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Annual periodicity of the $^{18}O/^{16}O$ and $^{13}C/^{12}C$ ratios in the coral *Montastrea annularis**

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Abstract—The isotopic ratios $^{18}O/^{16}O$ and $^{13}C/^{12}C$ show an annual periodicity in the coral *Montastrea annularis* from Bermuda, Jamaica and Barbados. The abundances of ^{18}O and ^{13}C are positively correlated in the Jamaica and Barbados samples, but inversely related in the Bermuda sample. Annual high density growth bands are formed during the season of warmest water temperature at all 3 sites and are enriched in ^{16}O. *M. annularis* has a constant displacement from oxygen isotopic equilibrium and accurately records seasonal temperature variations via the temperature-dependent aragonite–water fractionation factor. Light intensity, through the activity of the coral's endosymbiotic algae, regulates the depth-dependent and seasonal variations in the skeletal carbon isotopic composition.

1. INTRODUCTION

SCLERACTINIAN corals have proven to be useful monitors of surface ocean chemistry and environmental conditions for several reasons: (1) They deposit density bands which provide an annual chronology much like tree rings; (2) Corals incorporate many trace elements in their skeletons with a distribution coefficient close to unity; (3) Corals are suitable for ^{14}C, $^{238}U/^{230}Th$ and U/He dating methods; (4) Coral reefs are widely distributed throughout tropical and temperate regions of the world's oceans; and (5) Living coral specimens 200–500 yr old as well as extensive deposits of unaltered Holocene and Pleistocene specimens are available for study.

For this study we show the scleractinian coral *Montastrea annularis* (Ellis and Solander) apparently records seasonal temperature variations via the temperature dependent oxygen isotope fractionation factor for the aragonite–water system.

We have also found that the skeletal carbon isotopic composition of hemispherical-shaped *M. annularis* is strongly depth-dependent upon light intensity. Based upon these results we have analyzed *M. annularis* to determine if there are predictable intra-annual variations in carbon isotopes which can be related to seasonal insolation variations. In order to provide a time framework with which to compare our chemical results, we have established the season of deposition of skeletal carbonate for the coral species that we have used.

The cycle of high and low density skeletal material in *M. annularis* has been demonstrated to be annual by radiochemical analysis (DODGE *et al.*, 1974), comparison of growth rate determined by density bands and measurements in the field (MACINTYRE and SMITH, 1974; VAUGHAN, 1915), comparison of growth rate determined from stain lines and from density bands (STEARN *et al.*, 1977), and by observation of banding sequence in corals collected throughout the year (HUDSON *et al.*, 1976). WEBER *et al.* (1975) have conducted a comprehensive study involving approx 1400 corals from different areas including observations of band portion type at the growth surface on the date of collection, and the seasonal cycle of water temperatures and solar radiation in the collection area. They found *M. annularis* to be in line with their general conclusions for all corals. The high density (HD) band is considered to form in months of warmest water temperature and not to be related to variations in solar radiation.

An accurate chronology is requisite for interpreting our chemical results. Therefore, we have similarly tested these assumptions of time of dense band formation for our *M. annularis* collection from Jamaica, Barbados and Bermuda.

2. MATERIALS AND METHODS

Corals from the reef at Discovery Bay, Jamaica were collected in March 1973 from approx 10 m depth on the fore-reef and from approx 3 m depth on the eastern back-reef. In Barbados *M. annularis* corals were collected at 3 m depth from the reef off Bellairs Institute in July 1974. In Bermuda, several specimens of *M. annularis* were collected in May 1973 from approx 3 m depths on the reefs near North Rock.

Each available specimen was sectioned and X-radiographed to expose annual density bands (see Fig. 1). Annual band widths were assigned years of formation and measured along one or two transect lines oriented normal to growth band boundaries and in regions of the coral which most closely approximate the axis of maximum

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growth. An annual band was defined as the linear distance (normal to growth band boundaries) from the top edge of an HD band to the next lower HD band top edge. The type of the outermost incomplete annual band [low density (LD), high density (HD) or LD and HD], was noted and measured as the linear distance along the transect line from the former growth surface to the top edge of adjacent HD band. For Bermuda *M. annularis*, although portions of all specimens showed good banding, only one gave a clear record to the coral surface that was suitable for measurement.

In order to test the accuracy with which *M. annularis* skeletal oxygen isotopic composition records seasonal temperature fluctuations, annual growth bands were finely subsampled sequentially along transects oriented in the direction of upward growth. Using X-radiographs as templates, as many as fifteen evenly spaced samples per year of coral skeleton were taken from three specimens of *M. annularis* collected on reefs off Bermuda, Jamaica, and Barbados. Oxygen and carbon stable isotopic compositions were determined simultaneously on a triple collector Micromass 903 mass spectrometer. The results are reported in the standard $\delta(‰)$ notation relative to the Chicago PDB standard. Precision is $\pm 0.06‰$ (SD) for oxygen and carbon based on multiple analyses of a laboratory standard. All samples were precleaned in a low temperature oxygen plasma surface for 1 hr to remove organic material.

3. RESULTS AND DISCUSSION

3.1 *Density banding*

The results of band width measurements are presented in Table 1. For Jamaica *M. annularis* an LD band was observed at the surface in mid-March. This LD portion in six specimens was on the average 40.0% of the mean width for all internal bands of each specimen. Under an assumption of constant linear growth, the data suggest that the outer incomplete annual band (only LD showing) will complete formation in 60% of a year (approx 7.2 months) or near the end of October.

For Barbados *M. annularis*, an LD band was observed at the surface in the first part of July. This LD portion for eight specimens was on the average 74.8% of the mean width of complete internal annual bands for each specimen, indicating that the outer incomplete annual band will be fully formed in 25.2% of a year (approx. 3 months) or in the first part of October. Detailed densitometry of specimen B-3 (specimen in Fig. 1) revealed the outer LD band had a width (0.480 cm) which was 80% of the mean of all 17 internal LD bands ($\bar{X} = 0.608$ cm; SD = 0.131). Again under the assumption of constant linear growth, the data imply that the partially complete outer LD band will be complete in 20.0% of a year (2.4 months) or near mid September.

