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## DECADE-SCALE TREND IN SEA WATER SALINITY REVEALED THROUGH $\delta^{18}\text{O}$ ANALYSIS OF *MONTASTRAEA ANNULARIS* ANNUAL GROWTH BANDS

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### ABSTRACT

Stable oxygen isotope ratios ( $\delta^{18}\text{O}$ ) of coral skeletons are influenced by ambient water temperature and by the oxygen isotope ratio in the surrounding sea water, which, in turn, is linked to evaporation (salinity) and precipitation. To investigate this relationship more thoroughly, we collected hourly temperature data from the Hen and Chickens Reef in the Florida Keys between 1975 and 1988 and compared them to the  $\delta^{18}\text{O}$  of *Montastraea annularis* skeleton that grew during the same interval. To ensure that we obtained the correct oxygen isotopic range in the skeleton we typically sampled the coral at a resolution of 20–30 samples in 1 year; in 1 year we sampled the coral at a resolution of 70 samples·year<sup>-1</sup>. Despite our high-resolution sampling, we were unable to obtain the full temperature-induced  $\delta^{18}\text{O}$  range in the skeleton. Our data suggest that, during the summer, evaporation causes isotopic enrichment in the water, partially masking the temperature-induced signal. Our data also show that oxygen isotopic composition of seawater at the reef has increased since 1981. This increase indicates that salinity has increased slightly during the past decade, perhaps as a result of increased evaporation in waters of Florida Bay and the Keys. This phenomenon is probably not caused by a decrease in the outflow of freshwater into Florida Bay from the Everglades but may be related to the measured deficit in precipitation that has occurred over the past decade.

Corals incorporate tracers of sea water chemistry and environmental conditions into their skeletons that are characteristic of the time of skeletal growth. As early as the 1930's, Ma (1933, 1937) described cyclical patterns of coral skeletal growth related to environmental fluctuations. These cycles were not easily viewed directly, but Knutson et al. (1972) discovered that X-radiography revealed skeletal density banding in several Pacific species. By comparing autoradiographs of the skeleton which revealed the radionuclide signature produced by atomic weapons testing with the density bands, they determined that the banding faithfully records calendar years. Known age of bomb tests and density band counts indicated the bands were annual. During the two decades since this publication, a variety of methods have demonstrated that many massive corals produce density variations that are annual. Methods have included analysis for radioactive decay (Dodge and Thompson, 1974), skeletal staining (Stearn et al., 1977), dated marks on the skeleton (Macintyre and Smith, 1974), sequential collection (Hudson et al., 1976) and incorporation of tracers (Noshkin et al., 1975) with characteristic time histories.

One particularly useful tracer in coral skeletons is the ratio of the two common oxygen isotopes,  $^{18}\text{O}$  and  $^{16}\text{O}$ , measured as a ratio relative to a standard and expressed as  $\delta^{18}\text{O}$  or delta  $^{18}\text{O}$  in units of parts per thousand (per mille). In water, McCrea (1950), Epstein et al. (1953), and O'Neil et al. (1969) demonstrated that the  $\delta^{18}\text{O}$  content of inorganically precipitated calcium carbonate is determined by the  $\delta^{18}\text{O}$  of the water from which it precipitates and the temperature of precipitation. For the temperature range in which corals live, this relation is nearly linear. Weber and Woodhead (1972) found that for many species of corals, the relation between  $\delta^{18}\text{O}_{\text{coral}}$  and temperature was similar to that of O'Neil and others (1969) with a species dependent, negative offset. The relation can be expressed as:

$$\delta^{18}\text{O}_{\text{coral}} - \delta^{18}\text{O}_{\text{water}} = +bT + c \quad (1)$$

where T is water temperature in °C, and b and c are constants (Weber and Woodhead, 1972; Aharon, 1991). Aharon (1991) determined c to lie between 2 and 4 for many skeletal marine carbonates and b to vary from -0.11 to -0.30.

Using these relations, several researchers have reconstructed inter- and intra-annual temperature records by detailed sampling of corals within annual growth bands. For this approach, it is assumed that  $\delta^{18}\text{O}_{\text{water}}$  is constant and that  $\delta^{18}\text{O}_{\text{coral}}$  largely reflects temperature variation. Examples are Fairbanks and Dodge (1979) working in the Caribbean and North Atlantic, Dunbar and Wellington (1981) working in the eastern Pacific, Druffel (1985) in the central Pacific and Patzolt (1984) in the western Pacific.

