C. PROPOSAL NARRATIVE

Results from Previous NSF Support

1. Swart OCE-8900095($260K)/OCE-9217993($460) The control of banding and C&O isotopic compositions in Scleractinian coral skeletons: An experimental approach; P.K. Swart, A. Szmant, R. Dodge (NOVA Southeastern); Duration 3-1-89 to 3-1-97

Theses

Leder J.J., 1994. High-resolution, climate proxies in coral skeletons, Unpublished Ph.D thesis, University of Miami.(Ph.D. thesis defended, but final draft has not been submitted)

Papers

Nine papers in Peer Reviewed Journals

Abstracts

Nine abstracts at national and international meetings.

2. OCE- 9529838: Acquisition of a stable isotope mass-spectrometer

Two stable isotope mass spectrometers (Europa GEO and Europa 20-20) were acquired in 1998. These are interfaced to a CN analyzer, an automated water equilibrator, and a GC. The instruments have been installed and are working to specifications.

3- OCE-9819147: A Multi-tracer calibration study of sclerosponges

Detailed description of accomplishments are included in this proposal.

Papers

Swart, P.K., Thorrold, S., Rubenstone, J., Rosenheim, B., Harrison, C.G.A., Grammar, M., Latkoczy, C., (In Review) Intra-annual variation in stable oxygen and carbon and trace element composition of sclerosponges.

Abstracts

Rosenheim, B., Swart, P.K., Thorrold, S., and Rubenstone, J. 2001.Annual variations in the Sr concentration and oxygen isotopic variation in the skeleton of sclerosponges, GSA Boston.

4- OCE- 0081770 : Inter-annual to Century-scale Climate Records from the Atlantic

This proposal started in October 2000. Field activities are planned for March 2001. A Ph.D. student has started re-analyzing and sampling material in hand. A collection trip has just been completed and corals in excess of 100 years collected. Additional sites have been identified.

Abstracts

Moses, C., Swart, P.K., Dodge, R.E., Gilliam, D., and Helmle, K. 2001. Climate records in corals from the eastern Atlantic, GSA Boston.

5- OCE: -0082562: Acquisition of Kiel Device and Stable Isotope Mass Spectrometer

Equipment (Delta Plus and Kiel Device) has arrived at RSMAS and has been installed (April 2001). The equipment is not yet operating at specifications.

Introduction

This is a second submission of a proposal to NSF to continue a project initially funded in 1999 for a two year period. Funding from our current award has allowed us to start the important task of calibrating the chemical composition of the skeleton of sclerosponges as proxy indicators of temperature and salinity. This work, which is being carried out at the Discovery Bay Laboratory in Jamaica, is entering its third year and here we present data collected to date on the temperature and δ^{18}O of the water. In this version of the proposal we address legitimate concerns of the reviewers of the proposal submitted in February 2001 for the continuation of this work and concentrate specifically on the calibration of geochemical proxies in the skeletons of sclerosponges with modern environmental data.

Sclerosponges possess hard calcareous skeletons which contain 100's to 1000's of years of continuous growth records and have the potential to allow climate reconstructions over extended time scales using geochemical proxies (Figure 1). They represent arguably one of the most exciting new paleoclimate proxies of recent years and offer the potential to surpass corals in providing more accurate and longer proxy climate records. For instance, the sample shown in figure 1 is approximately 400 years old.

In the past several years there has been increasing interest in using the chemical composition of sclerosponges as proxy indicators of climate. Several papers in the past 18 months have reported advances in our understanding of certain aspects of the geochemistry of skeletons of these invertebrates [1-3]. These build on several older studies on the stable isotopic composition [4-10]. In addition we have used NSF funding to make some exciting discoveries including documenting (i) the presence of annual cycles in δ^{18}O and Sr/Ca ratio, and (ii)evidence of a a highly variable growth rate. These results have been submitted for publication [11]. In this proposal we present a summary of our proposed work and detailed advances made during our past 24 months of NSF funding.

Summary of Proposed Work

In this section we restate goals laid out in the previous funded proposal (italics), detail the progress has been made towards these goals and outline additional work (bold italics).

- *Monitor the environment of sclerosponges from Jamaica over a two year period, collecting monthly information on the water chemistry and temperature after staining them with Calcein.* ***Samples of sclerosponges have been stained at localities near the Discovery Bay Marine Laboratory in Jamaica, water temperature sensors deployed and water samples collected monthly. All samples collected thus far have been analyzed and suggest only minimal annual variations in the*** δ^{18}O ***of the water. These data are discussed below (Figure 12). We will also analyze the waters for variations in the Mg/Ca and Sr/Ca ratios.***
- *Collect sclerosponges and perform stable isotopic and trace element analysis (ion-microprobe and TIMS).* ***Samples are still in the field as the growth rate is extremely slow and we wish to leave the sclerosponges for at least 3 years after staining to allow***

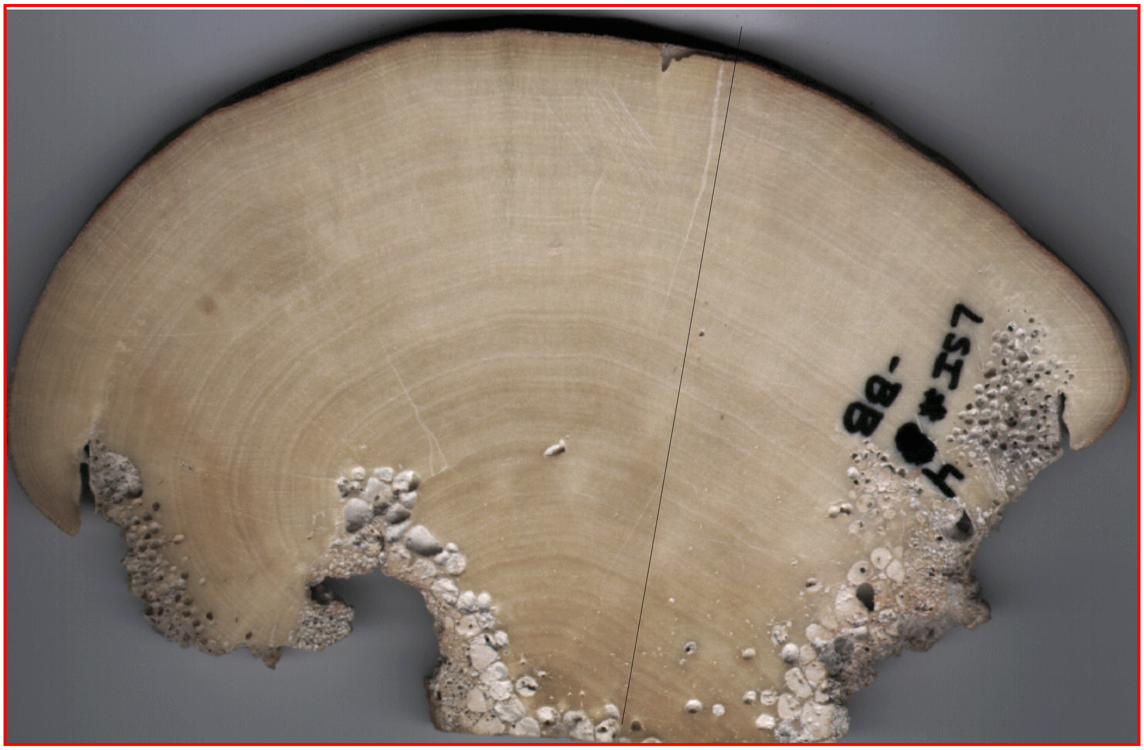

Figure 1: Polished slab of a section of a sclerosponge from Lee Stocking Island in the Bahamas. The variation in banding can be clearly seen. There is further discussion of this banding in this proposal. The line shows the approximate location of the scan using the LIFA instrumentation discussed later in the proposal. The age of this specimen is about 400 years old based on preliminary U/Th dates.

sufficient material for analysis. Analyses will be carried out using laser ablation ICP-MS rather than the ion probe, as originally proposed. In addition we propose to examine the trace element content and stable isotopic composition of five other sclerosponges from the same locality and determine the extent to which these species are reflecting the same chemical signatures.

