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CHAPTER 2

THE RELATIONSHIP BETWEEN STABLE ISOTOPIC VARIATIONS (O, H, and C) AND SALINITY IN WATERS AND CORALS FROM ENVIRONMENTS IN SOUTH FLORIDA: IMPLICATIONS FOR READING THE PALEOENVIRONMENTAL RECORD

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ABSTRACT

The oxygen isotopic composition of calcareous material secreted by organisms is often used for the reconstruction of salinity values in past environments. Implicit in this reconstruction is the assumption of a constant relationship between salinity and the $\delta^{18}O$ value of water. In this paper, we demonstrate through the analysis of water samples collected from several estuaries situated adjacent to the Florida mainland that varying relationships exist between these two parameters depending upon the extent of evaporation experienced by the freshwater which influences the salinity. We further show that these relationships are translated into the $\delta^{13}C$ and $\delta^{18}O$ values of corals growing in these environments. Water samples collected from Florida Bay, Whitewater Bay, and the Ten Thousand Island area between October 1993 and December 1998 show a range of correlations between the $\delta^{18}O$ of the water and salinity. These varying correlations arise because while water from the Everglades possesses a low salinity it has a relatively positive $\delta^{18}O$ value. In contrast, precipitation has a more negative $\delta^{18}O$ value. Consequently, areas in which the salinity is significantly influenced by freshwater derived from the Everglades tend to have different $\delta^{18}O$ to salinity relationships compared to regions where salinity variations are caused solely by inputs of precipitation. These variations must be recognized if one is to use proxy indicators of salinity such as the $\delta^{18}O$ value of skeletal carbonates to accurately reconstruct past salinity records.

The $\delta^{13}C$ of estuarine waters is related to both the input of isotopically depleted runoff from the Everglades and the local remineralization of organic material. Areas far removed from Everglades runoff, where variations in salinity resulted from input of precipitation, show little relationships between salinity and $\delta^{13}C$ because $\delta^{13}C$ variations arise from the local remineralization of organic material. In contrast, areas closer to the Everglades show stronger relationships between salinity and $\delta^{13}C$. These relationships are manifested in the isotopic composition of the coral skeleton as an absence of correlation between $\delta^{13}C$ and $\delta^{18}O$ in more marine areas compared to areas more directly influenced by runoff.

INTRODUCTION

The $\delta^{13}C$ and $\delta^{18}O$ values of calcareous organisms (ostracods, foraminifera, molluscs, and corals) have been used in the South Florida environment to ascertain changes in past environmental conditions, in particular salinity (Swart *et al.*, 1996; Swart *et al.*, 1999; Halley and Roulier, 1999; Nelsen *et al.*, 2000). The results of these studies indicate a change in salinity patterns commencing in Florida Bay as early as 1900. A concurrent shift in the $\delta^{13}C$ in both corals and molluscs suggest that a reduction in the hydrodynamic circulation of Florida Bay may be responsible for the observed changes in salinity. Construction of the Overseas Railway from Miami to Key West from 1906–1914, followed by water management practices which diverted the natural flow of water from the Everglades into Florida Bay have been suggested as possible causes for the reduced circulation within Florida Bay (Smith *et al.*, 1989; Swart *et al.*, 1996, 1999).

Anthropogenic changes in South Florida occurred synchronously with climatic variability. Regional droughts have been recorded in every decade from 1950 to 1990 resulting in salinity exceeding 50 in the central portions of Florida Bay (Fourqurean and Robblee, 1999; Fourqurean *et al.* 1992). In contrast, the 1997 El Niño, termed the "El Niño of the Century" produced above average rainfall during the winter dry season in South Florida. Decoupling these natural climatic conditions from anthropogenic conditions is important in deciphering the paleoenvironmental record.

This paper examines the associations between salinity, precipitation, and the $\delta^{18}O$, δD, and $\delta^{13}C$ of surface waters from 'fresh', estuarine, and marine environments of South Florida and relates these data to the interpretation of the $\delta^{13}C$ and $\delta^{18}O$ record of two corals growing in Florida Bay. In order to study these relationships, we have conducted a temporal and spatial investigation of the $\delta^{18}O$, δD, and $\delta^{13}C$ composition of

waters from the Everglades, Florida Bay, Whitewater Bay, and the Ten Thousand Islands areas. These data were then correlated with salinity measurements made on the same samples (Boyer et al., 1999).

BACKGROUND

HYDROLOGICAL SYSTEM IN SOUTH FLORIDA

South Florida experiences a subtropical climate with a hot, wet season during the summer (mid-May–October), and a mild, dry season during the winter (November–mid-May). Annual precipitation is approximately 130 to 150 cm across the region, with approximately 70% received during the summer wet season (Leach et al., 1972). The seasonality of precipitation and evaporation causes a seasonal fluctuation in surface water levels in South Florida. Water levels rise during the summer rainy season, with highest levels commonly observed in September and October. During the winter dry season, water levels decline slowly. Surface water can be absent from many areas of the Everglades at the end of the dry season (April and May) as evapotranspiration exceeds rainfall (Kushlan, 1990).

The Everglades depression extends southward from Lake Okeechobee to Florida Bay and is bounded to the east by Pleistocene limestones and quartz sands of the Atlantic Coastal Ridge and to the west by exposed Pliocene limestones of the Big Cypress Ridge. Holocene freshwater peats and marls partially fill the Everglades trough, decreasing in thickness southward from 4 m at the southern end of Lake Okeechobee to 0.7 m along the coastline of Florida Bay (Kushlan, 1990). Under natural, pre-development conditions, most surface water flowed southward in the Everglades from Lake Okeechobee to the Gulf of Mexico via the Shark River Slough (Fennema et al., 1994). A smaller drainage area, Taylor Slough, discharged locally derived freshwater into Florida Bay. Beginning in the late 1800s and throughout the 1900s, a complex network of canals, levees, pump stations, and impoundment areas were constructed throughout South Florida in an effort to manage water levels and flow throughout the region. Because of the resultant impoundment of water in what are known as conservation areas, evaporation is high, with estimates of rainfall lost to evapotranspiration being as high as 70% to 95% (Leach et al., 1972). This decreased surface water flow from Lake Okeechobee, through the Everglades to the marine systems of the Gulf of Mexico and Florida Bay, and increased drainage eastward toward Biscayne Bay (Fennema et al., 1994).

