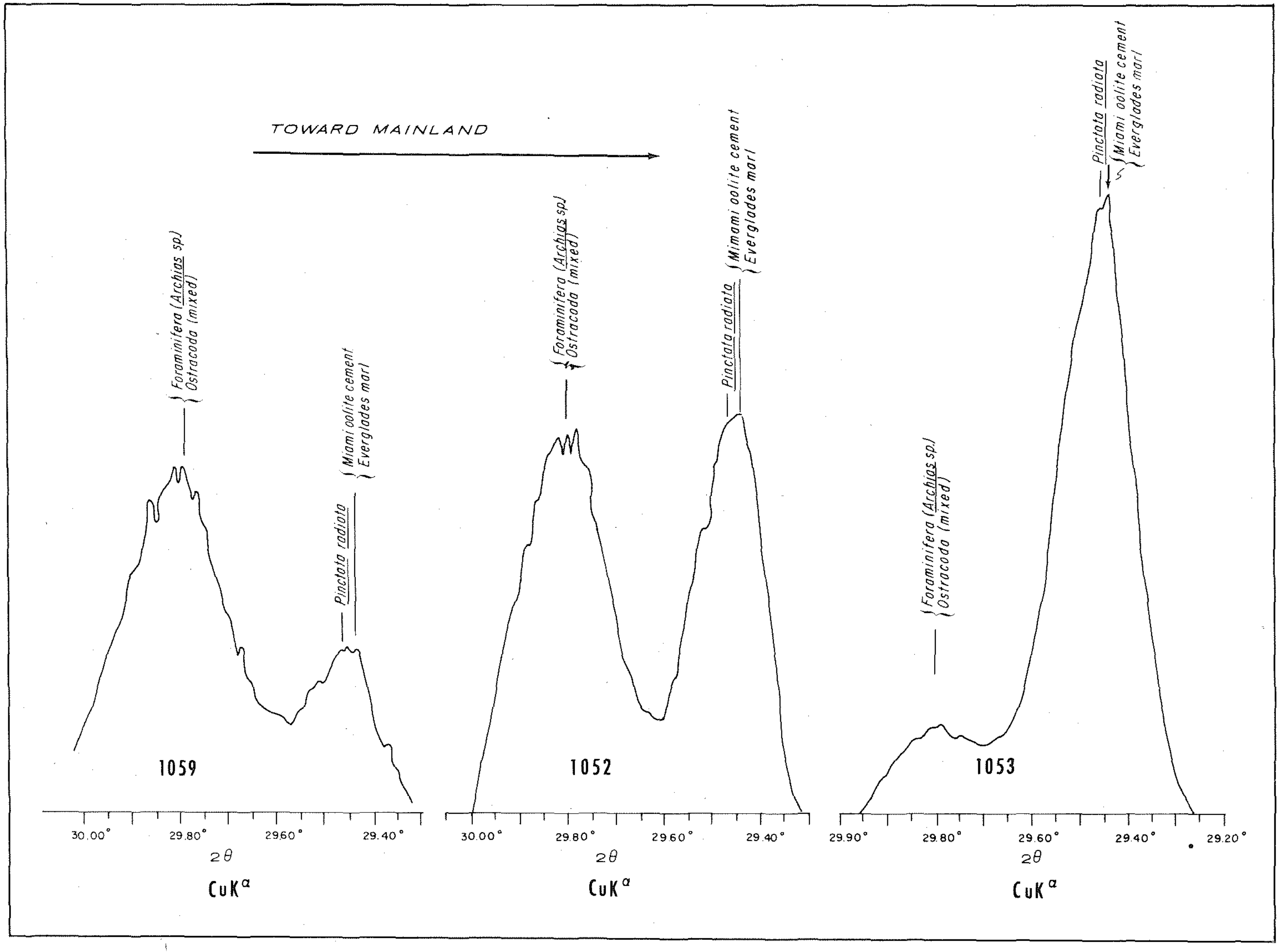


Figure 54. - Calcite x-ray peaks of Florida Bay sediment

Table 8

Composition of Florida Bay fine-grained sediment and approximate composition of possible source materials

Sediment

Sample	δO^{18}	δC^{13}	Calcite %	Mg in calcite
1053	-0.4	-0.4	62	Some high; most low
1052	0.0	0.6	49	High and low equal
1059	-0.3	1.6	38	Most high; some low

Possible Source Materials

Aragonite	Mollusks	1.0	-1.0	0	
	Green algae	0.1	-0.4	0	
	Miami Oolite	-1.8	2.5	0	
Calcite	Foraminifera	1.0	-1.0	100	High
	Ostracoda	1.0	-1.0	100	High
	Pinctata radiata	1.0	-1.0	30	Low
	Everglades marl	-1.3	2.5	100	Low
	Miami Oolite cement	-5.0	2.0	100	Low

The locations of the sediment samples are shown in fig. 2. They are representative of the three ecologic zones deduced from faunal data (fig. 14) - the northern zone, the interior zone, and the marginal zone.

A number of distinct gradients appear in the sediment analyses. Going from the northern to the marginal zone there is a decrease in % calcite, an increase in δC^{13} and a change from predominantly low Mg calcite to predominantly high Mg calcite. The latter relationship can be inferred quantitatively from the relative peak heights in fig. 54.

Examining first the calcite data one finds a very steep decreasing gradient going toward open water. The only really important faunal contributions of calcite in the Bay come from foraminifera and ostracods and one might look at the gradient as a decreasing contribution of these forms to the sediment. However, forams and ostracods are both high Mg forms and there is a relative increase in high versus low Mg calcite in the same direction. The calcite gradient must be due primarily to a decreasing low Mg calcite contribution to the sediment. The possible sources of low Mg calcite are Pinctata radiata debris, Everglades marl, and Miami oolite cement. Pinctata radiata is an unlikely source as it is at the most only 30% calcite and could not manufacture a sediment with 62% calcite as at 1053. The choice is between Everglades marl, a dark grey to tan sediment collected in a fresh water pond about 15 miles north of the Florida Bay coast, and Miami oolite cement, a clear sparry calcite that can make up as much as 60% of the Miami oolite rock underlying the Bay.

Looking at the δO^{18} data for the sediment, not only are the values all very much alike but they are all somewhat lower than would be expected for $CaCO_3$ precipitated in equilibrium with heavy Florida Bay water. Both Everglades marl and Miami oolite cement are lower than normal Bay precipitates but the cement is so much lower it would be difficult to accommodate it in the bulk sediment composition. To illustrate this point at station 1053 assume that all of the aragonite and the high Mg calcite have been precipitated in equilibrium with Bay water and have an average δO^{18} composition of 1.8%. Taking the calcite to consist of 20% of the high and 80% of the low Mg form, the bulk sediment at 1053 would have a δO^{18} of -1.5% if cement were the main contributor to the low Mg calcite. Using Everglades marl as the low Mg calcite source the sediment would have a calculated δO^{18} of about 0.3% which is much closer to the measured value.

If Everglades marl is the main low Mg calcite contributor it should be possible to accommodate the rather high δC^{13} of the marl in the bulk sediment. If the low Mg calcite has a δC^{13} of 2.5%, the remaining sediment must have an average δC^{13} of about -3.0% in order to have a bulk composition of -0.4%. This is not an unreasonable value for carbonates precipitated at 1053.

Similar calculations for the other sediment samples become more complicated because of the introduction of non-equilibrium precipitating forms such as green algae (22) and the greater difficulty of deriving average composition values for the equilibrium forms.

The data suggest that the fine-grained sediment of Florida Bay consists of the comminuted remains of organisms living in the Bay mixed with increasing proportions of Everglades marl as the mainland is approached from the Keys.

CONCLUSIONS

Variations in the water chemistry of the south Florida area are directly related to factors of climate and geography. The water data are not complete enough to show all of the possible variations that can occur but they do suggest three factors as the most important contributors to the variations. They are: (1) the isolation of Florida Bay from free exchange with open ocean water, (2) the seasonal influx of fresh water drainage from the coastal swamps, and (3) the high rate of evaporation in the shallow waters of Florida Bay and the coastal swamps. Other factors such as seasonal winds and seasonal sea level variations are effective on a smaller scale. The rare occurrences of hurricanes and northern storms are also recognized as sources of abrupt radical changes but no data are available on them.

The isolation of Florida Bay from free exchange with open sea water acts to maintain the variations in water chemistry introduced by other factors. This serves to contrast the highly variable conditions in the Bay with the uniform conditions along the reef tract.

The amount of exchange with open ocean water decreases toward the interior of the Bay and excess evaporation acts to produce a gradients of increasing salinity and increasing δO^{18} toward the mainland. Local fractional distillation processes operating in the coastal swamps enrich fresh water in H_2O^{18} to even higher values than normally occur in the Bay. The "flushing out" of this heavy water during the rainy season produces gradients of increasing δO^{18} and decreasing salinity toward the mainland.

The net effect on shell materials is that those forms which have a high degree of salinity tolerance record the gradient of increasing δO^{18} toward the mainland within the Bay and have a generally higher δO^{18} content than specimens of the same species growing along the reef tract. Differences in δO^{18} among different species from the same locality probably reflect shell growth under different environmental conditions which might be related to water chemistry but could be related to other factors such as temperature, spawning cycles, or nutrient supply. Analyses of only a few specimens or of a number of specimens of a species which has a limited ecological distribution are of little value in interpreting the environments except perhaps to contrast the Bay with the reef tract.

Two analyses of the δC^{13} of bicarbonate ions in Florida waters show Florida Bay water to be much lower than reef tract water. A similar contrast is noted in the C^{13} composition of the mollusk shells. In addition a gradient of decreasing δC^{13} toward the mainland was noted in the Bay. The C^{13} values all fall below a value proposed for $CO_2(atm) \longrightarrow HCO_3 =$ (water) equilibrium indicating that equilibration of the water is with CO_2 that is lighter than atmospheric CO_2. The large concentration of organic detritus in the Bay sediments as compared to the reef tract suggests that the partial oxidation of this detritus is the source of the light CO_2. The gradient in the Bay is mainly due to mixing of reef tract water which is near equilibration with atmospheric CO_2 with Bay water which equilibrates mostly with locally produced CO_2. A progressive decrease in the δC^{13} of the organic residue in the sediment reflects an increase in the relative contribution of mangrove debris toward the mainland. This may also account for a portion of the gradient found in the shells.

Extrapolation from analyses of brackish water indicates that the fresh coastal swamp water has an ionic composition much different from sea water. The Sr/Cl ratio is about the same but the Ca/Cl ratio is much higher and the Mg/Cl somewhat lower than normal sea water. Mixing of this water with reef tract or Gulf water in the Bay could produce a gradient of decreasing Sr/Ca and Mg/Ca ratios in the direction of the mainland.

Mg/Ca ratios in the shells are too low for precise measurement. The Sr/Ca ratios yield significant differences but the values have an erratic distribution with no clear gradients. This suggests that (1) there are other factors influencing the ionic ratios in the water (2) the selective mechanism of the organism is upset under variable salinity conditions, or (3) the selection of samples may reflect a greater mixing of environmental conditions than is implied by the O^{18} data.

Point (3) above has some interesting implications relative to the whole problem of sampling in an area such as Florida Bay. Each specimen analyzed represents the environmental conditions at a given location during the period of growth of the individual. The growth rates are not known but it is unlikely that any of the specimens are more than two or three years old. Considering the random nature of sample selection, the short life span of the individuals, and the many other ecological factors that might control the growth of the organisms it is clear that the only gradients in water chemistry that will be reflected in the shells are those which persist over long periods of time. The δO^{18} gradient is one of these because geographic isolation and evaporation produce the same kind of gradient as the introduction of fresh water from the mainland reservoir. The δC^{13} gradient also belongs in this class because it is related to the more or less permanent features of geographic isolation and density of mangrove growth. The Sr/Ca ratio would not be as persistent a gradient because of the small reservoir of Sr and the fact that the gradient will only exist during periods of fresh water influx.

The data from mollusks retrieved from cores in the mud banks indicate that the present environmental framework of Florida Bay has persisted for at least the last 3700 years. A gradual increase in the δO^{18} composition with depth at a location near the Bay margin indicates either the proximity of the mainland or a blocking off of reef tract water exchange which is presently taking place through shallow channels.

Gradients in the mineralogy and Mg composition of the fine-grained mud of Florida Bay show no obvious relationship to gradients in the sea water chemistry but do suggest the transport of a characteristic Everglades marl into the Bay.

Part II

The Shell Chemistry of Some Pleistocene Mollusks from South-Central Florida and Its Environmental Interpretation

INTRODUCTION

In part I it was shown that the chemical composition of mollusk shells can reflect certain aspects of the environment of shell growth. In this report mollusk shells from some Pleistocene rocks are subjected to similar analysis to determine if any environmental conclusions can be drawn from the much more limited information available in a rock outcrop.

The rock unit chosen for study is the Caloosahatchee formation, a very fossiliferous marl and limestone exposed along the Caloosahatchee River in south-central Florida. The Caloosahatchee marl was recently studied by DuBar (53) as part of a more comprehensive study of the stratigraphy and paleontology of the entire Neogene section in the Caloosahatchee River area. An excellent presentation of his work can be found in Geological Bulletin No. 40 of the Florida Geological Survey. Most of the descriptive information and faunal data given below are summarized from this bulletin.

