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CARBON CYCLE TRENDS RECORDED BY ORGANIC CARBON STABLE ISOTOPES IN PALEOCENE STRATA, BENTON COUNTY, MISSISSIPPI: IMPLICATIONS FOR CHRONOSTRATIGRAPHY OF THE PORTERS CREEK AND NAHEOLA FORMATIONS

A Thesis presented in partial fulfillment of requirements for the degree of Master of Science in the department of Geology and Geological Engineering The University of Mississippi

By

ERICA D. GERWECK

May 2017

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ABSTRACT

The Paleocene-Eocene Thermal Maximum (PETM) is one of the most studied carbon isotope excursions in Earth's history. The PETM occurred 55 million years ago when excess isotopically heavy carbon (C¹³) was added into Earth's carbon cycle, resulting in ecological and environmental changes. The PETM is marked by a negative stable carbon isotope excursion (CIE) in marine and continental strata around the globe. The Paleocene and Eocene boundary is contained in the sedimentary fill of the Mississippi Embayment so there is high potential to produce new PETM stable isotope datasets. The purpose of this project is to analyze the boundary for evidence of the PETM and other CIEs at the Flat Rock Church Paleobotanical Site and a nearby core from Benton County, Mississippi. Fieldwork at the Flat Rock Church site was conducted in order to observe the stratigraphic and lateral relationships of the Paleocene Porters Creek Formation and Naheola Formation and the Eocene Meridian Sand and to collect samples for preliminary stable carbon isotope analysis. Continuous, high-resolution data were produced from samples from the Rollison Core, which were decarbonated and analyzed for stable organic carbon isotopes ($\delta^{13}C_{TOC}$), percentage of carbonate, and total organic carbon. The resulting $\delta^{13}C_{TOC}$ curve shows an overall increase in $\delta^{13}C_{TOC}$ values upsection with five superimposed high-magnitude positive CIEs. Two of the five are discounted as the result of procedural error and the remaining three are interpreted as representing a combination of increased organic carbon burial and Caribbean volcanism. The upsection trend in $\delta^{13}C_{TOC}$ enrichment likely correlates to a segment of a larger, global Paleocene trend known as the Paleocene Carbon

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Isotope Maximum. Correlation of the $\delta^{13}C_{TOC}$ curves allows the establishment of a more precise chronostratigraphy, revising the previously established depositional range of the Porters Creek and Naheola from 63.8-56 Ma to 60.5-56.6 Ma.

DEDICATION

This thesis is dedicated to my parents, Reece, and all of the people who have given me encouragement and shown me love on this journey of graduate school and thesis writing.

LIST OF ABBREVIATIONS AND SYMBOLS

¹⁴C- Carbon-14

¹²C- Carbon-12

¹³C- Carbon-13

CIE- Carbon isotope excursion

T-OAE- Early Toarcian Oceanic Anoxic Event

OAE- Early Aptian Oceanic Anoxic Event

OAE2- Cenomanian-Turonian Oceanic Anoxic Event

PETM- Paleocene-Eocene Thermal Maximum

IETM- Initial Eocene Thermal Maximum

ME- Mississippi Embayment

 $\delta^{13}C_{TOC}\text{-}$ organic carbon stable isotopes

KPESIL- W. M. Keck-Paleoenvironmental and Environmental Stable Isotope Laboratory

TOC- Total organic carbon

Ma- million years (mega-annum)

PCIM- Paleocene Carbon Isotope Maximum

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First, I would like to thank my parents for their constant positive words and endless reminders of what proud parents they are. Without their support, this thesis would not have been possible.

Second, I would like to thank my advisor, Dr. Brian Platt. You have helped me to become a better geologist as well as a better person throughout the time of working on this project. Your expertise and passion for geology is inspiring. I one day hope to be as great of a geologist and educator as you are.

The other two members of my committee, Dr. Louis Zachos and Dr. Andrew O'Reilly, deserve a special thank you for their advice and encouragement along the way and taking their time to be a member of my project. Without their expertise, my research would not have been possible.

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A special thank you to the following people, without their assistance, this thesis would not have been possible. Jon Smith at the Kansas Geological Survey, Bruce Barnett at KPESIL,

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and my undergraduate helper, Lauren Klingel, as well as the Gulf Coast Association of Geological Societies and the University of Mississippi Investment Grant. Without their funding, my research would not have been possible.

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INTRODUCTION

The carbon cycle traces the circulation of carbon as it changes forms because of various chemical reactions throughout the environment. A large segment of the carbon cycle involves reactions in Earth's atmosphere, a critically important component for regulating climatic and biological processes. Carbon is exchanged with Earth's atmosphere via many mechanisms, including photosynthesis, respiration, volcanism, and burning of fossil fuels. Although the Earth has a finite quantity of carbon in its ecosystems, the state of the carbon is constantly changing into different compounds as it is exchanged between the four main carbon reservoirs: the lithosphere, hydrosphere, atmosphere, and biosphere (Koch et al., 1995).



Figure 1- Partial carbon cycle showing fractionation as carbon moves between the atmosphere, continental and marine reservoirs. After Koch et al. (1995).

Presently, humans are impacting the carbon cycle by introducing large volumes of CO_2 and CH_4 into the atmosphere (Siegenthaler and Oeschger, 1987). Although volcanism and other natural Earth processes influence the carbon cycle, humans have made the greatest change by the addition of excess carbon into the cycle through the burning of fossil fuels (Koch et al., 1995).

Carbon can be found in three naturally occurring isotopes, two of which (Carbon-12 and Carbon-13) are stable, and one of which (Carbon-14) is radioactive. Carbon-14 (14 C) is important for radiocarbon dating, however, it is not applicable to the research performed in this project because the ages of the strata are far beyond the limits of radiocarbon dating. Carbon-12 (12 C) is isotopically the lightest carbon isotope and is the more abundant of the two stable carbon

isotopes. Carbon-13 (13 C) is less abundant in nature, but its abundance relative to 12 C in different reservoirs is largely dependent on fractionation during carbon exchange (Fig. 1).

The long-term future impacts on the carbon cycle from anthropogenic activities can only be estimated, but these estimations are best guided by similar scenarios in deep time. Thus, finding ancient analogs of change is useful for predicting the long-term impacts of anthropogenic activities.

Throughout Earth's history there have been many carbon cycle fluctuations related to climate change. Stable isotope data from continental and marine records indicate that multiple hyperthermals, or short-lived periods of intense warming, that have occurred during deep time. Some well-studied carbon isotope excursions (CIEs) are associated with the Early Toarcian Ocean Anoxic Event (T-OAE), the Early Aptian Ocean Anoxic Event (OAE), and the Cenomanian-Turonian Oceanic Anoxic Event (OAE2) (Erbacher et al., 2005). The T-OAE, OAE and OAE2 are all characterized by positive carbon isotope excursions that can be located in cores and outcrops throughout the world (Erbacher et al., 2005). Although many hyperthermals have occurred, this study will focus on the Paleocene-Eocene Thermal Maximum (PETM), because of the apparent Paleocene-Eocene boundary exposed in the study area.

The PETM or the Initial Eocene Thermal Maximum (IETM) was a ~200,000-year-long period ~55 Ma when the Earth experienced rapid warming (Harrington et al., 2004). This change in Earth's climate is recorded as a negative carbon CIE. The PETM CIE is a trend that can be correlated in samples taken in both terrestrial and marine sediments from locations all over the world (McInerney and Wing, 2011). The PETM is recognized by the Intergovernmental Panel on Climate Change as one of the best ancient analogs for projected global climate change because of the influx of isotopically light carbon that is added into the carbon cycle (Zachos et al., 2001).

