A New Look at the Organic Geochemical Variability in the Woodford Shale of the Ardmore Basin: Paleoweathering and Organic Matter Source*

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Abstract

The Woodford Shale (Devonian-Mississippian) of the southern United States has become one of the most important unconventional hydrocarbon reservoirs in the country. Chiefly responsible for its efficacy as a resource are its remarkably high TOC, brittle structural nature, and an abundance of Type II marine kerogen. Recently the Woodford has been placed within a sequence stratigraphic framework in order to understand the subtle heterogeneities throughout the formation, and organic geochemical analyses may be able to increase the resolution of this ambition. Our study, which has the goal of using biomarkers to assess weathering and paleoenvironment, has determined that a number of aromatic hydrocarbons occur in the bitumen recovered from the Woodford Shale in southern Oklahoma, notably pyrosynthetic compounds including benzo[e]pyrene and benzo[ghi]perylene. Additionally, the hopanoid and steroid hydrocarbons display significant levels of biodegradation. The nature of these altered compounds, along with several other aromatics, may be indicative of modern weathering, paleoweathering, and an influx of weathered terrigenous organic matter into the depositional system. In terms of hydrocarbon producibility, delineating the boundaries of such a zone within the Woodford Shale may provide some benefit to those parties actively looking to utilize it as a resource play.

References Cited

Blakey, R., 2014, Colorado Plateau Stratigraphy and Geology, Global and Regional Paleogeography. Website accessed April 25, 2016. https://www2.nau.edu/rcb7/.

Cardott, B.J., 2012, Thermal maturity of Woodford Shale gas and oil plays, Oklahoma, USA: International Journal of Coal Geology, v. 103, p. 109-119.

Frederickson, E.A., 1957, Geologic Map of the Criner Hills Area, Oklahoma: Oklahoma Geological Survey.

Johnson, J.G., G. Klapper, and C.A. Sandberg, 1985, Devonian eustatic fluctuations in Euramerica: Geological Society of America Bulletin, v. 96, p. 567-587.

Kaiho, K., S. Yatsu, M. Oba, M. Gorjan, and J. Casier, 2013, A forest fire and soil erosion event during the Late Devonian mass extinction: Palaeogeography, Palaeoclimatology, Palaeoecology, v. 392, p. 272-280.

Roberts, C.T., and R.M. Mitterer, 1992, Laminated black shale-bedded chert cyclicity in the Woodford Formation, Southern Oklahoma: Oklahoma Geological Survey, Circular 93, p. 330-336.

Serna-Bernal, A., 2013, Geological characterization of the Woodford Shale, McAlister Cemetery Quarry, Criner Hills, Ardmore Basin, Oklahoma: M.S. Thesis, The University of Oklahoma.

AAPG Midcontinent Meeting 2015: The Art of Discovery

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Clifford DeGarmo

Outline

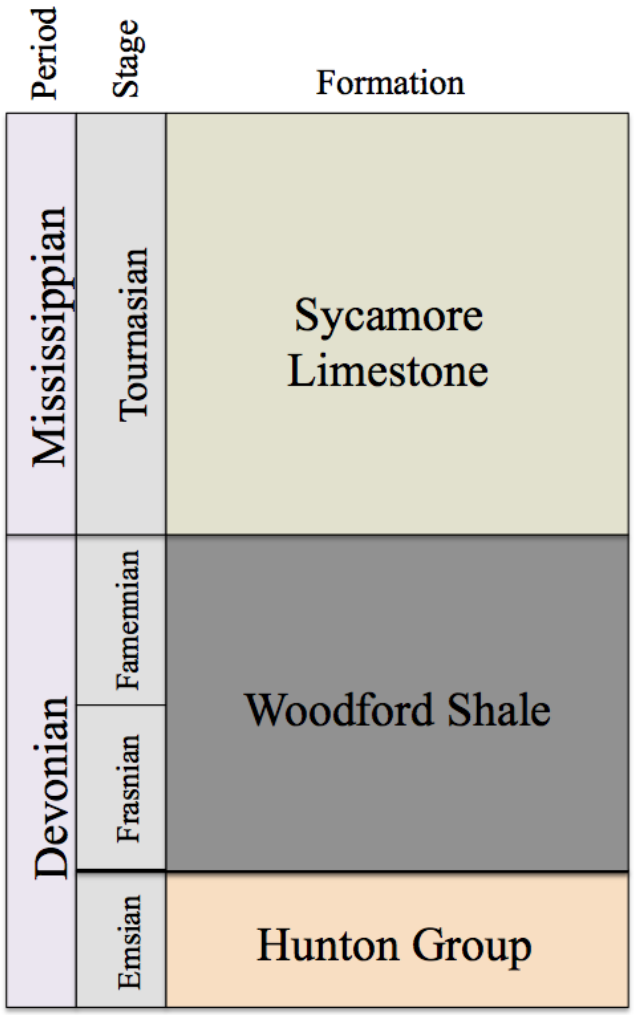
- Objectives
- Introduction
  - Facies
  - Current Sequence Stratigraphic Interpretation
- Geologic Setting
  - McAlister Cemetery Quarry
- Methods
- Results and Discussion
  - TOC/Rock-Eval data
  - Biodegradation
  - Biomarkers
  - Sequence Stratigraphy
- Conclusions