Marine environments that bound the southern peninsula of Florida include the Gulf of Mexico to the west, Biscayne Bay to the east, and Florida Bay to the south. The west coast from Cape Romano in the north to Cape Sable in the south, is characterized by mangrove swamps, tidal channels and small bays. The northern section contains numerous mangrove islands separated by tidal channels with strong currents and is referred to as the Ten Thousand Islands (TTI) area. South of the TTI, tidal currents are more sluggish and freshwater runoff from the Big Cypress Swamp and the Everglades is transported to the Gulf of Mexico by numerous streams (Davis, 1997).

Florida Bay is a large (2,000 km^2) triangular shaped estuary lying between the Southern Peninsula of Florida and the Florida Keys. Florida Bay is relatively shallow and underlain by a complex system of Holocene carbonate mud-banks that subdivide Florida Bay into smaller basins. Water in Florida Bay is a mixture of precipitation, freshwater runoff from the Everglades, and seawater from the Gulf of Mexico and the Florida Straits. These sources combined with evaporation results in salinity variations from 4 to 50 (Nuttle et al., 2000).

STABLE ISOTOPES

The major influence on variations in the ratio of ^{18}O to ^{16}O and D to H in the water cycle occurs during the processes of evaporation and precipitation (Craig and Gordan, 1965). During evaporation, the concentrations of ^{18}O and D are reduced in the water vapor while these same species are enriched in the condensate. As a consequence, restricted bodies of water become enriched in the heavier isotopes during evaporation while precipitation is typically enriched in ^{16}O and H. Precipitation throughout the world has been measured by the International Atomic Energy Authority (IAEA) and this data set shows that precipitation values become increasingly depleted towards the north and south poles (Rozanski et al., 1993). In South Florida the IAEA data estimates that rainfall should have a $\delta^{18}O$ value between -2 and $-4‰$. The behavior of the isotopic composition of water during evaporation and
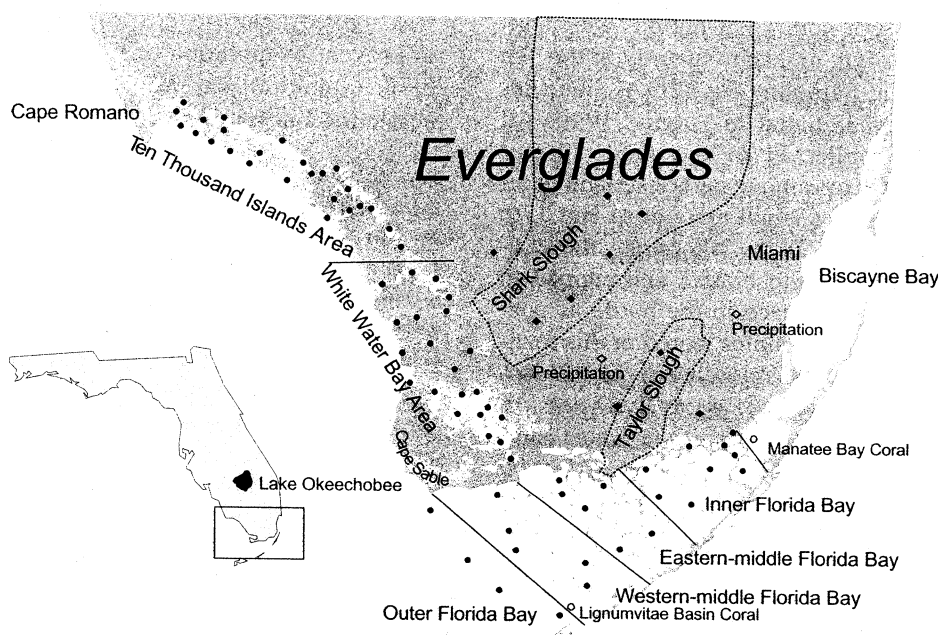
Text-figure 1.—Location map of water sampling stations within each geographic region.

precipitation can be modeled using the Rayleigh Distillation Equation. However, the maximum amount of enrichment in the heavier isotope that can be experienced by an evaporating water body is limited by subsequent exchange between the atmospheric moisture and the water body. The resulting isotopic composition that can be attained during evaporation is a function of the relative humidity, temperature of evaporation, and the isotopic composition of the atmosphere. The principals which govern the isotopic composition of such water bodies have been well studied and for further discussion the reader is referred to Gat (1981) and Gonfiantini (1986). For an environment such as South Florida where the mean relative humidity is 75%, the maximum $\delta^{18}O$ and δD that can be attained by the water body undergoing evaporation are approximately +4‰ and +42‰, respectively. Although the δD vs. $\delta^{18}O$ of most precipitation throughout the world falls along a line known as the meteoric water line (MWL) (Craig and Gordan, 1965), data from evaporating water basins, when plotted on a similar diagram, fall on lines which deviate from the MWL depending upon the relative humidity. For example, environments with high relative humidity fall close to the MWL with a slope of 8, while waters evaporated into an environment with a lower relative humidity will plot on a line with a slope significantly less than 8 (Gonfiantini, 1986).

The dissolved inorganic carbon (DIC) pool is composed of CO_2, HCO_3^-, and CO_3^{2-}. In waters of pH between 7 and 9, the DIC is dominated by HCO_3^-. Although there is a large fractionation factor between CO_2 and HCO_3^- (e = 8‰), the measured isotopic composition of the DIC reflects that of the HCO_3^- fraction. Hence when CO_2 is added to water the isotopic composition of the HCO_3^- will be approximately 8‰ heavier than that of the CO_2.

The $\delta^{13}C$ of the DIC is governed by the input of respiratory carbon delivered to the system through the respiration of organic material and the consumption of CO_2 through the process of photosynthesis. As organic material contains less ^{13}C than DIC which is in equilibrium with the atmosphere, addition of oxidized material will cause the $\delta^{13}C$ of the DIC to become enriched in the lighter isotope of C (^{12}C). Terrestrial organic materials tend to have more negative $\delta^{13}C$ values than marine material, and therefore waters derived from terrestrial sources associated with the oxidation of organic material often have more negative isotopic signatures than waters derived from marine sources. In a relatively closed system, the utilization of CO_2 in the process of photosynthesis can cause the residual pool of carbon in an environment to become enriched in ^{13}C. Hence algal blooms for example could lead to more positive DIC $\delta^{13}C$ values.

METHODS

WATER SAMPLE COLLECTION

Surface water samples were collected monthly since October 1993 in Florida Bay (Text-fig. 1). In October

1996 and February 1997, additional stations were added first in Whitewater Bay and subsequently in the Ten Thousand Islands area. Sampling for $\delta^{18}O$ at nine sites in the Everglades was initiated in August 1996. All water samples were collected in the field, filtered through a 0.45 μm filter to remove carbonate and other particles, and treated with a small amount of $HgCl_2$ to suppress biological activity. In the laboratory, the samples were transferred to serum bottles and capped to exclude as much of the air space in the bottle as possible. Repeated analyses of samples stored in this manner have not detected appreciable change in the isotopic composition over periods of up to five years.

