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SERENDIPITOUS OBSERVATIONS OF ORGANIC MATTER IN METEORIC CALCITE CEMENT IN HOLOCENE EOLIAN CALCARENITES, SAN SALVADOR ISLAND, BAHAMAS

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ABSTRACT

A study was conducted on San Salvador Island, Bahamas, examining mechanisms of tafoni development, which was presumed to be salt wedging given the Bahamian marine setting. For this study samples from Holocene and Pleistocene eolian calcarenites were collected and preserved in a desiccating environment, then subsequently cut and ground into thin sections using oil-based procedures to preserve any evaporite minerals. Thin section analysis showed no evaporate minerals present; however, Holocene samples showed 17.2 % porosity and 25.4% meteoric cement, very different results than the 25.9% porosity and 10% cement found in similarly-prepared Pleistocene samples. These results contrast with earlier reports from other studies, which show Holocene eolianites to have higher porosity and less cement than Pleistocene samples. Meteoric cement in Holocene eolian calcarenites in the Bahamas initiates on organic-rich allochems. In thin sections cut with oil, we believe relict organic matter is preserved in association with the equant spar. Organic matter is also present within equant spar based on subtle brown color in transmitted light, dull white color in reflected light, and bright red color in the confocal microscope, which shows organic matter within both peloids and cement. Some cement material is suspended in the biofilms, such that upon decay of the organic material with time, these cements collapse, decreasing apparent cementation and increasing porosity, which explains the change in those values over time in Holocene versus Pleistocene eolianites as the organics decay. Thin-sectioning with a water saw removes the organic material from Holocene samples, creating an observational bias avoided by our technique. Under the scanning electron microscope (SEM) some of these equant crystals have a smooth face; however, where crystal growth is incomplete, small spheres (100 nm) are visible throughout the crystals. Both petrographic and SEM microscopy reveal meteoric meniscus cement morphology identical to the meniscus formed by biofilms cultured in sandstone. The very small (100 nm) spherical structures are interpreted as nannobacteria and associated organic matter suggests that some of these meteoric cements are formed in association with microbial biofilms and that the role of organic matter in cementation should be explored further.

INTRODUCTION

The topography of San Salvador Island, Bahamas (Figures 1 and 2) is dominated by suites of eolian calcarenites, which form all topography over 7 m in elevation, as well as some of the topography at lower elevations (Carew and Mylroie, 1997). The

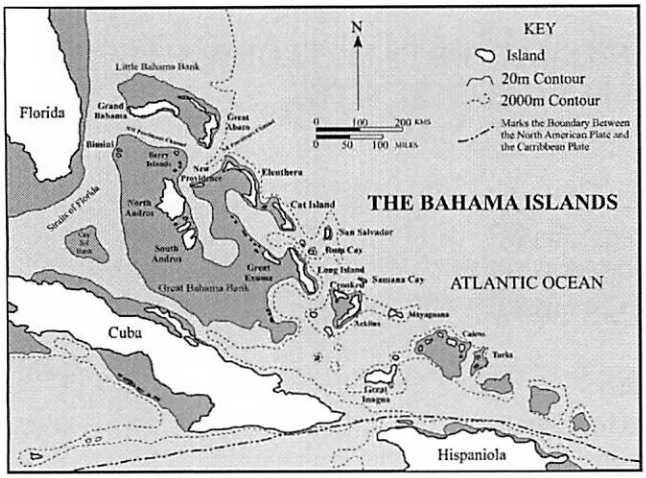

Figure 1. A map of the Bahamas showing San Salvador Island on the eastern side of the archipelago (Carew and Mylroie, 1995).

eolianites fall into two main stratigraphic units: Holocene dunes and Pleistocene dunes. Specifically, the eolianites studied consist of Holocene dunes of the North Point Member of the Rice Bay Formation (which have a calcrete crust but lack a terra rossa paleosol) and Pleistocene dunes of the Cockburn Town Member of the Grotto Beach formation (which have a calcrete crust and a terra rossa paleosol). The North Point Member has a few ooids low in the section, but is primarily peloidal-bioclastic, whereas the Cockburn Town Member dunes tend to have more ooids (Carew and Mylroie, 1997).

