

Memorandum For: Virginia Fay, Assistant Regional Administrator for Habitat Conservation
NOAA Fisheries Service, Southeast Region

From: Jocelyn Karazsia, Fish Biologist
NOAA Fisheries Service, Southeast Region, West Palm Beach field office

Date: July 22, 2016

RE: Final report from Dr. Peter Swart, University of Miami, describing results
of analysis of sediments collected from coral reefs at the Port of Miami

Enclosed please find the final report from Dr. Peter Swart of the University of Miami describing analysis of 20 sediment samples collected by NOAA divers in April 2016 from sediments that accumulated on coral reef and hardbottom habitats near the Port of Miami Entrance Channel. The sampled locations included sites adjacent to the channel known to be impacted by sedimentation and samples collected at various distances from the channel (up to 1,050 meters north of the channel) where NOAA divers observed signs of sedimentation and impacts to coral reef organisms. The reference samples were collected at sites approximately nine kilometers north of the channel (locations the permit from the Florida Department of Environmental Protection specifies as reference sites for the Middle Reef and Outer Reef), and 2.2 kilometers south of the channel (selected by NOAA divers after the permit-specified reference site appeared affected by sedimentation). Dr. Swart used X-ray diffraction and isotopic composition to examine the mineralogy of the sediment samples to examine their similarity to samples from the reference sites versus the geologic formations the dredge was excavating. Dr. Swart used his extensive knowledge and published studies of the composition of geologic layers to make this distinction. This study indicates the material accumulated on the coral reefs surrounding the federal channel at eight sites is not similar to that of the reference sites and is most likely from the underlying Fort Thompson and Anastasia formations penetrated during the dredging of the Port of Miami Entrance Channel. At another six sites, the accumulated sediments also appeared similar to those from the Fort Thompson and Anastasia formations, but the similarity was not as strong as observed in the previous eight stations. Figure 2 and the Appendix of the report show the locations of these stations. The general pattern being stations closer to the channel were more likely to be similar to the purported dredged material, and the dredged material appeared to extend at least 1,050 meters away from the channel on Middle Reef North and 700 meters away on Middle Reef South. The results reported by Dr. Swart strongly agree with the observations by NOAA divers and discussed in previous reports on the location and extent of sedimentation impacts on coral reef habitat along the Port of Miami Entrance Channel.

Report on the Mineralogy and the Stable Carbon and Oxygen Isotopic Composition of Samples Supplied by NOAA

Final Report

Date: 28 June 2016

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Executive Summary

- The carbonate mineralogy and stable C and O values was determined on 20 samples supplied by NOAA from reference sites and sites impacted by dredging adjacent to the Port of Miami and Miami Beach. Samples were collected by NOAA divers from sediments covering coral reef framework.
- The reference sites had relatively high concentrations of (>90%) aragonite and high-Mg Calcite and lower concentrations of low-Mg calcite (<10%). These sites also had higher carbon and oxygen isotope values.
- In contrast sites which were presumably affected by dredging contained higher concentrations of low-Mg calcite (up to 27%) and more negative carbon and oxygen isotope values. These values are indicative of the sediments being influenced by an allochthonous source of carbonate. These sites also had higher amounts of quartz.
- The stable carbon and oxygen isotopes as well as the mineralogy of the affected samples are consistent with the source of contamination being the underlying Anastasia and Fort Thompson formations.

Introduction

Twenty samples were provided by NOAA for the determination of the carbonate mineralogy (low-magnesium calcite (LMC), high-Magnesium calcite (HMC), and aragonite) as well as a qualitative determination of the abundance of quartz. The stable isotope ratios of carbon (^{13}C and ^{12}C) and oxygen (^{18}O and ^{16}O) were also determined. These analyses were made to determine the amount of non-indigenous materials in the supplied samples. As such samples were supplied from presumed pristine sites (reference) and from sites presumed to be impacted by dredging.

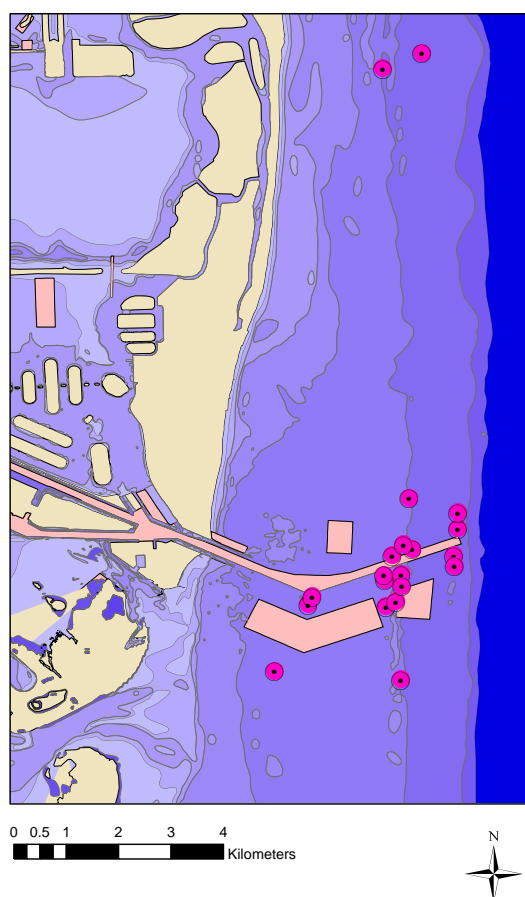


Figure 1: Location of samples collected in this study.