Salinity was measured at each surface water sampling location (except for the Everglades locations) by Florida International University/Southeastern Environmental Research Program (FIU/SERP). A summary of these data has been published by Boyer *et al.* (1999). Automated water salinity monitors were deployed at three locations in Florida Bay: Lignumvitae Basin, East Key and Manatee Bay. Hourly salinity data were obtained using a Hydrolab Datasonde 3 between 1995 and 1998 in Lingnumvitae Basin. Similar data from East Key and Manatee Bay were collected over shorter time periods. Each instrument was serviced at 6 to 8 week intervals. Servicing consisted of cleaning organisms which encrusted the housing and sensors, replacing batteries, and calibrating the instrument for salinity. Drift in the instrument within a given sampling period was corrected by measuring the salinity and temperature with the instrument at the beginning and end of each deployment period and assuming a linear instrument drift during the deployment period.

Precipitation samples were collected between August 1997 and December 1998 from two locations on the South Florida mainland. At the Redlands site, located southwest of Miami, precipitation was collected in a bottle equipped with funnel and tube. On a daily basis, the contents of the bottle were transferred to another bottle that was kept indoors and capped to form a bi-weekly to monthly composited sample. Daily amounts of precipitation were recorded with a standard wedge gage. Precipitation was also collected behind the Iori Building within Everglades National Park from December 1997 through December 1998, using an Aerochemetrics Wet/Dry collector. This collector consisted of two buckets, one to collect dry deposition and the other to collect wet deposition. The instrument was equipped with a heated sensor that when wet activated a mechanical arm that moved a cover from the wet collection bucket to the dry collection bucket, thereby exposing the wet collection bucket to rainfall. The heated sensor allowed for evaporation of rainfall that collected on it, and once dry, the mechanical arm was moved again to cover the wet collection bucket to prevent evaporation of the rainfall sample. Amount of precipitation was measured directly from the wet collection bucket using a ruler.

Carbon Isotopic Composition of Dissolved Inorganic Carbon (DIC)

The $\delta^{13}C$ of waters was measured using two methods.

Method 1: The $\delta^{13}C$ of the DIC for samples collected early in the project were determined by acidification under vacuum. Prior to analysis a sample (5 cc) was withdrawn from the serum bottle through a septum. The displaced volume of water was replaced by nitrogen gas. To acidify the sample it was injected into a sealed vessel through a septum which contained 0.5 cc of H_3PO_4. The sample and acid were then removed from the vacuum line and thoroughly shaken. The vessel was then reattached to the vacuum line and after evacuation the CO_2 produced was allowed to expand through a water trap and then frozen with liquid nitrogen into a vacuum vessel. The vessel was subsequently attached to a stable isotope mass spectrometer (Finnigan-MAT 251) and the ratios of $^{13}C/^{12}C$ and $^{18}O/^{16}O$ determined in a similar manner to the CO_2 produced from the acidification of carbonate. Standards were made by dissolving $NaHCO_3$ of known $\delta^{13}C$ in 18.3 Mohm water to make a 4 mM solution. Standardization is relative to PDB and data are reported in conventional δ units. Reproducibility was determined by replicate analysis of the same sample and has been measured at $\pm$ 0.1‰.

Method 2: The $\delta^{13}C$ of the DIC for samples collected during the latter stages of the project was determined using a continuous flow mass spectrometer. In this technique a vial with a septum containing 0.5 cc of ortho-phosphoric acid was evacuated. Two-cc of the sample was injected into the vial and thoroughly shaken. The sample was then placed along with other samples and standards in an autosampler (Gilssen) attached to a continuous flow isotope ratio mass spectrometer (Europa 20–20). Each sample in turn was purged by helium and the water removed using magnesium perchlorate. The CO_2 produced by the reaction of the acid with the dissolved inorganic carbon (DIC) was passed through a packed GC column (75°C) and then analyzed using the mass spectrometer. In this method up to 200 samples can be processed in one batch. The precision of this method is approximately the same as in the acidification under vacuum method ($\pm$ 0.1‰).

OXYGEN ISOTOPIC COMPOSITION OF WATERS

The $\delta^{18}O$ of water was determined using the Epstein and Mayeda (1953) method of equilibration. Two adaptations of this method were used.

Method 1: In this technique, 1 cm^3 of sample was placed in a vacuum vessel and all air removed through a process of freezing, pumping and thawing. After all air was removed, each flask was flooded in turn by 1 atm of CO_2 and the flask sealed. The water and the carbon dioxide were then allowed to equilibrate at 40°C overnight. In this process the oxygen in the water isotopically exchanged with the CO_2. The CO_2 then attained an isotopic composition representative of the water, although offset through a fractionation factor. In each run 14 samples and 2 standards were equilibrated with CO_2. Standards are related to V-SMOW through simultaneous equilibration with samples of V-SMOW distributed by the National Bureau of Standards (NBS). Reproducibility was determined by replicate analysis of the same sample and has been measured at ± 0.1‰.

Method 2: In this method the entire process including the flushing of the samples with CO_2, equilibration, and extraction was handled automatically. The process was controlled by a computer interfaced to a mass spectrometer (Europa GEO) and an equilibration unit (Europa WES). In each experiment, 0.5 cc of sample was placed in a small serum vial with a septum top. These samples were flushed with CO_2 at atmospheric pressure and allowed to equilibrate for 12 hours at 35°C. The CO_2 was then extracted through a cryogenic water trap and the isotopic composition determined using a mass spectrometer. A series of 59 specimens (including samples and standards) was analyzed in a 12 hour period. The reproducibility was approximately 0.08‰.

HYDROGEN ISOTOPIC COMPOSITION OF WATERS

The δD of the water was determined using two methods. Initial samples were analyzed using the first method described for each of the elements. Later samples, 1995 to the present, were analyzed using the second method. In both methods, data are reported relative to V-SMOW.

Method 1: The first method utilized the reduction of H_2O to H_2 gas using uranium at 800°C (Friedman, 1953). The hydrogen gas was then analyzed using a stable isotope mass spectrometer (Finnigan MAT 251).

Method 2: The second method used an equilibration technique between H_2 gas and H_2O in the presence of a platinum catalyst (Hokko beads) (Coplen *et al.,* 1991). This method was used in conjunction with the second method of determining the $\delta^{18}O$ of water using the GEO and WES. In this method the same samples which were used for the determination of the $\delta^{18}O$ were flushed with H_2. The equilibration between H_2 and H_2O occurred in a period of 30 minutes, allowing for analysis of the first equilibrated samples immediately following flushing of the last sample H_2. Precision of this method determined by replicate analyses of the standards within each run is approximately 1.5‰.