This study grew out of a project designed to determine how tafoni (singular: tafone) formed in Quaternary eolian calcarenites. Tafoni have been defined in many ways depending on the rock type, size, and forming mechanisms (Owen, 2007 and references therein), but are essentially erosional hollows in cliffs that are from tens of centimeters to meters in size. The tafoni of the Bahamas are cuspate erosional features that occur in the eolian calcarenite rocks along current coastlines being intermittently cliffed by Holocene wave activity, in inland positions where cliff formation occurred during the last interglacial sea-level highstand (MIS 5e), as well as in cave collapses, road cuts,

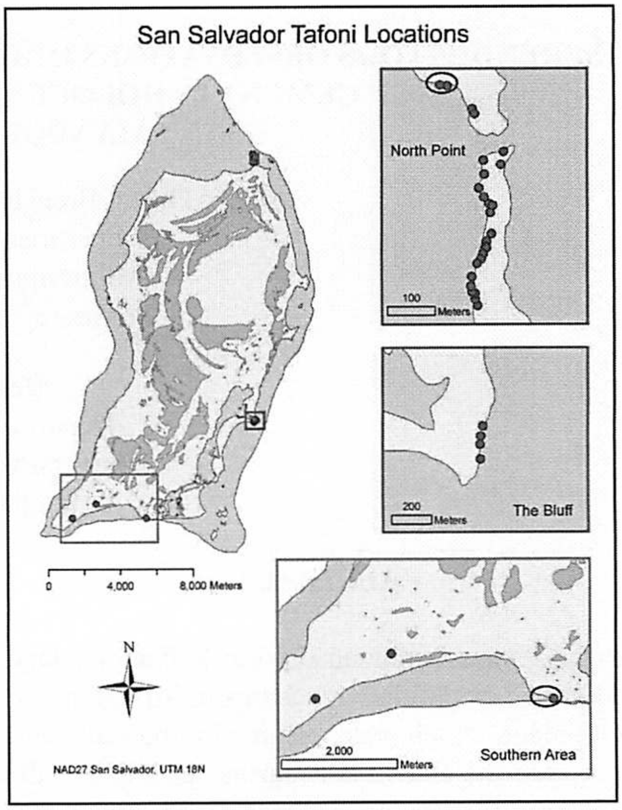

Figure 2. A map of San Salvador showing the locations of tafoni, sample locations discussed in this paper are circled (Owen, 2007).

and in quarried building blocks. The tafoni features are of various sizes (Owen, 2007 and references therein) (Figures 3, 4, and 5) and are formed by surficial erosional processes acting from the outside inward. The cliff formation, quarrying, or road cut activity creates vertical bedrock faces that lack the protective cemented calcrete crust that forms on the exterior of eolian calcarenites. The poorly-cemented dune interior is thusly exposed to surficial weathering processes. The vertical nature of this exposure prevents rapid re-cementation of the rock surface by meteoric waters, allowing surficial processes to continually attack the soft interior. This process results in large tafoni along eolian calcarenite cliffs, with smaller tafoni occurring in eolian calcarenites on younger quarry faces, road cuts, and in building stones. From the literature it was determined that the most probable cause of erosion forming the tafoni in this

Figure 3. View of tafoni in Holocene eolian calcarenites at North Point on San Salvador Island, Bahamas.

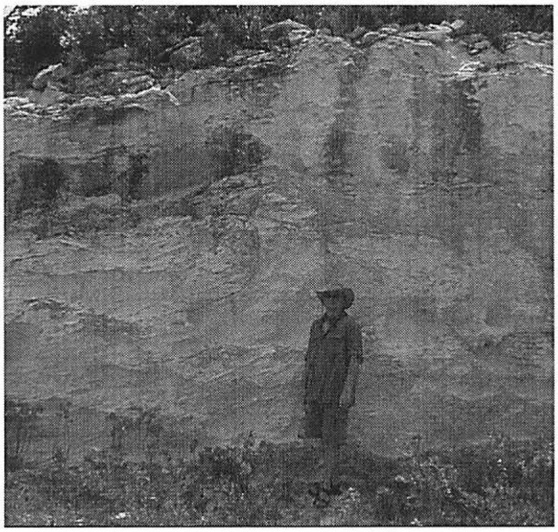

Figure 4. Tafoni in a road cut at the south end of San Salvador Island.

environment may have been salt wedging due to the proximity of the rock surfaces to the ocean environment in the Bahamian setting (Owen, 2007).