- *Assess the ability to retrieve intra-annual temperature signals from sclerosponges using the Sr/Ca and* δ^{18}O. ***We have performed high resolution minor element and*** δ^{18}O ***analyses on samples of sclerosponges from the Bahamas. These data are described in the proposal.***
- *Determine the extent of reproducibility of stable isotopic and geochemical trends within the skeletons of sclerosponges.* ***Replication has been started on Sr/Ca and Mg/Ca profiles. These data are shown in Figure 8. Replication of isotopic trends within sclerosponges has been attempted , but results to date have not been satisfactory as a result of sampling and analytical problems. These problems have been addressed and this work will be carried out in this proposal.***
- *Assess the ability of sclerosponges to provide information on variations in the depth of the thermocline.* ***We have attempted to perform high resolution measurements for stable C and O isotopes and trace elements from sclerosponges from two depths in the Bahamas. These data are discussed in this proposal (Figure 11).***

Background

It has been more than three decades since Goreau [12] described the ecology of the deep Jamaican reefs and found them to contain large populations of the sponge *Ceratoporella nicholsoni*. Although such sponges have been known for a long time, the extent of their diversity has only been evident in the last several decades [13 - 29]. Sponges with siliceous spicules and an additional calcareous basal plate, were initially ascribed to a separate class, the sclerospongiae. However, a variety of similarities with sponges lacking that calcareous basal plate, led to their incorporation into pre-existing groups of Demospongiae [24,29-34]. At the present time 16 species belonging to 2 classes, 4 subclasses, 9 families, and 12 genera are known. The biology and ecology of the sponges has been well described by Lang et al.[35] , Dustan et al. [36], Hartman and Goreau [18], Scoffin and Hendry [37], Wood [38], while their growth has been studied by Dustan and Sacco [39] and Benavides and Druffel [40], Reitner et al.[41],

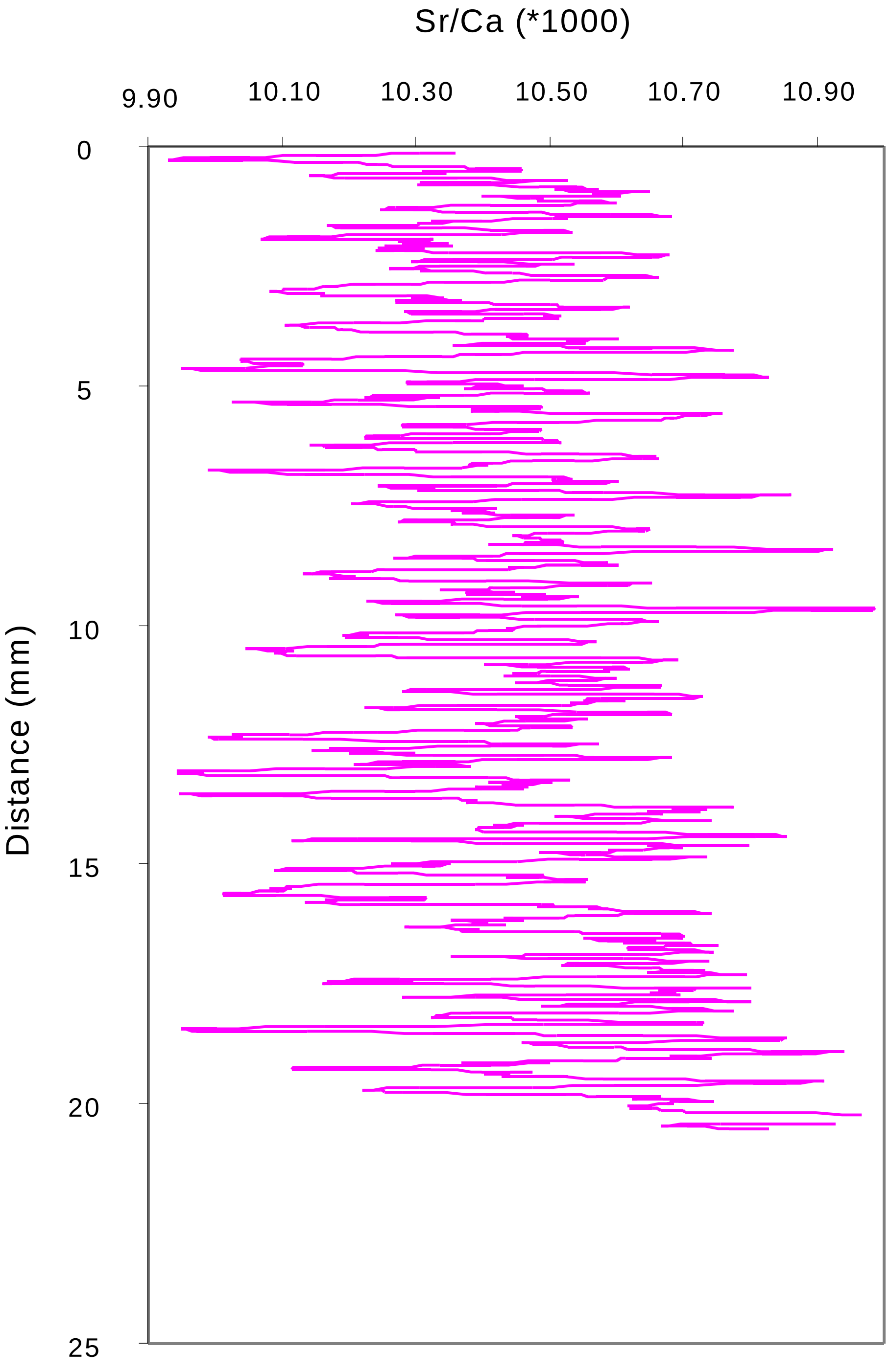

Figure 2: Variation in the Sr/Ca of sample from Tongue of the Ocean. Variations are much larger than would be suggested if the relationship between Sr/Ca and temperature were the same as in scleractinian corals. Assuming that the Sr/Ca variations are annual in nature variations in the annual growth rate can be determined.