to the sediment collection location. Sediments were scooped from the reef framework into the bottle until the sample bottle was approximately 3/4 to 7/8 full, depending on the amount of

Methods

Samples

Two sediment samples were collected at each of the sites shown in Figure 1. Sediment sample bottles were labelled with the site number and date, then filled with water to reduce their buoyancy before each dive. Sample sites correspond to locations where NOAA divers conducted line intercept and roving transect assessments of benthic community conditions and sedimentation. After completing a 50-m line intercept transect, divers opened the bottle to collect sediment. Metal rulers (30 cm by 2.6 cm) were used to collect a cross-section of the sediment layer covering the reef framework into a 400 ml, C-QEC certified clean, HPDE bottle. The sediment was collected from the entire sediment profile.

Sample bottles were tilted to be close

sediment available at the location. This method of sampling resulted in collection of turf algae and cyanobacteria along with sediments. The cap was replaced on the bottle and the bottle placed into the diver's tool bag. Samples were brought to the boat where they were stored in a locked cabin until the end of field operations. Sediment samples were brought to the NOAA Fisheries office in West Palm Beach, Florida, where they were stored at room temperature. The samples were brought to the stable isotope laboratory at the University of Miami, Rosenstiel School of Marine and Atmospheric Sciences where subsamples were taken for X-ray diffraction (XRD) and stable isotope analysis. One sample bottle from each location was randomly selected to take a subsample from. The selected sample bottle was decanted to remove excess water prior to taking the subsample. Each subsample was placed on a drying disc labelled with the location name from the respective sample bottle. Sediment sample bottles were recapped and remained in the custody of NOAA Fisheries staff during the subsample removal. Subsamples were retained by the UM Faculty for preparation, grinding and analyses.

X-Ray Mineralogy

The percentages of aragonite, HMC, and LMC of bulk and different size fractions were determined using X-ray diffraction analysis after the method of Swart et al. (2003). The purpose of these analyses is to assess whether there are amounts of non-indigenous carbonates influencing the reef. In this method the sample is assumed to be completely composed of aragonite, HMC, and LMC. Areas of the appropriate peaks for each mineral are determined using a scan between 23 and 32° 2θ (CuKα radiation). These areas are then compared to standard relationships between peak area and percentage mineral and the percentage of the mineral in the sample determined.

Stable Isotopes

The stable carbon and oxygen isotopic composition ($^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$) of the carbonate materials was also measured as these values can give clues to the origin of the carbonate minerals found on the coral framework surfaces. These isotopic values were determined using dissolution in phosphoric acid using the common acid bath method (Swart et al., 1991) at 90°C. The gas produced was analysed using a Finnigan-MAT 251. Data produced using both methods were corrected for isobaric interferences using the procedures (Craig, 1957) modified for a triple collector mass

spectrometer. Data are reported in the conventional $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ notation in parts per thousand (‰) relative to Vienna Pee Dee Bee (V-PDB) as defined by equations 1 and 2.

$$\delta^{13}\text{C} = \left[\frac{^{13}\text{C}_{\text{sample}}}{^{13}\text{C}_{\text{VPDB}}} - 1 \right] * 1000 \quad (1)$$

$$\delta^{18}\text{O} = \left[\frac{^{18}\text{O}_{\text{sample}}}{^{18}\text{O}_{\text{VPDB}}} - 1 \right] * 1000 \quad (2)$$

Average standard based on replicate analyses of internal standards obtained from both methods is < 0.1‰. Negative values indicate that the samples contain more of the rare isotope relative to the

