High-Resolution Chemostratigraphic Analysis of Wolfcamp D Shale-Unit in Upton and Midland Counties – Is it possible to identify stratigraphically significant surfaces using $\delta^{13}C_{carb}$?*

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Abstract

The Late Paleozoic Ice Age represents a dynamic period in Earth system history recording a shift from icehouse to greenhouse conditions. Concomitant with this change was a series high-frequency, high-amplitude sea level fluctuations leading to the deposition of “Kansas type” cyclothems in the Mid-Continent, and a similar rhythmic expression of interbedded shales and carbonates in the Midland Basin. Geochemistry has the potential to highlight certain environmental conditions that may not be readily apparent at the core or outcrop scale. Stable isotope geochemistry is a particularly powerful tool when examining mud-rich successions, because changes in organic matter partitioning may be recorded first in δ^{13}CDIC of seawater and consequently in $\delta^{13}C_{carb}$ of marine rocks. Provided significant post- depositional alteration has not occurred, $\delta^{13}C_{carb}$ may also be used to document distinct chronostratigraphic time horizons within the subsurface. Here we use principle component analysis of a high- resolution XRF dataset in tandem with $\delta^{13}C_{carb}$ measurements to document periods of organic matter enrichment as well as post-depositional organic matter destruction. We identify several thin bed intervals (<6 in.) marked by sharp negative $\delta^{13}C_{carb}$ excursions and sedimentary features consistent with low sedimentation. These intervals are interpreted to have undergone significant bacterially mediated diagenesis and may mark periods of limited or non- deposition. We hypothesize these intervals also have the potential to be used as chemostratigraphic tie-points within the basin. Results of this study indicate that while post-depositional diagenetic processes in these Late Pennsylvanian mudstones have altered the primary $\delta^{13}C_{carb}$ signal, $\delta^{13}C_{carb}$ may still be used to capture potential correlations intra-basin. The workflow presented herein may aide correlation in mud-rich environments of deposition.

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Adaptation of Southwest Section AAPG Poster Presentation

April 6-9th, 2019

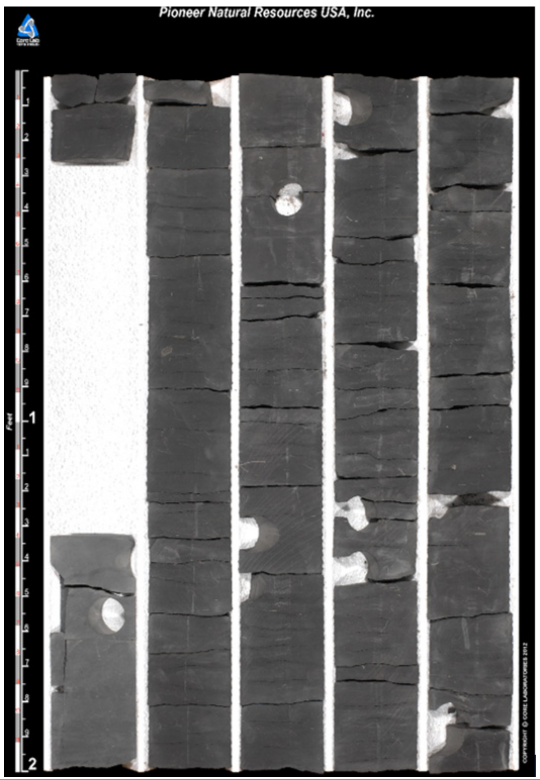
Stable
Isotope
Geochemistry
Laboratory

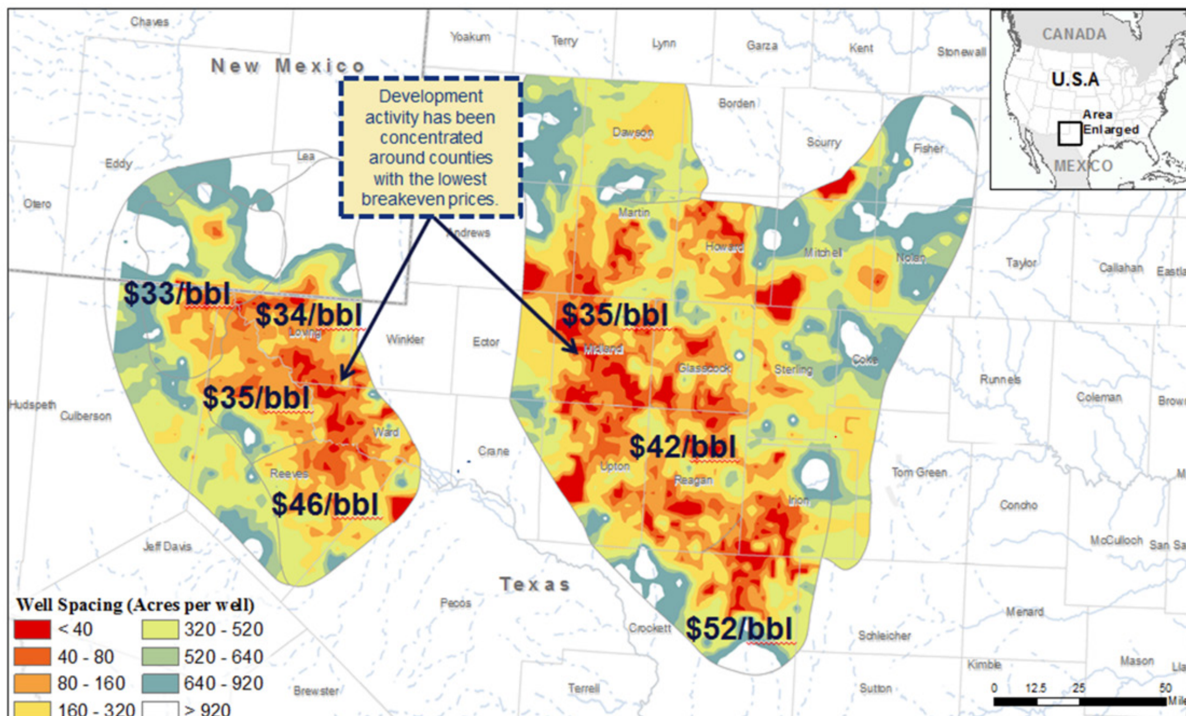
Outline

1. Introduction
   - Motivation, Midland Basin, Carbon Isotopes
2. Methods
   - Stable Isotope Geochemistry, PCA
3. Results
   - $\delta^{13}C_{CARB}$ Midland and Upton Counties
4. Discussion
   - $\delta^{13}C_{CARB}$ record, Potential Correlations
5. Conclusions

Motivation

- Heterogeneity is inherent in mudstone dominated successions
- This heterogeneity may not be apparent using traditional methods of characterization
- Since geologic factors have been shown to have the greatest affect on expected ultimate recovery (EUR), there is a need for detailed characterization of mudstone-dominated successions



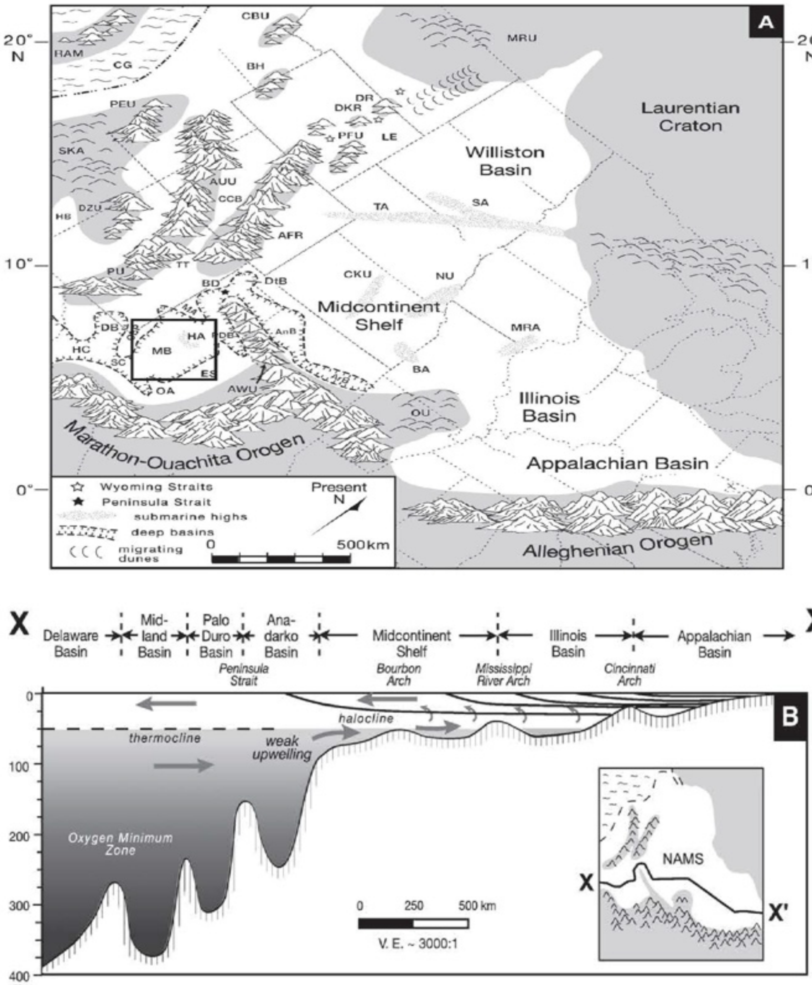


https://www.woodmac.com/news/editorial/delaware-wolfcamp/

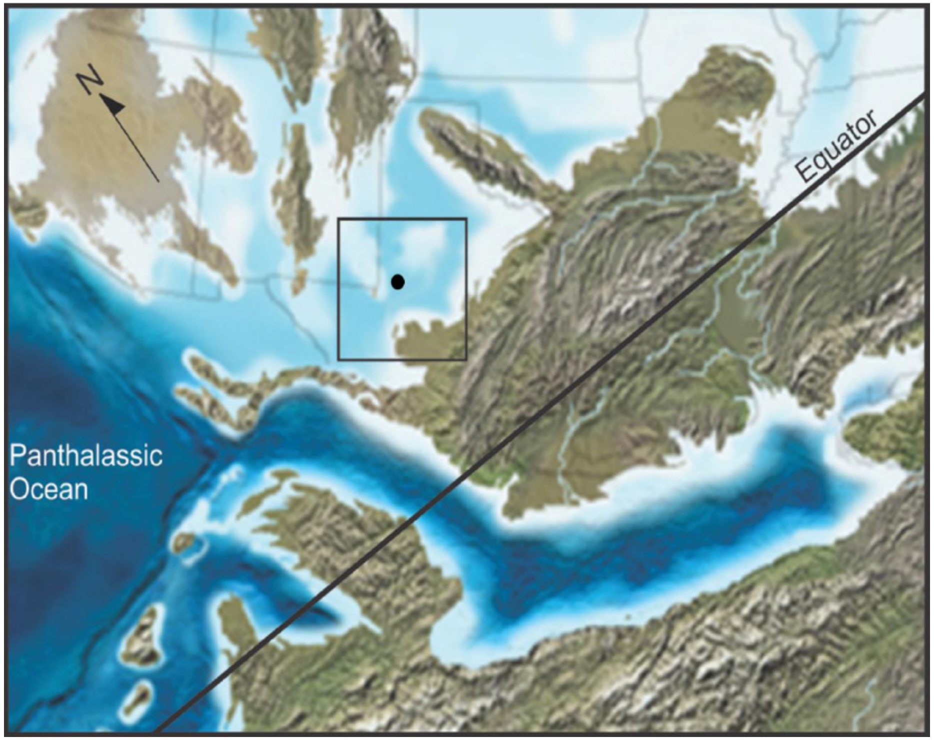
Objectives

1. Determine if carbon isotopes can illuminate paleo-environmental processes associated with the deposition of the Midland Basin WCD
2. Given this understanding, determine if a high-resolution (every 2 in.) carbon isotope ($\delta^{13}C_{CARB}$) record can aide in correlation within the basin