For the one *M. annularis* specimen from Bermuda, a thin HD band overlying an LD band was observed at the growth surface in mid May. This apparent incomplete cycle was 67.7% of the mean annual band width for all internal bands suggesting it will be com-

Table 1. Outer band portion analysis for *M. annularis*

Jamaica M. annularis; collected March 19, 1973

Specimen	Mean Band Width (cm)	s.d.	# of bands	Width of outer LD (cm)	% of Mean B.W.
D3	.866	.176	21	.275	31.7%
D6	.769	.070	16	.330	42.9
C2	1.004	.149	4	.462	46.0
C3	.699	.149	7	.340	48.7
C5	.790	.058	6	.207	26.2
C7	1.015	.194	9	.450	44.3
					40.0% = Mean

Under the assumption of constant linear growth, this suggests that the outer incomplete annual band (only LD showing) will be complete in 60.0% of a year (7.2 months) or near the middle of October.

Barbados M. annularis; collected approximately July 8, 1974

Specimen	Mean Band Width (cm)	s.d.	# of bands	Width of outer LD (cm)	% of Mean B.W.
B1	.967	.224	25	.781	80.8%
B2	1.221	.224	14	.968	79.3
B3	.828	.125	18	.687	83.0
B4	1.313	.173	21	.807	61.5
B11	1.004	.128	38	.760	75.7
B12	.995	.130	28	.692	70.0
B14	.962	.164	21	.701	72.9
B15	1.041	.138	32	.786	75.7
					74.8% = Mean

Under the assumption of constant linear growth, this suggests that the outer incomplete annual band (only LD showing) will be complete in 25.2% of a year (3. months) or near the first part of October.

Bermuda M. annularis; collected May 12, 1973

Specimen	Mean Band Width (cm)	s.d.	# of bands	Width of outer LD+HD (cm)	% of Mean B.W.
N9	.388	.048	17	.261	67.7%

Under the assumption of constant linear growth, this suggests that the outer incomplete annual band (LD and thin HD showing) will be complete in 32.3% of a year (approx. 4 months) or near mid. September.

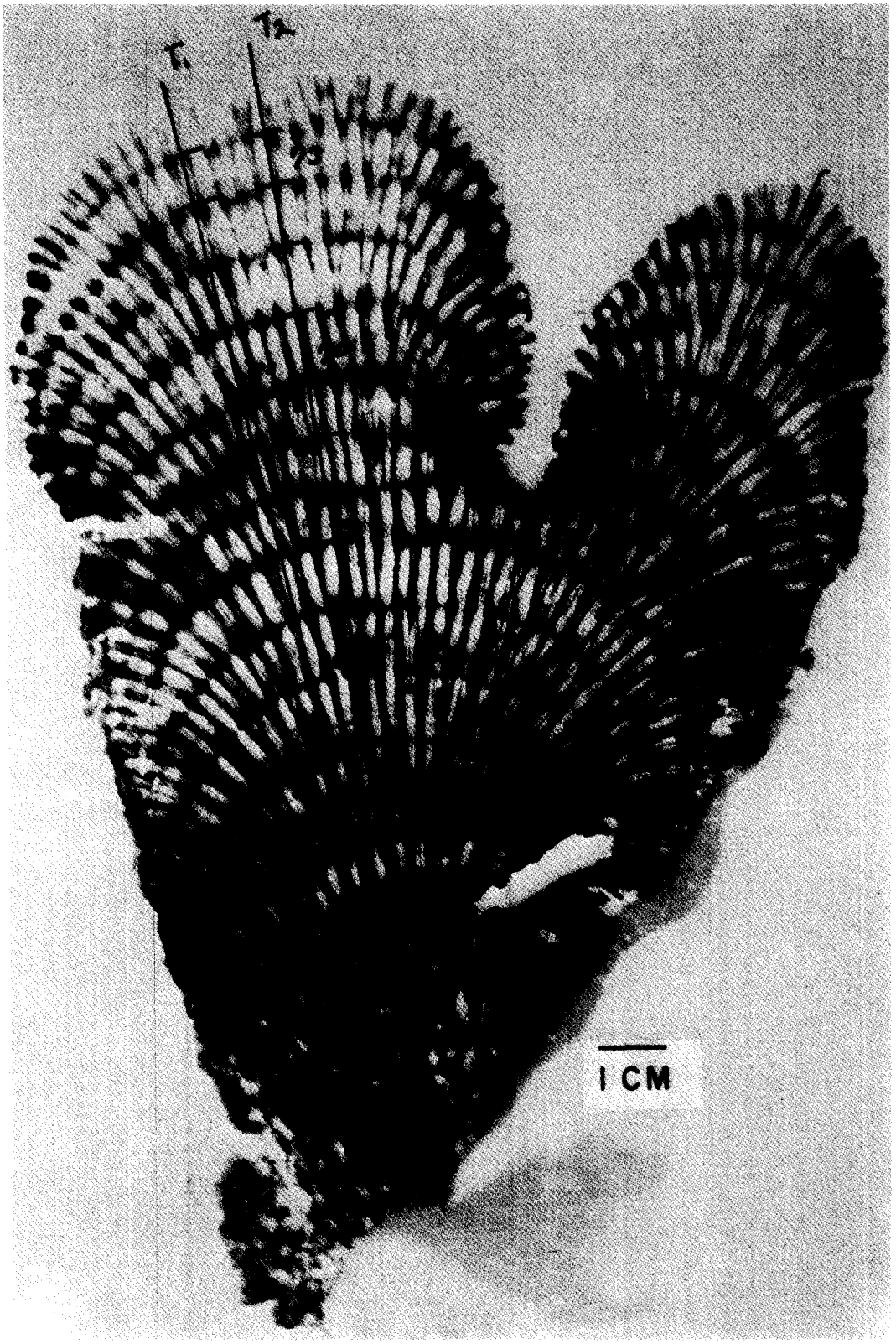

Fig. 1. X-radiograph positive of Barbados *M. annularis* (specimen B3) in column form. Annual density banding is well developed.

