Intra-annual variation in the stable oxygen and carbon and trace element composition of sclerosponges

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[1] This paper presents data to support the presence of (1) intra-annual signals in the chemical composition ($\delta^{18}O$ and Sr/Ca) of the skeletons of sclerosponges from the Bahamas and (2) variable rates of skeletal accretion. These conclusions are based on data obtained by using a microsampling method for the stable oxygen and carbon isotopes in which material was extracted at a resolution of one sample every 34 μm and a laser microprobe which obtained trace element data every 20 μm (Sr, Mg, and Pb). An age model was established using a combination of changes in the concentration of Pb, the change in the $\delta^{13}C$ of the skeleton of the sclerosponges, and U/Th isotopic measurements. These methods yield a mean growth rate of 220 μm/yr but suggest that the growth rate in this particular sclerosponge was not constant. The calculated growth rate is within error identical to that determined by U/Th methods. The variable growth rate was confirmed through spectral analysis of the $\delta^{18}O$ and Sr/Ca data that showed peaks corresponding to the annual cycle in these parameters as well as peaks corresponding to growth rates of approximately 128, 212, 270, and 400 μm/yr. The presence of these additional frequencies suggests a growth rate between approximately 100 and 300 μm/yr. These conclusions were supported by modeling of oxygen isotopic data measured on a scleractinian coral as well as model isotope data generated on synthetic time series. These findings have important implications for the use of sclerosponges as proxies of paleoclimate because they emphasize the need for a precise yearly chronology in order that proxy data can be compared with climatic variables. *INDEX TERMS:* 4215 Oceanography: General: Climate and interannual variability (3309); 4804 Oceanography: Biological and Chemical: Benthic processes/benthos; 4825 Oceanography: Biological and Chemical: Geochemistry; 4835 Oceanography: Biological and Chemical: Inorganic marine chemistry; 4875 Oceanography: Biological and Chemical: Trace elements; *KEYWORDS:* sclerosponge, strontium, stable isotopes, lead

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1. Introduction

[2] Sclerosponges are hard calcareous organisms which secrete skeletons composed primarily of $CaCO_3$ (aragonite) and a small amount of siliceous spicules. One aspect which has been particularly intriguing about these organisms is their low growth rate (0.1 to 0.3 mm/yr) [*Dustan and Sacco*, 1982; *Willenz and Hartman*, 1985; *Benavides and Druffel*, 1986] which means that even moderately sized individuals can be extremely long-lived. However, while this attribute makes sclerosponges valuable for providing geochemical data over longer time periods, sclerosponges do not contain annual growth bands like corals and therefore precise dating must rely on radiometric means with their inherent assumptions and uncertainties. Nevertheless, several workers have shown that sclerosponges can be successfully dated using a variety of methods and contain proxy records of their environment which can be interpreted to yield climatic and environmental information. These studies have used a range of sampling resolutions, from a fairly coarse sampling interval [*Druffel and Benavides*, 1986; *Benavides and Druffel*, 1986], to progressively finer sampling [*Böhm et al.*, 1996, 2000; *Moore et al.*, 2000]. The latest studies of *Fallon et al.* [1999] and *Lazareth et al.* [2000] have employed a laser microprobe coupled to an ICP-MS, allowing them to sample at resolutions approaching 20 μm. The principal question which is addressed in this paper is whether intra-annual variation in chemical composition exists within the skeletons of sclerosponges.

[3] Sclerosponges appear to grow in a manner analogous to scleractinian corals with the living organism only occupying the upper portion of the skeleton and the lower part being devoid of living sponge tissue. In the species used in this study, *Ceratoporella nicholsoni*, the tissue layer occu-

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pies the upper 1 mm of the skeleton which corresponds to a period of about five years. In contrast, the tissue layer in scleractinian coral occupies only approximately 50% of one year of skeletal growth [*Swart et al.*, 1998]. If calcification is taking place at multiple sites throughout the tissue layer, is it reasonable that an annual signal in temperature can be obtained? In this study we have attempted to obtain intra-annual samples using both a laser microprobe attached to an ICP-MS as well as a microsampler in which samples were physically milled from a slab of a sclerosponge at increments of 20 and 34 μm respectively.

[4] The growth rate of *Ceratoporella nicholsoni* has been studied on sclerosponges from Jamaica by both direct staining using Alizarin Red-S [*Dustan et al.*, 1976] and Calcein [*Willenz and Hartman*, 1985] and by using ^{14}C and ^{210}Pb [*Benavides and Druffel*, 1986]. In the study by *Dustan and Sacco* [1982], specimens of sponges were stained and collected some six years later. *Dustan and Sacco* [1982] estimated a growth rate of between 100 and 200 μm/yr, while *Willenz and Hartman* [1985] reported a value of 184 ± 20 μm/yr. The radiometric methods gave slightly higher growth rates (270 μm/yr using ^{14}C and 220 μm/yr using ^{210}Pb). Another technique used by various workers [*Böhm et al.*, 1996; *Lazareth et al.*, 2000] was to match the decrease in the $\delta^{13}C$ of the skeleton of the sclerosponge with the known increase in the CO_2 in the atmosphere or increases in the concentration of Pb [*Lazareth et al.*, 2000]. In all these cases it was assumed that the growth rate was approximately constant throughout the record.

[5] The first work on the $\delta^{13}C$ and $\delta^{18}O$ of sclerosponges [*Druffel and Benavides*, 1986] analyzed a 160 year old specimen of *C. nicholsoni* collected from Jamaica. This sclerosponge was dated using ^{14}C and sampled at a resolution of approximately one sample every 2.5 years. In contrast to nonzooxanthellate corals, which normally possess a positive covariance between $\delta^{13}C$ and $\delta^{18}O$ in their skeletons, the study of *Druffel and Benavides* [1986] showed no correlation, which they suggested was proof of the absence of vital isotopic effects in the secretion of the skeleton. While they did not observe any age dependent trend in the $\delta^{18}O$ data, their results showed an average 0.5‰ decrease in the $\delta^{13}C$ toward the present day. This decrease is similar to the decline in $\delta^{13}C$ seen in a coral skeleton from Bermuda [*Nozaki et al.*, 1978], and is probably a result of CO_2 added to the atmosphere from fossil fuel burning. Similar findings have been reported by *Swart et al.* [1994], *Moore et al.* [1996], *Böhm et al.* [1996], and *Lazareth et al.* [2000] in sclerosponges from the Caribbean and the Pacific. The most recent work on sclerosponges reported a calibration between the $\delta^{18}O$ and temperature [*Böhm et al.*, 2000] which is similar to that reported for aragonite and has approximately the same slope with respect to temperature as relationships reported for scleractinian corals [*Weber and Woodhead*, 1972; *Leder et al.*, 1996] and inorganic aragonite [*Grossman and Ku*, 1981].