Regional Paleogeography



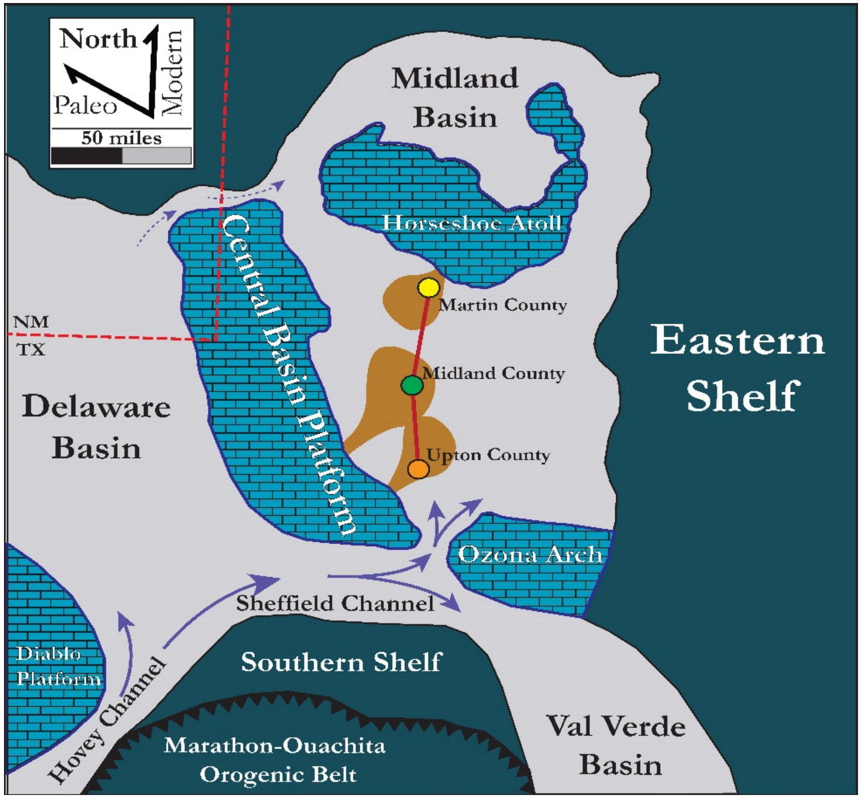
Modified from Algeo and Heckel, 2008



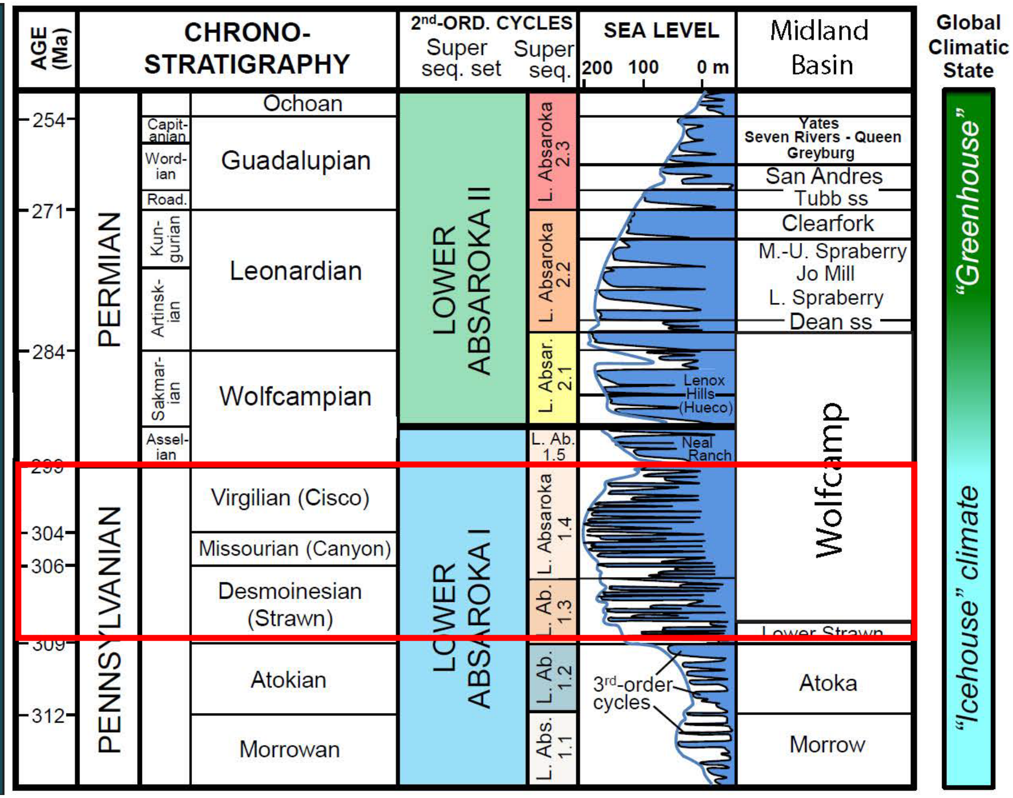
Modified from Blakey, 2013

- Position of the Midland Basin during Late Pennsylvanian led to the development of a monsoonal climate, impacting circulation and sedimentation patterns within the basin

Study Area



Reis, 2018



Modified from Waite and Reed, 2014

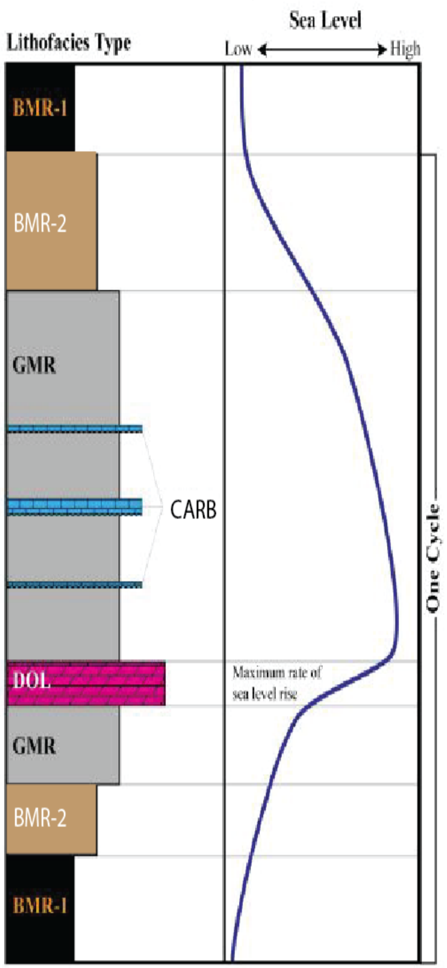
- Two cores in varying degrees of proximity to carbonate buildups within the basin
- High frequency, high amplitude sea level fluctuations associated with L. Absaroka Super Sequences 1.3 & 1.4

WCD vs Kansas Type Cyclothems

Lithofacies Description

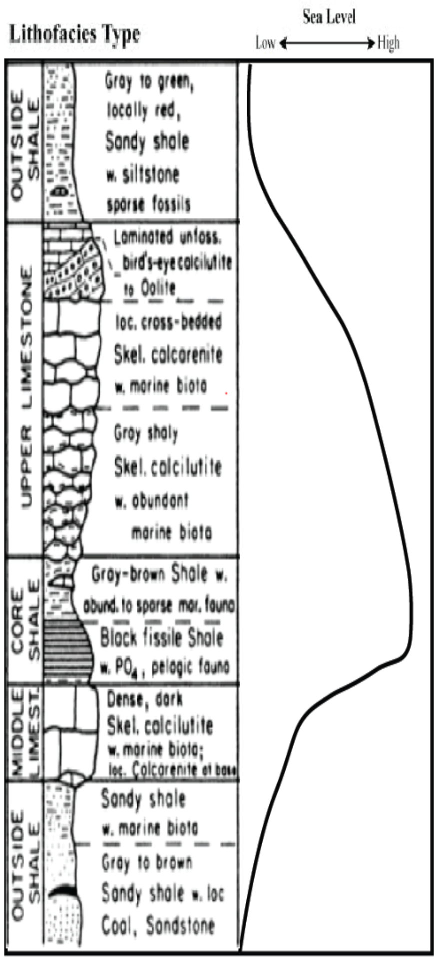
- ❑ BMR-1 (siliceous OM-rich mudstone)
  High Si%, Low Al%, High TOC Wt%, abundant phosphate nodules
- ❑ BMR-2 (clayey OM-rich mudstone)
  High Al%, moderate TOC Wt%, absence of phosphate nodules
- ❑ GMR (calcareous mudstone)
  High Ca%, normal grading
- ❑ CARB (carbonate)
  allochthonous fossil hash, sharp scoured bases
- ❑ DOL (dolomite)
  microcrystalline-cement texture