In areas where there is little temperature variation, isotopic variation in coral skeletons could be used to estimate the oxygen isotopic composition of seawater. Rainfall, runoff, and evaporation strongly effect  $\delta^{18}\text{O}_{\text{water}}$ . Evaporation increases  $\delta^{18}\text{O}$  of sea water and in the open oceans is directly related to salinity (Craig and Gordon, 1965; Broecker, 1974). Rainfall and runoff may also effect  $\delta^{18}\text{O}_{\text{water}}$  in reef areas, typically decreasing the isotopic ratio. Aharon (1991) noted similarity between rainfall and  $\delta^{18}\text{O}$  of coral records from Great Palm Island on the Great Barrier Reef. Cole et al. (1992) has used  $\delta^{18}\text{O}$  of coral as a proxy for rainfall during ENSO fluctuations in the equatorial Pacific.

We have analyzed  $\delta^{18}\text{O}_{\text{coral}}$  from a coral growing at Hen and Chickens Reef, a site strongly influenced by water from Florida Bay. Thermograph data is also available for this site from 1975 to 1988. In this paper, sea water temperature and coral isotope ratios are used to calculate changes in sea water isotopic composition from 1975 to 1988, using published relations between coral isotopic composition, temperature, and water isotopic composition. The oxygen isotopic composition of sea water has not been systematically measured anywhere in the south Florida region.

## MATERIALS AND METHODS

In March of 1989, a core boring, 5.5 cm in diameter and 28 cm long was taken from a colony of *Montastraea annularis* at Hen and Chickens Reef (Fig. 1) using equipment and techniques described by Hudson et al. (1994). This species is morphologically variable and a colony of morphotype 2 (Knowlton et al., 1992) was selected from 3 m depth near the center of the reef. A 4 mm thick slab was cut from the core parallel to the growth axis using a diamond bladed rock saw. X-radiographs were prepared from the slab to reveal density variation and assign a chronology to annual growth bands (Fig. 2), as well as measure extension and calcification rates following the methods of (Dodge and Kohler, 1985). Approximately 0.10 mg samples of aragonite were drilled from exothecal skeletal aragonite. Samples were taken from a coral slab parallel to the direction of growth at a frequency of about 20 samples per annual growth band. These samples were analyzed for  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  following methods described by Leder et al. (1991).

An intra-annual chronology for intervening samples was estimated by linear interpolation between annual, high density markers assuming a constant extension rate during the year. This assumption introduces error because extension almost certainly varies during the growth year as do many other physiological aspects of coral life. Most workers believe extension slows during dense band formation. However, this variation is poorly known and not quantified at this time.

Hourly seafloor temperature records from Hen and Chickens Reef (Hudson et al., 1991) were reduced to monthly averages. These data were used to predict the  $\delta^{18}\text{O}_{\text{coral}}$  variation in the sample due to temperature using the relation:

$$0.22 \Delta \text{T}^\circ\text{C} = -\Delta \delta^{18}\text{O}_{\text{coral}} \quad (2)$$

Equation 2 is derived from data presented by Fairbanks and Dodge (1979) for samples of *Montastraea annularis* from Jamaica and Bermuda, areas of small  $\delta^{18}\text{O}_{\text{water}}$  variation. Isotopic variation of sea water at Hen and Chickens Reef is estimated by subtracting temperature-induced variation from measured skeletal values. Although 0.22 is a good approximation of the constant b in Equation 1, the offset, c, must be estimated for *Montastraea annularis*.