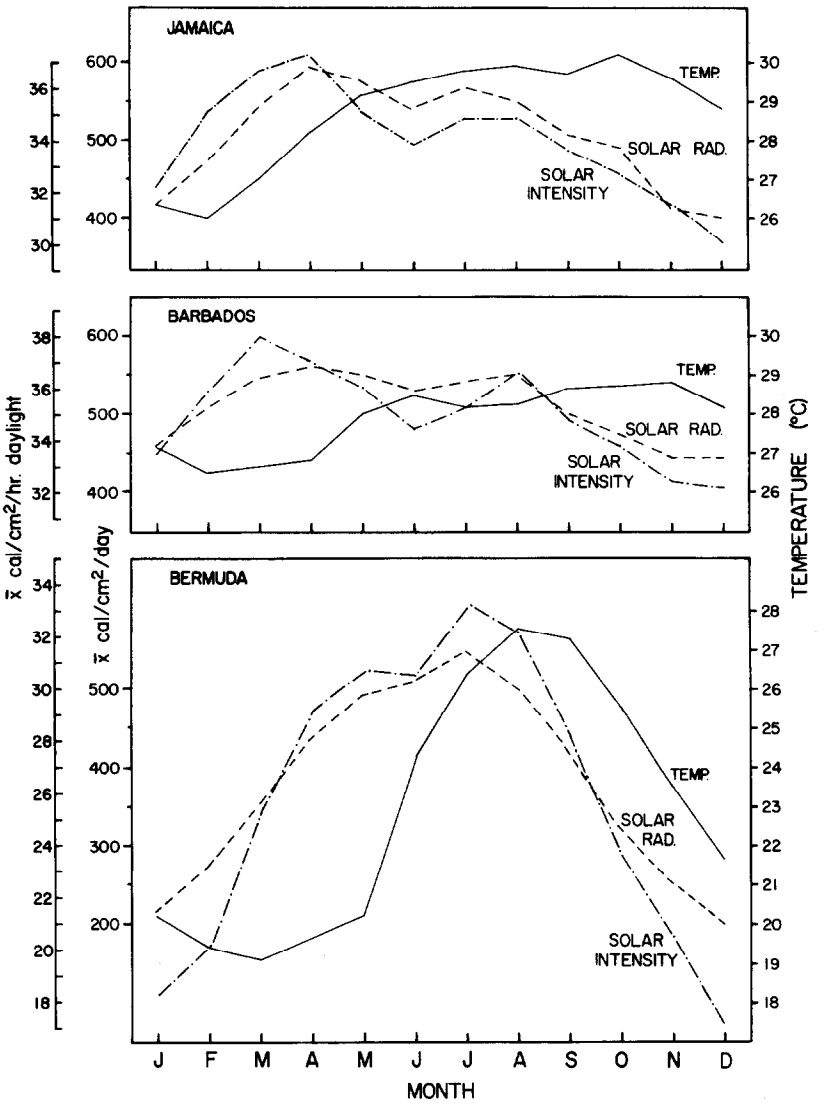

Fig. 2. Plots of average monthly water temperature and solar radiation for Jamaica, Barbados and Bermuda. Jamaica water temperature is from REISWIG (1971) and JACKSON (1972) and covers the period 1968–1970. Barbados water temperature is from SANDER and STEVEN (1973) and BEERS *et al.* (1968) for the period 1961-1964, 1968–1970. Temperatures for the North Rock locality at Bermuda are estimated using ocean data from station S off Bermuda from MORRIS (1977) during 1954–1957. Solar radiation data was calculated by the method of DEJONG (1973) which is $R = R_o\,[a + b\,(n/N)]$ where R (expressed in cal/cm^2/day) is the solar radiation reaching the Earth's surface at a particular lattitude, R_o is the actual duration of sunshine, N is the maximum possible duration of sunshine over the same period (average day length per month), and a and b are constants. Actual sun hours per day information (n) came from MACKY (1956) for Bermuda, C. C. SKEET (no date a + b) for Barbados, the the Jamaica meteorological office for Jamaica. The constants a and b required in the formula are $a = 0.31$, $b = 0.49$ for Jamaica, $a = 0.27$, $b = 0.49$ (Trinidad) for Barbados, and $a = 0.23$, $b = 0.48$ (world average) for Bermuda (DEJONG, 1973). Solar 'intensity' = R/N (expressed) in cal/cm^2/hr daylight).

plete in 32.3% of a year (approx 4 months) or near the middle of September.

It would appear that in *M. annularis* from Barbados and Jamaica that the HD band portion forms principally in the late summer–early fall months possibly over a 1–2 month period. If the one specimen from Bermuda is characteristic, the data suggest the HD band forms over the summer months (May–September). These time periods correspond on Fig. 2 to months of warmest water temperature and lowest solar radiation for Barbados, warmest water temperature and intermediate to lowest solar radiation for Jamaica, and warmest water temperature and high solar radiation for Bermuda.

3.2 *Oxygen isotopes*

WEBER and WOODHEAD (1972) have demonstrated that the average oxygen isotopic composition of scleractinian corals collected from 0–6 m water depth is temperature dependent. The $\delta^{18}O$ vs temperature curves for all of the eighty genera and sub-genera studied by WEBER and WOODHEAD (1972) are linear

and parallel or near parallel to the oxygen isotope 'paleo-temperature' scale established by McCREA (1950) and EPSTEIN *et al.* (1953). In all cases, however, the scleractinian curves are displaced toward more negative $\delta^{18}O$ values. The biochemical mechanisms operative in scleractinian corals which systematically produce an oxygen isotopic displacement from equilibrium values are not well understood. Thus, in order for *M. annularis* to be a useful paleothermometer it must be demonstrated empirically that its oxygen isotope disequilibrium displacement (vital effect) is invariant with depth and time of year of skeletal deposition.