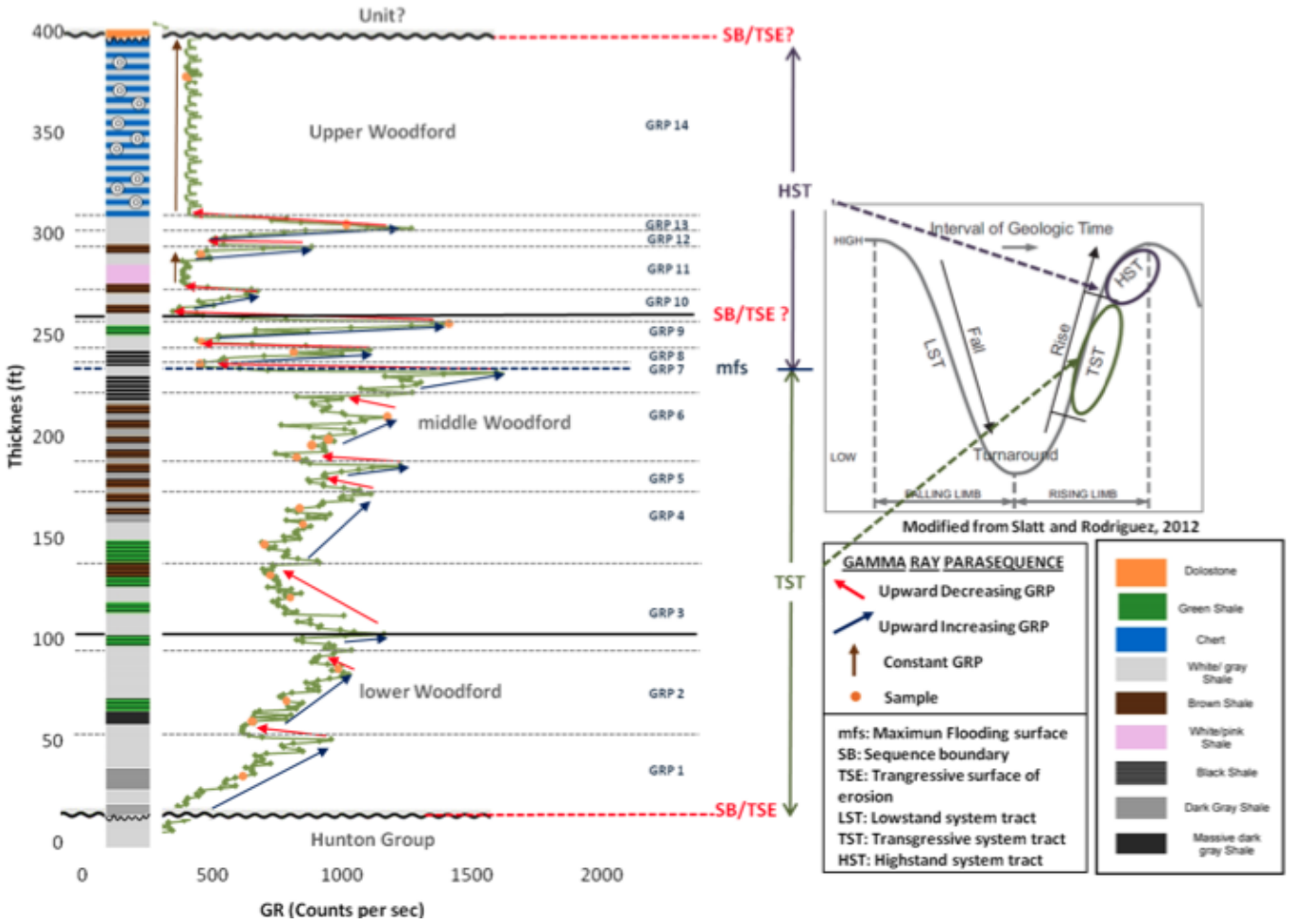
Objectives

- Report biomarker concentrations for Woodford Shale in McAlister Cemetery Quarry
- Evaluate apparent weathering in the Upper Woodford
- Correlate geochemical data to sequence stratigraphic framework of Serna-Bernal (2013)