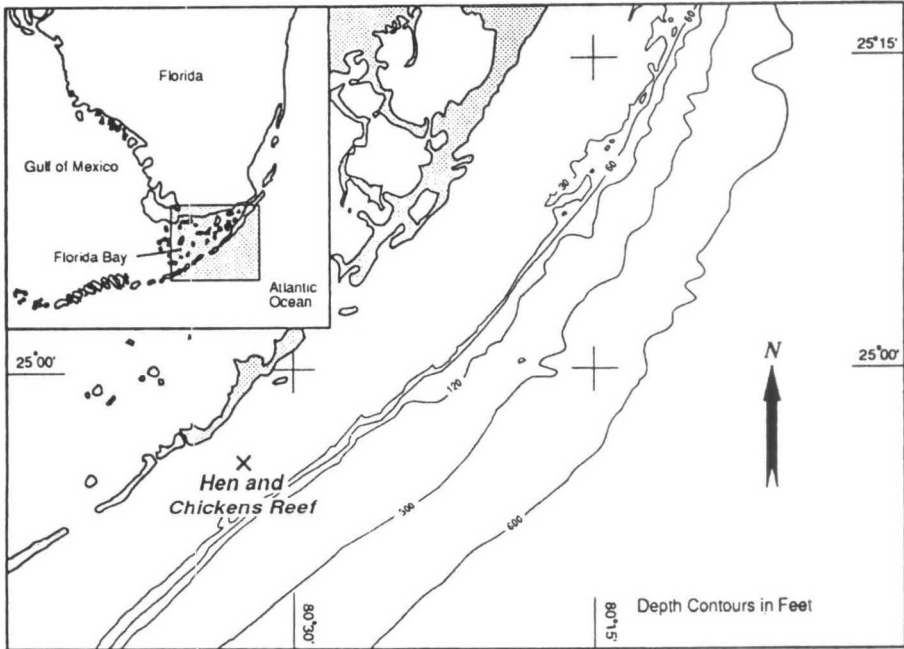


Figure 1. Location of Hen and Chickens Reef in the Upper Florida Keys.

Based on a comparison of the minimum  $\delta^{18}\text{O}$  values for the same species between Jamaica and Florida (Carysfort Reef), Leder et al. (1991) concluded that approximately 1 per mille was missing from the summer portion of the coral record at 30°C and that the correct  $\delta^{18}\text{O}$  of the coral at this temperature should be  $-5.6$  per mille. For corals from Hen and Chickens Reef, where summer water temperatures are approximately 2°C warmer than at Carysfort Reef, the correct  $\delta^{18}\text{O}$  should be approximately  $-6.0$ . In fact, the lightest values we measured were approximately  $-4.6$  per mille, a 1.4 per mille difference. Using  $-6.0$  as a summer value, the winter oxygen isotopic compositions are between 2 and 3 per mille heavier than the true summer values equating to a temperature range equivalent to that observed at Hen and Chickens Reef. Hence these corals appear to record approximately the correct winter temperature assuming  $\delta^{18}\text{O}_{\text{water}}$  of approximately 0 per mille (standard mean ocean water). This assumption means that the oxygen isotopic composition of the coral skeleton is approximately 3 per mille offset toward more negative values than equilibrium. If the winter isotopic composition of the Florida Reef tract water is heavier than 0 per mille, then this offset would be larger. We used an estimate of 3 for the offset,  $c$ , to calculate relative trends in sea water at Hen and Chickens Reef.

## RESULTS

Results of the isotope and density analysis are shown in Figure 3a and 3b. Comparisons of sampling locations to density banding shows that annual high density band portions correspond with minimal  $\delta^{18}\text{O}$  coral values. The correspondence occurs because high-density bands form during the summer when water temperatures are at the annual maximum (Hudson et al., 1976; Fairbanks and Dodge, 1979). Both highest density and lowest  $\delta^{18}\text{O}_{\text{coral}}$  are used to place an annual marker in the skeletal record. Slight variations in correspondence of high density and low  $\delta^{18}\text{O}_{\text{coral}}$  are believed to result from sampling unequal intervals and sampling across growth zones in the fine structure of the skeleton (Risk and Pearce, 1992).

Monthly average sea water temperatures at Hen and Chickens Reef are shown in Figure 3c for the years 1975–1987 and are substituted in Equation 1 with  $-.22$