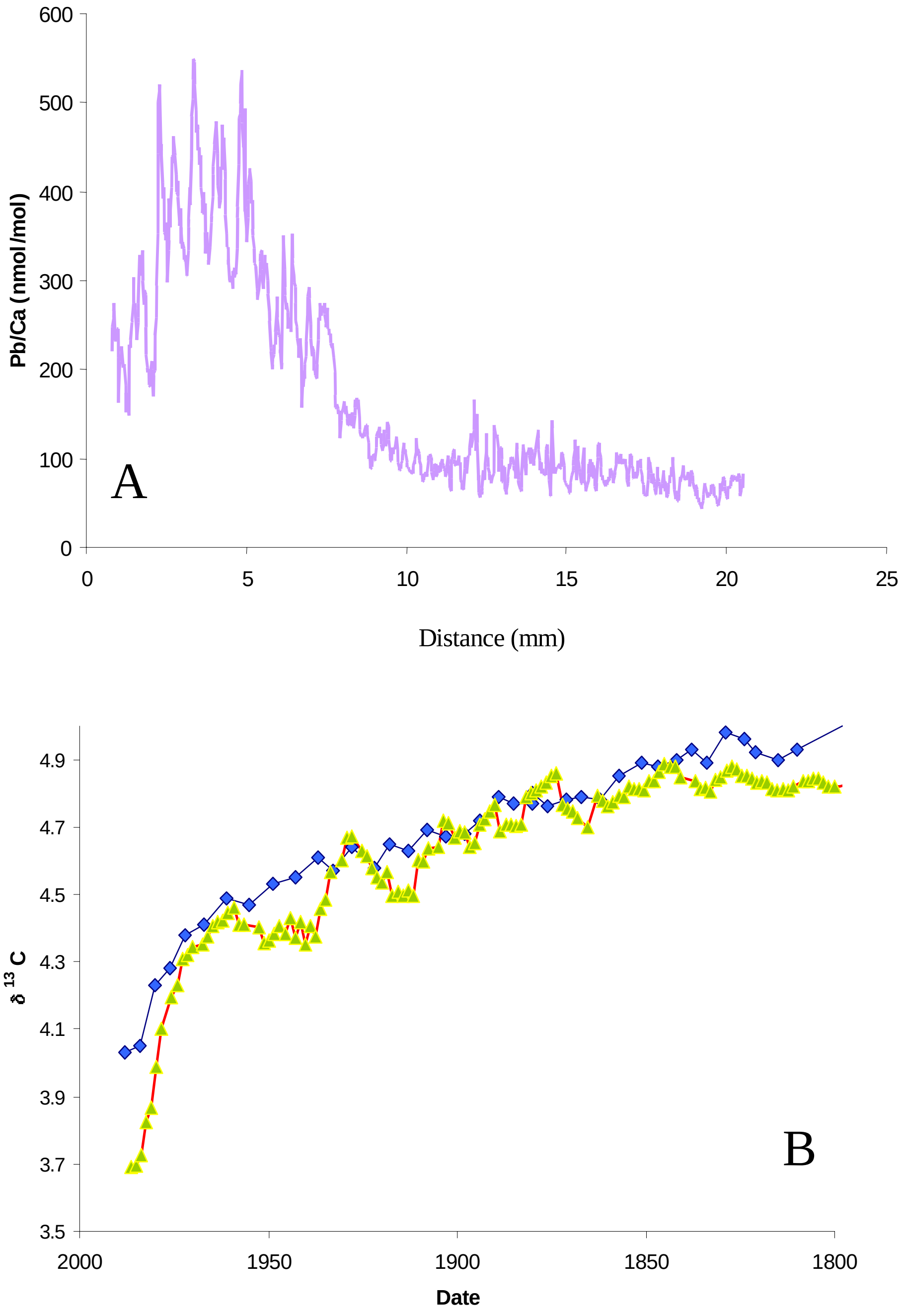

***Figure 3:** A) The Pb/Ca ratio in a sclerosponge from TOTO . The approximate age can be derived by matching the curve with published changes in the Pb/Ca ratio in the ocean [1,44,45]; B) Changes in the carbon isotopic composition of a sclerosponge from the Bahamas (unpublished, Swart) compared to a published carbon isotopic record from Jamaica [7]. The approximate age can be derived by matching the trend in the $\delta^{13}C$ between these two sclerosponges and is consistent with a mean growth rate of 0.250 mm/yr.*

Wörheide & Reitner, [42]. Lang et al. [35] found the sponges growing within the framework and under coral talus in the shallower portions of the reef (above 55m), while below 55m they are found on the steep surfaces of the deep fore-reef. They have been reported growing to depths of 145 m. Of the six species of sclerosponges reported by Lang et al. [35], the largest and most visible is *Ceratoporella nicholsoni*, which in Jamaica, was estimated to cover between 25 to 50% of the available substrate attaining sizes in excess of 1 m in diameter. The ultra-structure of the living tissue has been described by Willenz and Hartman [43]. *Stromatospongia vermicola* also grows to a reasonable size (40 cms in diameter) and can be locally more abundant than *C. nicholsoni*. The remaining species of Caribbean sclerosponges (*Hispidopetra miniana*, *S. norae*, *Goreauiella auriculata*, and *Merlia sp*.) are relatively small, but can be locally abundant.

Sclerosponges as Proxy Indicators

Intra-annual Geochemical Variation: Recent work [2,3] has shown a significant correlation between temperature and the δ^{18}O isotopic composition of sclerosponges. One of our goals, in addition to refining this relationship between temperature and δ^{18}O, is to attempt to establish the presence or absence of intra-annual signals in both δ^{18}O, the Sr/Ca ratio, and perhaps other geochemical climate proxies (Mg/Ca). A brief summary of this work, which has been submitted to *Paleoceanography*, is included here (At the time of the last submission this paper had just been submitted to *Paleoceanography*. It is still in review although no fault of the authors). The skeleton of a sclerosponge (*Ceratoporella nicholsoni),* collected from a depth of 143 m was sampled for C and O stable isotopes at a resolution of one sample every 32 μm using a computer controlled microdrill.