Introduction

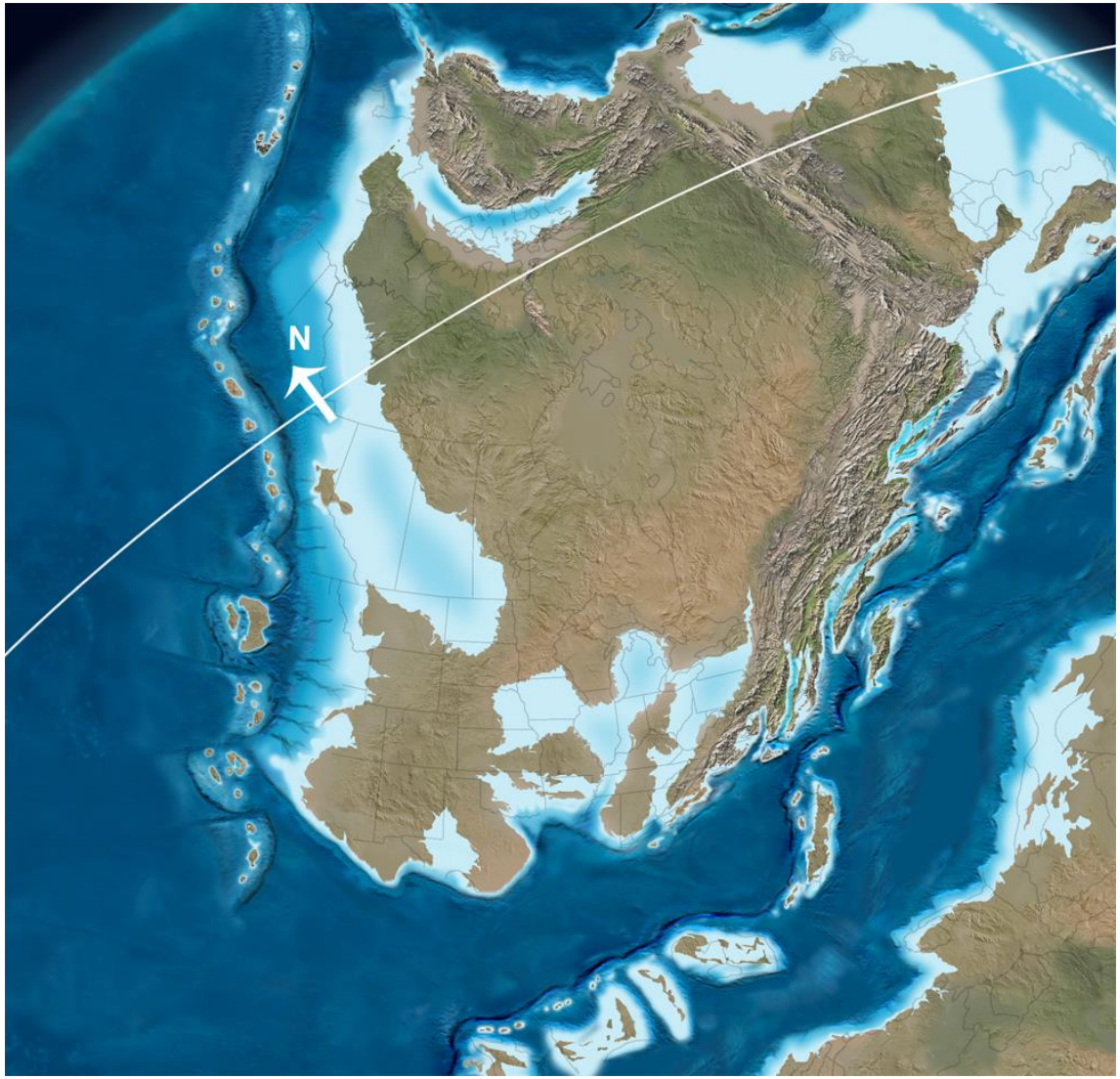
- Woodford is one of the most important hydrocarbon source rocks in OK
- 388-359 Ma
- 2nd order depositional sequence (~29 Myr) (Serna-Bernal, 2013)
- Dark gray, marine, siliceous and carbonaceous shale
- Typically high TOC (7-15 wt.%)
- Mostly Type II Kerogen
- Varying degrees of thermal maturity

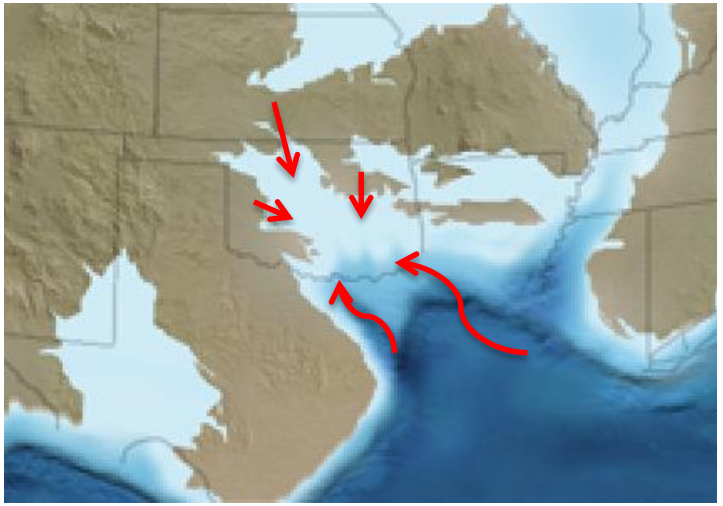




- Woodford Shale displays various lithofacies (siltstone, dolomite, chert) and 3rd order parasequences (Serna-Bernal, 2013).

Geologic Setting (385 Ma)





- Middle-Late Devonian deposition influenced by glacial eustasy, ocean upwelling, and terrigenous sediment influx
- OK Basin was within shallow, epicontinental sea