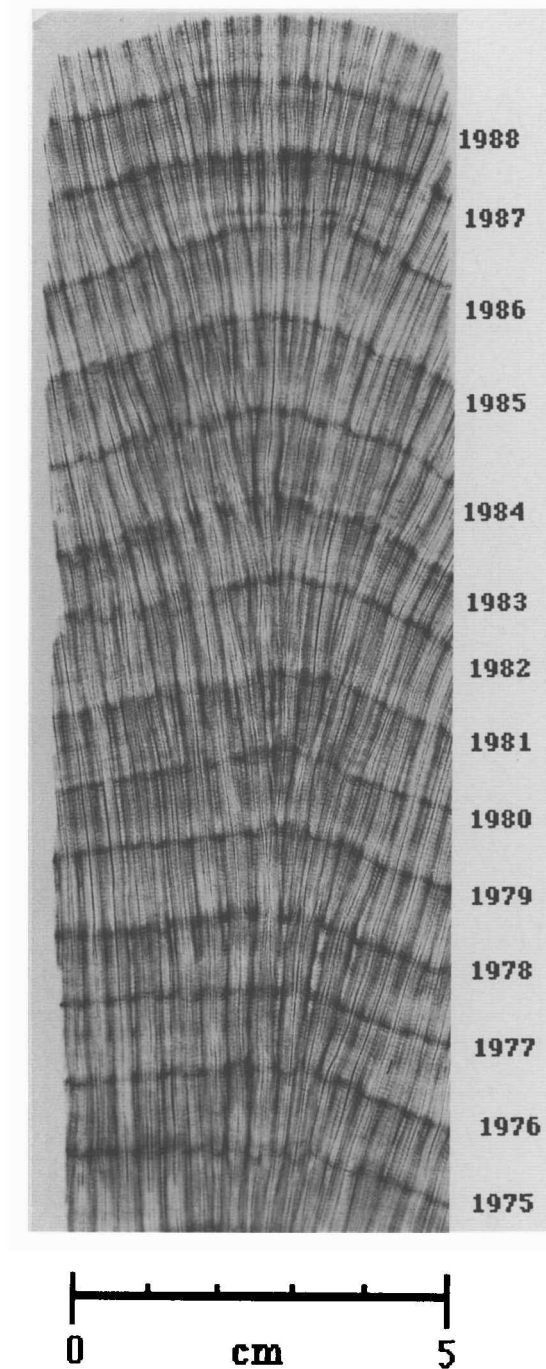
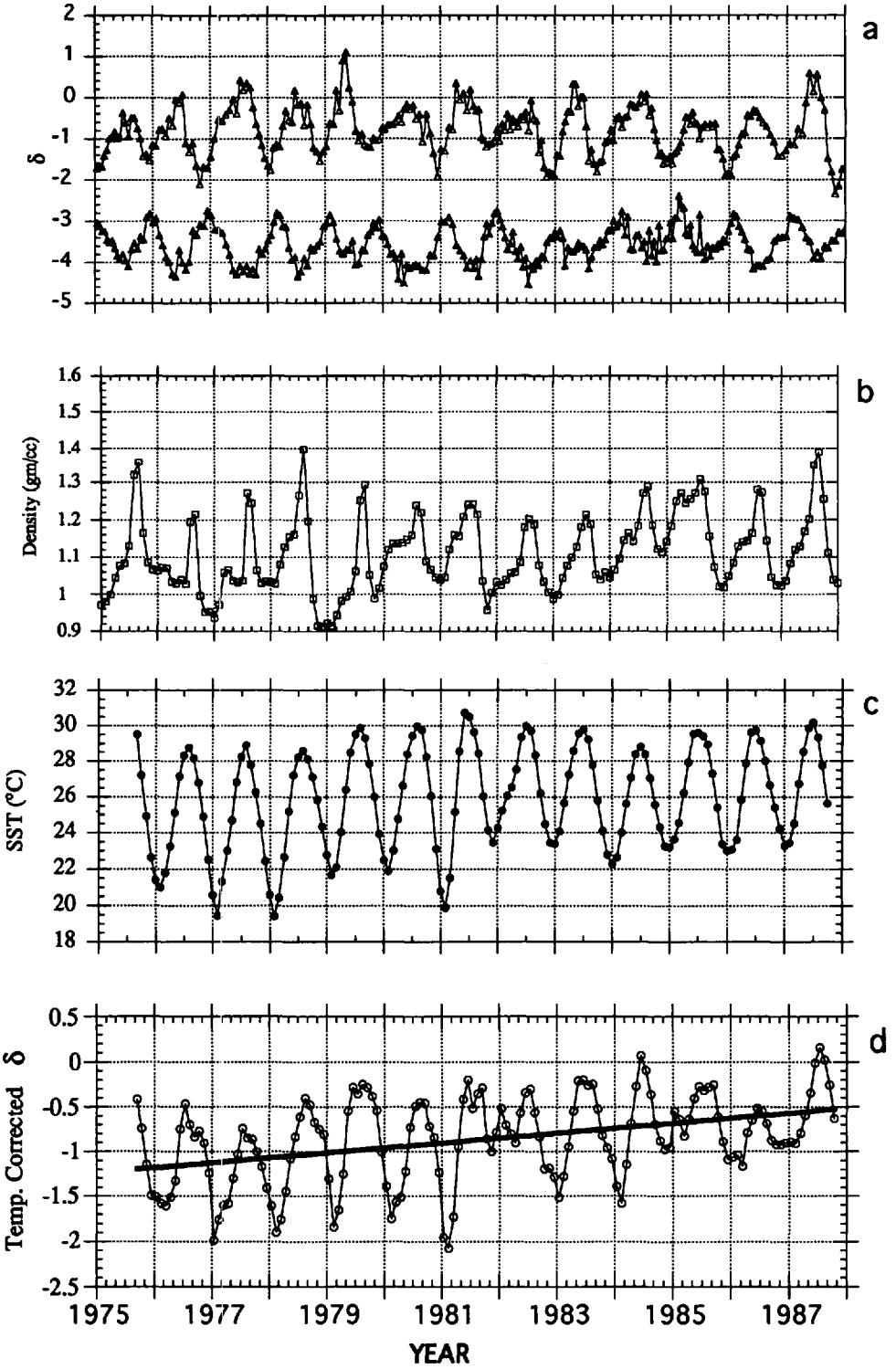


