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Controls on the oxygen and hydrogen isotopic composition of the waters of Florida Bay, U.S.A.

PETER K. SWART[1], LEONEL D.S.L. STERNBERG[2], RANDOLPH STEINEN[3] and STEVEN A. HARRISON[1]

[1]*Division of Marine Geology and Geophysics, Rosentiel School of Marine and Atmospheric Science, University of Miami, Miami, FL 33149 (U.S.A.)*
[2]*Department of Biology, College of Arts and Sciences, University of Miami, Coral Gables, FL 33134 (U.S.A.)*
[3]*Department of Geology, University of Connecticut, Storrs, CT 06268 (U.S.A.)*

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Abstract

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The oxygen and hydrogen isotopic composition have been measured of waters in Florida Bay and fluids squeezed from sediments which make up Holocene islands in the bay. Although, these waters ranged in salinity from 27 to 120 g kg^{-1}, most were found to have very similar hydrogen and oxygen isotopic compositions ($\delta^{18}O = +2$ to $+4‰$, $\delta D = +5$ to $+25‰$). In order to explain these observations we have applied the Craig-Gordon and Gonfiantini evaporation models which account for oxygen and hydrogen isotopic fractionation during the desiccation of saline water bodies. These models provide excellent agreement for the evaporation of water into an environment with a relative humidity of 77%, a temperature of 25°C and atmospheric water vapor possessing $\delta^{18}O$- and δD-values of -11 and $-75‰$, respectively.

The salinity of fluids from one core on Cluett Key (26.9 g kg^{-1}) was well below that of the surrounding bay (>40 g kg^{-1}) and the water from this locality was depleted in both D and ^{18}O. These $\delta^{18}O$- and δD-values, plotted together with other data from this study, fall on a line possessing a slope of 4.90 (±0.41), similar to what would be expected from the evaporation models. This line intersects the meteoric water line at $\delta^{18}O$- and δD-values which are within error, similar to average $\delta^{18}O$- and δD-values measured for rainfall in the Miami area.

1. Introduction

The origin and subsequent evaporation history of natural waters can be frequently constrained by the relationships between the isotopes of oxygen and hydrogen (e.g., Craig and Gordon, 1965; Fontes and Gonfiantini, 1967; Gat and Levy, 1978; Zimmermann, 1979; Fröhlich et al., 1988). During evaporation as a result of both kinetic and equilibrium processes, water vapor becomes depleted in the heavier isotopes of oxygen and hydrogen, ^{18}O and D. The magnitude of the depletion is dependent upon: (1) the relative humidity of the atmosphere into which the water is being evaporated; (2) the temperature of evaporation; (3) interactions with other ions in the fluid (ionic strength); and (4) the H and O isotopic composition of the water vapor in the atmosphere. This paper uses such models to constrain the origin and controls of the H and O isotopic composition of waters in Florida Bay, waters imponded on Holocene islands in the bay and interstitial fluids in the sediments which compose these is-

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lands. Such models are of interest because despite the wide reported range in salinities of the bay, previous workers have reported a narrow range of values (see Section 4).

Florida Bay is a large (20,000 km^2) shallow mud-dominated body of water, lying between peninsular Florida to the north and the Florida Keys to the south (Fig. 1). The principal inputs of water are from the Everglades in the north and from the Gulf of Mexico and Straits of Florida to the south and east. A mixture of these sources together with an annual rainfall of ~115 cm (data from Tavernier, Florida; Lloyd, 1964) and an equivalent or greater amount of evaporation produces variations in salinity in the bay of between 4 and 50 g kg^{-1} (Lloyd, 1964; Robblee et al., 1987). Although the magnitude of the contributions from the respective sources are highly variable, only rarely does evaporation not exceed runoff and rainfall and therefore hypersaline conditions generally prevail throughout the year (salinity >35 g kg^{-1}) (Robblee et al., 1987). Lloyd (1964) measured salinity and δ^{18}O-values of Florida Bay waters and found them to vary between 11.4 and 39.4 g kg^{-1} and +1 and +2.9‰, respectively. In his data there were no apparent trends between salinity and δ^{18}O. He interpreted the spread of data as reflecting the mixing between freshwater isotopically enriched in ^{18}O from the Everglades and marine water derived from the Gulf of Mexico and the Florida reef tract.

