

A SUBMERGED STALACTITE FROM BELIZE: PETROGRAPHY, GEOCHEMISTRY, AND GEOCHRONOLOGY OF MASSIVE MARINE CEMENTATION

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ABSTRACT: Submerged sink holes and cave systems associated with oceanic limestone platforms often contain speleothems and dripstone features which formed during subaerial exposure during glacially lowered sea level. A large stalactite, collected from a 50 meter deep terrace within the "Blue Hole" on Lighthouse Reef, offshore from Belize, records the geochronology of the transition from subaerial exposure to marine submergence during Holocene sea level rise. The stalactite originally formed on the ceiling of a large cavern when sea level was at least 60 meters below its present stand. As sea level rose, flooding the cavern, the fresh water phase of dripstone formation terminated and a 12 cm-thick rind of botryoidal splays of radial-fibrous marine aragonite coated the stalactite. This is the most massive encrustation of Holocene marine cement known, and it precipitated from seawater which had been considerably modified during circulation through the carbonate platform. By approximately 3000 yBP, when sea water flooded the bank top, cement accretion had ended, and the complex speleothem was encrusted by a marine biolithite prior to falling to the mud-covered floor of the cavern.

INTRODUCTION

An exceptionally large collapsed cavern (the Blue Hole) exists near the center of "Lighthouse Reef" (Fig. 1), the outermost atoll on the Belize limestone platform (Latitude N17°18.6'; Longitude W87°32'). When viewed from the air, the water in the cavern has a dark blue color, in sharp contrast with the

light greenish-blue of the 5 m deep shallow bank surrounding it. The large flooded cavern on Lighthouse Reef is well known to the diving community because of the clear, warm, calm water, and because of its depth. In 1970 a team of divers aboard R/V Calypso visited Lighthouse Reef for the purpose of making an undersea documentary film on sea level changes for the Cousteau television series. The first author participated as a staff geologist to record the findings of the expedition.

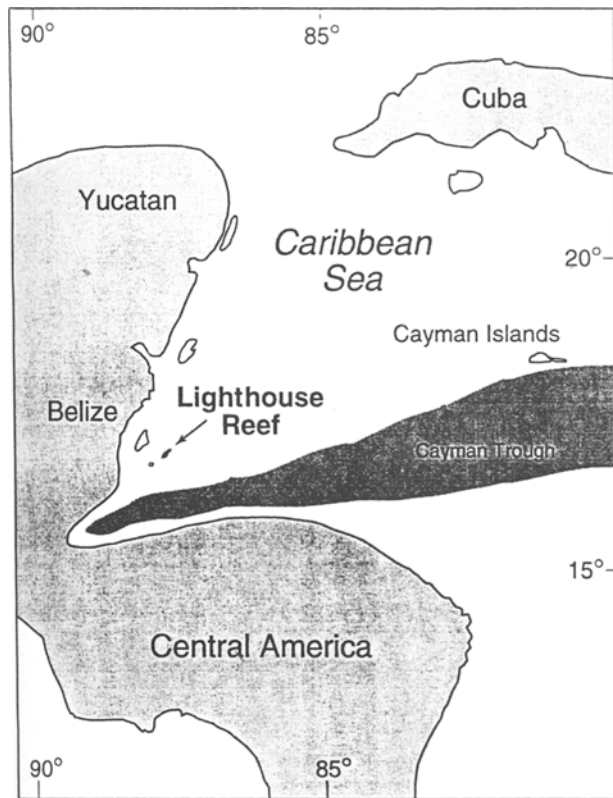


Figure 1. Location map of Lighthouse Reef and the Blue Hole in the western Caribbean east of Belize (formerly British Honduras) where the stalactite for this study was retrieved. Note the proximity of the study area to the Cayman Trough, a tectonically active spreading plate boundary.