Wolfcamp D Cyclothem



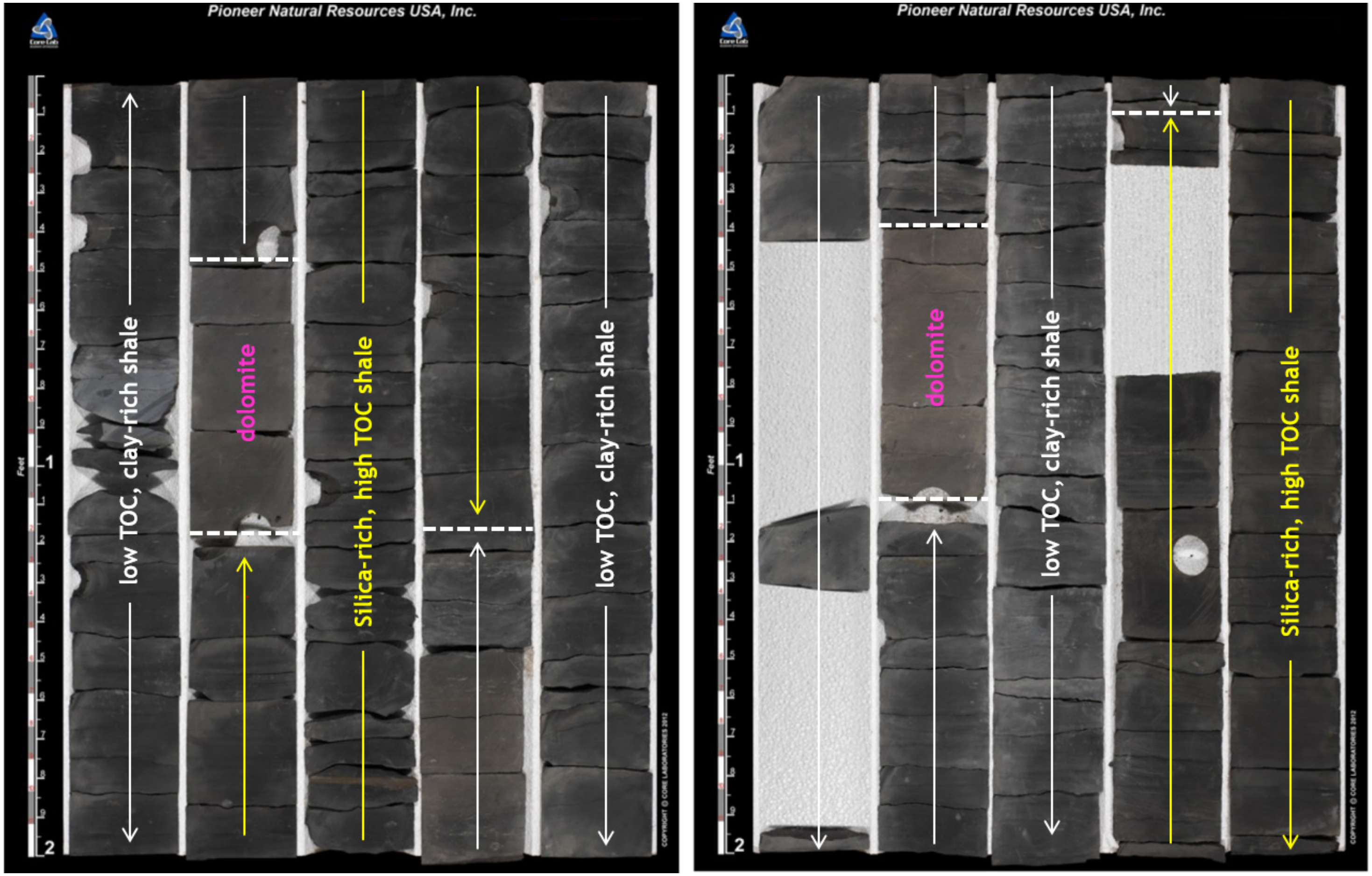
Modified from Ryan, 2016

Kansas Type Cyclothem



Modified from Heckel, 1977

WCD Cyclothem Example



Waite, 2014

WCD Depositional Packages 20-30 ft. in thickness

Organic Matter Enrichment

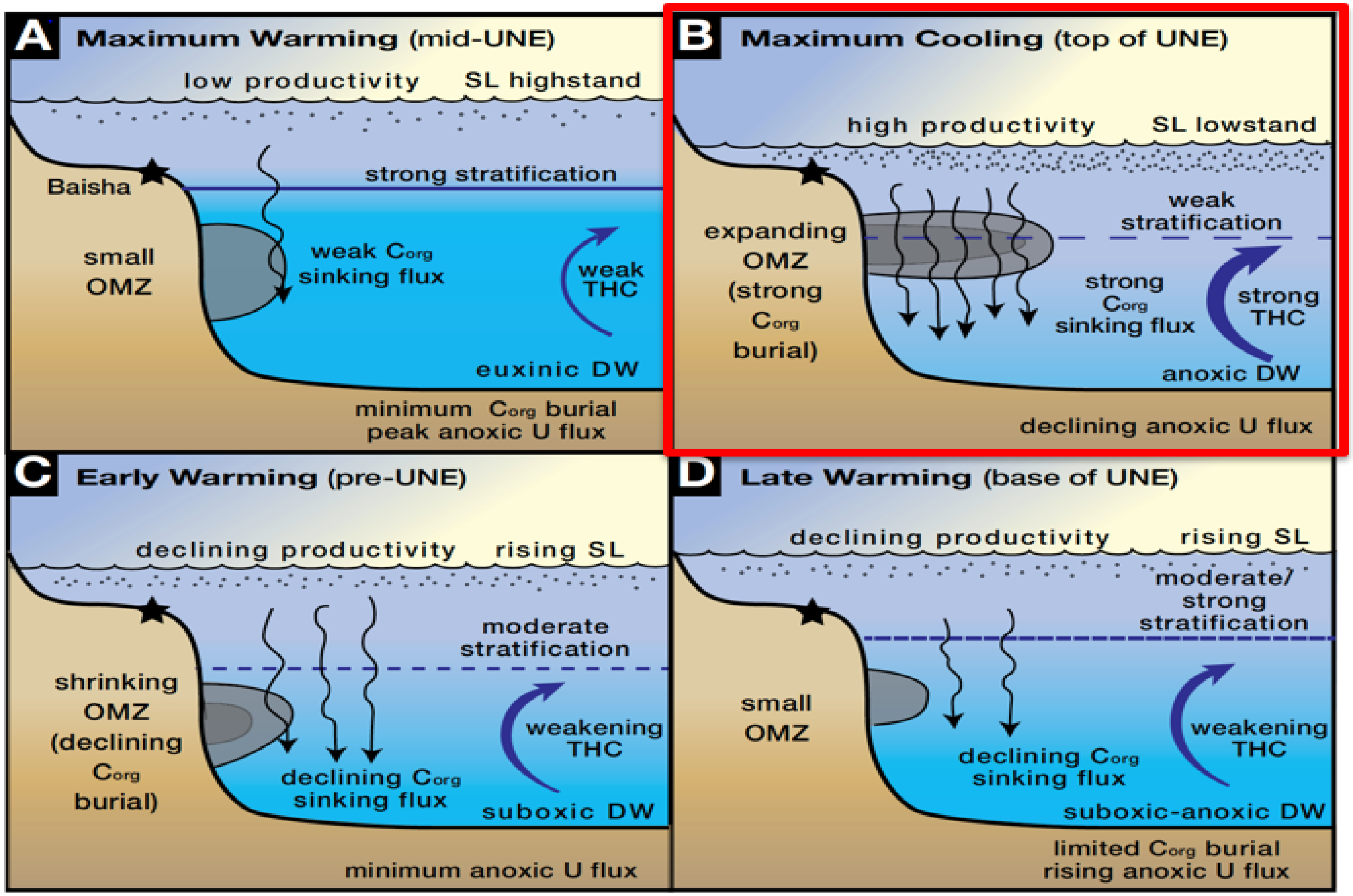
OM enrichment may be attributed to a function of:

- **Productivity**
  - -Rate at which OM is exported from surface waters
- **Destruction**
  - -Rate at which OM is destroyed
  - -Function of oxygenation
- **Dilution**
  - -Defined by non OM sedimentation rate

Bohacs et al., 1997

Conceptual Model for OM enrichment

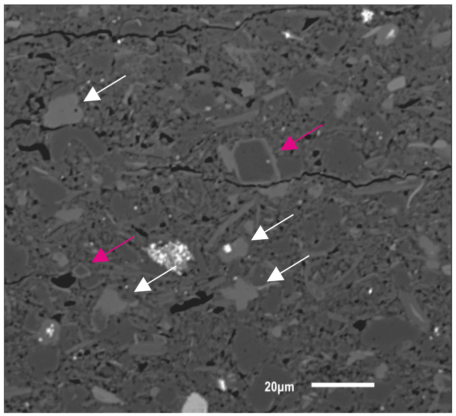
Stratification is a catalyst for OME

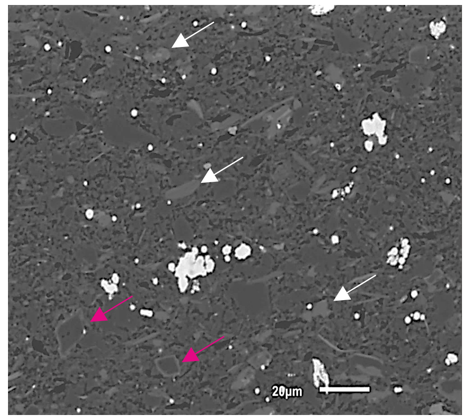


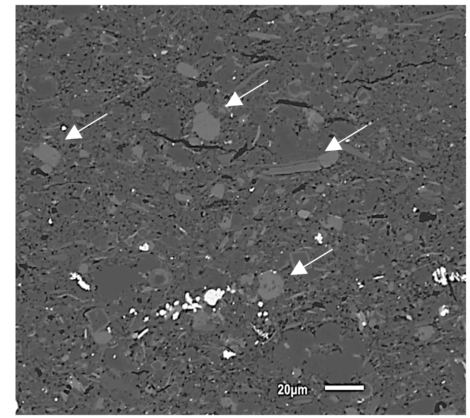
Song et al., 2017

Carbon Isotopes ($\delta^{13}C_{CARB}$)

Carbon isotopes can be used to track changes in OM partitioning







Positive $\delta^{13}C_{CARB}$ Excursions

- OM Enrichment results in burial and preservation of ^{12}C rich OM

^{12}C	^{13}C	^{14}C
12.00000	13.00335	14.0
98.89%	1.11%	t½ = 5715yrs
Stable	Stable	Radioactive Cosmogenic/ anthropogenic

$$\delta^{13}C = \left(\frac{\left(\frac{^{13}C}{^{12}C}\right)_{sample}}{\left(\frac{^{13}C}{^{12}C}\right)_{standard}} - 1 \right) \times 1000 ‰$$

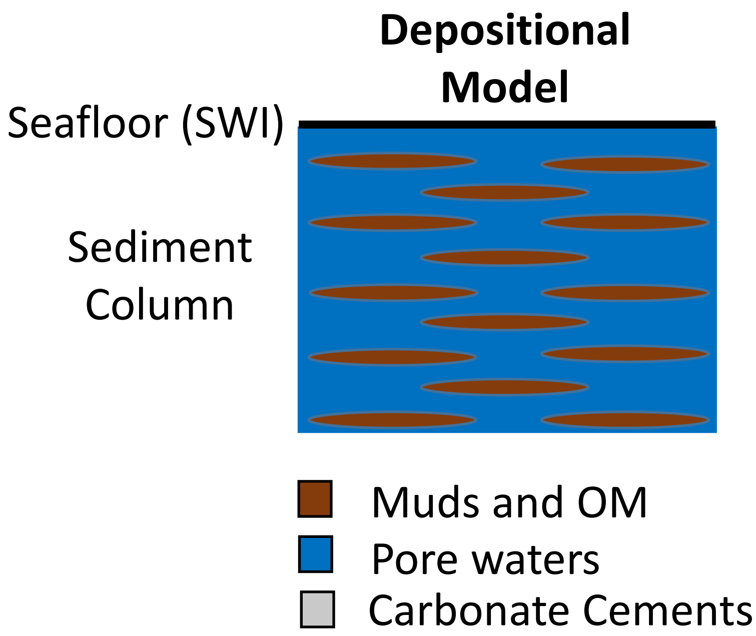
Negative $\delta^{13}C_{CARB}$ Excursions

- Destruction of ^{12}C rich OM
- Releases ^{12}C rich CO_2 resulting in carbonate cements ^{12}C

Process

1. Muds and OM deposited at SWI

2. Carbonate cements precipitate out from the marine DIC pool
   - ❑ OM enrichment and burial of OM results more positive δ^{13}C in the marine DIC reservoir
   - ❑ Diagenesis results in the destruction of OM and production of carbonate cements rich in ^{12}C



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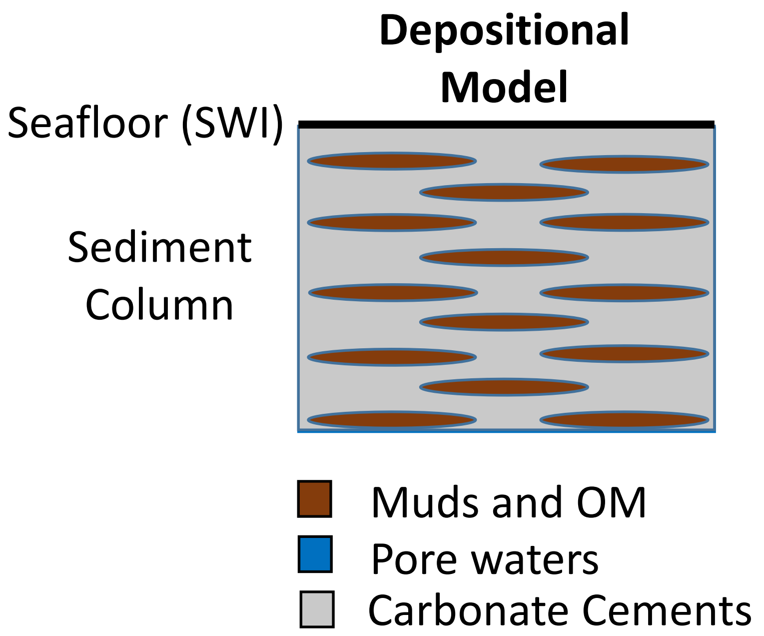