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The PETM can be related to modern times because the changes that occurred are similar to the changes being brought on by greenhouse gasses of present day. The cause of the PETM is debated, but previous interpretations include changes in tectonic processes and changes in orbital parameters. These changes led to rapid aberrant shifts and extreme climate transients the PETM is known for (Zachos et al., 2001).

The hypothesis of this study is that Paleocene/Eocene aged rocks exposed in Benton County, Mississippi preserve evidence of the PETM CIE. The justification for this is the presence of exposed Paleocene and Eocene rock, and the presence of kaolinite, a paleoclimate proxy. If evidence of the PETM is found, then it will be confirmed that the ME may be a good target for further studies in PETM research. Even if the hypothesis is rejected and no evidence of the PETM is found, the organic carbon stable isotope ($\delta^{13}C_{TOC}$) results will still be evaluated for previously identified trends that can enhance chronostratigraphy of the studied units.

In order to test the hypothesis, a field site and nearby core were selected from a locality where the Paleocene-Eocene contact is believed to be exposed between the Naheola Formation and the Meridian Sand. Stratigraphically, if the PETM CIE is captured in the core, it should be within the youngest strata of the studied core interval. To ensure an adequate background signal would be present in the results, samples were taken deeper into the Paleocene units in the core, ensuring that if a CIE was captured it could be easily distinguished. These additional samples would also yield enough data to reveal long-term trends that will be useful in chronostratigraphic analysis.

GEOLOGIC SETTING

The Mississippi Embayment

The ME is a southwest plunging syncline filled with Jurassic-Quaternary strata (Fig. 2). It encompasses nearly 160,935 mi² (259,000 km²) in the Gulf Coastal Plain and includes parts of Alabama, Arkansas, Illinois, Kentucky, Louisiana, Mississippi, Missouri, Tennessee, and Texas (Cushing et al., 1964). Beginning in the Jurassic, and persisting through the Miocene, this area was occupied by an extension of the Gulf of Mexico (Bicker, 1969).



Figure 2- PETM location within Mississippi and Benton County

The ME contains many types of rock and unconsolidated sediment, including gravel, sand, silt, clay, lignite, marl, chalk, and limestone. Some individual formations range in thickness from inches to thousands of feet toward the fold axis of the embayment (Cushing et al., 1964). Paleocene ME strata comprise the Midway and part of the Wilcox Groups, with Eocene strata in the upper Wilcox. Above the Wilcox is the Claiborne Group, which is entirely Eocene in age. This stratigraphic interval is the focus of this study (Fig. 2).

The lower most unit observed in outcrop and core is the Paleocene Porters Creek Formation, a member of the Midway Group, which is interpreted as a relatively deep marine deposit that represents the inundation over the entirety of the ME of the Gulf of Mexico. Its extent includes western Tennessee, western Kentucky, southwestern Illinois, southeastern Missouri, much of Mississippi, and southwestern Alabama (Dockery and Thompson, 2016). It ranges in thickness from a few hundred feet to greater than 1,400 ft. (426 m) (Dockery and Thompson, 2016). The overall lithology of the Porters Creek Formation is dark gray clay with blocky fracture. When weathered, the clay takes on a gray, tan, or white color. Common fossils within this formation include fish scales, shark teeth and gastropods (Dockery and Thompson, 2016).

The Naheola Formation overlies the Porters Creek within the Midway Group and is thought to represent a shallow marine to fluvial environment (Johnson et al., 1988). It is predominantly sand in the uppermost part of the formation (Johnston et al., 1988). It extends across Alabama and Mississippi, and ranges in thickness from 75 to 200 ft. (22.86 – 60.96 m) (Dockery and Thompson, 2016). The Naheola Formation is divided into two members: the Coal Bluff Member, which consists of glauconitic sand, silty clay and sandy marl, and the Oak Hill Member, which contains sand, silt, and clay, as well as a prominent bed of lignite toward the top.

The Midway Group is typically overlain by the Wilcox Group in Mississippi (Dockery and Thompson, 2016), but in the field area, the Naheola Formation is unconformably overlain by what is interpreted to be the Eocene Meridian Sand. The Meridian Sand is described as representing a near shore marine environment (Dockery and Thompson, 2016). It varies in

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thickness from 14.9 to 70.0 ft. (4.54 to 21.33 m) in Meridian, Mississippi. It is found in both Mississippi and Alabama and consists of tan or light gray, fine to course sand and fine gravel.

Study Area

Preliminary field data were collected from the Flat Rock Church paleobotanical site, also referred to in older literature as Hurley's Schoolhouse, in Benton County, Mississippi (Fig. 3; Berry, 1917; Zachos et al., 2015).





This locality exposes a large deposit of the mineral kaolinite, which was determined to be some of the highest quality in Benton County, making it a site of economic interest (Lusk, 1956). This site is also known for its well-preserved fossil leaves, which were first identified before the American Civil War (Fig. 4; Hilgard, 1860; Berry, 1917; Zachos et al., 2015).



Figure 4- Fossil leaf from Flat Rock Church Locality (Photo by L. G. Zachos)

This site was selected because its kaolinitic paleosols and fossil leaves provide paleoclimate proxies that can be used to corroborate paleoclimate interpretations from stable isotope results. Kaolinite is formed in soils from weathering in warm, wet climates and is linked to the PETM boundary. Kaolinite is a 1:1 phyllosilicate clay mineral where each layer consists of one tetrahedral sheet of oxygen and silicon, and one octahedral sheet of oxygen and aluminum atoms. Kaolinite is formed from the weathering of such silicate minerals as feldspar. Kaolinite is abundant in such highly weathered soils as Ultisols and Oxysols (Brady and Weil, 2008). Kaolinite can be found in samples taken from Antarctica, eastern North America, North Africa and Pakistan (McInerney et al., 2011; Wing, 2003). In some studies of the PETM, the changes in clay mineral composition that mark the initial onset of this climatic shift have been used to assess regional changes in humidity, soil erosion, temperature changes, and also seasonality of precipitation, thus locating the onset and end of the PETM (Harrington et al., 2004).

Another commonly used paleoclimate proxy is leaf margin analysis. Leaf margin analysis is performed by comparing the physiognomy of the leaf, or the number of smooth edged leaves to the number of jagged edged leaves in a sample and then using those percentages to generate a

linear function of the average annual temperature of the environment from which the leaves were produced (Wilf, 1997). Preliminary results were presented by Zachos et al. (2015), who calculated a mean annual temperature of 78.8° F (26° C) and a mean annual precipitation of 10.3 ft. (315 cm) based on leaf fossils collected from the Flat Rock Church site. Compare these values the modern MAP and MAT in Benton County, which are 4.75 ft. (145.0 cm) and 59.1° F (15.1° C), respectively.

METHODS AND MATERIALS

Field Work

Field work at the Flat Rock Church site was conducted in order to observe the stratigraphic relationships of the units of interest as well as to make lateral observations. This was particularly important for observing the nature of the contact between the Naheola Formation and the overlying Meridian Sand channel, which scours into the Naheola. Samples of plant fossils, kaolinite, and other strata were collected from exposed outcrops. Pictures detailing the outcrop located to the east side of the road, as well as the surrounding area were also taken (Fig. 5).



Figure 5- Panoramic image of the Flat Rock Church outcrop where preliminary samples were collected, near Blue Mountain, MS.

Outcrop samples were used to obtain preliminary stable isotope data to ensure that sufficient organic carbon was present to carry out a full organic carbon stable isotope study.