2. Methods

[6] In order to assess whether sclerosponges could record intra-annual changes in water chemistry and temperature, we analyzed a specimen of *C. nicholsoni* collected from the Tongue of the Ocean in the Bahamas (23°55′N, 76°50′N; Figure 1) from a water depth of 146 m. The water temperature at this depth is approximately 24°C and has an annual variation of 2 to 3°C [*Grammer*, 1991]. The specimen was slabbed, and sampled for its $\delta^{13}C$ and $\delta^{18}O$ values at a resolution of one sample every 34 μm. Based on our expectation that the growth rate of this coral would be approximately 250 μm/yr, this sampling resolution was sufficient to provide about 8 samples per year. The sampling was carried out using a computer-controlled microdrill. Each sample was milled along a line 1.7 mm long parallel to the oral surface of the animal to a depth of 340 μm. Each successive sample was taken by incrementing the drill 34 μm toward the interior of the skeleton (see Figure 2). The material produced during the drilling is theoretically approximately 60 μg (assuming a density of 2.94 gm/cm^3) although in practice the samples analyzed were somewhat smaller as a result of sample losses incurred during the transfer of the powder from the drill to sample boats used in the stable isotope mass spectrometer. A total of 667 samples was extracted from a continuous 21 mm section of the sclerosponge. These samples were processed using an automated common acid bath attached to a Finnigan-MAT 251 at the University of Miami. Data have been corrected for drift of the standard during the analysis and the usual isobaric interferences and are reported relative to V-PDB in the conventional notation. External precision, calculated by measuring replicate samples of an internal laboratory standard, is 0.08‰ for $\delta^{18}O$ and 0.03‰ for $\delta^{13}C$. A parallel section of the sclerosponge was analyzed using a Finnigan-MAT Element at Old Dominion University. The sclerosponge skeleton was initially mounted on a petrographic slide, scrubbed with a nylon brush in a solution of ultrapure H_2O, sonified for 5 min in Milli-Q water (Millipore Water Systems), tripled rinsed with an ultrapure 1% HNO3 solution, and finally triple rinsed again with Milli-Q water. The section was then dried under a positive flow hood for 24 hrs. The section was then transferred to the laser cell for all subsequent analyses, which were conducted with a Finnigan MAT Element2 magnetic sector field ICP-MS and Merchantek EO LUV266X laser ablation system. The laser sampled a single line, approximately 600 μm long and perpendicular to the growth axis of the sclerosponge, for each assay. Each sample was, in turn, separated by approximately 20 μm (see Figure 2). The analytical method we used to quantify the data followed the approach outlined by *Rosenthal et al.* [1999] for precise element/Ca ratios using sector field ICP-MS. We used a He gas stream to transport matter from the sample cell to the mass spectrometer. The carrier gas was then mixed with the Ar sample gas and a wet aerosol (1% (w/w) HNO3), and introduced to a Scott double pass spray chamber via a PFA micro-flow nebulizer [*Günther and Heinrich*, 1999]. The nebulizer was, in turn, attached to an autosampler. A liquid standard, containing all isotopes of interest at concentrations such that count rates were approximately equal to those obtained from the laser analysis of the sclerosponge, was analyzed every 5 samples to account for variations in mass bias and instrumental fluctuations of the ICP-MS. Quality control was maintained by assays of an aragonite reference material [*Yoshinaga et al.*, 1999, 2000]

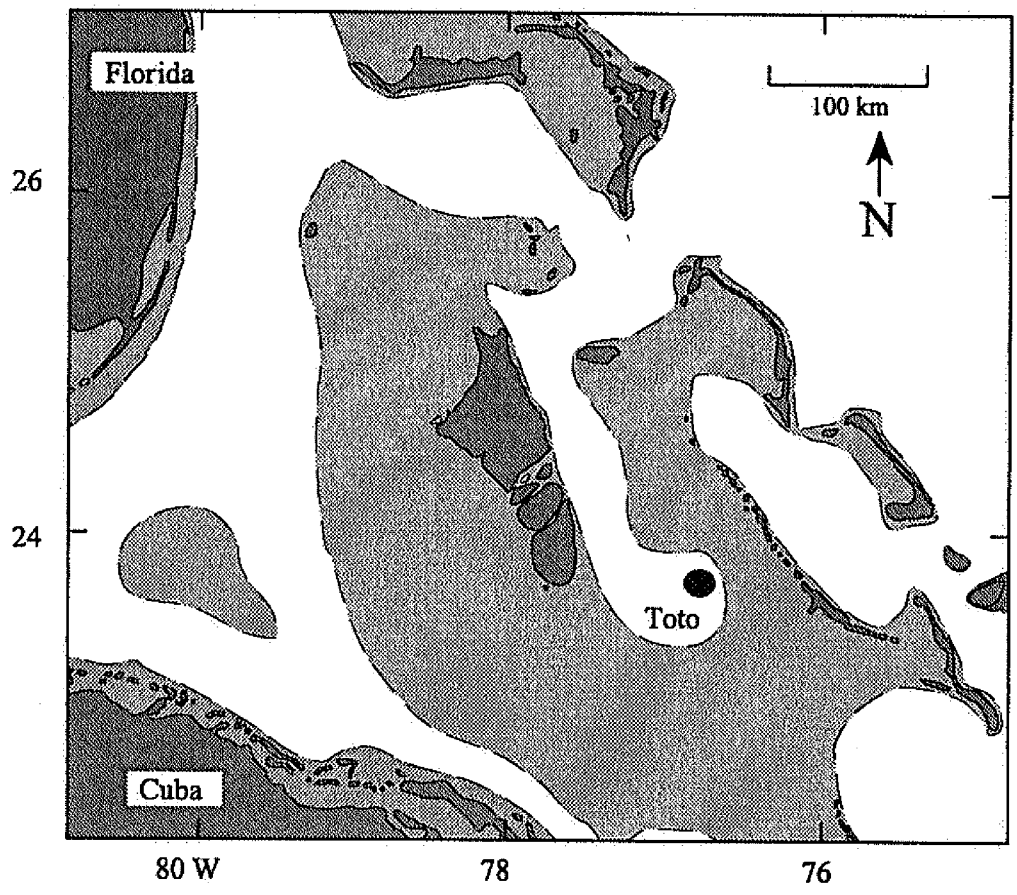


Figure 1. Location map of Bahamas. The samples were collected from a depth of 146 m in the Tongue of the Ocean in 1990 (TOTO) (23°55'N, 76°50′W). The location is indicated by the solid circle.

every 20 samples. Precision (%RSD) of the multielement technique, obtained by analysis of 5 replicate samples in a line perpendicular to the growth axis, are Mg/Ca 1.0%, Sr/Ca=0.6% and Pb/Ca 1.4%.

[7] About 0.25 g of the sponge carbonate were chemically prepared for U/Th measurements. The chemical purification procedure closely followed previous procedures [*Chen et al.*, 1986; *Edwards et al.*, 1987]. The U/Th measurements were performed at the GEOMAR mass spectrometer facilities on a Finnigan MAT 262 RPQ+ multicollector mass spectrometer. As a control, the $^{234}U/^{238}U$ activity ratio of U in the NBL standard 112a was measured to be $-32.82 \pm 3‰$. Latter value is in accord with previously published values [*Edwards et al.*, 1993; *Eisenhauer et al.*, 1996; *Cheng et al.*, 2000a, 2000b].

3. Results

3.1. Dating

[8] Three samples from different depths below the oral surface were subjected to U series dating. These data (Table 1) yield an average growth rate of 0.171 mm/yr and show an intercept indistinguishable from zero. The ^{238}U concentrations of the TOTO samples are typical for coralline sponges. The $^{234}U/^{238}U$ activity ratio reflects the $^{234}U/^{238}U$ activity ratio of modern seawater (about 145‰ [*Cheng et al.*, 2000a]). The measured ^{232}Th concentrations are low and in the range of values expected for areas away from continental margins.

3.2. Oxygen Isotopes

[9] The $\delta^{18}O$ of the skeleton of the sclerosponge showed an average value of +0.39‰ with range of 1.8‰ (Figure 3a). Assuming a $\delta^{18}O$ versus temperature relationship in sclerosponges similar to corals [*Leder et al.*, 1996], a variation of 1.8 ‰ would equate to a range in temperature of about 7°C or a combination of change in temperature and the $\delta^{18}O$ of the water.