SETTING

The Caloosahatchee River flows from Lake Okeechobee in the center of the state of Florida south and west discharging into the Gulf of Mexico south of Sanibel Island (fig. 55). Along at least half of its length it occupies a drowned river valley. The river and its tributaries have cut into the surficial Pleistocene rocks producing well-exposed vertical cliffs 10 to 15 feet high. These are the only really usable outcrops in the area. The immediate area on either side of the river is an almost featureless plain covered by very late Pleistocene sands and marls.

McNeil (54) has described a series of marine terraces at various altitudes over the Florida Peninsula which are thought to represent sea level stands during Pleistocene time. On both sides of the Caloosahatchee River at distances of 3 to 10 miles there is a 25 foot terrace which is believed to represent the shoreline during deposition of the Pamlico sand, the latest deposit in the area which forms a ubiquitous cover over the older Pleistocene rocks. A 100 foot terrace about 30 miles north of the river is believed to be the northernmost advance of shore during deposition of the Caloosahatchee formation (53). Many shorelines of intermediate position are thought to have been destroyed by transgressing seas.

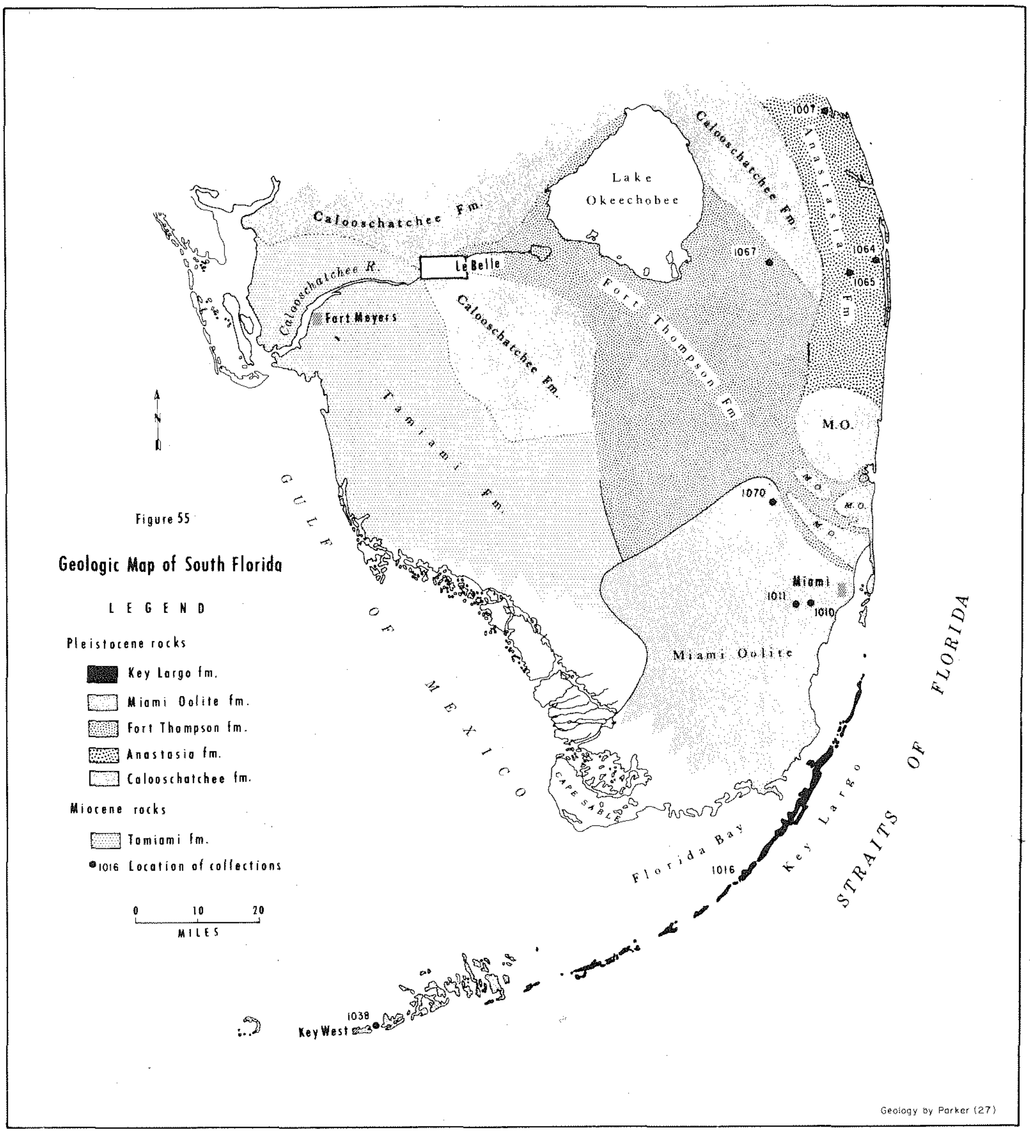


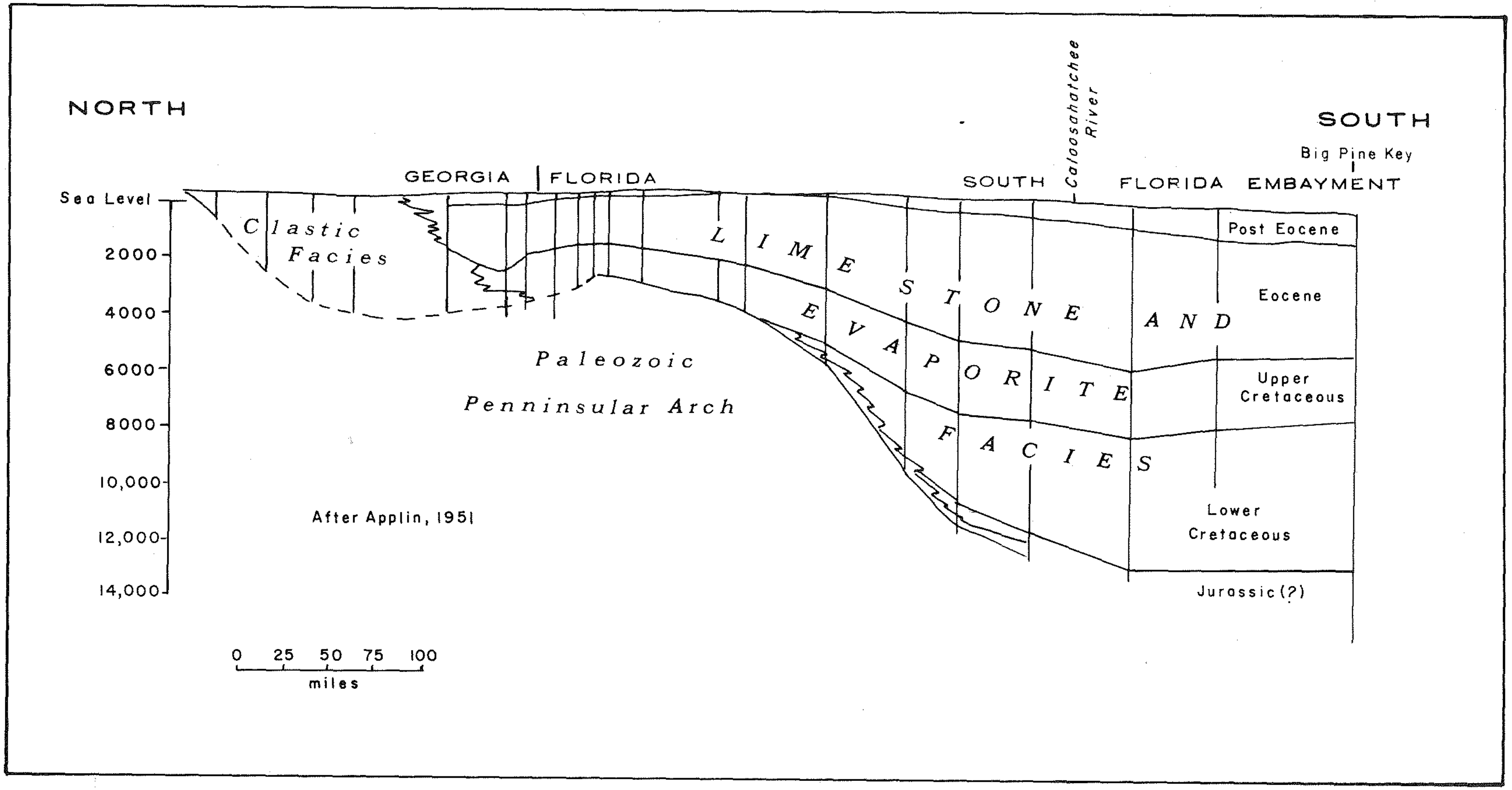
Figure 55

Geologic Map of South Florida

Geology by Parker (27)

REGIONAL GEOLOGY

The Floridan Plateau consists of a thick sequence of Mesozoic and Tertiary rocks which lap on a major structural feature, the Peninsular Arch (fig. 56). The arch is a sequence of flat-lying Paleozoic sediments. The post-Paleozoic beds are more than 12,000 feet thick near the Caloosahatchee River but thin to less than 4,000 feet near the Florida-Georgia border. They are almost entirely carbonates and evaporites Jurassic to Tertiary in age. Presslar (55) has grouped these beds with similar sequences in the Bahamas and Cuba in a common depositional basin which he designates the South Florida Embayment.



After Applin, 1951

Figure 56. - North-south geologic cross-section of the Floridan Plateau

LOCAL GEOLOGY

All of the rocks exposed in the area of interest are Miocene or younger in age (fig. 55). The oldest rock unit, the Tamiami formation, is upper Miocene. The Caloosahatchee formation was considered to be Pliocene by most early workers (56, 57) but vertebrate remains found by DuBar indicate that it belongs to the later sequence of Pleistocene strata that cover most of the South Florida peninsula.

Correlation within the Pleistocene beds is very difficult as they are rarely exposed through the cover of very late Pamlico sand and Lake Flirt marl and faunal distinctions are not clear. DuBar considers the Caloosahatchee formation to be Sangamonian in age, formed during the last great interglacial high sea level. The Anastasia formation, poorly cemented high beach dunes and bars along the east coast; the Key Largo formation, a fossil coral reef limestone; the Miami oolite; and the Fort Thompson formation, a series of alternating fresh water and marine limestones, are considered to represent minor fluctuations in sea level during advances and retreats of the Wisconsin Ice sheet and hence are in part time equivalents and younger than the Caloosahatchee formation.

CALOOSAHATCHEE FORMATION

A series of very fossiliferous beds exposed along the Caloosahatchee River were first described by Heilperin (58) and called the Floridan beds. Later Dall (56) described these same beds but gave them the name Caloosahatchee marl which has since come to be accepted. The approximate extent of the Caloosahatchee marl is shown in fig. 55.

The Caloosahatchee formation is defined by DuBar as being: "All the dominately marine strata which are younger than the Tamiami formation and older than the Fort Thompson formation...". In the field the lower boundary is usually clearly marked by an unconformity between the yellow to olive-green poorly fossiliferous clays and sands of the Tamiami formation and the very fossiliferous limestone and marls of the Caloosahatchee formation. The upper boundary is generally, though not always, marked by an unconformable contact with a fresh water marl of the Fort Thompson formation. Where marine beds of the Fort Thompson formation are lying directly on the Caloosahatchee formation the contact is difficult to detect.

The thickness of the Caloosahatchee formation varies considerably. It was deposited on the undulating topography of the Tamiami formation, and is thick in the lows and thin or absent on the highs. Subsequent erosion has removed additional section at some locations.

DuBar recognizes three members in the Caloosahatchee formtion: the Ayers Landing member, the Bee Branch member and the Fort Denaud member (fig. 58). The Fort Denaud member consists of a number