Rollison Core

In order to obtain a thick, continuous, vertical stratigraphic sample of the area, I selected the Rollison core because of its close proximity to the outcrop. The Rollison core was drilled by the Mississippi Mineral Resources Institute in June 1997, in Benton County, Mississippi (34.654722° N, 89.098611° W). The core reached a total depth of 355 ft. (108.20 m) and is predominantly clay, with sandstone, kaolinite and lignite, as originally logged by Swann (2015). For this particular study, the top 121 ft. (36.88 m) of the core were studied and sampled to obtain enough data to allow correlation to other Paleocene records and provide enough background data to be able to locate any excursions in the data.

Lab Work

All 121 ft. (36.88 m) of sampled core was unwrapped from its protective plastic wrapping to allow observation of the core. Each box of core was photographed to capture the color and broad-scale features before sampling (See Appendix I). All colors were described using a Munsell Soil Color Book (1975). Visual inspection ensured that the studied material matched the original core log.

Samples were taken at high-resolution, 5.9 in. (15 cm) intervals for the first 28 ft. (8.53 m) of core because this portion of the core was considered most likely to contain the PETM. Due to the unconformity between the Meridian Sand and the Naheola Formation, there was a chance that the PETM interval was absent as a result of erosion and would not be captured in the sable carbon isotope results, but the higher resolution sampling toward the top of the core increased the chances of locating the PETM or any other excursions. For the remaining 93 ft. (28.34 m), the sample interval was increased to 9.84 in. (25 cm).

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At each interval, the core was split to reveal a fresh surface from which a sample was taken. Samples were collected by scraping with a metal spatula, or drilling with a hammer drill and masonry bit until about 3 g of powered sample was obtained. Each sample was weighed on a model SLF303 Fisher Scientific balance to ensure each sample weighed at least 3 g and then each was placed into a labeled sample bag. All tools were wiped down with alcohol and a Kimtech wipe between samples to prevent cross contamination.

Outcrop samples were decarbonated at the University of Kansas and all core samples were decarbonated in the sedimentology lab at the University of Mississippi as described below; this also provided estimates of sample carbonate content. Samples were decarbonated following a method modified from Boutton (1996) to remove all carbonate, ensuring that all remaining carbon was organic carbon. All samples were powdered with mortar and pestle, and one-gram subsamples were placed into weighed centrifuge tubes. Once a sample was placed into a tube, it was reweighed to record the mass of the sample and the test tube. All test tubes were placed into an oven, lid off, at 113° F (45°C) and dried for about 30 hours. Samples were reweighed after drying to use for percent carbonate calculations.

Carbonate dissolution was achieved by adding 10 mL of 0.05N HCl to each centrifuge tube. Tubes were agitated vigorously to ensure complete reaction and centrifuged at 2,000 rpm for eight minutes to concentrate the solid fraction. Samples were decanted and rinsed with DI water three times to return sample pH to neutral. After rinsing, all samples were oven dried and reweighed. Initial and final weights were used to calculate percent carbonate by mass loss.

Dry decarbonated samples were ground with a corundum mortar and pestle to ensure that all samples were free of aggregates and that each was ground as finely as possible to so that all analyses provided results that were representative of the homogenized sample. All samples were

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transported to the W. M. Keck-Paleoenvironmental and Environmental Stable Isotope Laboratory (KPESIL), at the University of Kansas. At KPESIL, samples were analyzed for $\delta^{13}C_{TOC}$ values and total organic carbon (TOC) on a Costech EA interfaced to a Finnigan MAT 253 Isotope Ratio Mass Spectrometer. All samples were analyzed with primary and secondary standards at KPESIL to ensure quality control.

Chronostratigraphic Estimation

In order to compare my stable isotope results to the correct chronostratigraphic interval of existing δ^{13} C data, I needed to obtain estimates of the ages of the studied units in Benton County. The stratigraphic column from Dockery and Thompson (2016) was used to calculate the time span of deposition of both the Porters Creek and Naheola Formations. These units correspond to biostratigraphic zones NP3, NP4 and NP5, indicating deposition between ~63.8 Ma and ~56 Ma.

RESULTS

Lithologic Descriptions

Flat Rock Church Outcrop

At the Flat Rock Church outcrop there are five beds present (Fig. 6).

Porters Creek Formation. —At the base of the outcrop is a layer of kaolinite that varies in thickness between 2.5 ft. (0.76 m) and 5 ft. (1.52 m) that transitions into a light gray color towards the top. No fossils were observed.

Naheola Formation. — Above the kaolinite is gray siltstone that is ~1.5 ft. (0.45 m) thick and contains impressions and natural casts of horizontal and vertical plant roots.

The siltstone is overlain by a 1 ft. (0.30 m) thick yellow sandstone that contains petrified wood. No sedimentary structures or other fossils were observed, but note that much of this bed is weathered and covered by colluvium.

The sandstone is overlain by a ~1.5 ft. (0.45 m) thick bed of iron rich claystone. The bed contains the fossilized leaves that made the Flat Rock Church locality famous. Burrows up to 0.5 cm in width are present near the top of the bed. Many of these burrows are filled with coarse sand from the overlying unit and many are inclined to the upper bedding plane and are parallel to each other. The bed also contains abundant, thin, horizontal Leisegang bands.

Meridian Sand. — The Meridian Sand caps the outcrop at the field location. Its thickness varies from 1 m to a few cm. The sand is tan, scour-based, shows trough cross bedding and unconformably overlies the claystone.



Figure 6- Photo of Flat Rock Church Outcrop (Photo by L.G. Zachos)

Description of Rollison Core (Appendix I)

Porters Creek Formation:

Depth range 121.5 ft. - 81.5 ft. (37.03 m - 24.84 m). — Micaceous, dark reddish-brown

(5YR 4/2) clay, shows some evidence of lamination to thin bedding.

Depth range 81.5 ft. - 81.0 ft. (24.84 m - 24.68 m). — Gray (10YR 4/1), very fine

grained micaceous sandstone with Fe/Mn cement. No apparent sedimentary structures and no

evidence of bioturbation. Abrupt lower and upper contacts.

Depth range 81.0 ft. - 62.5 ft. (24.68 m - 19.05 m). — Dark gray (5YR 4/1) claystone, locally micaceous and silty with thin bedding and lamination.

Depth range 62.5 ft. – 61.0 ft. (19.05 m – 18.59 m). —Kaolinite-rich base that grades upward into the typical clay of the Porters Creek Formation. This means the clay contains some kaolinite and is the characteristic gray (10YR 7/1) color associated with the Porters Creek (Dockery and Thompson, 2016).

Depth range 61.0 ft. -43.0 ft. (18.59 m -13.10 m). — The top of the Porters Creek Formation is kaolinite rich, white (10YR 8/1), and contains possible siderite grains (Fig. 7) which form thin beds and also filled burrows.



Figure 7- Piece of Rollison core containing kaolin and siderite grains.

Naheola Formation:

Depth range 43.0 ft. – 35.5 ft. (13.10 m – 10.82 m). — Very fine, pale brown (10YR 8/2) sandstone that contains some carbonized plant roots towards the top. Massively bedded with a gradational lower contact.

Depth range 35.5 ft. – 34.0 ft. (10.82 m – 10.36 m). — Friable, black (N3), somewhat laminated lignite.

Depth range 34.0 ft. -30.0 ft. (10.36 m - 9.14 m). —Micaceous, white (5Y 8/1) claystone, locally silty and carbonaceous. Some parts of the bed are pure clay. Thinly bedded with a sharp lower contact.

Depth range 30.0 ft. – 27.5 ft. (9.14 m – 8.38 m). — Thinly bedded ironstone with micaceous intervals. Sandy in some areas with a sharp lower contact. Some iron nodules are present.