The Blue Hole has a diameter of 320 meters (1050 ft.) and a depth of 125 m (410 ft.). The upper 80 meters (260 ft.) was investigated using SCUBA and the deeper parts explored using two small submersibles (Dill 1977). The submersible dives revealed stalactites, stalagmites, dripstone curtains, and an extensive cave system leading away from the main cavern at the bottom and from the walls of the Blue Hole. At the base of the east and west sides of the Blue Hole, giant jumbled blocks of wall and ceiling rock have accumulated which contain attached speleothems. In contrast, the southern and northern perimeters preserve intact remnants of the original cavern walls and parts of the overhanging ceiling with attached speleothems. The entire cavern must have been dry at one time in order to permit the development of stalactites and stalagmites down to at least 125 meters. The flat floor at the center of the Blue Hole today is blanketed with sediment of unknown thickness. The morphology indicates that the Blue Hole had been deeper in the past but is now filling with biogenic carbonate sediment derived from the organically productive upper rim. During SCUBA dives along the upper lip, sediment containing abundant *Halimeda* plates rained over the edge of the Blue Hole. Submersible dives revealed that the rain of sediment has formed a ring-shaped sedimentary mound under the overhanging walls of the upper rim. The mound of unlithified *Halimeda* packstone shown in the profile of the Blue Hole (Fig. 2) has a relief of up to 30 m.

Remnants of an old cave ceiling crop out between depths of 30 and 55 meters along the northern and southern perimeters of

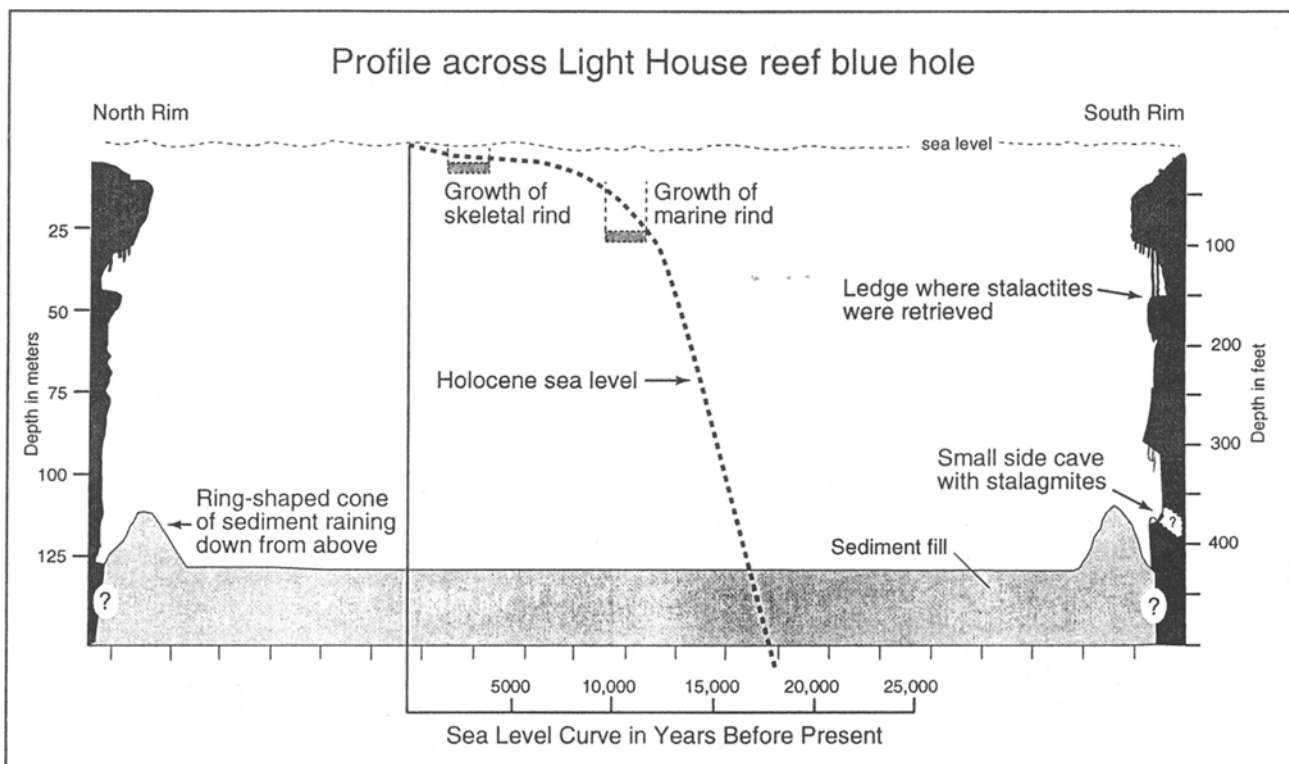


Figure 2. Cross-section of the Blue Hole showing depths, diameter and shape of the cavern where the stalactite was found. Note the mounds of sediment that have built up under the overhanging ceiling remnants. The high production of *Halimeda*-rich biogenic sediment around the upper rim of the Blue Hole is rapidly filling the sinkhole. Samples taken from the sediment filling the lower part of the Blue Hole smelled strongly of H_2S . Also included is a schematic sea level curve relating the zonation seen in the stalactite to times of exposure and development.