Early Diagenesis

1. Bacterial Sulfate Reduction

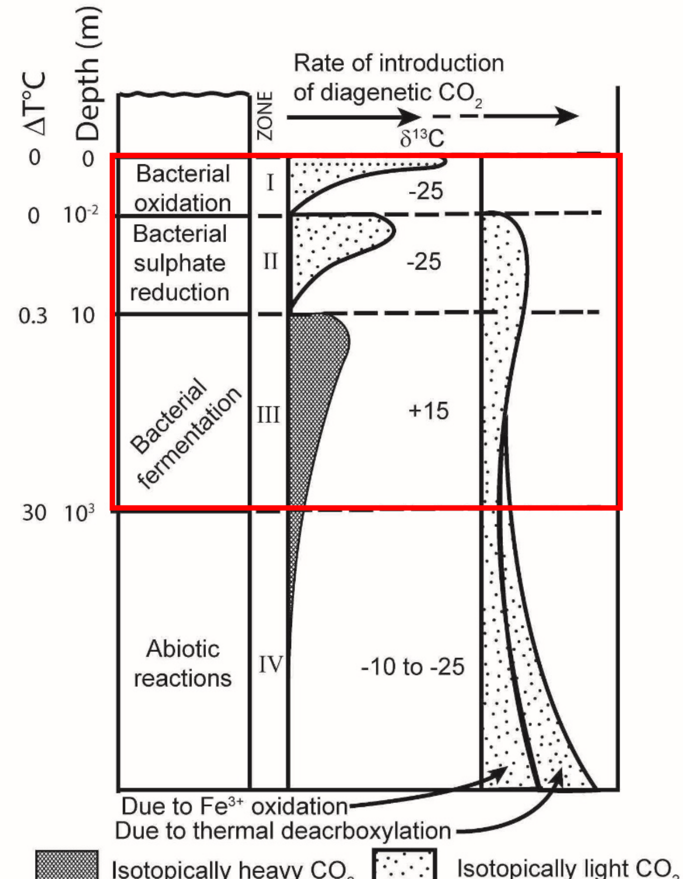
$$2CH_2O + SO_4^{2-} \rightarrow 2HCO_3^- + H_2S$$

- ❑ Sedimentary features: Iron rich minerals including pyrite and Fe-carbonates

2. Methanogenesis

$$CH_3OOH \rightarrow CH_4 + CO_2$$

- ❑ Sedimentary features: ferroan dolomite



Modified from Irwin and Curtis, 1977

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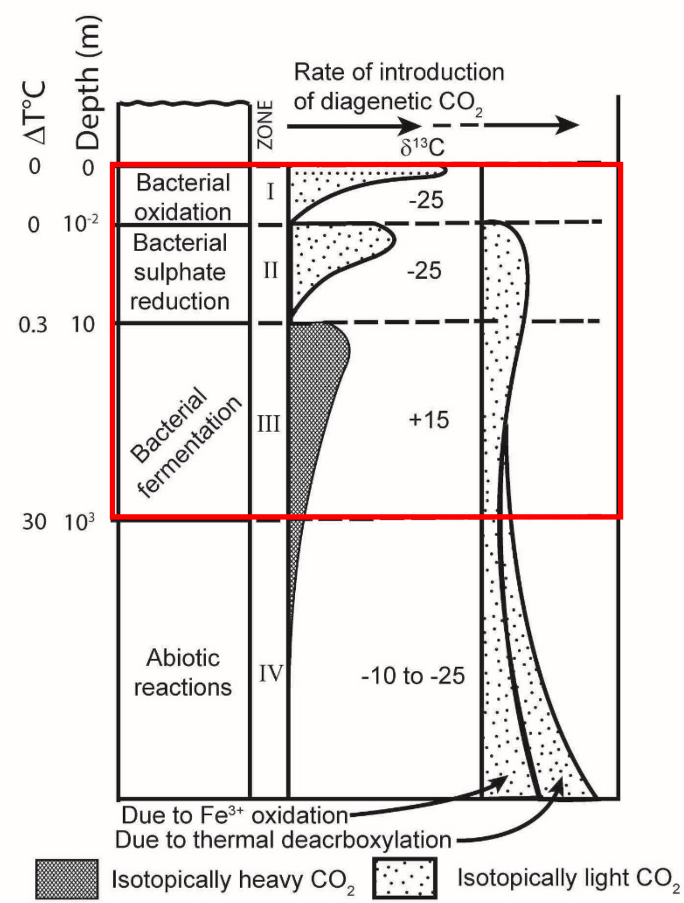
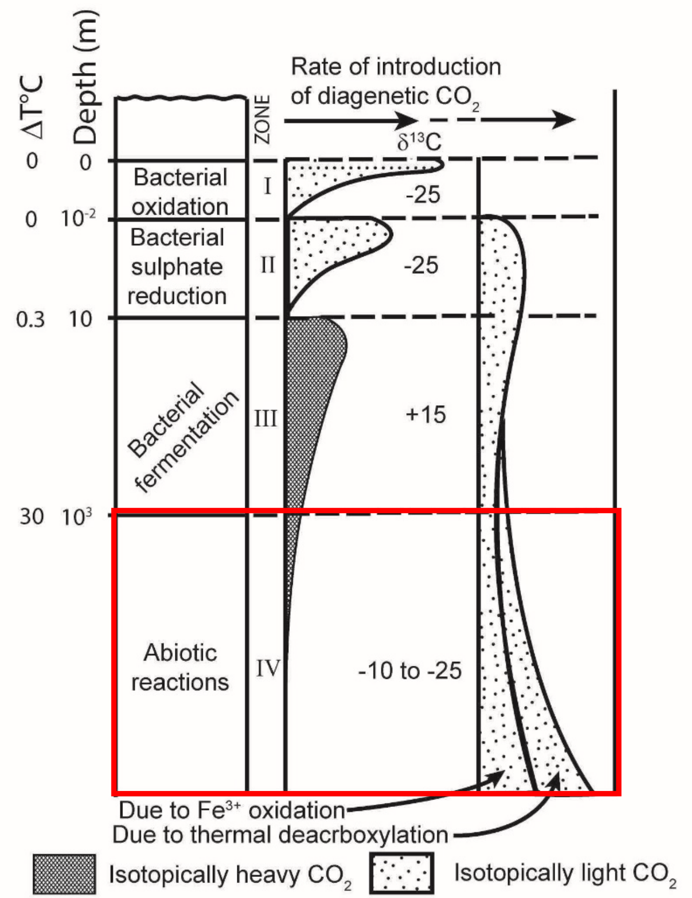


Modified from Irwin and Curtis, 1977

Late-Stage Diagenesis

1. Burial Diagenesis
   - ❑ Conversion of smectite to illite consumes K and releases Fe and Mg
   - ❑ Sedimentary features: ferroan dolomite
2. Brine Influence
   - ❑ Brine migration in the Triassic



Modified from Irwin and Curtis, 1977

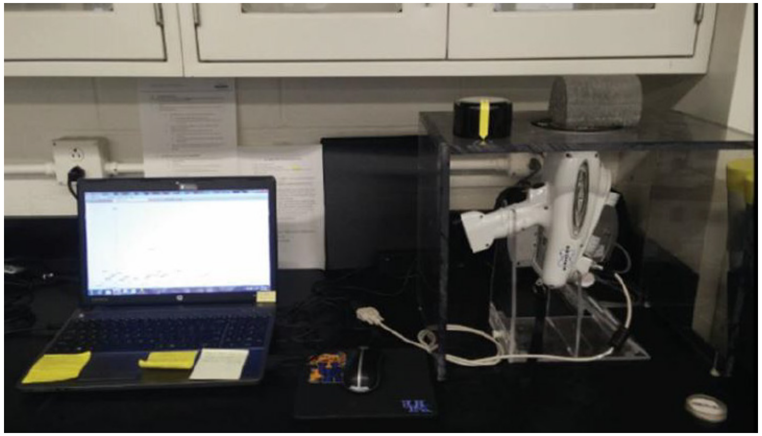
Methods

Stable Isotope Analysis

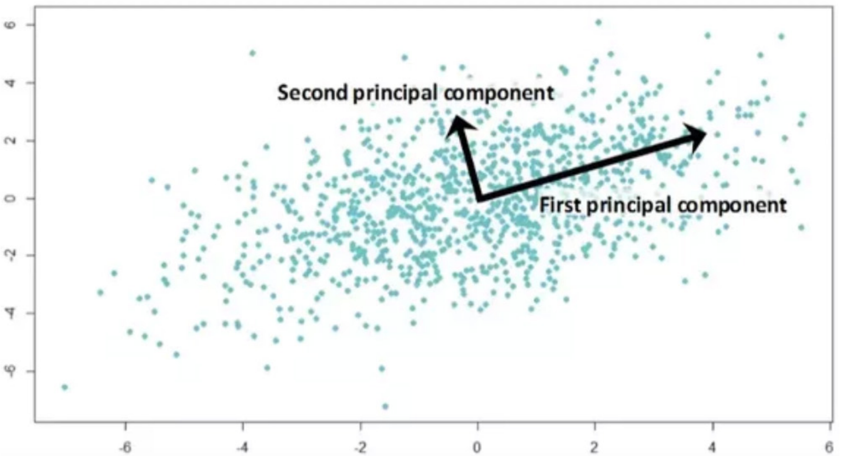
- ❑Bulk samples were homogenized and collected using a dremel
- ❑$\delta^{13}C_{CARB}$ measurements collected using ThermoFinnegan GasBench 2 connected to a Delta Plus IRMS

Methods

XRF data collected by previous students on handheld device



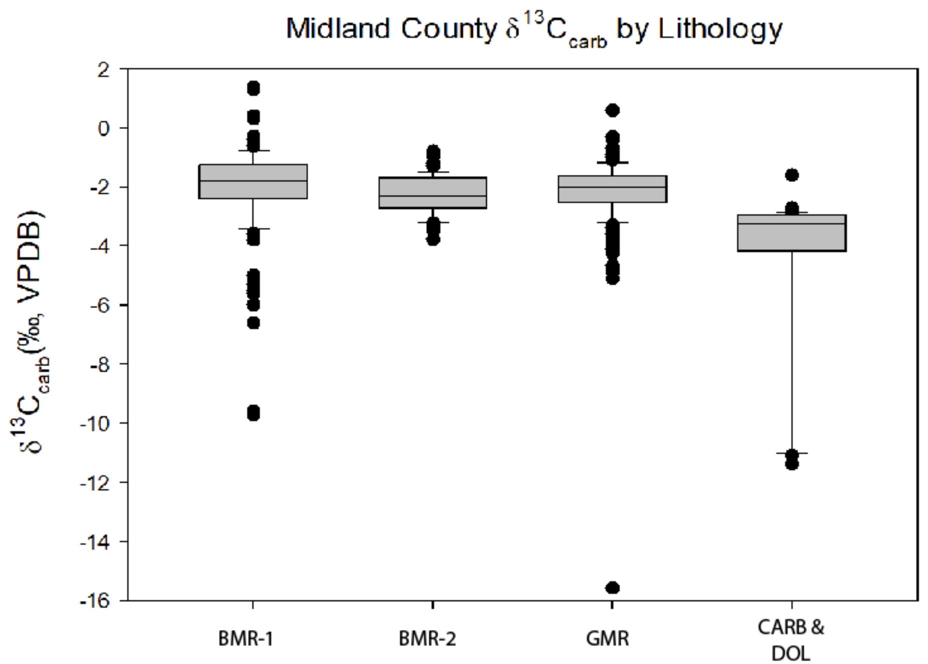
Principal Component Analysis on previously collected XRF data



SEM Image Analysis

Midland County $\delta^{13}C_{CARB}$

- BMR-1 $\delta^{13}C_{CARB}$ measurements more positive in comparison to other measurements
- There are several anomalously negative $\delta^{13}C_{CARB}$ measurements within the BMR-1, GMR, and CARB and DOL lithofacies