Florida Bay is also occupied by numerous Holocene islands, which are seasonally flooded by bay water during extremely high tides and storms. Such water becomes imponded on the islands and mixes with fluids buried within the sediments through diffusive processes and gravity infiltration (Swart et al., 1988). The salinities of such waters vary greatly as a result

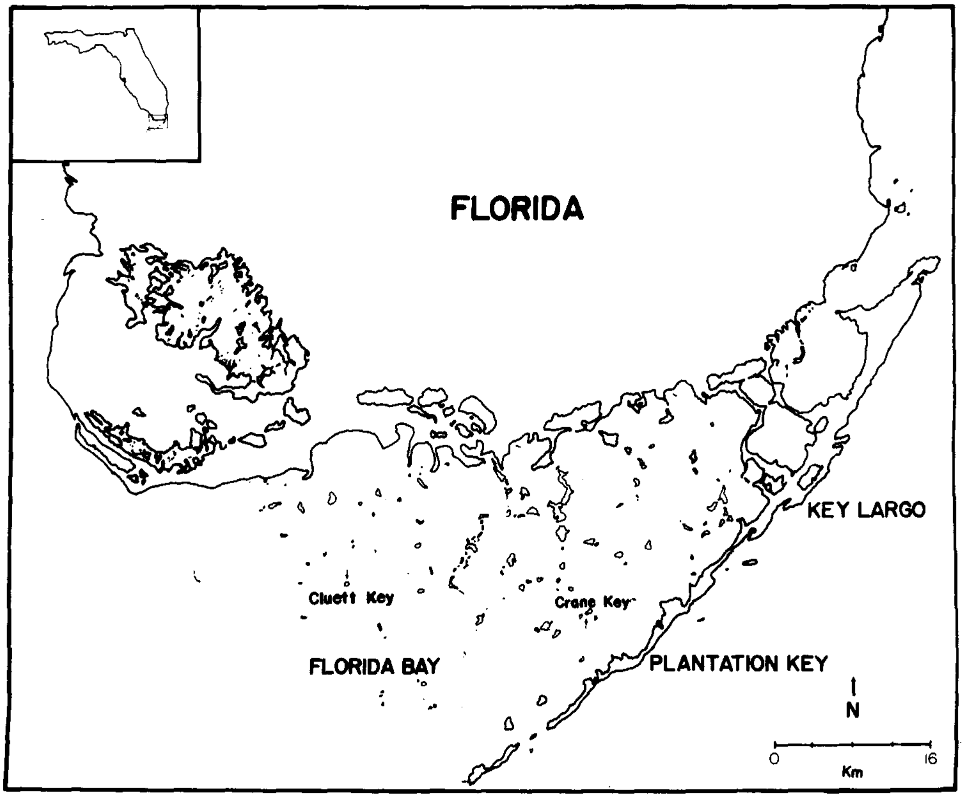

Fig. 1. Map showing the location of Florida Bay and the two islands studied, Crane Key and Cluett Key.

of evaporation and dilution by local rainfall resulting in ranges of salinity between 0 and > 160 g kg^{-1} (P.K. Swart, unpublished data, 1987).

The two islands from which interstitial water samples were collected for this study have been the subject of several previous investigations. Crane Key is situated in the southeastern portion of Florida Bay and has been described by Enos and Perkins (1979) (Fig. 1). Sub-surface diagenetic reactions have been investigated by Swart et al. (1989). Cluett Key is located in west Florida Bay. Its sedimentology and diagenesis have been studied by Steinen et al. (1978) and Videlock (1983). The H and O isotopic composition of water utilized by plants on this island have been investigated by Sternberg and Swart (1987).

2. Methods

Waters were collected from two islands, Cluett and Crane Key, and from Florida Bay on several occasions throughout 1986 and 1987. Two push cores were taken from Cluett Key and one from Crane Key. On Crane Key the core penetrated ~2 m of sediment before encountering Pleistocene bedrock. On Cluett Key one core (230 cm in depth) was taken in a shallow saline pond (CL-*27*) in the center of the island and the other (CL-*26*) (130 cm in depth) from an elevated area which possessed plants characteristic of fresher water (Sternberg and Swart, 1987; R.P. Steinen, unpublished data, 1977). Waters were extracted from the sediments at 10-cm intervals using a hydraulic press and squeezer similar to that used by Manheim and Sayles (1974). All samples were stored in sealed glass ampoules until the time of analysis. The oxygen isotopic composition was determined on CO_2 equilibrated with 1 cm^3 of sample in a shaking water bath at 25°C for 24 hr. (after the method of Epstein and Mayeda, 1953). Sixteen samples were equilibrated at one time including two internal laboratory standards. Experiments using this technique showed that equilibrium was attained in samples of normal seawater salinity in <5 hr. As a result of uncertainty regarding the precise correction factors to apply for the presence of dissolved salts (Gonfiantini, 1986), we have not corrected our data for these effects. Hydrogen was prepared from 1–5 μl of sample by reduction over zinc or uranium (Friedman, 1953). The isotopic ratios of both gases were determined using a Finnigan-MAT *251*® in the Stable Isotope Laboratory (SIL) at the Rosenstiel School of Marine and Atmospheric Sciences, University of Miami. Reproducibility of oxygen isotopic analyses determined by replicate analyses of standards within a single batch of equilibrations is ~ ±0.2‰ and hydrogen ~ ±1‰.