METHODOLOGY

Samples were collected on San Salvador Island, Bahamas, from the interior of tafoni features in Holocene and Pleistocene eolian calcarenites to study the nature of the erosional process forming them. This examination included looking for evaporite minerals pertaining to crystal wedging. The Holocene samples were taken from the Graham's Harbour side of Cut Cay located off the end of North Point, at the north end of the island, and the Pleistocene samples were taken from the south end of San Salvador near The Gulf (Figure 2). The samples were collected high and low within the tafoni, near the back wall where evidence of the active erosional process would most likely be fresh. The Holocene tafoni sampled were slightly larger than the Pleistocene tafoni, the high Holocene samples were collected approximately 4 to 5 meters above the tafone floor, with low samples collected half to one meter above the floor. Pleistocene high samples were collected aproximatly 3 to 4 meters above the floor, while low samples were collected half to one meter above the floor.

A total of 64 samples were collected. Samples were taken starting from the rock surface, and mining inward a total of 20 cm to obtain up to four additional successive samples not in direct contact with the outside air, for a total of 5 samples per location for most locations. The samples were immediately packaged in sealed plastic bags with silica gel desiccant to preserve any evaporite minerals present.

Thin sections were prepared from selected samples, two sample sets from tafoni in Holocene eolian calcarenites, and two from tafoni in Pleistocene eolian calcarenites. Blanks were prepared from the collected samples. The blanks were sent to Spectrum Petrographics, where they were impregnated and cut using oil techniques, which do not involve water, in a manner similar to that used to prepare water-sensitive soil samples. The thin section surfaces were protected by cover slips to prevent air moisture from penetrating the thin sections. The thin sections were point counted by standard petrographic procedures.

Figure 5. Tafoni (arrows) in eolian calcarenite quarried rock for building blocks for colonial period buildings, Watlings Castle, San Salvador Island, Bahamas.

Further examination was done using the scanning electron microscope (SEM). The samples were broken in small pieces and hot glued to pegs that could be placed in the SEM. Care was given to acquire fresh surfaces and not to contaminate the samples with human skin oil. The samples were then vacuum pumped down and coated with a gold-palladium alloy using a Polaron E5100 Sputter Coater for 30 seconds, resulting in a thin coat that prevented the formation of artifacts (Folk and Lynch, 1997). Samples were examined with a JEOL JSM-6500 F field emission scanning electron microscope, using a voltage of 5.0 KV and a working distance of 7.0 mm. Fluorescent images were acquired using a Zeiss LSM 510 Confocal Laser Scanning Microscope (Carl Zeiss Microimaging, Inc) with an Inverted Zeiss Axiovert 200 M Light microscope and a plan Apochromat 5X/0.16 NA objective lens. A FITC/TRITC (Fluorascein/Rhodamine/Transmission) filter set was used in Single and Multi Track channel mode imaging. Excitation wavelengths of 488nm/543nm and Emission wavelenghts of 505-530nm (Green) and 560nm (Red) were acquired at 512x512 or 1024x1024 pixel format for imaging purposes.

RESULTS

The results of the thin section analysis showed grain types reported by other petrographic studies previously done on San Salvador Island (Schwabe, 1992; Carney and Stoyka, 1993; White, 1995; Hutto and Carew, 1984; Stowers, 1988). Allochems found include: peloids, benthic foraminifera, coral fragments, bivalve, gastropod and other miscellaneous mollusk pieces, red algae, Halimeda sp., ooids, coated grains and bryozoans. Isopachous elongate marine and equant meteoric cements are present, but meteoric cements, sometimes with preserved meniscus geometries, are more common.

Analysis of the thin sections revealed no evaporites present. Initial results of point counting were surprising (Tables 1 and 2). For the Holocene samples the average was 25.4% cement and 17.2% porosity, while for Pleistocene samples the average was 10% cement and 25.9% porosity (see Figure 6). Not only were Holocene values for cement higher and porosity values lower than for the older Pleistocene samples, but the Holocene values were higher for cement and lower for porosity than values reported from previous studies (e.g. White, 1995), which used standard water-based thin section preparation, of the same Holocene eolianite units. When using transmitted light, there was observed some subtle brown color within the equant spar. In the reflected light a dull white color was obvious, and in the confocal microscope a bright red color was present. All of these indicate the presence of organic matter; it is visible under the confocal microscope within both peloids and cement (Figure 7). When viewed with the SEM, some of the equant crystals have smooth faces while in other areas where the crystal growth is incomplete, there are bacteria and small spheres in the size range of ~100 nm (Figures 8 and 9).