Depth range 27.5 ft. -26.0 ft. (8.38 m -7.92 m). — Micaceous, yellowish-red claystone that is strongly laminated at the base with thin lamination towards the top. Sharp lower contact.

Depth range 26.0 ft. -21.3 ft. (7.92 m -6.49 m). — Micaceous, white (5Y 8/1) claystone that is silty in some areas. Poorly bedded with a sharp lower contact.

Depth range 21.3 ft. -20.3 ft. (6.49 m - 6.18 m). — Very fine, argillaceous, yellow (10YR 7/6) siltstone with a gradational lower contact.

Depth range 20.3 ft. – 19.8 ft. (6.18 m - 6.03 m). — Reddish-brown (5YR 4/4) ironstone that is inducated. Sandy in some areas with sharp upper and lower contacts.

Depth range 19.8 ft. – 19.0 ft. (6.03 m – 5.79 m). — Micaceous, argillaceous, yellow

(10YR 7/6) siltstone with areas of very fine sand. Massive bedding, with a sharp lower contact.

Depth range 19.0 ft. – 15.0 ft. (5.79 m – 4.57 m). — Carbonaceous, micaceous, pale

yellow (5Y 7/3) claystone. Massively bedded with gradational lower contact.



Figure 8- Correlation of Flat Rock Church Outcrop (A) and Rollison Core (B).

Analytical Results

The resulting curves of percent carbonate, TOC and $\delta^{13}C_{TOC}$ from the outcrop and core are presented in Figures 9 and 10.



Figure 9- Stratigraphic column, TOC and Percent carbonate from the Flat Rock Church outcrop

Flat Rock Church Outcrop

Percent Carbonate. — Percent carbonate in outcrop samples varies from 0.5% to 17%. The Porters Creek Formation contained the highest percent carbonate at the outcrop locality with values between 15% and 17%.

TOC. — The TOC curve has two sharp peaks, both towards the top of the Naheola Formation, with one peak at 0.75% and another at 1.4%. The peaks correspond to the strata that contain petrified wood. The lowest TOC values are in the kaolinite rich layers. Stable Isotopes. — The $\delta^{13}C_{TOC}$ values range from ~-27.0‰ to ~-24.5‰. The highest values are located within the claystone, sandstone and the red claystone of the Naheola Formation. Although the data are sparse, there is still an overall trend in the curve, which becomes more positive towards the top of the outcrop (Fig. 9).



Figure 10- Stratigraphic column, $\delta^{13}C_{TOC}$, percent carbonate, and TOC from Rollison core with excursions highlighted in gray and labeled A-E.

Rollison Core

Percent Carbonate. — In the core, the values of percent carbonate vary between -1.25% and 1.5%. The samples that contained the most carbonate were located in the Porters Creek Formation and those with the least amount of carbonate were in the Naheola Formation. Overall, the values decrease upward.

TOC (Appendix II, Tables 1-4). — Total organic carbon values in the core are low, with little variation. The only exception is a spike associated with the lignite bed.

Stable Isotopes (Appendix II, Tables 1-4). — The $\delta^{13}C_{TOC}$ values range from -26‰ to 4‰ and the data exhibit overall upsection enrichment. All deviations from background values are positive, defining five main excursions (A-E, Fig. 10).

Excursion A is located about 82.02 ft. (25.0 m) into the core from ground surface and is a spike that reaches a value of 5‰ within the micaceous, fine grained gray sandstone. It is defined by a single point.

Excursion B starts at a depth of 59.05 ft. (18.0 m) and returns to background values at 47.57 ft. (14.5 m). This excursion has four peaks at -13‰, -9‰, -15‰ and -17‰. This particular excursion is confined to one facies of white to light gray clay.

Excursion C is at a depth of 39.37 ft. (12.0 m) and is the lowest magnitude excursion within the $\delta^{13}C_{TOC}$ curve. It is associated with the pale brown, fine grained sandstone that contains carbonized plant roots. This excursion reaches a value of -23‰.

Excursion D is located at a depth of 27.88 ft. (8.5 m) and ends at 24.60 ft. (7.5 m). The excursion has one peak that reaches a value of 2‰, and a peak that reaches -10‰. It is contained within the white claystone bed.

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Excursion E is located at a depth of 19.68 ft. (6.0 m) and reaches a peak of -18‰. It corresponds to a bed of yellow siltstone. It is defined by a single point.

DISCUSSION

Depositional Environments

Flat Rock Church Outcrop

The kaolinite layer located at the base of the outcrop is interpreted to have originated from an environment that experienced high weathering rates (Docker and Thompson, 2016). Since kaolinite is a secondary mineral, it is usually found as a weathering product near a weathered surface. Kaolinite is also commonly found in tropical to subtropical areas, and according to Zachos et al.'s (2015) calculations of average temperature, the climate represented by leaf fossils at the Flat Rock Church outcrop is conducive to the accumulation of a thick authigenic kaolinite bed.

The rooted silt overlies the kaolinite bed at the outcrop locality. The fossilized roots indicate that this bed was once host to vegetation and corroborates the pedogenic interpretation of the kaolinite. Together, the silt and kaolinite constitute a paleosol with the silt likely representing the A horizon and the kaolinite likely representing the B horizon.

The yellow sandstone could represent a transgression as higher-energy nearshore marine sediments were deposited over the paleosol or fluvial deposition (Dockery and Thompson, 2016).

The iron-rich red claystone seemingly represents contradictory environments. The abundant oxidized iron indicates a well-oxygenated environment, while the exquisitely preserved

leaf fossils indicate an anoxic environment, which would be required to prevent decay of the leaf material. The presence of Liesegang banding indicates diagenetic oxidation of the strata (Racz, 1999), so it is sensible to interpret the original depositional environment as an anoxic, low-energy setting. This may have been a protected nearshore or upland lacustrine environment.

The uppermost bed exposed at the Flat Rock Church outcrop, interpreted as the Meridian Sand, is based by a scour surface that likely represents a significant unconformity as the Wilcox Group is entirely absent. Previous studies of the Meridian interpret a nearshore marine depositional environment and the channelized nature of the unit at the outcrop represents a significant episode of incision.

Rollison Core

The dark, micaceous clay of the Porters Creek Formation, is interpreted as a deeper marine environment relative to the underlying strata (Dockery and Thompson, 2016). This represents marine transgression of the Mississippi Embayment sea with abundant terrigenous input.

The Naheola Formation represents a transgression and its gray, sandy beds with trough cross bedding are interpreted as a shallow marine environment (Dockery and Thompson, 2016). The Naheola also contains a lignite bed interpreted as a estuarine environment. The overall depositional environments for the Rollison core represent multiple fluctuations in relative sea level.

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Percent Carbonate

Flat Rock Church Outcrop

The consistently low percent carbonate values indicate that little to no carbonate was present in the strata. The highest value is found in the Porters Creek Formation, which likely corresponds to carbonate deposition within a marine environment. The Porters Creek Formation is described as being very shallow marine, so a minor amount of carbonate may be expected (Johnson and Bush, 1988). Percent carbonate values peak near the petrified-wood-bearing sandstone; this may be the result of the influence of porosity and permeability on precipitation of carbonate cement from pore fluids.

Rollison Core

In the Rollison Core, the amount of carbonate varied between -1.15% to 1.53%. All negative percent carbonate values are considered errors likely due to sample loss during decarbonation. The amount of carbonate in the samples decreases upward within the Porters Creek Formation and increases slightly in the Naheola Formation. Since this change occurs at the contact between the red mudstone and the gray mudstone, the percent carbonate could correspond to a changing depositional environment.

