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## BARIUM CHRONOLOGIES FROM SOUTH FLORIDA REEF CORALS - ENVIRONMENTAL IMPLICATIONS

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## ABSTRACT

Benthic algal blooms (e.g., *Codium isthmocladum*) have become increasingly common on reefs and hardgrounds of Southeast Florida. The contribution from possible responsible nutrient sources, including natural upwelling and local pollution, has not been quantified. In an attempt to differentiate each potential source, lattice-bound barium concentrations in the skeletons of two common Southeast Florida stony coral species (*Montastraea faveolata* and *Solenastrea bournoni*) were measured by isotope dilution inductively coupled mass spectrometry (ICP/MS). Specimens were collected offshore between 26°01'-57'N at shallow (10 m) and deep (20 m) reefs. X-rays of skeletal slabs revealed annual density bands which guided annual and subannual chemical sampling over 20 years. Selected specimens were analyzed for oxygen and carbon isotope content to gauge water temperature and salinity. Results demonstrate historical Ba levels in corals and variability among species, seasons, years, and sites.

## INTRODUCTION

In recent years there have been widespread summer algal blooms (*C. isthmocladum*) on Southeast Florida reefs (Palm Beach, Broward, and Dade Counties). Algae have overgrown, smothered, and removed substrate for natural settlement from the coral reef communities. The recurrent summertime *Codium* blooms have impacted over the 54 nautical miles of coastline, from northern Broward through Palm Beach County. Extensive accumulations were first noticed in 1989, when anecdotal reports of algae accumulations up to 1.5 m thick were reported off of Boca Raton in 25 m depth.

## Proposed causes

Several sources of nutrients could be fueling the algal blooms. These include 1) man-induced (agricultural runoff, sewage) and 2) natural (upwelling). Unfortunately, little quantitative data exist on the spatial and time distribution or sources of nutrients off the Southeast Florida coast.

Anthropogenic nutrient sources of significant magnitude currently impact the coastal waters of Palm Beach, Broward, and Dade Counties. Six outfalls at depths greater than 30 m discharge approximately 400 million gallons per day of secondarily treated, nutrient-rich wastewater (Proni and Damann, 1989). Inlets to the intracoastal waterways along this stretch of coastline may act as additional point sources for pollution, particularly for large volumes of storm-water runoff (Hauert and Startzman, 1985). Additionally, canals discharging through the inlets contain waters draining Lake Okeechobee and extensive surrounding agricultural areas.

In Southeast Florida, upwelling of nutrient rich water occurs. While this is not as intense as the general phenomena on west sides of continents, upwelling can be a significant source of nutrient supplies (Yoder et al., 1983; Smith, 1983; Chew et al., 1985). Thus, a clear mechanism exists for upwelling-induced nutrient enrichment of Florida's waters.

## Objectives of the study

We have compared barium,  $\delta^{13}\text{C}$ , and  $\delta^{18}\text{O}$  oxygen records of sampled coral skeletons from different depths and latitudes along the northern Broward and Palm Beach coastline. The objectives of this study were to: 1) evaluate the necessity and efficacy of skeletal cleaning procedures prior to analysis and 2) attempt to differentiate potential sources of nutrients contributing to the algae blooms.

## Background

The history of nutrient enrichment may be indicated by the trace elements Cd, Mn, and Ba (Shen, 1986; Shen and Boyle, 1988; Lea et al., 1989; Shen and Sanford, 1990). Cd and Ba are nutrient analogs (e.g., Boyle et al., 1981; Millero and Sohn, 1992) exhibiting

strong nutrient type profiles with depth. These trace elements may be incorporated in the calcium carbonate lattice of coral skeletons by substitution with calcium (Shen and Boyle, 1988; Shen and Sanford, 1990). Shen and Sanford (1990) define elements that "cannot be added or removed unless mineral dissolution or alteration occurs" as "lattice substituted", and it is these elements that have the highest potential as permanent markers of historic nutrient conditions. Cd and Ba in dated coral skeleton samples have been shown to reflect former nutrient conditions, especially in regions marked by strong upwelling events such as the Galapagos (Shen and Sanford, 1990; Lea et al., 1989) or the coast of southern Oman (Tudhope et al., in press). Furthermore, barium is also thought to be of value as a chemical tracer delivered to the oceans by rivers (Shen and Sanford, 1990; Boyle, 1976; Hanor and Chan, 1977; Edmond et al., 1978).

The C and O isotopic composition of coral skeletons has been studied by numerous workers (Weber and Woodhead, 1970, 1972; Land et al., 1975a, 1975b; Weber et al., 1975, 1976, Goreau, 1977; Fairbanks and Dodge, 1979; Swart and Coleman, 1980; Swart, 1983; Weil et al., 1981; Patzold, 1984; McConnaughey, 1986, 1989b; Swart et al., in press). For review, see Swart (1983) and McConnaughey (1989a). It has been reasonably established that the O isotopic composition of the skeleton is negatively correlated with temperature as a result of normal equilibrium or perhaps kinetic processes (Weber and Woodhead, 1972; Fairbanks and Dodge, 1979; Weil et al. 1981; McConnaughey, 1989a,b). The C isotopic composition of zooxanthellate coral skeletons frequently exhibits no relationship to easily quantifiable environmental variables such as temperature and insolation. Because of the eventual breakdown of organic matter in the deep ocean, upwelled waters should generally be lighter (more depleted) than the surface waters they are mixing with. Therefore, depleted  $\delta^{13}\text{C}$  of the skeletal material could indicate 1) freshwater, 2) upwelling, or 3) a combination of both.