Blakey, 2009

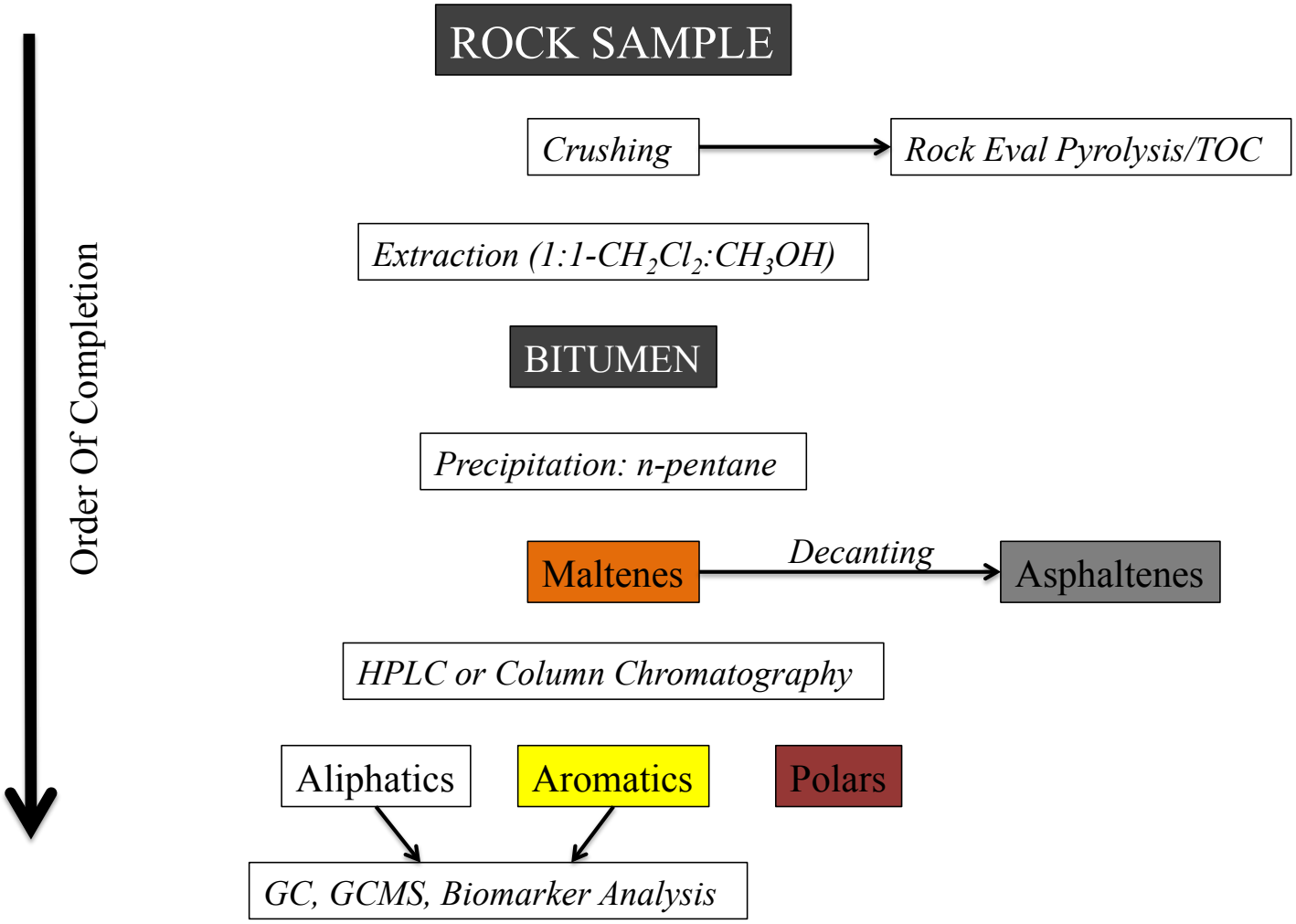
McAlister Cemetery Quarry

- 34.079° N, 97.156° W
- 122 m section
- ~320°, 35-55° NE
- East limb of Rock Crossing Anticline