3.3. Carbon Isotopes

[10] The $\delta^{13}C$ of the skeleton of the sclerosponge showed patterns similar to those seen by previous workers [*Druffel and Benavides*, 1986; *Böhm et al.*, 1996] with a trend of progressive enrichment with increasing age (Figure 3b) with the most negative values occurring in the most recent portion of the skeleton.

3.4. Strontium

[11] The mean Sr/Ca ratio of the sclerosponges is 10.44 mmol/mol, significantly higher than that measured in other

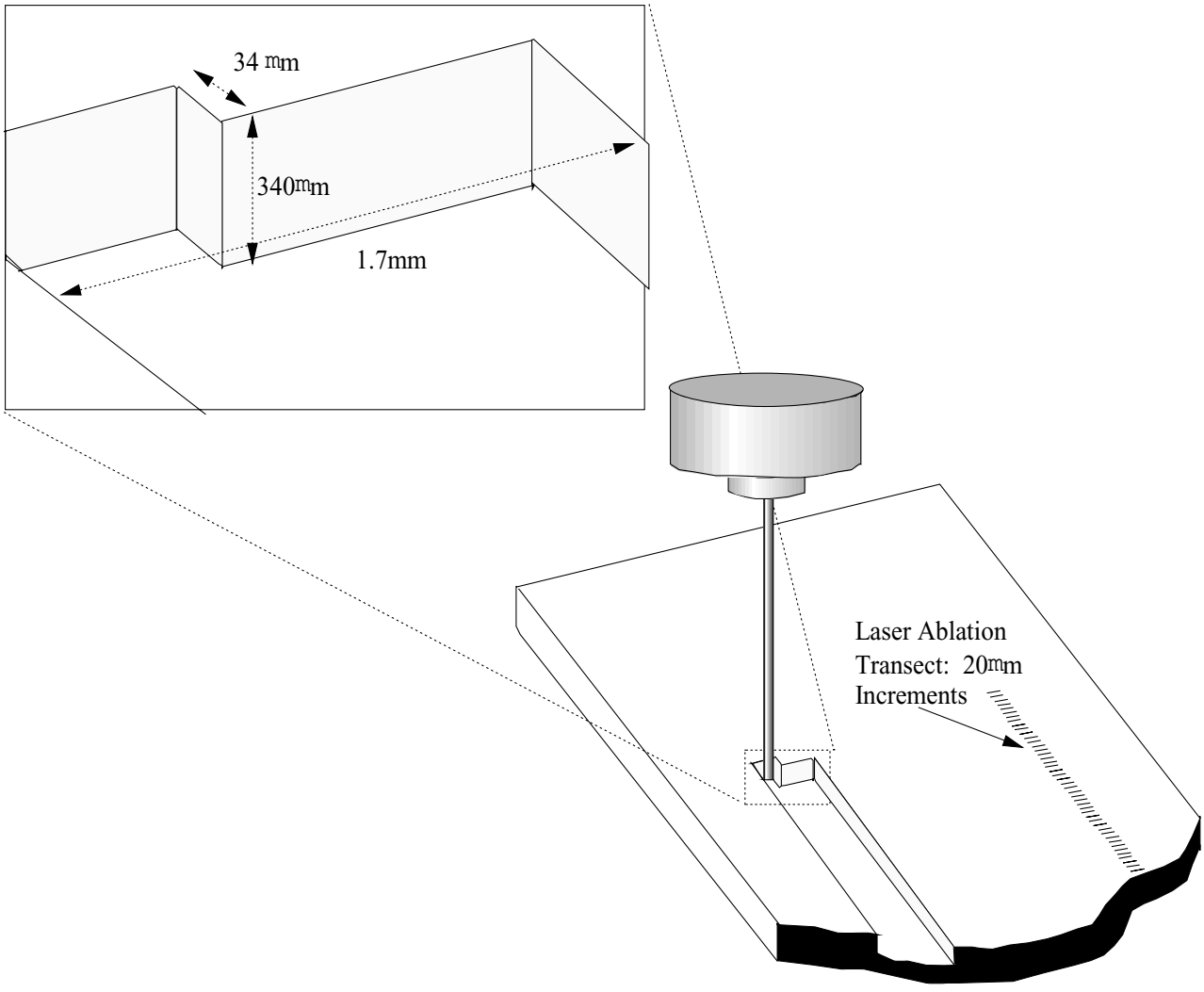


Figure 2. Schematic representation of the sampling of the skeleton of the sclerosponge for $\delta^{18}O$ and Sr/Ca. Each sample for $\delta^{18}O$ and $\delta^{13}C$ is milled from a section of the sponge 1.7 × 0.34 × 0.034 mm. Each sample for Mg/Ca, Sr/Ca, and Pb/Ca analysis is measured on a 0.1 mm long swath separated by 0.02 mm.

aragonitic organisms such as corals [*Swart*, 1981; *Beck et al.*, 1992]. This finding is similar to that made by previous studies [*Fallon et al.*, 1999]. The Sr/Ca ratio exhibits regular variations of amplitude of about 0.5 to 0.8 mmol/mol (Figure 3c).

3.5. Magnesium

[12] The Mg/Ca ratio showed a strong positive covariance with the Sr/Ca ratio similar to that documented by *Fallon et al.* [1999] for sclerosponges ($r^2 = 0.21$, n = 1020, $p > 0.001$). Values ranged from 0.7 to 1.05 mmol/mol.

3.6. Lead

[13] The Pb/Ca ratio ranges from below 100 to over 500 nmol/mol reaching a maximum about 1 cm from the oral surface of the sclerosponge (Figure 4). Values then declined from this point onwards. These values are

Table 1. Data Used for Calculated Uranium Series Ages[a]

Sample	Distance From Oral Surface	Activity Ratio $^{234}U/^{238}U$	Activity Ratio $^{230}Th/^{234}U$	^{232}Th Concentration	Age, years
1	10.9	1.148 ± 0.003	0.001165 ± 0.000665	1.19168 ± 0.0023	127 ± 72
2	4.8	1.147 ± 0.003	0.000805 ± 0.000157	1.9511 ± 0.0232	88 ± 17
3	3.05	1.148 ± 0.002	0.000768 ± 0.000037	2.3163 ± 0.0051	84 ± 10

[a] All given statistical errors are two standard deviations of the mean (2). The used decay constants are $\lambda_{234\ U} = 2.8262 \times 10^{-6}\ a^{-1}$ [*Cheng et al.,* 2000b]; $\lambda_{238\ U} = 1.55125 \times 10^{-10}\ a^{-1}$ [*Jaffey et al.,* 1971]; $\lambda_{230\ Th} = 9.158 \times 10^{-6}\ a^{-1}$ [*Cheng et al.,* 2000b]. Ages were calculated using an equation previously published [*Edwards et al.*, 1987]. Ages were calculated for the initial conditions under which ^{230}Th was associated with ^{232}Th assuming that the $^{232}Th/^{238}U$ ratio is 3.8.