## MATERIALS AND METHODS

## Collection area

The study site is located between N lat. 26°01'-57' along South Florida's eastern coastline (see Fig. 1). Reefs of this area parallel the shoreline in a series of ridges or terraces separated by plains of sand (Goldberg, 1973). The reefs are divided into three reef terraces which are approximately 100, 800, and 2000 meters offshore, and in depths of 4-7, 7-14, and 17 to 23 m, respectively. The deepest reef terrace is biologically and geologically the most well developed (Goldberg, 1973). The tracts are marked by few interruptions until West Palm Beach, where the inshore reefs all but disappear. Only the third and deepest reef remains past Juno Beach.

## Experimental design and sampling site

Six stations were sampled: two control sites unaffected by *Codium* blooms (Hollywood Beach-H and Commercial Pier-C) and four affected sites (Boca Inlet-B, West Palm Beach-W, Juno-J, and Jupiter-JP). Using SCUBA, we collected coral specimens (10-40 cm diameter) of *Montastraea faveolata* and *Solenastrea bournoni* from the second-M (10 m) and third-D reefs (20 m). The first reef was not sampled because of low coral abundance. The species were chosen for their abundance on Southeast Florida reefs and because they usually demonstrate good density banding.

## Collecting, slabbing, and x-radiographing

After collection, colonies were air dried and then sectioned parallel to the axis of growth into slabs approximately .5 cm thick with a masonry diamond bit saw. Slabs were X-radiographed to expose density banding. Transects for subsampling were oriented normal to growth band boundaries. Skeletal subsamples were obtained in two ways. For *S. bournoni*, small (1-2 g) wafers representing a full year's growth were cut with a hand-held dental drill equipped with a circular blade (0.05 mm thickness), then crushed with an agate

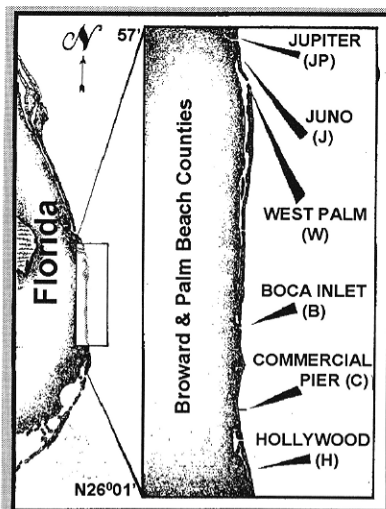


Fig. 1: Map of collection area.

to avoid potential tissue contamination.

#### Cleaning experiment design

Shen and Boyle (1988) and Linn et al. (1990) have demonstrated the importance of cleaning coral samples of pre-existing surface or occluded contamination (organic and detrital). Colonies (both species) from several sites and depth were used to assess the need of a cleaning protocol. The most recent growth years of specimens—where contamination effects were most likely to occur—were sampled (Flor and Moore, 1977; Buddemeier et al., 1981; Lea and Boyle, 1992). Skeleton for at least 20 analyses (5 to 8 g) was removed and crushed. One fraction of the powder was cleaned, the other was not. Ten samples of each fraction were analyzed. This experiment was also performed with 10- to 12-year-old skeletal samples from one *S. bournoni* specimen.

#### Treatment design and efficacy

Cleaning treatment of the coral samples for barium analysis was done according to the method of Lea and Boyle (1992):

Step 1: Distillation and sonication in distilled water, and 0.016 N dist. HNO<sub>3</sub> (3 times).

Step 2: Treatment with boiling 50/50 30% H<sub>2</sub>O<sub>2</sub> and 0.2 N NaOH (3 times).

Step 3: Leaching with 0.1 N Distilled HNO<sub>3</sub> (2 times).

Experiments were also performed on two *S. bournoni* colonies to determine at what point further cleaning of the coral became unnecessary. Two extra acid leaches were added to the protocol (with .16 N distilled HNO<sub>3</sub>).

#### Dating and sampling

A continuous record of skeletal density near the chemical sampling transect was obtained using image analysis densitometry of coral X-radiographs (see Dodge and Kohler, 1985; Dodge and Kohler, 1993). The highest annual values found were considered to have occurred in September (highest temperature month) of that particular growth year. Since subsamples for *M. faveolata* were systematically taken at 800  $\mu$ m intervals, interpolation to a common time was necessary to develop Ba and isotope records of equal intervals (3 months) to allow comparisons.

#### Ba sample preparation.

A total of 18 barium chronologies, from 1985 to 1994 (or 1995) were determined for 9 *M. faveolata* and 9 *S. bournoni*. Barium was determined by ICP/MS. Each sample comprised approximately 0.1 to 1.5 g (.500 g on average). Coral powder was dissolved in 200  $\mu$ L of 2N (the acid was distilled in a sub-boiling still; one distillation was enough to produce no measurable barium blank). To the solution, 100  $\mu$ L <sup>138</sup>Ba spike at 81 ppb (total) barium was added and the sample was brought to a final volume of 1.5 mL. Attempts were made to keep <sup>138</sup>Ba/<sup>137</sup>Ba sample ratios around unity to avoid under- or over-spiking (see Klinkhammer and Chan, 1990), but this sometimes proved difficult as ratios varied from .2 to 10 and occasionally much higher. A consistency standard

mortar and pestle. Subsamples with obvious non-skeletal material were sonicated prior to crushing. Each sample was then transferred directly into a 1.5 ml acid-leached vial and cleaned (to be described). For *M. faveolata*, coral slabs were fixed to a computer-driven moveable XYZ platform and "dragged" in 800  $\mu$ m increments (around 500  $\mu$ g coral powder) across a small carbide tip dental drill. The resulting groove was typically 3 to 4 mm deep. The powder was collected into acid-leached 1.5 ml polyethylene vials. Efforts were made to choose a continuous coralite, and to sample exothecal elements only

(cocktail) made up of <sup>135</sup>Ba spike and reagent grade Ba Cl<sub>2</sub>.H<sub>2</sub>O was analyzed after every 10 to 20 sample readings.