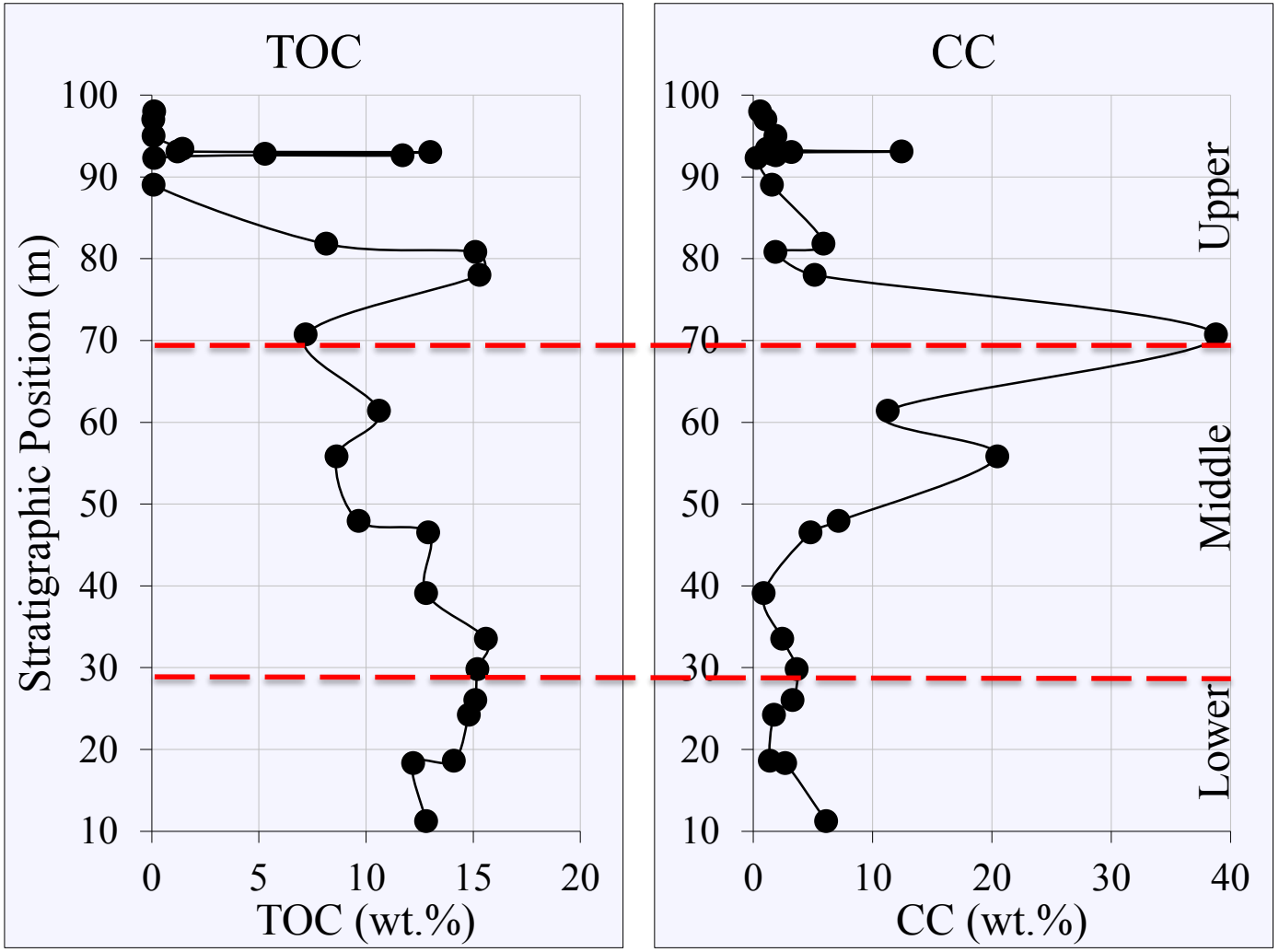
Sampling

- 6 profiles were utilized in the quarry, modified after Serna-Bernal (2013)
- 22 rock samples excavated at depth of ~1 m from quarry floor
- 4 samples were used from remnant Serna-Bernal samples (2, 10, 13, 19)