Figure 3. An upward view from -30 meters at the southern perimeter of the overhanging ceiling, showing the stubs of broken stalactites and the encrusted nature of the ones still attached.

the Blue Hole. Along the southern rim, beneath the over-hanging ceiling, a 5 m-wide ledge occurs at a depth of 50 m (164 ft.), probably as the result of dissolution during a still-stand of sea level at that depth. Large stalactites hang down from the roof above this ledge into the water column. A number of the stalactites hanging from the ceiling are tilted to the south at between 5 and 13 degrees, others are vertical, and several are curved with the upper portion tilted and the lower part vertical (Fig. 3). Thus regional tilting must have occurred sometime in the past after cave decoration had begun. Subsequent to tilting of previously emplaced features, vertical stalactite growth continued. The cavern must have remained dry for a considerable length of time after tilting because several very large stalactites managed to fuse with underlying stalagmites to form large vertical columns. Several of these columns extend down from a ceiling depth of 30 m (98 ft.) to the ledge at 50 m. The ledge is also coated with dripstone curtains that have in several places grown out over the bases of large vertical columns. Thin sheets of dripstone encase both sediments and speleothems where carbonate-depositing water once flowed across the ledge, and then formed a dripstone curtain that coats the walls of the cavern to depths beyond 60 m.

The surface of the ledge has accumulated a number of stalactites fallen from the over-hanging ceiling above. The diving team retrieved one of these fallen stalactites from the 50-meter deep terrace on the southern rim. The retrieved stalactite had an overall length of 2.84 m (7 ft., 10 in.) and a maximum diameter of 0.42 m (17 in.). Stalactites that had fallen to the ledge were half buried in a dark grey, gelatinous, *Halimeda* coral packstone which smelled strongly of hydrogen sulfide. The retrieved stalactite was matched with a 30 meter deep stub extending down from the ceiling above the ledge upon which it was found. When sectioned, geopetal fills within the cavities of the core of the stalactite were found to be tilted approximately 10 degrees to the vertical axis, confirming the origin of the stalactite core prior to regional tilting.

PETROGRAPHY

The upper one meter of the studied stalactite was slabbed perpendicular to its long axis, starting at its thick end (the end originally attached to the ceiling) in 15 cm-thick sections. The remaining part was cut along the long axis to show variations in the internal structure of the stalactite as it grew (Fig. 4). One side of the stalactite is quite porous whereas the other side displays much denser internal structure. The porous zone was the part of the stalactite that was buried in the reducing sediment blanketing the ledge from which it was retrieved.

The nearly circular slabs cut perpendicular to the long axis show that the stalactite consists of the following three more-or-less concentric zones (Figs. 5 and 6), from which numerous thin sections and SEM stubs were examined:



Figure 4. Longitudinal section of the studied stalactite (oriented in original growth position) showing its internal structure. The porous half was buried in unlithified sediment as it rested horizontally on the ledge from which it was retrieved. Ruler is 6 inches long. "C" is the calcite core; "s" is the skeletal rind.

1) An inner "core" of calcite, approximately 18 cm (7 in.) in diameter is present at the thickest part of the stalactite where it broke from the ceiling. The core tapers down to about 10 cm (4 in.) at its tip. Based on the presence of vague asymmetrical concentric growth rings, the core seems to consist of two coalesced stalactites which may have grown faster on one side than on the other. The calcite core is petrographically complex. In places it appears to be a neomorphosed replacement of radial fibrous aragonite, in other places it is micritic, whereas elsewhere it is a spar mosaic possibly representing an original vadose speleothem. We suspect the core represents a multiple generation stalactite, similar to others found in the Blue Holes of the Bahamas (Benjamin 1970; Spalding and Mathews 1972). It may have first formed as two pendant stalactites in a dry cavern. It was then coated by marine cement during immersion in sea water during an interglacial high stand. Upon subsequent re-exposure it