A Perkin-Elmer Elan 5000 ICP/MS (with a Gilson 212B autosampler) was utilized for all barium analyses. Ca was analyzed by flame atomic absorption spectrophotometry (AAS).

#### Carbon and oxygen

Carbon and oxygen samples were sampled with a carbide tip dental drill combined with an XYZ stage. As with sampling for barium with this instrument, corals were drilled as far as possible along a continuous polyp tract, chosen as closely as possible to the barium transects. Smaller sample size was utilized for isotopes (approximately 350  $\mu$ m intervals). This allowed 10 samples per year on faster growing corals. Samples were analyzed for  $\delta^{13}C$  and  $\delta^{18}O$  values using standard methods (Swart et al., 1991).

#### RESULTS

Results are organized into three parts: 1) Cleaning experiments, 2) barium chronologies, and 3) preliminary isotope chronologies.

#### Cleaning experiment

Fig. 2 shows *S. bournoni* mean barium concentrations of recent growth band samples from uncleaned (untreated-U) and cleaned (treated-T) corals (n = 10 in each case). Cleaning of the *S. bournoni* samples produced considerable decrease in mean barium concentrations. In some corals (3rd reef at Hollywood-HD, 2nd and 3rd reefs at Commercial Pier-CM, CD) extreme variations occurred. Only one coral (Juno Beach 3rd reef-JD) did not demonstrate a statistically significant difference in mean barium concentration after cleaning. This was caused by a single outlier. Omission of this value from the average resulted in a statistical difference (p < 0.006).

Means of uncleaned *S. bournoni* samples were highly variable (7 to 54  $\mu$ Mol Ba/Mol Ca) and significantly different when tested by ANOVA. Once cleaned, means of these samples were less variable (4 to 7  $\mu$ Mol Ba/Mol Ca) but still significantly different when tested by ANOVA.

There was no obvious relationship between *S. bournoni* samples within or between control and affected areas. The 2nd reef coral from the Hollywood control site (HM) showed the least contamination, while the 3rd reef coral from same site (HD) showed the most (Fig.2). This increase with depth (47  $\mu$ MOL Ba) is not mirrored in corals from the Commercial Pier control site immediately to the north, where contamination levels for 2nd (CM) and 3rd (CD) reef corals were high and almost equal (~38  $\mu$ Mol Ba) (Fig.2). The algae bloom area coral from the 3rd reef at Juno Beach (JD) showed relatively low contamination of uncleaned samples (Fig.2).

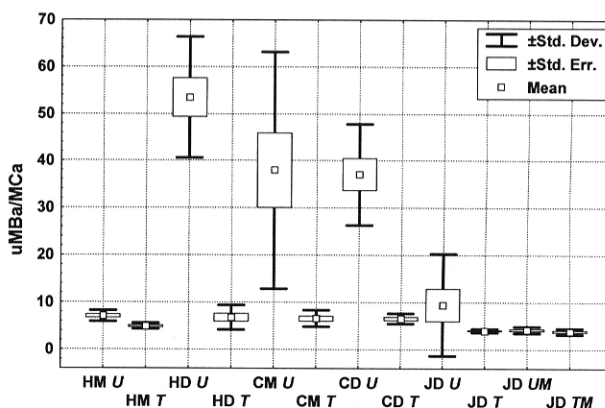


Fig. 2: *S. bournoni* cleaning experiment. Means are for 10 analyses. U: untreated; T: treated; HM: Hollywood 2nd reef; HD: Hollywood 3rd reef; CM: Commercial Pier 2nd reef; CD: Commercial Pier 3rd reef; JD: Juno Beach 3rd reef; UM: untreated middle of coral skeletal elements; TM: treated middle of coral skeletal elements.

Older skeletal elements (10 to 15 years back from collection date of colony) of *S. bournoni* from the affected area of Juno Beach were cleaned and compared. No significant differences between means were found (see JD UM and JD TM in Fig. 2). For this colony at least, contamination was a problem confined to the most recently deposited skeletal structures, as noted by other researchers (Tudhope et al., 1995; Hart and Cohen, in press).

Significantly higher mean barium levels found in uncleaned *S. bournoni* (Fig. 2) clearly mandated that all coral samples from this species be cleaned.

Six *M. faveolata* were analyzed in the same fashion as *S. bournoni*. Three colonies were from the control site (HM, CM, and CD) and three from the affected areas (BD, WM, and WD) (see Fig. 3 below). No differences were found by ANOVA between cleaned and uncleaned samples from any site. The cleaning protocol for *M. faveolata*, therefore, was not needed and not used prior to dissolution and spiking of barium transect samples.

**Cleaning efficacy**

We tested to determine if extra cleaning of *S. bournoni* samples would cause barium levels to significantly decrease. Additional acid leaches were performed on coral powder from two colonies of *S. bournoni*, both known to contain high surface barium. One was from a control site (Commercial Pier-CD), while the other was a large (1-1.5 m in diameter) specimen from Florida Bay (FB) (Hudson et al., 1989). Fig. 4 shows results. ANOVA revealed significant differences between cleaned and uncleaned samples from both sites, and a small significant increase in mean barium levels of the Commercial Pier coral with additional cleaning, perhaps caused by sample heterogeneity. Most importantly, further cleaning of the Commercial Pier and the more contaminated Florida Bay coral did not show a decrease in measured barium levels. Consequently, the full cleaning treatment without additional acid leaches was judged sufficient.

It should be noted that the extremely high barium levels recorded in the untreated Florida Bay coral samples are underestimated due to underspiking (their elevated concentrations were not anticipated -see Klinkhammer and Chan, 1989).