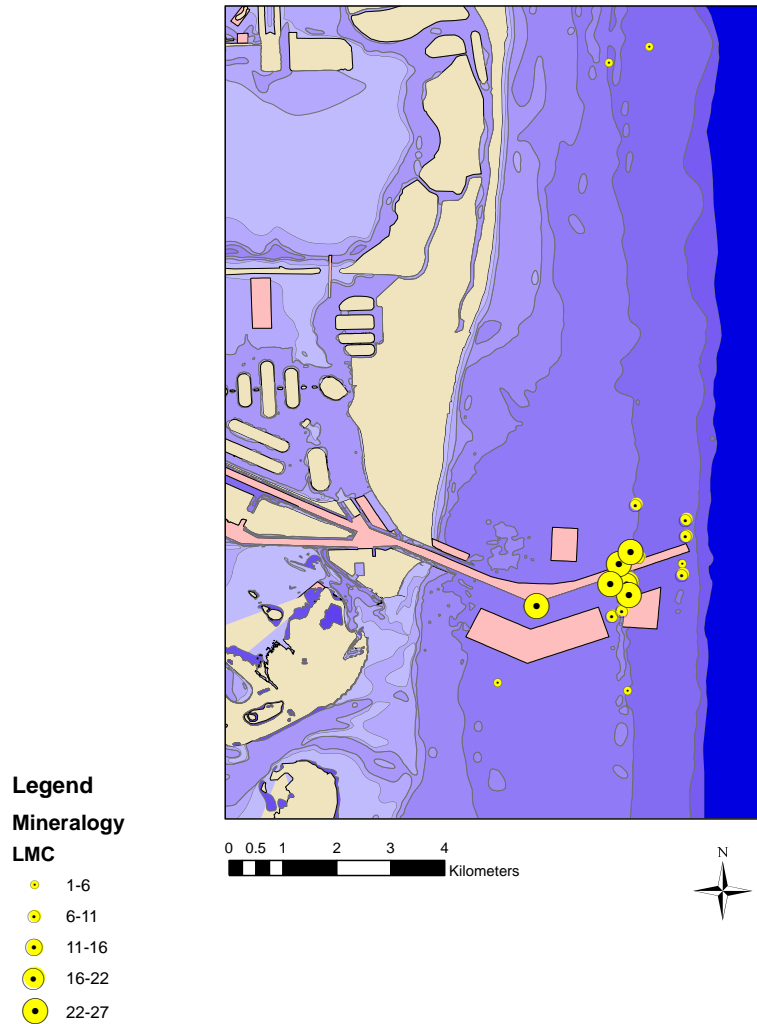


Figure 2: Concentration of LMC are various sites. Values are in percent of the total carbonate at each location.

standard and positive values indicate that the samples contain more of the more of the heavier form.