Salinity measurements were made on the waters at the time of collection using a Goldberg refractometer calibrated using IAPSO* seawater.

As at the time of this study there had been no investigation of the isotopic composition of rainfall in the south Florida area, we also report data on the H and O isotopic composition of precipitation in the Miami area, over a 3-yr. period between 1985 and 1987.

3. Results

The oxygen and hydrogen isotopic composition of rainfall in south Florida is extremely variable with $\delta^{18}O$-values ranging from −8 to +0.0‰ (P.K. Swart, unpublished data, 1987). For a total of 110 samples collected over a 3-yr. period, the weighted mean for $\delta^{18}O$ is −2.67‰ and for δD, −11.36‰ (number of samples analyzed for $\delta D = 22$). Although there is a considerable variability, the $\delta^{18}O$ and δD of the rain samples fall within error on the meteoric water line (MWL) as defined by Craig and Gordon (1965) (see Fig. 4).

The salinity of the water samples collected in Florida Bay ranges from 26.9 g kg^{-1} in the subsurface of one core (CL-*26*) from Cluett Key to

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> 120 g kg^{-1} in the center (CL-*27*) of the same island. In contrast, the salinities from Crane Key only attain values as high as 88 g kg^{-1} and the bay waters range from 42 to 46 g kg^{-1}. These data are shown in Table I and Fig. 2; data from Lloyd (1964) are shown for comparison. In spite of these large ranges in salinities, most of the waters possess rather restricted H and O isotopic compositions. The exceptions were waters from Cluett Key which could be considered to be largely meteoric in origin in that they possessed salinities lower than Bay water. A plot of δD vs. δ^{18}O for all analyses shows that the data fall off the MWL on a line with an equation given below; values shown in brackets represent one standard error (Fig. 3):

TABLE I

Salinity and oxygen and hydrogen isotope data

(A) Cluett Key (CL-*26*)

Depth (cm)	Salinity (g kg^{-1})	δ^{18}O (‰)	δD (‰)
10-20	28.6	−0.90	−7.8
20-30	33.2	−1.02	−5.6
30-40	47.8	+0.10	−0.4
40-50	49.8	−0.30	
50-60	51.4	−0.40	
60-70	51.4	−0.54	−6.7
70-80	52.4	−0.76	
80-90	51.9	−0.83	
90-100	51.4	−1.33	−6.6
100-110	47.2	−0.80	
110-120	45.2	−1.35	
120-130	39.5	−0.52	−9.0

(B) Cluett Key (CL-*27*)*

Depth (cm)	Salinity (g kg^{-1})	δ^{18}O (‰)	δD (‰)
10-20	93	+3.34	
20-30	103	+3.34	
30-40	118	+3.00	
40-50	108	+3.64	
50-60	116	+3.24	+9.2
60-70	118	+2.14	
80-90	118	+2.80	+9.9
90-100	119	+2.65	+9.9
100-110	119	+2.75	
110-120	120	+2.80	+10.2
120-130	120	+2.40	+9.2
130-140	118	+2.70	+5.8
140-150	117	+2.90	
150-160	116	+2.70	+10.3
160-170	114	+2.70	
170-180	113	+2.70	
180-190	110	+2.70	+9.1
220-230	103	+2.70	

(C) Florida Bay

Sample No.	Salinity (g kg^{-1})	δ^{18}O (‰)	δD (‰)
1	44	+3.23	+16.3
3	45.5	+3.51	+16.0
4	46	+3.23	+17.8
5	45.5	+3.61	+19.4
6	43	+3.61	+18.2
7	45	+3.74	+22.0
8	45	+3.99	+22.8
9	45.5	+3.84	+21.4
10	44.5	+3.88	+20.6
11	44.5	+3.82	+22.3
12	45	+4.26	+21.2
13	42	+2.87	+12.7

(D) Crane Key

Depth (cm)	Salinity (g kg^{-1})	δ^{18}O (‰)	δD (‰)
0-10	85.3	+2.81	+7.3
10-20	80	+3.75	+23.3
20-30	80.8	+3.14	+10.1
30-40	82.4	+3.08	+10.1
40-50	83.1	+2.76	+8.0
50-60	84.2	+3.21	
60-70	86.3	+2.44	
70-80	87.5	+2.79	
80-90	88	+2.61	+7.8
90-100	88.2	+2.61	+10.9
100-110	87.9	+2.6	
110-120	88.3	+2.55	+16.1
120-130	88	+2.84	
130-140	87.5	+3.53	+14.9
140-150	86.7	+2.8	
150-160	86	+2.84	
160-170	85.9	+2.93	
170-180	85	+2.5	+13.0
180-190	83.8	+2.1	+10.3

