

KECK GEOLOGY CONSORTIUM

**PROCEEDINGS OF THE TWENTY-SECOND
ANNUAL KECK RESEARCH SYMPOSIUM
IN GEOLOGY**

April 2009
Franklin & Marshall College, Lancaster PA.

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2008-2009 PROJECTS

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(GRENVILLE PROVINCE, NEW YORK)**

Faculty: *WILLIAM H. PECK, BRUCE W. SELLECK* and *MARTIN S. WONG*: Colgate University

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ONTARIO AND QUEBEC, CANADA**

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**BLOCK ISLAND, RI: A MICROCOSM FOR THE STUDY OF ANTHROPOGENIC & NATURAL ENVIRONMENTAL
CHANGE**

Faculty: *JOHAN C. VAREKAMP*: Wesleyan University and *ELLEN THOMAS*: Yale University & Wesleyan University

Students: *ALANA BARTOLAI*: Macalester College; *EMMA KRAVET* and *CONOR VEENEMAN*: Wesleyan University; *RACHEL NEURATH*: Smith College; *JESSICA SCHEICK*: Bryn Mawr College; *DAVID JAKIM*: SUNY.

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Keck Geology Consortium: Projects 2008-2009
Short Contributions – RHODE ISLAND

BLOCK ISLAND, RI: A MICROCOSM FOR THE STUDY OF ANTHROPOGENIC AND NATURAL ENVIRONMENTAL CHANGE

Project Director: *JOHAN C. VAREKAMP*: Wesleyan University

Project Faculty: *ELLEN THOMAS*: Yale University & Wesleyan University

RECONSTRUCTING THE PALEOENVIRONMENT OF THE GREAT SALT POND: A STABLE ISOTOPE ANALYSIS OF FORAMINIFERA *ELPHIDIUM EXCAVATUM* OVER THE LAST 1750 YEARS

ALANA BARTOLAI: Macalester College

Research Advisor: Kelly MacGregor

FORAMINIFERA AS PROXIES FOR SALT MARSH ESTABLISHMENT AND EVOLUTION ON BLOCK ISLAND, RHODE ISLAND

EMMA KRAVET: Wesleyan University

Research Advisors: Ellen Thomas and Johan Varekamp

ATMOSPHERIC MERCURY DEPOSITION IN AN ISOLATED ENVIRONMENT: A 300-YEAR RECORD AT BLOCK ISLAND, RHODE ISLAND

RACHEL NEURATH: Smith College

Research Advisor: Robert Newton

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JESSICA SCHEICK: Bryn Mawr College

Research Advisor: Donald Barber

A 3.5 KY SEDIMENTARY RECORD OF THE GREAT SALT POND ON BLOCK ISLAND, RI

CONOR VEENEMAN: Wesleyan University

Research Advisor: Johan Varekamp

Funding provided by: Keck Geology Consortium Member Institutions and NSF (NSF-REU: 0648782)

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ALANA BARTOLAI: Macalester College
Research Advisor: Kelly MacGregor

INTRODUCTION

Marine sediments collected from lake cores can record past climatic change through proxies for water salinity, temperature, oxygenation, and the local carbon cycle. Microfossil foraminifera, as well as other marine invertebrates which leave calcium carbonate shells, are frequently utilized for paleoclimate studies because they interact with the environment during life and are preserved in the substrate material. Foraminifera are single-celled marine organisms possessing calcium carbonate shells and are abundant in the fossil record. These organisms extract elements such as carbon and oxygen from the ocean water to build their tests and stable isotope analysis on the shell composition can reveal changes in ocean chemistry over time (Finelli 1998). The most frequently used ratios of isotopes for forams are $^{18}\text{O}/^{16}\text{O}$ and $^{13}\text{C}/^{12}\text{C}$.

This study examines two sediment cores from the Great Salt Pond, on Block Island, Rhode Island. Stable isotope analysis on the shells of foraminifera *Elphidium excavatum* from sediment cores will provide insights into the oscillations of the pond from fresh to saltwater environments as well as overall climate variation. The cores cover the last 1800 years, which provide information on the Little Ice Age, the Medieval Warm Period and evidence for eutrophication as a reflection of the impact of island inhabitants.