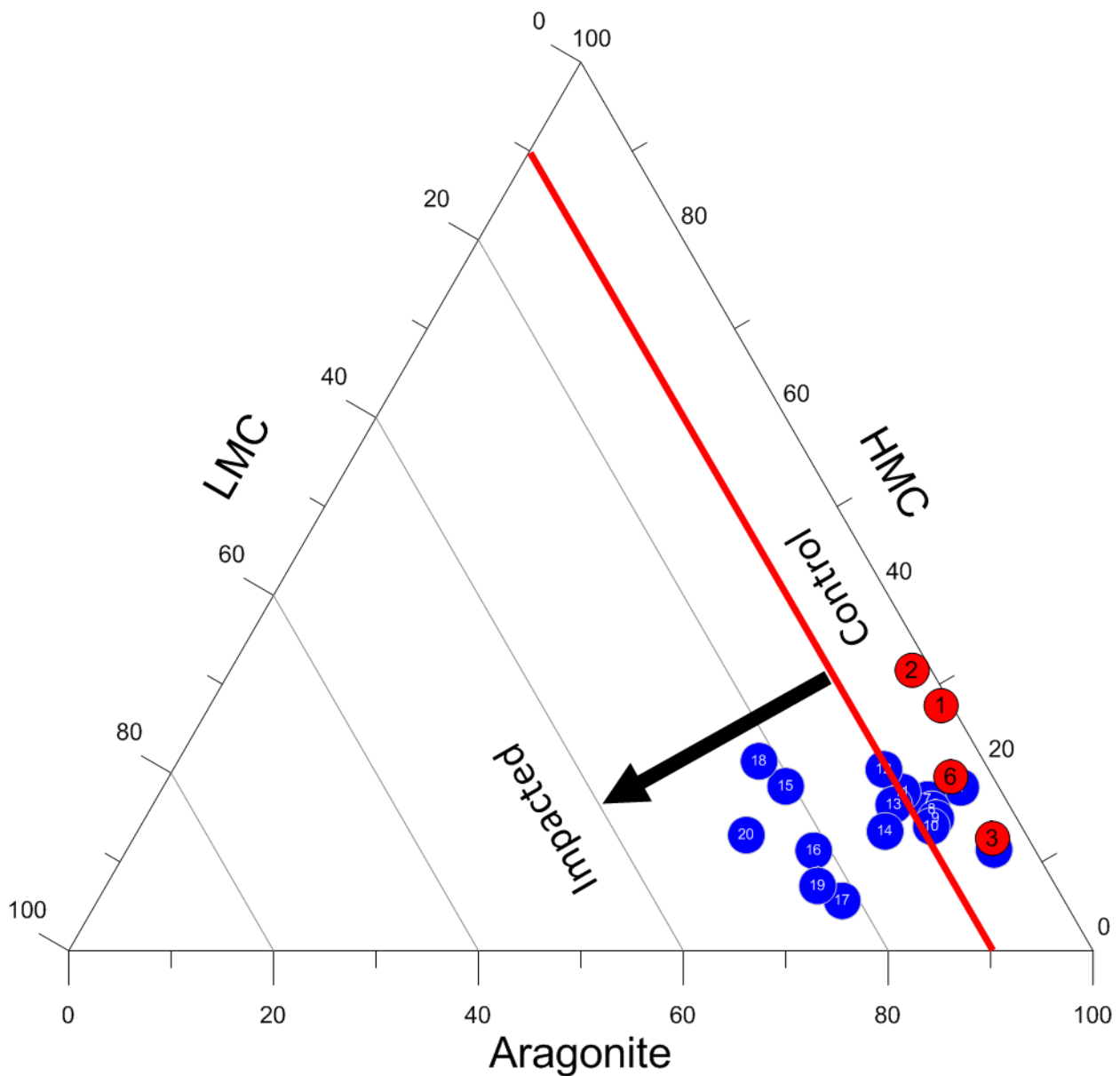


Figure 3: Ternary diagram showing the percentage of carbonate mineralogy from each sample. The identities of the samples are given in Table 1. The red symbols represent the reference sites. The red line represents a LMC content of 10% above which samples are considered to be influence by allochthonous carbonate material.

Results

All data are shown in Table 1. Correlation coefficients between the various measured parameters are shown in Table 2.

X-ray Mineralogy

Aragonite: The percentage of aragonite varied from between 57 to 85% with a mean concentration of 72%. The highest concentrations were found at the reference sites, while the lowest concentrations were present at the dredge affected sites.

High Mg Calcite: The percentage of HMC varied from 6 to 21% with the highest values associated with the reference sites.

Low Mg Calcite: The percentage of LMC varied from 2 to 27% with the lowest values associated with the reference sites (Figure 2 and 3).

Stable Isotopes

Carbon: The carbon isotopic composition ($\delta^{13}\text{C}$) varied from +1.09 to +2.76‰. The values were inversely correlated with the concentration of LMC ($r=-0.88$, $n=20$, $p<0.01\%$) and quartz ($r=-0.54$, $n=20$, $p<0.05$) and positively correlated with concentration of aragonite ($r=+0.55$, $n=20$, $p<0.05$) and HMC ($r=+0.52$, $n=20$, $p<0.05$). The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values were positively correlated ($r=+0.91$, $n=20$, $p<0.01$).

Oxygen: The oxygen isotopic composition ($\delta^{18}\text{O}$) varied from -0.71 to -1.58 ‰. The values were inversely correlated with the concentration of LMC ($r=-0.79$, $n=20$, $p<0.01\%$) and positively correlated with concentration of aragonite ($r=+0.55$, $n=20$, $p<0.05$). There were no statistically significant correlations between $\delta^{18}\text{O}$ and the concentration of quartz and $\delta^{18}\text{O}$ and the concentration of HMC.

Discussion

Mineralogy

Modern Reefal Environments: The mineralogy of Modern carbonate sediments is dominated by aragonite which typically comprises as much as 90-95% of the sediment (Bathurst, 1971; Milliman, 1974). Aragonite is produced by a wide a variety of organisms on a coral reef including the majority of the corals and green algae. A secondary naturally occurring component is HMC. This mineral, produced by many calcareous algae as well some foraminifera and echinoderm, is a form of calcite, but as the name implies contains high amounts of the element Mg in its structure. Typically the amount of HMC is between 10-15%. The most stable form of calcite (LMC) is the least abundant in carbonate environments, usually less than 5%. Low-Mg calcite is formed by molluscs and foraminifera and typically only comprises < 5% of reefal sediments. Based on descriptive studies of sediments in the Florida Keys (Lidz et al., 1985; Swinchat, 1965) it might be expected than the

sediments analysed in this study would be consistent with these values unless they were influenced by an additional source.

In normal carbonate dominated environments quartz is not a common constituent. However, in the case of the Florida coast there has been significant input of quartz sand from the

