The Biogenic Hypothesis: Microbial Acids and Gas as an Explanation for the Dissolution and Forming of Pores and Caves in Limestone*

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Abstract

The current explanation for the formation of pores, holes and caves in marine limestone is the combination of acidic meteoric water and mixing of $CaCO_3$-supersaturated seawater with $CaCO_3$-saturated groundwater creating under saturated mixed water. We now know that the mixing of these bodies of water cannot dissolve limestone unless there is a continuous source of acids to overcome the buffering effects of the limestone. Similarly, rainwater that is slightly acidic via incorporation of atmospheric and soil CO_2 cannot remain acidic during its passage through marine-limestone.

Large numbers of interstitial bacteria are the obvious sources of acid and gas needed to initiate and maintain acidic meteoric and ground-water conditions. We have shown that rainwater over San Salvador Island before contact with the ground has a pH of 5.6 and is buffered within three minutes to 8.6 following contact with local limestone. Buffered rainwater passing through 3 meters of limestone arrives in vadoses cave as acidified drip-water with a pH of 6.7. We hypothesize that the dissolution capacity of meteoric-water is controlled by the assimilation of bacterially generated acids and gas, produced in the pores of the host rock. Heterotrophic bacteria also produce large quantifies of gas in unconsolidated rock and can generate blisters or pores. The gas they generate is temporarily trapped in their mucilage causing a ballooning effect and subsequent displacement of the surrounding unconsolidated grains. The resulting sedimentary textures formed by microbial acid and gas, in modern carbonate rocks, appear to match textures observed in ancient carbonate cores.

Selected Reference

Garrison, B.V., and B.E. Urband, 2003, The effects of OCTG (Oil Country Tubular Goods) connection swaging and stress relieving on SSC (Sulfide Stress Cracking) resistance : NACE International Corrosion Conference, San Diego, California, March 16-20, 2003, paper 03111, 18 p.

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Making holes in rocks via rain water

The solution of CO_2 (g) in water is as follows:

$$CO_2 (g) + H_2O \longleftrightarrow H_2CO_3 (aq)$$

If carbonic acid dissociates:

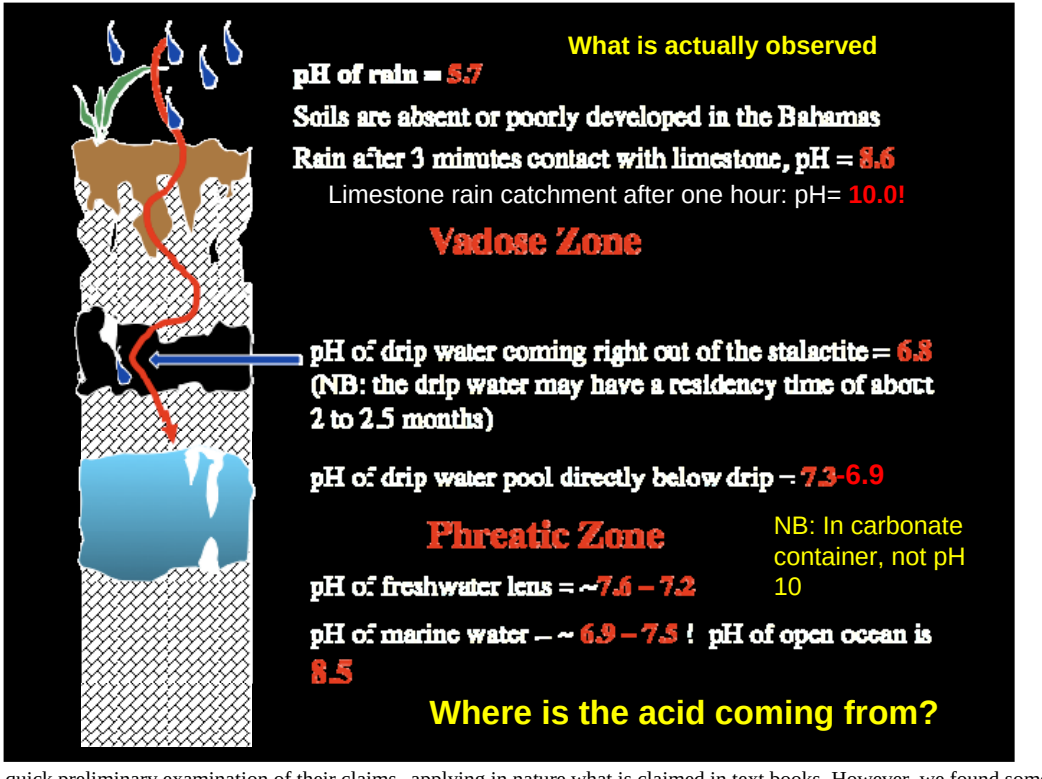
$$H_2CO_3 \longleftrightarrow H^+ HCO_3$$

$$HCO_3^- \longleftrightarrow H^+ + CO_3^{2-}$$

$$Ca + CO_3^{2-} \longleftrightarrow CaCO_3^{2-}$$

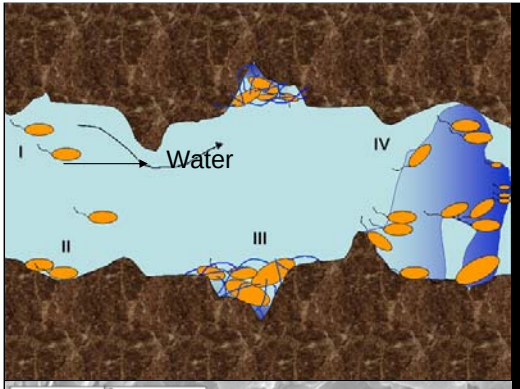
Abiotic approach

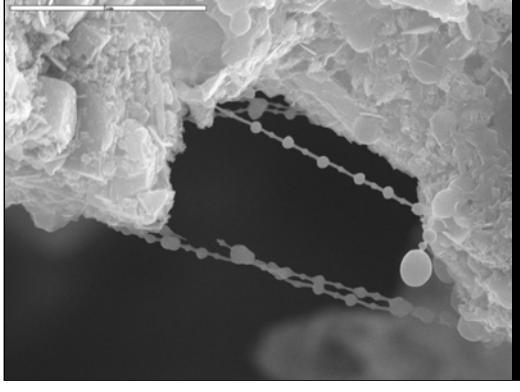
Presenter's Notes: Additional CO2 is picked up in the soil (no comment as to the origin of the CO2); this carbonic acid solution now is supposed to makes its way through meters of rock and dissolve massive caves?? IF so effective, what about the rock between the surface and the water table? Dissolution stops a few meters from the top of the rock and picks up again at depth??