*This core was taken in the saline pond in the center of the island.

$$\delta D = 4.902(\pm 0.418)\delta^{18}O - 2.66(\pm 3.29) \quad (1)$$

Although this line intersects the MWL at a $\delta^{18}O$-value of −4.4‰, significantly lower than the average rainfall value in Miami of −2.67‰, the large errors of the intercept and the slope indicate that there is no statistical significant difference between this intersection with the MWL and the average $\delta^{18}O$ of the rainfall in Miami. The equation of this line is also similar to a line fitted to isotopic analyses of plant water taken from the same islands, which in turn reflects the isotopic composition of the groundwater in these locations (Sternberg and Swart, 1987). There were no apparent trends in the isotopic composition of either H or O with increasing depth in the cores (Table I).

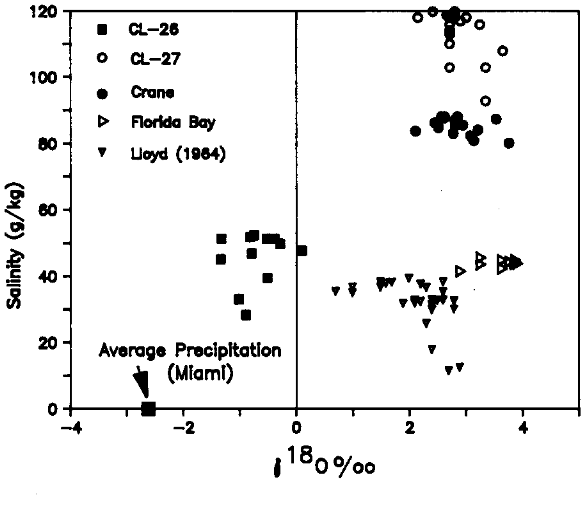

Fig. 2. Plot of salinity vs. $\delta^{18}O$ for all samples measured in this study; data from Lloyd (1964) are shown for comparison. Average rainfall (P.K. Swart, unpublished data, 1987) is also shown for comparison.

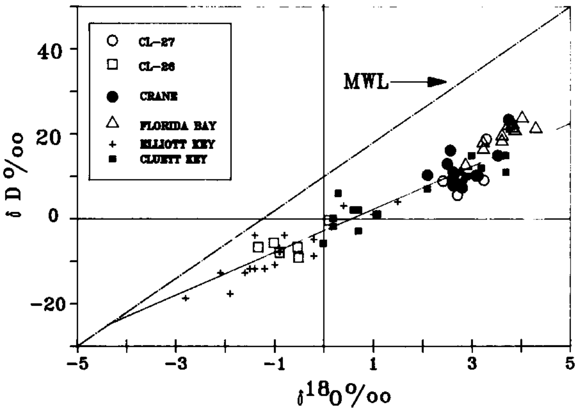

Fig. 3. Relationship between $\delta^{18}O$ and δD for samples collected in this study. A best-fit line through all the data has a regression coefficient 0.98 and a slope of 4.90 (±0.41). This line intersects the MWL at a $\delta^{18}O$ of −4.4‰ and a δD of −22.7‰. Also shown are data from a study by Sternberg and Swart (1987) for waters extracted from plants from Cluett and Eliott Keys. These data exhibit similar correlations.

4. Discussion

The water in Florida Bay can be considered to be mixtures of three principal sources: (1) local rainfall; (2) water from the Everglades to the north; and (3) ocean water from the Gulf of Mexico and the Gulf Stream (Lloyd, 1964). For the purposes of this study we shall assume that the H and O isotopic compositions of rainfall are equal to the average composition of precipitation measured in Miami ($\delta^{18}O = -2.67$‰ and $\delta D = -11.32$‰). Ground- and surface waters from the Everglades, although being highly variable in both H and O isotopic composition ($\delta^{18}O = -3$ to $+3$‰; P.K. Swart, unpublished data, 1987), are ultimately derived from precipitation and therefore have similar isotopic compositions. The $\delta^{18}O$- and δD-values of Gulf Stream water are relatively constant, possessing a $\delta^{18}O$-value of between +1.0 and +1.7‰ and a δD-value of between +7 and +14‰ (Sternberg and Swart, 1987; this study). In this study we shall consider the Florida Bay water to be formed from mixtures of fresh water (rainfall and runoff from the Everglades) with original $\delta^{18}O$- and δD-values of −2.67 and −11.63‰, and Gulf Stream water with $\delta^{18}O$- and δD-values of +1 and +10‰, respectively.

Although, the high salinity in Florida Bay is caused by evaporation, variations in salinity of the interstitial pore fluids and imponded waters on the islands may also be influenced by the dissolution of salts in the sediment profiles by bay water and inundation by rainwater. As it is probable that a complex sequence of evaporation, dilution by oceanic and meteoric waters, subsequent evaporation and further mixing takes place, the salinity of these waters can only be used as an estimate as to the amount of evaporation which has taken place.