3.2.1 *Average oxygen isotopic composition of* M. annularis *vs depth.* Figure 3 presents data on the mean $\delta^{18}O$ of *M. annularis* vs depth from Jamaica (LAND *et al.*, 1975) and St. Croix (WEBER *et al.*, 1976). The data plotted in Fig. 3 represent only those samples taken from the axis of maximum growth, which leads us to different conclusions than those derived by the original authors. This means that 'hemispherical or columnar shaped' colonies are sampled from the top of the corallum, while 'flattened shaped' colonies are sampled along the margin or edge. The oxygen isotopic composition of slowly growing portions of a specimen show greater isotopic variability (LAND *et al.*, 1975) and are avoided in this study. The mean isotopic composition of *M. annularis* collected from 10 to 60 m off Jamaica is $-4.49 \pm 0.14‰$ ($n = 22$). The mean oxygen isotopic composition of *M. annularis* collected from 0 to 28 m depth off St. Croix is $-4.06 \pm 0.09‰$ ($n = 210$). The slopes of the linear regression lines plotted in Fig. 3 for Jamaica and St. Croix are -0.0016 and 0.0056, respectively. These data demonstrate that the average oxygen isotopic composition of *M. annularis* is constant over the depth intervals studied. The study areas are isothermal over the depths sampled. Therefore, we may assume that the 'vital effect' is also constant with depth.

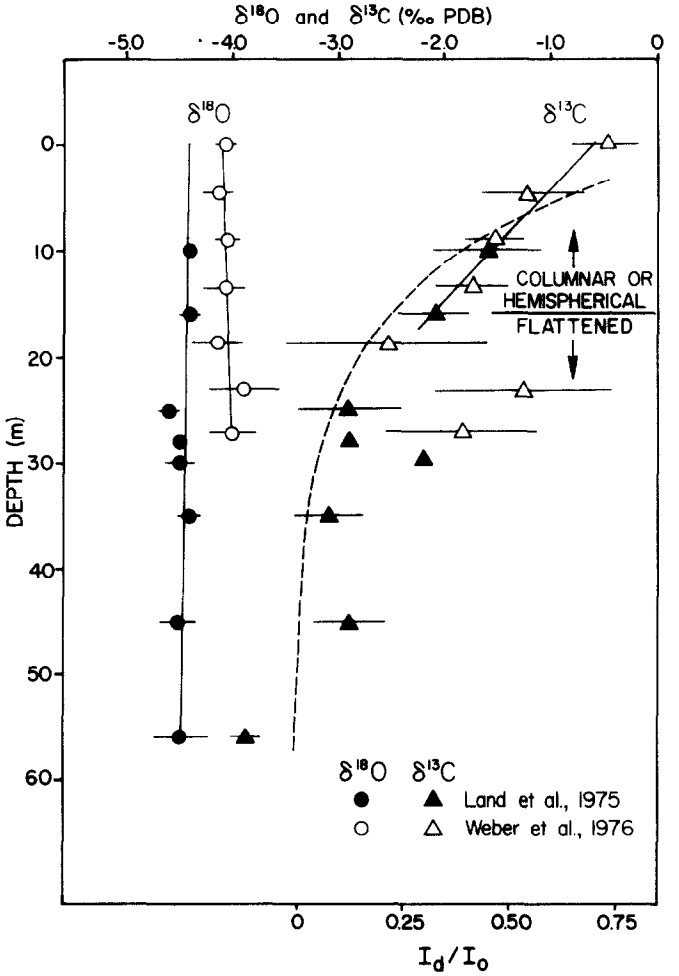

Fig. 3. Oxygen and carbon isotopic composition of skeletal carbonate from rapidly growing sections (sampled along axis of maximum growth) of *M. annularis* as a function of water depth. Length of error bar corresponds to one standard deviation from the mean. The solid symbols are data for Jamaica from LAND *et al.* (1975) and the open symbols are data for St. Croix from WEBER *et al.* (1975). The solid lines are linear regression lines. The dashed line approximates relative light intensity vs depth using an equation for the attenuation of light expressed as a function of the extinction coefficient (k): $I_d = I_o e^{-k\delta}$ where I_d and I_o are the radiant energy at a depth (δ) and the surface, respectively.