Presenter's Notes: A quick preliminary examination of their claims--applying in nature what is claimed in text books. However, we found something different.

BIG problem: acid is not a constant source

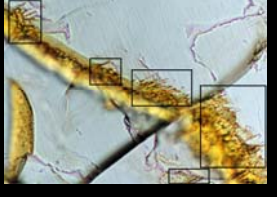




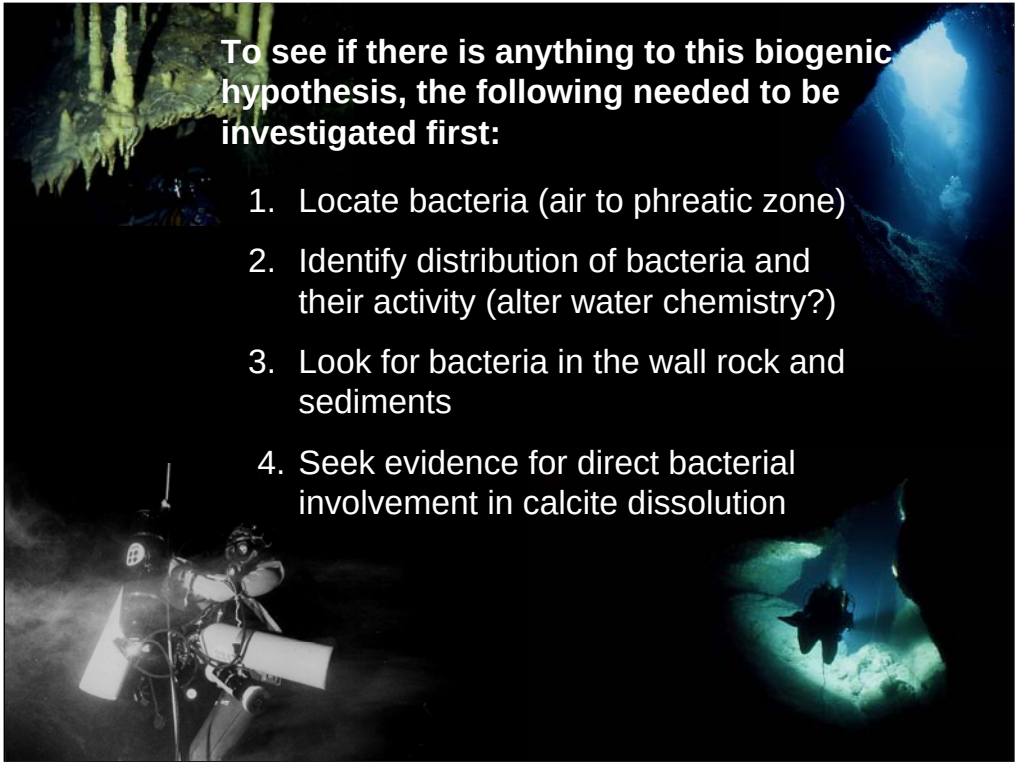
Acids made by bacteria and fungi:

Carbonic acid oxalic, gluconic, nitric and sulfuric……(provide and continues assault on the host rock (surface and interior)

Oxalic acid is 10,000 times stronger than acidic acid….



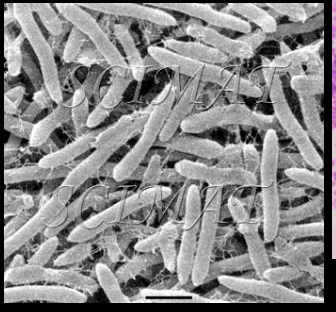
Presenter's Notes: Hole-making bacteria in your mouth?? Teeth are a mineral. Important: the acid source has to be continuous to make holes, whatever the size. As a result, we have come up with a biogenic hypothesis that may solve, or assist in solving, the problem.


To see if there is anything to this biogenic hypothesis, the following needed to be investigated first:
1. Locate bacteria (air to phreatic zone)
2. Identify distribution of bacteria and their activity (alter water chemistry?)
3. Look for bacteria in the wall rock and sediments
4. Seek evidence for direct bacterial involvement in calcite dissolution

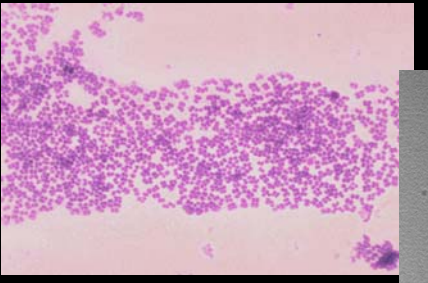
..we start with the rain…

Its Raining Bacteria!

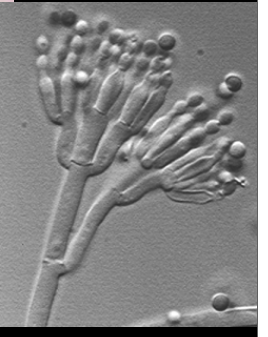
So far, 4 different isolates:



Bacillus megaterium

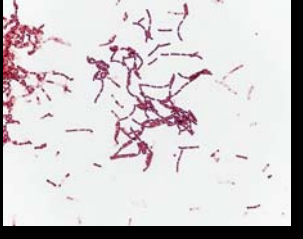


Micrococcus



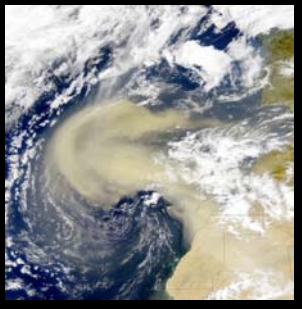
Penicillium

1000 bacterial cells / ml of rainwater



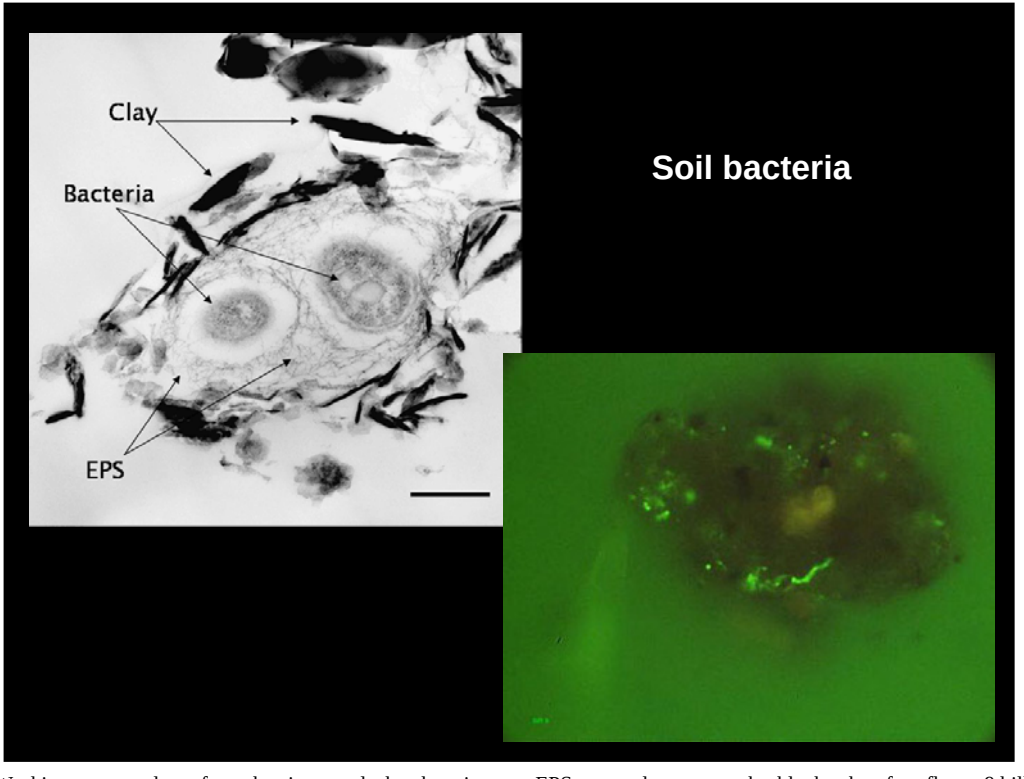
Klebsiella

Presenter's Notes: 1 cubic centimeter of dry air from the surface of the Earth to the top of the atmosphere weighs 1.04kg as it relates to CO2 pp. Why are they (bacteria) in the air?



Dust carries between a million and a billion microbes (¼ tsp).

>300 kinds of microorganisms cultured from air samples collected during Saharan dust storm events. This is approximately 2 to 3 times more than during non-dust events. Of the cultureable bacteria identified thus far, 10% are known animal pathogens, 5% are plant pathogens, and 27% are opportunistic human pathogens (Garrison et al., 2003).



Presenter's Notes: Working our way down from the air towards the phreatic zone. EPS can wedge apart rocks, block subsurface flows; 9 billion bacterial cells per gram of soil on average; 1 billion per ml of ocean water.

Epifluracent AODC, Acridine Orange Direct count (DAPI)

Bacteria in rocks in dry caves?.....

CO_2 Flux Meter

CO_2 coming out of the rock is on initial examination 2 to 3 fold higher than what is coming out of the cave floor sediments.

$\delta^{13}C$ (DIC) values suggest biological source

~52g/m^2/day (r^2 value 0.74)

Presenter's Notes: Unconventional use of a CO_2 flux meter, but recent results are considered to be reasonable when samples are incubated in oxygen free-environments.

New Findings in dry caves!

Cave wall rock incubated in anaerobic environment resulted in the dominant gas production being N_2, (8.2×10^{-7} to 2.1×10^{-4} µM per g). The next interesting discovery was the production of N_2O. Concentration of this gas was insufficient to measure isotopically but the N_2 signature ranged from -2 to 3 ‰, while the carbon isotope composition of CO_2 ranged from -29 to -6‰

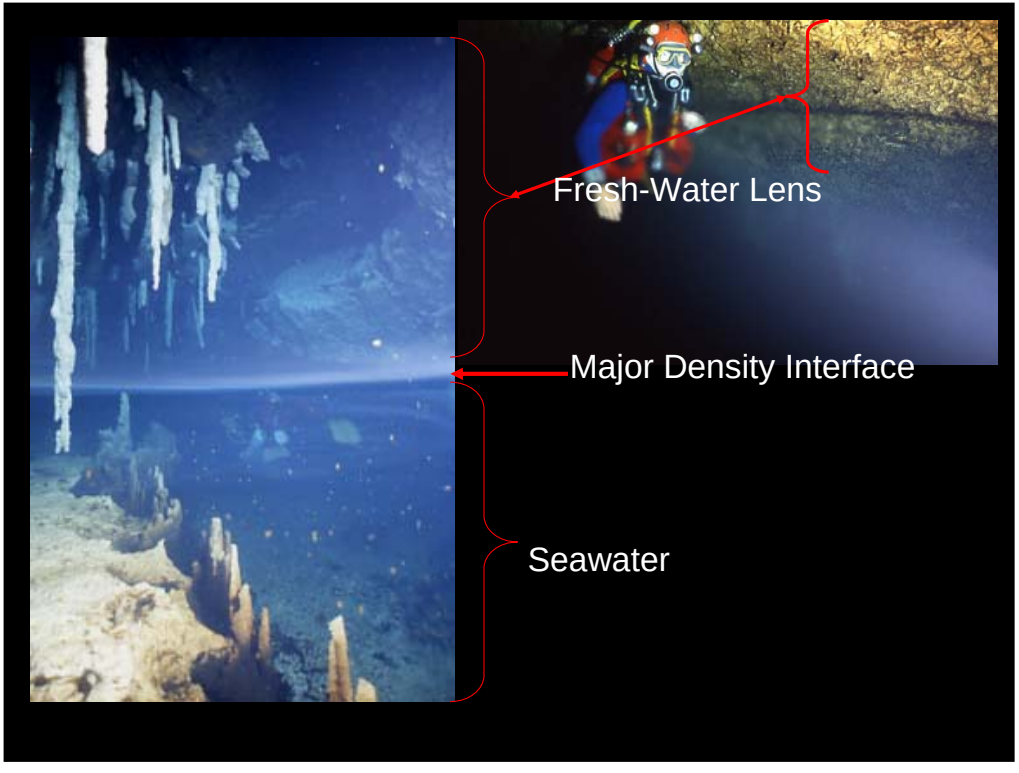
Before taking you Into the phreatic zone, some definitions…..