Table 1 Thin Section Point Count Results

Slide #	Tafoni Location	Age	Depth (cm)	Sample #	Count	Porosity Percent	Allochems Percent	Cement Percent
1	E2 Low	Pleistocene	0 to 4	E2 #2	100	32	58	10
2	E2 Low	Pleistocene	16 to 20	E2 # 6	100	29	60	11
3	E2 High	Pleistocene	0 to 4	E2 # 7	100	22	70	8
4	E2 High	Pleistocene	8 to 12	E2 # 9	100	21	67	12
5	E2 High	Pleistocene	16 to 20	E2 # 11	419	25.54	65.63	8.83
6	Z Low	Holocene	0 to 4	Z # 2	101	18.81	55.45	25.74
7	Z Low	Holocene	16 to 20	Z # 6	100	11.00	63	26
8	Z High	Holocene	0 to 4	Z # 7	101	16.83	55.45	27.72
9	Z High	Holocene	8 to 12	Z # 9	102	19.61	56.86	23.53
10	Z High	Holocene	16 to 20	Z # 11	104	17.31	52.88	29.81
11	Between Z and Y	Holocene	0 to 4	C ZY # 1	107	19.63	60.75	19.63

Table 2 Thin Section Averages

	% Porosity	% Allochems	% Cement
Holocene Averages	17.20	57.40	25.40
Pleistocene Averages	25.91	64.13	9.97
Crust Averages	23.49	62.92	13.59

SEM analysis also indicated the presence of biofilms (similar to the sandstone example of Figure 10).

DISCUSSION

The suprising results of this work are the unusual low levels of porosity, and high levels of cement, found in the Holocene eolian calcarenites on San Salvador. This became even more surprising when the values for older Pleistocene eolian calcarenites were considered; their porosity is higher and the cementation lower than for the Holocene material (Tables 1 and 2). The assumption had been that Holocene eolian calcarenites, being young, would show substantial primary porosity and low amounts of cement (White, 1995; Carney and Stoyka, 1993). Then, as the rocks aged, and meteoric water was able to invade the eolianite mass, cementation would progress at the expense of the porosity, as the Pleistocene eolianites were expected to display. But the results, as observed, were the opposite of this expectation. Given that previous studies (Schwabe, 1992; Carney and Stoyka, 1993; White, 1995; Hutto and Carew, 1984; Stowers, 1988) had shown the expected result of young eolianites being porous and weakly cemented, and older eolianites being less porous and better cemented, suspicion fell on the collection and thin section processes. The dry preservation techniques used in this study apparently preserved organic material that otherwise would have been lost in a moist collection regime, and/or by the water thin-section cutting process, which is

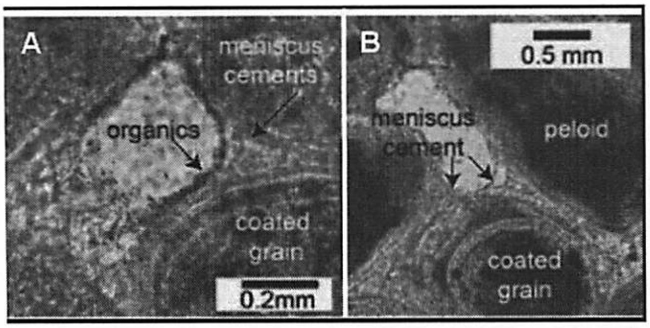

Figure 6. A) Image from a Holocene North Point Member eolianite thin-section, showing no evaporite minerals, but more cement and less porosity relative to image 6B. B) Image from Late Pleistocene Cockburn Town Member eolianite thin-section, again showing no evaporite minerals, less cement than in 6A, but more porosity.

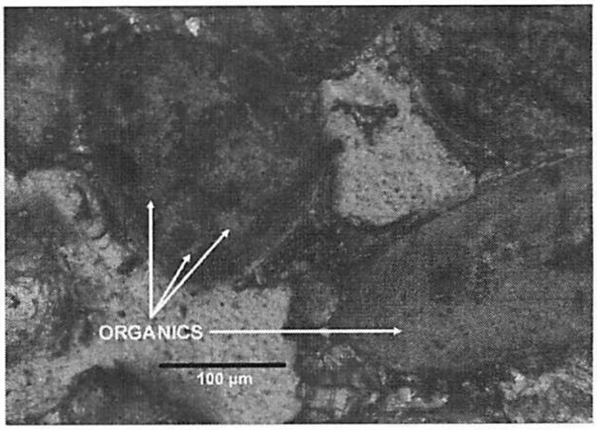

Figure 7. Photomicrograph taken using a confocal microscope showing organic matter (arrows) within peloids and meniscus cements. This image is created by stacking three digital images (plane light and two types of laser light). The laser light causes red luminescence in the organic matter. In this black and white view the organic material is identifiable as light gray areas within the peloids.

more commonly used. These results suggest that the organic matter-bearing cements were preserved by the oil-based sample preparation.