Experimental



Carbon Content



AVG. TOC

- Upper – 5.6 wt.%
- Middle – 12.2 wt.%
- Lower – 13.8 wt.%

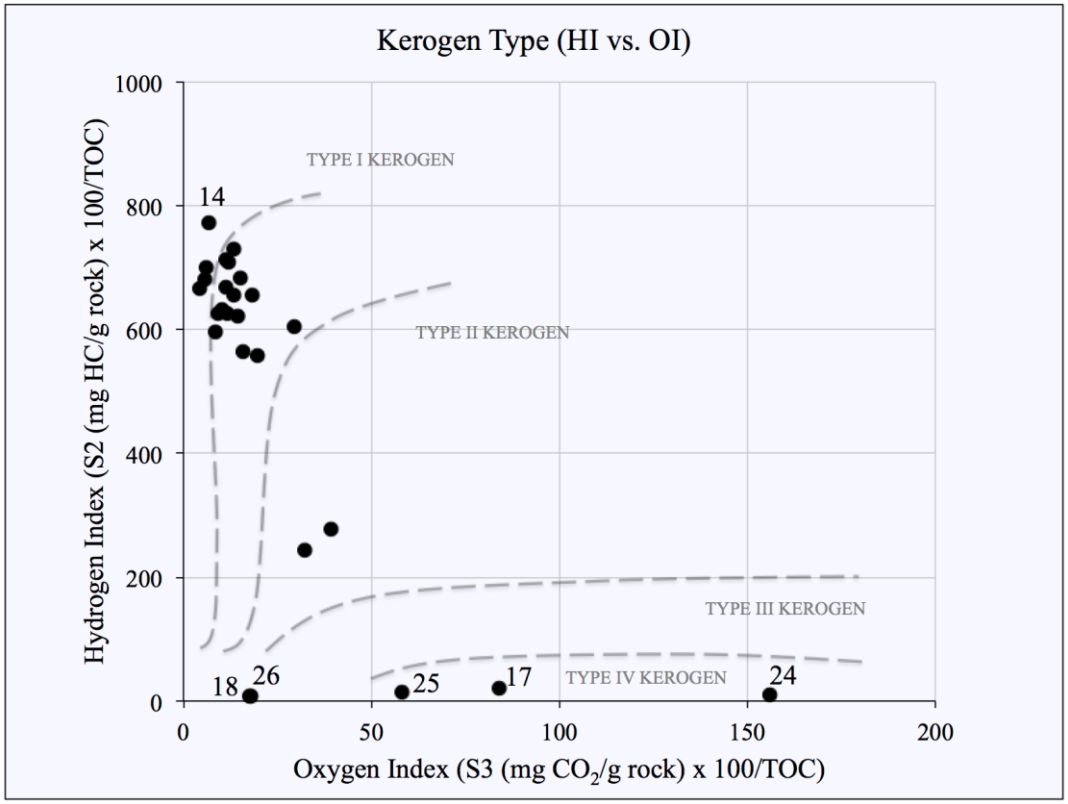
AVG. CC

- Upper – 5.5 wt.%
- Middle – 7.2 wt.%
- Lower – 3.1 wt.%

- High TOC samples generally dark in color

TOC measured by LECO method; "CC" is carbonate content

Kerogen Type



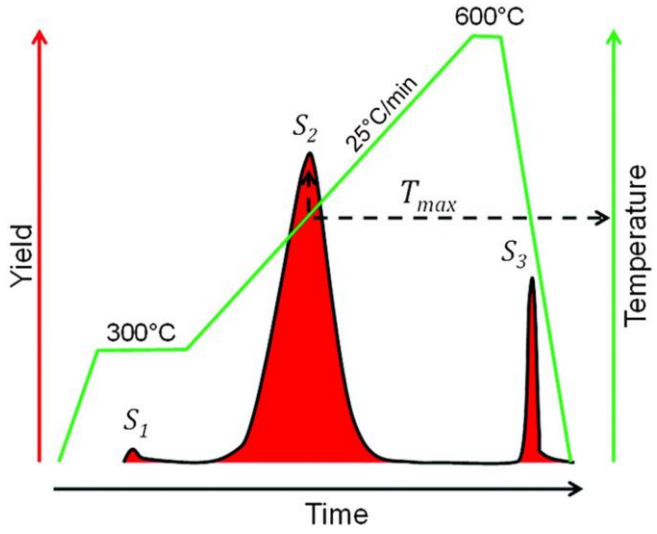
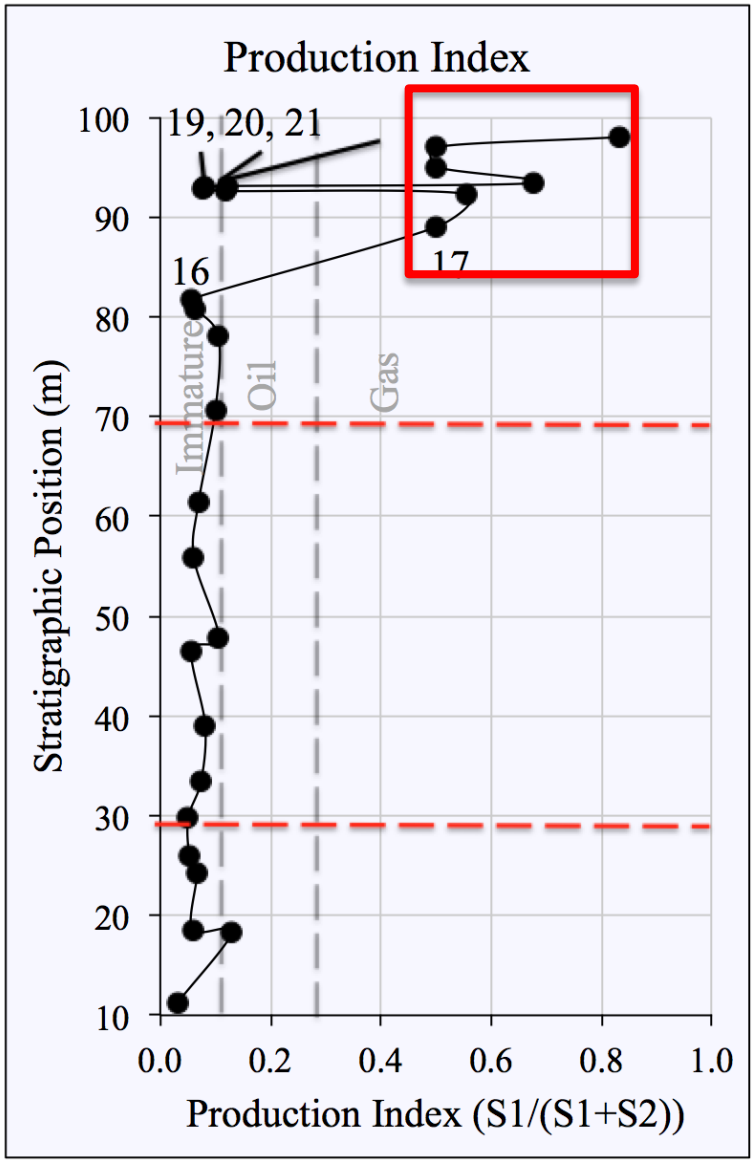


Image from geoscienceworld.org

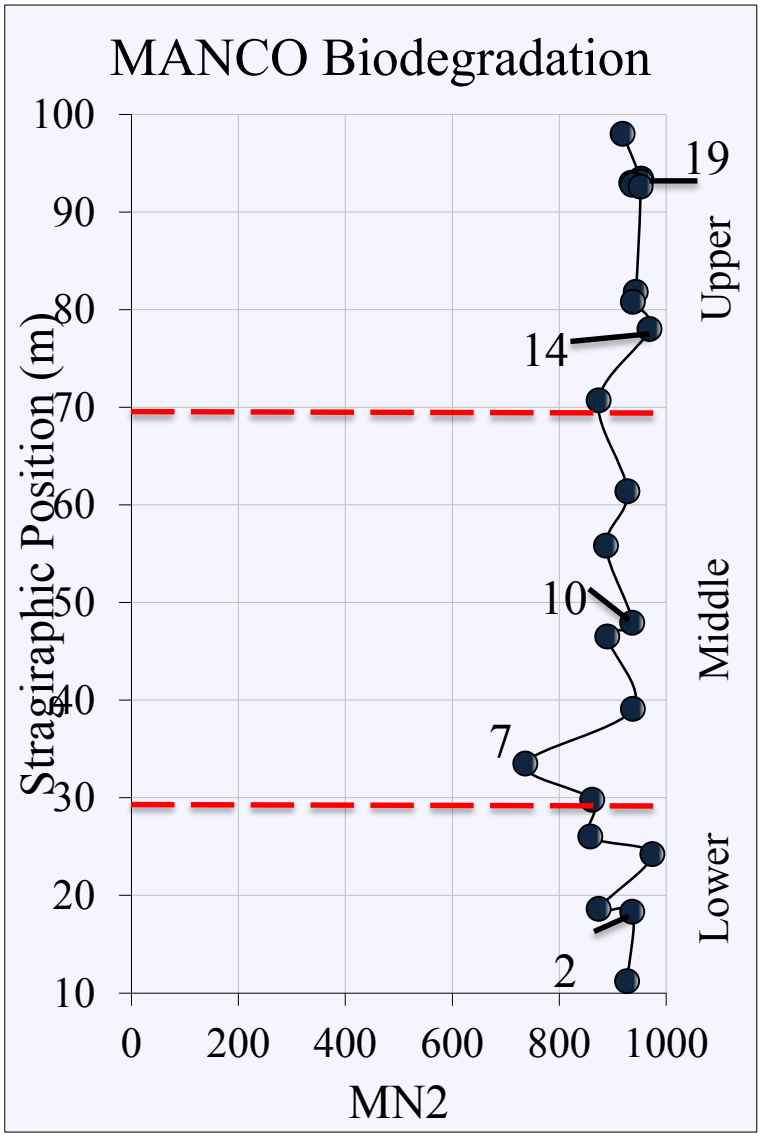
Thermal Maturity



- T_{max} values 413-429
- Thermal maturity close to oil-window threshold
- Gas-window samples artifacts of low TOC and weathering
- Measured %Ro values ~0.53 (Cardott, 2012)