Stable Isotopes: Carbon and Oxygen

Oxygen isotopes use the ratio of heavy to light oxygen in marine sediments, ice cores, or fossils

and compare it to an international standard known as the PeeDee Belemnite standard for carbonates. Ocean waters rich in heavy oxygen, ^{18}O , inform us that light oxygen was being trapped in ice sheets, indicating a generally cooler climate (Nurnberg 2000). Ocean waters rich in light oxygen, ^{16}O , are associated with generally fresher, less saline water. On a global scale this can indicate warmer temperatures and on a local scale can indicate heavier rainfall. Oxygen isotope proportions are expressed by the following equation:

$$(1) \quad \delta^{18}\text{O} = [(^{18}\text{O}/^{16}\text{O})_{\text{sample}} - (^{18}\text{O}/^{16}\text{O})_{\text{std}} / (^{18}\text{O}/^{16}\text{O})_{\text{std}}] \times 10^3$$

The result of this equation can either be negative values that indicate a higher ratio of ^{16}O or positive values referring to larger amount of ^{18}O in the ocean (Parrish, 2002).

Carbon isotopes ratios reflect changes in ocean circulation and productivity. The photosynthetic process preferentially uses lighter ^{12}C isotope. In a lake or pond, this means that the plant material is enriched with ^{12}C and the water has higher ratios of ^{13}C . Higher ratios of ^{13}C indicate a warmer climate, with more photosynthetic processes (Nurnberg). Carbon isotope proportions are measured similar to equation (1) replacing $^{18}\text{O}/^{16}\text{O}$ with $^{13}\text{C}/^{12}\text{C}$.

FIELD SETTING

Block Island is located approximately 15 km south from the Rhode Island coastline. The exact age of formation is not known but it was formed as a terminal moraine between 21,000 and 24,000 years BP as the Laurentide ice sheet retreated (Boothroyd,

Sirkin 2002). Approximately 6000 years BP, Block Island consisted of two islands separated by a glacial channel that is now the Great Salt Pond (Sirkin 13). A number of coastal processes have since connected the two islands by tombolos, and the Great Salt Pond is enclosed with the exception of a breach.

The Great Salt Pond has an area of 573 acres making up approximately 9% of the area of the island. There are no streams running into the pond and the water is a mixture from the Atlantic Ocean and precipitation. Historical documents and archaeological data suggest that the connection of the Great Salt Pond to the Atlantic Ocean has been closed in the past by drifting sand and later opened as a breach by the inhabitants of the island. The detailed history of the oscillations between fresh, brackish and salt water environments is unknown.

Currently, the GSP is connected to the Atlantic Ocean by a breach, with modern salinity averaging between 30-32 ppt. This is slightly lower than average oceanic salinity of 33-37 ppt (Hale 2002). In the 1900's, Block Island became a popular tourist destination, averaging more than 800 boats anchoring in the pond each day, increasing the threat of pollution (Littlefield 2002). Block Island's rich history provides the Great Salt Pond as an interesting location for paleoenvironmental reconstruction.

METHODS

Field Methods

Sediment cores were taken at 11 different locations throughout the Great Salt Pond, collected at water depths between 18 to 30 ft. Locations for sediment cores were chosen from grab samples that yielded fine dark clay suggesting deeper water with lower deposition rates and the least chances of human-induced erosion. Two methods of coring were used, hammer coring and vibracoring. Seven hammer cores ranging from 59cm to 119 cm in length and four vibracores ranging in core length from 117 cm to 232 cm were collected. Figure 1 shows the location of all cores taken from the Great Salt Pond.

This study focuses on two hammer core samples

Core Locations

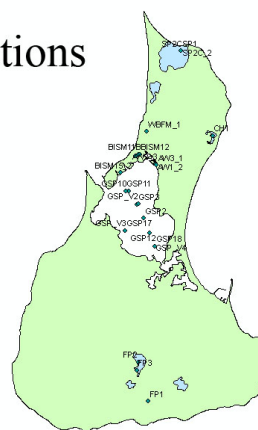


Figure : A map of core sample locations taken in the Great Salt Pond of Block Island, RI. Map from Conor Veeneman.

from the Great Salt Pond, GSP2 and GSP3. GPS locations for the cores were (N41°11.384;W 071°34.660) and (N41°11.550 and W071°34.766), respectively at water depths of 30ft. The lengths of the sediment cores were 59 cm for GSP2 and 112 cm for GSP3.

Lab Methods

The cores were vertically extracted, using a core plunger and sampling occurred at 2 cm intervals continually throughout the entire core. Each 2 cm section was separated into two samples for geochemical and foraminiferal analysis. The samples for foraminiferal analysis were wet sieved through a 63 micron screen, then gently washed with deionized water and an all purpose cleaner. Blue dye was used to stain the samples to prevent cross contamination of further samples and then placed in formaldehyde for preservation.