5. Stable oxygen and hydrogen isotopes

The hydrogen and oxygen isotopic compositions of waters in isolated basins have been modelled by various workers (e.g., Brutsaert, 1965, 1975; Craig and Gordan, 1965; Merlivat and Coantic, 1975; Gat, 1981; Gonfiantini, 1986). As the effects involved are well known only brief details are given here. For the evaporation of saline water, the H or O isotopic composition of the residual water body (δ) can be shown to be equal to the following equations (Gonfiantini, 1965, 1986):

$$\delta = (\delta_o - A/B) f^{B} + A/B \tag{2}$$

$$A = \frac{h/\alpha_w \delta_a + \Delta\epsilon + (\alpha - \tau)/\alpha}{1 - h/\alpha_w + \Delta\epsilon} \tag{3}$$

$$B = \frac{h/\alpha_w - \Delta\epsilon + (\alpha - \tau)/\alpha}{1 - h/\alpha_w + \Delta\epsilon} \tag{4}$$

where h = relative humidity, δ_a = H or O isotopic composition of atmospheric moisture; δ_o = oxygen or hydrogen isotopic composition of the original water; α = equilibrium fractionation factor for H or O between water and water vapor; f = fraction of water evaporated; $\epsilon = \alpha - 1$, $\Delta\epsilon$ = kinetic enrichment factor; α_w = activity coefficient of water; and τ = ratio of the activity coefficients for D/H and $^{18}O/^{16}O$. The values used for α and ϵ can be calculated for any particular temperature using the following equations (Kakiuchi and Matsuo, 1979):

Oxygen:

$$\ln \alpha = 5970.2T^{-2} - 32.801T^{-1} + 0.05223 \tag{5}$$

Hydrogen:

$$\ln \alpha = 2408T^{-2} + 64.55T^{-1} - 0.1687 \tag{6}$$

The effect of ion hydration has been discussed by Sofer and Gat (1972, 1975) and can be explained by the term τ. For a multi-component solution such as seawater, τ can be defined by eq. 6 and the following equation for H and O, respectively (Sofer and Gat, 1972, 1975):

$$(\tau^{-1} - 1) \times 10^{-3} = 6.1 m_{CaCl_2} + 5.1 m_{MgCl_2} + 2.4 m_{KCl} + 0.4 m_{NaCl} \tag{7}$$

$$(\tau^{-1} - 1) \times 10^{3} = 0.47 m_{CaCl_2} + 1.107 m_{MgCl_2} - 0.16 m_{KCl} \tag{8}$$

where m = molality of the species involved and may be calculated from the salinity of the solution being evaporated. The modification of the activity coefficient of water (α_w) can be accounted for using the tabulation of Robinson and Stokes (1959). For the purposes of this study we have used the relationship for a sodium chloride solution as detailed in the following equation:

$$\alpha_w = -0.000543 f^{-2} - 0.018521 f^{-1} + 0.99931 \tag{9}$$

The kinetic enrichment factor ($\Delta\epsilon$) is dependent upon the relative humidity of the atmosphere and a constant (k) determined by Merlivat (1978) to approximate the square root of the ratio of the diffusion coefficients of the relevant isotopes:

$$\Delta\epsilon = k(1 - h/\alpha_w) \tag{10}$$

(k = 14.2 for O and 12.5 for H; k-values determined experimentally by Merlivat, 1978 at 21°C).

Using this equation it is possible to generate relationships between evaporation and either the O or H isotopic composition of the remaining solution with different relative humidities, temperatures, initial fluid isotopic compositions and atmospheric isotopic compositions.

6. Temperature and relative humidity

The average daily temperature for the study area is taken from the weather station at Key West, ~160 km to the southwest. Average

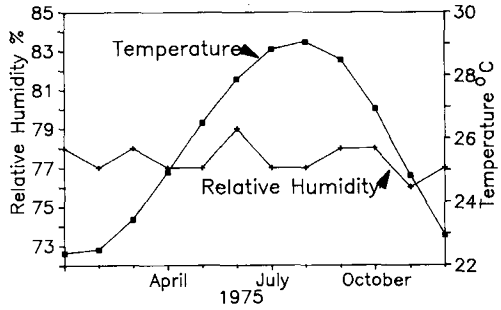

Fig. 4. Yearly variation (1975) in temperature and relative humidity from Key West, Florida (NWS, 1975).

monthly temperatures varied between 22° and 30°C, with a yearly average of 25°C (Fig. 4). Variation in temperature alters the α and ϵ terms in the above equations so that α for oxygen ranges between 1.008532 and 1.009727 and for hydrogen between 1.066586 and 1.08005 (30° and 20°C, respectively). For demonstrative purposes we shall use the average temperature of 25°C, but will examine the effect that temperature has on the relationship between δD and δ^{18}O (e.g., Fig. 5 for precipitation) of an evaporating solution later.