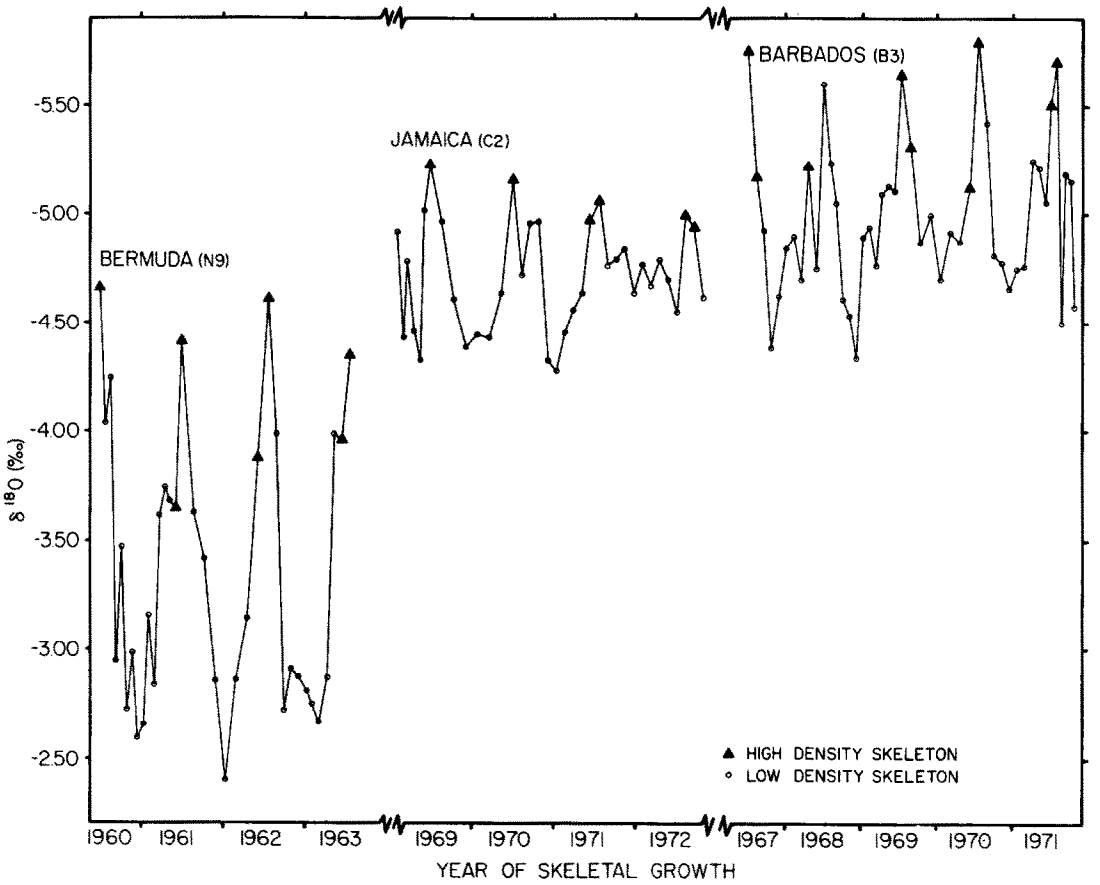

Fig. 4. Oxygen isotope transects across annual growth bands in *M. annularis* plotted against year of skeletal growth. Samples are evenly spaced and were taken along the axis of maximum growth. The year of formation of a particular growth band was determined by growth band chronology.

3.2.2 *Seasonal temperature-dependent variations in* M. annularis *oxygen isotopic composition.* On the basis of the information outlined above and assuming that the skeletal oxygen isotope fractionation will occur seasonally in a manner analogous to bulk samples from corals collected from widely separated temperature regions, we have tested the hypothesis that seasonal temperature variations will be recorded via the oxygen isotopic composition within annual coral growth bands. Figure 4 presents the results of $\delta^{18}O$ transects which span 4–5 yr of growth in each of three corals from Barbados, Jamaica and Bermuda. In all three records an annual periodicity in the $\delta^{18}O$ composition occurs as was previously observed by EMILIANI (1978) for *M. annularis* from Florida. In both studies the high-density skeletal portion generally coincides with the lightest $\delta^{18}O$ values, as would be expected if HD bands are deposited during the warmest time of the year.

In order to estimate the accuracy with which these isotope transects record annual temperature variations at the site of collection we have computed the average annual $\delta^{18}O$ range for corals deposited in oxygen isotopic equilibrium with local seawater. In Table 2 these values are compared to the average annual range in oxygen isotopes of *M. annularis*. The equilibrium range is based on ambient temperature data and the oxygen isotopic composition of local seawater. The equilibrium range was computed using the oxygen isotopic fractionation factor for the $CaCO_3$–H_2O system which was experimentally determined by EPSTEIN *et al.* (1953) and is expressed as:

$$t = 16.5 - 4.3(\delta^{18}O_{carb.} - \delta^{18}O_{H_2O}) + 0.14(\delta^{18}O_{carb.} - \delta^{18}O_{H_2O})^2$$

where t = temperature °C and $\delta^{18}O_{carb.}$ and $\delta^{18}O_{H_2O}$ are the $\delta^{18}O$ values, respectively, for CO_2 extracted from the $CaCO_3$ and for CO_2 equilibrated with the H_2O at 25.3°C. An accurate absolute value for seawater is not required when determining the annual oxygen isotope range. At Jamaica and Bermuda $\delta^{18}O_{water}$ varies slightly on a seasonal basis and is corrected for according to the ^{18}O-salinity relationship: Jamaica $d\delta/dS = 0.11$; Bermuda $d\delta/dS = 0.60$ (EPSTEIN and MAYEDA, 1953; CRAIG and GORDON, 1965). Substantial seasonal $\delta^{18}O_{water}$ variations occur at the Barbados site which were corrected using a $d\delta/dS = 0.23$.

The seasonal occurrence of low-salinity water in the eastern Caribbean and western tropical Atlantic is due to runoff from the Orinoco and the Amazon rivers (CALEF and GRICE, 1967; RYTHER *et al.*, 1967; SANDER and STEVEN, 1973). The $\delta^{18}O$ of Amazon river water is $-8.0 \pm 0.2‰$ (LONGINELLI and

Table 2. Annual $^{18}O/^{16}O$ aragonite equilibrium range vs annual $^{18}O/^{16}O$ range in *M. annularis*

	$\bar{X}_R\delta^{18}O_{Equil.}$ * (‰)	$\bar{X}_R$Temp. (°C)	$\bar{X}_R\delta^{18}O_{M.A.}$ (‰)	$\bar{X}_R$Temp.$_{M.A.}$ (°C)	$\bar{X}_R\delta^{18}O_{Equil.} - \bar{X}_R\delta^{18}O_{M.A.}$ (‰)
Bermuda	1.97±0.12	8.9±0.6	1.95±0.20	9.3±1.0	-0.02
	n = 20		n = 6		
Jamaica	0.67±0.03	3.3 **	0.69±0.20	3.1±0.9	0.02
	n = 6		n = 7		
Barbados	0.94±0.16	2.7 **	1.17±0.14	***	-0.23
	n = 8		n = 8		

* $\bar{X}_R$ = average range.
** Not enough data for a reliable estimate of the standard deviation of the mean.
*** Not computed due to a substantial seasonal $\delta^{18}O$ water variation.