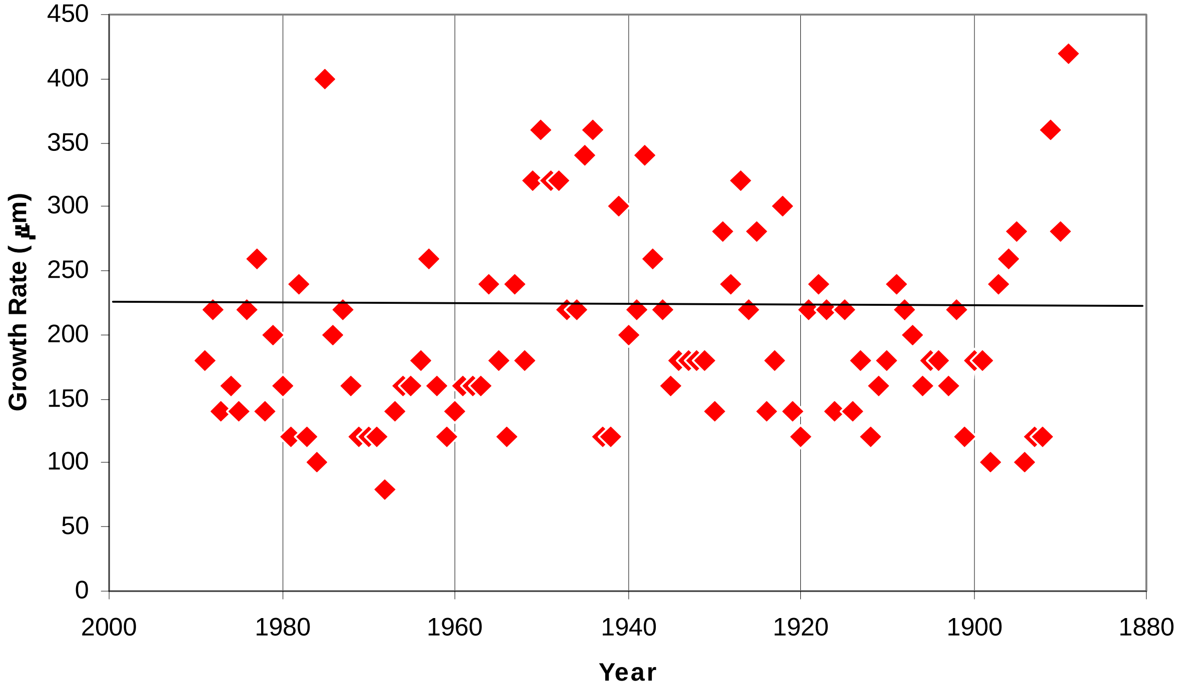

Figure 4: Growth rate calculated by assuming the variations in the Sr/Ca ratios shown in figure 2 are annual in nature. The overall age (0.22 mm/yr) of the specimen calculated using this technique is essentially identical to that measured using U-Th methods.

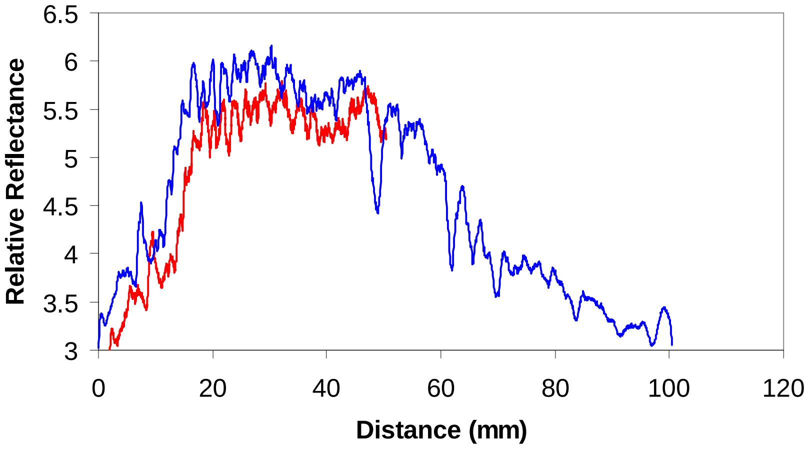

Figure 5: Results from two transects on the sample shown in Figure 1 made using the LIFA instrument designed by Milne and Swart[50]. The monochromator is set to zero allowing all the reflected light to enter the detector thus measuring the reflectance of the surface of the sample. The two scans have been offset slightly to allow the correspondence of the two scans to be seen.

In addition a parallel section of the same sample was ablated using a Finnigan MAT Element2 magnetic sector field ICP-MS and a New Wave EO LUV266X laser ablation system. The following elements were analyzed; Sr, Mg, Ba, Pb, and U although only the Sr, Mg, and Pb data are discussed in the paper (Figure 2 [11]). Samples of the skeleton were also dated using the multicollector Plasma 54 (VG Elemental) at Lamont-Doherty Earth Observatory. Using a combination of the changes in the δ^{13}C (Figure 3b) (related to the C-13 Suess effect [4,7]), the change in the concentration of Pb (Figure 3a) [1, 44,45] and the uranium series isotopic measurements, we established a mean growth rate of 220 μm/yr for this specimen. However, it was clear that a constant growth rate could not be applied to the entire record. This was confirmed by the presence of additional peaks in the power spectrum of the δ^{18}O data which corresponded to rates of 128, 270, and 400 μm/yr (Figure 5). Similar additional peaks were also present in the spectra of the Sr/Ca data. We interpreted these additional peaks in the power spectra of the Sr/Ca and δ^{18}O data as a reflection of variable growth rate. Support for this interpretation was provided both by examining spectra from a coral skeletal record, to which a uniform growth rate had been applied, and also by modeling synthetic data [11]. While these results have implications on the use of sclerosponges for the purposes of correlation to instrumental climate records on annual and decadal time scales, use of mean growth rates in sclerosponges is still useful for the interpretation of long term changes in climate .

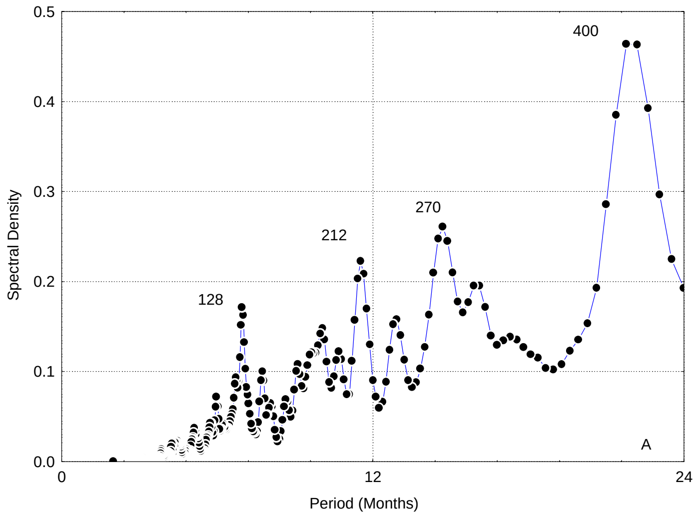

Figure 6: Spectral analysis of the δ^{18}O of samples from a sponge collected from the Tongue of the Ocean in the Bahamas. Samples were collected every 32 μm and were then interpolated to a sampling resolution of 1 sample every month assuming a growth rate of 220 μm/yr. The multiple peaks correspond to growth rates of 128, 212, 270, and 400 μm/yr

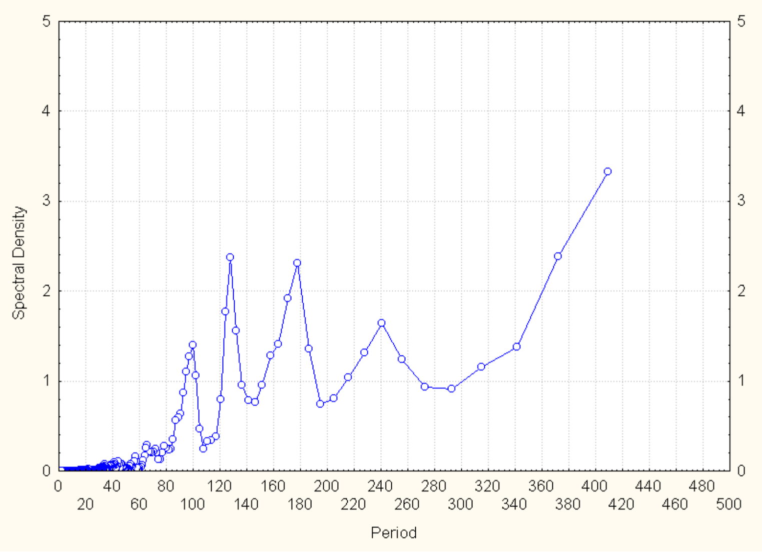

Figure 7: Spectral analysis of data shown in figure 6. Peaks shown correspond to a frequency of between 9 to 15 years. Period is shown in months.