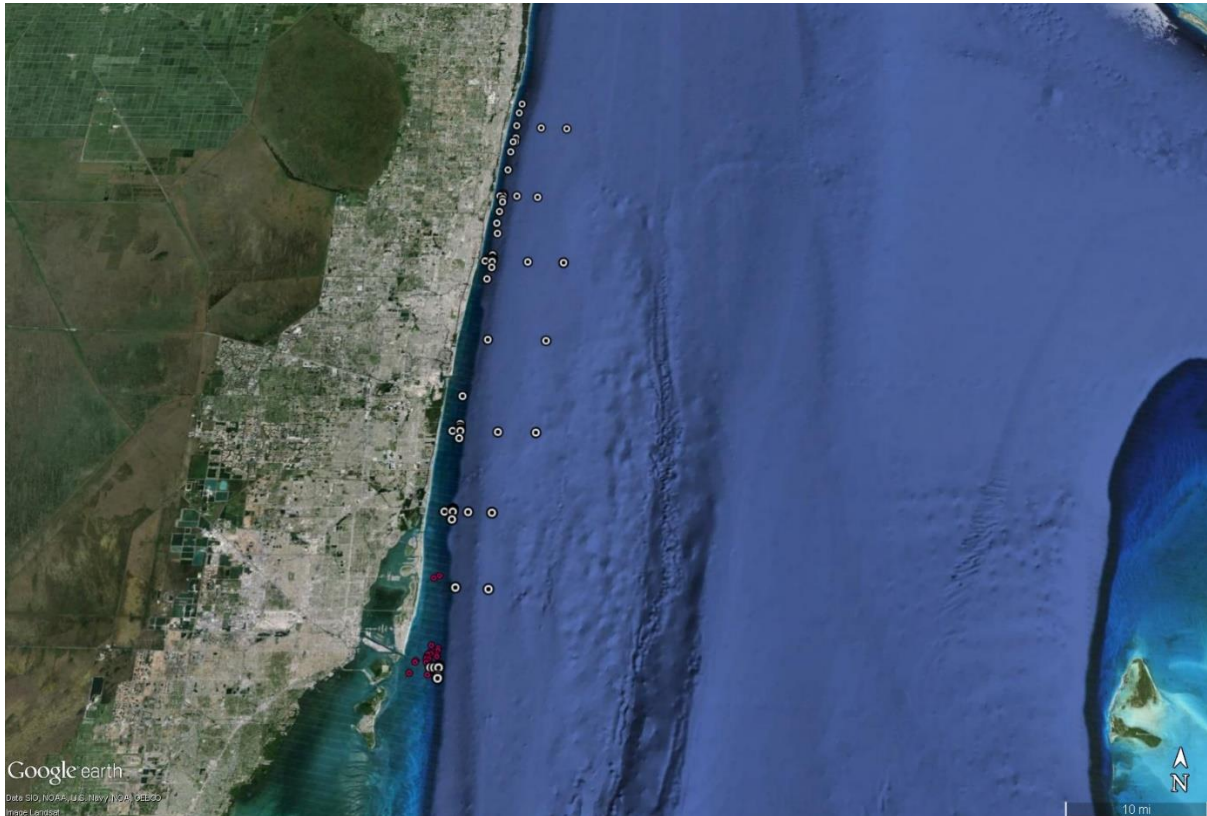


Figure 4: Distribution of samples from this study (purple symbols) as well as material from the NOAA FACE (white symbols) project for which the C and O isotope data are presented in Figure 5.

north, brought down the coast by long-shore drift.

Stability of Carbonate Minerals: Both aragonite and HMC are metastable, meaning that with time they will dissolve and be converted to LMC (Morse and Mackenzie, 1990) (pg. 425-431). This takes place over millions of years in the marine environment, but is greatly accelerated when sediments are exposed to freshwater. Therefore when sea level varies, as it has done so many times over the past 1 to 2 million years, reefal sediments composed of aragonite and HMC are converted to LMC (Land, 1973). In fact the majority of the underlying rocks (Fort Thompson and Anastasia) in the port of Miami have been altered and are exclusively LMC with intercalated layers of quartz sand.

Stable Isotopes: Carbon and oxygen both have more than one stable isotope. The abundance of these isotopes is controlled by the formation process as well the same processes which convert aragonite and HMC to LMC. Generally speaking unaltered reefal materials have characteristic $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values (Gischler et al., 2009) which change when the sediments are exposed to freshwater water (Morse and Mackenzie, 1990). Hence as the carbonate mineralogy of the Fort Thompson and Anastasia formations are exclusively composed of LMC (with interbedded quartz), these units contain $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values which are distinct (more negative) from the Modern sediments. Although there have not been to our knowledge any stable isotope studies of the Fort Thompson and Anastasia, their $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values are likely to be similar to those of the younger Miami Limestone, for which there are several studies.

Interpretation of the Data

Low-Mg Calcite: The concentration of LMC in the studied samples ranges from 2 to 27%. The lowest concentrations were associated with the project selected reference sites. Although I would consider concentrations greater than ~10% unusual for a carbonate dominated environment, one must consider that there might be some contribution from the material used to renourish Miami Beach in the 1970s. These materials were excavated from off shore of the Beach and probably contained material that was exclusively composed of LMC. Such material could have moved off shore from Miami Beach and transported by long-shore drift to the south. However, the reference sites in this study, which also presumably may have received some of the renourishment material, only contained 2-8% LMC. Therefore, I think it is fair to assume that these high amounts of LMC are not natural and presumably were derived from dredged material originating from the Anastasia and Fort Thompson formations. Based on core borings made for the Port of Miami tunnel project, these formations are present in the area at depths of < 60 ft (Meyer, 2011). Assuming that the natural sediment is composed of ~ 2 % LMC while the contaminant material is 100% LMC a simple mixing model can be constructed, then up to 25% of the sediments at some sites can be considered to have been derived from a non-natural source.

Aragonite and HMC: As the concentration of aragonite is inversely correlated with the concentration of LMC similar conclusions can be reached using these data.