Additional observations show upon examination of prepared samples that the meteoric meniscus cement morphology appears strikingly similar to the morphology of meniscus films grown in a laboratory environment as seen in Figure 10 (Fratesi, 2002). There were brown inclusions seen in thin section and the very small (100 nm) spherical structures seen in SEM which are interpreted as nannobacteria and associated organic matter. There was a biofilm-like morphology and the presence of nannobacteria and organics throughout the calcite crystals, suggesting that at least some of these meniscus cements formed in association with microbial biofilms and mandates that the role of organic matter in cementation be explored further.

Somewhat as a counter point of the famous bathybius of Thomas Henry Huxley, where in the1870s a preservation technique artificially created deep-sea samples that indicated the ocean floor was covered by a living gelatinous mass (Garrison, 2002), the artifice of humid sample collection, and thin-section cutting with water, removed evidence of important biological activity in the tafoni eolianite samples. As observed on San Salvador, the calcareous particles (allochems) making up these eolianites are created by living organisms, it is not surprising that organic material ends up in, and on, the carbonate grains at the time of dune deposition. A study done by Pelle and Boardman (1988) showed no significant concentrations of trace elements associated with residual soil organic matter. They also found that the early–formed, impermeable and laminated calcretes are effective seals against the movement on meteoric waters through eolian units, to create a closed system. Therefore the organic material seen in thin section is likely inherited from the initial deposition of the grains, a closed system. Therefore the organic material seen in thin section is likely inherited from the initial deposition of the grains, and not from additional organic material infiltrating the dune from overlying soils at a later time. The lack of percolation also does not allow for significant additional cementation of the dune interior. Observation of Pleistocene eolianites, as

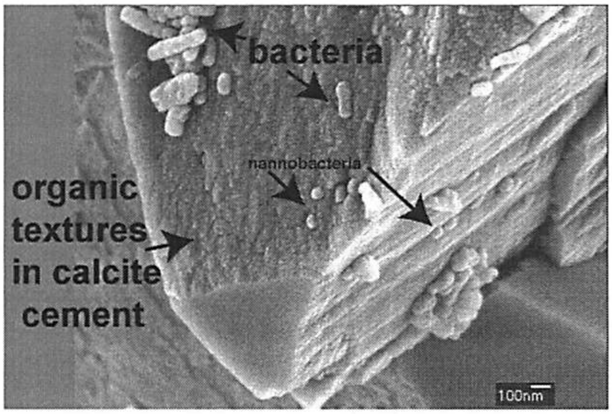

Figure 8. SEM photomicrograph of Holocene samples collected on Cut Cay, showing bacteria and nannobacteria on a calcite surface with organic texture.

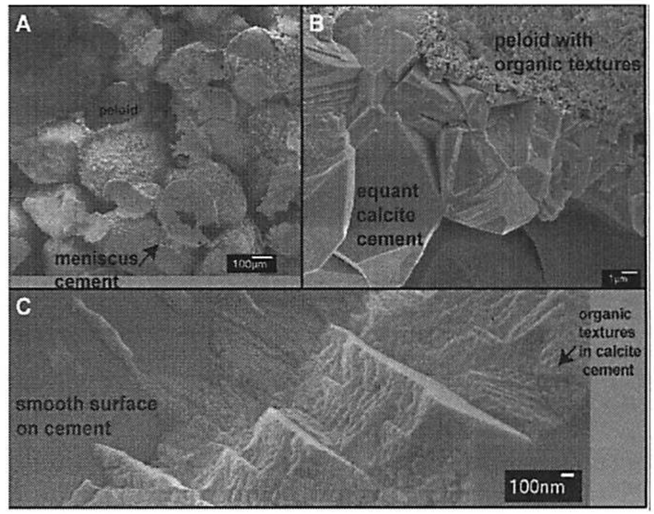

Figure 9. SEM photomicrographs of Holocene samples collected on Cut Cay, showing: A) peloids with rough, clearly organic textures; B) equant calcite cement with mostly smooth surfaces in contact with organic peloid surface; C) calcite cement showing both smooth and organic textures.

seen in quarries and road cuts, demonstrates that despite their greater age compared to Holocene dunes, their interiors crumble and degrade easily as a result of weak cementation.