CORALS

A specimen of *Solenastrea bournoni* was cored in Lignumvitae Basin of Florida Bay in 1986 and 1993. Isotopic analyses from this specimen were reported by Swart *et al.* (1996, 1999). In 1996, a specimen of *Solenastrea hyades* was collected from Barnes Sound, near the mouth of Manatee Bay in northeast Florida Bay.

Coral cores were sliced into sections parallel to the axis of coral growth. Core sections were then subjected to X-radiography to facilitate the construction of annual coral chronologies. Skeletal coral carbonate was sampled for $\delta^{13}C$ and $\delta^{18}O$ using methods described previously (Swart *et al.*, 1999). A powdered calcium carbonate was collected in transects from coral slabs using a computer-controlled drilling apparatus. All carbonate samples were processed on a Finnigan MAT 251 Mass spectrometer connected to an automated extraction devise at the University of Miami. Data are presented in standard delta notation relative to PDB.

RESULTS

ISOTOPIC COMPOSITION OF WATERS

The $\delta^{18}O$ of precipitation reported in this study in the South Florida area is highly variable. Despite this variability, the data fall near the MWL and have volume weighted mean values for $\delta^{18}O$ and δD of −2.9‰ and −9.9‰, respectively (Table 1). The $\delta^{18}O$ data agree well with precipitation data collected between 1983 and 1988 (Swart *et al.*, 1989) that have mean $\delta^{18}O$ and δD values of −2.7‰ and −11.4‰, respectively. Actual $\delta^{18}O$ values of the precipitation ranged from values as negative as −6‰ during the wet season to values close to 0‰ during the drier portions of the year.

Water from the Everglades is significantly enriched in ^{18}O and D with respect to precipitation (Table 1). Mean $\delta^{18}O$ for the Everglades samples is +0.55‰, compared to −2.9‰ for precipitation. The highest values occur during the end of the dry season (March–May) with isotopically more negative values in the late wet season (Text-fig. 2). The $\delta^{18}O$ and δD data fall on a line with a slope of 5.8 ($R^2 = 0.75$), less than the slope of 8 for the MWL (Text-fig. 3). Although $\delta^{13}C$

Table 1.—Statistical summary of stable isotope and salinity data for surface waters by area and precipitation in South Florida.

Area	Number of samples	Mean $\delta^{18}O$	S.D. (a) $\delta^{18}O$	Mean δD	S.D. δD	Mean $\delta^{13}C$	S.D. $\delta^{13}C$	Mean Salinity	S.D. (a) Salinity
Everglades	221	0.55	1.59	6.75	10.83	−6.9*	1.9*	(c)	(c)
Florida Bay (total)	1318	1.62	1.00	11.35	6.66	−2.87	2.32	27.9	9.6
Inner	427	1.76	1.06	11.83	7.30	−3.39	2.16	21.6	9.2
Eastern Middle	240	1.80	0.96	11.64	7.39	−2.95	2.45	31.5	6.8
Western Middle	194	1.55	0.67	10.99	5.63	−2.77	2.35	33.9	3.6
Outer	151	1.41	0.60	9.50	4.99	−2.29	2.39	33.8	2.9
Whitewater Bay	247	1.58	1.19	10.07	8.07	−7.33	1.85	13.5	10.1
Ten Thousand Islands	259	1.06	1.31	7.12	7.89	−5.76	2.34	21.6	11.6
Precipitation (b)	23	−2.9	1.48	−9.95	11	(c)	(c)	(c)	(c)

(a) Standard deviation.
(b) Isotopic means for precipitation are weighted by the amount of precipitation.
(c) Not measured.
* Meyers (1990).

of Everglades waters were not measured in this study, they were reported in Meyers (1990) and included in Table 1 for comparative purposes. In general, the isotopic composition of DIC in Everglades waters were negative with a mean $\delta^{13}C$ of −6.9‰ (Meyers 1990).

The $\delta^{18}O$ of the water in all of the Florida Bay samples ranges from −2.9 to +5.7‰ with a mean of +1.62 (Table 1). The $\delta^{13}C$ for all of the Florida Bay samples (−2.87‰) is higher than that reported for the Everglades (−6‰; Table 1). A time series of the mean d¹³C values for all stations in South Florida indicate a minimum in 1996 (Text-fig. 4).

The mean $\delta^{18}O$ for the Whitewater Bay and Ten Thousand Islands areas are positive and +1.58‰ and +1.06‰, respectively (Table 1). In contrast, the mean $\delta^{13}C$ for both Whitewater Bay and the Ten Thousand Islands area is significantly negative with values of −7.33‰ and −5.76‰, respectively (Table 1). These values are similar to those reported for the Everglades (Table 1) by Meyers (1990).

COMPARISON OF OXYGEN AND CARBON ISOTOPIC COMPOSITION WITH SALINITY

In order to examine the variation in the relationships between $\delta^{18}O$, $\delta^{13}C$, and salinity further, we have separated Florida Bay into four regions: Inner Florida Bay, Eastern-middle, Western-middle, and Outer Florida Bay (Text-fig. 1). Salinity within these regions increases from east to west across Florida Bay (Table 1), typical of an estuary. The Inner Florida Bay region has the lowest mean salinity of 21.6, while the Western-Middle and Outer Florida Bay regions have a similar mean salinities of 31–33. In general, the mean $\delta^{18}O$ decreases from east to west across Florida Bay from +1.8 to +1.4‰ (Table 1).

The relationships between $\delta^{18}O$ and $\delta^{13}C$ with salinity of South Florida estuarine waters are investigated by using $\delta^{18}O$ vs salinity and $\delta^{13}C$ vs salinity plots and

then fitting a linear regression through the data (Table 2). When the $\delta^{18}O$ for each site in Florida Bay is averaged on a monthly basis and compared to the corresponding mean monthly salinity for each station, there is a positive linear correlation ($R^2 = +0.36$; $p < 0.01$) (Text-fig. 5). There is a positive linear relationship between $\delta^{18}O$ and salinity for each of the four regions of Florida Bay (Table 2; Text-fig. 6). Although the linear regression can explain only 30 percent or less of the variation between $\delta^{18}O$ and salinity in the Florida Bay regions (Table 2), each of the linear regressions are significant at $p < 0.01$. The linear relationship between $\delta^{18}O$ and salinity was strongest for the two middle regions of Florida Bay ($R^2 = 0.3$), and weakest for the Outer region of Florida Bay ($R^2 = 0.09$).