TOC

Flat Rock Church Outcrop

Peaks within the TOC curve of the outcrop data correspond to the petrified-wood-bearing sandstone and the fossil-leaf-bearing claystone. This relationship is sensible because the high

concentration of plant material in these strata and the nature of preservation suggest that a greater volume of organic carbon should be present.

Rollison Core

The TOC values are very low with little change, except for some minor variation in some dominantly clay beds and a large peak in the lignite bed, which is expected due to the high carbon content of lignite. Higher values of TOC indicate a greater abundance of plant matter, which is evident in the TOC curve where plant life is expected to have been concentrated within ancient soils. The near-exponential decline in TOC with depth in the paleosol beneath the lignite is characteristic of vertical profiles of modern soil TOC (Hiederer, 2009). This suggests that TOC content in these strata was not diagenetically altered. If the TOC curve is compared with the depths of modern soils, the Naheola Formation does not match the predicted pattern. This could indicate that the bed could have been altered by diagenesis. The effect of diagenesis on TOC values shows that diagenesis causes enrichment of ¹³C (Wynn, 2007). The enrichment of organic carbon in the soil would lead to increased values like the spikes in the Naheola.

Stable Carbon Isotopes

Flat Rock Church Outcrop

Stable isotope values increase upsection. The data are too sparse, however, to determine whether any apparent variation represents true high-resolution trends. The suggestion of an overall positive trend is a pattern that can be better examined within core data.

Rollison Core

Background trend. — As suggested by the outcrop data, the $\delta^{13}C_{TOC}$ curve for the Rollison Core shows a positive trend upsection (Fig. 10). Based on previous calculations for relative ages for these units, the Rollison Core isotope curve contains a fraction of the calcareous nanoplankton-indicated Paleocene isotope curve (Fig. 11). The age of the Porters Creek and Naheola combined matches the timing as well as the positive trending arm of the Paleocene Carbon Isotope Maximum (PCIM).

The comparison of organic carbon curves and carbonate carbon curves in Figure 11 is reasonable due to the relatively consistent difference between organic carbon and carbonate carbon reservoirs (see Fig. 1). This is due to the averaging of isotopic values form the mixing and dispersing of plant tissues and organic compounds (Magioncalda et al., 2004). The previous calculations performed on the Naheola and Porters Creek Formations gave us a window of time that the studied formations fit into the upward increasing arm of the overall Paleocene curve. This calculation and comparison allows for improvement of the chronostratigraphic constraints on deposition of the combined strata of the Naheola and Porters Creek Formations and their overall placement within the Paleocene curve. The original estimation for the depositional age was ~63.8 Ma to ~56.0 Ma. The new age estimation as a result of this study is ~60.5 to ~56.6 Ma.



Figure 11- Comparison of Paleocene curve, Porters Creek and Naheola Formation curves and curves produced from Flat Rock Church Paleobotanical Site.

Excursions.—Within the overall trend, there are five apparent excursions (labeled A-E in Fig. 10). These will each be discussed individually below.

CIE-A consists of a single point on the $\delta^{13}C_{TOC}$ curve. Due to this, and a magnitude that is unrealistically high for organic carbon stable isotopes, I interpret this as the result of contamination by carbonate from incomplete decarbonation during lab work. This excursion, therefore, will not be considered further in this discussion.

CIE-B is made up of four smaller peaks with in the one excursion. Of all excursions in the $\delta^{13}C_{TOC}$ curve, this is likely a true signal due to its realistic magnitude and multiple point makeup.

CIE-C is located within the sandstone bed at the base of the Naheola Formation. Due to this excursion's close proximity to the carbonized roots, as well as the lignite bed, this particular excursion is one of interest. This excursion is also one of interest because it has a corresponding excursion in the TOC curve. This curve's magnitude is realistic and likely a true signal.

CIE-D reaches unusually large values, similar to CIE-A. Not only does the large value give reason to question this excursion, but it is located at a place in the core that is rich in siderite. Siderite reacts more slowly with HCl than typically encountered carbonate minerals such as calcite and dolomite (Hirmas et al., 2012), so it is likely that the peak represents carbonate carbon contamination as a result of incomplete decarbonation. This apparent excursion, therefore, is discounted and will not be discussed further.

CIE-E is the uppermost excursion in the core. The values are similar to those of CIE-B and CIE-C, thus making it a valid excursion. All in all, excursions A and D will not be considered in the overall conclusions of the $\delta^{13}C_{TOC}$ curve. However, the conditions responsible for excursions B, C and E will be discussed further.

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Positive CIEs

There are multiple possible explanations for the presence of the CIEs within the core data. Positive organic carbon isotope excursions occur with ¹²C sequestration resulting from an increased burial rate of organic matter (Ludvigson et al., 2004).

Differential organic carbon burial rates can be attributed to changes in thermohaline circulation. Thermohaline circulation is the result of the formation of polar ice, which causes an increase in the salinity of the remaining seawater. The increase in salinity causes an increase in density so the water sinks toward the sea floor. Less dense water then moves to the shallower area where the water with increased salinity once was. This constant circulation of seawater is responsible for Earths deep-water ocean currents (Bryan, 1986).

If the excursions in the Rollison core resulted from changes in Earth's thermohaline circulation, they suggest decreased circulation, resulting in decreased nutrient circulation and therefore, increased burial of organic carbon. The stopping or decreasing of circulation can cause anoxic conditions to occur, thus leading to increased preservation and burial (Kump et al., 1999).

Another cause of positive CIEs is changes in the relative abundances of plants employing different metabolic pathways. In the process of photosynthesis in plants, there are three main pathways for the conversion of CO₂ and water to energy: C₃, C₄, and CAM (Forseth, 2010). Higher $\delta^{13}C_{TOC}$ values are associated with C₄ plants. Fractionation during the carbon cycle results in $\delta^{13}C_{TOC}$ enrichment in C₄ plants. Once the plants are buried, their $\delta^{13}C_{TOC}$ enriched tissues decompose and are incorporated into the sediment deposited in the area. Terrigenous strata associated with dominantly C₄ flora will thus be reflected in the isotopic record. C₄/C₃ plant abundances are not a valid explanation for the positive excursions in the Rollison Core,

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however, due to the fact that there is no evidence of C_4 plants before the Oligocene/Miocene (Koch et al., 1995).

Volcanism is another cause of positive CIEs in the geologic record. Increased volcanism leads to increased amounts of ¹³C enriched CO₂ in the atmosphere, where it reenters the carbon cycle. Interestingly, there is evidence of increased Caribbean volcanism in the late Paleocene (Zachos et al., 2001; Bralower et al., 1997). Twelve tephra layers have been identified in surrounding locations, each representing a separate eruption. All twelve layers are relatively thick (~13 cm), as well as a significant distance from the initial eruption, indicating that these eruptions were large scale and powerful. Eruptions during this time as well as in the location of the North American igneous province are considered effusive eruptions due to the voluminous CO_2 degassing that resulted (Bralower et al., 1997).

Volcanic CO₂ release into the atmosphere can be an explanation for the positive excursions in the Rollison Core. The CO₂ released from volcanoes is enriched with ¹³C. For example, other paleosols have been observed from localities close to volcanic eruptions near the Somma-Vesuvius area in Italy. The paleosols show an increase in $\delta^{13}C_{TOC}$ values (Zanchetta et al., 2000).

Caribbean volcanism occurred during the late Paleocene between ~56.0 Ma and ~55.55 Ma (Bralower et al., 1997). From the previous calculations, the Naheola and Porters Creek Formations were deposited between ~63.8 Ma and ~56.0 Ma. Since the Caribbean eruptions were described as being large scale, this means that the timing of the eruptions in the Caribbean and the excursions at the Flat Rock Church site could coincide (Bralower et al., 1997).