It is well established that the Holocene eolian calcarenites form quickly after their allcohems are deposited in Bahamian lagoons. The allochem 14C ages for the North Point eolianites cluster at 5,000 yBP, yet sea level was already encroaching on these dunes by 3,000 yBP, thus showing the rapid development of these dunes (Carew and Mylroie, 1995; 1997). Therefore, the allochems were deposited and blown up into dunes while very young. A calcrete crust formed quickly over the surface of these dunes preventing infiltration of meteoric waters and other atmospheric processes, such that substantial organic material was retained on and within the allochems, without later organic addition from the soil above. Microbiological activity is known to occur in subsurface sedimentary rocks and could be expected in this scenario. Such activity apparently created biofilms that assisted not only in occluding porosity, but also in precipitating calcite cements within the biofilm. Removal of the biofilm and therefore the cements present within the film, by standard sample preparation techniques, including water cutting to make blanks and then the thin sections, created the previously reported high porosity and low cement amounts seen in the literature.

The Pleistocene eolian calcarenite samples show a higher porosity and lower cement amount than the Holocene samples described in this study. That outcome is a result of the biological material of the biofilm-precipitated cements being used up and decaying away over the 120 ka time between their deposition during the last interglacial (MIS 5e), and their sampling today. This outcome is also evident in the physical act of sample collection, where once the outside crust on the Pleistocene rocks was broken, the interior eolianite was much easier to sample than its Holocene counterpart. So while the Pleistocene rocks show more cementation, and less porosity than do water-cut Holocene eolianites on San Salvador, they show the opposite relationship to Holocene eolianites that have not had their biological material, and attached biofilm cements, degraded by water-based preparation techniques.

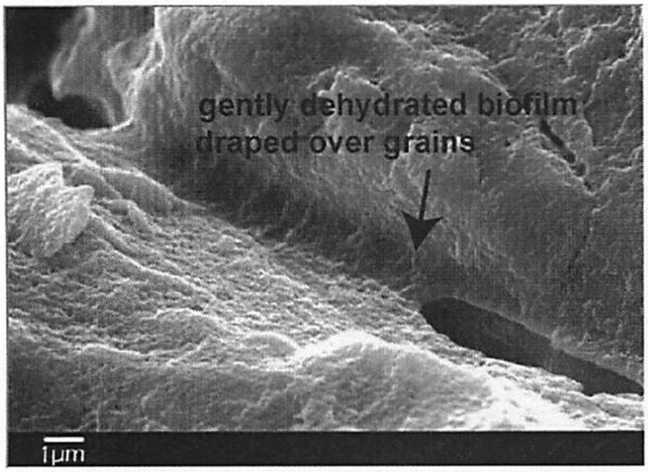

Figure 10. SEM photomicrograph shows that biofilm, induced in the laboratory by placing a sandstone sample in a dilute nutrient solution, has a morphology similar to meniscus cement. Results from this study suggest that precipitation might occur within similar, natural biofilms (Fratesi, 2002).

CONCLUSIONS

The unique sampling and sample preparation regime used for this tafoni study shows that evidence of organic participation of cements in biofilms, resulting in less porosity than shown by previous studies. The biofilms and their precipitated cements are lost when standard water-based thin section preparation procedures are used, and the biofilms are no longer available to serve as a structure for binding cements. The organic biofilm-precipitated cements seem to have a more important roll in cementation on the interior of the dune, than on the outside crust over the dune, where other cementation processes occur. When a comparison is made with Holocene eolian calcarenites and similarly prepared Pleistocene eolian calcarenites, the indication is that through time, there is loss of organic material in the Pleistocene eolianites; and therefore the loss of organically-bound cement which reduces the overall level of cementation of these older rocks and results in increased porosity. This decay of organic material results in softer rocks as the Pleistocene samples were much easier to collect once the initial crust was broken than were the Holocene samples.

As with any research, once results are found, it causes more questions to be asked. Is this situation unique to eolianites, which have never seen phreatic water, or can these interpretations be equally applied to meteoric or marine carbonate cementation environments? Do biofilms create a unique microenvironment that organizes cementation? Does organic matter promote calcite precipitation? When and how does the loss of organic matter occur and how does this affect the geochemical signature of the calcite cement?

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