**Barium chronologies**

Fig. 5 shows the mean of each *M. faveolata* over a 10 year growth period. All barium data have been interpolated (four samples per year). Figs. 6A and 6B present chronological barium levels for each *M. faveolata* coral. ANOVA revealed that there were significant differences between mean barium level for each *M. faveolata*, as well as between yearly means for the 1993.5-1984 barium ensemble chronology (not shown). Post Hoc testing (Newman-Keuls) pointed to significant differences between the means of 1990 and 1984, partly caused by markedly higher barium levels in 1990 for both Boca Inlet corals (see Fig. 6B). Concentrations showed high variability within and between corals of same or different depth and location (Fig. 6A, B). FFT analyses of each time series did not show a readily identifiable seasonal cycle.

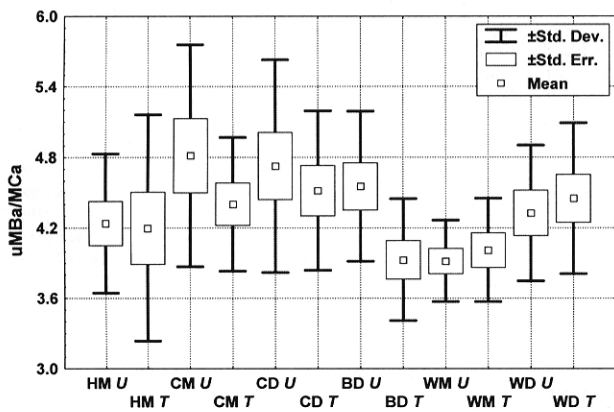


Fig. 3: *M. faveolata* cleaning experiment. Means are for 10 analyses. BD: Boca Inlet 3rd reef; WM: West Palm 2nd reef; WD: West Palm 3rd reef.

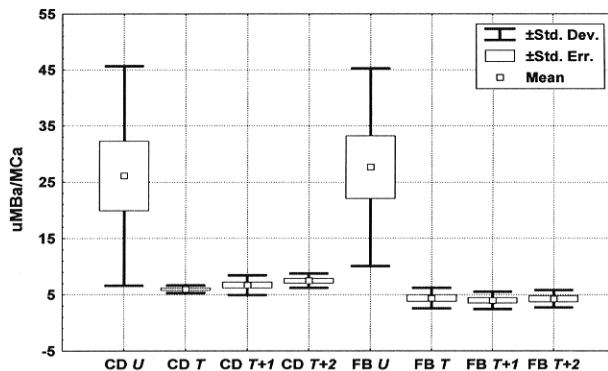


Fig. 4: Cleaning efficacy. Means of *S. bournoni* untreated (U), after full treatment (T), and two additional acid leaches (T+1, T+2). FB: Florida Bay (lower Mattacumbe). FB U mean (27.65 $\mu$ MolBa) should be multiplied by 100.

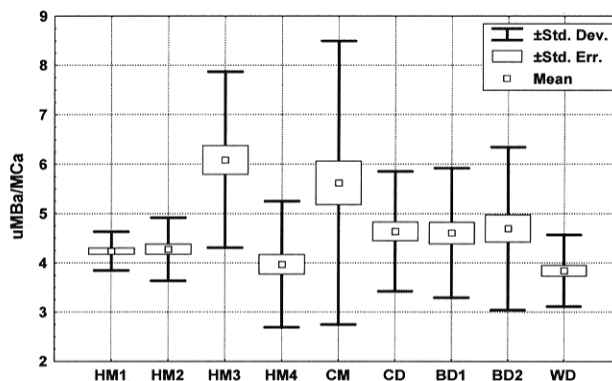


Fig. 5: Mean (n = 40 samples and 10 years) of *M. faveolata* chronologies. BD1 and BD2: two different *M. faveolata* colonies from the 3rd reef at Boca Inlet.

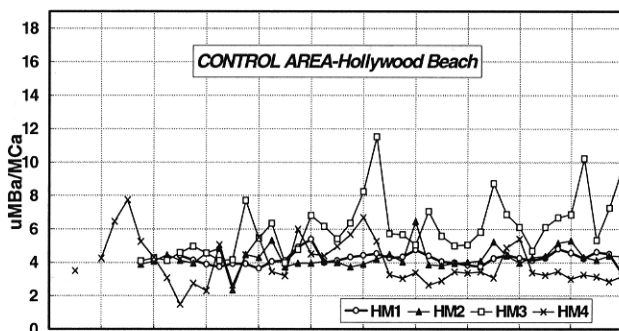
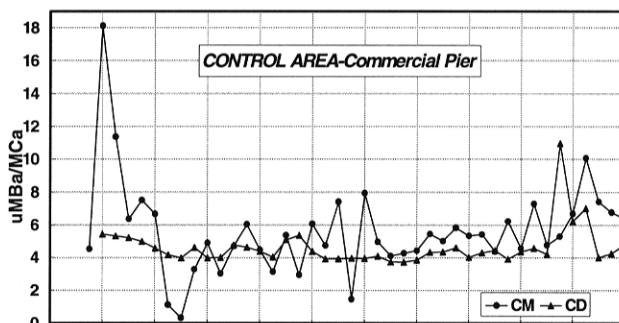


Fig. 6A: Barium chronologies for control area *M. faveolata*.