To further expand the scope of this research, comparison of all curves were conducted with a neighboring core, Hill #2 (Klingel, unpublished data). Though the Hill #2 core showed variation of percent carbonate, TOC, and $\delta^{13}C_{TOC}$ curves, no excursions were able to be correlated. As a recommendation for future work, samples that correspond to the CIEs should be re-decarbonated and rerun for stable isotope analysis.

Comparison of Outcrop and Core Results

When comparing the results of the outcrop data and core data, many differences were found. The first variation is the data from the outcrop includes two samples from the Meridian Sand, whereas the core data does not. Second, is the number of samples that were tested. At the outcrop locality, 12 samples were collected for analysis. The samples were collected at low resolution: one to two samples per bed for the preliminary sampling. Future research could assess the outcrop locality at a higher resolution. Although the outcrop data are not useful when compared to the high resolution core data, they do include samples taken from the Meridian Sand, a unit located above the Naheola Formation.

Surficial concentration of carbonates, also known as case hardening, is a possible cause of the extreme differences in percent carbonate curves from the outcrop to core. Case hardening occurs when the addition of a cementing agent such as manganese, sulfate, carbonate, silica, iron, oxalate, or organisms, solidifies on the surface of the substrate (Dorn, 2013). Carbonate case hardening is caused by the buildup of minerals from ground water or rainwater when it washes over or penetrates the substrate's surface. Carbonate case hardening would result in more carbonate being present in the outcrop.

Case hardening would explain why the percent carbonate curve of the outcrop looks so different than the curve of the core. The outcrop has been subjected to meteoric diagenesis, whereas the core has not.

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Another possibility for the higher levels of percent carbonate in the Porters Creek Formation is the result of soil carbonates from weathering processes. The precipitation of $CaCO_3$ from either the saturation of the soil solution or evapotranspiration of soil moisture would result in the high levels of carbonate in the soil (Birkeland, 1999). This is unlikely to be the cause of the observed carbonate, however, because the climate of the region is not conducive to accumulation of a carbonate-rich horizon.

Another major difference in the data comparison is the $\delta^{13}C_{TOC}$ values. The $\delta^{13}C_{TOC}$ values from the outcrop only span ~3.0‰, whereas variations in the core data can reach spans of close to 30‰. The reason for this is that there are no lignites present in the outcrop.

CONCLUSIONS

This research was conducted to test the hypothesis that the Paleocene/Eocene aged rocks exposed in Benton County contain evidence of the PETM CIE using stable carbon isotope analysis. To accomplish this goal, an outcrop at the Flat Rock Church paleobotanical site was chosen along with the Rollison Core because they were thought to contain strata that spanned the Paleocene-Eocene boundary.

Preliminary samples were taken from outcrop to assure enough data were present to carry out a full stable carbon isotope analysis. Results proved that there was adequate data to carry out a full analysis. Samples from the Rollison Core were decarbonated at the University of Mississippi and then taken to the University of Kansas for full stable isotope analysis. Results from the core yielded values for TOC and $\delta^{13}C_{TOC}$ and values for percent carbonate were calculated at the University of Mississippi. Although the core data did not contain any evidence of the negative CIE associated with the PETM, three positive excursions were noted. The overall trend of the $\delta^{13}C_{TOC}$ curve was towards more positive values upsection. This was compared with the overall carbonate carbon curve for the Paleocene and correlated with the timing of the Porters Creek and Naheola Formation. The excursions that were recorded within the Rollison core are thought to be smaller excursions captured within one larger, global Paleocene trend known as the PCIM, proved by the chronostratigraphic constraints used. The chronostratigraphic correlation that was used to locate the Naheola and Porters Creek Formations in the Paleocene curve can be used to give more precise ages to the formations. The three positive excursions are likely the result of multiple factors. The most plausible cause of excursion B is the influence of Caribbean volcanism. Since excursion B is located in the center of a bed and is not associated with any facies change, ¹³C enriched volcanic CO_2 is the most probable cause. Excursion C is located near the first paleosol in the Naheola Formation and may be the result of volcanism or possibly ¹²C. Excursion E is within an argillaceous siltstone bed and is likely influenced by the increased burial and sequestration.

Results from the research conducted at the Flat Rock Church Paleobotanical Site and the Rollison Core have enhanced the understanding of the paleoenvironment in Benton County, Mississippi. The resulting $\delta^{13}C_{TOC}$, percent carbonate, and TOC curves from the core data all show that this locality underwent substantial environmental and potentially gradual climatic changes. This is also shown through the presence of kaolinite, fossil leaves, petrified wood and siderite grains.

All accepted excursions that have been researched have been influenced by either volcanism or organic carbon burial in marine basins.

Even though the PETM was not found at this locality in Mississippi, new depositional ages of the Porters Creek and Naheola Formations has been achieved based on the identification of the positive trend within the PCIM. Original calculations estimated deposition between ~63.8 Ma and ~56.0 Ma. After stable carbon isotope analysis and correlation of results to the global Paleocene curve, the depositional age has been revised to ~60.5 Ma to ~56.6 Ma.

Overall, this research can help to further understanding of the changes being seen in the carbon isotope ratio levels of present day atmospheric CO_2 . Anthropogenic influences on the Earth in recent years have caused CO_2 levels to rise exponentially. With the knowledge of the ecological impact of Earth's carbon isotope ratios in the past, it is likely that anthropogenic

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influences will produce similar changes. All in all, the research presented in this thesis has improved understanding of Mississippi Embayment paleoenvironments in the late Paleocene, and has also provided more precise time constraints on the deposition of the Porters Creek and Naheola Formations. REFERENCES

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LIST OF APPENDICES

APPENDIX I

Figure 12- Upper Naheola formation, depths 15'-25'

Figure 13- Naheola formation, depths 25'-35'

Figure 14- Lower Naheola formation, depths 35'-50'

Figure 15- Upper Porters Creek formation, depths 50'- 60'

Figure 16- Porters Creek formation, depths 60'- 71'

Figure 17- Porters Creek formation, depths 71'- 81'



Figure 19-Porters Creek formation, depths 100'- 111.1'

Figure 18- Porters Creek formation, depths 81'- 100'



Figure 20- Lower Porters Creek Formation, depths 111.1'-121'