A series of 80 samples were chosen for foraminiferal analysis from two cores from the Great Salt Pond. This included the entire core of GSP2 and the upper 50 samples of GSP3. Based on previous studies of benthic foraminifera in the Long Island Sound, the species *Elphidium excavatum* for carbon and oxygen isotopes since it is abundant throughout the core and typical of estuarine environments (McGann, 2008). Samples were first dry sieved through a 150 micron screen and using a microscope foraminifera were picked from all 80 samples with a damp non-

synthetic brush. The sample at 32-34 cm depth contained fewer than 10 forams and was not analyzed. Special attention was given to choose *E. excavatum* that were undamaged. Approximately 10-15 specimens of *E. excavatum* were picked for stable isotope analysis. Oxygen and carbon stable isotopes were analyzed in specimens of *E. excavatum* at the University of Minnesota's Limnological Research Center. Preparation for analysis included placing samples in a test tube with ethanol in a sonicator for 15 seconds followed by another 15 seconds in the sonicator with de-ionized water. The samples were run on a mass spectrometer (MAT252).

RESULTS

Core Stratigraphy:

The cores are composed of fine dark clay with abundant shell fragments, some identifiable as *Lucina* and slipper limpets. Plant material is found in samples of the core and the upper section of both GSP2 and GSP3 contain dark gray clay enriched with organics. Intermittent sand layers mixed within the sequence of clay layers are also apparent that range from 2-4 cm in width.

Age Data

Radiocarbon-14 dating on core GSP3 resulted in two age dates. GSP3-32, a sample that is 62-64 cm from the top of the core has a carbon-14 date that calibrates to 1059 years before present, and GSP3-55, which represents the sample at depth 108-110 cm from the top of the core, has a carbon-14 date that calibrates to 1728 years BP. Mercury analysis on core GSP3 yielded an age date of 68 years BP at 7 cm depth. Figure 2 represents an age model for the core GSP-3 using a stepwise linear function based on the radiocarbon and mercury data. This age model assumes constant sedimentation rate between these data points.

Foraminiferal Data

Stable oxygen isotopes ($\delta^{18}\text{O}$) values measured in the tests of *E. excavatum* in core GSP3 range from

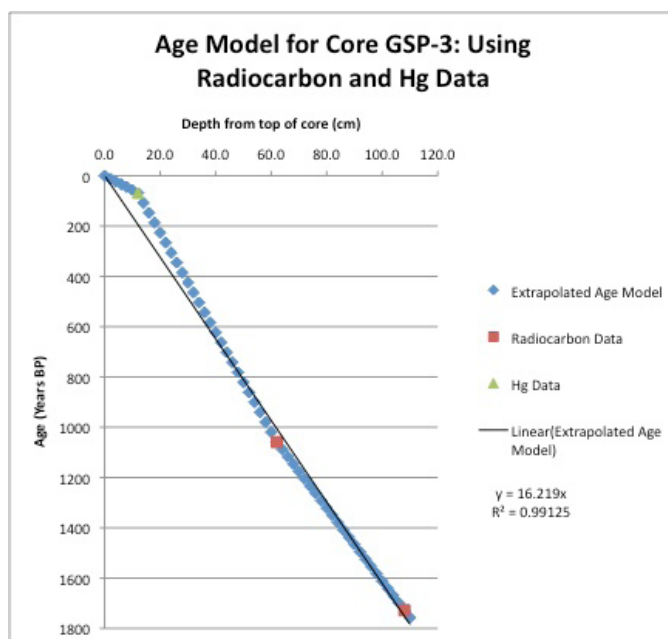


Figure 2: This represents an age model for core GSP3 under the assumption of a constant sedimentation rate between known age data points from radiocarbon dating and mercury analysis.

-0.11‰ to 1.35‰ based on the Vienna PeeDee Belemnite (VPDB) standard, with mostly positive values. The values oscillate over time, reaching its largest value of 1.35‰ at 30-32cm depth, 425 years BP. The lowest value of -0.11‰ occurs at 68-70cm depth, at an age of 1146 years BP. Values of $\delta^{18}\text{O}$ can be used to measure salinity of the Great Salt Pond by using the Kim and O'Neil expression. Stable carbon isotope ($\delta^{13}\text{C}$) values in core GSP-3 range from -2.23‰ to 0.90‰, with mostly negative values. $\delta^{13}\text{C}$ values can be a useful indicator of percent dissolved oxygen saturation values using an isotope mass balance equation. Table 1 records the age, depth, $\delta^{18}\text{O}$ values, $\delta^{13}\text{C}$ values, salinity, and percent saturation values for core GSP3.