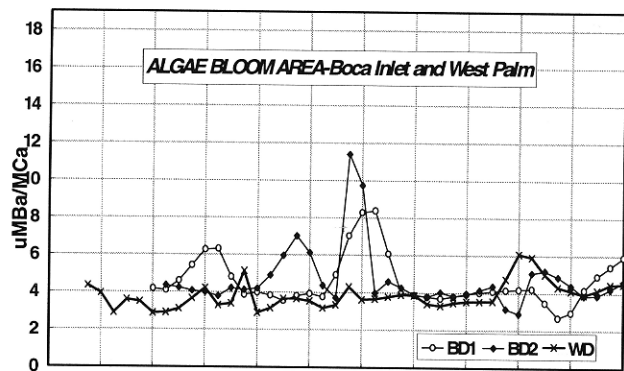


Fig. 6B: Barium chronologies for algae bloom area *M. faveolata*.

Fig. 7 gives means for each *S. bournoni* over a ten year period (1985-1994). ANOVA revealed no differences between individual coral mean barium levels for *S. bournoni*. Figs. 8A and 8B contain values for barium chronologies for each *S. bournoni*. The dominant feature of the annual *S. bournoni* transects is the marked increase of barium levels in samples representing the year 1993 and later. Post Hoc (Newman-Keuls) testing of ANOVA on the 1994-1985 ensemble chronology singled out the 1994 mean as significant. Despite our cleaning experiments showing no decrease in barium with successive acid leaches on samples from the most recent years of coral growth in the Commercial Pier 3rd reef coral (CD) (Fig. 3), the mean *S. bournoni* values for 1994 and 1995 hint at potential contamination, as seen by other researchers (Tudhope et al., in press; Cohen and Hart, 1985). The reason for this barium-rich phase is unknown. Tissue barium concentrations can be up to 10 times those of the skeleton; thus, insufficient reductive cleaning possibly accounts for this contamination.

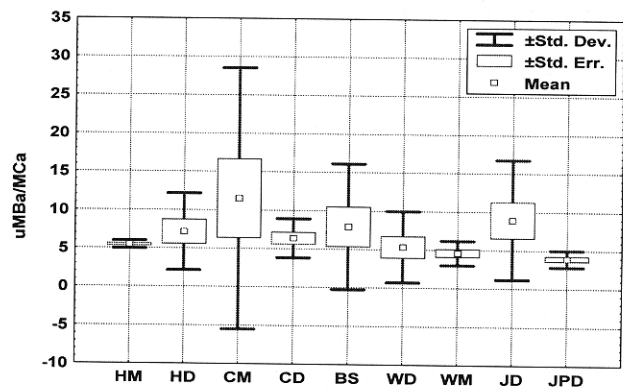


Fig. 7: Mean (n = 10 samples and 10 years) of *S. bournoni* chronologies. JPD: Jupiter Beach 3rd reef.

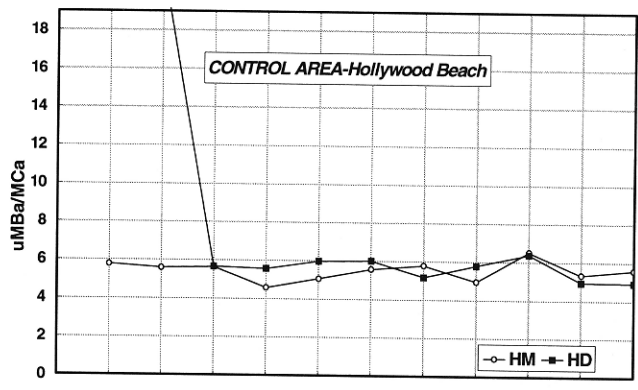


Fig. 8A: Barium chronology for control area *S. bournoni*.

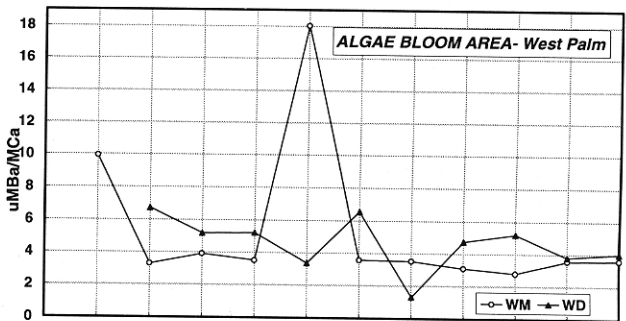
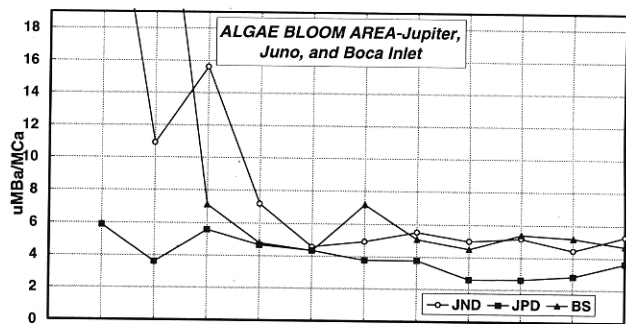
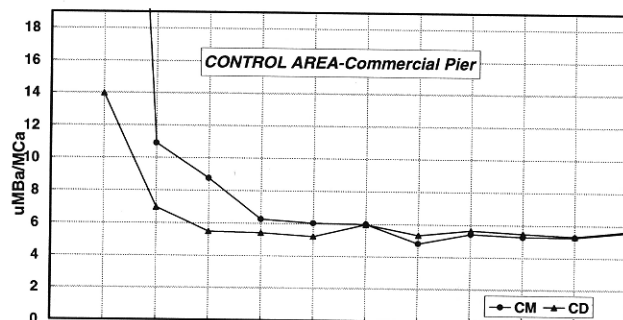


Fig. 8B: Barium chronologies for control and algae bloom area *S. bournoni*.