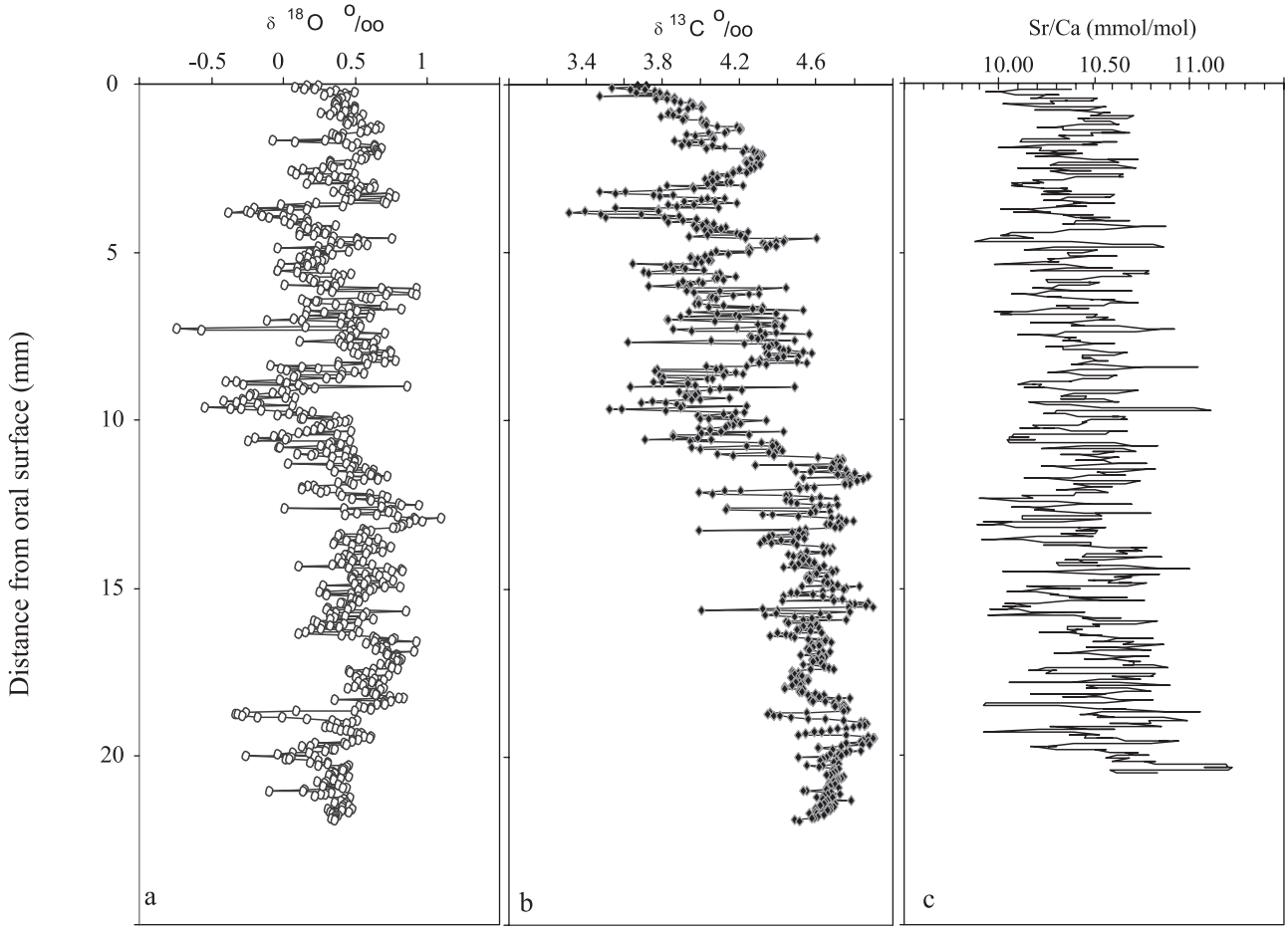


Figure 3. Variation in the (a) $\delta^{18}O$, (b) $\delta^{13}C$ of the skeleton of a sclerosponge, and (c) Sr/Ca ratio. Samples for stable isotopes were taken every 34 μm using a computer controlled microdrill. Samples for Sr/Ca were taken from an area parallel to where $\delta^{18}O$ and $\delta^{13}C$ were collected (see Figure 2).

slightly lower than those reported by *Lazareth et al.* [2000] who measured maximum Pb values of between 2.5 to 3 ppm.

4. Discussion

[14] The first step in the interpretation of the high-resolution data is the establishment of an age model for the sclerosponge. In the preparation of this chronology we have used three approaches (1) the Pb concentration, (2) the $\delta^{13}C$ record, and (3) uranium series age dates.

4.1. Lead Data

[15] There have been numerous workers who have documented the increase of lead in the atmosphere as a result of industrial input and the combustion of leaded gasoline. These records are contained in ice cores [*Murozumi et al.*, 1969; *Candelone et al.*, 1995; *Rosman et al.*, 2000], corals [*Shen and Boyle*, 1987, 1988; *Dodge and Gilbert*, 1984], and sclerosponges [*Lazareth et al.*, 2000]. Using the data presented by *Shen and Boyle* [1987, 1988], we can match the maximum concentration in lead measured in our sclerosponge to that measured in the coral skeleton (Figure 4). This maximum in the coral skeleton has been shown to be a result of use of alkyl Pb in gasoline which reached a peak in 1971 [*Shen and Boyle*, 1987] and can be dated extremely accurately by simply counting the number of annually formed density bands in the coral skeleton. The comparison between the sclerosponge and the coral yields an average growth rate for the sponge of 220 μm a year.

4.2. Carbon Isotopic Data

[16] The decrease in the $\delta^{13}C$ of atmospheric CO_2 as a result of the addition of isotopically depleted fossil fuel derived CO_2 has been well documented and is recorded in the skeleton of corals [*Nozaki et al.*, 1978] and sclerosponges [*Druffel and Benavides*, 1986; *Swart et al.*, 1994; *Böhm et al.*, 1996; *Lazareth et al.*, 2000]. This change has been used in previous studies to confirm the age estimates of sclerosponges dated by radiometric means [*Böhm et al.*, 1996] and also to date the sclerosponge directly [*Lazareth et al.*, 2000]. The change in the $\delta^{13}C$ of the sclerosponge analyzed in this study when matched to the known change of the CO_2 concentration in the atmosphere sclerosponge