EDMOND, 1978). $d\delta/dS$ of 0.23 is derived assuming a dilution of seawater of 34.7‰ salinity at $\delta^{18}O = 0.0$‰ with fresh water at −8.0‰ $\delta^{18}O$ (EPSTEIN and MAYEDA, 1953).

The predicted annual range in the oxygen isotopic composition of calcium carbonate deposited in isotopic equilibrium with Bermuda seawater is 1.97 ± 0.12‰ which agrees with the observed average annual range of 1.95 ± 0.20‰ recorded by *M. annularis*. Jamaica's predicted vs observed annual calcium carbonate oxygen isotope ranges are 0.67 ± 0.03‰ and 0.69 ± 0.20‰, respectively. Barbados' predicted and observed average annual $\delta^{18}O$ range in *M. annularis* are 0.94 ± 0.16‰ and 1.17 ± 0.14‰, respectively.

3.2.3 *Oxygen isotope fractionation.* An *in situ* study of calcification and photosynthetic carbon fixation in *M. annularis* has been made in Jamaica and Miami by BARNS and TAYLOR (1973). These authors concluded that oxygen production and CO_2 fixation increase in proportion to increasing light intensity until saturating light values are reached at or near 400 ft candles, at which point their respective rates reach a maximum. BARNES and TAYLOR (1973) conclude that light saturation of the *M. annularis* host-symbiont complex prevail during most of the day from the surface to 9 and 15 m on the reefs in Jamaica and Miami, respectively.

The constant oxygen isotopic composition of *M. annularis* to depths greater than 50 m rules out any simple relationship between symbiotic zooanthella activity as measured by BARNES and TAYLOR (1973) and skeletal oxygen isotopic composition. BARNES and TAYLOR (1973) have shown that rates of oxygen production and CO_2 fixation by the algal symbionts vary by almost an order of magnitude between 0 and 50 m and yet the skeletal oxygen isotopic composition remains constant.

Our results show that high resolution sampling (greater than 12 samples per year of growth) is required for an accurate reconstruction of the local annual temperature range. These results are not in complete agreement with the conclusions of GOREAU (1977) and EMILIANI *et al.* (1978). Although EMILIANI *et al.* (1978) suggest that the ^{18}O depletion in HD layers is probably in part due to higher temperatures of calcification, both GOREAU (1977) and EMILIANI *et al.* (1978) conclude that the annual temperature effect is obscured by physiological perturbations of the oxygen isotopes. They both cite as evidence for physiological control of the annual ^{18}O signal, the fact that the annual range in their oxygen isotope data is equal to approximately half the annual range predicted by equilibrium ^{18}O-temperature fractionation. The fact that EMILIANI *et al.* (1978) sampled only four samples per year of skeletal growth and that Goreau (1977) sampled approximately six samples per year of skeletal growth necessitates an attenuation of the true annual ^{18}O amplitude in their samples.

M. annularis' constant displacement from oxygen isotopic equilibrium and temperature dependent oxygen isotopic fractionation permits accurate determination of annual temperature range independent of the isotopic composition of ocean water, provided $\delta^{18}O$ seawater does not vary annually.

3.3 *Carbon isotopes*

3.3.1 *Average carbon isotopic composition of* M. annularis *vs depth.* Figure 3 includes a plot of the average carbon isotopic composition of *M. annularis* (sampled from the major growth axis) vs depth from Jamaica (LAND *et al.*, 1975) and St. Croix (WEBER *et al.*, 1976). The $^{13}C/^{12}C$ composition of columnar or hemispherically-shaped specimens which grow in less than 18 m depth, decreases linearly by 2‰ in the upper 18 m. The $\delta^{13}C$–depth relationship may be described at these localities by the equation: depth (m) = $-10.37\ \delta^{13}C_{PDB} - 6.21$, and has a correlation coefficient of −0.97. The flattened-variety of *M. annularis*, which occurs at depths greater than 18 m, shows considerable $\delta^{13}C$ variability between 20 and 30 m, and is probably due to the difficulty in identifying the major growth axis as the coral shape grades from hemispherical to flattened variety. *M. annularis* approaches a minimum $\delta^{13}C$ value below 30 m.

For hemispherical and columnar shaped specimens, annual calcification rate and skeletal density increases with increasing water depth and the polyp spacing

shows little change (WEBER *et al.*, 1976, tables 2 and 4; BARNES and TAYLOR, 1972). Included in Fig. 3 is a plot (broken line) approximating light penetration at these sites. The adsorption of light is expressed as a function of the extinction coefficient (K):

$$I_d = I_o e^{-k\delta}$$

where I_d and I_o are the radiant energy at a depth (δ) and the surface, respectively (PARSONS and TAKAHASHI, 1973). There exists a first order relationship between *M. annularis bulk skeletal* $\delta^{13}C$ composition and radiant energy levels.

3.3.2 *Seasonal variations in* M. annularis *skeletal carbon isotopic composition.* We have taken a similar approach in our interpretation of seasonal carbon isotopic variations in *M. annularis* as we did for interpreting seasonal oxygen isotope variations. We tested the assumption that the skeletal carbon isotopic fractionation will occur seasonally in a manner analogous to the observed $\delta^{13}C$ depth variation.

Figure 3 shows that in the upper 18 m, light intensity is reduced by approx. 50%. Figure 2 indicates that seasonal light variations of comparable magnitudes also occur at our study sites. Assuming light is the principal factor regulating skeletal $\delta^{13}C$ fractionation as a function of water depth, mediated by endosymbiotic algae, then we would expect ^{13}C depleted values to occur during months of reduced light levels and ^{13}C enriched values during months of increased light intensity.