**Preliminary carbon and oxygen time series**

Fig. 9 shows isotope and density chronologies for corals from Juno and Jupiter. Figs. 10A and 10B show carbon and oxygen chronologies for corals from Hollywood, Commercial Pier, and West Palm Beach. The two Commercial Pier corals were sampled coarsely at 4 samples per year, while all others were sampled at 7 to 12 samples per year. Caution should be used when interpreting records for the Juno and Jupiter Beach corals from the affected area because poor density banding in these made assignment of years difficult.

The range of the complete  $\delta^{13}C$  data set was from  $-0.5\text{‰}$  to  $-4.5\text{‰}$ .  $\delta^{13}C$  measurements within chronologies varied considerably, displaying a maximum of almost  $3.5\text{‰}$  in Hollywood Beach (2nd reef). The range of the complete  $\delta^{18}O$  data set was between  $-1.5$  and  $-4\text{‰}$ . The range of  $\delta^{18}O$  for corals from Juno, Jupiter, Commercial Pier (3rd reef), and Hollywood Beach was nearly  $2\text{‰}$ , except for the 2nd reef Commercial Pier *S. bournoni* and West Palm Beach *M. faveolata* which were  $1\text{‰}$ . Individual coral carbon and oxygen chronologies were significantly positively correlated, with the 3rd reef Commercial Pier coral exhibiting the highest coefficient. No clear annual or seasonal cycle was noted except in the more recent carbon isotope measurements of the Hollywood Beach (2nd reef) *M. faveolata*. From 1990 to 1995, at this site, carbon showed a broader range of values and a pronounced seasonal cycle.

**DISCUSSION**

The four *M. faveolata* 2nd reef coral chronologies from the Hollywood Beach control site (Figure 6A, B) show no clear patterns of barium level over time or with depth. One 2nd reef coral had a concentration range of  $2\text{ }\mu\text{Mol Ba/Mol Ca}$  while another located 5 m

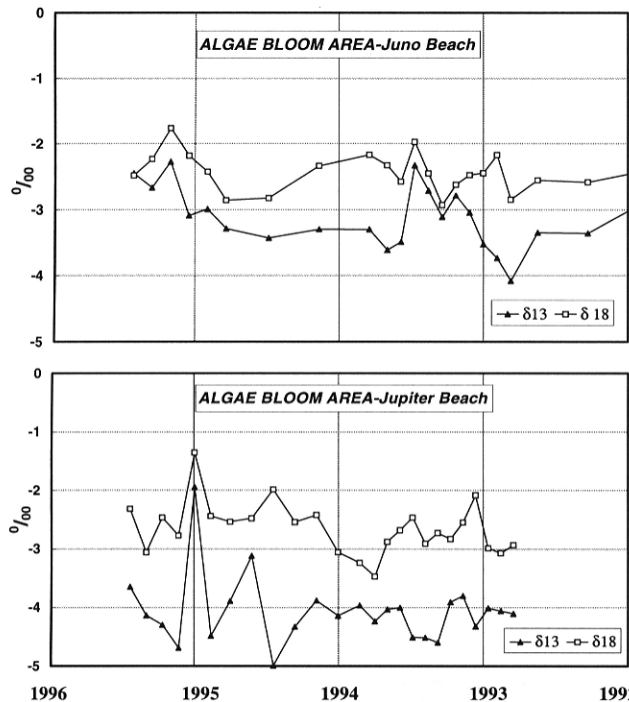


Fig. 9: Carbon and oxygen isotope records for Juno 3rd reef (JD) and Jupiter 3rd reef (JPD). Growth band year assignment questionable.

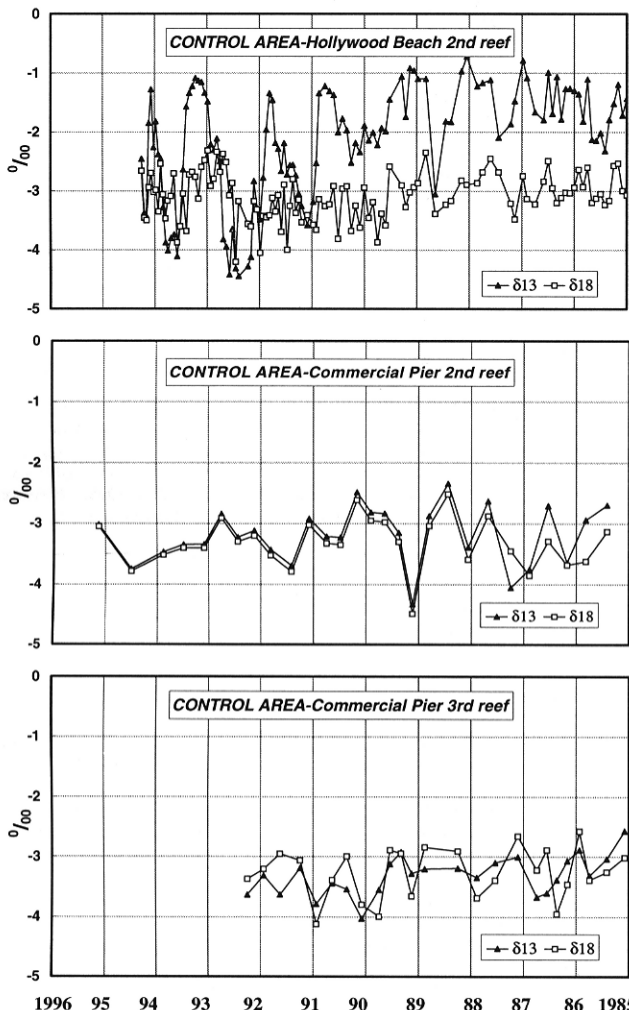


Fig. 10A: (See Fig. 10B caption).