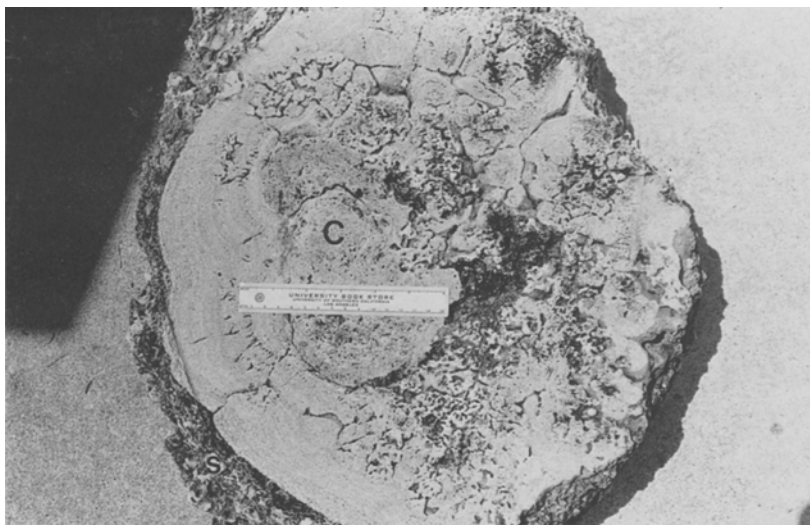
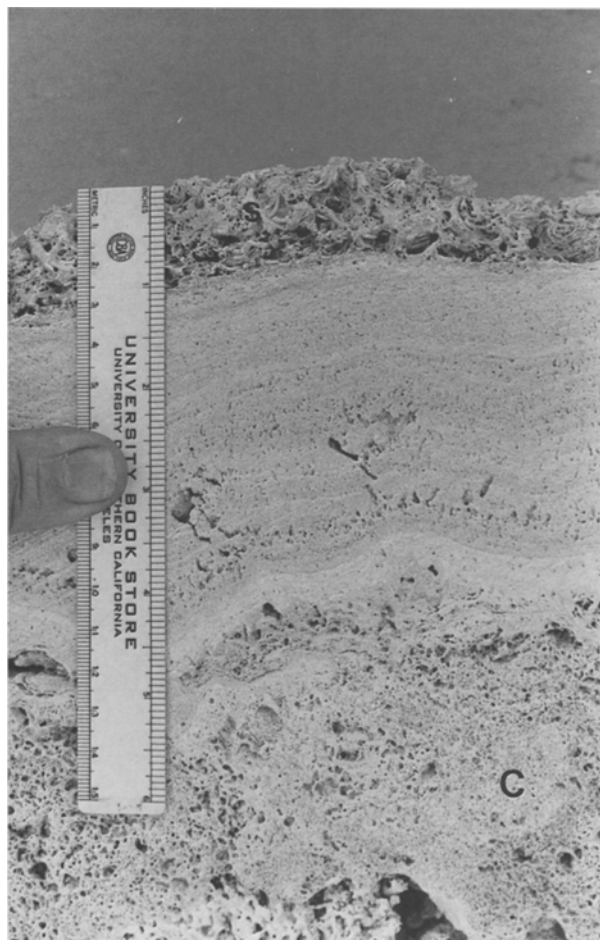


Figure 5. Photograph of a slab of the stalactite cut perpendicular to the long axis near to where it had been attached to the roof of the cave and showing the three internal zones. The calcite core (C) is spanned by the 6-inch ruler. To the left is the dense, laminated marine botryoidal aragonite rind with also contains microbial "bushes". To the right the porous "bushes" dominate. The outer skeletal rind (s) is a serpulid-mollusc biolithite, in sharp contact with the botryoidal aragonite rind.



↑Figure 6. Close-up of the slabbed section in Figure 5 showing the branched, microbial "bushes" formed within the dense laminated marine botryoidal aragonite cement zone. The boundary with the central core (C) of the original speleothem is sharp, as is the boundary with the outer skeletal rind (s).

experienced additional vadose growth and neomorphic meteoric alteration of the marine components to calcite.

2) The calcite "core" is surrounded by a 10 to 15 cm-thick (4 to 6 in.) laminated rind composed of overlapping botryoidal radial fibrous splays of aragonite with crystals up to 2.5 millimeters in length (Fig. 7). Minor amounts of Mg-calcite micrite are present between some of the botryoids, commonly arranged in concentric zones. Concentric zoning is also visible within some of the aragonite crystals, and separation of zones by between 2 and 20 μm is consistent with growth of each zone during a single tidal cycle. The tips of small aragonite crystals are pointed, whereas the large crystals always have square-ended terminations (Loucks and Folk 1976). One side of the stalactite is relatively dense and concentrically laminated whereas the other side is quite porous and chalky in places. The porous side has a pronounced branched cauliflower-like pattern (Figs. 4, 5, and 6), resembling features described from travertine deposits (Chafetz and Folk 1984). The dense side is laminated in the outer part but also contains cauliflower-like structures, especially near the boundary with the central core.