Stable Isotopes: In Figure 5 data are shown from this study as well as the mean data from 72 samples collected by NOAA during the FACE program (Figure 4). The stable C and O isotopic composition of the samples measured in this study lie on a mixing line between the unaffected sediment and material likely to be representative of the dredged material. For the purposes of this comparison I have used data analyses made on the Miami Limestone. These are likely to be

representative of material which has been exposed to freshwater diagenetic processes. Using a two component mixing model similar calculations can be made to that obtained from the model constructed using LMC. However, there are uncertainties because of a greater natural variability in the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of the natural system and uncertainties regarding the precise values of the contaminant end member.

Summary

There is evidence to suggest that at least 25% of the material on some of the impacted reefs is not indigenous. Based on its mineralogy and stable O and C isotopic composition, the most likely source is the underlying Fort Thompson and Anastasia formations, penetrated during the dredging operations.

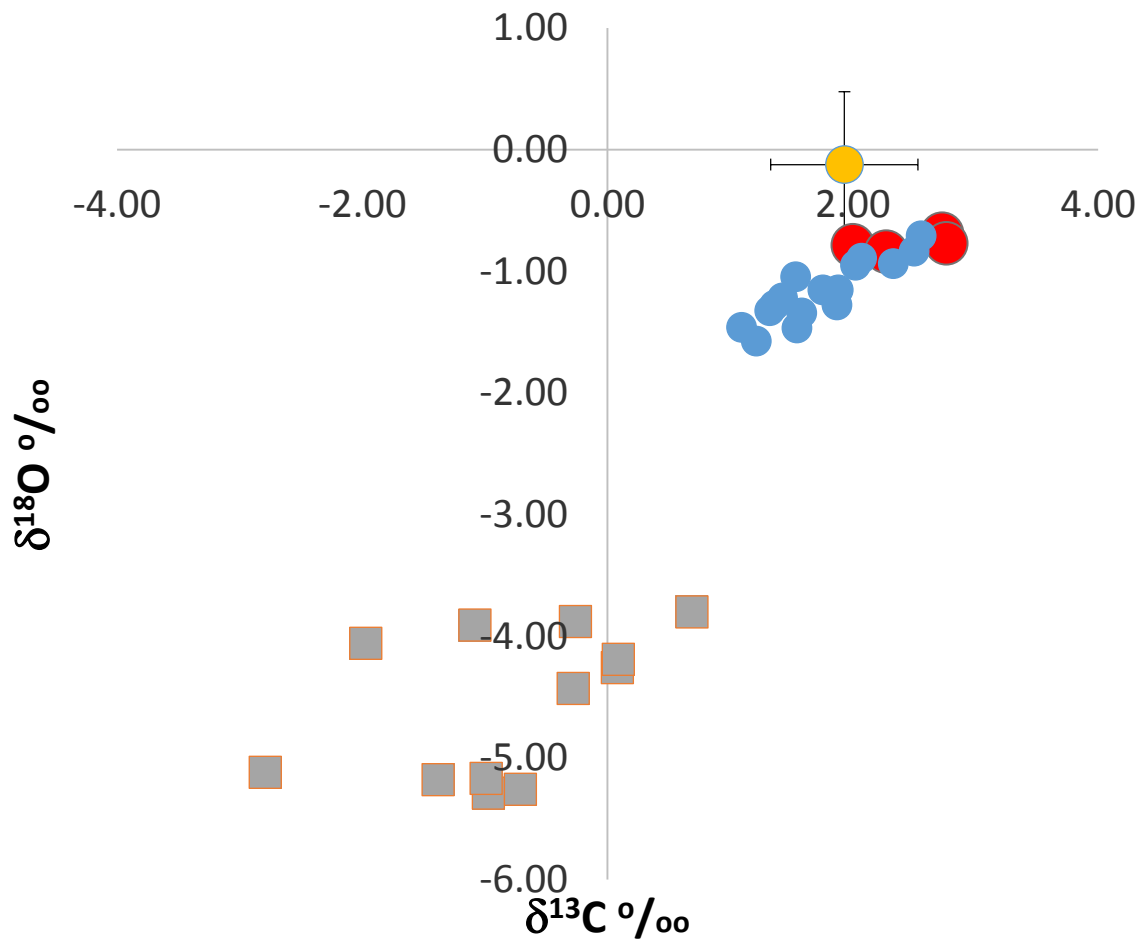


Figure 5: Samples from dredge sites (blue solid circles), and reference sites (red solid circles), relative to the mean values of 72 samples of sediments from Dade and Broward counties during the FACE program (orange circle with error bars), and samples from the Miami Limestone (grey squares). The FACE data are comparable to the material from the reference sites. Their elevated oxygen isotope values reflect the more northerly location (cooler water temperature).