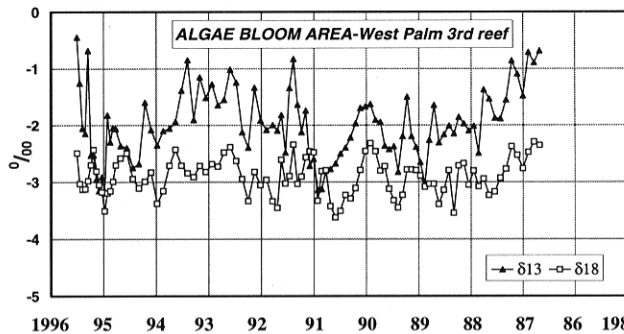


Fig. 10B: Carbon and oxygen records for Hollywood 2nd reef *M. faveolata* (HM), Commercial Pier 2nd and 3rd reef *S. bournoni* (CM and CD), and West Palm 3rd reef *M. faveolata* (WD).

away had a range over 7.5  $\mu\text{Mol Ba/Mol Ca}$  (see Fig. 6A). Occasional similarities existed between chronologies such as large barium increases shown by two Boca Inlet 3rd reef *M. faveolatas* in 1990 (see Fig.6B). Nevertheless, there was generally poor correlation among chronologies. Significant differences found between the 10 year means of some *M. faveolata* were not apparently related to specimen depth or latitude.

A purpose of our study was to evaluate the use of barium concentration in Southeast Florida corals for identifying nutrient sources potentially fueling *Codium* algal blooms on northern reefs. For our corals, we generally did not find consistent differences in barium between seasons, depths, or the *Codium*-affected area versus control areas. This may be because seasonal upwelling of water along the Southeast Florida coast is not sufficiently intense or does not carry sufficient differential barium to be recorded by the corals. While local upwelling still remains a possibility for introducing differential nutrients to fuel algal blooms in northern Broward and Palm Beach Counties, the corals do not support this hypothesis. Support would have been provided with possibly higher barium concentrations in the corals with depth and in algal infested locations, which did not occur. Preliminary oxygen and carbon isotopic data for five corals also do not support differential temperatures (from upwelling) at depth or location.

A competing alternative hypothesis for nutrient source might invoke terrestrial runoff emanating to the reefs via inlets. Because the *Codium* blooms were localized north of Boca Raton, higher nutrients might be expected to be emanating from Boca Inlet and consequently producing elevated barium levels in those northern corals. The corals of our collections at and north of Boca inlet do not demonstrate elevated barium by location or time. It is possible that the runoff does not carry an increased barium concentration in contrast to other riverine waters (Shen and Sanford, 1990). Carbon isotopic measurements, which might be indicative of organic matter from increased inlet nutrients, do not show differential values in the Boca or north corals.

*Codium* algal blooms pulsed in the early 1990s in Florida's northern Broward and Palm Beach Counties on offshore reefs. Our results do not suggest a long term upwelling event or a localized point source. It is possible that *Codium* ecology coupled with relatively abundant and pervasive nutrients from the major sewage outfalls and other sources, well mixed by coastal eddies of the Gulf Stream, were responsible and that precise identification of sources will be difficult with the barium coral tool. Further research may involve additional isotopic measurements, trace metals, and collections in an attempt to define nutrient sources and evaluate the utility of the barium skeleton tool in coastal waters.

REFERENCES

Boyle EA (1976) The marine geochemistry of trace metals. Ph.D. thesis, Massachusetts Inst. Technol./Woods Hole Oceanogr. Inst., Mass., 156 pp

Boyle EA, Husted SS, Jones SP (1981) On the distribution of copper, nickel and cadmium in the surface waters of the North Atlantic and North Pacific Ocean. *J Geophys Res* 86:8048-8066