There is a variation in the intercepts of the linear regressions for each of the regions in Florida Bay. The linear regressions for the Inner and Eastern-middle areas of Florida Bay predict a $\delta^{18}O$ at zero salinity of +0.33‰ and −0.83‰, respectively. The predicted intercept of the linear relationship at zero salinity for the Western-middle and Outer areas of Florida Bay are
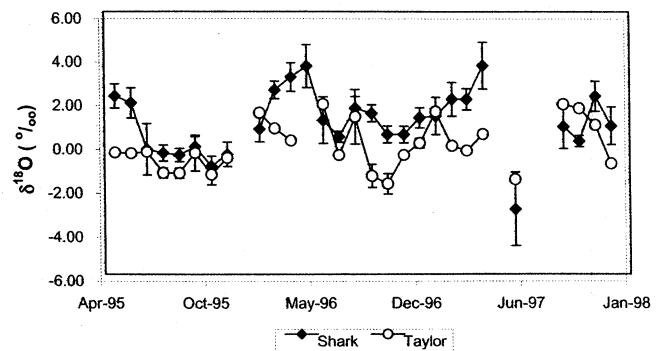
Text-figure 2.—Time series of mean $\delta^{18}O$ for Everglades. Error bars represent ± 1 standard deviation.
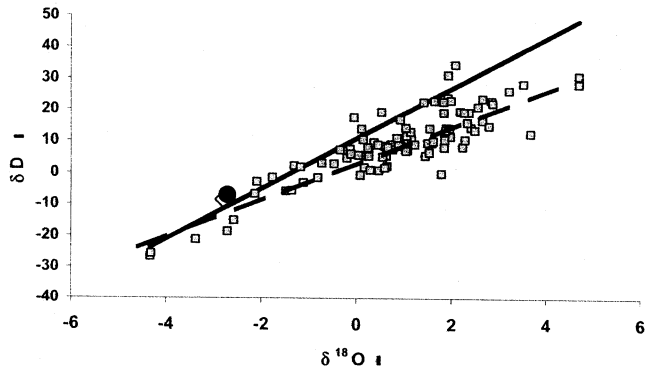
Text-figure 3.—Oxygen and hydrogen isotopic composition of Everglades water. Black circle represents volume weighted average isotopic composition of rainfall collected in this study. Open triangle represents isotopic composition of rainfall reported by Swart *et al.*, 1989.
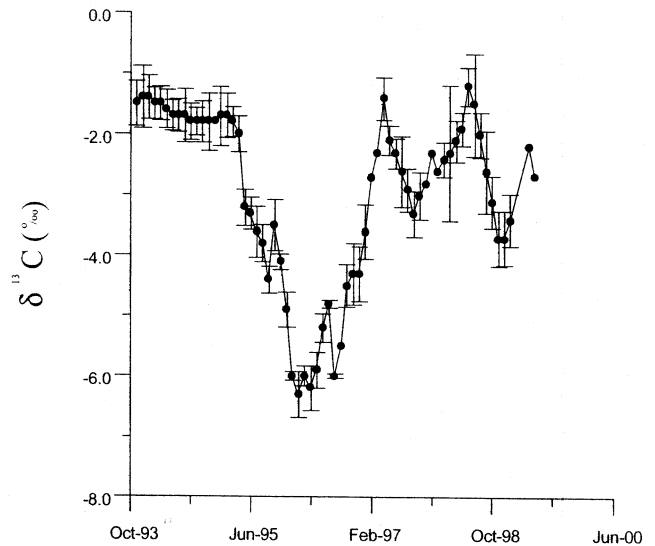

Text-figure 4.—Five month running mean of the $\delta^{13}C$ composition of the DIC in all regions studied. Error bars represent ± one standard error.

significantly more negative than zero at $-2.39\%o$ and $-1.07\%o$, respectively.

A positive linear relationship exists between $\delta^{18}O$ and salinity for the Whitewater Bay and Ten Thousand Islands areas (Table 2). The linear correlation coefficient (R^2) for the Whitewater Bay and Ten Thousand Islands is 0.34 and 0.28, respectively (p < 0.01). The predicted intercept of the linear relationship at zero salinity is close to zero for both the Whitewater Bay ($+0.35\%o$) and Ten Thousand Islands areas ($-0.2\%o$, Table 2).

There is no strong linear correlation between $\delta^{13}C$ and salinity throughout all of Florida Bay (Text-fig. 7). Similarly there is no strong linear correlation between $\delta^{13}C$ and salinity within the four regions of Florida Bay (Table 2; Text-fig. 8), except for the Inner Florida Bay area. The Inner Florida Bay area, Whitewater Bay area and the Ten Thousand Islands areas have similar correlations ($R^2 = 0.2$; p < 0.01) between $\delta^{13}C$ and salinity.

CORALS

The $\delta^{13}C$ and $\delta^{18}O$ data for the skeleton of the coral collected from Lignumvitae Basin have been reported previously (Swart *et al.*, 1996; 1999). The average an-

nual values for both corals are shown in Text-figure 9. The Manatee Bay coral ($-2.58 \pm 0.3\%o$) is slightly isotopically enriched in $\delta^{18}O$ relative to the Lignumvitae coral ($-2.04 \pm 0.5\%o$), and has more negative $\delta^{13}C$ values ($-6.45 \pm 0.43\%o$ vs. $-3.25 \pm 0.58\%o$ for the Manatee Bay coral).

CONTINUOUS SALINITY MONITORING DATA

Continuous salinity data collected from Lignumvitae Basin in Florida Bay are shown in Text-figure 10. The continuous data from Lignumvitae Basin have been averaged into monthly values and are plotted with the FIU/SERP data. The FIU /SERP data represent water samples collected on a single day within the month. Generally the agreement between the two datasets is excellent considering the different temporal resolution between them.

DISCUSSION

SOURCES OF SALINITY VARIATION

Relatively few studies have examined the $\delta^{18}O$ and δD of precipitation in South Florida. The data pre-

Table 2.—Results of linear regression analyses.