Strontium: At the time of the submission of our last proposal there had been no published data on the strontium concentration of sclerosponges, with the exception of data presented by Fallon [46]. He reported that sclerosponges contain significantly higher concentrations than corals (9000 ppm vs. 7000 ppm). In the data from our recent publication [11] the Sr/Ca (Figure 2) covaried with δ^{18}O. However, if the Sr/Ca ratio in skeletons of sclerosponges possessed the same temperature dependence as in corals [47,48], then the observed range in Sr/Ca values would equate to a temperature variation of 8°C. Obviously this range is too large for the depth from which this particular sclerosponge was collected which only manifests a temperature range of 2-3°C [11]. Our present data therefore suggest that while there is an inverse correlation between the Sr/Ca ratio and temperature, there is quite different slope between temperature and δ^{18}O compared to scleractinian corals.

Magnesium: The Mg/Ca ratio in the skeleton is weakly positively correlated with the Sr/Ca ratio, but does not show any evidence of an annual cycle. The absence of annual cycles in Mg/Ca despite the positive association with Sr/Ca (which does show evidence of annual cycles) indicates that there are additional metabolic controls governing the concentration of Mg, perhaps related to temperature, but which do not affect Sr. In addition, the presence of a positive correlation with Sr/Ca means that the Mg/Ca ratio in sclerosponges must exhibit the opposite relationship with temperature when compared to corals [49].

Other Geochemical Proxies: There was no evidence of intra-annual signals in any of the other constituents examined including carbon isotopes, Ba, Pb, and U.

Skeletal Growth Rate

Growth Rate: The growth rates of *Ceratoporella nicholsoni* have been studied on sclerosponges from Jamaica by both direct staining using Alizarin Red-S [39], Calcein [43] and by using ^{14}C and ^{210}Pb [40]. In the study by Dustan and Sacco [36], specimens of sponges were stained and collected some six years later. Dustan and Sacco [39] estimated a growth rate of between 0.1 to 0.2 mm/yr, while Willenz and Hartman [43] reported a value of 0.184 +/- 0.02 mm/yr. The radiometric methods gave slightly higher growth rates (0.27 mm/yr using ^{14}C and 0.22 mm/yr using ^{210}Pb). Based on the assumption that the cyclicity which we observe in the Sr/Ca ratio (Figure 2) is annual, then it is possible not only to age date the sclerosponge to an accuracy of +/- 1 year, but also to measure changes in the growth rate and relate these to environmental variations. This method suggests that the growth rate of the sclerosponge may vary between 100 to 400 µm/yr (Figure 4). Strikingly, the method calculated an age for the sclerosponge which agrees to +/- 1 year with that obtained by the uranium-thorium technique.

Banding: Skeletons of a number of sclerosponges, including *Ceratoporella nicholsoni* (Figure 1), show concentric growth bands apparently on a 9 to 15 year time scale, although the significance of such banding is not known. These concentric growth patterns suggest that there are no significant diagenetic reactions which might obscure this banding. As part of the work carried out under the existing award, we have started to analyze the visible banding using a modification of an instrument designed to measure fluorescence in coral skeletons [50]. This particular instrument uses a laser to illuminate the surface of the sclerosponge and measures the reflected light. The reflected light signal is normalized to the illuminating signal and outputted as a non-dimensional ratio. An example of this output is shown in figure 6. By initially assuming a constant growth rate of 220 µm/yr (for argument's sake), the spectral characteristics of the signal can be determined as a periodicity of between 9 and 15 years (Figure 7). While this suggests the presence of one or more cycles on a decadal scale frequency, it must not be forgotten that there is significant data suggesting that growth rates of sclerosponges are non-uniform. Thus spectral analysis of any parameter where uniform growth rates have been assumed probably yields a prismatic separation of one frequency - in this case an unknown frequency as it cannot be guessed as to the physical cause of the concentric banding. Nonetheless, the banding offers promise for using sclerosponges as proxy indicators of decadal scale climate changes.

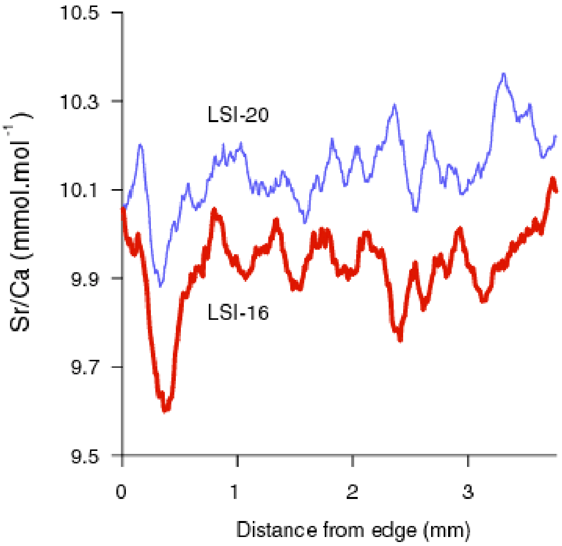

Figure 8: The transects of Sr/Ca ratios measured in two samples from Exuma collected at depths of 136 m (LSI-20) and 67 m (LSI-16); both these sclerosponges are in excess of 200 years old. Similar patterns are evident in the two transects although they are offset by the difference in temperature between 137 and 67 m. This difference is converted to temperature in figure 11.

Can Sclerosponges Provide Retrospective Information on the Thermocline?