#	ID	Lat	Lon	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	A	HMC	LMC	Quartz
1*	R2N-C	25.845	-80.102	2.00‰	-0.79‰	71%	28%	1%	21.49
2*	R2S-2200-LR	25.741	-80.099	2.73‰	-0.69‰	67%	32%	2%	66.25
3*	HBS-C	25.742	-80.121	2.27‰	-0.84‰	84%	13%	3%	173.27
4	R3S-150-SG	25.762	-80.090	2.33‰	-0.94‰	78%	18%	4%	179.34
5	HBS-200	25.753	-80.115	2.56‰	-0.71‰	85%	11%	4%	279.12
6*	R3N-C	25.848	-80.095	2.76‰	-0.77‰	76%	20%	4%	27.92
7	R3S-350-SG	25.760	-80.090	2.50‰	-0.84‰	75%	17%	8%	38.71
8	R3N-100-LR	25.766	-80.089	2.02‰	-0.95‰	76%	16%	8%	110.65
9	R3N-400-LR	25.769	-80.089	1.88v	-1.16‰	77%	15%	8%	35.86
10	R2N-1050-LR	25.772	-80.098	1.87‰	-1.28‰	77%	14%	9%	117.35
11	R2S-700-RR	25.753	-80.102	2.07‰	-0.89‰	72%	18%	10%	83.53
12	R2S-700-LR	25.754	-80.100	1.76‰	-1.15v	69%	20%	10%	87.92
13	R2N-50-LR	25.763	-80.097	1.58‰	-1.34‰	72%	16%	11%	135.57
14	R2S-200-RR	25.758	-80.102	1.43‰	-1.22‰	73%	13%	14%	167.67
15	R2N-200-LR SSS2 On Reef	25.759	-80.099	1.21‰	-1.58‰	61%	19%	21%	222.38
16	R2N-50-RR	25.762	-80.101	1.09‰	-1.46‰	67%	11%	22%	189.12
17	R2N-200-LR SSS2 Sand Channel	25.764	-80.099	1.54‰	-1.47‰	73%	6%	22%	255.33
18	R2S-400-LR	25.757	-80.099	1.36‰	-1.28‰	57%	21%	22%	284.08
19	HBS-CP	25.755	-80.114	1.54‰	-1.05‰	69%	7%	23%	448.19
20	R2S-100-RR	25.759	-80.102	1.32‰	-1.33‰	60%	13%	27%	219.73

Table 1: Stable C and O isotope analyses and percentage of aragonite (A), high-Mg calcite (HMC), and low-Mg calcite (LMC) as proportion of the carbonate fraction of the sediment. The amount of quartz is indicated by the peak area of the 101 peak. This is not quantitative, but higher peak areas are correlated with greater amounts of quartz. Samples marked with an asterisk are reference sites.

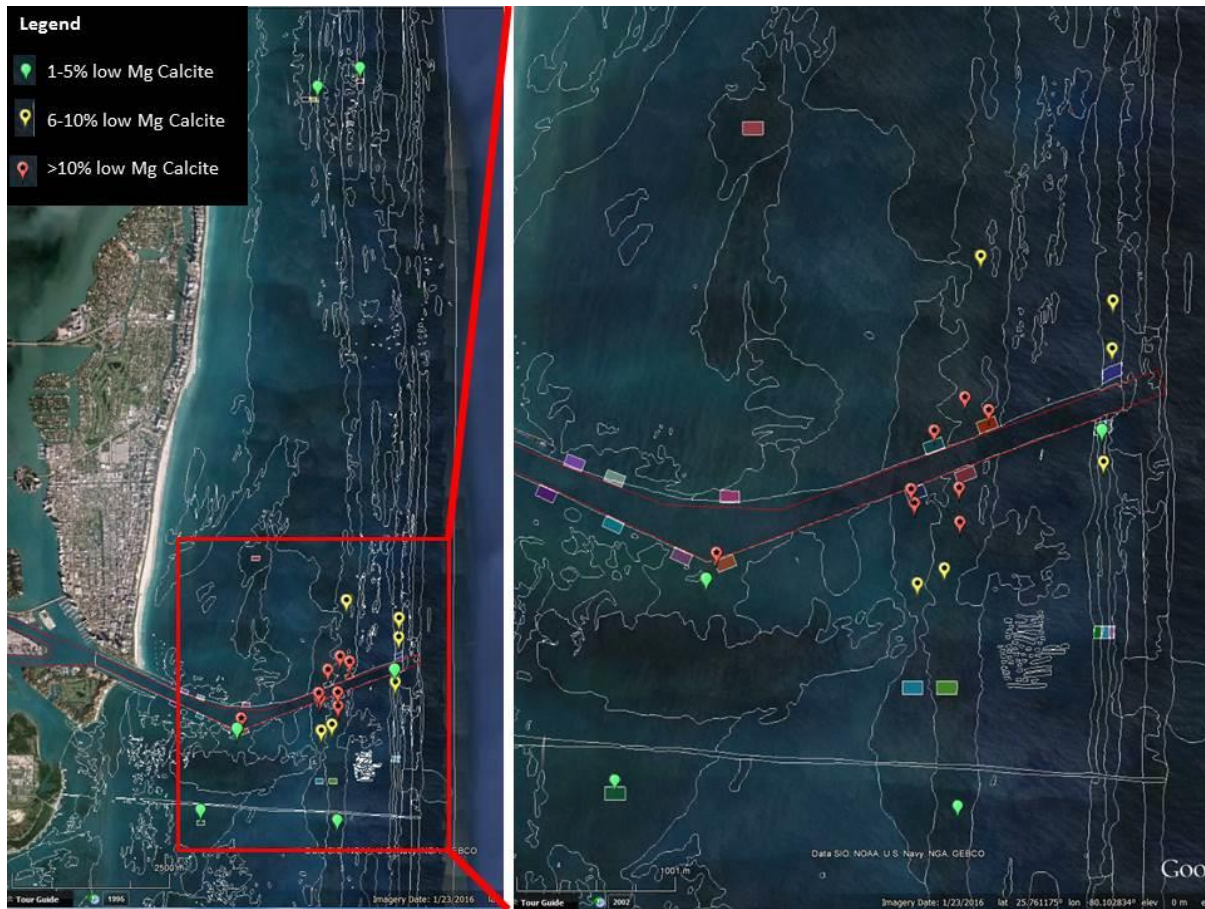
Correlations (Spreadsheet1) Marked correlations are significant at $p < .05000$ N=20 (Casewise deletion of missing data)								
Variable	Means	Std.Dev.	C	O	A	H	LMC	Q
C	1.9424	0.5674	1.00000	0.91488	0.55336	0.52200	-0.88036	-0.54095
O	-0.7430	0.2780	0.91488	1.00000	0.53085	0.43004	-0.79202	-0.35850
A	0.7201	0.0733	0.55336	0.53085	1.00000	-0.26034	-0.69706	-0.24453
H	0.1640	0.0611	0.52200	0.43004	-0.26034	1.00000	-0.51081	-0.59285
LMC	0.1155	0.0823	-0.88036	-0.79202	-0.69706	-0.51081	1.00000	0.65800
Q	157.174	108.073	-0.54095	-0.35850	-0.24453	-0.59285	0.65800	1.00000

