

**KECK GEOLOGY CONSORTIUM**

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

April 2009  
Franklin & Marshall College, Lancaster PA.

Dr. Andrew P. de Wet, Editor  
Keck Geology Consortium Director  
Franklin & Marshall College

Dr. Stan Mertzman  
Symposium Convenor  
Franklin & Marshall College

Kelly Erb  
Keck Consortium Administrative Assistant

Diane Kadyk  
Academic Department Coordinator  
Department of Earth & Environment  
Franklin & Marshall College

*Keck Geology Consortium  
Franklin & Marshall College  
PO Box 3003, Lancaster PA 17604-3003  
717 291-4132 [keckgeology.org](http://keckgeology.org)*

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(GRENVILLE PROVINCE, NEW YORK)**

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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**  
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**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

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*RACHEL NEURATH*: Smith College

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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)**

Keck Geology Consortium  
Franklin & Marshall College  
PO Box 3003, Lancaster Pa, 17603  
Keckgeology.org

# USING CARBON AND NITROGEN ISOTOPES AND LOSS-ON-IGNITION TO RECONSTRUCT THE LAND USE HISTORY OF BLOCK ISLAND, RHODE ISLAND

JESSICA SCHEICK: Bryn Mawr College  
Research Advisor: Donald Barber

## INTRODUCTION

Lacustrine sediments provide an important proxy for studying paleoenvironments and land use history. Variability in the quantity and character of organic material trapped in accumulating sediments can preserve records of a variety of environmental factors. Sedimentary organic matter generally includes the remains of primary producers and decomposers of organics living in the water column, such as plants, algae, and cyanobacteria, as well as nutrients and plant material washed into lakes from the surrounding watershed (Perry and Taylor, 2007). Records preserved include sedimentation rates, oxic and anoxic conditions, lake productivity, the growth of plants and organisms in situ and on land nearby, and nutrient loading based on anthropogenic land use (Haberzettl, et al., 2005; Perry and Taylor, 2007; Sage and Monson, 1999; Tylmann, 2005).

The carbon and nitrogen isotopic compositions of organic matter, reported here as  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values, as well as the C/N ratio, have been used extensively to study paleoenvironmental conditions and changes in land use (Haberzettl, et al., 2005). Fixed nitrogen, which causes eutrophication, is characterized by elevated  $\delta^{15}\text{N}$  values; thus, increases in the  $\delta^{15}\text{N}$  composition of lacustrine organic matter can indicate increases in human and cattle waste input. Similarly, cultivated soils have been shown to be isotopically heavier than non-cultivated ones (Bremner and Tabatabai, 1973 fide Peters, 1978), so higher  $\delta^{15}\text{N}$  values may correspond to increased allochthonous soil input (Haberzettl, et al., 2005). A comparison of relative  $\delta^{13}\text{C}$  values provides evidence for lake level changes and variations in terrestrial and marine organic carbon from plants. Plants can be broadly categorized into C3 and C4 plants based on how they interact with  $\text{CO}_2$  in the atmosphere.

C4 plants, such as marsh grasses and maize, have less negative  $\delta^{13}\text{C}$  values than C3 plants (Meyers, 1999; Sage and Monson, 1999). Thus, an increase in  $\delta^{13}\text{C}$  values, especially concurrent with an increase in  $\delta^{15}\text{N}$  and increased allochthonous sedimentation, can indicate the introduction of maize cultivation to a locality (Sage and Monson, 1999).

Block Island (BI), Rhode Island was first inhabited by humans over 3000 years before present and first appears in written European records in 1524, though it was not explored by Europeans until 1612 (Anderson, 2002; Lanman, 1876; Mendum, 1897; Tveskov, 1997). Since the arrival of the Europeans, both land cover and land use have changed drastically. BI transitioned from dense deciduous oak forest to a clear cut landscape for agriculture and livestock. The island is now predominantly grassland.

This study aims to use a combination of  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  isotope and C/N abundance data together with sediment loss-on-ignition (LOI) analysis and historical records to reconstruct the plant habitat and land-use changes on Block Island since the island's habitation by humans over 3000 years ago.