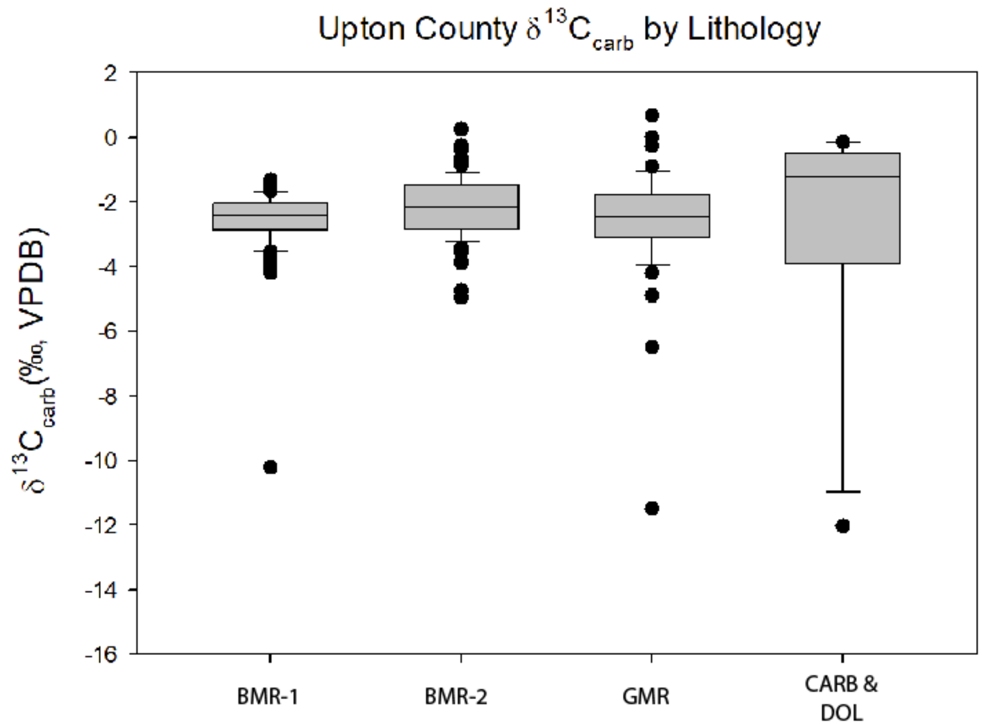


405 Samples, 108 BMR-1, 81 BMR-2, 208 GMR, 32 CARB & DOL

Upton County $\delta^{13}C_{CARB}$

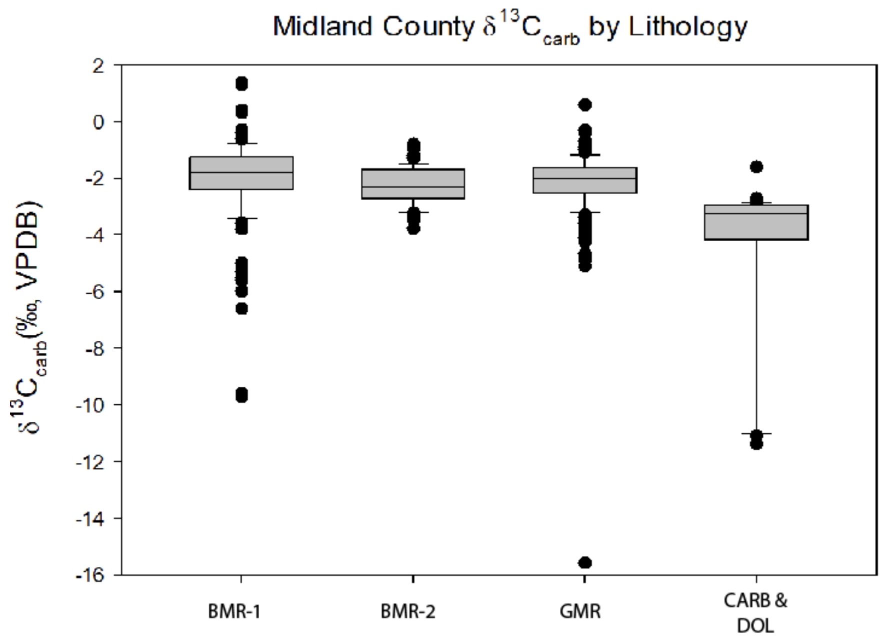
- Lack of positive BMR-1 $\delta^{13}C_{CARB}$ measurements in comparison to other lithofacies

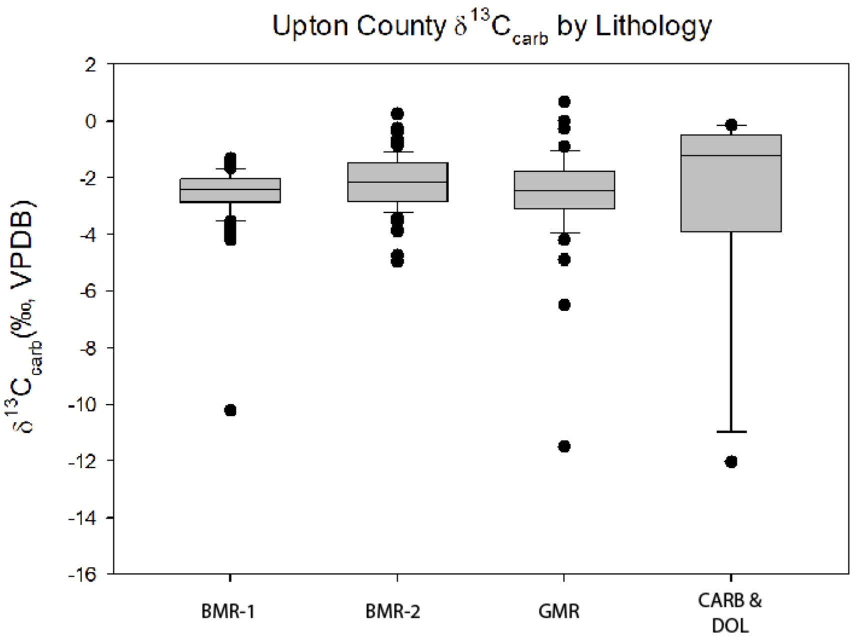
- Anomalously negative $\delta^{13}C_{CARB}$ measurements within the BMR-1, GMR, and CARB and DOL lithofacies



225 Samples, 75 BMR-1, 50 BMR-2, 36 GMR, 13 CARB & DOL

Midland vs Upton $\delta^{13}C_{CARB}$



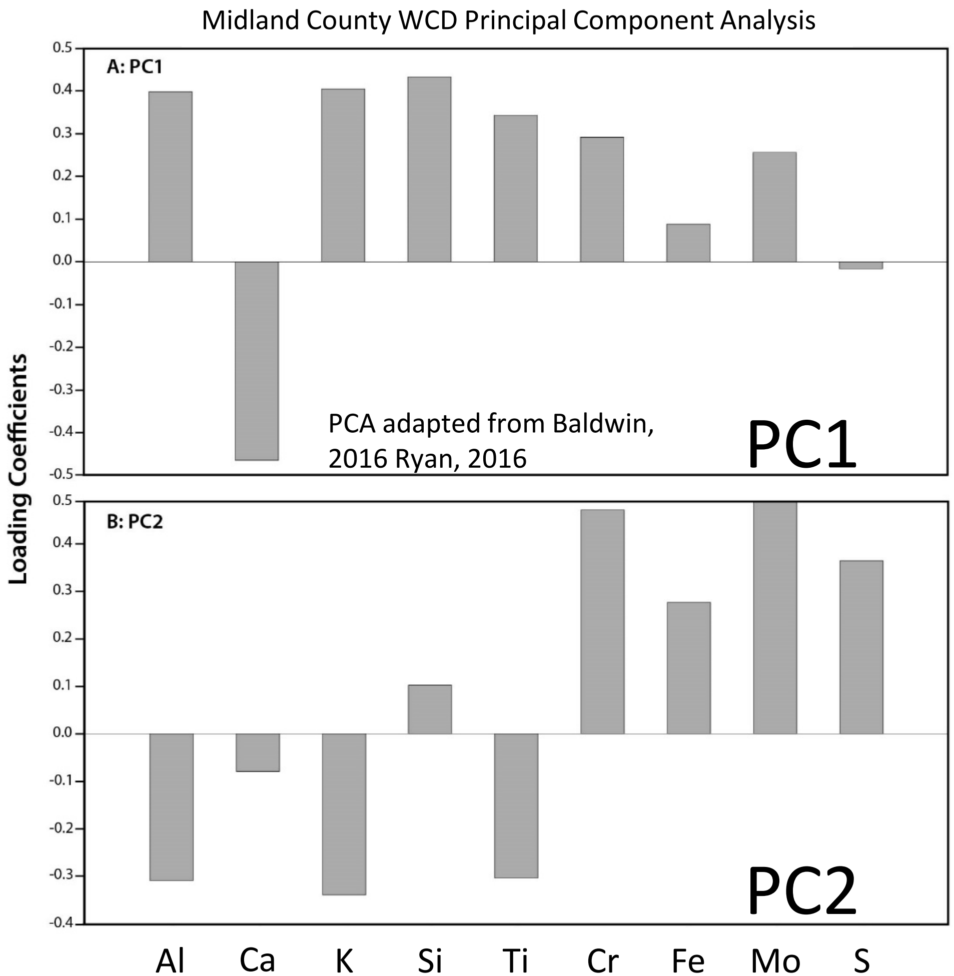


- Midland County $\delta^{13}C_{CARB}$ measurements within BMR-1 are elevated in comparison to Upton County

Principal Component Analysis

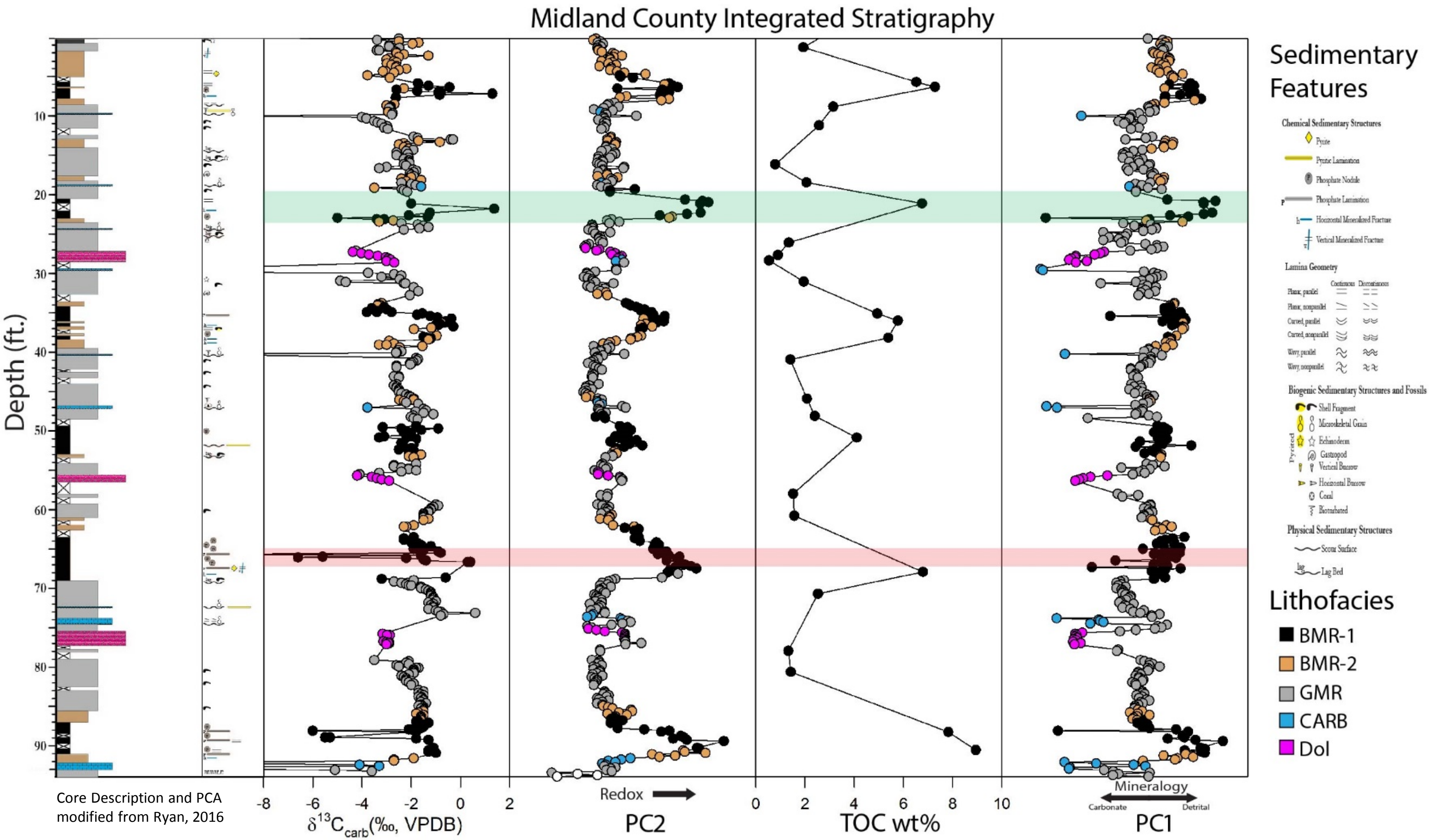
PCA reduced the dimensionality of major rock forming and redox elements in this study