Table 2: The regression coefficients between the various parameters measured in this study. Values which are significantly significant at the 95% confidence limits are shown in red.

References

- Bathurst, R.G.C. (1971) Carbonate sediments and their diagenesis, 2nd ed. Elsevier, Amsterdam.
- Craig, H. (1957) Isotopic standards for carbon and oxygen and correction factors for mass-spectrometric analysis of carbon dioxide. *Geochim. Cosmochim. Acta* 12, 133-149.
- Gischler, E., Swart, P.K. and Lomando, A.J. (2009) Stable isotopes of carbon and oxygen in modern sediments of carbonate platforms, barrier reefs, atolls and ramps: patterns and implications, in:
- Swart, P.K., Eberli, G.P., McKenzie, J.A. (Eds.), *Perspectives in Carbonate Geology: A Tribute to the Career of Robert Nathan Ginsburg*, pp. 61-74.
- Land, L.S. (1973) Holocene meteoric dolomitization of Pleistocene limestones, North Jamaica. *Sedimentology* 20, 411-424.
- Lidz, B.H., Robbin, D.M. and Shinn, E.A. (1985) Holocene carbonate sedimentary petrology and facies accumulation, "Looe-Key-National Marine -Sanctuary, Florida". *Bull. Mar. Sci.* 36, 672-700.
- Meyer, M. (2011) Geotechnical/geologic experience within the Fort Thompson formation, Langan Project 300054001, Miami.
- Milliman, J.D. (1974) *Marine carbonates*. Springer Verlag, Berlin.
- Morse, J.W. and Mackenzie, F.T. (1990) *Geochemistry of Sedimentary Carbonates*. Elsevier, p. 707 p.
- Swart, P.K., Burns, S.J. and Leder, J.J. (1991) Fractionation of the stable isotopes of oxygen and carbon in carbon dioxide during the reaction of calcite with phosphoric acid as a function of temperature and technique. *Chem. Geol.* 86, 89-96.
- Swart, P.K., James, N.P., Mallinson, D., Malone, M.J., Matsuda, H. and Ilmo, T. (2003) Data Report: Carbonate Mineralogy of Sites Drilled during Leg 182 in: Feary, D.A., Hine, A.C., Malone, M.J. (Eds.), *Proceedings of the Ocean Drilling Program Scientific Results*. Ocean Drilling Program, College Station.
- Swinchat, J.P. (1965) Significance of constituent composition texture and skeletal breakdown in some recent carbonate sediments. *J. Sed. Pet.* 35, 71-8.

Appendix



After the report was received, the NMFS noted Figure 2 was not displaying properly on some computers. To address this issue, the NMFS made a new version of Figure 2 using the same data as the original figure but with symbols more likely to display correctly across a broader range of computer platforms. Green balloons indicate concentrations of low Mg Calcite (LMC) up to 5 percent. Yellow balloons indicate LMC concentrations of 6 to 10 percent. Red balloons indicate LMC concentrations greater than ten percent.