Stable isotope values for two samples, GSP3-22 and GSP3-23, remained unanalyzed at the University of Minnesota and stable isotopes for the core GSP2 are still being analyzed and once received can be compared to the results from GSP3.

ID # GSP3	GSP3 slice interval (cm)	Estimated Core Age (years BP)	d13C (permil)	d18O (permil)	Temp C	salinity	% saturation
1.00	0-2	0.00	-1.13	1.08	12.00	35.12	62.15
2.00	2-4	11.33	-1.48	0.83	12.00	34.13	50.86
3.00	4-6	22.67	-0.85	0.64	11.97	33.38	73.14
4.00	6-8	34.00	-1.56	0.98	11.99	34.71	47.14
5.00	8-10	45.33	-0.67	1.01	11.99	34.84	78.10
6.00	10-12	56.67	-2.13	0.86	12.00	34.27	27.02
7.00	12-14	68.00	-1.55	0.95	11.93	34.56	47.82
8.00	14-16	107.64	-1.58	0.52	11.87	32.80	49.33
9.00	16-18	147.28	-1.62	1.09	11.78	34.96	45.35
10.00	18-20	186.92	-0.63	0.85	11.63	33.90	80.32
11.00	20-22	226.56	-1.68	0.67	11.57	33.14	46.29
12.00	22-24	266.20	-0.87	0.82	11.52	33.70	72.79
13.00	24-26	305.84	-0.45	0.86	11.58	33.89	86.07
14.00	26-28	345.48	-1.01	0.80	11.56	33.64	68.33
15.00	28-30	385.12	-0.48	0.44	11.60	32.25	85.87
16.00	30-32	424.76	-0.52	1.35	11.66	35.86	82.80
17.00	32-34	464.40	No Data	No Data			
18.00	34-36	504.04	-1.13	1.33	11.71	35.84	62.08
19.00	36-38	543.68	-2.04	0.98	11.69	34.47	31.02
20.00	38-40	583.32	-2.06	-0.03	11.58	30.39	37.80
21.00	40-42	622.96	0.23	0.80	11.76	33.81	106.93
22.00	42-44	662.60	N/A	N/A			
23.00	44-46	702.24	N/A	N/A			
24.00	46-48	741.88	-0.35	0.79	11.60	33.64	89.38
25.00	48-50	781.52	-0.92	0.79	12.14	34.11	69.86
26.00	50-52	821.16	-1.74	0.93	12.28	34.77	39.64
27.00	52-54	860.80	-0.69	0.84	12.21	34.38	77.42
28.00	54-56	900.44	0.25	0.93	12.33	34.80	107.88
29.00	56-58	940.08	-0.04	0.36	12.77	32.97	98.87
30.00	58-60	979.72	0.23	0.19	12.96	32.44	107.25
31.00	60-62	1019.36	-0.85	1.09	12.85	35.91	70.08
32.00	62-64	1059.00	-0.92	0.20	12.51	32.11	70.80
33.00	64-66	1088.09	-1.48	0.94	12.40	34.93	48.93
34.00	66-68	1117.17	-1.15	0.80	12.27	34.26	61.53
35.00	68-70	1146.26	-1.25	-0.11	11.98	30.41	62.82
36.00	70-72	1175.35	-0.81	0.75	11.63	33.51	74.57
37.00	72-74	1204.43	-0.60	0.90	11.41	33.91	81.28
38.00	74-76	1233.52	-0.59	1.04	11.45	34.49	81.31
39.00	76-78	1262.61	-0.19	0.99	11.68	34.49	94.14
40.00	78-80	1291.70	0.51	0.74	11.86	33.67	115.22
41.00	80-82	1320.78	0.56	0.46	11.78	32.48	116.28
42.00	82-84	1349.87	0.25	0.78	11.92	33.85	107.59
43.00	84-86	1378.96	0.90	0.84	12.26	34.39	127.54
44.00	86-88	1408.04	0.49	1.25	12.39	36.12	116.07
45.00	88-90	1437.13	-0.49	0.68	12.39	33.88	84.10
46.00	90-92	1466.22	-0.17	0.58	12.47	33.56	94.69
47.00	92-94	1495.30	-1.21	0.44	12.73	33.23	59.68
48.00	94-96	1524.39	-0.60	0.47	13.19	33.75	79.66
49.00	96-98	1553.48	-2.23	0.50	12.74	33.48	21.99
50.00	98-100	1582.57	-0.40	0.42	12.74	33.15	87.11

Table 1: This table contains Core depth, estimated core age (cal years BP), oxygen and carbon isotope values measured in *Elphidium excavatum*, estimated water temperature (°C), salinity in psu, as well as oxygen consumption index in percent saturation from the upper 50 samples of core GSP-3.