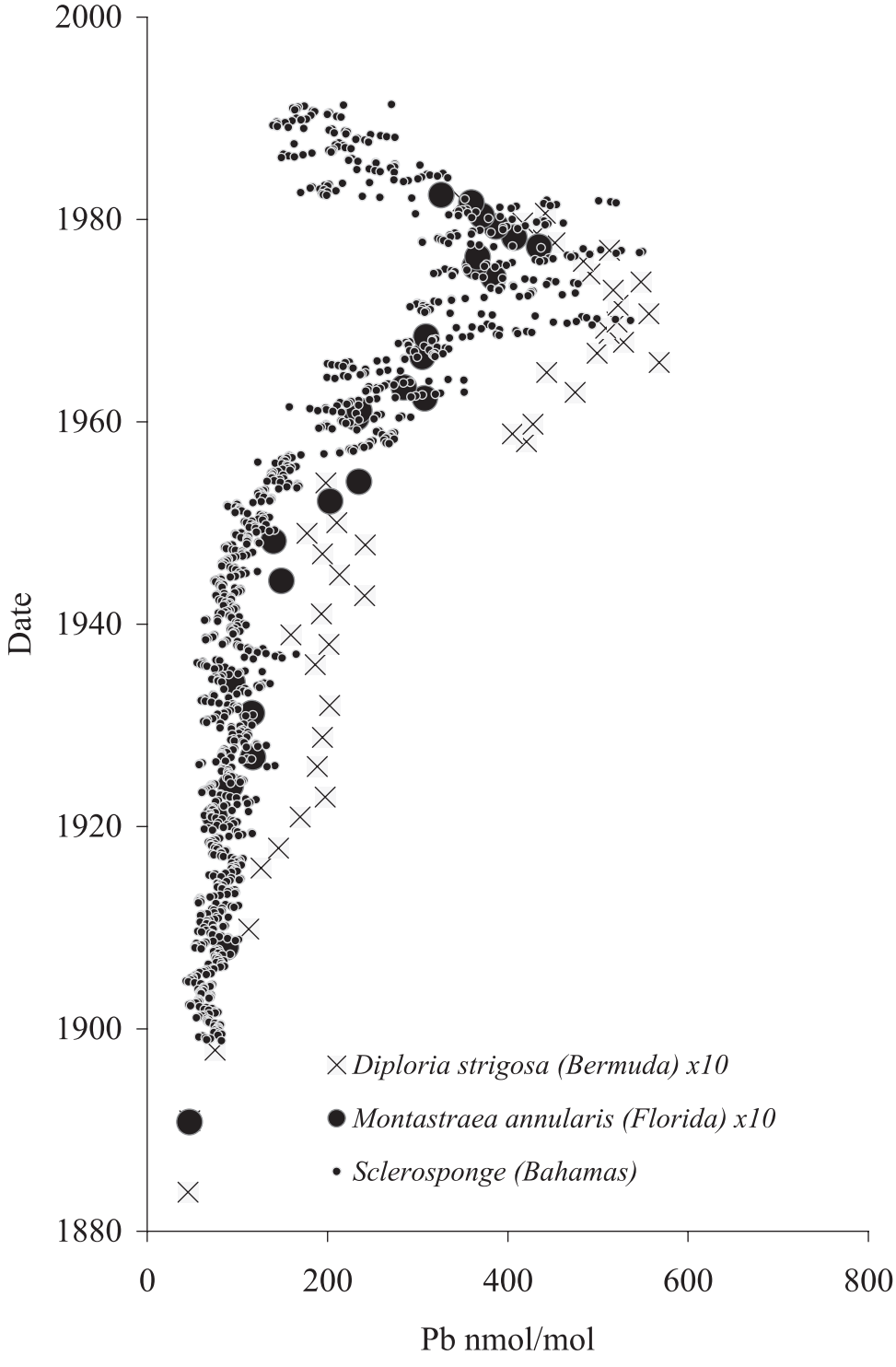


Figure 4. Variation in the Pb/Ca ratio measured along the same transect as the Sr/Ca and Mg/Ca ratios were measured. The distance has been converted to age using a growth rate of 220 μm/yr and has been estimated by matching the Pb/Ca ratio and $\delta^{13}C$ value in the sclerosponge with known changes in these parameters [*Dodge and Gilbert*, 1984; *Lazareth et al.*, 2000; *Böhm et al.*, 1996; *Shen and Boyle*, 1987, 1988]. For comparison, data from *Shen and Boyle* [1987, 1988] obtained from specimens of *Diploria strigosa* in Bermuda and *Montastraea annularis* in the Florida Keys are plotted in addition to the sclerosponge data. Note the concentrations from these corals have been multiplied by a factor of 10 to make the scales comparable to the sclerosponge sample. Although these data show lower absolute concentrations in Pb when compared to the sclerosponge, the increase in the Pb coincident with the advent of Pb in fuel is unambiguous.

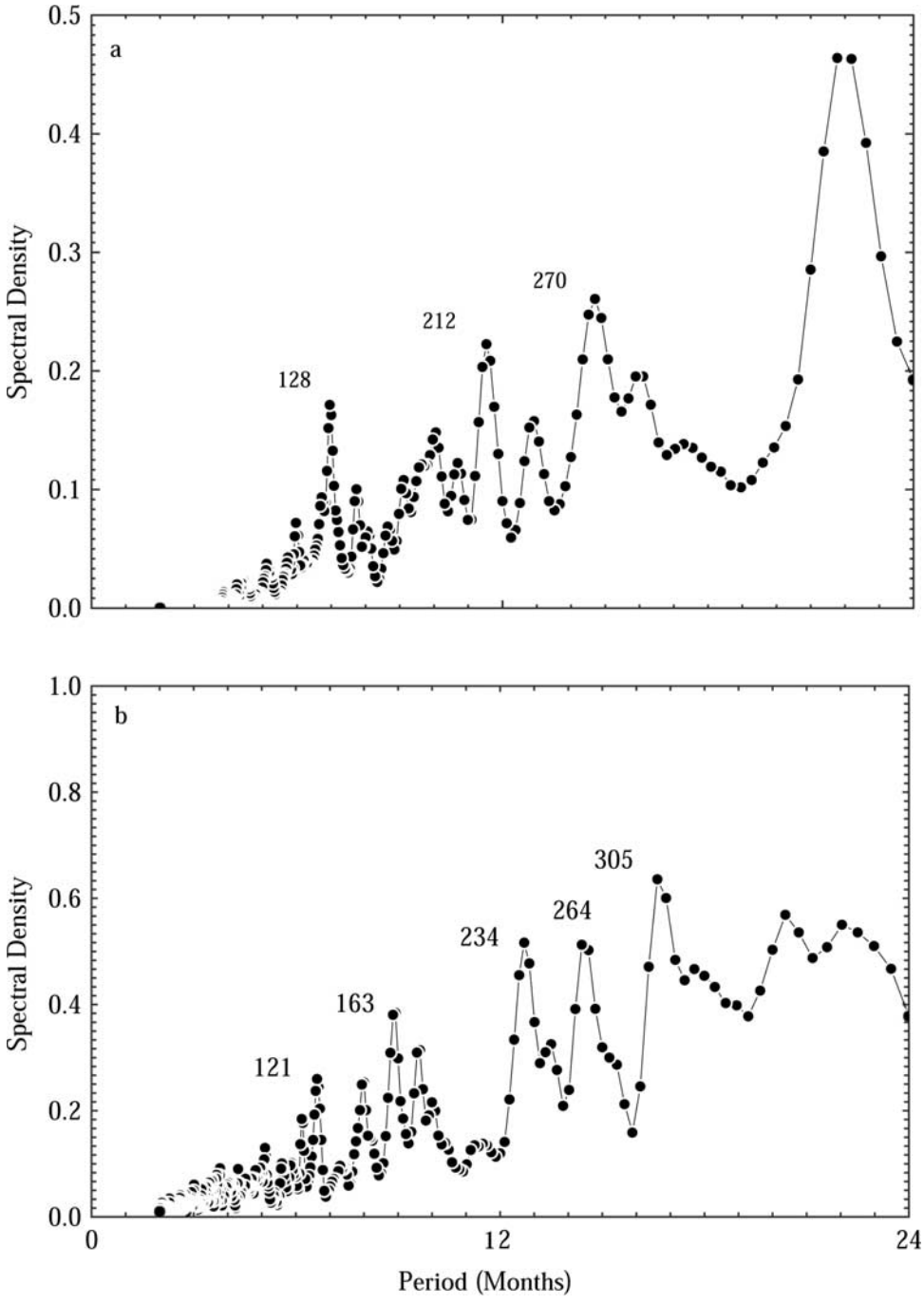
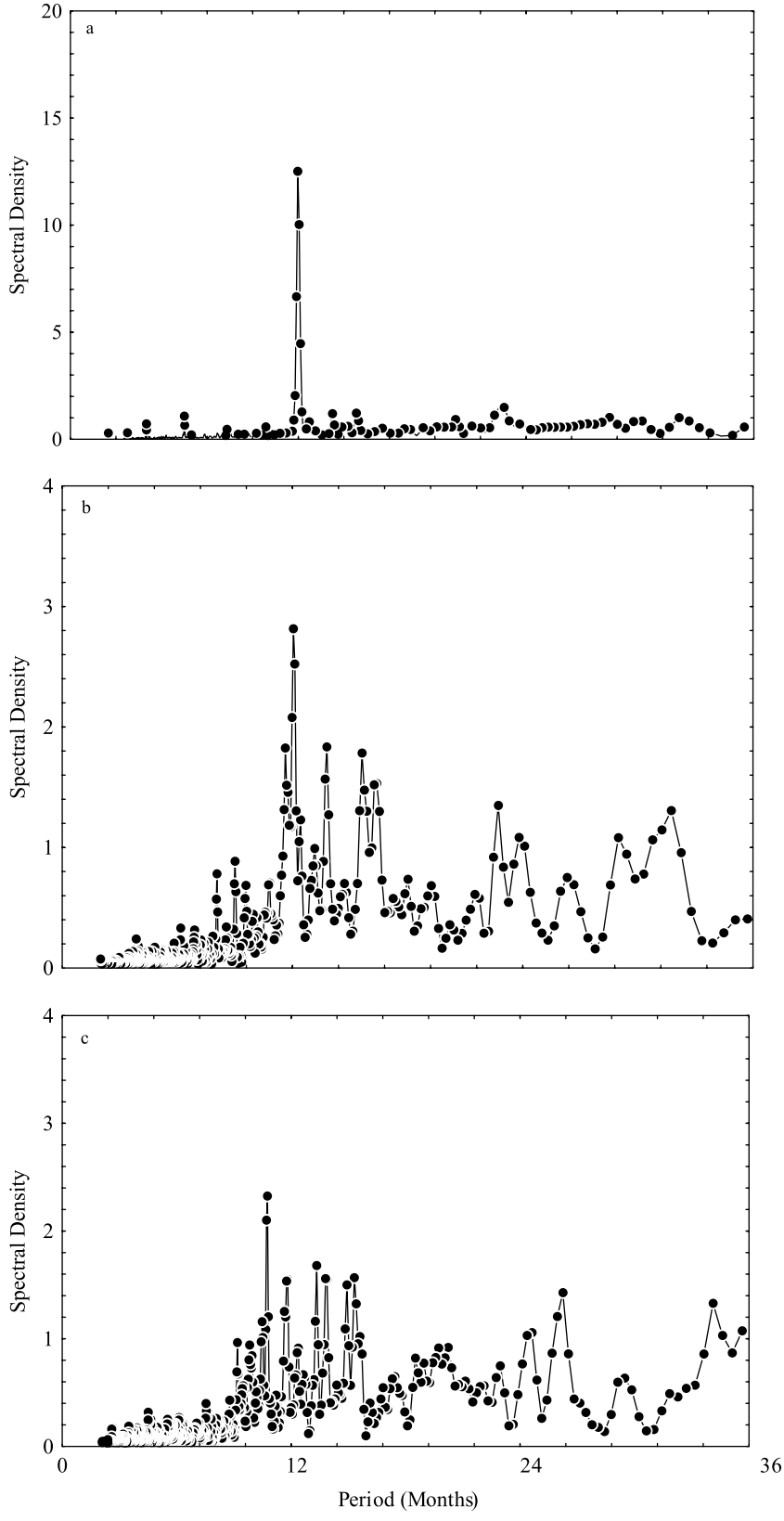