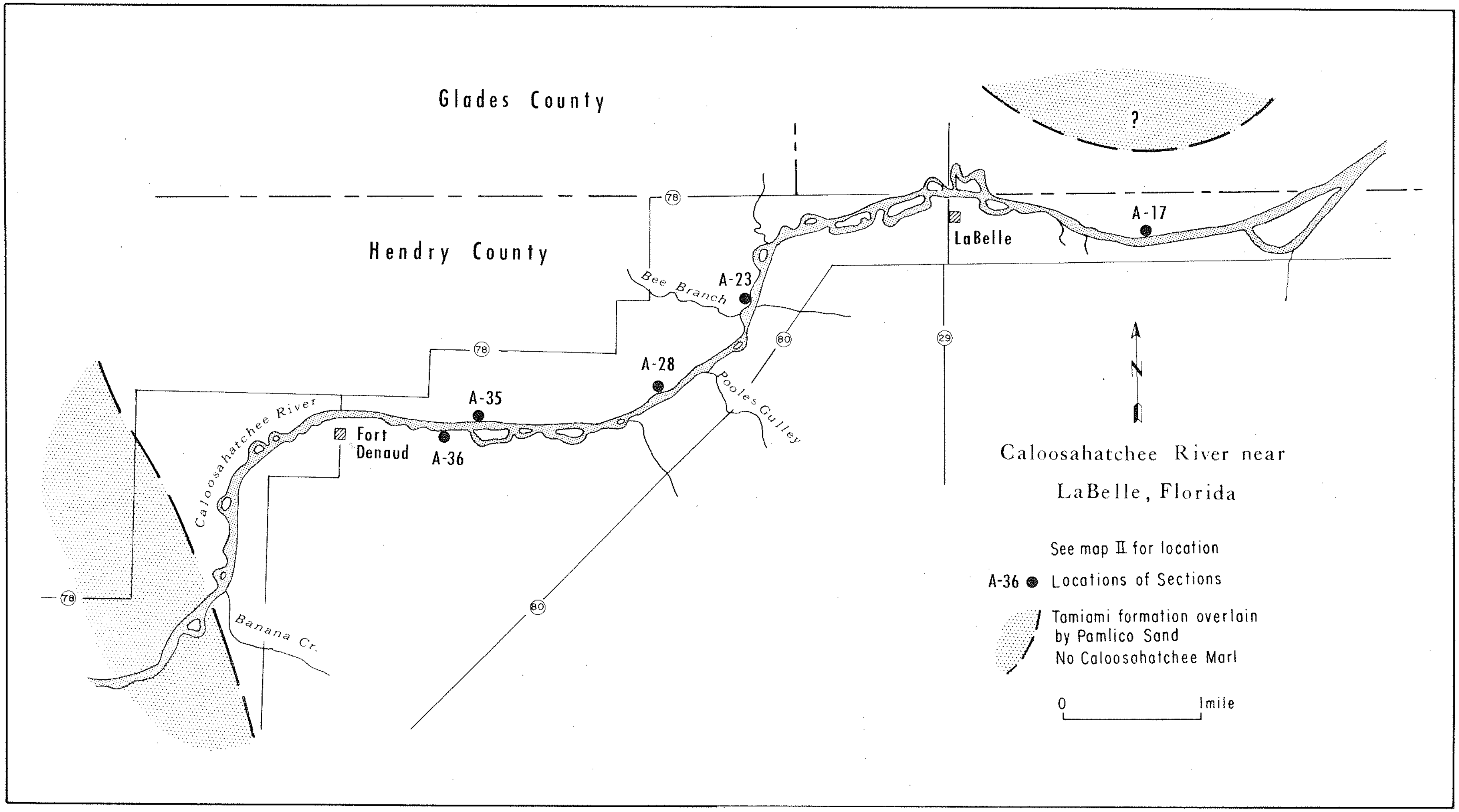


Figure 57. - Map of the Caloosahatchee River near La Belle, Florida

of distinct zones which are discontinuous over the area studied. One or two of the zones can be found at the base of almost all of the exposures of the Caloosahatchee formation, but rarely do all appear in the same section. One of the more consistent zones is a brackish water marl which was found underlying the Bee Branch member at all of the localities studied. The fauna of this zone includes *Rangia nasuta*, which is considered to occupy a very low salinity niche similar to its related Recent forms, and a variety of marine, polyhaline and fresh water forms. The zone was obviously one of great environmental fluctuation.

The Bee Branch member is one of the most distinctive units of the entire Neogene section. It consists of a hard bioclastic limestone and concretionary marl. It is usually less fossiliferous than the other members of the Caloosahatchee formation and the faunal composition, according to DuBar, is indicative of a deep water shelf environment of 10 to 20 fathoms.

The Ayers Landing member is a poorly consolidated, slightly sandy shell marl. *Chione cancellata*, *Phacoides multilineatus* and *Calyptrae centralis* occur in great abundance. Corals belonging to the genera *Siderastrea*, *Dichocoenia*, *Diploria* and *Manicina* are locally abundant at the base. The unit usually fills depressions in the underlying Bee Branch member. DuBar interprets the assemblage as having lived "...offshore on the continental shelf or in the environment of a fairly broad deep bay." He suggests a depth of water of 5 to 20 fathoms initially with salinities of 30 to 36‰; then gradual shoaling as

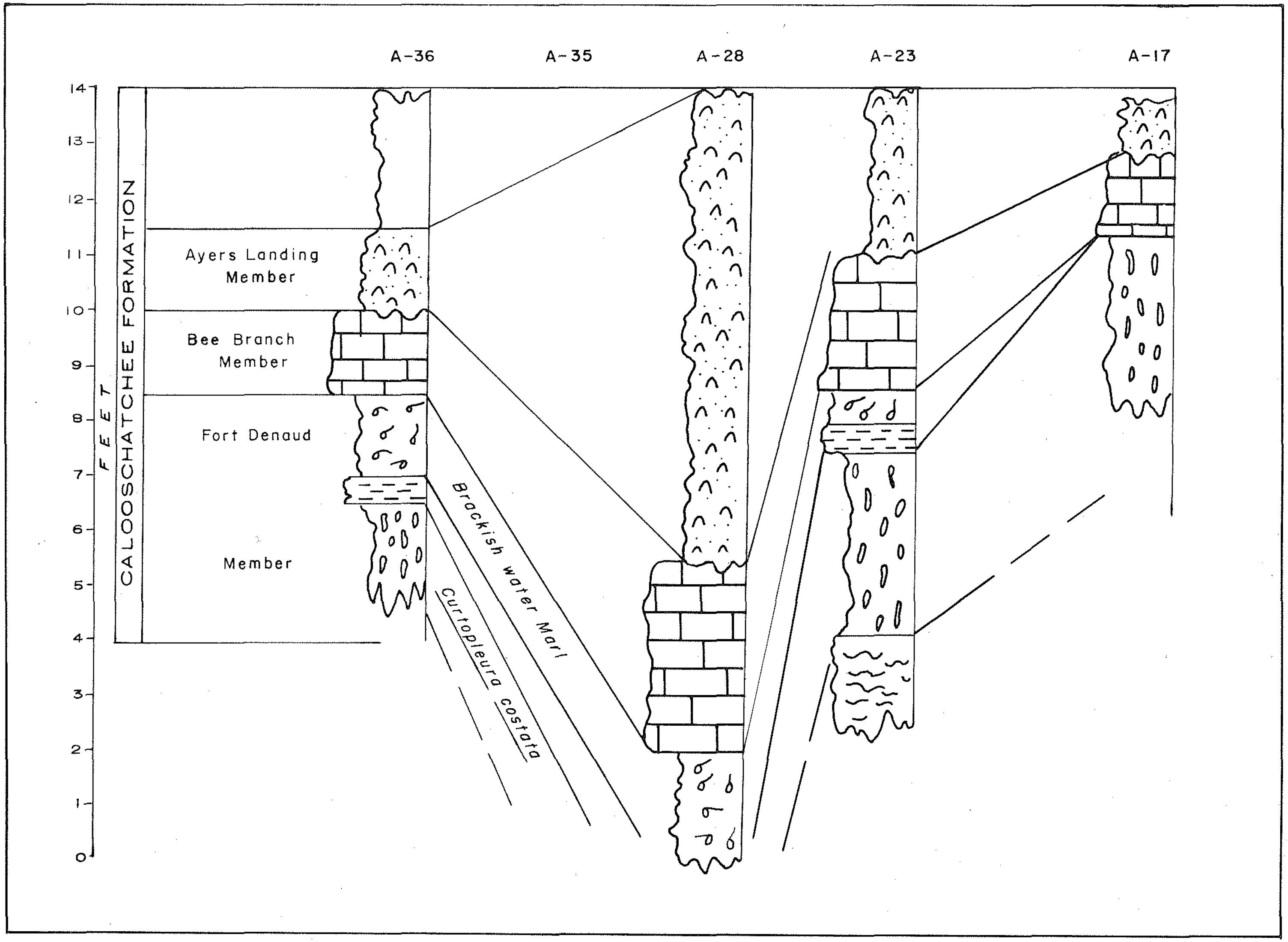


Figure 58. Stratigraphic sections of the Caloosahatchee formation

deposition continued, leading to the introduction of "high salinity bay species such as Chione cancellata."

Collections of fossils from the three members of the Caloosahatchee formation were made at five locations along the river. The locations are shown in fig. 57. Additional material was furnished by Dr. DuBar from his collections at these same locations. Representative sections of the collecting localities are shown in fig. 58.

THE FAUNA OF THE CALOOSAHATCHEE FORMATION

All of the Caloosahatchee marl faunal elements are related to Recent tropical and sub-tropical forms with at least 40 per cent of the molluscan species extant. Recent species such as Chione cancellata and Calyptrea centralis are very abundant in many of the beds.

No attempt was made by the present writer to repeat the detailed faunal analyses made by DuBar. The ease with which sections were located and individual units recognized attested to the accuracy of his descriptions. The faunal data given below are taken directly from DuBar's paper.

The particular units selected for analysis in this report are easily distinguished on the basis of faunal composition. Variation in the gastropod and pelecypod fauna at location A-36 are shown in fig. 59 as cumulative bar graphs. Of particular interest is the contrast in the character of the pelecypod fauna between the brackish water units (Cyrtopleura costata zone and brackish water marl zone) and the normal to high salinity units (Bee Branch member and Ayers Landing member). The distinctive gastropod assemblage of the Bee Branch member is also notable.

In addition to the faunal variation between beds there are detectable lateral variations within some of the beds. The most striking is the Cyrtopleura costata zone of the Fort Denaud member. Faunal analyses from this bed at three locations are shown in fig. 60. The differences are so great that DuBar divided the unit into three facies:

1. A-35 Brackish water facies
2. A-17 High salinity bay facies
3. A-23 Turritella facies

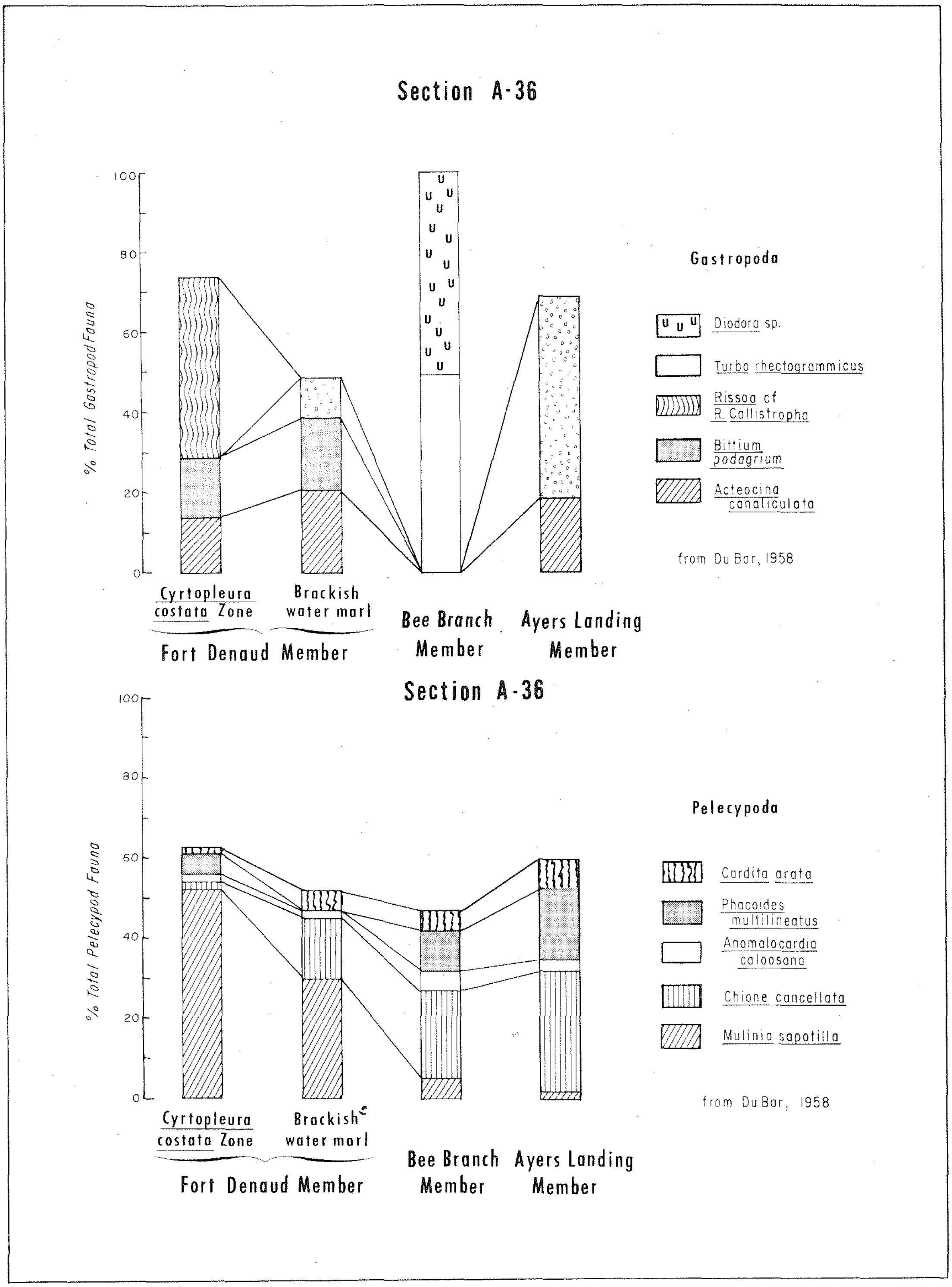
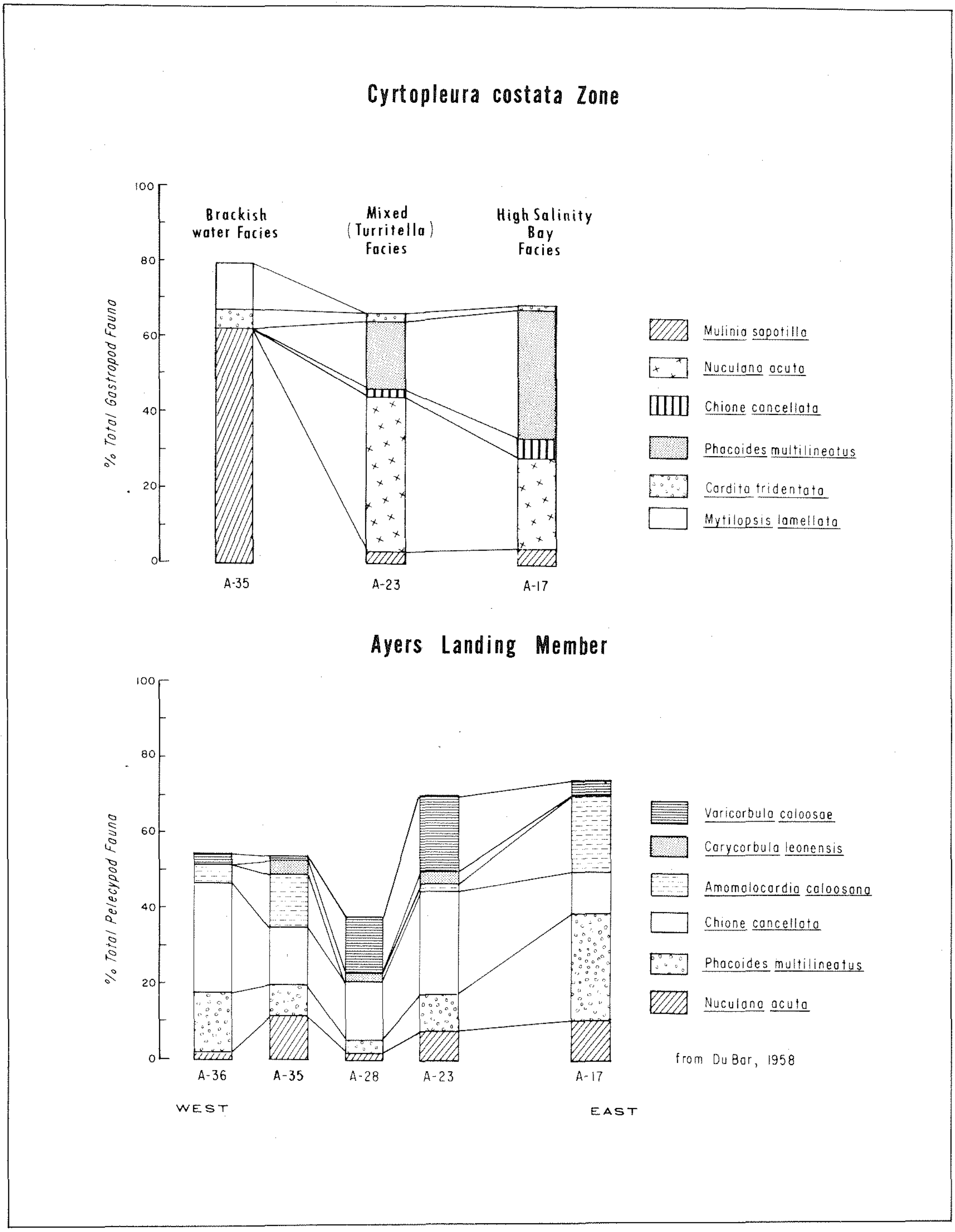