Figure 5 is a plot of the ^{18}O and ^{13}C transects of samples C2 (Jamaica), B3 (Barbados), and N9 (Bermuda). Like the oxygen isotope data, the carbon isotope data also shows a distinct annual periodicity. However, the phasing of the carbon isotope curves with respect to the dense skeletal bands and thus the oxygen isotope data is not the same for all three samples.

As we might expect from observations of skeletal ^{13}C depth dependence, the oxygen and carbon isotope plots in Fig. 5 of the Jamaica and Barbados samples are approx 180° out of phase, which agrees with the phase relationships for temperature and solar radiation for Jamaica and Barbados in Fig. 2. Solar radiation is reduced at Barbados and Jamaica during months of warmest water temperatures due to increased cloud cover. Therefore, the Jamaica and Barbados data is consistent with our predictions that during the months of reduced solar radiation and warmest annual water temperatures the skeletal ^{18}O and ^{13}C should be isotopically light. Unlike Barbados and Jamaica, Bermuda's annual water temperature and solar radiation are approximately in phase (see Fig. 2). Figure 5 shows that our Bermuda isotope data are generally consistent with our model with the exception of the isotopically heavy carbon isotope values which occur during the 1961–1962 winter months.

3.3.3 *Carbon isotope fractionation.* The $\delta^{13}C$ values for our three samples range from +0.1 to −3.1‰ which overlaps the range of bulk $\delta^{13}C$ values of *M. annularis* collected in the upper 20 m. It is apparent that *M. annularis* skeletal carbon isotopic composition is depleted in ^{13}C compared to aragonite deposited in isotopic equilibrium with local seawater. The $\delta^{13}C$ ΣCO_2 content of seawater at these three sites is approx. +2.0‰ (KROOPNICK *et al.*, 1972). For surface seawater in equilibrium with atmospheric CO_2, the expected $\delta^{13}C$ value for the $-HCO_3$ ion at 25°C can be determined using published equilibrium constants reported in RUBINSON and CLAYTON (1969; EMRICH *et al.* (1970). We use the average value for KEELING's (1961) $\delta^{13}C$ of atmospheric CO_2 of −6.6‰ as corrected by BOTTINGA and CRAIG (1969). The bicarbonate ion is enriched in ^{13}C by approx. 7.8‰ relative to gaseous CO_2 (EMRICH *et al.*, 1970; VOGEL *et al.*, 1970). Therefore, the bicarbonate ion, which is believed to be the chemical species utilized during calcification, has a $\delta^{13}C$ value of +1.2‰ (PDB). RUBINSON and CLAYTON (1969) measured the fractionation between aragonite and bicarbonate in NaCl solution and found 2.7‰ ^{13}C enrichment in the aragonite at 25°C. This gives an aragonite $\delta^{13}C$ equilibrium value of approximately 4‰. The temperature effect is only −0.035‰/°C (RUBINSON and CLAYTON, 1969).

Annual variations in the physical and chemical factors regulating carbon isotope equilibrium chemistry could not produce the annual carbon isotope cycles in *M. annularis*. Biological factors, therefore, must regulate the annual carbon isotope cycle in *M. annularis skeletons*. There is no evidence to suggest that the annual carbon isotope cycle in *M. annularis* results from an endogenous rhythm of coral metabolism.

Recent studies suggest sunlight, through the action of the endosymbiotic alga, *Gymnodinium microadriaticum*, may regulate skeletal $\delta^{13}C$ composition. It has been shown in hermatypic corals, that photosynthesis by the endosymbiont greatly enhances rates of calcification in the light (GOREAU, 1959; 1961; GOREAU and GOREAU, 1959; CHALKER 1975; CHALKER and TAYLOR, 1975; VANDERMEULEN *et al.*, 1972). By contrast, non-symbiotic ahermatypic corals calcify slowly and their rates are unaffected by illumination (GOREAU, 1959; 1961; GOREAU and GOREAU, 1959). Experimental evidence reported by EREZ (1978) suggests a positive correlation between skeletal ^{12}C enrichment and ^{14}C measured rate of photosynthesis by algal symbionts in several hematypic corals from the Gulf of Elat. BARNES and TAYLOR (1973) have shown that photosynthetic carbon fixation by *M. annularis* in the upper 15 m at Jamaica increases as the corals are shaded, suggesting photosynthetic rates may increase with depth to a subsurface maximum.

WALSH (1975) first noted a strong positive correlation between skeletal ^{13}C enrichment and 'number of sunshine hours' during skeletal growth of several *priorities* species from the Pacific. Compilation of ^{13}C-depth profiles (see Fig. 3) for *M. annularis* data