At the time of writing we have completed Sr/Ca and δ^{18}O analyses of two sclerosponges collected from different depths (136m; LSI-20 and 67 m; LSI-16) collected from Lee Stocking Island (LSI), as well as the sclerosponge collected from TOTO (143 m). All three of these sclerosponges have Sr/Ca ratios which are inversely related to temperature, that is to say the shallower sclerosponge has the lowest Sr/Ca ratios indicating the highest temperature. The Sr/Ca data from TOTO is shown in Figure 2 and the two transects from Exuma is shown in Figure 8. An immediately obvious aspect of these data is that the trends in the Sr/Ca ratio in these two sclerosponges, which are separated by 60 m in water depth, are coherent. The variations in the Sr/Ca ratio is clearly responding to inter-annual environmental forcing. This result addresses one of the goals of the current award, that is the replication of geochemical patterns in different specimens of sclerosponges. As in the case of the TOTO sclerosponge, the range in the Sr/Ca values are greater than expected if the Sr/Ca vs temperature relationship is the same as in scleractinian corals. Although the precise temperature range at the depth from which the sclerosponges were collected is not known, based on the temperature measurements made at Lee Stocking Island at depths of 105' and 340', the temperature range should be between 4 and 6°C. As there is a statistically significant positive correlation between the Sr/Ca ratio and δ^{18}O (Figure 9 and Figure 10) and assuming that the temperature vs. δ^{18}O is similar to those recently published [2,3], it is possible to obtain a preliminary relationship between Sr/Ca and temperature for sclerosponges. In an attempt to utilize sclerosponges for the purposes of thermocline reconstruction at LSI, we have taken the two sclerosponge records (LSI-16 and LSI-20) and assigned ages based on the assumption that the high frequency signals, which are visible in the Sr/Ca and δ^{18}O records, are related to annual changes in temperature. It is then possible to subtract the two signals and the resultant variation measures the difference in temperature between 67 and 136 m (Figure 9). We suggest that these differences are related to the depth of penetration of surface water. Seasonal patterns can be clearly seen as during the winter, there is minimal difference in temperature between these two water depths. Interestingly, there are clearly longer term variations, probably related to long term variations in wind strength, with greater wind strengths allowing deeper penetration of surface waters [51].

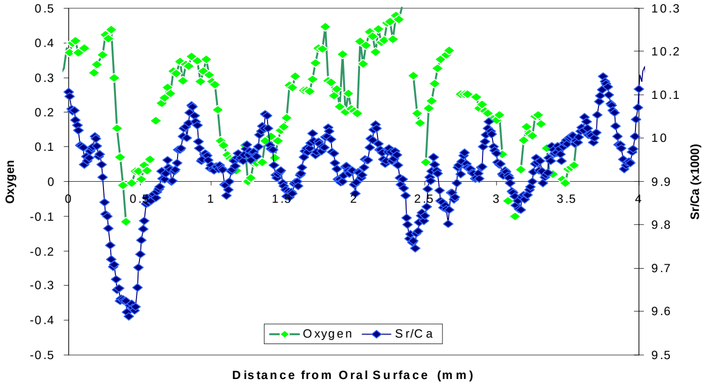

Figure 9: Transect of Sr/Ca and δ^{18}O ***in LSI-16, a sclerosponge collected from a depth of 67 m near Lee Stocking Island in the Bahamas. Two transects were made at slightly different positions at right angles to the surface of the sponge. The variation in the*** δ^{18}O ***is clearly associated with variations in the Sr/Ca ratio. Slight variations in the relationship between the Sr/Ca and*** δ^{18}O ***may be a result of the different locations of the transects. The Sr/Ca measurements were made every 10 µm while the*** δ^{18}O ***samples were taken every 20-30 µm.***

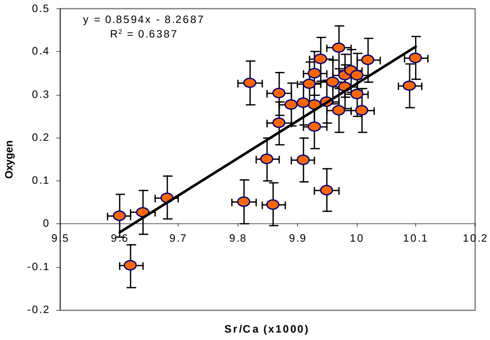

Figure 10: Relationship between Sr/Ca and δ^{18}O ***in the skeleton of the sclerosponge (LSI-16). The correlation was achieved by tuning the data shown in figure 9. Using the relationship between temperature and*** δ^{18}O ***published by Bohm[3] we can derive a preliminary relationship between Sr/Ca and temperature (T=56.55-3.79Sr/Ca) Error bars represent approximately ½ standard deviation of the analytical methods used.***

Methods, Approach , Objectives and Importance

Task 1: Collection of previously stained sclerosponges: During summer of 2002 we will collect portions of the previously stained sclerosponges growing at Discovery Bay. These samples will be sectioned and replicate portions of the section

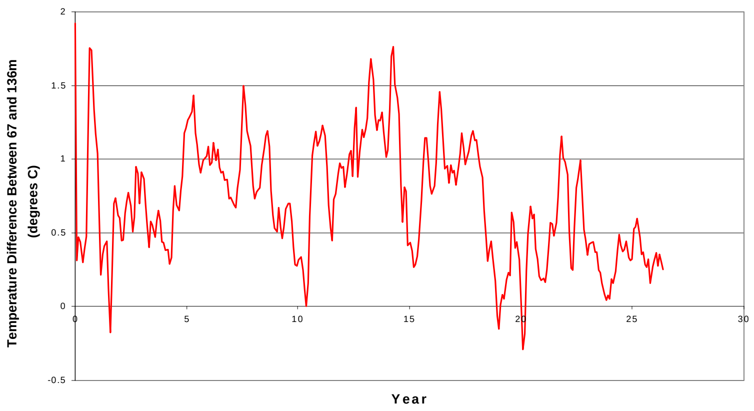

Figure 11: Difference in temperature between sclerosponges growing at 67 and 136 m using the data shown in figure 8 and the correlation calculated in figure 10. The maximum difference in temperature occurs during the summer and the minimum difference during the winter when strong winds promote deep mixing of surface and deep waters. Spectral data shows there to be a 9- 10 year cyclicity in these records. This has the same period as the temperature in the southern sub-tropical Atlantic (SATL) [51,52] which is linked to variation in wind strength in the northern sub-tropical Atlantic (NATL).

sampled for trace elements (using laser ablation ICP-MS) and for stable isotopes. In contrast to the existing work which we have carried out, we will ensure that both types of analyses will be carried out on mirror transects from the same sclerosponge. Sampling for isotopes will be carried out using our new micromill and analyzed using our new Delta-plus and Kiel device. With the funding provided by our existing NSF grant we have been able to show the presence of intra-annual signals within the skeletons of sclerosponges [11]. In addition to Sr/Ca and δ^{18}O we may be able to use these data to ascertain the significance of changes in the Mg/Ca, Ba/Ca, and U/Ca ratios in the sclerosponges. These data will for the first time present a rigorous calibration between temperature, water composition and proxy indicators in the skeletons of sclerosponges. Data on the temperature, δ^{18}O, and carbon isotopic composition at the site between the start of the experiment and May 2001 are shown in figure 12. Based on these analyses there appears to be little change in the δ^{18}O of the water that would mask temperature induced variations in the skeletal δ^{18}O values. There do appear to be changes in the δ^{13}C of the dissolved inorganic carbon and these may be visible in the δ^{13}C of the skeleton. These samples have been preserved for cation analysis and variations in the Mg/Ca and Sr/Ca of the waters will be also measured on these samples. Based on changes in the salinity and δ^{18}O, we expect these changes to be minimal. In order to ascertain whether sclerosponges from this locality show temperature ranges similar to those which we observed during the calibration study, we have measured the C and O isotopic composition in the upper 1 mm of growth from a specimen which we collected in 1998 (Figure 13). The δ^{18}O shows possibly five cycles indicating a growth rate of about 0.2 mm/yr and a range of δ^{18}O values similar to that expected based on the data presented in figure 12.