Figure 59. - Relative percent of molluscan species in the Caloosahatchee formation



from Du Bar, 1958

Figure 60. - Lateral distribution of molluscan species in members of the Caloosahatchee formation

The *Turritella* facies is thought to represent a high salinity environment but differs from the high salinity bay facies in that it contains fewer brackish water and fresh water forms. In the writer's opinion A-23 and A-17 could both be considered mixed facies of brackish water and high salinity forms.

Though no numerical data were presented on lateral variation in the Bee Branch member, DuBar notes in his text a distinction between the fauna of a marly facies and a hard limestone facies in the unit indicating the marl was formed shoreward of the limestone. The lateral distribution of marl and limestone is not clear from his descriptions.

Lateral variations in the faunal composition of the Ayers Landing member are more subtle than the variations found in the other units. Cumulative bar graphs of the pelecypod fauna from a number of stations are shown in fig. 60. Most of the important species are present at each of the localities but the relative abundances of certain species show significant changes. A-36, A-35 and A-17 are relatively high in *Phacoides multilineatus* and *Anomalocardia caloosana* but low in *Varicorbula caloosaea*. At station A-23 and A-28 there are considerably more *Varicorbula caloosaea* but fewer *A. caloosana* and *P. multilineatus*. Some areas of Florida Bay support large numbers of *A. cuneimeris*, a very close relative to *A. caloosana*, and *P. multilineatus* while Recent species of *Varicorbula* are known to inhabit more open water. This suggests more restricted circulation in the vicinity of A-36, A-35 and A-17 during Ayers Landing time.

SHELL CHEMISTRY

Selected specimens of Pleistocene mollusks were analyzed for δO^{18} and δC^{13}. Chione cancellata and Lucina pennsylvanica were collected from the Fort Thompson, Anastasia, Key Largo and Miami oolite formations in a band of locations along the east coast. Locations of the samples are shown in fig. 55 and the areal distribution of values is given in figs. 65 and 66. The recorded values are grouped under the heading of "open shelf" in figs. 61 to 64.

Specimens representing seven species of mollusks were collected from the three members of the Caloosahatchee formation at the locations shown in fig. 57. Separate plots for each stratigraphic unit showing the δO^{18} and δC^{13} values for each species by location are shown in figs. 61 to 64. A complete listing of the isotopic data is given in tables VII and VIII, appendix B.

Strontium analyses of selected specimens of Chione cancellata are listed in table 9.

The precision for carbon and oxygen isotopes is ± 0.1% and for strontium ± 10% of amount present. Techniques are described in appendix A.

Oxygen Isotope Composition

The specimens analyzed from the collections made along the east coast are used here as representatives of an open shelf environment to be compared to the Caloosahatchee marl specimens. The rocks sampled are younger than the Caloosahatchee formation but a gross

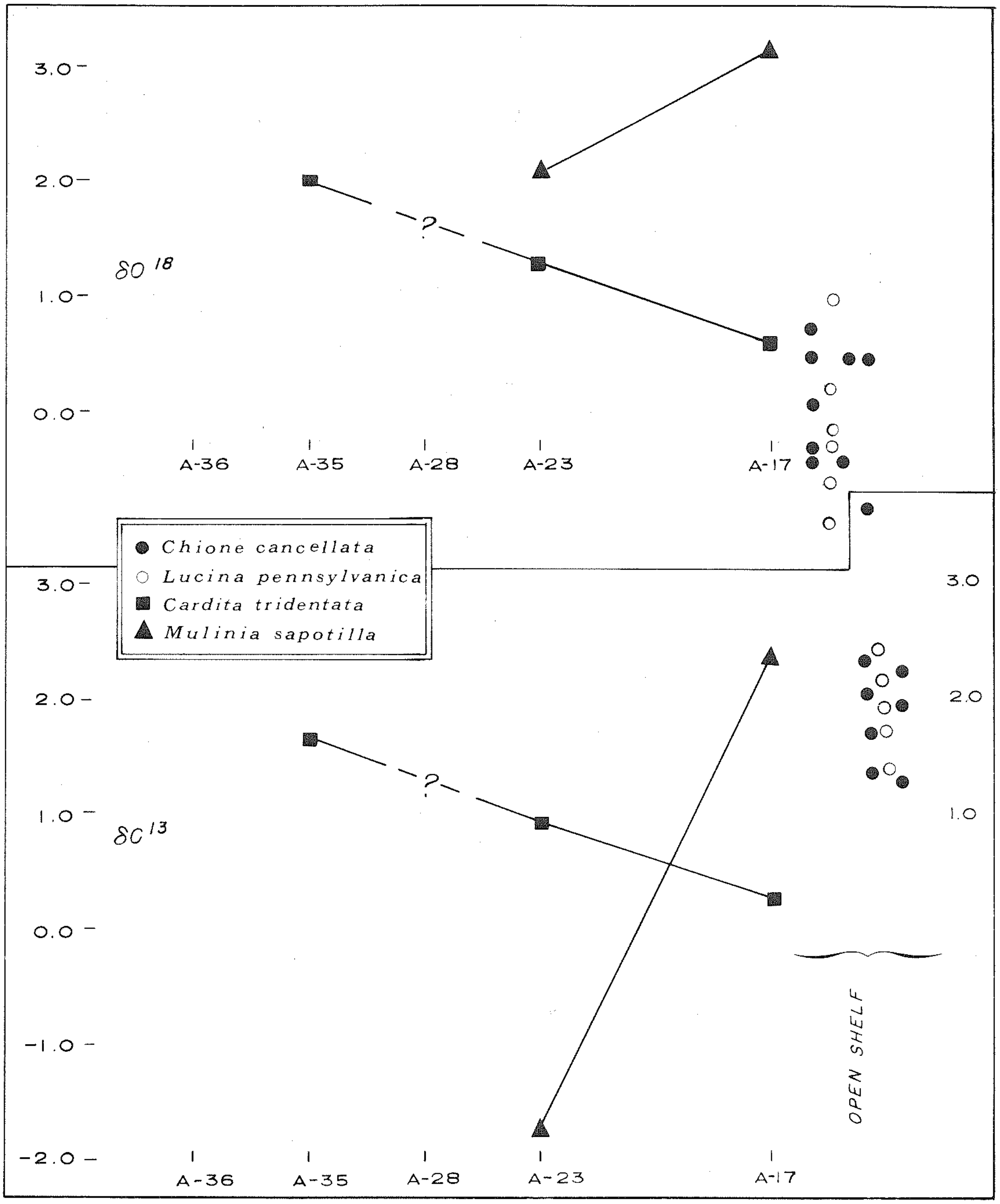


Figure 61. - δO^{18} and δC^{13} of mollusks from the <u>Cyrtopleura costata</u> zone