Figure 5. Spectral analysis performed on (a) $\delta^{18}O$ and (b) Sr/Ca data. Data have been converted from the spatial to the time domain assuming a growth rate of 220 μm/yr and interpolated to a spacing interval of 12 samples a year. Hence if the sclerosponge grew consistently at 220 μm/yr, a strong peak at 12 samples a year would be evident. Peaks corresponding to slower growth rates occur at frequencies of less than 12 samples a year, and peaks corresponding to faster growth rates correspond to frequencies of greater than 12 samples year. These peaks are labeled in units of μm/yr.

(Figure 3b) and provides an age which is consistent with the age estimate based on the Pb concentration.

4.3. Uranium Series Model

[17] Uranium-thorium dating has been previously used successfully to provide age estimates of sclerosponges [*Moore et al.*, 1996, 2000; *Böhm et al.*, 2000]. The data shown in this paper indicate a mean growth rate of 0.171 mm/yr. This is lower than previous growth estimates in sclerosponges which average around 0.22 mm/yr and slightly lower than the age estimate provided by the Pb concentration data (Figure 4) and the match to the $\delta^{13}C$ of the skeleton (Figure 3b). However, considering the errors on the U/Th age estimates (Table 1), the growth rate calculated


a
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Spectral Density
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20
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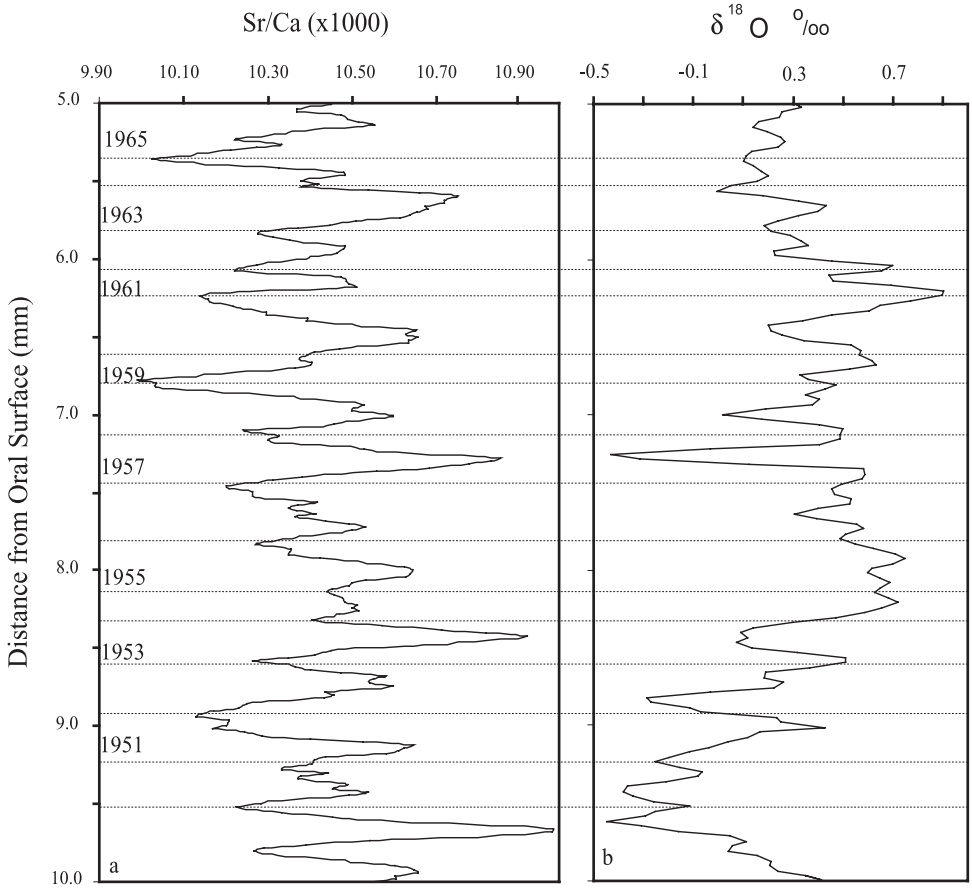

Figure 7. A portion of the Sr/Ca in a portion of the sclerosponge between 5 and 10 mm from the oral surface in order to demonstrate the apparent annual cyclicity in the ratio. The chronology can be determined assuming each cycle in the Sr/Ca ratio approximates 1 year. In some years, however, the Sr/Ca ratio does not exhibit a clear interannual signal suggesting that there is interannual variability in the temperature at the depths from which the sclerosponges were recovered.

by U/Th can be considered to be identical to that estimated using the Pb and $\delta^{13}C$ data.