- **Previous UK Graduates used PCA to identify depositional cycles within core**
- **PC1 Mineralogy**
  - -Positive Loading: Al, K, Si, Ti (Detrital)
  - -Negative Loading: Ca (Carbonate)
- **PC2 Redox**
  - -Positive Loading: Cr, Mo, S (Restriction)
  - -Negative Loading: Al, K, Ti (Detrital)
- **Midland County**
  - -First two principle components account for more the 60% of the variance within the dataset (PC1:44%, PC2: 23%)
- **Upton County**
  - -First two principle components account for more the 80% of the variance within the dataset (PC1:60%, PC2: 21%)



Midland County Integrated Stratigraphy

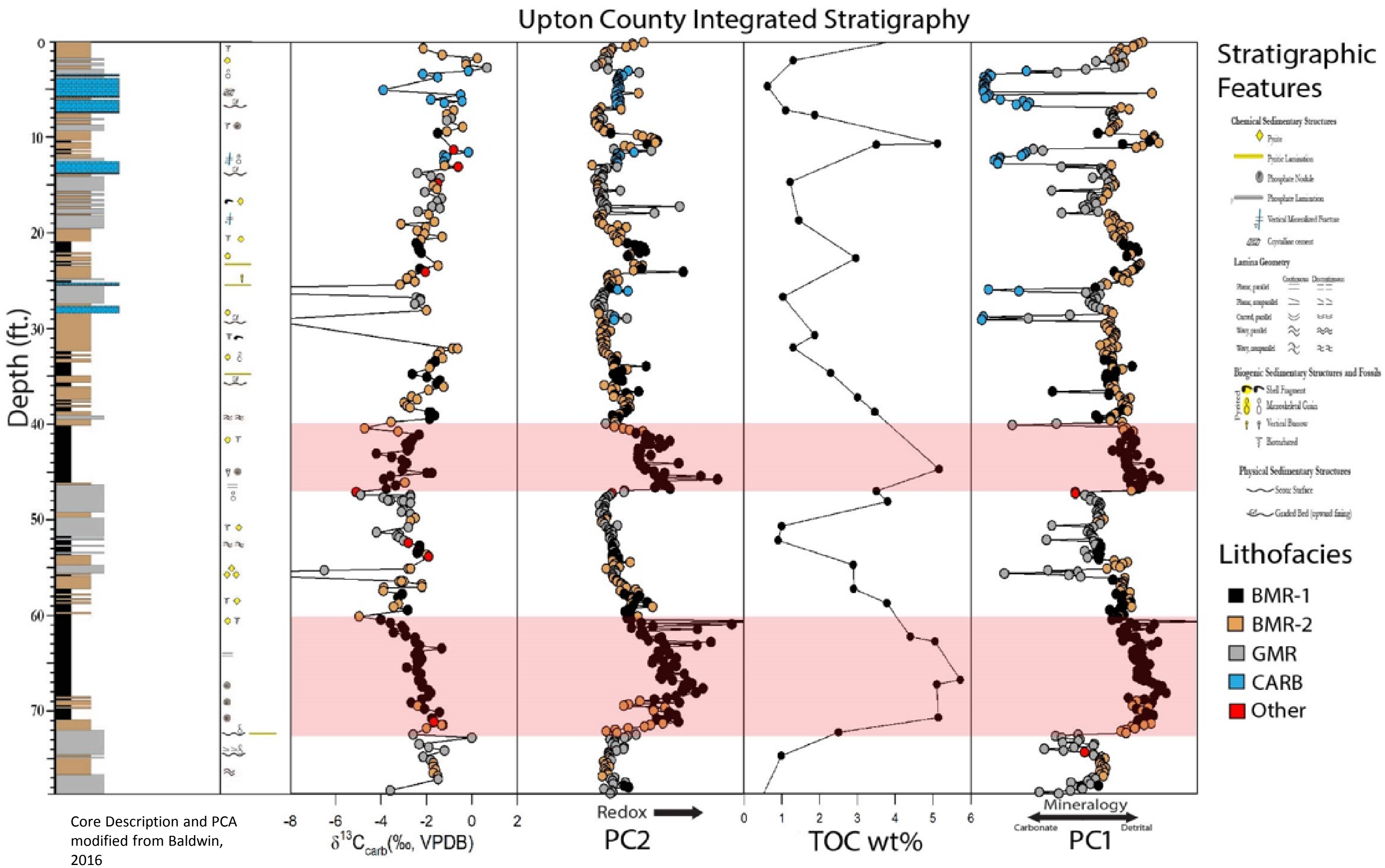
A signal reflecting OM enrichment



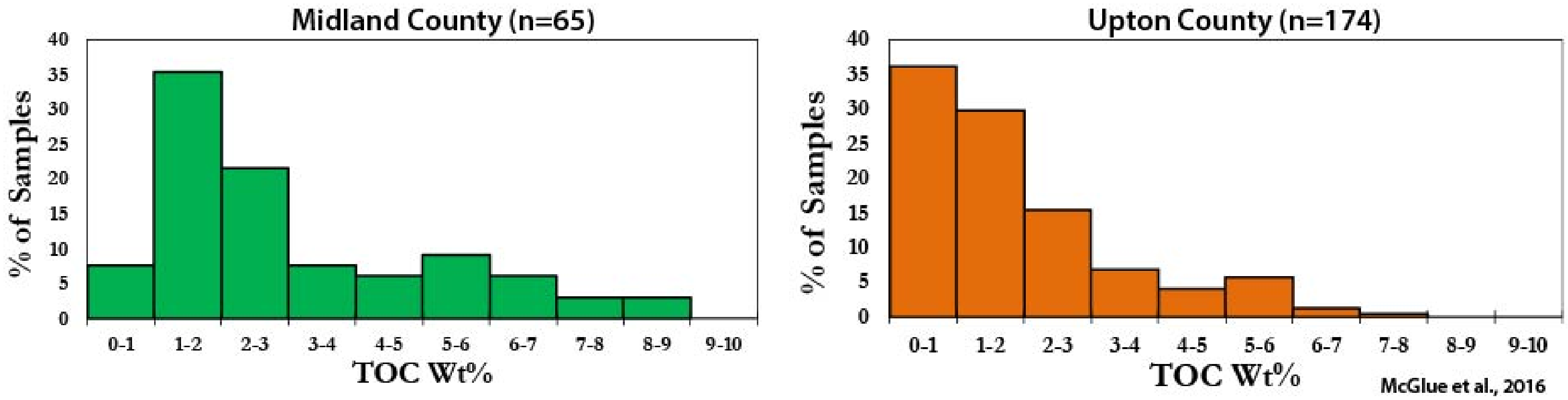
Core Description and PCA modified from Ryan, 2016

Upton County Integrated Stratigraphy

A signal reflecting the destruction on OM



Midland vs Upton County



- A marked difference exists in TOC Wt% measurements between Midland and Upton County

- Differences in OM enrichment may be attributed to a function of:
  - -Productivity
  - -Preservation
  - -Dilution

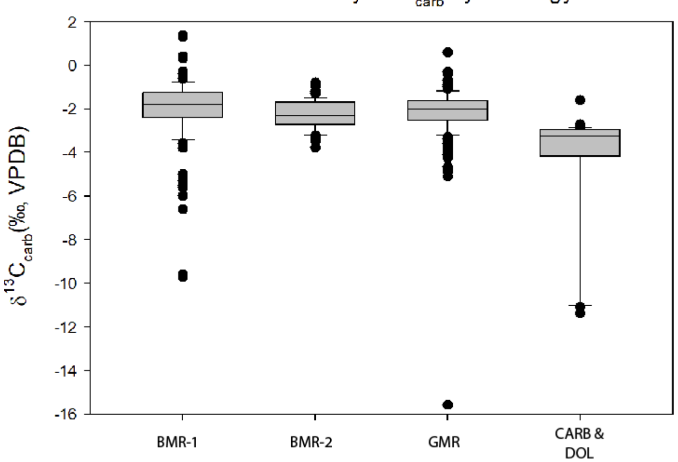
Midland vs Upton County Preservation and Dilution

- Redox measurements suggest a more oxic bottom waters and less preservation in Upton County in comparison to Midland County
- More positive $\delta^{13}C_{CARB}$ measurements in Midland County within BMR-1 suggest increased preservation of OM

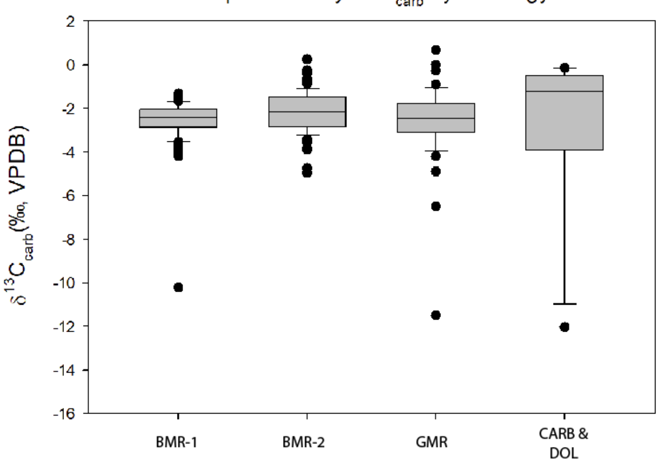
Enrichment Factors within BMR-1 in Midland and Upton Counties

Indicator	Midland County	Upton County
Average BMR-1 Cr Enrichment Factor	4.7	3.0
Average BMR-1 Mo Enrichment Factor	31.1	32.1
Average BMR-1 U Enrichment Factor	9.8	6.5
Average BMR-1 V Enrichment Factor	2.7	2.1
Average BMR-1 Mn Enrichment Factor	0.4	0.7