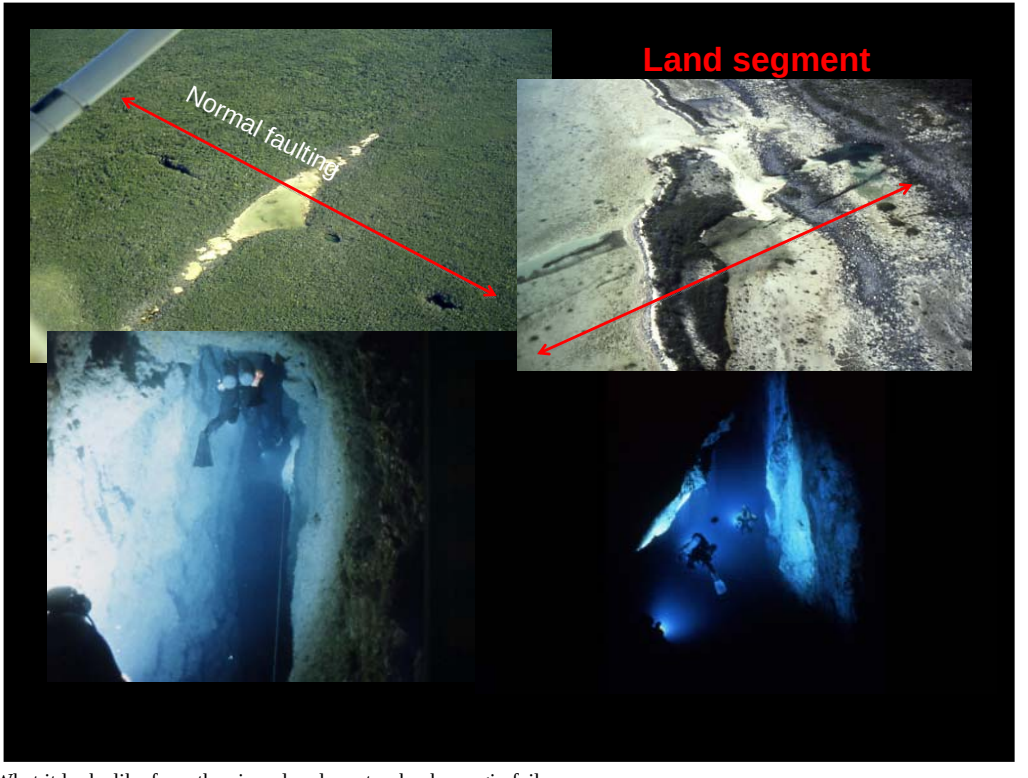
Blue Holes ?

Basic Classification of Caves in the Bahamas

1. Horizontal Caves
2. Fracture-guided Caves
3. Vertical Caves

Presenter's Notes: Sea-level drop, hole is no longer blue--reason for better scientific classification along with new information gained from cave diving. No reason to assume that the caves currently above sea-level are different from those that are currently flooded.


Fresh-Water Lens
Major Density Interface
Seawater



Presenter's Notes: What it looks like from the air and underwater; bank margin failure.

Basic Classification of Caves in the Bahamas

1. Horizontal Caves
2. Fracture-guided Caves
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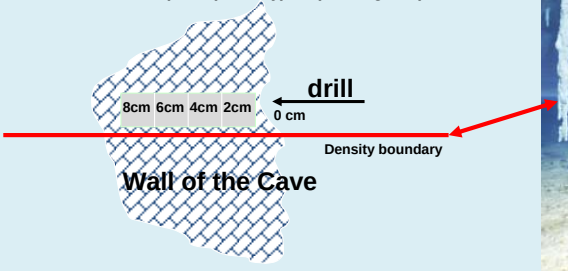
Bacteria in wall rock, sediments and water?.....

Rock

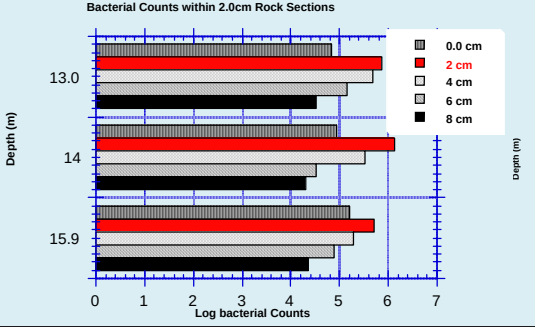
13.0m vertical depth (10-15% porosity) (~0.963g/cm^3)

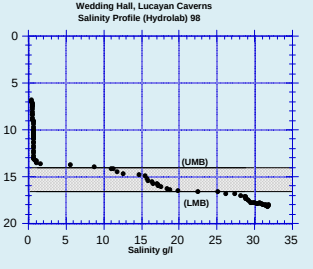
14.0m (20-30% porosity) (~0.631g/cm^3)

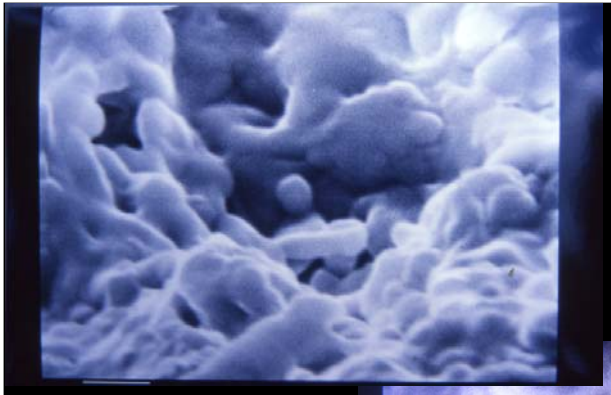
15.9m (1-3% porosity) (~0.815g/cm^3)