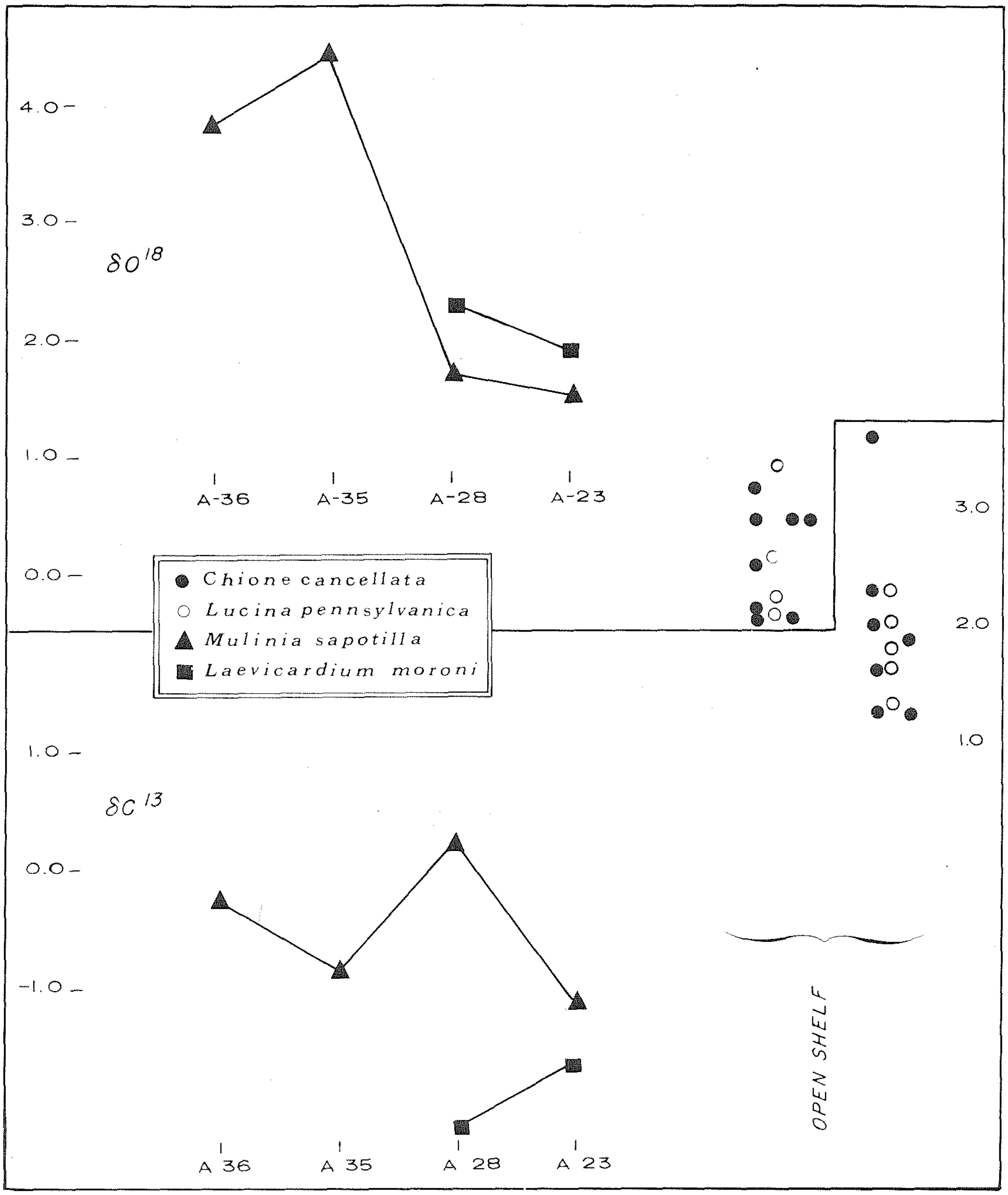


Figure 62. - δO^{18} and δC^{13} of mollusks from the brackish water marl

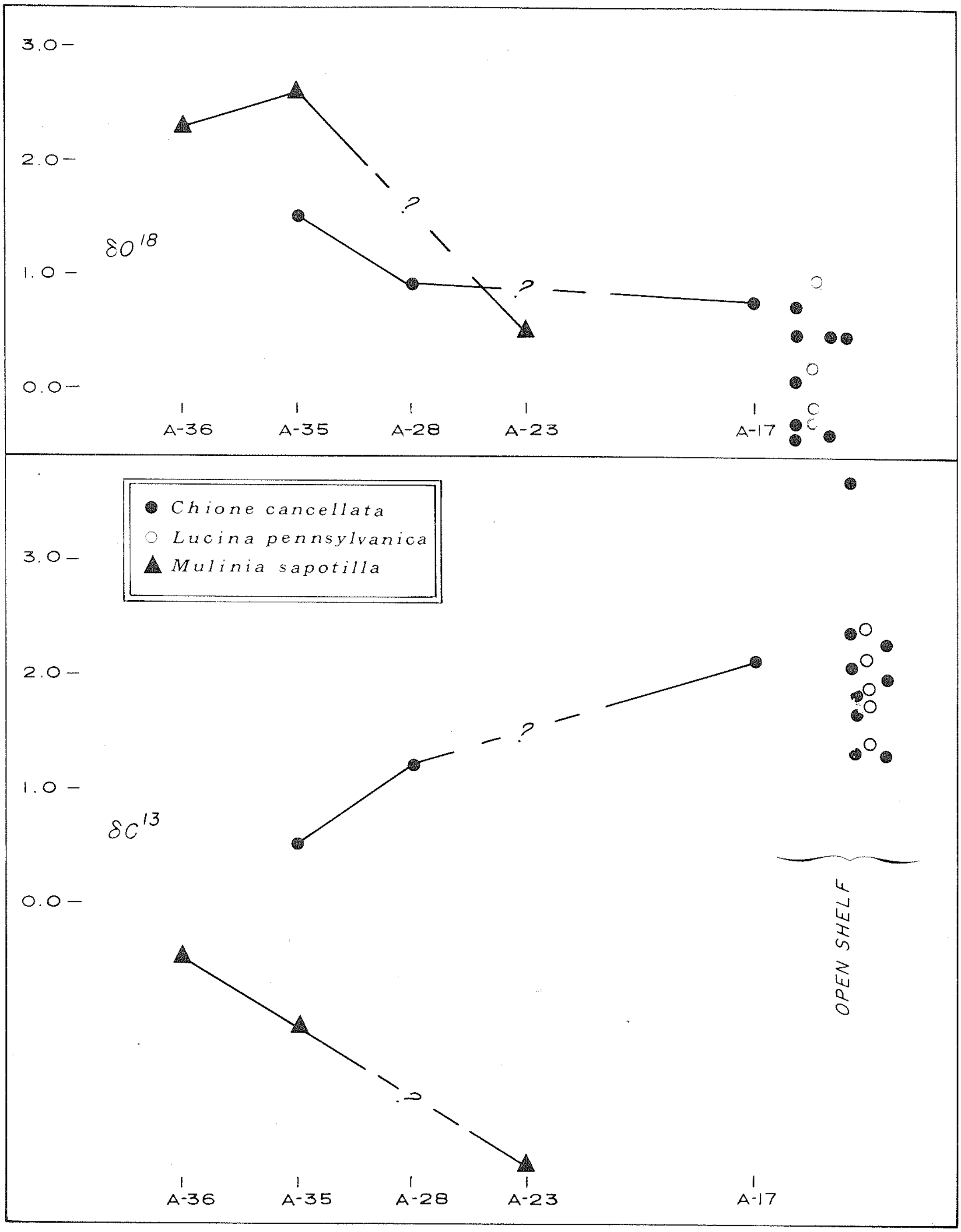


Figure 63. - δO^{18} and δC^{13} of mollusks from the Bee Branch member

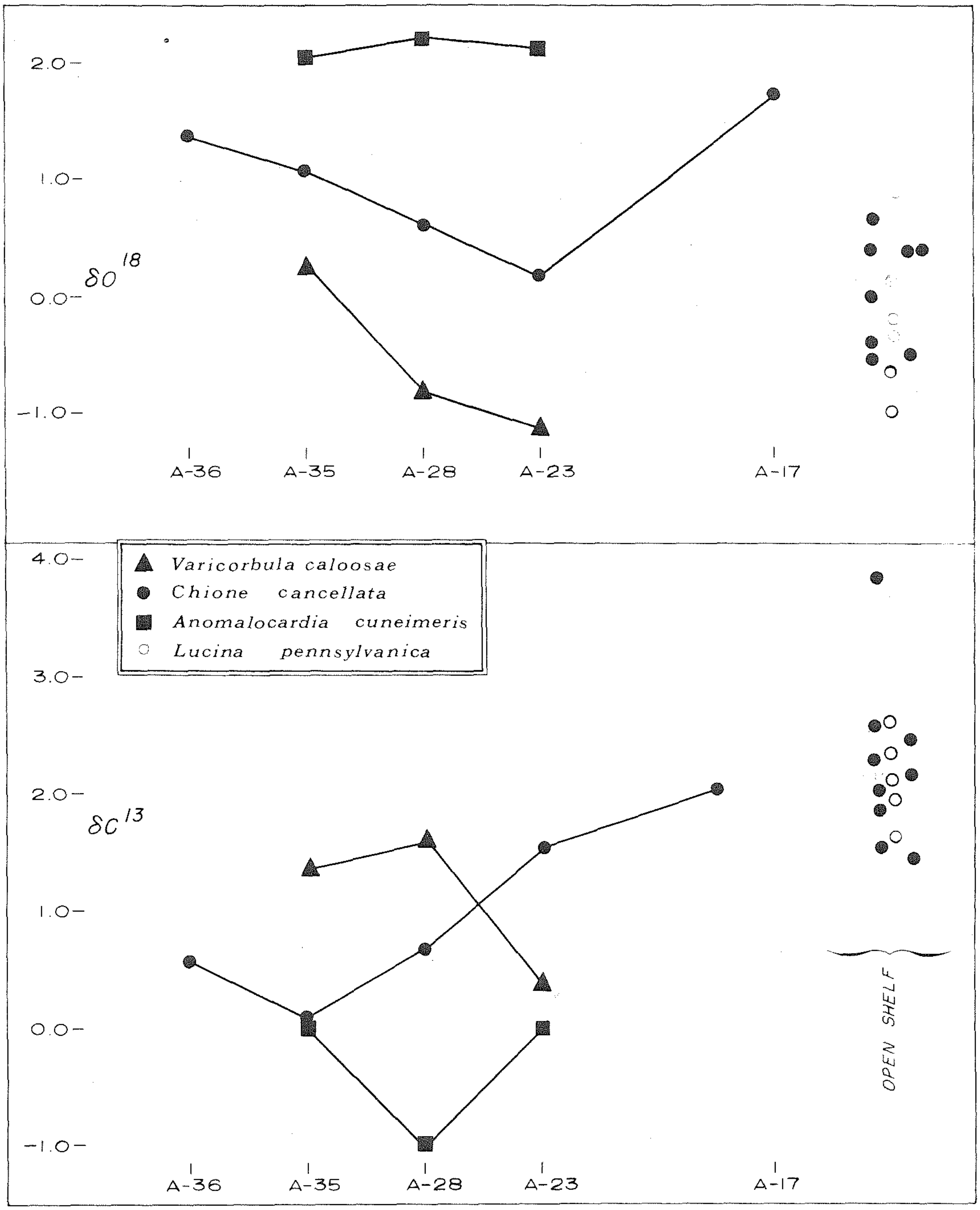


Figure 64. - δO^{18} and δC^{13} of mollusks from the Ayers Landing member

similarity in the faunal composition indicates that there are no radical differences in the environments represented (53).

Considering the geographic spread of the collections and the fact that the beds sampled are only roughly time equivalent units the values show remarkably little variation (fig. 65). The average is close to the values found in specimens living along the present-day reef tract.

In looking at the plots for the four units of the Caloosahatchee marl that were studied the following points are noted:

1) There are wide variations in δO^{18} both geographically and stratigraphically for the same species.

2) Most of the O^{18}/O^{16} ratios of the Caloosahatchee specimens are higher than those collected along the east coast.

3) There are wide variations among the various species from a given collection.

4) There is a general trend of decreasing δO^{18} going from A-36 at the west to A-23 at the east. The trend appears in all units though not in all species from a given unit.

The δ values of the Caloosahatchee shells range from -1.0 to 4.0‰ . If all the specimens had grown in water of the same isotopic composition the temperature range represented would be 25°C! Clearly, there must have been large variations in the isotopic composition of sea water during Caloosahatchee time at the locations studied.

Fort Denaud member - The two zones of the Fort Denaud member, the Cyrtopleura costata zone (fig. 61) and the brackish water marl (fig. 62), exhibit a consistent trend of decreasing δO^{18} in going from section

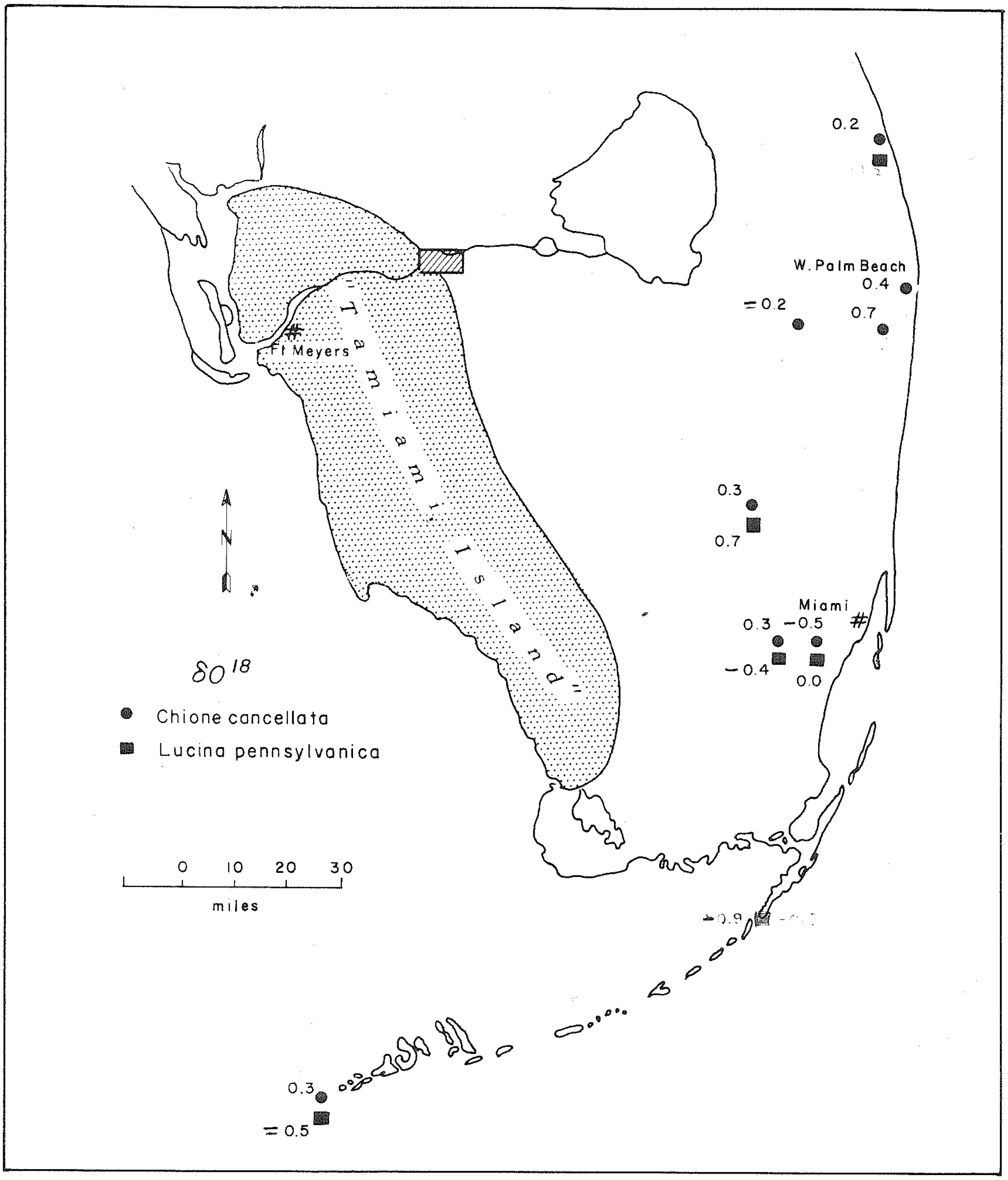


Figure 65. - δO^{18} of Pleistocene mollusks from the open shelf.