Figure 2. X-radiograph of core slab from *Montastraea annularis* illustrating skeletal density variation and dates assigned to high density bands.



and 3.0 for the constants  $b$  and  $c$  respectively, to estimate water isotopic variation. That is:

$$\delta^{18}\text{O}_{\text{water}} = \delta^{18}\text{O}_{\text{coral}} + 0.22(T) - 3 \quad (3)$$

estimates isotopic variation in seawater. In practice, isotopic measurements are interpolated to 12 equally spaced values for comparison with other monthly data. The resulting estimate of water variation is shown in Figure 3d. This analysis reveals an average annual seawater variation of about 1.5‰ in water at Hen and Chickens Reef, with most negative values occurring in the winter and positive values occurring in the late summer and fall. In addition, a linear regression of the data indicates that there has been an irregular but overall increase in  $\delta^{18}\text{O}_{\text{water}}$  of about 0.7‰ at this site during this 13-year period. Most of this increase appears to have occurred since 1981. An F-test of the slope of this regression indicates it is significant at  $P = 0.05$ .

Four measurements of the oxygen isotopic composition of sea water are available seaward of the Florida Keys. Lloyd (1964) analyzed three samples collected in August, 1958. One of Lloyd's samples, from about 15 km SW of Hen and Chickens Reef seaward of a wide channel between the Keys, had  $\delta^{18}\text{O}_{\text{water}}$  1.5‰. The other two samples collected about 20 km NE of Hen and Chickens Reef and seaward of central Key Largo, were 0.9 and 1.0‰. Da Silveira and others (1987) analyzed one sample collected along the eastern shore of Elliot Key, about 50 km NE of Hen and Chickens Reef. This sample, collected 15 August, 1986, was 1.2‰. These four measurements, although insufficient for direct comparison with estimates from coral skeletons, are 1–2‰ higher than our summer estimates and indicate that the coral record is missing part of the summer record as suggested by Leder and others (1991).

#### DISCUSSION

The data presented in this paper support the notion of decade-scale changes in the oxygen isotopic composition of sea water affecting Hen and Chickens Reef. In a normal reef environment such an increase would be interpreted as reflecting an increase in salinity and this is probably the most likely explanation here. However, there is at least one other possibility, namely that the increase could reflect enhanced addition of isotopically heavy water from the Everglades (Lloyd, 1964; Swart et al., 1989). This would necessitate a significant increase in flow from the Everglades during this period and present data does not support this contention (Smith et al., 1989; Roblee, pers. comm.). Furthermore, as the Hen and Chickens coral is located on the Atlantic side of the Keys, it is likely that variations in freshwater flow from the mainland would have only a minimal influence.