Midland County $\delta^{13}C_{carb}$ by Lithology

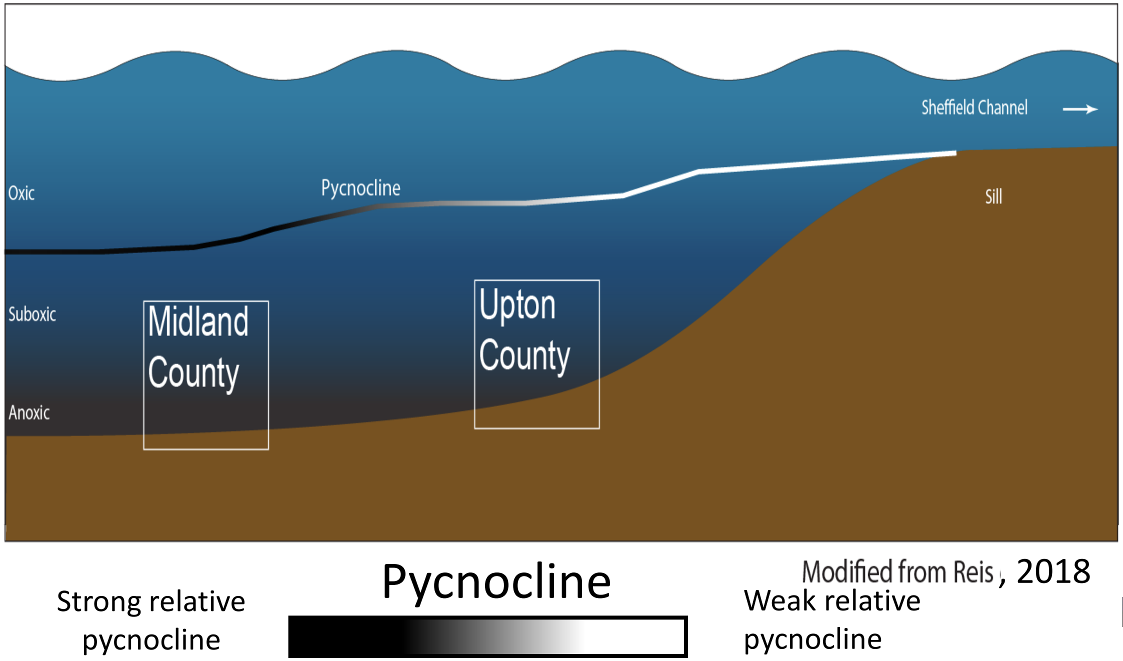


Upton County $\delta^{13}C_{carb}$ by Lithology

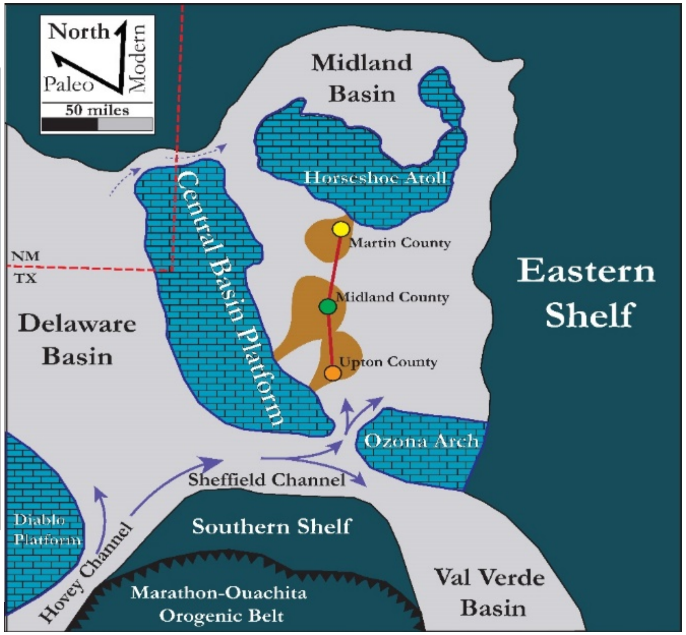


Midland vs Upton County Preservation and Dilution

Redox and $\delta^{13}C_{CARB}$ measurements suggest more oxic bottom waters and less preservation in Upton County in comparison to Midland County



Modified from Reis, 2018

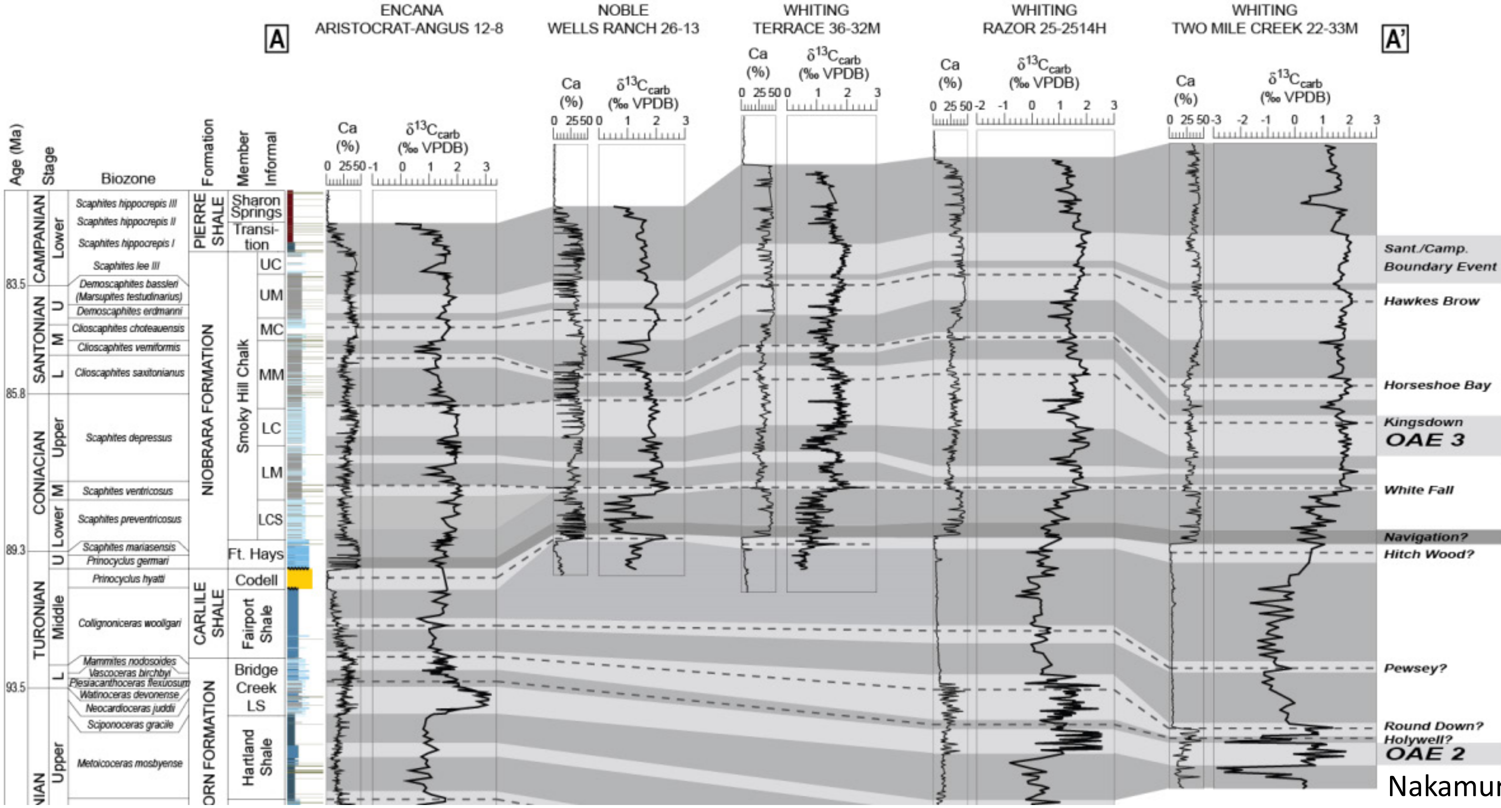


- ❑ A weaker relative pycnocline in Upton County may have led to more vertical mixing with oxygenated waters in the photic zone
- ❑ Periodic oxygenation from carbonate gravity flows could have led to more oxygenation in Upton County.

Stratigraphy

Positive $\delta^{13}C_{CARB}$ excursions reflecting a primary signal can be used for correlation

- ❑ Ocean $\delta^{13}C_{DIC}$ is well mixed and varies on short time-scales
- ❑ Positive $\delta^{13}C_{CARB}$ excursions may represent primary OM burial events



Nakamura, 2015

Stratigraphy

SEM images of microbially-mediated diagenesis

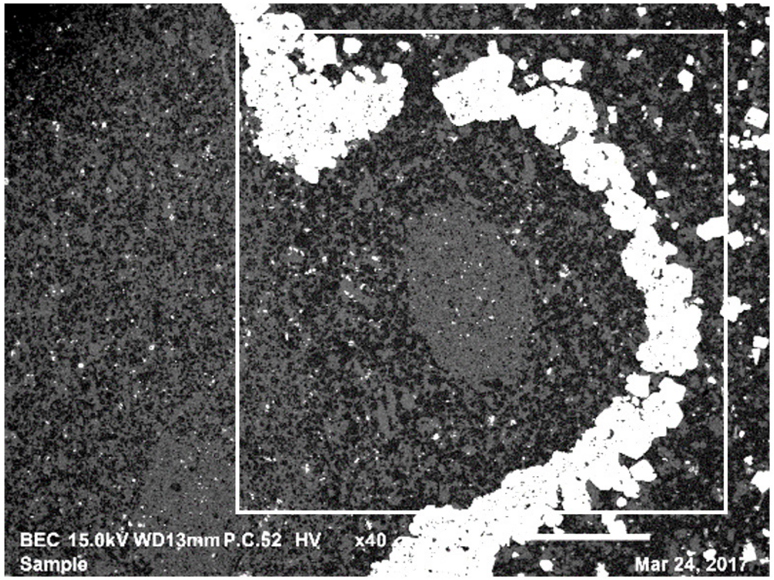
"Existence of an early 'cement' may represent a pause in sediment accumulation"

"Extent of cementation may represent duration of hiatus in sediment accumulation"

Using $\delta^{13}C_{CARB}$ we can effectively measure the extent of cementation

Lazar et al., 2015
Mudstone Primer

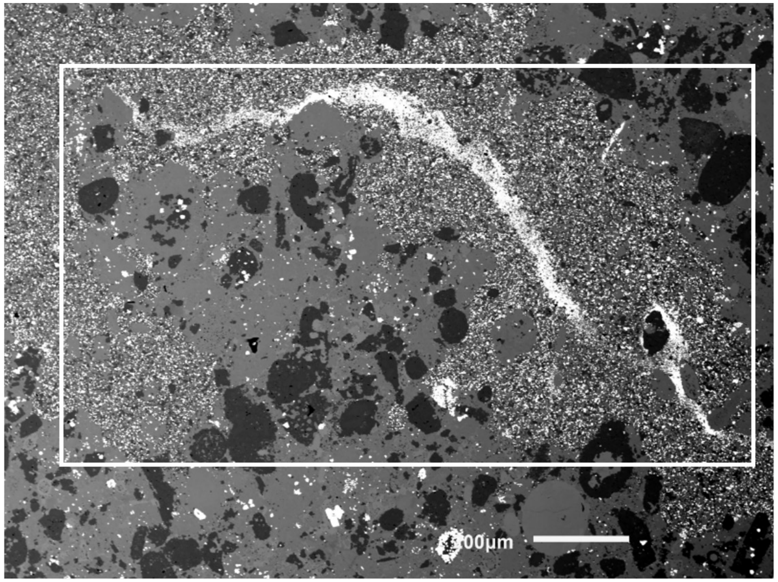
Midland County



Modified from Reis, 2018

10ft. $\delta^{13}C_{CARB}$ value of -8.5 ‰

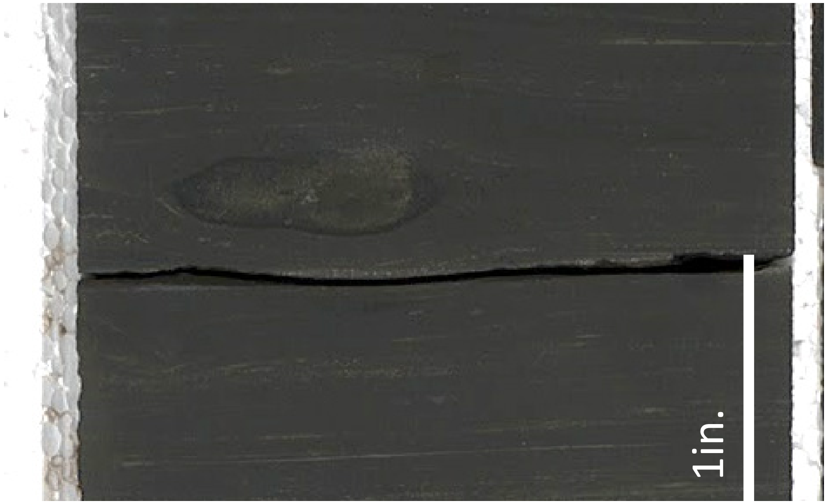
Upton County



29ft. $\delta^{13}C_{CARB}$ value of -9 ‰

Stratigraphy

Early diagenesis at the SWI is near instantaneous with respect to geologic time
Several sedimentary features in hand sample exist pointing early-diagenetic processes