3) A 3 cm-thick rind of marine-cemented serpulid-mollusc biolithite composed of aragonite and Mg-calcite encrusts the outermost surface of the stalactite. This zone and the outermost part of the second zone have been subjected to bioerosion and marine boring.

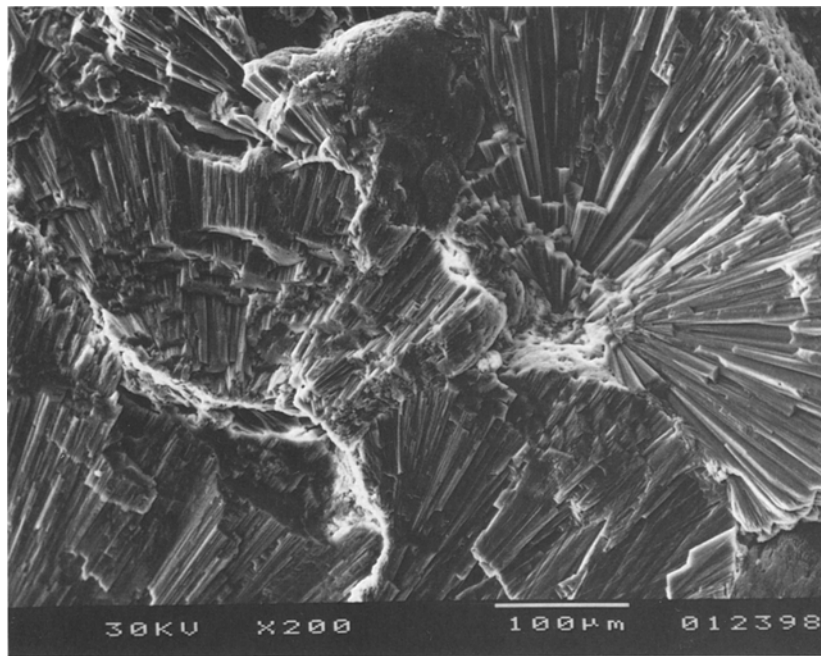


Figure 7. SEM image of aragonite botryoids. Note how some of the crystals have fractured concentrically, corresponding to the lines of inclusions (zones) visible in thin section.

ELEMENTAL AND STABLE ISOTOPIC GEOCHEMISTRY

The calcite core is enriched in sodium, strontium, magnesium, ^{13}C , and ^{18}O (Table 1) relative to stalactites from other oceanic provinces (Gross 1964). A reasonable explanation for the chemistry of the core of this speleothem is that it formed at a time when the shallow-water marine carbonate deposits, which constitute the carbonate platform, were being altered by meteoric water in the vadose zone.

Dissolution of aragonite and incongruent dissolution of Mg-calcite within the subaerially exposed platform released "marine" components (Sr, ^{13}C , ^{18}O) to the carbonate rich, downward flowing meteoric groundwater. When this water encountered the cavern it evaded CO_2 to the cave atmosphere, resulting in speleothem formation. Additionally, some areas within the calcite core contain relict marine textures, and thus the chemistry today may also reflect the primary marine aragonite and/or Mg-calcite which encrusted an early-formed vadose stalactite and which subsequently stabilized to calcite.

Table 1. Geochemical analyses from the sectioned stalactite (Fig. 8)