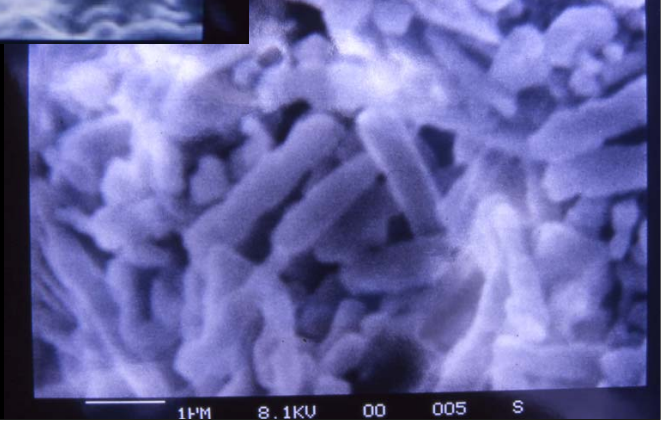
Horizontal Cave: Lucayan Caverns



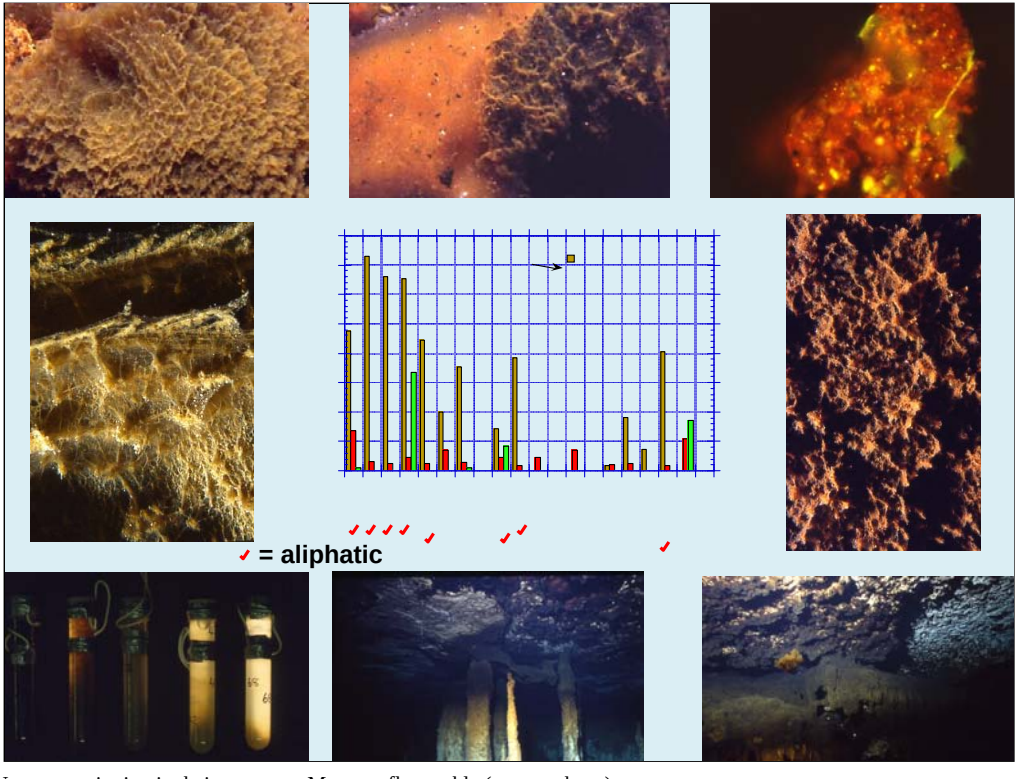




SEM



Biofilm in a pore of a rock: Note bacteria beneath the film



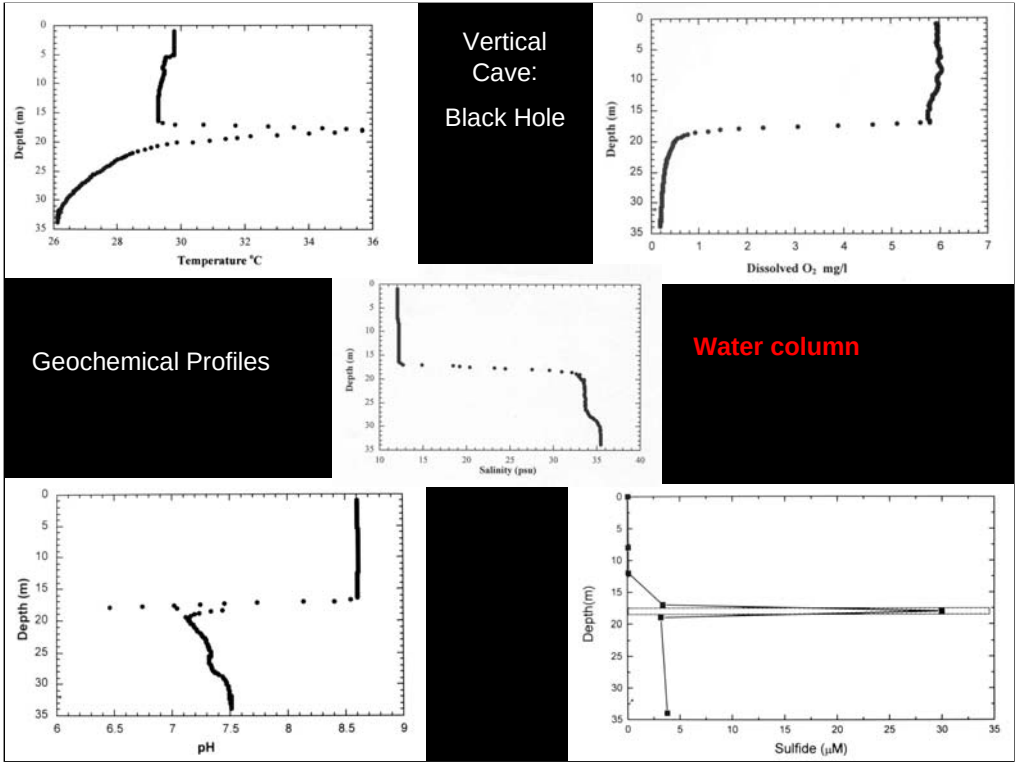
Presenter's Notes: Non-aromatic ring in their structure. Most are flammable (e.g., methane).

Vertical cave:
The Black Hole

Total mass of purple bacteria ~ 5 tons dry weight!

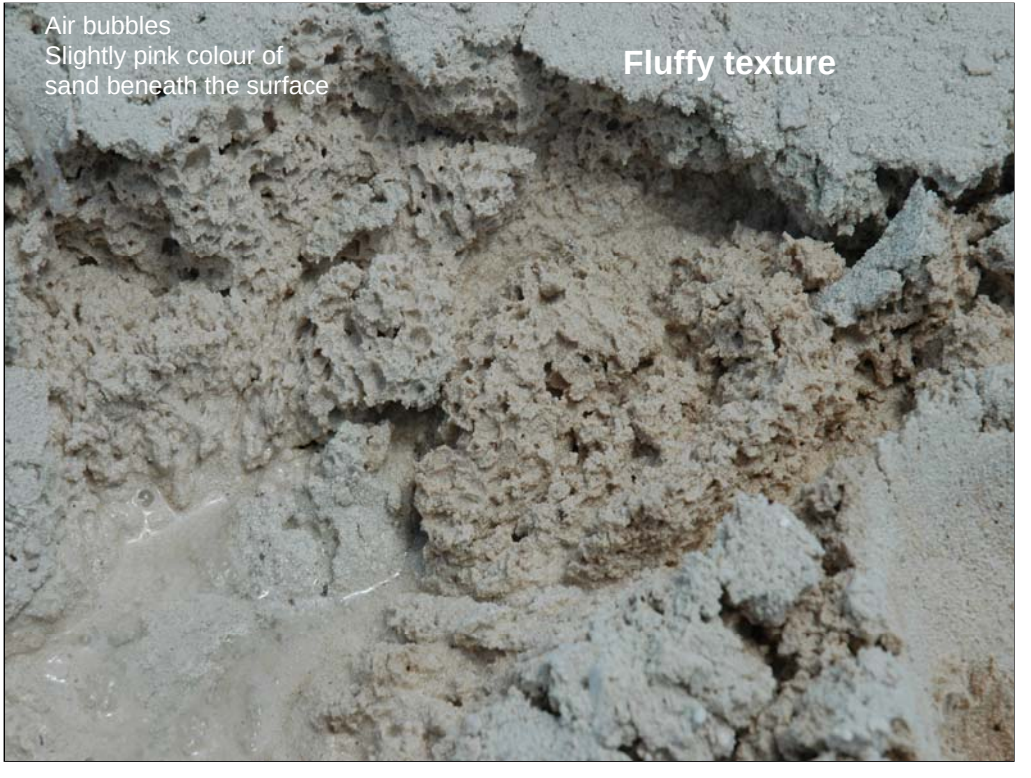
Can these numbers change the water chemistry?