## METHODS

### Sample Collection and Processing

Cores from three ponds on Block Island are being analyzed in this study. Core FP1 is a hammer core from Fresh Pond, a freshwater pond located just south of the airport that serves as a reservoir for the island (Fig. 1). Hammer core SP2-C was extracted from Sachem Pond, a slightly saline pond located at the northern tip of the island (Fig. 1). Sachem Pond is protected from the ocean by a barrier spit



Figure 1. Block Island, RI. The location of cores included in this study are indicated by red dots. Sailboat markers display corresponding pond names. Map of New England area shows the location of Block Island with respect to the coastline, Long Island, and Martha's Vineyard, all part of the terminal moraine of the Laurentide Ice Sheet during the Last Glacial Maximum. Images modified from Google Earth.

that is occasionally breached during large storms, so although the pond is usually fresh, it can become brackish following breaching. Vibracore GSPV3 was collected from the island's largest pond, the saline Great Salt Pond (Fig. 1).

The cores were extruded in 1-2cm intervals. Each slice of core was labeled, homogenized, observed, weighed, and set out on tables to air dry. After a period of 3-10 days, once the sediment had no color variations owing to moisture, it was reweighed and put into plastic containers for storage. A split of each section was ground into a fine powder using an agate mortar and pestle, and further splits were used for each type of analyses.

### Loss-on-Ignition, Isotope Ratio Mass Spectrometry, and Carbon/Nitrogen Abundance

Loss-on-ignition (LOI) analysis were performed on a selection of splits from core SP2-C. For core FP1, one sample was tested for LOI to ascertain whether carbonates were present prior to mass spectrometry. No analyses have yet been performed on the GSPV3

core.

LOI was done using a ThermoLyne 48000 Furnace, following the methods of Shuman (2003). Samples were selected at 2-6cm intervals. Crucibles were placed randomly in crucible trays to reduce bias based on location within the oven. Organic and inorganic content was calculated based on the difference between initial sediment weight and ash weights following each round of incineration (Heiri et al., 2001).

Mass spectrometry measurements are being carried out at the University of New Hampshire Stable Isotope Laboratory using a Costech 4010 Elemental Analyzer in conjunction with a Delta Plus XP Mass Spectrometer. Prior to analysis, SP2-C and GSPV3 samples will be treated with sulfurous acid to remove marine carbonates; this approach follows the methods of Steve Phillips, adapted from the USGS open file report.

## RESULTS

### Core SP2-C

LOI analysis reveals variable amounts of organic matter with depth in core SP2-C (Fig. 2). The weight percent of the water characterizing the sediments upon extraction closely follows the variations in organic content, as shown by a very strong correlation between the weight percent water and weight percent organic matter based on LOI ( $r^2 = 0.83$ ).

### Core FP1

Mass spectrometry was used to measure carbon and nitrogen isotopic ratios and the C/N ratio of organic matter in eleven samples selected at approximately 6cm intervals in core FP1. The weight percent carbon content corresponds very closely with the weight percent nitrogen content ( $r^2 = 0.98$ ), because both are contained in organic matter. Bivariate plots of  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ , and C/N demonstrate three distinct groups of values: one at high  $\delta^{13}\text{C}$  and intermediate  $\delta^{15}\text{N}$  values, one at intermediate  $\delta^{13}\text{C}$  and high  $\delta^{15}\text{N}$  values, and one at low  $\delta^{13}\text{C}$  and low  $\delta^{15}\text{N}$  values (Fig.

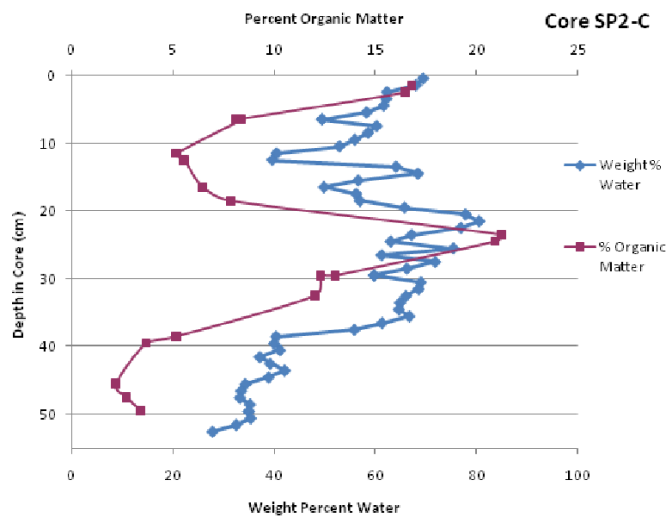


Figure 2. Sediment weight percent water and percent organic matter for core SP2-C plotted as a function of depth in core. Notice that both data sets display the same general trends, a function of sediment mineralogy.