Task 2: Establish variations in geochemical parameters as a function of depth: Paleoceanographic reconstructions using sclerosponge skeletons have a significant advantage compared to corals because sclerosponges are not restricted to surface waters. Hence it may be possible to reconstruct variations in the thermocline as a function of time which in turn may be related to features such as wind strength. We have started this work and preliminary results presented here for the first time show annual and seasonal differences. We intend to extend this concept to additional depths and correlate these data to records of temperature and wind strength. It is important that geochemical signals within sclerosponge skeletons can be replicated through additional analyses on the same specimen and also between additional samples collected from the same locality. This work is scheduled for the next six month period.

Task 3: New types of sclerosponges: There have been a number of studies using sclerosponges of different species from many different parts of the world. By analogy with scleractinian corals it is well known that different species have different responses to the incorporation of stable isotopes and minor elements[60,61]. Is this same for sclerosponges? The finding of interspecific differences would have significant implications on the comparisons of isotopic records measured on different organisms. The propose study will provide us an ideal opportunity to compare the stable isotopic and minor element composition of a variety of species from Jamaica and determine the extent to which there are species effects in sclerosponges. These organisms will be collected during our forth coming trip and the upper most portion of the skeleton sampled in the same manner as we intend to sample the calibration organisms. This will allow direct comparisons of the material formed by different sclerosponges over the same period of time.

Task 4: Additional Sclerosponges from a range of water depths: Unfortunately we do not have sclerosponges in the Bahamas from depths shallower than 63m, but we intend to search for additional specimens at suitable localities. We have requested funds from the NOAA/NURP program to collect additional sclerosponges from a range of water depths. The point of

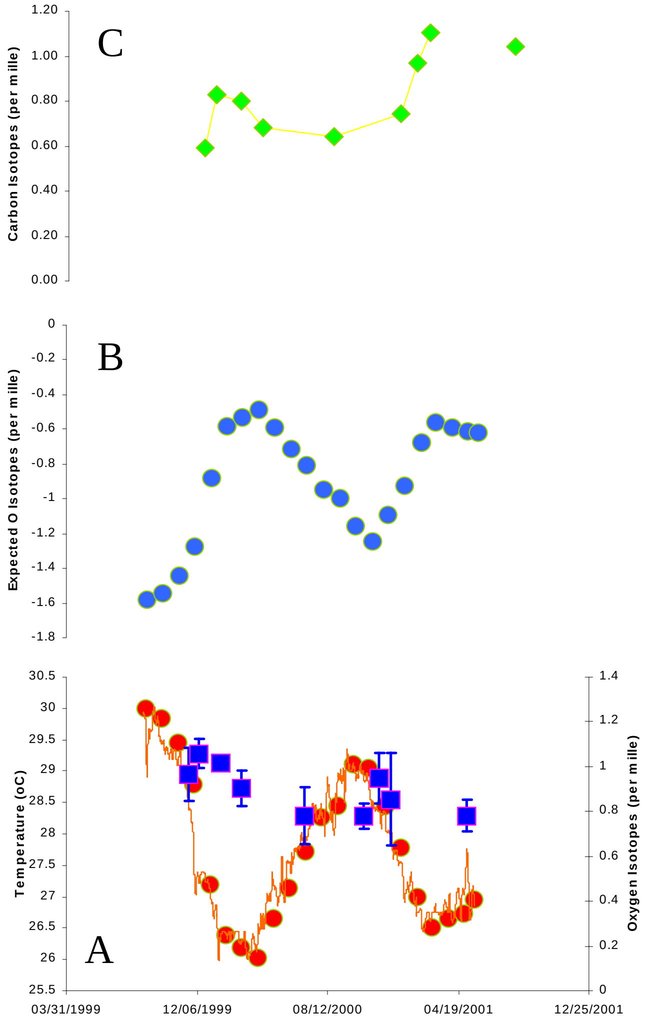

Figure 12: Results from the temperature loggers deployed at the calibration site since summer 1999 together with O and C isotopic data on water samples collected at DBML. A) Shows temperature data collected every 2 hours together with mean monthly temperature values (round symbols) and the δ^{18}O ***on water samples (solid squares with error bar). B) Shows the temperature data from panel A converted to the expected range in the*** δ^{18}O ***of the sclerosponges using the data measured on the*** δ^{18}O ***of the water shown in panel A and the temperature equation presented by*** **Böhm** ***et al [3]. C) Shows the C isotopic data measured on the DIC which should be expected to convert directly to a similar change in the carbon isotopic composition of the skeleton.***

collecting and measuring additional sclerosponges from different water depths is to provide additional confirmation that the chemical trends measured in sclerosponges can be replicated.

Analytical Aspects

Sample Extraction: Samples will be extracted from polished sections of sclerosponges using an automated XYZ computer New Wave microdrill. This device is similar in principal to our home built device, but has better software and drill control which enable us to follow any path which is marked on the specimen. This instrument has been recently purchased to complement our existing home built device with which all previous samples were taken.

Stable Isotopic Analyses: Stable isotopic analyses will be performed using conventional instrumentation. In addition to a Finnigan-MAT 251 interfaced to a Common-Acid Bath , we have just purchased a Delta-plus with Kiel device. The Kiel device and Delta-plus combination should offer better precision than our existing instrumentation. Water samples collected for their δ^{18}O will be processed using an automated water equilibration system interfaced to a Europa GEO (Figure 12). Precision for this method is better than 0.08‰. Carbon isotopic analysis of the DIC will be performed using an ANCA GSL interfaced to an Europa 20-20. Precision on this method is approximately 0.2 ‰.

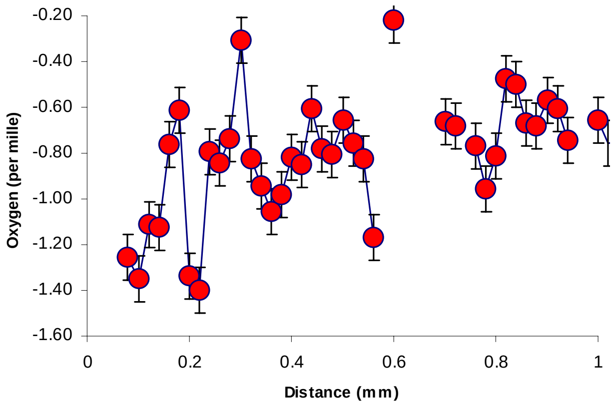

Figure 13: Oxygen isotopic composition of a sclerosponge taken from the same depth and locality where the calibration experiment is being performed. The skeleton was sampled at a resolution of one sample every 0.02 mm and the data have been treated with a two point moving average. The range in the isotopic data is similar to that expected based on temperature and the δ^{18}O ***of the water (Figrue 12).***

Elemental Analyses: Minor element and analyses will be performed using a Finnigan MAT Element2 magnetic sector field ICP-MS and New Wave 213 laser ablation system.. The analytical method we use to quantify elemental ratios follows the approach outlined by [11,59] for precise element/Ca ratios using sector field ICP-MS. We will use a He gas stream to transport matter from the sample cell to the mass spectrometer. The carrier gas is then mixed with the Ar sample gas and a wet aerosol (1% [w/w] HNO_3), and introduced to a quartz cyclonic spray chamber via a PFA micro-flow nebulizer [53]. The nebulizer is, 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, is analyzed every 5 samples to account for variations in mass bias and instrumental fluctuations of the ICP-MS. Quality control is maintained by assays of an aragonite reference material [54,55] every 20 samples. Precision (%RSD) of elemental ratios in a multi-element method is obtained by analysis of 5 replicate samples in a line perpendicular to the growth axis, is as follows: Mg/Ca =0.98, Sr/Ca = 0.58, Pb/Ca=1.36. Precision of a modified method for Sr/Ca assays only is considerably better (RSD<0.1%), and all analyses will be conducted in duplicate, with one run for the multi-elemental method and one run for Sr/Ca.