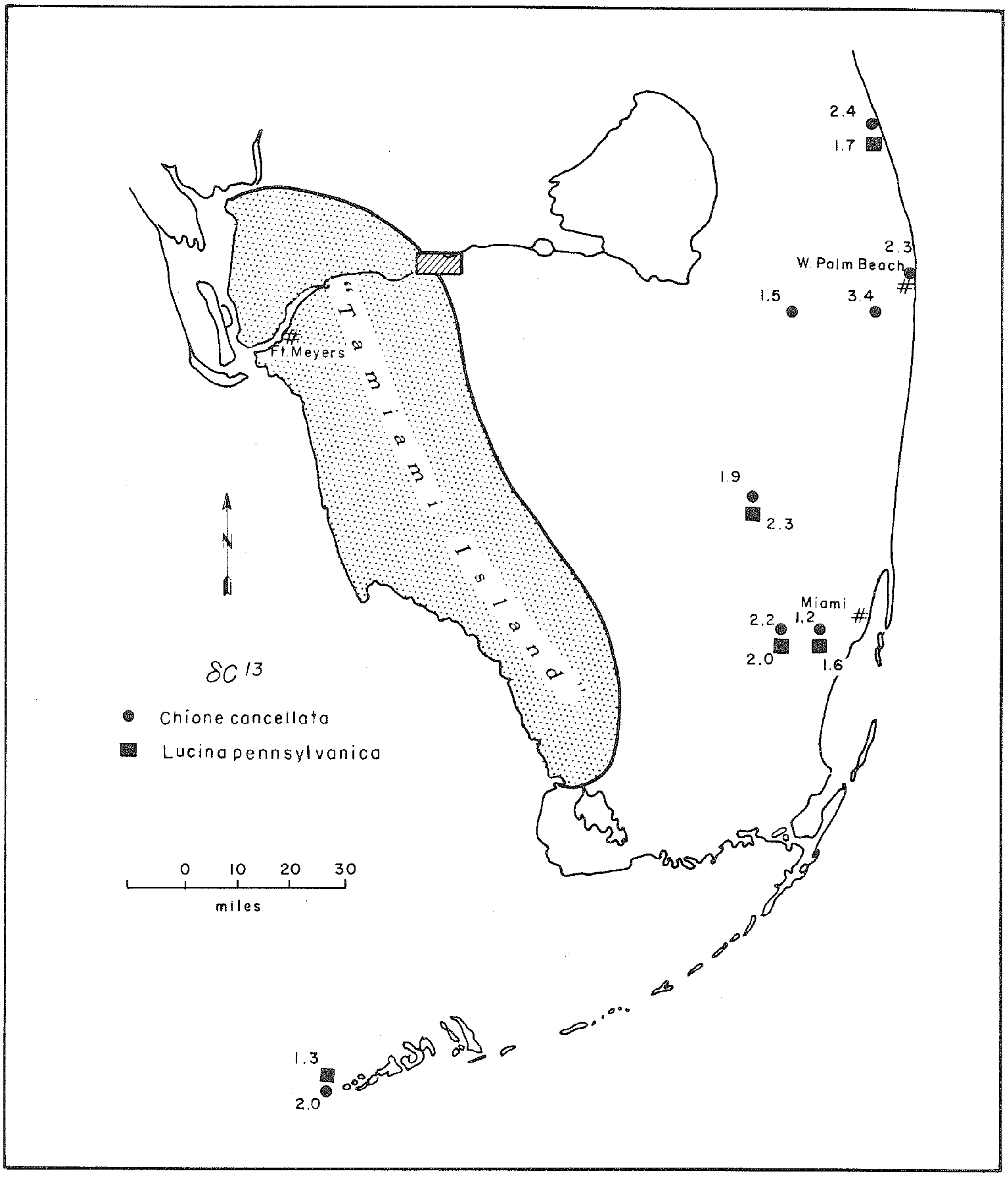


Figure 66. - δC^{13} of Pleistocene mollusks from the open shelf

A-35 to A-23. From A-23 to A-17 there is a divergence of values - *Mulinia sapotilla* getting heavier and *Cardita tridentata* getting lighter. The following relationships are also significant: (1) analyses from the brackish water marl are generally heavier than those from the *Cyrtopleura costata* zone (2) the heaviest value from the *Cyrtopleura costata* zone is from A-35 which is interpreted as being a brackish water facies and (3) the heaviest values are recorded by *Mulinia sapotilla,* a characteristic brackish water species. These three lines of evidence agree in suggesting that brackish water in the area had consistently greater values of δO^{18} than the normal sea water. The trend of decreasing δO^{18} to the east suggests that the introduction of the heavy brackish water was from a westerly direction.

Bee Branch member - The sample selection from this bed tends to bias the interpretation of the environment of deposition. The two species analyzed, *Chione cancellata* and *Mulinia sapotilla,* do not belong to the assemblage used by DuBar to characterize the environment as deep water. Characteristic deeper water specimens were not available for analysis. The shallow water forms examined yield a picture very similar to that found in the Fort Denaud member.

Ayers Landing member - The three species analyzed from this unit show a consistent wide spread of δO^{18} values at each location. *Anomalocardia caloosana* exhibits the highest values with almost no variation geographically. The species is closely related to *Anomalocardia cuneimeris* which was found to have a very limited distribution in Florida Bay. The Ayers Landing specimens are much larger than those from

Florida Bay and their relative contribution to the pelecypod assemblage is not overwhelming in any of the collections (fig. 60). There were apparently no "blooms" of this species in the sediments examined.

The values for Chione cancellata fall in a range characteristic of the east coast open shelf specimens. The trend of decreasing δO^{18} toward the east is still evident though there is a sharp upswing at the easternmost locality, A-17.

Varicorbula caloosae shows the lowest δO^{18} of any of the Caloosahatchee fossils analyzed. Recent species of this genus are found exclusively on open shallow shelves and the low values are probably indicative, in part, of good circulation. The fact that the values fall below many values of the east coast open shelf specimens suggests that only those specimens with low values in the east coast collections are really representative of open water circulation. The trend of decreasing δO^{18} from west to east is also evident in this species.

A number of specimens of Heliosoma disstoni, a fresh water snail, were found in the Ayers Landing collections. The scattered distribution of the specimens among marine forms suggests that they were washed into the area. The δO^{18} composition of one of the specimens is 7.0‰. There is no information in the literature on whether or not fresh water mollusks precipitate their shells in equilibrium with the water. The writer grew some common aquarium snails in water of known isotopic composition. Only a small increment of shell was added after three weeks at a temperature of 25°C. The isotopic temperature of the shell material was 21°C. There is no indication here that the precipitation was far enough out of equilibrium to account for the extremely high value found in the Caloosahatchee specimen. The specimen of Heliosoma disstoni apparently grew in fresh water enriched in O^{18} to a value of around 8% .

The evidence indicates that there was a persistent influx of fresh water with a high O^{18} content into the area during Caloosahatchee time. In this respect the environment of the Caloosahatchee formation resembles very closely the model described from Florida Bay in Part I. The geographic and climatic factors which control the process in Florida Bay may also apply to the Caloosahatchee formation. With this in mind the data can be examined in more detail to see how well the model fits.

The δO^{18} gradient found in each unit indicates that the fresh water was introduced from the west. In order to enrich fresh waters to such high values it is necessary that they be evaporated in ponds and lakes probably under the conditions of fractional distillation suggested for Florida Bay swamps. The steep gradient in δO^{18} and the rapid facies changes found in some beds indicate that the land area which shed the fresh water was, at times, near the sites of collection. This conclusion is consistent with the known geology in the area. Fig. 67 is a geologic cross section from data of Parker and Cooke showing variations in the Tamiami formation topography and Caloosahatchee formation thickness (59). The surfaces of both units have been greatly altered by erosion, yet the impression of a rise of the sea floor to the west in Caloosahatchee times is definitely evidenced. Though no core information is available immediately west of the area studied, it is known

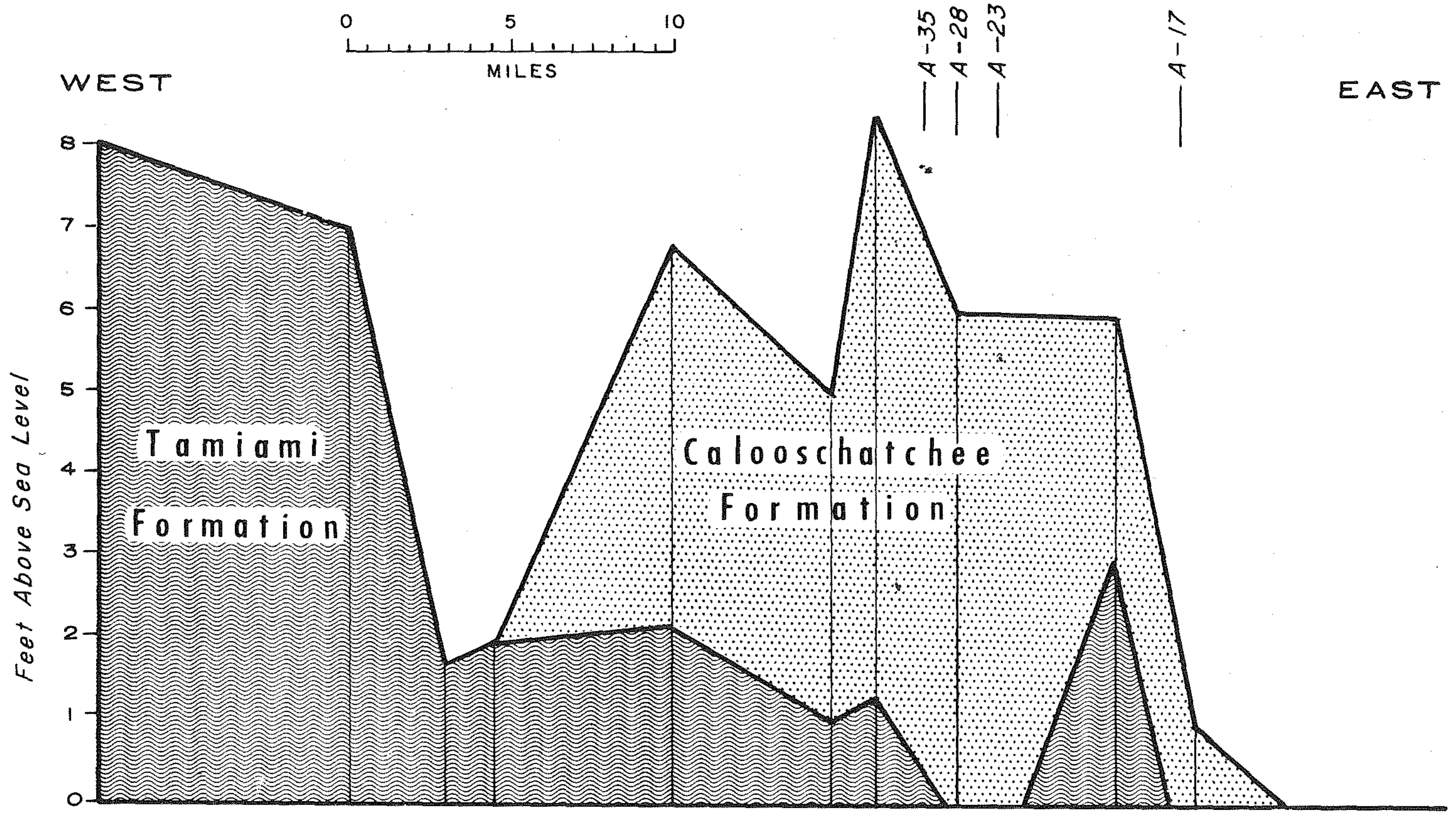


Figure 67. - Geologic cross-section along the Caloosahatchee River

that west of Fort Myers the Tamiami formation lies only a few inches below surfacial sands. South of Fort Myers the Tamiami formation is intermittently exposed in a wide band east of the present Gulf coast of Florida. Hence a considerable area of land was probably exposed during Caloosahatchee time. The approximate extent of the "island" as interpreted from the geologic map is shown in figs. 65 and 66.

In fig. 57 the approximate limits of the Caloosahatchee formation are shown in heavy dashed lines. The shaded areas indicate Tamiami formation overlain directly by Pamlico sand. The shaded area north of section A-17 is implied from the stratigraphic and topographic evidence. Fig. 67 shows a distinct rise in the Tamiami topography and fig. 58 shows a thinning of the stratigraphic section at A-17. The faunal composition at A-17 in the Ayers Landing member was also shown to bear a closer resemblance to A-35 and A-36 than to A-23 or A-28. The suggestion is supported to some extent by the isotopic data. The trend of decreasing δO^{18} to the east is reversed in Chione cancellata from the Ayers Landing member and Mulinia sapotilla of the Cyrtopleura costata zone. Cardita tridentata from the Cyrtopleura costata zone shows a continued decrease and the change in Chione cancellata from the Bee Branch member is not clear as there is no analysis from section A-23. The evidence for a land mass near A-17 is strong but the relationship of this mass to the mainland mass to the west is not clear.

The mixtures of species with widely varying ecology and the wide range of δO^{18} values found in all of the units suggest that the influence exerted by the Tamiami island on the marine environments varied.

Some of the variation could be accounted for by seasonal and super-annual climatic variations under a constant geographical framework such as is found in Florida Bay at the present time. The differences between Chione cancellata and Anomalocardia caloosana in the Ayers Landing member may be due to this. Radical changes such as the introduction of open shelf species in the Bee Branch member must be related to major sea level changes at the time which drowned the island and effectively eliminated its influence on environment in the area.

Carbon Isotope Composition

The δC^{13} values for the Pleistocene shells analyzed cover a large range and are more erratic than the δO^{18} values. The specimens collected along the east coast (fig. 66) and most of the specimens collected from section A-17 in the Caloosahatchee formation have values around 2.0‰ which is about the same value found in mollusks growing along the Florida reef tract today. The remaining Caloosahatchee specimens tend to be lighter with much local variation.

Comparison with the Florida Bay model suggests that the low C^{13} values of the Caloosahatchee marl fossils may be due to the equilibration of locally produced CO_2 with the carbonate cycle of the water. The evidence for a local source of CO_2 in the Caloosahatchee sediments is not good, however. The rocks are light tan to white in color and very coarse grained, with no sign of detrital organic material. It might be argued that any excess organic material that might have been associated with the original sediments and have contributed light carbon CO_2 to the water has since been completely oxidized. The lack of fine-grained sediment, however, indicates that the bottom sediments were well agitated and under these circumstances it is unlikely that any large amount of organic material would accumulate in them.