4.4. Intra-annual Variations in Stable Isotopes

[18] Based on a sampling rate for stable C and O isotopes of one sample every 34 μm, an annual growth rate of 220 μm/yr would yield about 6 samples within a calendar year. Sampling for trace elements was carried out using an interval of 20 μm, yielding 11 samples a year. In order to test for the presence of annual cycles in the skeleton we applied an annual growth rate to the sclerosponge of 220 μm and interpolated the position of the samples to a sampling interval of 12 samples a year. The data were then subjected to Spectral and Single Spectral Analysis (SSA) [*Vautard et al.*, 1992]. The spectral results for the higher frequency $\delta^{18}O$ data (Figure 5a) show a statistically significant peak at the annual cycle (12 samples/yr), but also peaks at about 60% of the annual cycle (128 μm/ yr) as well as peaks corresponding to growth rates of 270 and 310 μm/yr. Similar spectra were observed in the case of the Sr/Ca ratio, although the annual peak indicated a growth rate of between approximately 230 and 260 μm/yr (Figure 5b). There were no signals corresponding to yearly variation in the Mg/Ca ratio. We believe that these spectra not only reflect the presence of annual variations in the chemical composition of the skeletons of sclerosponges, but also reflect the

Figure 6. (opposite) Spectral analysis performed on (a) $\delta^{18}O$ data from a 250 year old specimen of *Montastraea annularis* from the Florida Keys [*Swart et al.*, 1996]. The chronology is based on the annual variation in the $\delta^{18}O$ and therefore exhibits a strong annual signal at 12 samples a years. If the chronology is based on the annual variation in the density band, then (b) a large number of peaks appear around the period of 12 months. This is caused by the fact that the density bands do not always exactly occur every 12 months, sometimes occurring on a periodicity shorter than 12 months and sometimes longer. If spectral analysis is performed on the same data but (c) with the chronology based on a constant growth rate for the entire record, then a number of small peaks are manifested around the annual signal. This is analogous to the situation seen in sclerosponges in which a signal constant growth rate would be applied to an entire sclerosponge.

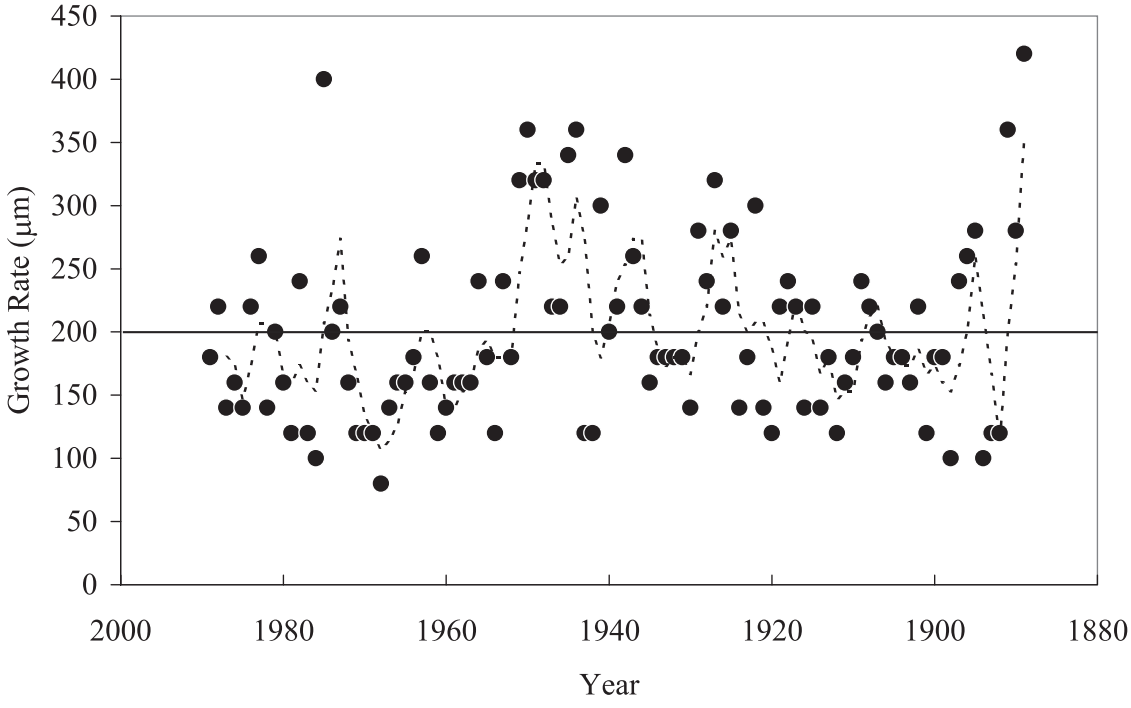

Figure 8. Annual growth rate of sclerosponge calculated from the Sr/Ca data. Each year is assumed to correspond to a cycle of Sr/Ca values. The dashed line represents a 3 year running average of the growth rate. The mean growth rate (horizontal line) calculated using this approach is 200 μm/yr and agrees with the estimate calculated using the Pb/Ca (Figure 4) and the $\delta^{13}C$ data (Figure 3b).

presence of a variable growth rate. In order to test the hypothesis that the additional peaks in the spectra shown in Figures 5a and 5b are a result of varying growth rate, we carried out two experiments. In the first we perform spectral analysis on a previously published $\delta^{18}O$ record from a 240 year old scleractinain coral collected from the Florida reef tract [*Swart et al.*, 1996]. In this record the annual cycles were chosen based on the cyclic variation in the oxygen isotopic records (Figure 6a) and the density of the skeleton (Figure 6b). The $\delta^{18}O$ data were then interpolated to a frequency of 12 samples a year and subjected to time series analysis. Obviously the spectral analysis of the $\delta^{18}O$ data, in which the annual cycle was chosen using the annual variation in the $\delta^{18}O$, shows an extremely strong peak at 12 months. In contrast the chronology determined using the density bands, although showing the strongest signal at 12 months, also shows peaks corresponding to shorter and longer than the yearly cycle (Figure 6b). The explanation for this is that density bands in corals do not always form at precisely the same time [*Buddemeier and Kinzie*, 1976]. Sometimes the period between density bands maybe 12 months but at other times it can be longer or shorter. If the chronology of the same coral is then assigned as we would a sclerosponge, on the basis of an average growth rate, a quite different spectral pattern is produced (Figure 6c). This pattern is very similar to the pattern observed in the sclerosponge. It is also possible to construct a synthetic time series in which varying growth rates are imposed on an annual cycle in $\delta^{18}O$ and the record subsequently sampled at a uniform sampling rate, as in the case of the sclerosponge. The result obtain from this modeling exercise is similar to both the coral and sclerosponge data.