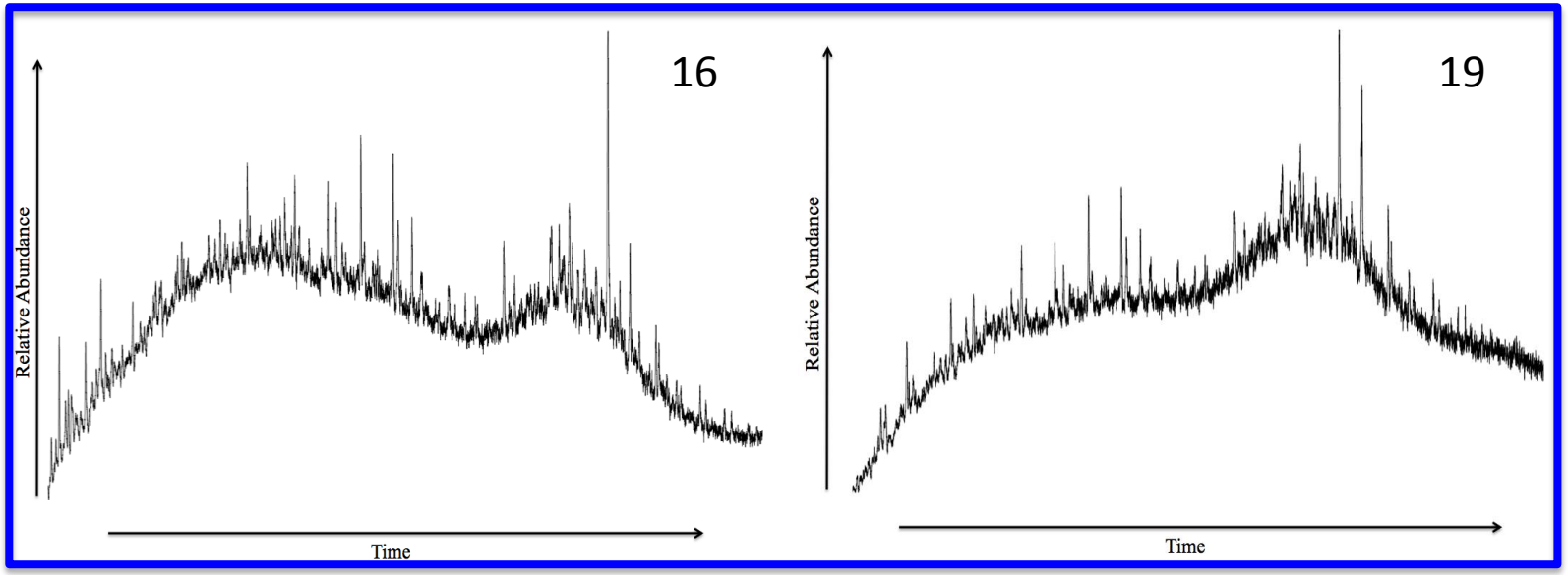
Sample	Position (m)	T_{max}	%Rc	PI
26	98.00			0.83
25	97.00			0.50
24	95.00			0.50
23	93.40	413	0.27	0.68
22	93.10	419	0.38	0.12
21	93.00	422	0.44	0.08
20	92.80	428	0.54	0.08
19	92.60	421	0.42	0.12
18	92.30			0.56
17	89.00			0.50
16	81.80	422	0.44	0.06