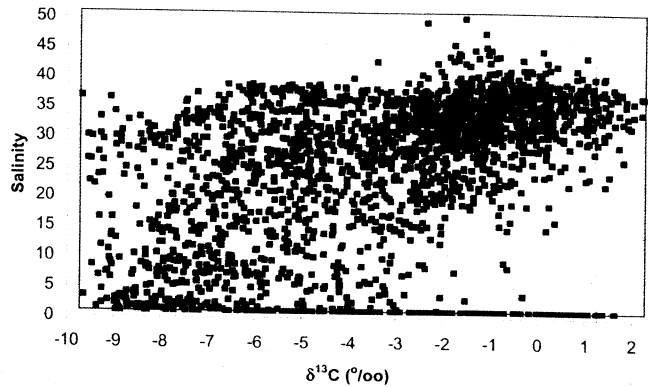| Area	$\delta^{18}O$ vs. salinity					$\delta^{13}C$ vs. salinity				
	Intercept	Slope	R^2	Number	P	Intercept	Slope	R^2	Number	P
Florida Bay										
Inner	+0.33	0.06	0.26	537	<0.01	−5.75	0.11	0.20	516	<0.01
Eastern Middle	−0.83	0.08	0.31	293	<0.01	−6.54	0.12	0.11	296	<0.01
Western Middle	−2.39	0.11	0.30	242	<0.01	−7.99	0.16	0.05	244	<0.01
Outer	−1.07	0.09	0.09	194	<0.01	−10.90	0.26	0.10	184	<0.01
Whitewater Bay	+0.35	0.07	0.34	395	<0.01	−8.33	0.10	0.20	364	<0.01
Ten Thousand Islands	−0.2	0.06	0.28	395	<0.01	−7.67	0.09	0.20	336	<0.01
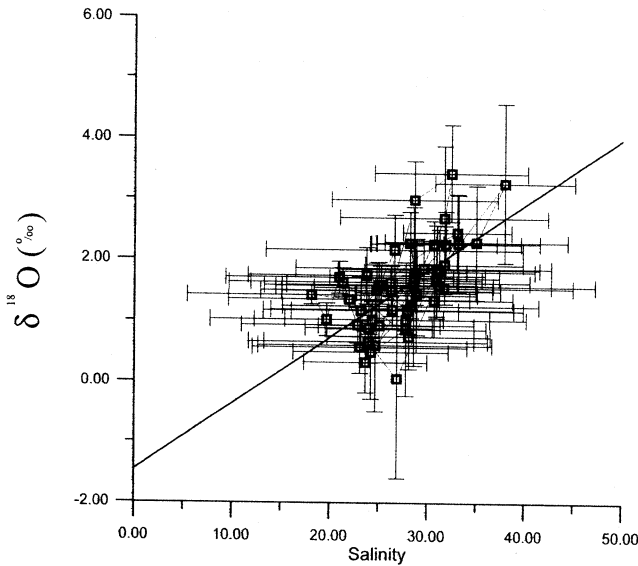
Text-figure 5.—Mean monthly $\delta^{18}O$ values versus salinity for all sites in Florida Bay. Error bars represent ±1 one standard deviation.

Text-figure 7.—Mean monthly $\delta^{13}C$ versus salinity for all sites in Florida Bay.

sented in this study show that the isotopic composition of South Florida precipitation falls near the MWL (Text-fig. 3). It is relatively depleted with volume weighted means of δD and $\delta^{18}O$ $-9.95\permil$ and $-2.90\permil$, respectively (Table 1).

Based on a correlation between δD and $\delta^{18}O$, the data from the Everglades plot below the MWL (Text-fig. 3). Deviation away from the MWL is a well-known phenomenon and arises through the differential influence of evaporation of the oxygen and hydrogen isotopes. In the case of the Everglades data, the closeness of the slope of the best fit line through the data

(5.8) to the slope of the MWL, suggests evaporation at a high relative humidity (Gonfiantini, 1986). Meyers *et al.* (1993) predicted a mean relative humidity of 80% for the Everglades based upon a stable isotope evaporation model. The time series trend of the Everglades data (Text-fig. 2) shows some seasonality with isotopically more positive values toward the end of the dry season when evaporation typically exceeds precipitation.

The intercept of the best fit line through the Everglades data with the MWL is similar to the isotopic composition determined for South Florida precipitation (Text-fig. 3). These results indicate that precipitation is the ultimate source of the evaporated water in the Everglades, Everglades water can be distinguished isotopically from its parent precipitation. The mean $\delta^{18}O$ and δD of the Everglades water is $+0.55\permil$ and
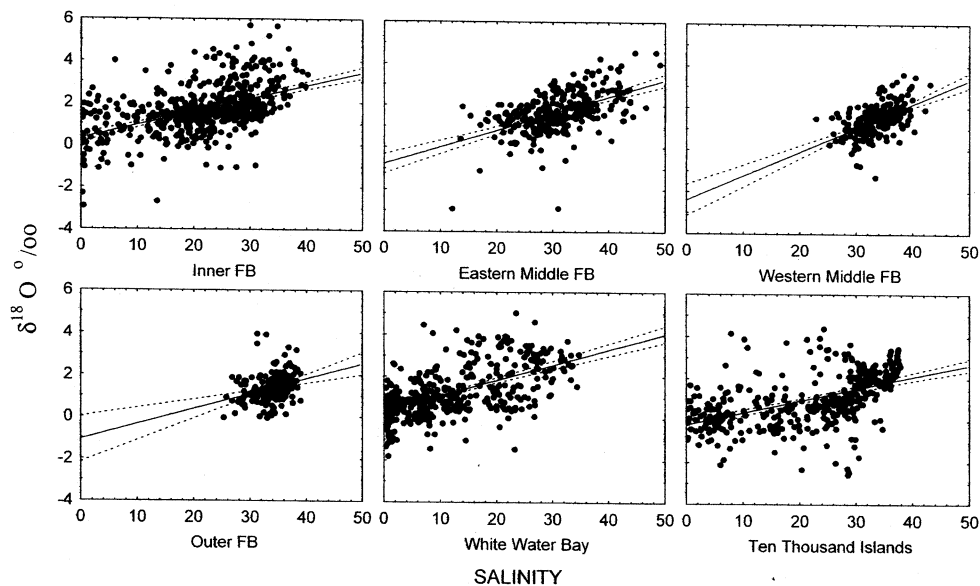
Text-figure 6.—Comparison of the linear relationship between $\delta^{18}O$ and salinity for the six major areas designated in Text-figure 1.
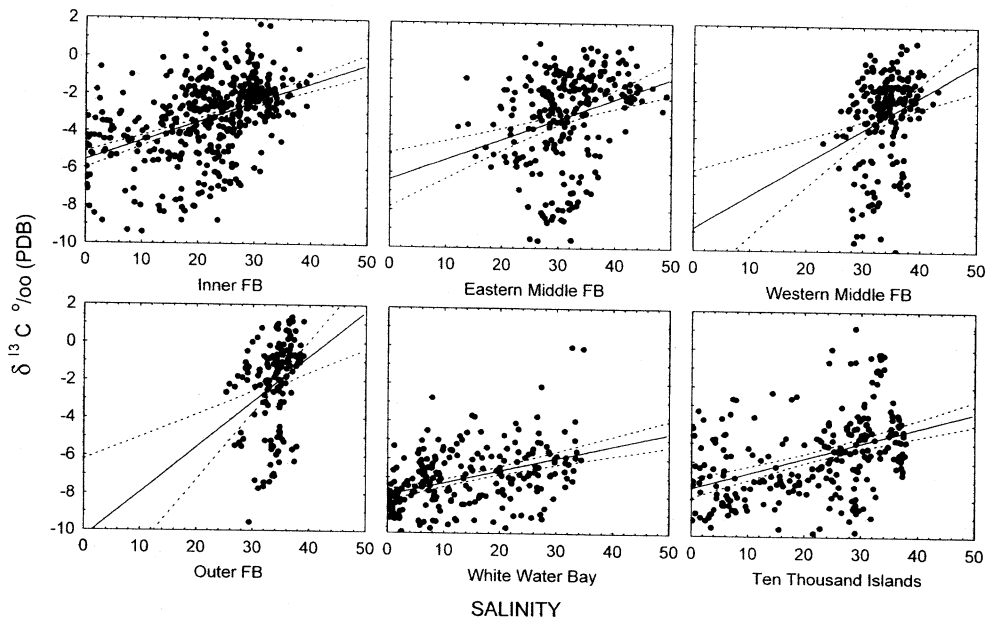
Text-figure 8.—Comparison of the linear relationship between carbon isotopic composition (DIC) and salinity for the six major areas designated in Text-figure 1.