The average monthly relative humidity in Key West varies between 77% and 78% (Fig. 4) with a yearly average of 77.4%.

7. Application of model

In this section we shall examine the sensitivity of the eq. 1 to variations in the initial H and O isotopic composition of the fluid being evaporated, temperature, relative humidity, atmospheric H and O isotopic composition, and fraction of the water evaporated. The criteria for judging whether particular environmental conditions "fit" the observed data is whether the maximum H or O isotopic composition attainable under such conditions is equal to the average H and O isotopic composition of a particular group of samples. As the samples collected from Florida Bay have the heaviest δ^{18}O- and δD-values, these shall be used as the limiting case. The following examples deal principally with the fractionation of O; however, similar calculations can and have been carried out for H.

As a first approximation only, let us consider a δ_a-value (−12‰) in equilibrium with the local rainfall at 25°C (−2.67‰), an initial starting composition of the water being evaporated (δ_0) of −2.67‰ and a salinity of 20 g kg^{-1}. The choice of initial salinity and O isotopic composition may appear somewhat arbitrary as different parts of Florida Bay will experience varying amounts of mixing between seawater, existing bay water, rainwater and water from the Everglades. However, it will be shown that a salinity of 20 g kg^{-1} is a reasonable approximation and that the final O isotopic composition is insensitive to the starting O isotopic composition.

Using these starting parameters, the resultant isotopic compositions of the residual fluids can be estimated for any fraction of water removed (f) and are shown in Fig. 6 for relative humidities of 10%, 25%, 50%, 77.4% and 95%. As can be seen from this figure, the O isotopic composition of the residual (δ) water under a relative humidity of 77% (the average relative humidity for the area) can only attain a maximum isotopic composition of ~ +2.3‰. As the fraction of water removed becomes higher, the ionic strength of the residual increases and the actual isotopic composition decreases as a result of changes in the thermodynamic activity of water, and partitioning between the hydration sphere of ions and free water. Although the

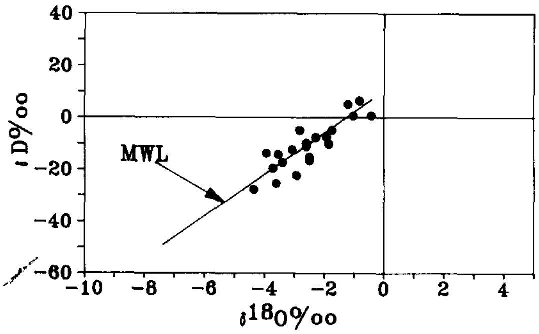

Fig. 5. Oxygen and hydrogen isotopic data for precipitation in the Miami area during 1986 and 1987. Data fall within error on the MWL.

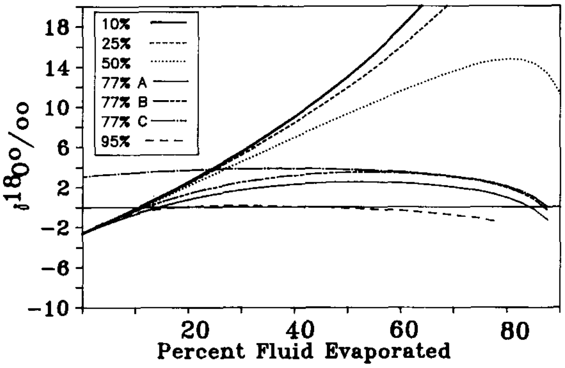

Fig. 6. Results of the evaporation of a fluid with an initial $\delta^{18}O$ of −2.67‰ and a salinity of 20 g kg^{-1} at 35°C into an atmosphere with humidity in equilibrium with the local rainfall (−2.67‰). The *dashed lines A, B* and *C* represent evaporation at a relative humidity of 77.4%. For line *A* the atmospheric moisture is in equilibrium with the local precipitation (−2.67‰); the maximum isotopic composition which can be attained is ~1‰ less than the average of the Florida Bay waters. Case *B* represents evaporation into an atmosphere with a $\delta^{18}O_a$ of −11‰ and a δD_a of −75‰ and provides the best fit with our data. Line *C* shows the path of evaporation taken under identical conditions to case *B*, but with a starting O isotopic composition of +3‰. Note that approximately the same isotopic compositions are reached regardless of the O isotopic composition of the starting fluid.

maximum H and O isotopic values attained using these parameters do not precisely coincide with the maximum mean H and O isotopic composition of Florida Bay waters, considering all the uncertainties involved, atmospheric moisture appears to be only slightly out of equilibrium with the local rainfall. In order to account for this difference a combination of the following conditions occur: (1) evaporation under conditions of lower relative humidity; (2) non-equilibrium between atmospheric water vapor and local precipitation; and (3) evaporation takes place at a lower temperature.