While our favored hypothesis is that the increase reflects enhanced salinity we cannot quantitatively hindcast how much of an increase occurred over this period. Although there is a well known relationship between salinity and oxygen isotopic composition in the open ocean, this relationship does not apply to south Florida coastal environments. In addition to the effects of isotopically heavy (evaporated)

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Figure 3. Measured and calculated skeletal and seawater parameters at Hen and Chickens Reef for the growth period 1975–1988. 3a)  $\delta^{18}\text{O}$  (solid triangles) and  $\delta^{13}\text{C}$  (open triangles) in *Montastraea annularis* skeleton; 3b) skeletal density (open squares); 3c) monthly mean sea surface temperatures; and 3d) calculated change in oxygen isotope ratio of seawater at Hen and Chickens. Heavy solid line is the regression indicating 0.7‰ increase for the period of record.

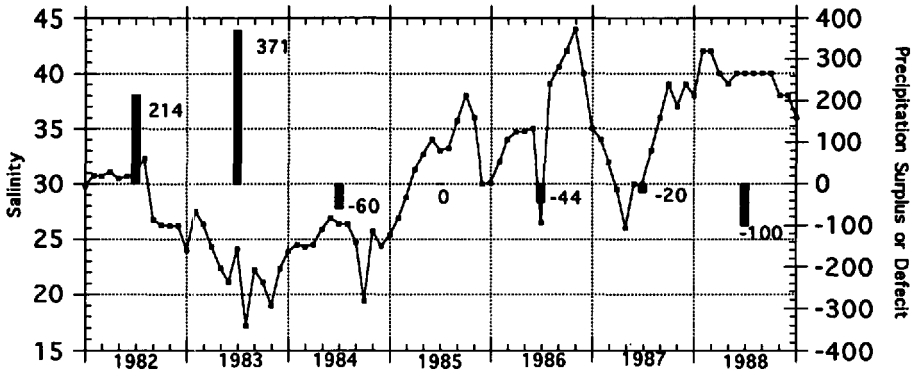


Figure 4. Salinity variation at latitude 25°05'08" and longitude 80°31'06" in Florida Bay (solid squares are approximately monthly measurements in parts per thousand) compared with annual surplus or deficit precipitation in millimeters (solid bars).

freshwater entering coastal areas, the oxygen isotopic composition of sea water is influenced by normal evaporation and precipitation processes. Generally precipitation reduces salinity and lowers  $\delta^{18}\text{O}_{\text{water}}$  whereas evaporation increases both these parameters. However, as a result of the high relative humidity and high evaporation in south Florida, the isotopic composition of the water quickly reaches an equilibrium with the atmosphere and even though salinity may continue to increase,  $\delta^{18}\text{O}_{\text{water}}$  does not (Swart et al., 1989). Notwithstanding these complications, we believe our data suggest an irregular but significant increase in salinity between 1976 and 1988.

The hindcast salinity increase most likely resulted from a decrease in precipitation experienced by this area (Fig. 4). The decades of the 1970s and 1980s were unusually dry in south Florida. Between 1975–1989 south Florida (Florida areas 5, 6, and 7 of the National Climatic Data Center) experienced below average or near average precipitation every year except 1982–1983 and overall was 48 mm (19 in) below normal. Salinity in the Florida Keys area is a function of sea water circulation as well as climate and cannot be predicted from climate alone. Although circulation in this region is complex, a comparison of precipitation and salinity from a point in Florida Bay (about 10 km from Hen and Chickens Reef) shows evidence of the relation between climate and salinity (Fig. 4). At this location in the bay salinity is relatively low during years of surplus precipitation and relatively high during dry years. The increase in salinity during the 1980's at this bay site may have influenced sea water at Hen and Chickens and the entire region may have responded in a similar way to the same general climatic conditions.

The lower rainfall affected salinity and oxygen isotopic composition in two ways. First, there was a reduction in isotopically light precipitation ( $-3$  per mille; Swart et al., 1989) into local waters. Second a reduction in the amount of precipitation is usually associated with reduced cloudiness and hence enhanced sunshine and evaporation. Both these affects would act to isotopically increase salinity and the  $\delta^{18}\text{O}$  of sea water. However, there is no evidence that salinity at Hen and Chickens reached levels sufficiently high to stress the corals.

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