Presenter's Notes: Geochemical changes in the water column.


Vertical Cave:
Black Hole
Geochemical Profiles
Water column
Depth (m)
Temperature °C
Dissolved O2 mg/l
Salinity (psu)
pH
Depth(m)
Sulfide (μM)

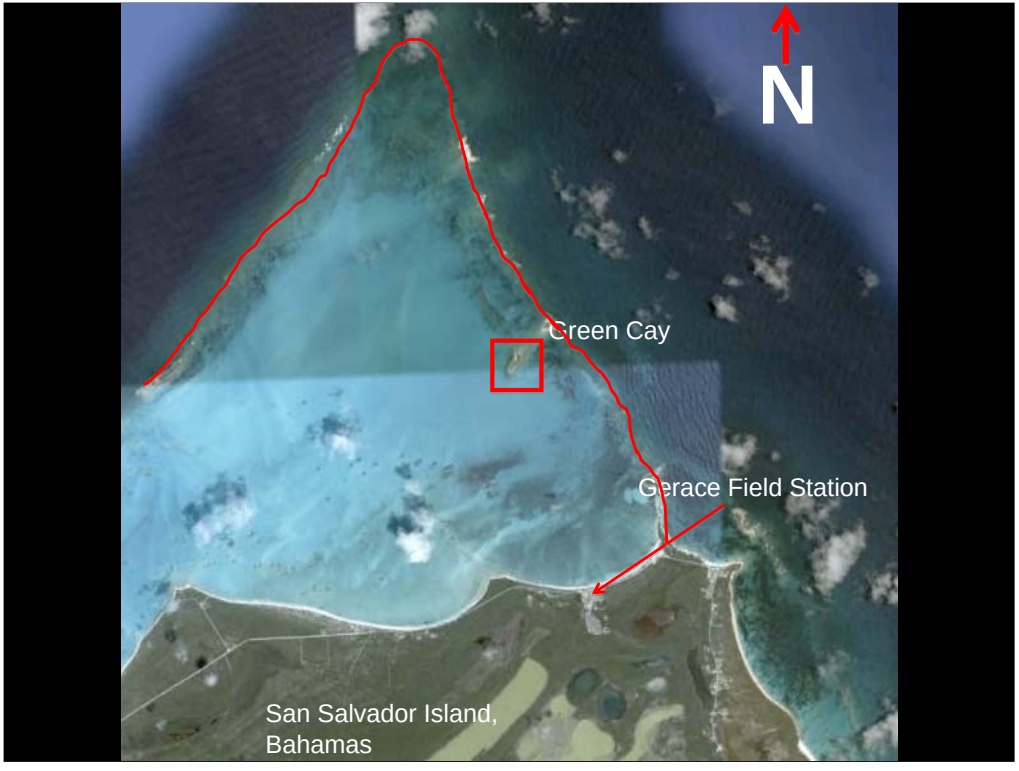
Gas, another way to make holes?……


Berry Islands
Joulters Cay,
North Andros
Image U.S. Geological Survey



Presenter's Notes: The sound of popping sand; found items decomposing, and sand was dark purple under the item.

Presenter's Notes: Fermenting? CO2 signature is pointing in that direction; H2, NH3, ethanol, ethylene…..


N
Green Cay
Gerace Field Station
San Salvador Island,
Bahamas

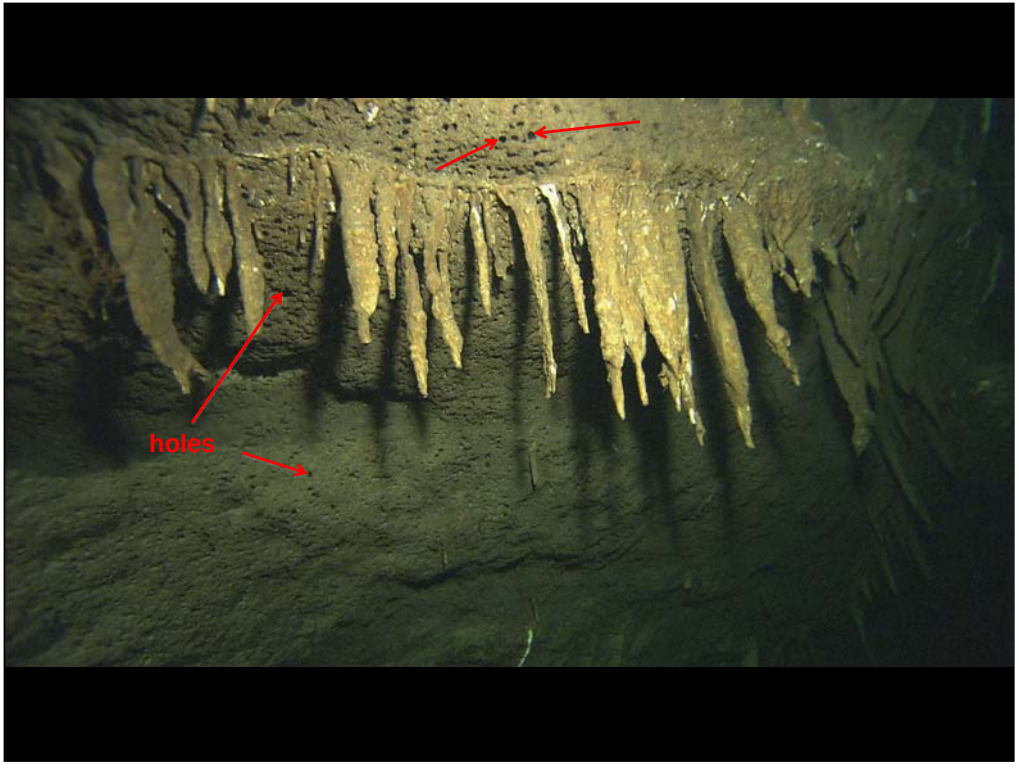

Green Cay
Armored limestone
(Saharan Dust)