- Buddemeier RW, Schneider RC, Smith SV (1981) The alkaline earth chemistry of corals. Proc 4th Int Coral Reef Symp, Manila, 2:81-85
- Chew F, Bane Jr. JM, Brooks DA (1985) On vertical motion, divergence, and the thermal wind balance in cold-dome meanders: a diagnostic study. J Geophys Res 90:C2,3173-3183
- Dodge RE, Kohler K (1985) Image analysis of coral skeletons for extension rate, calcification rate, and density. Advances in Reef Science, Joint Meeting of Atlantic Reef Committee and the Internat. Soc. of Reef Studies. pp 31-32
- Edmond JM, Boyle EA, Drummond D, Grant B, Mislick T (1978) Desorption of barium in the plume of the Zaire (Congo) River. Neth J Sea Res 12:324-328
- Fairbanks RG, Dodge RE (1979) Annual periodicity of the  $^{18}\text{O}/^{16}\text{O}$  and  $^{13}\text{C}/^{12}\text{C}$  ratios in the coral *Montastrea annularis*. Geochim Cosmochim Acta 43:1009-1020
- Flor TH, Moore WS (1977) Radium/calcium and uranium/calcium determinations for Western Atlantic reef corals. Proc 3rd Int Coral Reef Symp, Miami, Florida, 2:555-561
- Goldberg WM (1973) The ecology of the coral-octocoral communities off the southeast Florida coast: geomorphology, species composition, and zonation. Bull Mar Sci 23(3):465-472
- Goreau TJ (1977) Coral skeletal chemistry: physiological and environmental regulation of stable isotopes and trace metals in *Montastrea annularis*. Proc R Soc Lond B 169:291-315
- Hanisak MD (1979) Growth patterns of *Codium fragile* spp. *tomentosoides* in response to temperature, irradiance, salinity, and nitrogen source. Mar Biol 50:319-332
- Hanisak MD, Harlin MM (1978) Uptake of inorganic nitrogen by *Codium fragile* spp. *tomentosoides*. J Phycol 14:450-454
- Hanisak MD, Blair SM (1988) The deep-water macroalgal community of the East Florida continental shelf (USA). Helgolander Meeresunters 42:133-163
- Honor JS, Chan LH (1977) Non-conservative behavior of barium during mixing of Mississippi River and Gulf of Mexico waters. Earth Planete Sci Lett 37:242-250
- Hart SR, Cohen AL (1995) Sr/Ca in Corals: an ionprobe study of annual cycles and microscale coherence with other trace elements. Geochim Cosmochim Acta. In press
- Hauert DE, Startzman JR (1985) Short-term effects of a freshwater discharge on the biota of St. Lucie Estuary, Florida. Tech. Pub. 85-1. South Florida Water Management Dist. West Palm Beach, 38pp
- Hudson HD, Powell JVD, Robblee MB, Smith TJ (1989) A 107-year-old coral from Florida Bay: barometer of natural and man-induced catastrophes? Bull Mar Sci 44:283-291
- Klinkhammer GP, Chan LH (1990) Determination of barium in marine waters by isotope dilution inductively coupled plasma mass spectrometry. Analytica Chimica Acta 232:323-329
- Land LS, Lang JC, Bames DJ (1975a) Extension rate: a primary control on the isotopic composition of West Indian (Jamaican) scleractinian coral skeletons. Mar Biol 33:221-233
- Land LS, Lang JC, Smith EN (1975b) Preliminary observations on the carbon isotopic composition of some reef corals and symbiotic zooxanthellae. Limnol Oceanogr 20:283-287
- Lea DW, Shen GT, Boyle EA (1989) Coralline barium records temporal variability in equatorial Pacific upwelling. Nature 340:373-376
- Lea DW, Boyle EA (1992) Determination of carbonate-bound barium in foraminifera and corals by isotope dilution plasma-mass spectrometry. Chem Geol 103:73-84
- Linn LJ, Delaney MJ, Druffel ERM (1990) Trace metals in contemporary and seventeenth-century Galapagos coral: records of seasonal and annual variations. Geochim Cosmochim Acta 54:387-394
- McConnaughey TA (1986) Oxygen and carbon isotope disequilibria in Galapagos corals: Isotopic thermometry and calcification physiology. Dissertation, Univ. of Wash. 340 pp
- McConnaughey TA (1989a)  $^{13}\text{C}$  and  $^{18}\text{O}$  disequilibrium in biological carbonates II. In vitro simulation of kinetic effects. Geochim Cosmochim Acta 53:151-162
- McConnaughey TA (1989b)  $^{13}\text{C}$  and  $^{18}\text{O}$  disequilibrium in biological carbonates I. Patterns. Geochim Cosmochim Acta 53:151-162
- Millero FJ, Sohn ML (1992) Chemical Oceanography. CRC Press, Boca Raton, Florida, 531 pp
- Patzold J (1984) Growth rhythms recorded in stable isotopes and density bands in the reef coral *Porites lobata* (Cebu, Philippines). Coral Reefs 3:87-90
- Proni JR, Damann WP (1989) Final Report: Southeast Florida Outfall Experiments (SEFLOW). NOAA-AOCL, Miami, FL
- Shen GT (1986) Lead and Cadmium Geochemistry of Corals: Reconstruction of Historic Perturbations in the Upper Ocean. Ph.D. Dissertation. Woods Hole Oceanographic Institution. WHOI-86-37. 233pp
- Shen GT, Boyle EA (1988) Determination of lead, cadmium and other trace metals in annually-banded corals. Chem Geol 67:47-62
- Shen GT, Sanford CL (1990) Trace element indicators of climate variability in reef-building corals. In: Global Ecological Consequences of the 1982-1983 El Nino-southern Oscillation. Elsevier Oceanography series 52, Ed: Glynn FW. 255-283
- Smith NP (1983) Temporal and spatial characteristics of summer upwelling along Florida's Atlantic shelf. J Phys Oceanogr 13:1709-1715
- Swart PK (1983) Carbon and Oxygen isotope fractionation in Scleractinian corals. Earth Sci Reviews 19:51-80
- Swart PK, Coleman ML (1980) Isotopic data for scleractinian corals explain their paleo-temperature uncertainty. Nature 283:557-559
- Swart PK, Burns SJ, Leder JJ (1991) Fractionation of stable isotopes of O and C in  $\text{CO}_2$  during the reaction of calcite with phosphoric acid as a function of temperature and technique. Chem Geol 86:89-96
- Swart PK, Healy G, Dodge RE, Kramer P, Hudson H, Halley R, Robblee M (1995) The stable oxygen and carbon isotopic record from a coral growing in Florida Bay: a 160 year record of climatic and anthropogenic influence. Palaeogeograph, Palaeoclimatol, Palaeoecol. In press
- Tudhope AW, Lea DW, Schirrmield GB, Chilcott DP (1995) Monsoon Climate and Arabian Sea Coastal Upwelling Recorded in Massive Corals from Southern Oman. In press
- Weber JN, Woodhead PMJ (1970) Carbon and oxygen isotope fractionation in the skeletal carbonate of reef building corals. Chem Geol 6:93-117
- Weber JN, Woodhead PMJ (1972) Temperature dependence of oxygen-18 concentration in reef coral carbonates. J Geophys Res 77:463-473
- Weber JN, Dienes P, Weber PH, White EW (1975) Seasonal high and low density bands in reef coral skeletons. Nature 355:687-698
- Weil SM, Buddemeier RW, Smith SV, Kroopnick PM (1981) The stable isotopic composition of coral skeletons: control by environmental variables. Geochim Cosmochim Acta 45:1147-1153
- Yoder JA, Atkinson LP, Bishop SS, Hofmann EE, Lee TN (1983) Effect of upwelling on phytoplankton productivity of the outer southeastern United States continental shelf. Cont Shelf Res 1:385-404