+6.75‰, respectively, as compared to -2.90‰ and -9.95‰ for the precipitation.

Florida Bay exhibits a wide range of $\delta^{18}O$ values related to evaporation, precipitation, and mixing with water derived from the Everglades, the Gulf of Mexico, and the Florida Reef Tract. The wide range of $\delta^{18}O$ values was noted by Lloyd (1964) who was unable to exhibit any relationship between salinity and $\delta^{18}O$. In contrast to the study of Lloyd (1964), the data in this study were collected within a temporal and spatial framework and consequently the apparent poor correlation between salinity and $\delta^{18}O$ noted by Lloyd can be explained by mixing between different end-mem-

bers with similar salinity, but differing $\delta^{18}O$ values. These relationships can be visualized on a $\delta^{18}O$ vs. salinity plot (Text-fig. 11) comparing the $\delta^{18}O$ composition and salinity of the relevant end-members waters: Everglades, precipitation, and seawater. Data for the seawater end-member are derived from previous studies (Ortner *et al.*, 1995; Leder *et al.*, 1996; Swart,
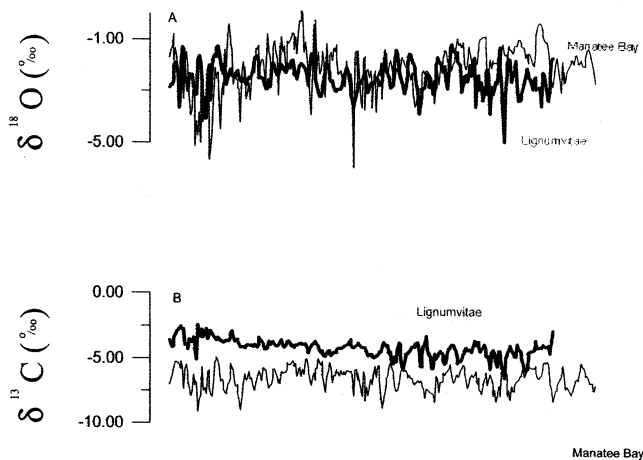
Text-figure 9.—Oxygen and carbon isotopic data from corals collected from Lignumvitae Bay and Manatee Bay.
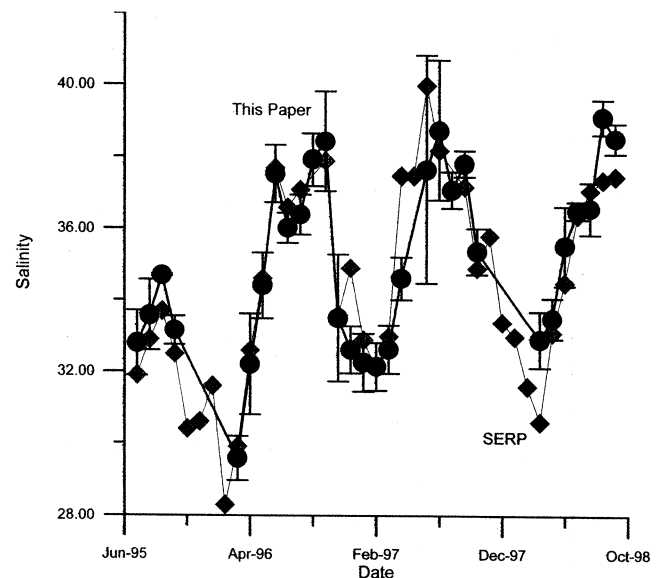
Text-figure 10.—Comparison of data collected from the continuous salinity monitoring stations and data collected by FIU on a monthly basis. Salinity data have been averaged from hourly data into monthly values. Error bars represent ± one standard deviation.

Text-figure 12.—Relationships between $\delta^{13}C$ and $\delta^{18}O$ in the coral skeletons from Lignumvitae Basin and from Manatee Bay. Note that in the Lignumvitae data there is no correlation between the two isotopes (R^2 = 0.04)as predicted from an absence of a correlation in the two isotopes in the water at that site. In Manatee Bay however there is a correlation between the two isotopes which is statistically significant at the 99% level (R^2 = 0.14).

their skeletons, while corals influenced by runoff should have a better correlation. These correlations can be seen in data from the coral collected from Manatee Bay which shows a strong positive correlation between skeletal $\delta^{13}C$ and $\delta^{18}O$ (R = .42, n = 362, p > .0001). In contrast, corals from Lignumvitae Basin show no correlation between the two isotopes (R = 0.003, n = 1894, p = not significant) (Text-fig. 12). These correlations are similar to the relationships seen between the $\delta^{13}C$ and $\delta^{18}O$ of waters. For example, results from a linear regression model between $\delta^{13}C$ of DIC and salinity has an R^2 of 0.2 (Table 2). In western-middle Florida Bay, where the Lignumvitae Basin is located, an R^2 of 0.05 is obtained (Table 2).