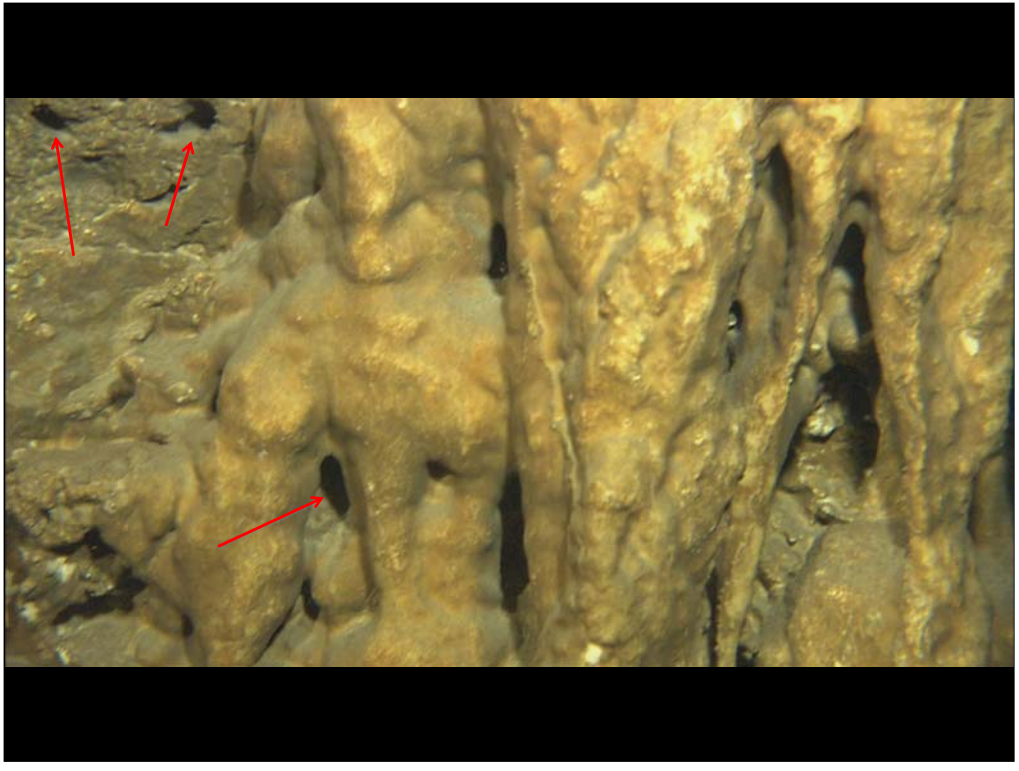
Green Cay (~125,000 yrs) frothy sand?

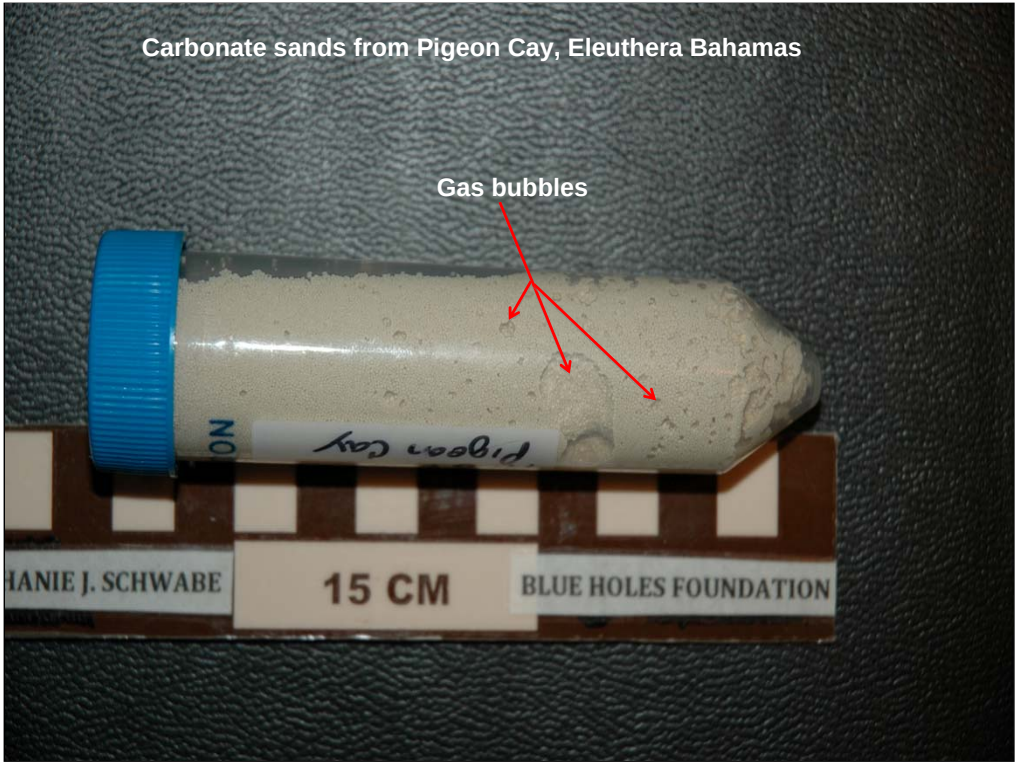
The same?