3).  $\delta^{13}\text{C}$  varies with depth in the core, whereas  $\delta^{15}\text{N}$  shows an overall decreasing trend downcore (Fig. 4). An age-depth model provided by Varekamp (personal communication, 2009) places the 53cm basal core sample at 1828 calendar years AD.

## DISCUSSION

### Core SP2-C

The correlations between weight percent water and organic matter are best explained based on sediment composition. Visual analysis indicates that core mineralogy is predominantly clay and quartz sand, with an overall increase in sand content downcore. The strong correlations between weight percent water and organic matter are easily explained by this lithology; not only is clay content indicative of the water holding capacity of sediment, but it also influences the amount of organic material adhering to the sediment. The organic matter also has the ability to hold water, further increasing the water holding capacity of the sediments beyond that allowed by clay content alone.

The observed variations in organic matter and water content are interpreted to indicate the influence of breaching on sedimentary material transport

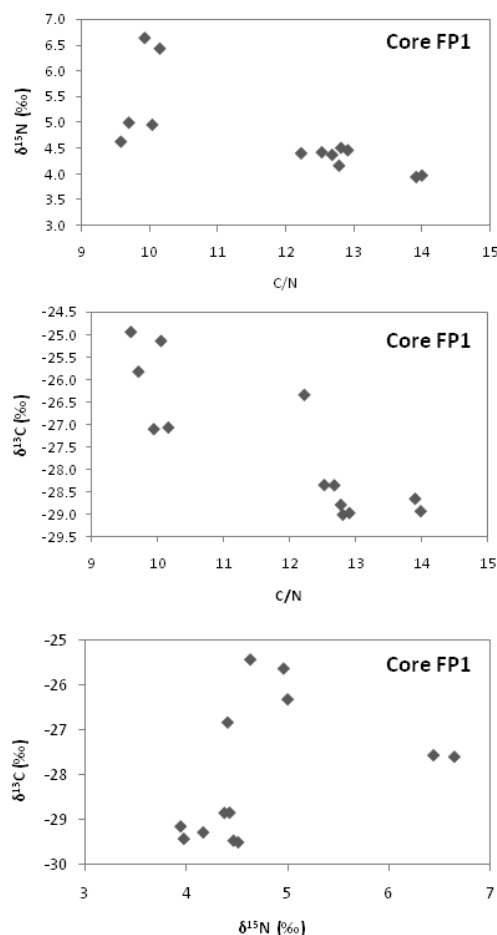


Figure 3: Bivariate plots of the three data parameters  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ , and C/N. Notice the three distinct groupings in the  $\delta^{13}\text{C}$  vs.  $\delta^{15}\text{N}$  plot (high  $\delta^{13}\text{C}$  and intermediate  $\delta^{15}\text{N}$ , intermediate  $\delta^{13}\text{C}$  and high  $\delta^{15}\text{N}$ , and low  $\delta^{13}\text{C}$  and low  $\delta^{15}\text{N}$ ). These groups suggest that three distinct types of organic matter are present in the core.

into the pond. Because Sachem Pond is a freshwater pond except for breaching episodes, we would expect the marine influence to create fluctuations in the carbon and nitrogen isotopic ratios as well as the C/N ratio in organic matter. Forthcoming mass spectrometry data could be used to test the hypothesis that high water content and high organic matter intervals reflect fresh conditions, while low water content and coarser-grained, low organic matter units reflect marine breaching events associated with storms.