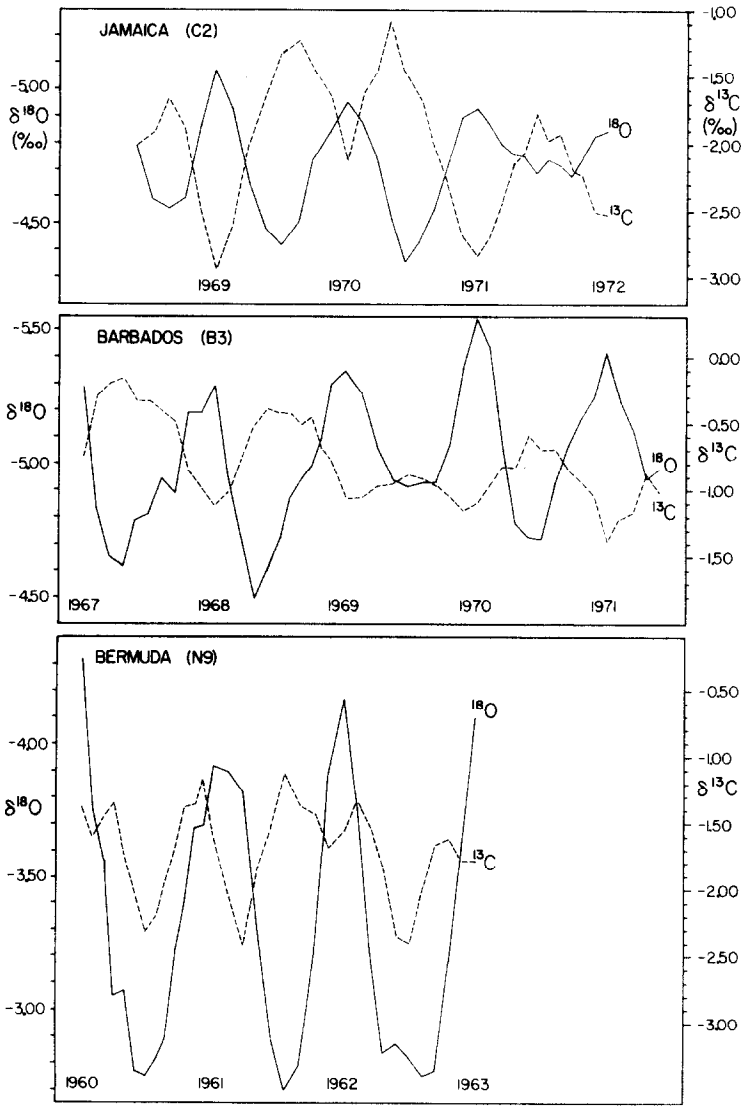

Fig. 5. Oxygen and carbon isotope transects across annual growth bands in *M. annularis* plotted according to year of skeletal growth. The data were filtered using a 3-point moving average to better illustrate phase relationships. The carbon isotope axes are plotted in the opposite direction to the oxygen isotope axes for the purpose of comparison to Fig. 2.

from the major growth axis reported by LAND *et al.* (1975) and WEBER *et al.* (1976) adds further support for a simple skeletal ^{13}C-radiant energy model. Consistent with these observations is the ^{13}C annual periodicity and the ^{13}C and temperature (^{18}O) phase relationships in *M. annularis* from Barbados, Jamaica, Bermuda and Florida (Fig. 5). EMILIANI *et al.* (1978) demonstrate that *M. annularis* from the Florida Keys shows a yearly signal in both ^{13}C and ^{18}O, and an inverse relationship between the two isotopes. Emiliani's 30-yr isotope record provides strong support for our ^{13}C-insolation model. In southern Florida annual solar radiation and water temperature are in phase (positively correlated) like the climate in Bermuda; therefore an inverse correlation between ^{18}O (temperature) and ^{13}C (solar radiation) are consistent with our isotope model prediction. The negative correlation of ^{18}O and ^{13}C for *M. annularis* from Bermuda and Florida as compared to the positive correlation of Jamaica and Barbados indicates the regional variation which must be considered when modeling coral isotope fractionation in hermatypic corals.

It is clear from the temporal and depth distribution data in Figs. 3 and 5 that the oxygen and carbon isotope fractionation mechanisms are decoupled. Therefore, a simple two component respiratory CO_2 and seawater HCO_3^- mixing model does not apply to *M. annularis*.

4. SUMMARY AND CONCLUSION

WEBER and WOODHEAD (1971) demonstrated the strict temperature dependence of the bulk skeletal oxygen isotopic composition of hermatypic corals.

We have combined their results with the discipline of coral chronology and identified temperature-dependent seasonal variations in the oxygen isotopic composition of *M. annularis*.

The wide distribution of modern coral reefs and their fossil counterparts (submerged and uplifted Holocene and Pleistocene reefs) preserve an abundance of oceanic and climatic information. Although numerous questions regarding stable isotope fractionation in the coral–symbiont system may remain an enigma for many years to come, studies of seasonal variations in oxygen and carbon isotopes can be usefully applied to may current research problems.

Coral specimens 400–500 yr old are available for retrieving precise average and seasonal temperature records and solar insolation phasing. Well-dated Holocene and Pleistocene reefs also contain unaltered coral for the study of paleotemperatures, paleoseasonality, and insolation–temperature phase relationships. These seasonal data are unique and particularly useful for Holocene or Pleistocene climate modeling because they provide input data on seasonal gradients as compared to seasonally or annually integrated data currently available.

Oxygen isotope chronology holds immediate promise for coral band dating. At some reef localities it is the rule rather than the exception that density banding is ambiguous or confusing at best. This results from a proponderance of secondary dense-bands whose origin is speculation at this point. These secondary bands can obscure identification of the annual dense-band. For many geochemical studies, the reduced accuracy of the coral growth chronology is unacceptable. Where banding is ambiguous, ^{18}O chronology (i.e. annual temperature record) offers a precise method capable of resolving annual or sub-annual growth chronology in areas where only a minimal annual temperature range (less than 1°C) occurs.

Our study indicates that skeletal carbon isotopic composition of *M. annularis* is dependent upon radiant energy (or light intensity), through the activity of the coral's endosymbiotic alga, *Gymnodinium microadriaticum*. Columnar and hemispherically shaped colonies of *M. annularis*, which are generally found in less than 20 m of water, show a strict ^{13}C-depth dependence. The bulk ^{13}C composition decreases linearly by 2‰ from the surface to 20 m. The attenuation of light with increasing water depth probably regulates the *M. annularis* ^{13}C-depth profile of St. Croix and Jamaica. We have not attempted to identify the metabolic processes responsible for ^{13}C fractionation; we believe, however, that it may be related to rates of algal symbiont photosynthesis. The results of our study on seasonal variations in skeletal carbon isotopes show that the $^{13}C/^{12}C$ ratio varies with an annual periodicity and its phasing is consistent with local annual insolution records. One critical check on the skeletal ^{13}C-insolation model would be a comparison of the amplitudes of the annual carbon isotope signal in specimens collected from 0–20 m. The annual carbon isotope signal should be attenuated with depth proportional to the decrease in seasonal light-intensity variations with depth.

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