Sample	ppm Na	ppm Sr	ppm Mg	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	Mineralogy
<u>Stalactite core</u>						
A		2770		-3.1	-0.6	calcite
B (V-III)	360	2910	6880	-3.3	-0.9	calcite
C (IX)	520	2960	6420	-3.3	-0.8	calcite
D (X)	310	2090	3670	-3.0	-1.2	calcite
<u>Marine cement rind</u>						
F (I)	2560	9810	560	+0.8	+0.5	aragonite
G (II)	2480	9500	290	+0.9	+1.7	tr. Mg-calcite
H(III)	1600	9690	1010	+0.4	+1.1	tr. Mg-calcite
I (IV)	2230	9480	2860	+0.7	+1.1	tr. Mg-calcite
J (V)	147	10080	3010	+0.6	+1.1	tr. Mg-calcite
K (VI)	2310	10200	450	+0.5	+1.7	aragonite
L (VII)	2440	8800	3990	+1.3	+0.6	tr. Mg-calcite
M (B)		9270		+1.2	+0.8	aragonite
N (C)		8770		+0.8	+0.8	aragonite
<u>Exterior skeletal rind</u>						
S (XI)	2310	3560	20300	+2.6	+0.1	70% aragonite

The botryoidal aragonite rind forming around the core is chemically nearly identical to coarsely-crystalline marine aragonite cement found farther south along the "drop-off" into deep water along the main reef system seaward of Belize (Ginsburg and James 1976), from Grand Cayman Island (LeBlanc 1979), Jamaica (Land and Moore 1980), and from several Cenozoic occurrences in the Pacific (Aissaoui 1985). Cation concentrations are typical of marine aragonite, whereas the oxygen isotopic composition is somewhat ^{18}O -enriched relative to an equilibrium marine precipitate, as is typical for marine cements. The carbon isotopic composition is somewhat depleted in ^{13}C when compared with other marine cements. Both carbon and oxygen isotopic systems are shifted away from the compositions of presumed inorganic crystals in the direction expected due to microbial influence.

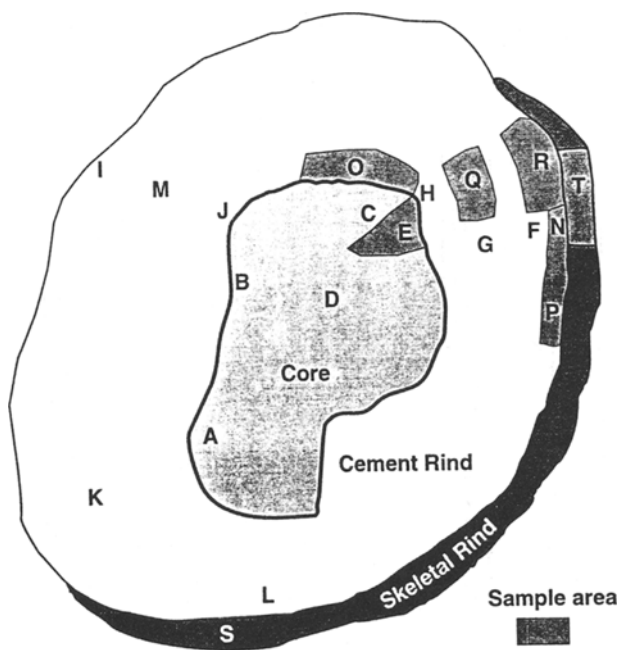


Figure 8. Drawing of a slab of the stalagmite adjacent to the one illustrated in Figure 5, showing lettered locations where samples were taken for geochemical analyses (Tables 1, 2 and 3).

GEOCHRONOLOGY

Portions of one of the basal sections of the stalactite (Fig. 8) were dated using standard ^{14}C methods at the University of Texas at Austin. U-series ($^{230}\text{Th}/^{234}\text{U}$) dating was also accomplished at McMaster University by dissolving samples in nitric acid to which a $^{228}\text{Th}/^{232}\text{U}$ tracer was added. U and Th were extracted from the filtered solution and were plated out and analyzed by alpha spectrometry (Gascoyne et al. 1979). Additional U-series geochronology, as well as strontium isotopic analysis, was conducted mass spectrometrically at the University of Texas. Data are presented in Tables 2 and 3.

The calcite core of the stalactite gave a ^{14}C "age" of 24,000 years. This minimum age merely confirms that the stalactite formed prior to the Holocene rise of sea level, when the cavern was already well formed.

The aragonite marine cement rind surrounding the central speleothem core yields apparent ^{14}C ages between 10,220 and 11,540 yBP. According to recent sea level curves (e.g. Edwards et al. 1993), sea level at 11.5 Ka should have been approximately 55m below its present level, and the stalactite, which grew at approximately -31m where we sampled it, should not yet have been submerged.