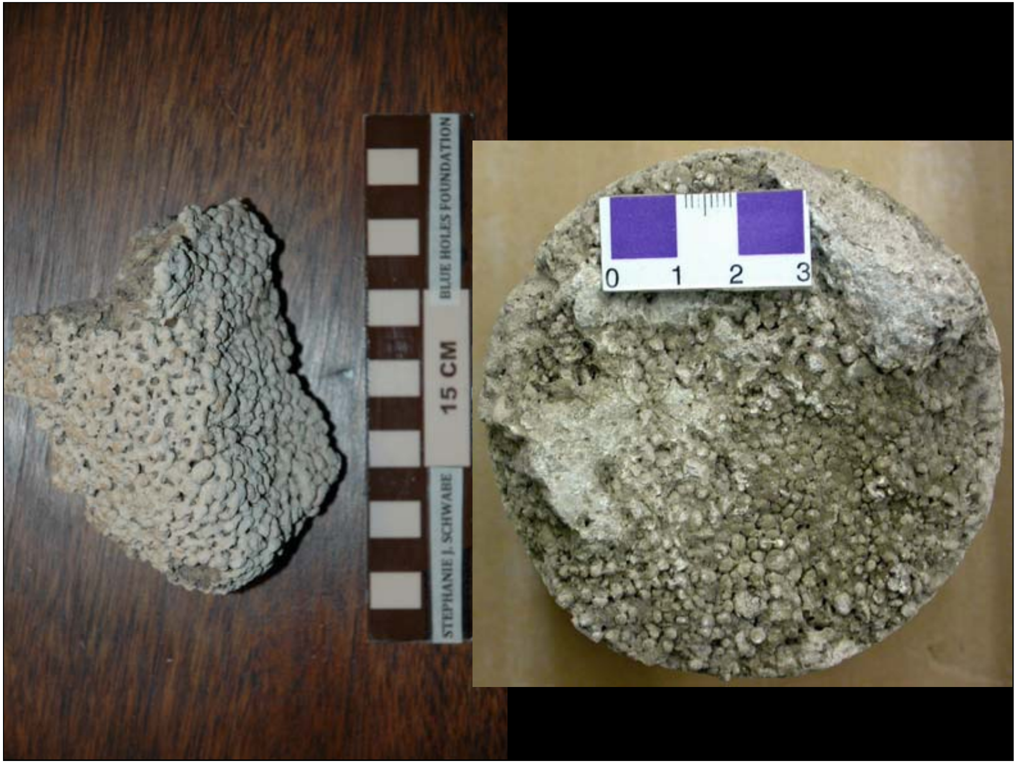
Holocene frothy sand

Presenter's Notes: Go under the mangroves.

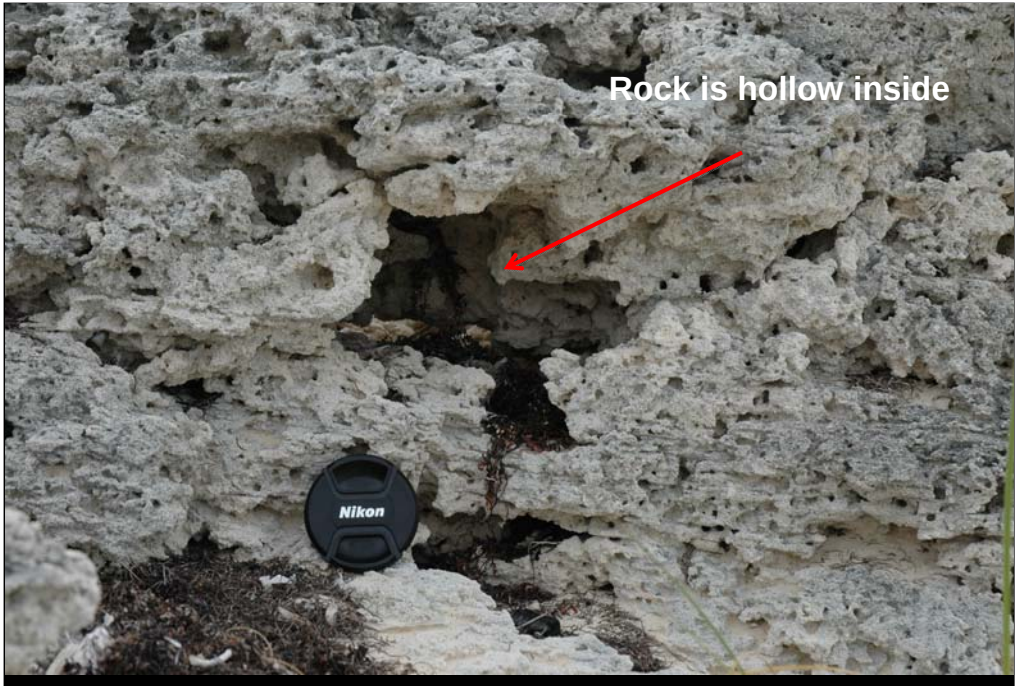

holes




Carbonate sands from Pigeon Cay, Eleuthera Bahamas
Gas bubbles
NO
Pigeon Cay
HANIE J. SCHWABE
15 CM
BLUE HOLES FOUNDATION

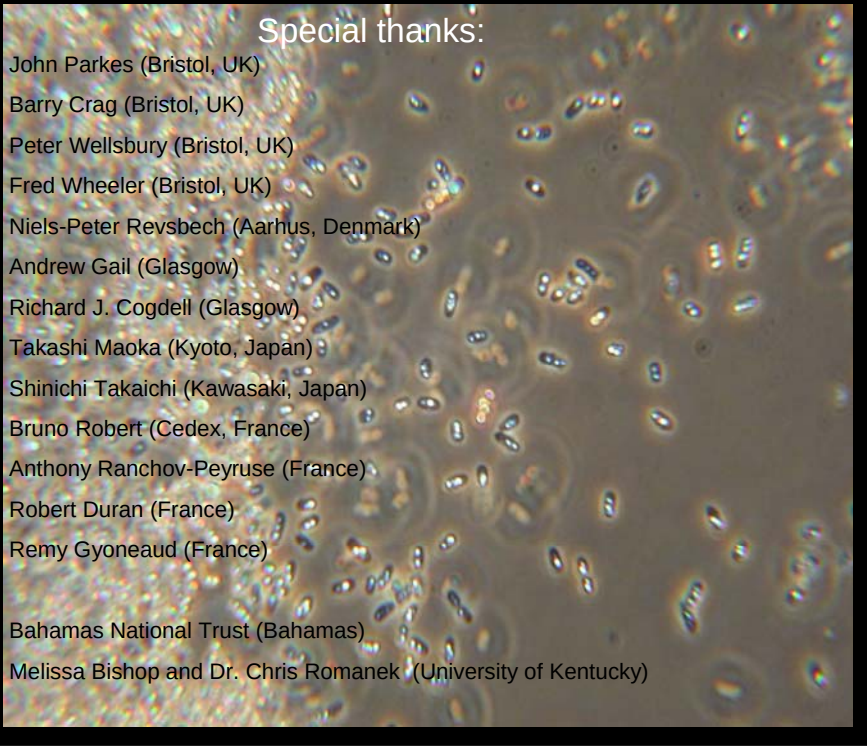

BLUE HOLES FOUNDATION
15 CM
STEPHANIE J. SCHWABE
0 1 2 3


0 1 2 3



San Salvador Island, Bahamas, Graham's Harbour

Presenter's Notes: Although we consider this research novel, by 1904 scientists had already discovered that interstitial bacteria on the surface and within the rock were responsible for the disintegration of building stones in England. Later in 1933 Pain et al. conducted a very detailed research project that identified the presences of bacteria and the acids they produced were identified. The argument of this process only being a tropical event is null and void. They called it bacterial disease of stones. We call it "the biogenic hypothesis."



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