DISCUSSION

Age Models

Figure 2 represents an age model based on radiocarbon data and mercury data for core GSP3. This model assumes a constant sedimentation rate between the known age data points and forms a stepwise linear function. Between zero and the Hg data point of 68 years BP, the sedimentation rate is 1.911 mm/yr. From 68 years BP to 1059 years BP a sedimentation rate of .4944 mm/yr is calculated and

between 1059 years BP and 1728 years BP, there is a sedimentation rate of .688mm/yr.

Stable Isotope Analysis: Oxygen

Paleotemperature reconstruction for the core GSP3 was based on the Greenland Ice Core GISP2. The Greenland Ice Core provides an exceptionally clear age and temperature model based on stable isotope analysis and ice accumulation (Alley 2004). Calculating the deviations from the mean throughout time for GISP2, these calculations can then be applied to the core and age model for GSP3. The mean annual temperature of Block Island is 12.65°C. This value was the average of the temperatures recorded from δ¹⁸O from *E. excavatum* from each of the 38, 5cm samples of core GSPV-3, assuming a constant salinity at 35 psu. Using the values of deviation from the mean from GISP2 and applying it to the mean temperature and core of GSP3, temperature values can be reconstructed for the Great Salt Pond. This acts as one of the best estimates of a paleotemperature record for Block Island.

δ¹⁸O values from GSP3 reflect salinity values of the pond over time by using the Kim and O’Neil expression for ¹⁸O fractionation. Salinity values range from 30-35 psu and are recorded in Table 1. Beginning 100 years ago, there is a gradual increase in salinity. This coincides with historical data from Livermore which documents a permanent breach being built in 1895. The influence of ocean sea water on the Great Salt Pond is shown by salinity values of 30 psu or above. Salinity, while fairly stable in the 30-35 psu range, does appear to fluctuate regularly perhaps as a result of the closing and opening of the breach due to drifting sand. Figure 3 shows the salinity of the Great Salt pond over time.

Figure 4 shows δ¹⁸O values as a result of age and depth of the core. There is an increase in the oxygen isotopic ratio starting around 600 years BP. This correlates with the beginning of the Little Ice Age which occurred between 150-600 years BP. This time period of the core shows the highest values of δ¹⁸O of 0.98‰, 1.33‰, and 1.35‰. These positive large values indicate an ocean rich in heavy oxygen,

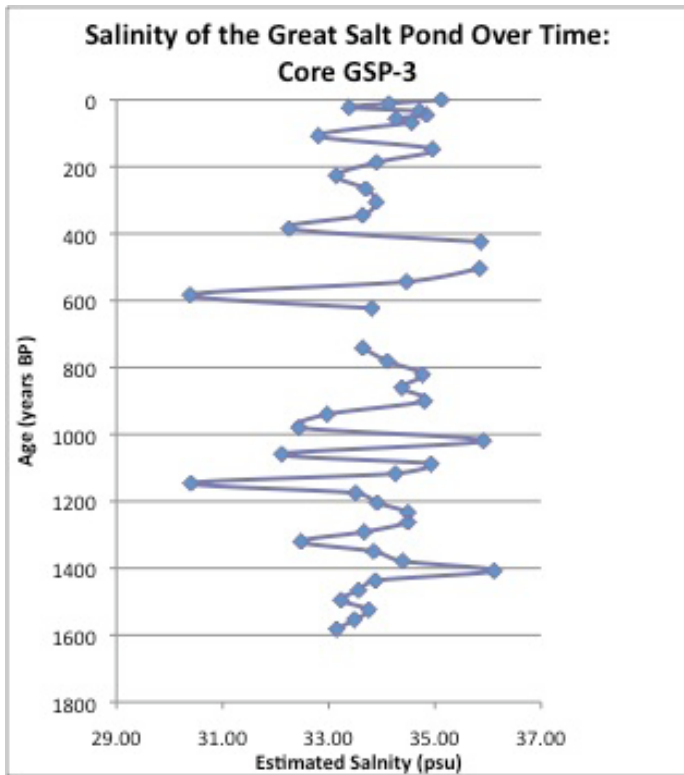


Figure 3: This shows the oscillations of salinity over time for core GSP-3

meaning that the lighter, ^{16}O , was being trapped in glaciers. This indicates an overall generally cooler climate.