Two samples from the aragonite marine cement rind yield $^{87}\text{Sr}/^{86}\text{Sr}$ values of 0.709043 and 0.709033, respectively (Table 3). These values are considerably less radiogenic than modern seawater (0.709187) or the outer skeletal rind (0.709163). Thus it is clear that the seawater that precipitated the aragonite had interacted with the pre-Holocene rocks which comprise the offshore platform, becoming "contaminated" with unradiogenic Sr.

The U and Th isotopic compositions of the aragonite marine cement rind are also incompatible with the formation of aragonite from unmodified seawater within the last 10,000 years. A present-day $\delta^{234}\text{U}$ of 45 (Table 2) corresponds to a ^{234}U disequilibrium age of about 0.4 Ma. U-Th isotopic ages can be brought into agreement with the anticipated age based upon sea level curves (ca. 8000 years) if the initial $\delta^{234}\text{U}$ of the modified seawater was about 46 and the initial $^{230}\text{Th}/^{232}\text{Th}$ was about 0.005. Thus the incorporation of unradiogenic C and Sr, and ^{238}U and ^{230}Th from surrounding platform carbonates accounts for the discrepancy between the position of the stalactite and its "age" relative to most sea level curves.

Despite the inaccuracy of the absolute "ages", the marine-cement rind, which is almost 15-cm thick in places, seems to have formed quite rapidly (see Fig. 2 and Table 2), and to have ceased growing long before sea level flooded the top of the platform. The fact that one ^{14}C age (sample O) seems to be out of stratigraphic sequence suggests that aragonite growth may have continued within the porous stalactite as it continued to accrete.

The outer biogenic rind of the stalactite has a ^{14}C age of 2,910 yBP, which corresponds favorably with a time when sea level rise began to slow (Bloom 1971; Adey et al. 1977; Neuman and Macintyre 1985). At about this time sea level would have crested the top of the Lighthouse carbonate platform, permitting the colonization of the speleothems and other hard cavern wall surfaces by marine organisms. The absolute age of this zone is also uncertain because the Sr isotopic composition is less radiogenic than is modern seawater (Table 3), suggesting that it may also have incorporated some unradiogenic carbon as it grew.

Table 2. Radiometric ages from the sectioned stalactite (Fig. 8)

¹⁴ C dates:					
Sample	Age (years BP)	Laboratory number			
O	10,220 ± 120 yBP	Univ. Texas	#1771		
P	11,540 ± 180 yBP	Univ. Texas	#1772		
T	2,910 ± 90 yBP	Univ. Texas	#1770		

Uranium series analyses by alpha counting:				
Sample	²³⁰ Th/ ²³⁴ U	²³⁴ U/ ²³⁸ U	U conc. (ppm)	Age (Ka)
E	0.195 ± 0.020	1.085 ± 0.019	0.30	24 ± 2
Q	0.101 ± 0.010	0.961 ± 0.005	26.43	11 ± 1
R	0.091 ± 0.009	1.060 ± 0.013	2.18	10 ± 2

Uranium series analyses by mass spectrometry:						
Sample	²³² Th (pg/g)	²³⁰ Th/ ²³² Th	²³⁸ U (ppm)	δ ²³⁴ (present)	²³⁰ Th/ ²³⁸ U	Age* (years)
I	445	0.0214	6.025	44	0.0960	10490±50
J	473	0.0253	7.381	46	0.0986	10750±50

*Assuming an initial ²³⁰Th/²³⁸U ratio of 0.000014 (Edwards et al., 1987)

Table 3. Strontium isotopic analyses from the sectioned stalactite (Fig. 8)

Sample	⁸⁷ Sr/ ⁸⁶ Sr	Seawater Sr age (Ma)*
I	0.709033	5.3
J	0.709043	5.1
S	0.709163	0.7
Modern coral	0.709187	

*Using the curve of Farrel et al., 1995.

DISCUSSION

Prior to Holocene marine flooding, a large cavern had dissolved into the carbonate platform that is now Lighthouse Reef. Because of the great size of this cavern it is reasonable to assume that it formed during several glacial low-stands (Pratt and Dill 1974). During one of the dry periods within the late Pleistocene, the Belize stalactite began to form. The stalactite does not provide information on the time of cavern formation or when growth began. The formation of speleothems at the deepest depths observed from the submersibles shows that sea level must have been at least 125 meters below its present elevation. The geopetal fills within the core of the studied stalactite, and other, *in situ*, tilted stalactites, indicate that tilting took place before rising sea level reached -60 meters. The abundant vertical columns and stalactites indicate that the region has not been subjected to tectonic tilting recently. Horizontal stability has apparently existed for at least the past 9,000 years.