Radiometric Growth analysis: Age dating will be performed on the sclerosponges collected from the Exuma Sound depth transect using methods described by Böhm et a. [3,7].

Time Schedule

The project is scheduled to start in March 2002 which will be six months after the termination of the existing grant. By the end of present grant we expect to have completed most of the tasks originally proposed. The sclerosponges which we have stained will not be collected until summer of 2002. During the time up to the collection of these sclerosponges we will continue to analyze the skeletons of the sclerosponges which comprise the depth transect at Lee Stocking Island. Our new mass spectrometer has been delivered and installed in March 2001. However, it is not performing to specifications and Finnigan-MAT is investigating a problem in the source which is providing poor precision data. All new samples for stable isotopes will be collected using our new micromill and analyses performed using the new mass spectrometer and the Kiel device. Once the sclerosponges which we have been growing under controlled conditions in DBML have been collected, an intense program will be initiated to analyze the C and O isotopic composition as well the trace elements and calibrate these data to the environmental data. We anticipate that this portion of the project will take at least 12 to 18 months. At this stage we will also analyze samples of the other five species of sclerosponges present at the site and compare these data to the stained sclerosponges. It must be emphasized that the process of sampling material from the skeleton which is only a fraction of a millimeter will require a significant effort and is not a trivial task. In our previous project we had a contract with LDEO for U-Th isotopic analyses. However, we have now developed a relationship with Dr. A. Eisenhauer of Geomar. We intend to duplicate the analyses which were performed at LDEO and complete the analyses that should have been completed under the existing project.

Personnel

The project will be supervised by Professor Peter K. Swart at the University of Miami. Dr. Swart has carried out a similar project with corals under field conditions. Dr. Swart will be assisted in the field by Dr. Philippe Willenz from Institut Royal des Sciences Naturelles de Belgique. Dr. Willenz has been working at the Discovery Bay Marine Laboratory for over 15 years and has previously carried out staining experiments using Calcein. Dr. S. Thorrold will be responsible for trace element aspects of the analyses. Dr. Swart and Dr. Thorrold have previously successfully collaborated resulting in several publications [11,56-58]. Finally dating aspects will be carried out in this project by Dr. A. Eisenhauer from GEOMAR in Kiel.

Analytical: Sampling of the sclerosponges for their stable $\delta^{18}O$ and $\delta^{13}C$ composition will be carried out by Dr. Swart and Amel Saied at the University of Miami using a micro-sampling device. All stable isotope analyses will be performed at the University of Miami. Trace elements will be performed at WHOI.

Thin sections for growth rate measurement will be prepared and analyzed in Brussels by Dr. Willenz.

Student Participation

Aspects of this project will be used for the Ph.D. thesis of Brad Rosenheim at the University of Miami. In addition various graduate and under graduate students will assist in analytical aspects of this research. The research will also be used as part of the University of Miami's INSTAR program, a program designed to teach scientific methods to K-12 teachers from South Florida.

Significance of Proposed Research

There have numerous papers which have recently started to explore the utility of the chemical record in sclerosponges [1-11] for the purposes of interpreting patterns in global climate change, atmospheric pollution, and oceanic circulation. There have been some important findings from this work. First, all of the sclerosponges analyzed to date clearly show the influence of the global increase in pCO_2 in the carbon isotopic composition of the skeleton [5,7,8]. Second, various workers have shown that the $\delta^{18}O$ of the skeleton is correlated to temperature [2,3], although the precise relationships for different species still need to be determined and no definitive relationships have been demonstrated between temperature and minor elements. Although it can be argued that scleractinian corals respond in a similar manner to climate, the significant improvements that sclerosponges offer are that (i) they are extremely long lived, (ii) they in habit a range of water depths (very shallow to over 100 m), and (iii) they apparently secrete their skeletons in C and O isotopic equilibrium. Therefore the importance of the proposed work is that it will:

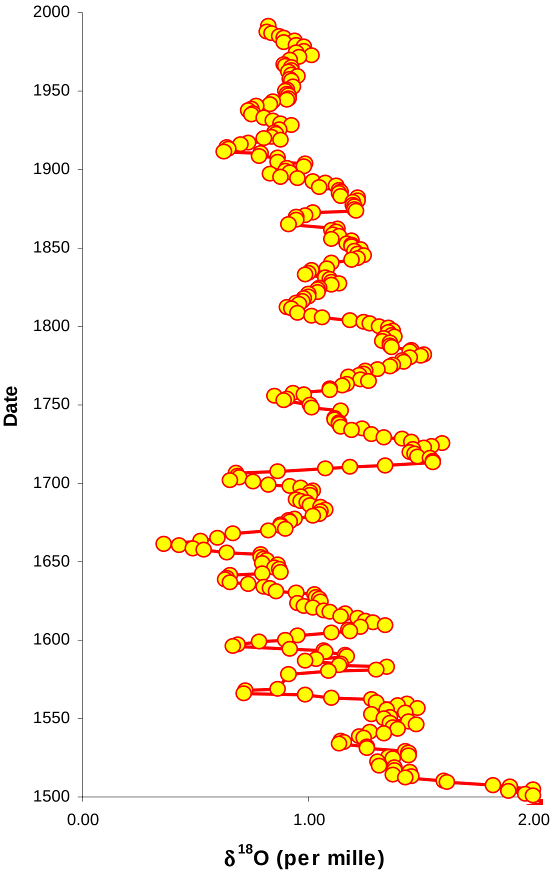

Figure 14: The $\delta^{18}O$ record from a sclerosponge obtained from the Bahamas which has been dated using a combination of uranium series isotopes and comparison to the C-13 Suess effect.

- Determine the response of the relationship between temperature and the important geochemical proxies for temperature (Mg/Ca, Sr/Ca, and $\delta^{18}O$) in the species *Ceratoporella nicholsoni*;
- Confirm whether annual cycles exist in these geochemical proxies within sclerosponges and consequently whether these can be used for dating purposes;
- Determine the extent of geochemical differences between various species of sclerosponges and whether all species in Jamaica secrete their skeletons in isotopic equilibrium;
- Determine which geochemical parameters are related to the concentric banding observed in sclerosponge skeletons;
- Provide a sound basis for future work obtaining proxy records of thermocline histories of globally significant oceanic circulations such as the N. Atlantic Subtropical Gyre;
- Allow for the interpretation of geochemical records obtained from sclerosponges such as shown in Figure 14.