APPENDIX II

| | 10 | Somelo Notor: | | Dolligge Coro | iddiecie | | |
|-------------|--------------|---------------|----------------|---------------|------------------------|-------|--------------------------------|
| 812312U | 0 | sample Notes: | Erica Gerwecks | Kollison Core | | | |
| 8 Samples | | Data File: | | | | | |
| dentifier 1 | Identifier 2 | Amount (mg) | Ampl 44 (mV) | Area 44 (Vs) | 8 ¹³ C VPDB | С% | Comments |
| - | | 54.899 | 4585 | 104.69 | -25.37 | 0.08 | |
| 0 | | 54.060 | 5549 | 128.46 | -25.15 | 0.10 | |
| ო | | 55.393 | 3581 | 84.52 | -24.94 | 0.07 | |
| 4 | | 53.281 | 3649 | 85.11 | -25.67 | 0.07 | |
| ъ | | 55.643 | 3040 | 71.75 | -26.08 | 0.06 | |
| 9 | | 53.027 | 3649 | 85.49 | -25.39 | 0.07 | |
| 7 | | 53.627 | 4082 | 95.66 | -24.46 | 0.08 | |
| ω | | 43.616 | 4249 | 97.01 | -19.51 | 0.09 | |
| ი | | 30.553 | 4566 | 101.96 | -17.51 | 0.14 | |
| 10 | | 29.793 | 2444 | 57.09 | -22.50 | 0.08 | |
| - | | 46.664 | 4311 | 100.75 | -25.05 | 0.09 | |
| 12 | | 56.938 | 4230 | 99.28 | -24.67 | 0.07 | |
| 13 | | 52.341 | 4984 | 114.59 | -24.98 | 0.09 | |
| 14 | | 52.288 | 4452 | 103.24 | -24.92 | 0.08 | |
| 15 | | 44.379 | 12658 | 278.46 | -23.98 | 0.26 | |
| 16 | | 52.916 | 6758 | 155.70 | -24.65 | 0.12 | |
| 17 | | 46.493 | 10126 | 223.43 | -24.23 | 0.20 | |
| 18 | | 50.263 | 8094 | 184.65 | -24.52 | 0.15 | |
| 19 | | 1.844 | 2840 | 63.07 | -10.02 | 1.48 | |
| 20 | | 2.459 | 2756 | 60.14 | -11.54 | 1.06 | |
| 21 | | 1.932 | 3884 | 83.65 | -7.84 | 1.84 | |
| 22 | | 5.951 | 6724 | 145.75 | 1.39 | 1.02 | |
| 23 | | 15.194 | 2181 | 49.31 | -23.47 | 0.14 | |
| 24 | | 14.015 | 2618 | 58.93 | -23.57 | 0.18 | |
| 25 | | 17.272 | 2582 | 58.08 | -23.77 | 0.15 | |
| 26 | | 14.855 | 3686 | 83.73 | -23.74 | 0.24 | |
| 27 | | 14.146 | 1793 | 40.40 | -24.28 | 0.13 | |
| 28 | | 1.603 | 49995 | 1664.35 | | | too large |
| 29 | | 1.753 | 49970 | 1745.02 | | | too large |
| 30 | | 1.817 | 25071 | 574.04 | | | too large |
| 31 | | 36.005 | 1775 | 46.45 | -22.61 | 0.06 | |
| 32 | | 35.411 | 1112 | 27.71 | | | too small |
| 33 | | 38.082 | 1161 | 27.97 | | | too small |
| 34 | | 37.479 | 835 | 19.86 | | | too small |
| Peach Leaf | QQ Std | 0.102 | 4833 | 106.89 | -26.12 | 44.10 | True δ ¹³ C= -26.20 |
| DORM | QQ Std | 0.080 | 3692 | 81.05 | -17.18 | 43.49 | True δ ¹³ C= -17.22 |

| Comments | | | | | | | | | | too large | | | | | | | | | | | | | | | | | | | | | | | | | True δ^{13} C= -17.20 | True δ ¹³ C= -26.20 | True δ ¹³ C= -17.22 |
|------------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|-----------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|------------------------------|--------------------------------|--------------------------------|
| С% | 0.07 | 0.07 | 0.08 | 0.08 | 0.08 | 0.08 | 0.10 | 0.07 | 0.10 | | 0.28 | 0.06 | 0.07 | 0.05 | 0.09 | 0.10 | 0.13 | 0.36 | 1.77 | 1.18 | 1.27 | 0.87 | 0.93 | 0.84 | 0.80 | 0.64 | 0.55 | 0.52 | 0.48 | 0.66 | 0.58 | 0.37 | 0.56 | 0.45 | 1.70 | 44.22 | 43.43 |
| 8 ¹³ C VPDB | -25.97 | -26.03 | -24.82 | -17.37 | -21.89 | -23.94 | -14.79 | -24.64 | -14.61 | | -8.42 | -20.98 | -13.03 | -26.14 | -25.37 | -25.61 | -25.21 | -25.08 | -25.68 | -25.63 | -25.79 | -25.85 | -25.78 | -26.21 | -26.25 | -26.03 | -25.76 | -26.06 | -26.05 | -26.05 | -25.58 | -25.66 | -25.91 | -26.02 | -17.32 | -26.36 | -17.13 |
| Area 44 (Vs) | 130.56 | 108.97 | 139.31 | 137.86 | 115.15 | 122.16 | 96.02 | 96.82 | 163.57 | 831.96 | 328.52 | 85.41 | 97.35 | 95.51 | 100.73 | 112.00 | 143.83 | 58.95 | 271.00 | 212.03 | 211.33 | 153.48 | 180.41 | 142.57 | 149.57 | 115.50 | 134.45 | 86.99 | 77.80 | 117.38 | 111.33 | 66.73 | 101.98 | 76.91 | 104.39 | 127.20 | 88.23 |
| Ampl 44 (mV) | 4818 | 3825 | 4641 | 5123 | 4545 | 4827 | 3887 | 3823 | 6595 | 35030 | 13978 | 2908 | 3569 | 2994 | 3560 | 4064 | 5446 | 2278 | 11124 | 8697 | 8789 | 6312 | 7373 | 5814 | 6062 | 4686 | 5533 | 3496 | 3170 | 4740 | 4413 | 2677 | 4091 | 3133 | 4247 | 5265 | 3713 |
| Amount (mg) | 72.014 | 60.689 | 69.720 | 64.657 | 54.912 | 61.439 | 38.621 | 53.810 | 60.996 | 65.186 | 44.553 | 56.478 | 51.323 | 69.958 | 42.580 | 43.764 | 41.124 | 6.654 | 5.786 | 6.824 | 6.361 | 6.752 | 7.442 | 6.562 | 7.174 | 7.018 | 9.499 | 6.526 | 6.451 | 6.956 | 7.483 | 7.239 | 7.126 | 6.828 | 2.396 | 0.111 | 0.080 |
| Identifier 2 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | QQ Std | QQ Std | Std |
| Identifier 1 | 35 | 36 | 37 | 38 | 39 | 40 | 41 | 42 | 43 | 44 | 45 | 46 | 47 | 48 | 49 | 50 | 51 | 52 | 53 | 54 | 55 | 56 | 57 | 58 | 59 | 60 | 61 | 62 | 63 | 64 | 65 | 66 | 67 | 68 | MT Soil | Peach Leaf | DORM |
| Analysis # | 118770 | 118771 | 118772 | 118773 | 118774 | 118775 | 118776 | 118777 | 118778 | 118779 | 118782 | 118783 | 118784 | 118785 | 118786 | 118787 | 118788 | 118789 | 118790 | 118791 | 118794 | 118795 | 118796 | 118797 | 118798 | 118799 | 118800 | 118801 | 118802 | 118803 | 118806 | 118807 | 118808 | 118809 | 118781 | 118793 | 118810 |