As sea level rose above about -38 m, a botryoidal aragonite rind began to encrust the tilted stalactite. Growth rates as high

as 2 to 20 μm/year apparently took place. We are unsure if sunlight was able to penetrate into the cave at this time. The large amount of rubble associated with the east and west walls of the Blue Hole demonstrate that considerable roof collapse took place at some time in the recent past, but the cave may have been dark at the time the stalactite was being encrusted. We propose that growth of the aragonite botryoidal rind was heavily microbially influenced, based on two lines of evidence. First, cauliflower-like textures (Figs. 4, 5, and 6) are difficult to explain by a purely inorganic mechanism. And second, the stable isotopic chemistry is consistent with a microbial influence. We are unsure why the two sides of the stalactite are so different. It is possible that the differences merely reflect the direction of flow of seawater in the flooded cavern, the dense side growing with fewer microbial "bushes". Asymmetrical flow within submerged caverns is well documented elsewhere (Whitaker and Smart 1993). Alternatively, the porous side may have been modified by dissolution after it fell and as it was buried in anoxic mud (Walter and Burton 1990). It seems unlikely, however, that such extensive modification could take place in a few thousand years, and evidence of corroded aragonite crystals is

lacking. The growth of the aragonite rind apparently terminated long before rising sea level flooded the platform top. We can only speculate as to why aragonite growth stopped. It is possible that roof collapse occurred approximately 8000 years ago, plugging the bottom of the cave and impeding circulation. It is also possible that sea level occupied new cave levels as it rose, reducing circulation in the more deeply submerged passageways.

CONCLUSION

The Belize stalactite not only yields information about late Pleistocene eustasy and tectonics, but is also an example of Holocene submarine cementation on a larger scale that has been previously described. The thick marine cement rind which encrusts the Belize stalactite is similar in some respects to ancient cement encrustations, albeit in smaller cavities, yet it is quite different from most other Holocene examples. Extremely thick layers and crusts of presumed marine aragonite have been described from many ancient carbonate shelf margins such as the Permian of West Texas and New Mexico (Mazzullo and Cys 1979). Thick aragonite cements are also postulated to have formed inorganically on the sea floor, especially during the pre-Cambrian (Peryt et al. 1990). Many investigators who have studied West Texas deposits have concluded that the Permian was also a time of worldwide eustatic fluctuation of sea level, and the Belize stalactite suggests that marine reef cement encrustation can continue to take place during rises and falls of sea level and not solely at highstands. Further, cementation can take place from modified seawater, deep within a carbonate platform. Attempts to relate cement chemistry, even if it is preserved, to the chemistry of open marine water, may thus be compromised.

One obvious difference between the massive rind of marine cement recovered from Belize and most Paleozoic and pre-Paleozoic examples is the size of the individual crystals. Despite the fact that the aragonite crystals in the Belize stalactite never exceed 10 μm in diameter and 2.5 mm in length, they are much larger than cement crystals from most other Holocene reefs. Yet aragonite crystals many centimeters long have been described from numerous ancient deposits. The differences between the morphology of Belize stalactite aragonite and other modern marine cements may reflect the modification of seawater which took place as the result of circulation through the carbonate platform. Whether the difference between the morphology and crystal size of Holocene and ancient cements reflects microbial evolution, changing seawater or atmospheric chemistry, or some other variable, is unknown.

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resting place for the stalactite at the Modern Carbonate Laboratory and Museum of the University of Miami at Fisher Island (Fig. 4). Jay Banner provided access to the laboratory facilities at the University of Texas for U-Th geochemistry. Reviewers Conrad Neumann and Sal Mazzullo provided constructive comments on the manuscript. The crew and divers of the R/V Calypso deserve special mention for making the retrieval possible. Special thanks and appreciation are extended to Albert Falco, Andre' Labon, and Richard Murphy who, along with the first author, conceived the idea of using a geological subject for a Cousteau TV series. Our greatest thanks and appreciation belong to the late Jacques-Yves Cousteau and his wife Simon, who together provided the funds and vessel that made it all possible.

This paper is dedicated to the memory of both Jacques and Phillip Cousteau who, as close friends and diving buddies of the first author, did so much to make the expedition to study "Blue Holes" a success.

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DILL, LAND, MACK AND SCHWARCZ

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