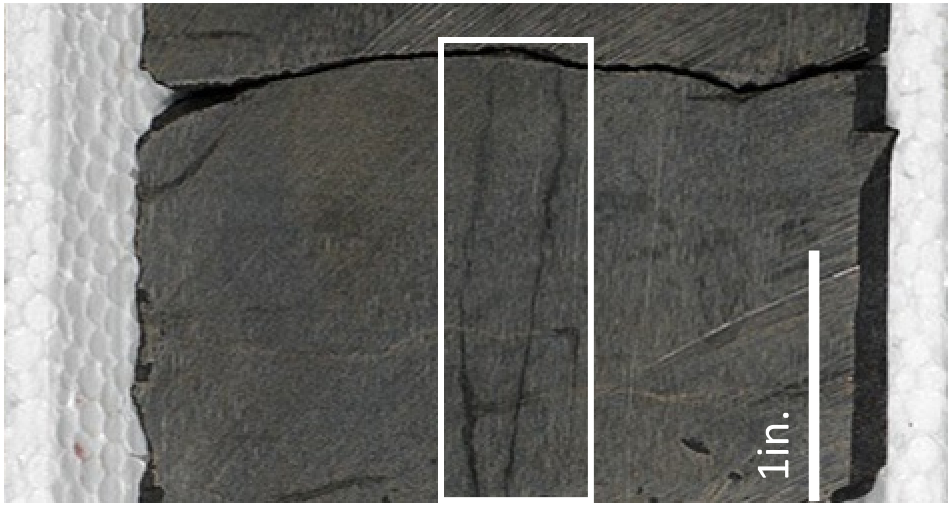


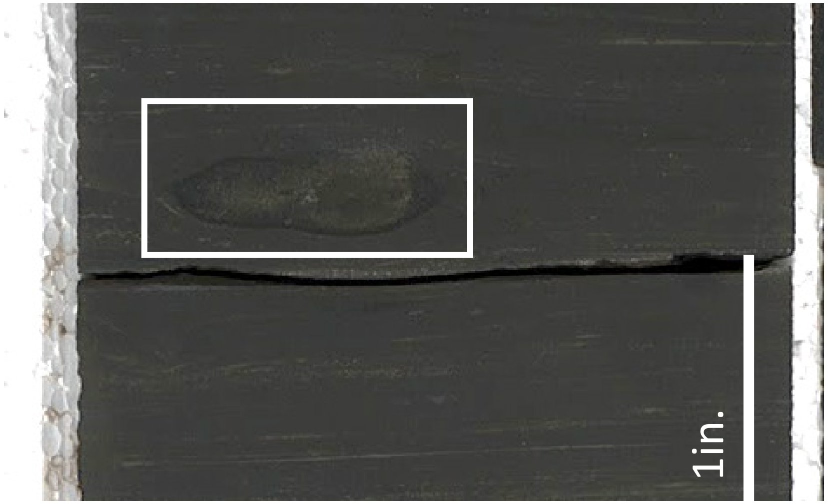
- ❑ Vertical burrow at 26 ft. in Upton County points to extended duration at or near the SWI
- ❑ $\delta^{13}C_{CARB}$ value of -12 ‰

- ❑ Phosphate nodules may signify exposure at or near the SWI resulting in anomalously negative $\delta^{13}C_{CARB}$ value

Stratigraphy

Early diagenesis at the SWI is near instantaneous with respect to geologic time
Several sedimentary features in hand sample exist pointing early-diagenetic processes





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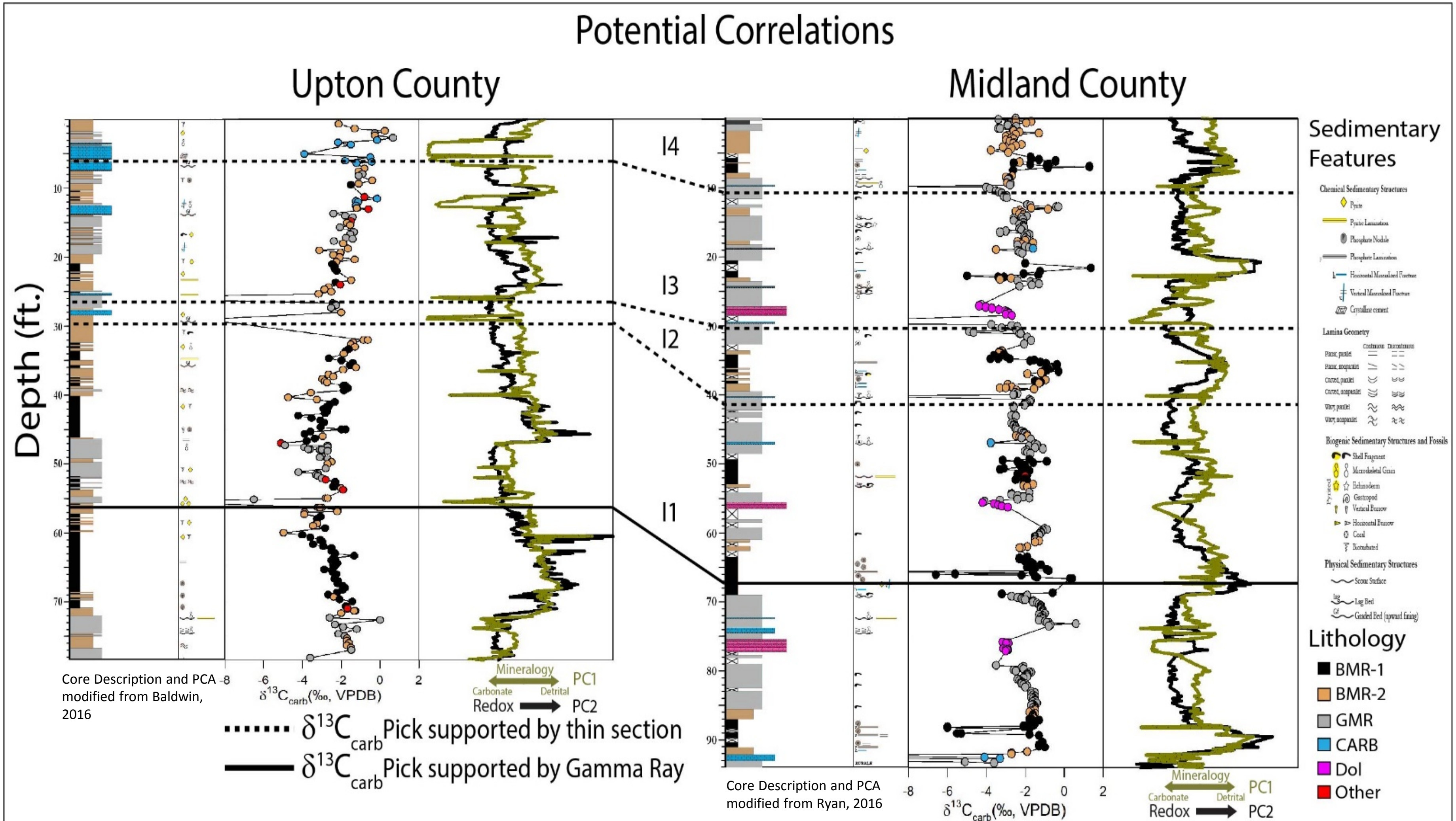
Stratigraphy

Sharp negative $\delta^{13}C_{CARB}$ excursions may aide in correlation



Conclusions

- $\delta^{13}C_{CARB}$ can be used to inform paleo-environmental processes
  - -Using the framework developed, the distribution $\delta^{13}C_{CARB}$ measurements observed suggests the Upton County locality was more heavily influenced by the destruction of OM relative to Midland County
- Sharp negative $\delta^{13}C_{CARB}$ excursions may aide in correlation within the basin
  - -Early diagenetic in nature
  - -Geochemical record at Midland and Upton localities
- Future work will be needed to determine the validity of correlations proposed in this study
  - -Sulfur Isotopes – Redox conditions and nature of sharp negative $\delta^{13}C_{CARB}$ excursions
  - -Access to more core can help determine the regional extent of the surfaces shown in this study

Acknowledgements

- Committee:
  - -Dr. Andrea Erhardt (Chair)
  - -Dr. Michael McGlue
  - -Dr. Ryan Thigpen
- KSIGL:
  - -Dr. Jordon Munizzi (Lab Manager)
  - -April Collins
  - -Bailee Morrison
  - -Rowan Rich
  - -Elizabeth Avery
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  - -Alex Reis
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  - -Lowell Waite
  - -Tom Spalding
  - -Dan Spaulding

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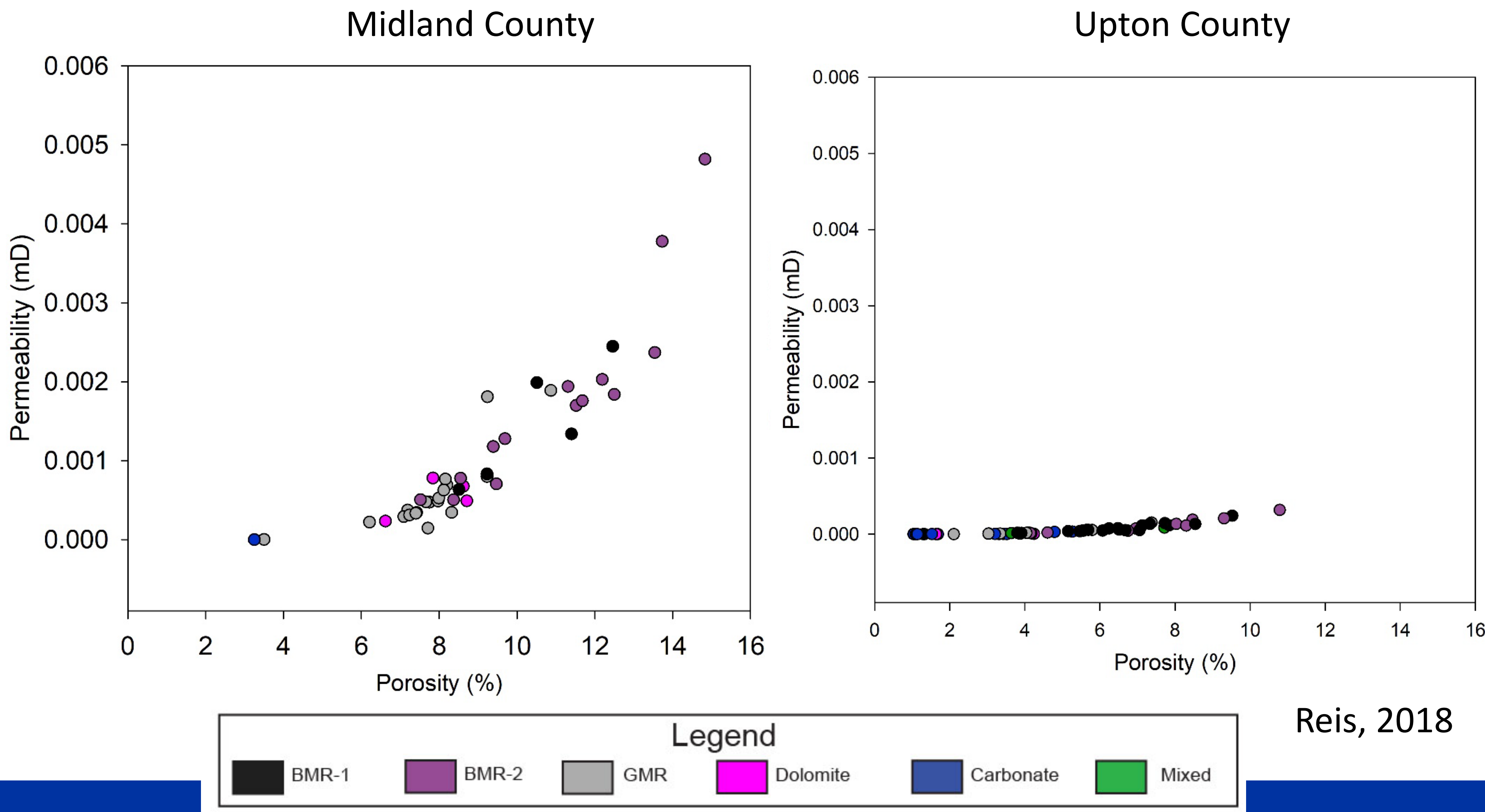
Backup

Porosity-Permeability



Reis, 2018

Spectral Gamma vs Carbon Isotopes