[19] A further confirmation of the variable growth rate can be obtained by counting the cycles in the Sr/Ca ratio and assuming that these are annual in nature (Figure 7). Using this method it is possible to ascertain that the annual growth rate, varies between 80 and 420 μm/yr (Figure 8) and has an average of 200 μm/yr. This is remarkably consistent with other estimates of extension rates considering the inherent errors in all of these methods. Based on this counting, the age of the oldest portion of the sclerosponge is 1893, compared to 1892 based on using an average growth rate of 220 μm/yr. In the counting exercise there were several years in which we measured relatively high growth rates for the sclerosponge (> than 400 μm/yr). It is conceivable that these higher growth rate years resulted from the fact that the sclerosponge may have missed a cycle in the Sr/Ca ratio leading to the representation of two years as one year's growth. The peak representing a growth rate of 400 μm/yr seen in the $\delta^{18}O$ data (Figure 5a) may therefore represent a 2 to 4 year cycle rather than an annual one. Although a similar exercise in peak counting can be carried out using the $\delta^{18}O$ data, the sensitivity of the $\delta^{18}O$ to temperature (0.25‰/°C) is relatively small compared to the apparent sensitivity of the Sr/Ca ratio (see later discussion). Consequently, a greater uncertainty exists in assigning variations in the data to specific years.

4.5. Interpretation of the Data

[20] Using SSA it is possible to estimate the temporal variation in the magnitude of the different growth rates and

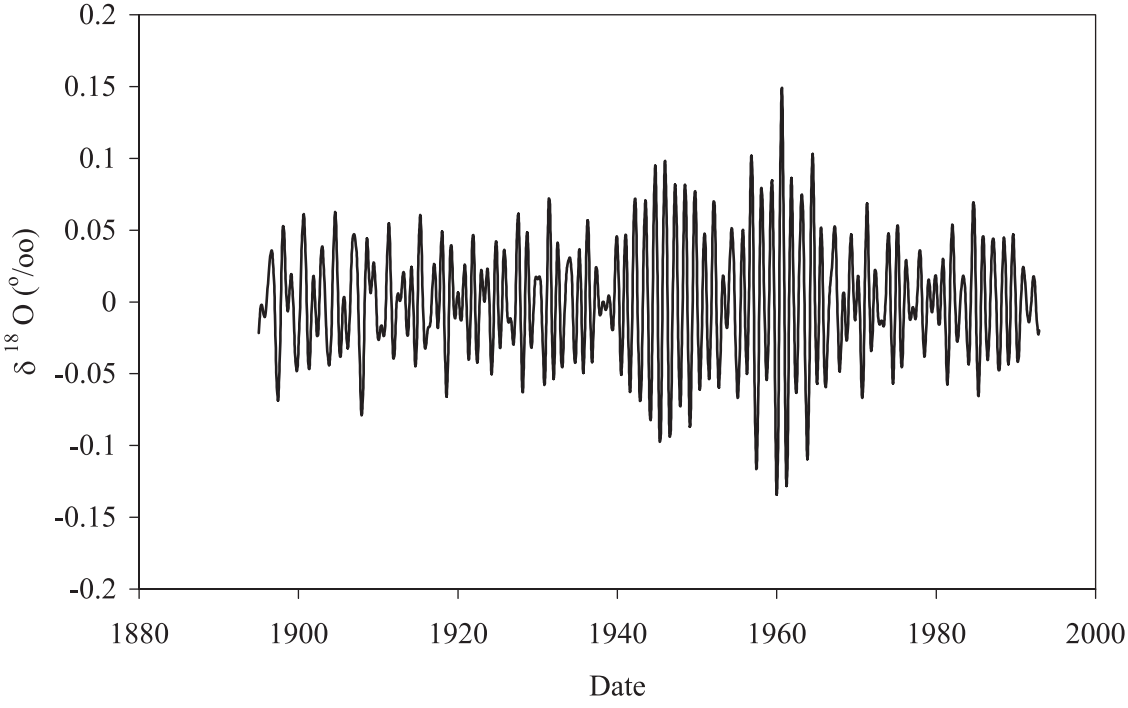

Figure 9. The annual signal of the oxygen isotopic composition extracted from single spectral analysis (SSA) of the oxygen isotopic data. This annual signal accounts for approximately 10% of the variance in the oxygen isotopic signal. The annual variation in the $\delta^{18}O$ signal ranges from <0.05 to 0.15‰, equivalent to an annual range in temperature from 0° to 2.5°C.

the contribution of these to the total variance in the oxygen isotopic signature. These data indicate that the magnitude of the yearly $\delta^{18}O$ varies between essentially 0 to 0.3‰ (Figure 9). It is well established that the $\delta^{18}O$ of the skeleton of sclerosponges records the temperature of growth [*Böhm et al.*, 2000; *Moore et al.*, 2000] and that the relationship is approximately similar to that observed in other aragonitic organisms. Therefore a variation of 0.3 ‰ is equivalent to about 1.5°C and is consistent with the annual change temperature observed at a depth of 143 m in the Tongue of the Ocean [*Grammer*, 1991]. The total combined variance of the $\delta^{18}O$ signal observed at the three principal frequencies, corresponding to growth rates of between 128 and 270 μm/yr is 11%. The remainder of the variance in the $\delta^{18}O$ record is accounted for by longer term changes, 3 years (3%), 4–5 years (13%), 6–10 years (15%) and longer cycles or trends, not resolved by the length of the record examined.

[21] Unlike the $\delta^{18}O$ signal, the precise interpretation of variations in the Sr/Ca and Mg/Ca signals in skeletons of sclerosponges are not yet clear. Assuming a temperature versus Sr/Ca ratio relationship similar to that measured in scleractinian corals [*Smith et al.*, 1979; *Beck et al.*, 1992], the annual range in the Sr/Ca data (Figure 3c) would appear equate to a temperature range of about 8°C. As this range is too great for the water depth at which the corals were collected [*Grammer*, 1991], it is obvious that the calibration between Sr/Ca and temperature in scleractinian corals is not directly applicable to sclerosponges. Another difference between sclerosponges and scleractinian corals, is that the Mg/Ca ratio in scleractinian coral skeletons is positively correlated with temperature [*Mitsuguchi et al.*, 1986] and therefore inversely correlated with the Sr/Ca ratio. In the sclerosponge investigated in this study however, there is a weak positive, but nevertheless statistically significant, correlation between Sr/Ca and Mg/Ca (r^2=0.21). A similar observation was made by *Fallon et al.* [1999] in specimens which they studied. As a result of this rather poor correlation, the Mg/Ca did not exhibit the clear variations which we observed in the Sr/Ca ratio.

[22] If the Sr/Ca ratio of skeleton is inversely related to temperature, there should be a positive correlation between the Sr/Ca ratio and the $\delta^{18}O$ records. Although similar spectral frequencies were observed in both signals suggesting a common forcing mechanism, the fact that the $\delta^{18}O$ and Sr/Ca were sampled from different portions of the sclerosponge and at different sampling resolutions precludes a rigorous correlation.

5. Conclusions and Implications

[23] The data presented in this paper show that, despite the slow rate of skeletal accretion of sclerosponges, intra-annual variations in the temperature and other water quality parameters can be obtained from these organisms if appropriate sampling techniques are used. However this work also emphasizes the need for a precise chronology in order to allow an interpretation of paleoenvironmental data from proxy indicators in the skeletons of sclerosponges to be made. In order for annual correlations to be made with sea surface temperatures and other climate phenomena, a precise method of obtaining annual growth rates is required. One such method is a high resolution transect of the Sr/Ca composition.

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