The importance of these effects can be assessed by using the measured annual average temperature and relative humidity and by comparing the association between $\delta^{18}O$ and δD in our data with that of the model. Oxygen isotopic compositions of the appropriate range can be achieved either by reducing the average relative humidity to 75% or reducing the average temperature 17°C. If the relative humidity in the model is reduced from 77.4% to 75%, then the slope of the line between $\delta^{18}O$ and δD becomes 3.84, significantly less than the measured relationship of 4.90. A reduction in temperature to 17°C also seems unlikely as temperatures this low are not normal for this area. Our data therefore suggest that atmospheric moisture is not in complete equilibrium with the Florida Bay waters and agree with the conclusions of Craig and Gordon (1965) and Craig and Horribe (1967) who determined that generally moisture and precipitation are not in isotopic equilibrium in oceanic and coastal regions.

Using the O isotopic data measured in this investigation and the average meteorological data for the study area, the isotopic composition of the atmospheric moisture can be estimated using eq. 2. These calculations indicate that a reasonable fit to the data is obtained using a $\delta^{18}O_a$ of −11‰ and $\delta D_a = -75$‰ (Fig. 6).

A further implication of the model of Gonfiantini (1965) is that H and O isotopic compositions of the final fluid are largely independent of the initial H and O isotopic composition (δ_0), so that if the water in the island sediments and surface waters is Florida Bay water, driven onto the islands by storms, approximately the same isotopic composition will be reached than if the waters were evaporated from rainwater. This is exemplified in this study by the case in which bay water ($\delta^{18}O = +3$‰) and meteoric water ($\delta^{18}O = -2.67$‰) are evaporated and similar end values attained (Fig. 6). With these parameters, the $\delta^{18}O$ is relatively insensitive to the amount of evaporation which has taken place. The only exceptions are that: (1) large changes in isotopic composition can occur relatively rapidly for small amounts of evaporation if δ_0 is significantly different than the maximum value; and (2) there is a gradual decrease in H and O isotopic composition with increasing ionic strength. This gradual decrease in iso-

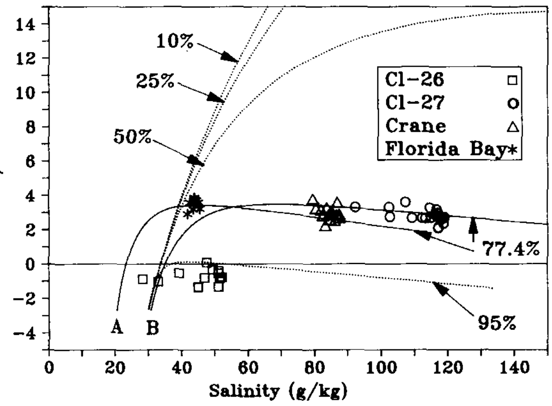

Fig. 7. The percentage of fluid evaporated has been converted to a salinity scale assuming an initial salinity of 20 g kg^{-1} (A) and 30 g kg^{-1} (B) and that all changes in salinity result from evaporation. The *dotted lines*, representing atmospheres of differing relative humidity as in Fig. 6, are shown for comparison.

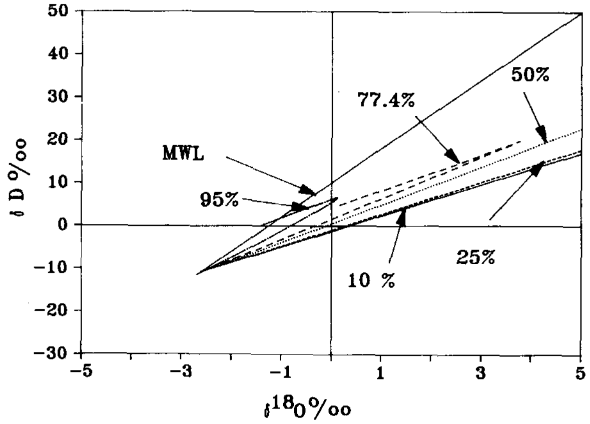

Fig. 8. Pathways of evaporation into atmospheres of varying relative humidities for a fluid with initial H and O isotopic compositions for $\delta^{18}O$ and δD of −2.67 and −11.32‰, and atmospheric isotopic compositions of −11 and −75‰, respectively, initial salinity of 20 g kg^{-1} and temperature of 25°C. The best-fit line to the data for evaporation into an atmosphere with a relative humidity of 77.4% is:

$$\delta D = 5.019(\pm 0.095) \times \delta^{18}O + 1.96(\pm 1.003)$$

(the *figure in brackets* represents one standard error). This equation is not statistically different from eq. 1 fitted to our data.

topic composition concurs with our measured data, which shows that those samples which have the highest salinity have lower δD- and $\delta^{18}O$-values (Fig. 7). These data indicate that Florida Bay waters could not have evolved simply from the evaporation of oceanic waters with a salinity of 35 g kg^{-1}, or from a mixture of oceanic water and fresh water with a salinity as low as 10 g kg^{-1}. The best fit to our data is achieved by the evaporation of an initial water with a salinity of between 20 and 30 g kg^{-1} (Fig. 7).