APPLICATION TO EXISTING PALEOENVIRONMENTAL DATA

Combining the salinity relationship beteen Lignumvitae Basin along with $\delta^{18}O$ record of the coral skeleton collected from Lignumvitae Basin, attempts have been made at estimating salinity variations in other regions of Florida Bay (Swart et al., 1996; 1999). Based on data presented in this paper, however, the equation linking the skeletal $\delta^{18}O$ and salinity in Lignumvitae Basin (Swart et al., 1999) is not valid for other areas of Florida Bay. Consequently different equations for estimating salinity from $\delta^{18}O$ need to be derived for every location. While this is impractical in

real terms, one can obtain an idea of the influence of the variations by calculating the relationships between salinity and $\delta^{18}O$ for the different geographic sub-regions designated for Florida Bay (Text-figs. 1, 6). As an example of the influence that these different relationships have on the calculation of the salinity from a $\delta^{18}O$ record, we examined the $\delta^{18}O$ record of a coral from Lignumvitae Basin and a coral of a similar genus growing in Barnes Sound near the mouth of Manatee Bay. In order to compare the salinity estimates, we used three methods to determine the salinity at the mouth of Manatee Bay. These are (1) the transfer function approach presented by Swart et al. (1999) using the $\delta^{18}O$ of coral skeletons growing in Lignumvitae Basin and the modern salinity correlations between the two basins, (2) using a coral actually growing in a site and the correlation between salinity and $\delta^{18}O$ for Lignumvitae Basin, and (3) using the Manatee Bay coral and the salinity vs. $\delta^{18}O$ relationship presented in this paper. We then compared these salinity estimates directly with measurements by FIU/SERP and the University of Miami in Barnes Sound. In the first comparison, the data from the coral growing in Lignumvitae Basin was converted to salinity using the equation presented by Swart et al. (1999) which related salinity to the temperature (T) and the $\delta^{18}O$ of the coral skeleton (equation 1). This provided an estimate of salinity with a slightly greater amplitude than the Lignumvitae coral, but significantly higher than the range in salinity measured in Manatee Bay (Text-fig. 13).

$$Salinity = 4.988\delta^{18}O_{coral} + 1.18T + 19.62 \qquad (1)$$

In the second approach equation 1 was also used, but in this case the data from the coral actually growing near the mouth of Manatee Bay was used (Text-fig. 13). This gave an estimate similar in pattern to the method used previously, but with much higher salinity estimates than the salinities actually measured (Text-fig. 13). The third method uses the new relationship between salinity and $\delta^{18}O_{water}$ shown in Table 4. In order to convert the $\delta^{18}O$ of the coral skeleton to salinity we used the relationship established by Leder et al. (1996) between temperature and skeletal $\delta^{18}O$ for the species *Monastrea annularis* and assumed an annual mean temperature of 25°C. Combining these two equations a new formula can be derived which is specific for corals growing in the inner portion of Florida Bay. This relationship is shown in equation 2.

$$Salinity = 4.14\delta^{18}O_{coral} + 0.978T + 9.33 \qquad (2)$$

The results of these three calculations together with the range of salinities actually measured at the site in Manatee Bay are shown in Text-figure 13. This visual comparison shows that the best estimate of salinities
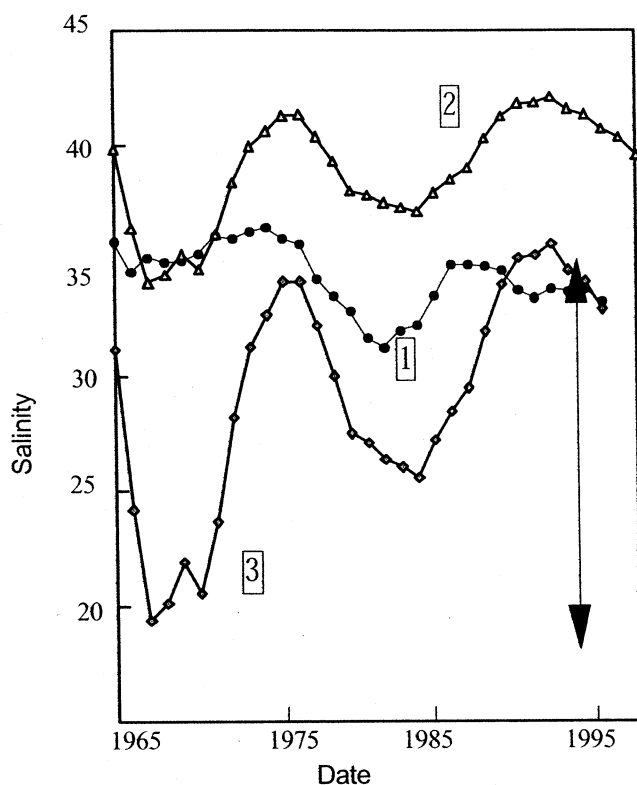
Text-figure 13.—Line (1) represents the salinity in Barnes Sound estimated using the $\delta^{18}O$ data from the coral in Lignumvitae Basin (Swart *et al.*, 1996, 1999). Line (2) represents the salinity estimate calculated from the $\delta^{18}O$ of the Manatee Bay coral using the relationship between salinity and $\delta^{18}O_{water}$ established for Lignumvitae Basin. Line (3) is the new relationship between salinity and $\delta^{18}O$ for the inner region of Florida Bay established in this paper (Table 4). The ranges in salinity measured by FIU and presented in this paper are indicated by the arrow.

measured at the site are provided by the method in which we used the correlation between salinity and $\delta^{18}O_{water}$ for inner Florida Bay. Previously estimates for the salinity in this portion of Florida Bay are therefore likely to have been too high (Swart *et al.*, 1999). However, in spite of the distance between the two locations (Lignumvitae Basin and Manatee Bay), the coral in Lignumvitae Basin shows a similar temporal pattern in $\delta^{18}O$ to the Manatee Bay Coral and with the appropriate calibration the Lignumvitae coral record (Swart *et al.*, 1996) can be used to estimate salinities in other portions of Florida Bay.

CONCLUSIONS

1) Relationships between salinity and $\delta^{18}O$ vary according to relative distance from the Everglades. This changing relationship is caused by an increasing influence of rainfall compared to runoff in controlling salinity variations. For example, the western portion of Florida Bay appears not to be significantly influenced by runoff from the Everglades and salinity variations there are related to changes in the amount of precipitation. Application of a constant salinity vs. $\delta^{18}O$ relationship in the interpretation of $\delta^{18}O$ values of calcareous organisms from South Florida estuaries is not appropriate.

2) Carbon isotopic variations in Florida Bay are related to the oxidation of organic material. Large variations in the $\delta^{13}C$ of the DIC occur both within saline and freshwater environments. Within the saline environments, there is little relationship between salinity and $\delta^{13}C$ while in the freshwater environment, there is a strong correlation between salinity and $\delta^{13}C$.

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