If locally produced CO_2 was a source of variation in the carbon isotope composition of the water it was not a persistent one as it is in present day Florida Bay. The erratic nature of the variations suggests that many processes were at work to alter the carbon isotope composition.

Strontium Composition

Ten specimens of *Chione cancellata* from various units and sections of the Caloosahatchee formation were analyzed for strontium as described in appendix A. Results of the analyses are given in table 9.

In Part I it was shown that systematic variation in the Sr/Ca ratio of Florida Bay water can occur as a result of dilution with fresh water rich in calcium ions. These variations are not reflected in any simple way in the Sr content of the Florida Bay shells because of either vital effects or the operation of some other mechanisms which alters the Sr/Ca ratio of the water.

The values for the Caloosahatchee specimens tend to be a little higher on the average than the Recent specimens from Florida Bay of the same species. This may be due to a generally higher temperature during Sangamonian time which would increase the proportion of Sr incorporated in the shell (8).

Table 9

Strontium Composition Pleistocene Fossil Shells

Chione cancellata

Member		Section	% Sr	$\frac{\text{Sr}}{1000\ \text{Ca}}$
Ayers Landing		A-36	.20	2.3
		A-35	.20	2.3
		A-28	.22	2.5
		A-23	.18	2.1
		A-17	.17	2.0
Bee Branch		A-35	.19	2.2
		A-17	.20	2.3
Fort Denaud	Brackish marl	A-35	.18	2.1
		A-23	.17	2.0
	C. costata mono	A-17	.21	2.4

Variations among the specimens analyzed are within the error of measurement. The factors that produced significant variations in the carbon and oxygen isotope chemistry of the water apparently had little influence on the Sr/Ca ratio.

CONCLUSIONS

The chemical data support the interpretation made by DuBar that the Caloosahatchee marl was deposited under a great variety of environmental conditions, most of which were characterized by restricted circulation, and that at various times the shoreline was very near the present Caloosahatchee River outcrop area. The chemical data provide the following additional information: The nearest shoreline was probably the eastern edge of a topographic high in the Tamiami formation, just a few miles west of the present outcrop area of the Caloosahatchee formation. During deposition of the Caloosahatchee formation the "Tamiami island" exerted a varying influence on the chemistry of the offshore water, at times providing dilution from fresh water run-off and at other times acting as a barrier to water circulation across the peninsula and causing hypersalinity conditions. These variations may represent seasonal or superannual climatic fluctuations at a more or less constant sea level such as is found in Florida Bay today or it may represent minor fluctuations in sea level which periodically flooded the island. In the case of the Bee Branch member the island must at one time have been deeply submerged to allow the influx of certain of the faunal elements.

δO^{18} and δC^{13} analysis appear then to be definitely useful tool for studying ancient environments. In the case cited above much of the ecological information available in the rocks could have been deduced from the faunal analyses. But faunal analysis coupled with the geochemical data provide a much more complete and exact picture of the nature of the environments, their lateral extent and their variations in time within a single unit as well as between units.

The model which was suggested by the Florida Bay situation and which seems to fit the deposition of the Caloosahatchee marl in part is, of course, not the only type of ecological framework which can be studied by these means. Estuaries, intercontinental basins, barred lagoons and other paleogeographic settings which result in variation in local water chemistry can be expected to place their stamp on the faunal composition and on the chemical composition of the organisms growing there.

With this kind of information and a proper knowledge of the geologic setting it should be possible to draw significant and far reaching conclusions about the paleogeography and paleoclimatology of an area.

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APPENDIX A

Collection and Preparation of Samples

Field Collection

Shell samples were collected by washing the sediment on nested 3/16" and 3/64" screens in the field. The sediment was scooped up in a shovel to a depth no greater than nine inches below the mud surface and placed on the top screen. The fine sediment was easily washed away by agitating the screen under water. The two sieve fractions were separately bagged and stored in a large jar with 95% alcohol.

Water samples were collected in polyethylene bottles by rinsing the bottle thoroughly in the sample water, then filling to the brim and tightly capping it.

Sediment samples were collected in a jar, fixed with 95% alcohol and tightly capped.

The sediment cores were obtained by pushing a length of 4" galvanized drain pipe into the mud, capping the pipe at the top with a stopper and lifting the pipe and sediment out of the mud. The pipe was cut into convenient lengths which were sealed at both ends with plastic sheets and tape.

Laboratory Preparation

The shell samples were thoroughly rinsed in hot tap water, then distilled water and placed in storage containers dry. Specimens used for analysis were carefully cleaned under a binocular microscope, then broken up into sand size pieces and placed in Clorox for two days. The samples were rinsed three times in hot tap water, then three times in distilled water and then dryed at 60°C. When dry the samples were powdered to pass 200 mesh and placed into vials.

Sediment samples were prepared by treating the wet sediment with Clorox for five days with periodic stirring. The sediment was washed by suspending in distilled water, allowing to settle and decanting the supernatant liquid a total of five times. After drying the sediment was ground to pass 200 mesh and stored in vials.

Organic residue from the sediments was obtained by digesting the total fresh sediment with 5% HCl until no further reaction was noted. The black residue was filtered out and washed on the filter paper with 5% HCl and then distilled water. After drying the material was ground and again allowed to soak in 5% HCl, then filtered, washed and dryed as above. The material was ground to less than 62 μ and stored in vials.

The core sections were opened by sawing lengthwise with a hacksaw. Half of the core was wrapped in polyethylene, sealed and stored. The remaining half was examined and shells removed at measured lengths. The shells were treated as above except for a preliminary soaking in a 30% Clorox-water solution to loosen sediment fillings.

Analytical Techniques

Salinity

Total salinity was determined by the standard Knudsen titration of halide with $AgNO_3$, using a potassium dichromate indicator. The burette was calibrated against Copenhagen sea water and duplicate analyses were made on each water sample. The precision is approximately ± 0.3%.

Isotope Analysis

Carbon and oxygen isotopes were analyzed on CO_2 gas produced from the samples as described below. A 60° sector 6" mass analyzer of the type described by McKinney et al (42) was used to determine the O^{18}/O^{16} (mass 46/mass 44) and C^{13}/C^{12} (mass 45/mass 44) ratios of the gas. Corrections for mixing in the values and contribution of O^{17} to mass 45 were made according to the suggestions of Craig (49).

During the period covered by the analyses given here approximately every tenth analysis made by the writer was of a primary standard. The standard was a $CaCO_3$ powder made from Recent ooliths collected in the Bahamas and all but two of the analyses were fresh preparations. The reproducibility of the standard over short periods was 0.1‰ for δO^{18} and 0.2‰ for δC^{13}. Over longer periods there were variations of the order of 0.5‰ - 0.8‰ . These appeared to be associated with changing the working standard, the standard used in the mass spectrometer to compare to the sample gas. Large drops in the oolite standard appeared when a new working standard preparation was placed in the machine.

All of the results given here were calculated against the oolite standard and then converted to the PDBI (Cretaceous Belemite standard) scale on the basis of two PDBI analyses made near the time of two oolite standard analyses. The precision is given as 0.2‰ for carbon and 0.1‰ for oxygen but the accuracy relative to the PDBI scale may not be that good.

Carbonates - CO_2 gas was evolved from carbonates by reaction with 100% phosphoric acid. Twenty mgm of cleaned and powdered sample were placed in a reaction tube. A side arm in the tube was filled with two ml of acid. The reaction tube was evacuated and then the acid allowed to react with the carbonate. The reaction proceded for 24 hours at 25°C. The CO_2 gas evolved was transferred to an analyzer sample tube after removal of air and water vapor.

Water - The oxygen isotope composition of water was determined on tank CO_2 which had been allowed to equilibrate with the water. Ten ml of the water was placed in a flask and dissolved gases removed by alternately freezing, pumping and thawing. Tank CO_2 at one atmosphere was introduced into the flask and allowed to equilibrate for one week at 25°C. Because there is about 100 times more water oxygen than CO_2 oxygen in such a system the CO_2 gas acquired the isotopic composition of the water. An aliquot of the CO_2 was transferred to an analyzer sample tube after removal of water vapor and air.

Organic material - The C^{13}/C^{12} ratio of organic materials was determined on CO_2 derived by combustion. About 25 mgm of the dry organic residue was placed in the cool section of a combustion tube attached to a gas line. The line was evacuated and the sample moved to the furnace section of the tube with a magnetic plunger. An excess of oxygen was admitted and the gases circulated through the line for one hour with a Toeppler pump. The furnace was kept at 600°C. A CuO baffle in the furnace assured complete conversion of CO to CO_2. The CO_2 produced was collected in an analyzer sample tube after removal of water vapor and air.

Mineralogical Analysis

Calcite and aragonite were determined by X-ray spectrometer. A small amount of the 200 mesh powder was allowed to fall on a very lightly greased sample disc which was then mounted in a rotating holder. The grease acted to hold the grains in their landing position and thus irradiated by CuK X-rays in a spectrometer and the peak heights recorded. The ratio of peak intensities for aragonite (26.2° 2θ) and calcite (29.4° 2θ) were compared to a plot of the same ratios determined on known mixtures of calcite and aragonite.

Trace Element Analysis

Sr and Mg were determined by emission spectrograph with a Molybdenum internal standard. Twenty-five mgm of powdered sample were dissolved in 1% HCl to which had been added a standard amount of ammonium molybdate. The solution was made up to 25 ml and allowed to equilibrate and mix for 12 hours. Standard amounts of solution were placed on each of three copper electrodes and allowed to dry under a heat lamp. The samples were excited by a D.C spark for 30 seconds on a Jarrel Ash spectrograph. In addition to the three aliquots from each sample a series of standards ranging from .05% to 2.5% Sr and Mg were also shot on each plate. After developing, the transmission of the MO 3903, MO 2848, Mg 2803, Mg 2796, Sr 4078 and Sr 4216 lines were determined. After converting transmission to intensities working curves were made from the data on the standards relating I_{Mg}/I_{MO} and I_{Sr}/I_{MO} to per cent Mg and per cent Sr respectively. Similar ratios were calculated for each of the samples and compositions read off the working curves. Compositions from all lines which had less than 5% or more than 95% transmission were discarded and the remaining values averaged to give the final Sr% and Mg%. The reproducibility of the determinations is ± 10% of the amount present.

Mg in calcite was determined by X-ray. A powdered sample was mounted in the X-ray goniometer as described in the mineralogy analysis. The counter was set for fixed count and a separate automatic timer and printer attached to the goniometer. After making 6400 counts at one position the time lapse was printed, the timer and counter set back to zero and the goniometer advanced by 0.02° 2θ, all automatically, and a new count begun. The times were plotted on reciprocal paper so that the peak position could be determined to within 0.02° 2θ. The position of the normal 29.4 calcite peak varies with the amount of Mg occupying Ca positions in the calcite lattice. The "peak shift" was compared to a calibration curve made from samples of known Mg concentration.

APPENDIX B

Table 1

Station	August, 1958 Salinity ‰	August, 1958 δO^{18} ‰	November, 1958 Salinity ‰	November, 1958 δO^{18} ‰	January, February, 1958 Salinity ‰	January, February, 1958 δO^{18} ‰
1017	36.4				31.7	1.9
1018	32.3	2.2	35.9			
1019	11.4	2.7	29.9	2.8		
1020	17.8	2.4			32.4	2.8
1021	22.7					
1022	30.0	2.4			33.2	
1023	29.8	2.4	31.5		31.5	
1024	38.2	2.6	35.3	0.7	32.7	2.6
1025	37.6	2.2			33.7	
1026	36.0				32.7	2.1
1027	31.8	2.1				
1028	17.2				31.3	2.4
1029	39.4	2.0				
1030	39.1				32.3	
1031	38.1	1.7			35.1	
1032	37.8	1.6			32.5	
1034	38.2	1.5				
1035	37.4					
1036	36.6	1.5				
1041	35.8				32.7	2.5
1042	35.2	2.6				
1043	37.4				34.6	
1044	16.6		24.5		38.4	
1050	35.7					
1051	36.5	2.3				
1053	11.8					
1054	12.5	2.9	32.8	2.4		
1055	16.4					
1056	22.6				25.6	2.3
1061	34.9	1.0			36.6	1.0
1062	35.0					
1063	36.9					

Miscellaneous Samples

Sample	Description	Date	Salinity ‰	δO^{18}
1078	Sea water from Gulf of Mexico	8/59	35.5	1.4
1080	Rain water, Everglades	8/59	0.0	-0.2
1081	Rain puddle, Everglades	8/59	0.0	0.7

Table IIa

Number* and relative percent of pelecypods in Florida Bay sediment.