8. Correlation between oxygen and hydrogen isotopes

Normally the δD and $\delta^{18}O$ of precipitation falls on the MWL (Craig and Gordon, 1965).

This relationship also appears to be valid for the south Florida area (Fig. 4). The results from the earlier calculations of evaporation into atmospheres of differing relative humidities plotted on such a diagram deviate considerably from this relationship. Similar behavior results from an increase in temperature. With increasing salinity, the relationship between δD and $\delta^{18}O$ can show a reversal as ionic interactions affect H and O to different degrees (Fig. 8). Using the atmospheric parameters discussed above (relative humidity = 77.4%, T = 25°C), a δ_a and δ_0 for H and O of (−11‰, −75‰) and (−2.67‰, −11.63‰), respectively, then a δD vs. $\delta^{18}O$ plot produces a line with a slope of 5.05 (±0.016) (Fig. 8), which is within error the same as that fitted to our data (Fig. 3).

The H and O isotopic composition of our samples shows a significant amount of deviation from a best fit line (Fig. 3). This scatter is suggested to be a result of a combination of three processes: (1) mixing of fluids which have evaporated from both meteoric and bay water; (2) increasing ion interactions at high ionic strengths (Fig. 8); and (3) evaporation at different temperatures and into atmospheres of differing relative humidities.

The similarity in the relationships of the δD- and $\delta^{18}O$-values observed for plant water (Sternberg and Swart, 1987) from the islands studied and the data in this investigation (see Fig. 3) suggests that either plants are utilizing water as it evolves in δD and $\delta^{18}O$ as a result of evaporation, or as previously suggested utilization of various mixtures of fresh water and ocean or bay water. For plants, the latter hypothesis seems more plausible, since there was a high correlation between isotope ratios of plant water and the location relative to ocean or bay water (Sternberg and Swart, 1987). With regard to the interstitial water samples, further studies will need to be carried out to determine whether the relationship between δD and δ^{18}O is determined solely by evaporation or mixing. This is particularly true for water samples from CL-*26*, which fall on a mixing line between local rainfall and water from CL-*27* (Fig. 2). The waters from CL-*26* have salinities ranging from 28.6 to 52.4 g kg^{-1}, but have extremely depleted H and O isotopic compositions. Despite such high salinities, these waters were probably derived from rainwater, the salt content being derived from the dissolution of minerals remaining in the sediment. These salts may have been left in the profile during previous periods of inundation by bay water and subsequent desiccation, or been selectively excluded from the roots of plants during uptake of water.

The data presented here show that although the H and O isotope hydrology of waters in Florida Bay is extremely complex, it can be interpreted as a first approximation using the models of Gonfiantini (1965, 1986). In this investigation no attempt was made to use combined mixing and evaporation models (Gonfiantini, 1986) because we lacked spatial and temporal data on the H and O isotopic composition and salinity of bay water. After collection of such information more complex models could be applied and information obtained on the hydrologic balance.

9. Conclusions

(1) The H and O isotopic compositions of waters from Florida Bay and squeezed from the sediments of islands in the bay range in salinity between 28 and 120 g kg^{-1}. Those waters which possess salinities equal to or in excess of the Bay, all show a narrow range of δ^{18}O- and δD-values (δD = +5 to +25‰, δ^{18}O = +2 to +4‰).

(2) Modelling of these data suggests that the compositions can be explained by evaporation into an atmosphere of 77.4% relative humidity at a temperature of 25 °C. These waters are not in isotopic equilibrium with atmospheric moisture.

(3) Correlation between the δD and δ^{18}O of all the data produces a slope of 4.90 (±0.41) and agrees within error with the results from the model. Although the correlation could also have been produced through mixing between meteoric and Florida Bay water, the coincidence between the slope of our data and that predicted by the model strongly indicates that the δD- and δ^{18}O-values of all the Florida Bay waters in the various environments investigated in this study are largely produced by evaporation rather than mixing.

(4) Variability in the H and O isotopic data results from: (1) evaporation at different temperatures and into atmospheres of differing relative humidities, (2) evaporation of solutions with a range of initial isotopic compositions and salinities; and (3) subsequent mixing of waters.

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