### Core FP1

The uniform variations in percent nitrogen and percent carbon content of the sediment indicate



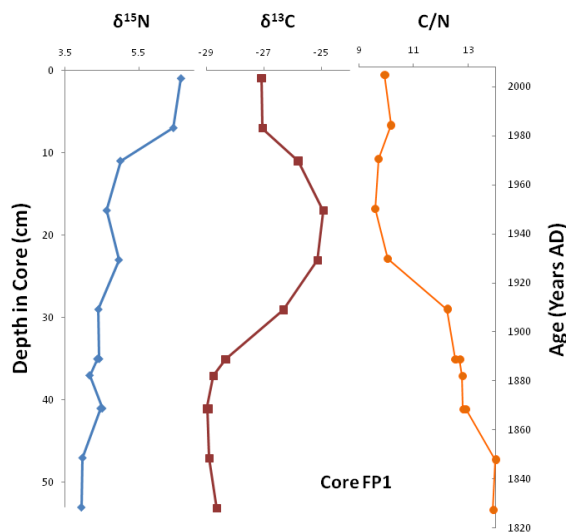


Figure 4: A plot displaying  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$  isotope values and C/N data depicted based on center interval depth in core and the corresponding age model for core FP1.  $\delta^{15}\text{N}$  values show an overall increasing trend upcore.  $\delta^{13}\text{C}$  values increase upcore to about 35cm, when they decrease again, most likely owing to a decrease in farming. C/N values are above  $\sim 10$  below 25cm core depth, indicating the presence of allochthonous materials. The more recent values around 10 indicate the presence of smaller amounts of terrigenous sediments, owing to a change in ground cover with the decline of farming. The age model applied to FP1 dictates calendar year dates of 2005 at 1cm and 1828 at 53cm, though the model is subject to change and the basal age may in fact be up to 100 years earlier.

that some intrinsic factor of sedimentation, perhaps sedimentation rate, is controlling the accumulation of both materials in organic matter. In the Fresh Pond, this control contrasts the trends observed in core SP2-C, where breaching is believed to exercise the dominant control on sediment and organic matter accumulation.

Based on the age model and historical accounts, we would expect to see an increase upcore in  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ , and C/N values. By 1828, the approximate date at the base of the core, BI had been completely clear-cut for over 100 years, the land was being used for farming and grazing, and livestock had been introduced and were established as a major export of the island (Mendum, 1897). The overall increase in  $\delta^{15}\text{N}$  from the core bottom can be explained by these changes in land use. The cultivation of soils tends to make them isotopically heavier (Peters et al., 1978), and the addition of fertilizers to farmland increases

the amount of  $\delta^{15}\text{N}$  that gets washed into the ponds. Increased  $\delta^{15}\text{N}$  values also indicate an increase in allochthonous material (Haberzettl, et al., 2005), in this case due to the lack of ground cover to prevent erosion. Maize, a  $\text{C}_4$  plant, is isotopically heavier in  $\delta^{13}\text{C}$  values than more common  $\text{C}_3$  plants (Sage and Monson, 1999). The steady increase in  $\delta^{13}\text{C}$  values is coincident with the presence of farming on BI, though we observe a decrease beginning circa 1950. This decrease is probably owing to a decrease in farming as BI's already strong tourist economy grew stronger. As in  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$ , we see further evidence in C/N ratios reflecting land use trends. A C/N value of  $\sim 10$  is the maximum value for which all organic matter can be considered autochthonous (Haberzettl et al., 2005). Unsurprisingly, given the prevalence of farming and the accompanying erosion, in the lower half of the core we observe high values of C/N ( $>12$ ), and as land cover returns with the decrease in farming in the 1950s, C/N values steadily decline to the present value of  $\sim 10$ .

## CONCLUSION

Mass spectrometry and LOI are important methods for reconstructing the land use of a region through time. LOI is an easy, cost effective method for measuring organic material in sediments, which can be compared to mineralogy and weight percent water to determine controlling factors on organic material accumulation in sediments.  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ , and C/N indicate the relative inputs of  $\text{C}_4$  plants, fertilizer, and terrigenous material, respectively.

Lithology was found to play an important role in controlling organic material content in Sachem Pond, while breaching is hypothesized to be the dominant influence on variations in organic material and water content. Changes in  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ , and C/N values in Fresh Pond coupled with an age model allowed a pattern between land use based on historical accounts to be corroborated by mass spectrometry data.

A great deal of further data and analysis is needed to completely constrain the exact timing and extent of the introduction of maize and livestock to

Block Island. Age models will need to be completed for cores to allow comparison to historical documents. Paleolimnological studies could provide details about the plants present on land and how they might have contributed to the total carbon and nitrogen inputs.

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