Smaller values of $\delta^{18}\text{O}$ in core GSP3 appear at 58-68 cm depth from the top of the core, which correlates with about 940-1117 years BP. Lower $\delta^{18}\text{O}$ values correlate with an increase in ^{16}O as glaciers melt and return the lighter oxygen to the ocean waters. This indicates a warming period. The warming period seen in core GSP3 correlates with the Medieval Warm Period that took place around 700-1100 years BP and is seen in other cores from around the world (McGann 2008). Figure 4 shows $\delta^{18}\text{O}$ values skewed to the left between 700-1100 with some outliers, confirming a warmer and more arid climate.

Carbon Isotope Analysis

$\delta^{13}\text{C}$ values in core GSP-3 are mostly negative. These values fall between the two end members of $\delta^{13}\text{C}$ values of river water, approximately 10‰, and open ocean water, 0‰ (McGann 2008). The Great Salt

Pond is a mixture of ocean water from the Atlantic that enters through the breach as well as precipitation predicting $\delta^{13}\text{C}$ values that are slightly negative. Figure 4 depicts $\delta^{13}\text{C}$ versus age showing values skewed to the left.

^{13}C values can also be used to calculate the dissolved oxygen percent saturation. Assuming that the $\delta^{13}\text{C}$ of bicarbonate in seawater is zero, the values of $\delta^{13}\text{C}$ in *E. excavatum* reflect an addition of light carbon, most likely through the oxidation of photosynthesis. By setting up an isotope mass balance equation using the salinity calculated from the $\delta^{18}\text{O}$ values, a calculation of how much organic carbon was added to the system can be found. This can be used as a direct correlation of eutrophication. Referring to Table 1, percent saturation values show a general decrease over time. Percent saturation from depths of 0-16cm, average around 53.43% whereas the average for the rest of the core is 79.11%, and the average for the whole core is 74.94%. Percent saturation is the amount of oxygen dissolved in the water sample compared to the maximum amount that could be present at that same temperature. Decreasing values show less oxygen in the water than there is potential. The input of nutrients, such as nitrogen and phosphorous, can decrease oxygen and water quality. This is otherwise known as eutrophication

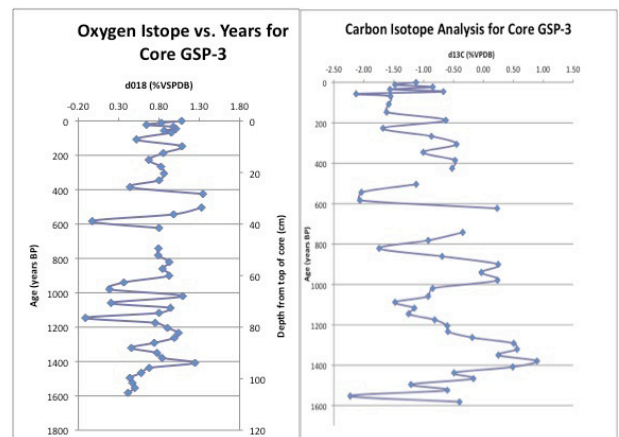


Figure 4: The graph on the left shows $\delta^{18}\text{O}$ values relative to the Vienna PeeDee Belemnite (VPDB) standard plotted with estimate age (cal years BP) and depth in core GSP-3. The graph on the right shows $\delta^{13}\text{C}$ relative to the VPDB standard plotted with estimate age (cal years BP).

and generally occurs due to human influences. This decrease in percent saturation occurs around 150 years ago, when tourism became more popular on Block Island.

CONCLUSION

The microfossil foraminifera acts a paleoenvironmental indicator by providing information about past temperature, salinity, and the local carbon cycle. Stable isotope analysis on the benthic foraminifera *Elphidium excavatum* indicates that the climate of the Great Salt Pond has oscillated numerous times between warm and dry, and cool and wet conditions over the past ~1750 years. Insight into the oscillation of the pond from fresh, brackish, and saltwater is shown through salinity levels gathered for isotope data. An increase in salinity occurring 100 years BP corresponds with historical data of Native American shell middens and documents about creating permanent breaches. The oxygen and carbon isotope data from the cores in the Great Salt Pond are contemporaneous with the Medieval Warm Period and the Little Ice Age with decreasing and increasing $\delta^{18}\text{O}$ respectively.

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