		1017	1018	1019	1020	1022	1031	1032	1034	1023	1024	1025	1028	1030
Brachidontes exustus	No.	245	42	149	39	22	28	149	26	123	206	103	16	12
	%	61	7	11	4	5	20	46	10	23	81	20	11	9
Chione cancellata	No.	14	1	1	2	5	15	88	43	2	2	5	27	55
	%	3	0	0	0	2	11	27	16	0	1	1	19	40
Anomalocardia cuneimeris	No.	3	46	913	860	199	1	4	0	218	1	220	3	0
	%	1	8	69	62	47	1	2	0	41	0	43	2	0
Laevicardium mortoni	No.	38	209	59	49	14	9	14	6	4	3	6	7	0
	%	9	34	4	3	3	7	4	2	1	1	1	5	0
Cardita floridana	No.	2	4	0	0	0	41	8	67	0	0	0	0	20
	%	1	1	0	0	0	30	3	25	0	0	0	0	15
Tellina spp.	No.	59	284	195	434	176	18	40	58	187	36	172	63	42
	%	15	46	14	31	41	12	12	21	35	14	34	44	31
Misc.	No.	41	26	9	0	6	26	20	71	0	6	4	26	7
	%	10	4	1	0	2	19	6	26	0	2	1	18	5
Total	No.	402	612	1326	1384	422	138	323	271	534	254	510	142	136
	%	100	100	100	100	100	100	100	100	100	100	100	100	100

*Number of valves divided by two.

Table IIb

Number and relative percent of gastropods in Florida Bay sediment

		1017	1018	1019	1020	1022	1031	1032	1034	1023	1024	1025	1028	1030
Bulla	No.	47	114	38	140	29	1	0	4	44	44	4	2	0
occidentalis	%	18	36	31	16	4	1	0	2	22	15	1	2	0
Prunum	No.	20	4	17	40	15	0	13	12	26	19	14	18	16
apicinum	%	8	1	14	5	2	0	9	6	13	6	2	17	13
Modulus	No.	72	101	66	8	71	5	33	50	19	99	170	7	24
modulus	%	28	32	55	1	10	4	24	27	9	33	30	7	20
Tegula	No.	0	0	0	0	0	0	0	13	0	0	0	0	1
fasciata	%	0	0	0	0	0	0	0	7	0	0	0	0	1
Calliostoma	No.	0	0	0	0	0	0	0	1	0	0	0	0	29
euglyptum	%	0	0	0	0	0	0	0	1	0	0	0	0	24
Cerithium	No.	0	0	0	318	324	0	42	10	102	85	227	73	12
spp.	%	0	0	0	36	48	0	30	5	51	28	39	71	10
Misc.	No.	115	98	0	369	247	131	52	98	10	53	152	3	37
	%	45	31	0	42	36	95	37	52	5	18	27	3	31
Total	No.	254	317	121	875	686	137	140	188	201	300	567	103	119
	%	100	100	100	100	100	100	100	100	100	100	100	100	100

Table III

Strontium Composition of Shells

Station	*Anomalocardia cuneimeris*		*Brachidontes exustus*		*Cardita floridana*		*Chione cancellata*	
	Wt %	$\frac{Sr}{1000\ Ca}$	Wt %	$\frac{Sr}{1000\ Ca}$	Wt %	$\frac{Sr}{1000\ Ca}$	Wt %	$\frac{Sr}{1000\ Ca}$
1018	0.19	2.2	0.17	2.0			0.14	1.6
1019	0.17	2.0	0.15	1.7			0.14	1.6
1020	0.17	2.0	0.15	1.7			0.14	1.6
1021	0.15	1.7					0.17	2.0
1022			0.19	2.2			0.17	2.0
1024			0.16	1.8			0.14	1.6
1026	0.18	2.1	0.14	1.6			0.14	1.6
1028			0.18	2.1			0.20	2.3
1030					0.27	3.1		
1031			0.16	1.8			0.16	1.8
1032			0.24	2.8			0.14	1.6
1034					0.24	2.7	0.19	2.2
1041	0.12	1.4	0.19	2.2			0.10	1.1
1043					0.28	3.2	0.08	1.0
1053	0.17	2.0	0.23	2.6			0.16	1.8
1062							0.16	1.8
1063								
7426			0.16	1.8	0.26	3.0		

Table III (Cont.)

Station	*Bulla occidentalis*		*Modulus modulus*		*Prunum apicinum*		*Tegula fasciata*	
	Wt %	Sr/1000 Ca	Wt %	Sr/1000 Ca	Wt %	Sr/1000 Ca	Wt %	Sr/1000 Ca
1018			0.14	1.6	.31	3.6		
1019	0.30	3.4	0.19	2.2	.28	3.2		
1020			0.16	1.8	.30	3.4		
1021	0.25	2.9	0.17	2.0				
1022					.31	3.6		
1024	0.14	1.6	0.13	1.5	.23	2.6		
1026			0.10	1.1	.22	2.5		
1028	0.20	2.3	0.12	1.4				
1030							0.27	3.1
1031			0.20	2.3	.29	3.3		
1032								
1034			0.13	1.5	.22	2.5	0.24	2.7
1041					.21	2.4		
1043	0.25	2.9	0.13	1.5			0.28	3.2
1053			0.14	1.6				
1062			0.19	2.2				
1063			0.15	1.7				
7426	0.20	2.3					0.26	3.0

Table IV

δO^{18} composition of shells from Florida Bay

Station	Anomalocardia cuneimeris	Brachidontes exustus	Cardita floridana	Chione cancellata	Bulla occidentalis	Modulus modulus	Prunum apicinum	Tegula fasciata
1017		1.4				2.1	2.7	
1018	1.5	1.8			-0.4	1.3		
1019	1.6	1.9		0.4	1.7	1.7	1.6	
1020		1.8		0.3		1.8	2.3	
1021	1.0			1.0	2.2	2.3	1.0	
1022	1.7	3.6			2.5	1.2		
1023		2.1						
1024		1.6		1.6	2.0	1.3		
1025								
1026	1.7	1.5		0.6		1.4	1.7	
1028		1.5		0.4	1.8	1.9	2.4	
1029				0.2		0.6		
1030			0.9					0.4
1031		0.9	1.0	-0.3		0.3	0.5	1.5
1032		1.2		0.6				
1034			1.0	0.0	1.7	-0.1	0.6	0.9
1041	1.3	1.5		0.4	0.1	0.9		
1042	1.5							
1043			-0.1	0.3	0.5	0.3	1.6	
1044	1.3	2.0		0.5		1.1		
1053		1.5		-0.4		0.2		
1061								
1062				-0.5		-0.4		
1063						0.6		1.0
7426			0.4	0.1		0.2	0.9	
7447	2.2		1.2	1.2		0.6		

Table V

δ C^{13} composition of shells from Florida Bay

	Anomalocardia cuneimeris	*Brachidontes exustus*	*Cardita floridana*	*Chione cancellata*	*Bulla occidentalis*	*Modulus modulus*	*Prunum apicinum*	*Tegula fasciata*
1017		-0.2				-1.4	-0.7	
1018	-1.2	1.4			0.9	-1.5		
1019	-2.6	-1.8		-3.5	-0.8	0.1	-2.6	
1020		-0.4		-1.9		-0.4	-0.7	
1021	-1.4			-1.3	0.5	-0.2	-0.5	
1022	-0.7	-3.4			-0.5			
1023		0.3						
1024		0.7		0.1	1.7	0.8		
1025								
1026	-0.1	-0.3		0.1		-0.1	-2.4	
1028		0.9		-0.1	-0.8	-1.8	0.9	
1029				-0.3		0.9		
1030			1.0					1.0
1031		0.7	1.4	1.6		0.2	1.4	2.0
1032		1.2		1.0				
1034			1.6	1.1	0.5	-0.1	1.2	1.3
1041		-0.5		0.0	-1.5	-0.9		
1042								
1043			0.2	0.1	-1.1	0.0	-0.4	
1044	-1.7	-0.5		-2.0		-0.4		
1053	-3.2	-1.7		-1.0		-2.6		
1061								
1062				1.2		1.4		
1063						0.3		0.6
7426			1.7	0.0		2.1	2.4	
7447	-0.7		0.2	-0.1		1.4		

Table VI

Chemical Composition of Shells from Florida Bay Cores

Station		1052	1057	1058	1059				
Depth inches		57	63	60	31	42	55	70	79
Anomalocardia cuneimeris	δO^{18}		1.0						
	δC^{13}								
Brachidontes exustus	δO^{18}		1.4	0.7					
	δC^{13}		0.3	0.0					
Chione cancellata	δO^{18}	0.8				0.3		0.1	
	δC^{13}	-0.8				1.2		1.2	
Modulus modulus	δO^{18}	2.0	1.3	1.8	0.3	0.3	0.3	0.8	1.3
	δC^{13}	1.3		1.1	1.3	2.1	3.0	1.7	1.9

Table VII

δO^{18} Pleistocene fossil shells

Member		Section	Chione cancellata	Mulinia sapotilla	Varicorbola caloosae	Anomalocardia caloosana	Leavicardium mortoni	Cardita tridentata
Ayers Landing		A-36	1.4					
		A-35	1.1		0.3	2.1		
		A-28	0.6		-0.8	2.4		
		A-23	0.2		-1.1	2.3		
		A-17	1.8					
Bee Branch		A-36		2.3				
		A-35	1.5	2.6				
		A-28	0.9					
		A-23	1.2	0.5				
		A-17	0.7					
Fort Denaud	Brackish marl	A-36	1.3	3.8				
		A-35		4.4				
		A-28		1.7			2.8	
		A-23		1.5			1.9	
	Cyrtopleura Costata zone	A-35						2.0
		A-23		2.1				1.3
		A-17		3.1				0.6

Formation	Location	Chione cancellata	Lucina pennsylvanica
Anastasia	1007	0.2	-1.2
	1064	0.4	
	1065	0.7	
	1067	-0.2	
Miami Oolite	1010	-0.5	0.0
	1011	0.3	-0.4
	1070	0.3	0.7
Key Largo	1016		-0.9
	1038	0.3	-0.5

Table VIII

δC^{13} Pleistocene Fossil Shells

Member		Section	*Chione cancellata*	*Mulinia sapotilla*	*Varicorbula caloosae*	*Anomalocardia caloosana*	*Leavicardium mortoni*	*Cardita tridentata*
Ayers Landing		A-36	0.3					
		A-35	-0.2		-0.2	1.1		
		A-28	0.4		-1.3	1.3		
		A-23	1.3		0.1	-0.3		
		A-17	1.8					
Bee Branch		A-36		-0.5				
		A-35	0.5	-1.1				
		A-28	1.2					
		A-23		-2.3				
		A-17	2.1					
Fort Denaud	Brackish marl	A-36		-0.3				
		A-35	0.8	-0.9				
		A-28		0.2			-2.2	
		A-23	1.0	-1.2			-1.7	
	Cyrtopleura costata zone	A-35						1.7
		A-23		-1.8				0.9
		A-17		2.3				0.2

Formation	Location	Chione cancellata	Lucina pennsylvanica
Anastasia fm	1007	2.4	1.7
	1064	2.3	
	1065	3.4	
	1067	1.5	
Miami Oolite fm	1010	1.2	1.6
	1011	2.2	2.0
	1070	1.9	2.3
Key Largo fm	1038	2.0	1.3

Table IX

Partial Faunal list of Florida Bay mollusks

- Class Pelecypoda
    - Order Protobranchia
        - Family Nuculanidae
            - *Nuculana acuta* (Conrad)
    - Order Filibranchia
        - Family Arcidae
            - *Barbatia cancellaria* (Lamarck)
            - *Anadara notabilis* (Roding)
        - Family Glycymeridae
            - *Glycymeris pectinata* (Gmelin)
        - Family Mytilidae
            - *Brachidontes exustus* (Linne)
            - *Volsella americana* (Leach)
        - Family Pteriidae
            - *Pinctata radiata* (Leach)
        - Family Pectinidae
            - *Pecten ziczac* (Linne)
        - Family Ostreidae
            - *Crassostrea virginica* (Gmelin)
    - Order Eulamellibranchia
        - Family Carditidae
            - *Cardita floridana* (Conrad)
        - Family Lucinidae
            - *Phacoides multilieatus* (Tuomey and Holmes)
            - *Codakia orbicularis* (Linne)
        - Family Cardiidae
            - *Laevicardium mortoni* (Conrad)
        - Family Veneridae
            - *Anomalocardia cuneimeris* (Conrad)
            - *Chione cancellata* (Linne)
        - Family Tellinidae
            - *Tellina similis* (Sowerby)
            - *Tellina alternata* (Say)
        - Family Sanguinolariidae
            - *Tagelus divisus* (Spengler)

- Class Gastropoda
    - Order Archeogastropoda
        - Family Fissurellidae
            - *Diodora* sp.
            - *Fissurella* sp.

Table IX (Cont.)

Family Trochidae
    Calliostoma euglyptum (A. Adams)
Family Turbinidae
    Astrea longispina (Lamarck)
Order Mesogastropoda
    Family Caecum
        Caecum floridanum (Stimpson)
    Family Modulidae
        Modulus molulus (Linne)
    Family Potamididae
        Batillaria minima (Gmelin)
    Family Cerithiidae
        Cerithium muscarum (Say)
        Cerithium variabile (C. B. Adams)
        Bittium varium (Pfeiffer)
    Family Calyptraeidae
        Crepidula spp.
    Family Eratoidae
        Trivia maltbiana (Schwengel and McGinty)
Order Neogastropoda
    Family Columbellidae
        Columbella mercatoria (Linne)
        Anachis avara (Say)
        Mitrella lunata (Say)
    Family Nassariidae
        Nassarius vibex (Say)
    Family Fasciolariidae
        Fasciolaria tulipa (Linne)
    Family Mitridae
        Mitra floridana (Dall)
    Family Marginellidae
        Prunum apicinum (Menke)
Order Tectibranchia
    Family Bullidae
        Bulla occidentalis (A. Adams)
    Family Atyidae
        Atys sandersoni (Dall)
    Family Acteonidae
        Acteon punctostriatus (C. B. Adams)
    Family Ellobiidae
        Melampus coffeus (Linne)