| ysis # | Identifier 1 | Identifier 2 | Amount (mg) | Ampl 44 (mV) | Area 44 (VS) | 8 ¹⁵ C VPDB | C% | Comments |
|--------|--------------|--------------|-------------|--------------|--------------|------------------------|-------|--------------------------------|
| 827 | 69 | | 7.993 | 3310 | 81.23 | -25.65 | 0.40 | |
| 828 | 70 | | 6.940 | 4222 | 105.34 | -25.79 | 0.59 | |
| 829 | 71 | | 7.409 | 3311 | 81.14 | -25.72 | 0.43 | |
| 830 | 72 | | 1.016 | 4261 | 99.32 | 3.40 | 3.81 | |
| 831 | 73 | | 6.858 | 2911 | 71.21 | -25.66 | 0.41 | |
| 832 | 74 | | 7.480 | 2621 | 64.56 | -25.72 | 0.34 | |
| 833 | 75 | | 7.053 | 2588 | 63.59 | -25.70 | 0.36 | |
| 834 | 76 | | 6.926 | 2688 | 66.47 | -25.87 | 0.38 | |
| 835 | 17 | | 7.185 | 3426 | 86.63 | -25.72 | 0.47 | |
| 836 | 78 | | 7.373 | 2072 | 51.27 | -25.88 | 0.28 | |
| 839 | 62 | | 7.528 | 3431 | 85.79 | -25.85 | 0.45 | |
| 840 | 80 | | 7.587 | 1846 | 46.91 | -25.60 | 0.25 | |
| 841 | 81 | | 7.390 | 4612 | 113.12 | -25.90 | 0.59 | |
| 842 | 82 | | 7.191 | 2637 | 65.40 | -25.94 | 0.36 | |
| 843 | 83 | | 7.458 | 3832 | 94.86 | -25.96 | 0.50 | |
| 844 | 84 | | 7.492 | 3926 | 97.39 | -25.93 | 0.50 | |
| 845 | 85 | | 7.752 | 3305 | 82.18 | -25.79 | 0.42 | |
| 846 | 86 | | 7.254 | 3077 | 77.34 | -25.81 | 0.42 | |
| 847 | 87 | | 7.596 | 3652 | 92.01 | -25.92 | 0.47 | |
| 848 | 88 | | 7.158 | 3113 | 78.43 | -25.99 | 0.43 | |
| 851 | 89 | | 7.755 | 3832 | 96.12 | -25.94 | 0.48 | |
| 852 | 06 | | 7.551 | 4085 | 101.59 | -26.05 | 0.53 | |
| 853 | 91 | | 7.245 | 4100 | 102.70 | -25.81 | 0.55 | |
| 854 | 92 | | 7.022 | 4765 | 118.02 | -25.84 | 0.65 | |
| 855 | 93 | | 7.062 | 3961 | 98.37 | -25.97 | 0.55 | |
| 856 | 94 | | 7.546 | 3890 | 98.13 | -25.98 | 0.51 | |
| 857 | 95 | | 7.213 | 4674 | 115.67 | -25.79 | 0.62 | |
| 858 | 96 | | 7.607 | 3406 | 85.17 | -25.83 | 0.44 | |
| 859 | 97 | | 7.275 | 4417 | 108.90 | -25.85 | 0.59 | |
| 860 | 98 | | 6.919 | 4566 | 113.41 | -25.72 | 0.64 | |
| 863 | 66 | | 7.457 | 4295 | 106.41 | -25.91 | 0.56 | |
| 864 | 100 | | 7.427 | 4126 | 102.72 | -25.88 | 0.54 | |
| 865 | 101 | | 7.359 | 3088 | 76.383 | -26.03 | 0.41 | |
| 866 | 102 | | 7.323 | 3398 | 85.124 | -26.10 | 0.46 | |
| 838 | MT Soil | QQ Std | 2.019 | 3517 | 84.50 | -17.11 | 1.63 | True 8 ¹³ C= -17.20 |
| 850 | Peach Leaf | QQ Std | 0.119 | 5623 | 133.38 | -26.16 | 43.36 | True 8 ¹³ C= -26.20 |
| 227 | Maca | | | 00,0 | 01.00 | | | -130 11 00 |

| Comments | | | | | | | | | | | | | | | | | | | | | | | | | | True δ ¹³ C= -17.20 | True δ^{13} C= -26.20 | True 8 ¹³ C= -17.22 |
|------------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|---------|---------|---------|--------|--------------------------------|------------------------------|--------------------------------|
| %D | 0.64 | 0.64 | 0.66 | 0.63 | 0.63 | 0.68 | 0.70 | 0.68 | 0.65 | 0.81 | 0.51 | 0.71 | 0.53 | 0.71 | 0.67 | 0.58 | 1.39 | 1.77 | 33.68 | 47.52 | 15.32 | 0.02 | 0.03 | 0.02 | 0.48 | 1.67 | 43.71 | 42.80 |
| δ ¹³ C VPDB | -26.30 | -26.13 | -26.13 | -26.28 | -26.39 | -26.33 | -26.45 | -26.44 | -26.47 | -26.49 | -26.23 | -26.14 | -26.12 | -26.13 | -26.14 | -26.24 | -9.91 | -8.13 | -25.43 | -26.07 | -25.17 | -26.36 | -25.90 | -26.09 | -10.37 | -17.10 | -26.29 | -17.16 |
| Area 44 (Vs) | 215.58 | 158.44 | 197.81 | 154.19 | 164.86 | 178.42 | 183.73 | 176.54 | 173.72 | 204.54 | 126.53 | 181.11 | 131.73 | 187.94 | 169.45 | 151.13 | 101.61 | 95.06 | 111.61 | 418.47 | 117.37 | 67.14 | 78.67 | 55.98 | 111.92 | 84.971 | 116.97 | 86.09 |
| Ampl 44 (mV) | 8770 | 6449 | 7822 | 6108 | 6335 | 7165 | 7257 | 6863 | 6932 | 8133 | 5015 | 7364 | 5353 | 7615 | 6703 | 6108 | 4239 | 4054 | 4602 | 16948 | 4816 | 2693 | 2987 | 2163 | 4829 | 3503 | 4900 | 3600 |
| Amount (mg) | 13.498 | 10.067 | 12.121 | 9.947 | 10.606 | 10.616 | 10.625 | 10.484 | 10.814 | 10.168 | 10.189 | 10.325 | 10.194 | 10.644 | 10.178 | 10.581 | 2.991 | 2.186 | 0.135 | 0.347 | 0.311 | 117.060 | 114.965 | 114.396 | 9.492 | 2.119 | 0.109 | 0.083 |
| Identifier 2 | | | | | | | | | | | | | | | | | | | | | | | | | | QQ Std | QQ Std | QQ Std |
| Identifier 1 | 103 | 104 | 105 | 106 | 107 | 108 | 109 | 110 | 111 | 112 | 113 | 114 | 115 | 116 | 117 | 118 | 19 | 21 | 28 | 29 | 30 | 32 | 33 | 34 | 44 | MT Soil | Peach Leaf | DORM |
| Analysis# | 118898 | 118899 | 118900 | 118901 | 118902 | 118903 | 118904 | 118905 | 118906 | 118907 | 118910 | 118911 | 118912 | 118913 | 118914 | 118915 | 118916 | 118917 | 118922 | 118923 | 118924 | 118931 | 118934 | 118935 | 118925 | 118909 | 118921 | 118936 |

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 Tables 1-4- Stable carbon isotope test results from KEPSIL. Primary (USGS-24, IAEA-600, ANU) and secondary (DORM, MT

 Soil, Peach Leaf) standards were used to reference isotopic composition to ensure the lab equipment was functioning properly as well as the values given for the core samples were outputting reasonable results.

VITA

Erica Gerweck was born in Wichita, Kansas and shortly after moved to Lee's Summit, Missouri. After graduating high school in 2011, Erica attended Longview Community College where she received her Associate in Arts in 2013. At Longview, Erica was a part of the Phi Theta Kappa national honors fraternity. Missouri State University is where Erica attended for her Bachelors of Science in Geology; she also received a minor in Environmental Science and Policy. She graduated from Missouri State University in 2015.

While attending Missouri State, Erica performed research under Dr. Gary Michelfelder. This research was focused on the volcanology of Crater of Diamonds State Park in Murfreesboro, Arkansas. Erica was awarded a scholarship from the College of Natural and Applied Science for her research. At the University of Mississippi, Erica was awarded the Gulf Coast Association of Geological Societies Research Grant for her research.

In the summer of 2014, Erica had a geology internship in Tulsa, Oklahoma at Chestnut Exploration and Production. Currently, she is a teaching assistant at the University of Mississippi teaching Environmental Geology.

Erica's professional memberships include the Young Professionals of Oxford, Mississippi, the Geological Society of America, American Association of Petroleum Geologists, and the Phi Theta Kappa national honor fraternity.