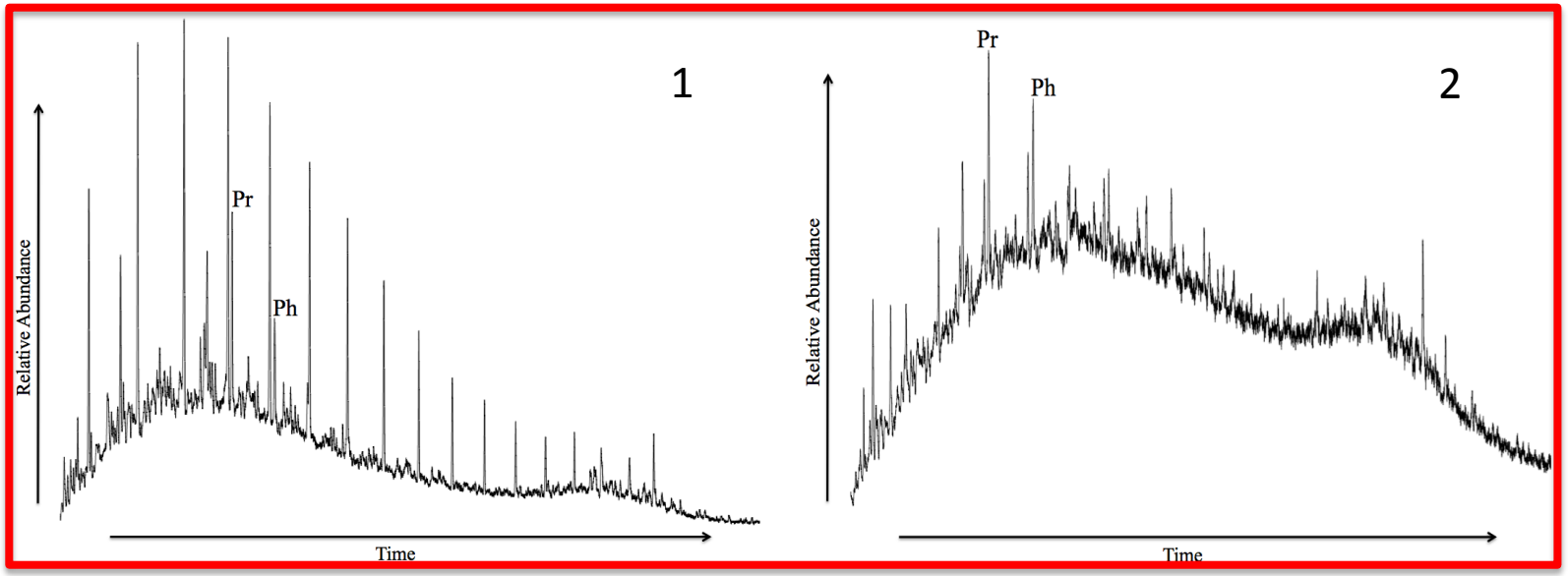
Biodegradation



- Classification scheme for oils, based on biomarkers with 0 (least degraded) to 1000 (most degraded) (Larter et al., 2012)
- Entire section >700, indicating heavy biodegradation throughout
- Serna-Bernal samples relatively more degraded than adjacent samples
- Uniform exposure at surface likely responsible for degree of degradation
- Universal heavy biodegradation suggests biomarkers affected equally throughout section

Saturates (GC)



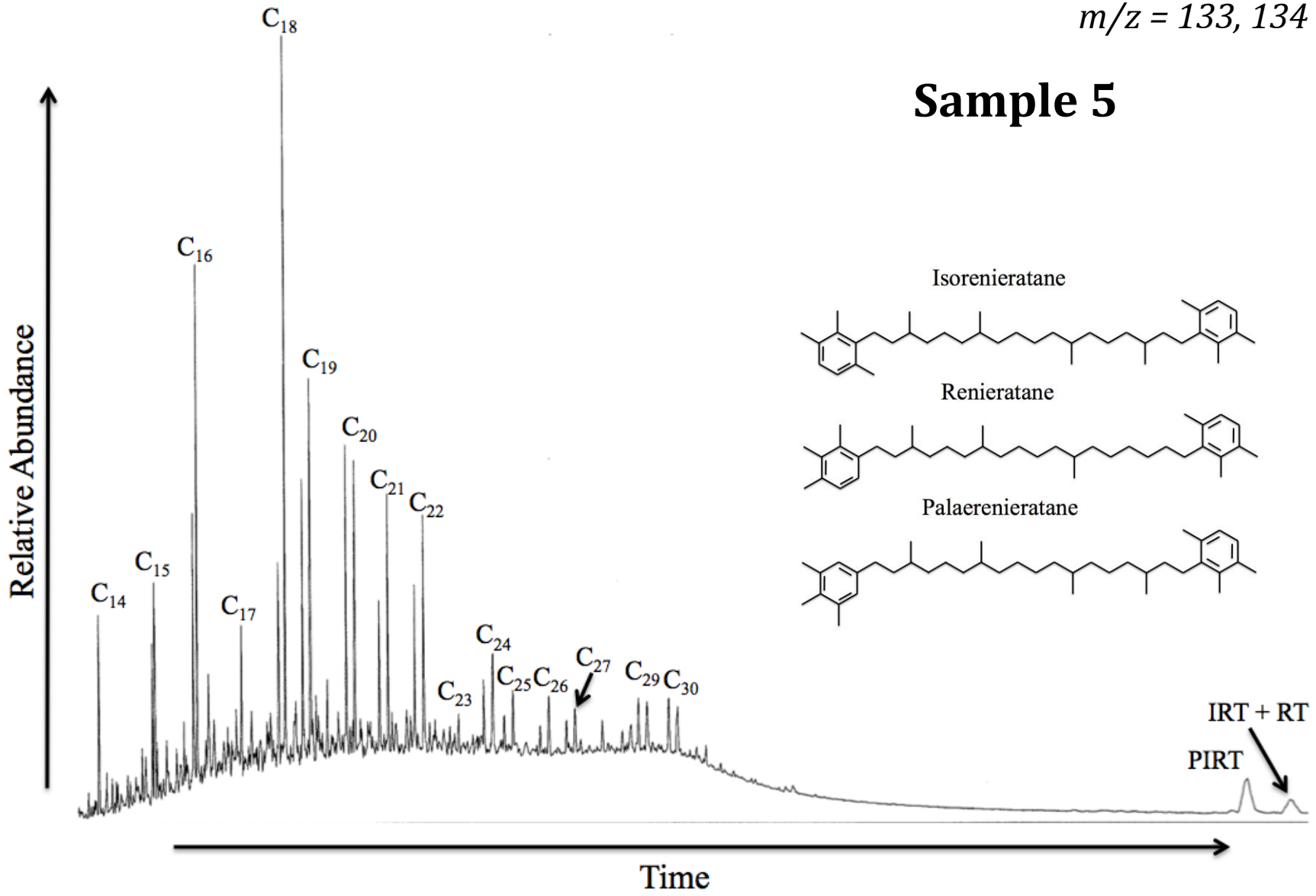


Sample
26
25
24
23
22
21
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1

Aryl Isoprenoids

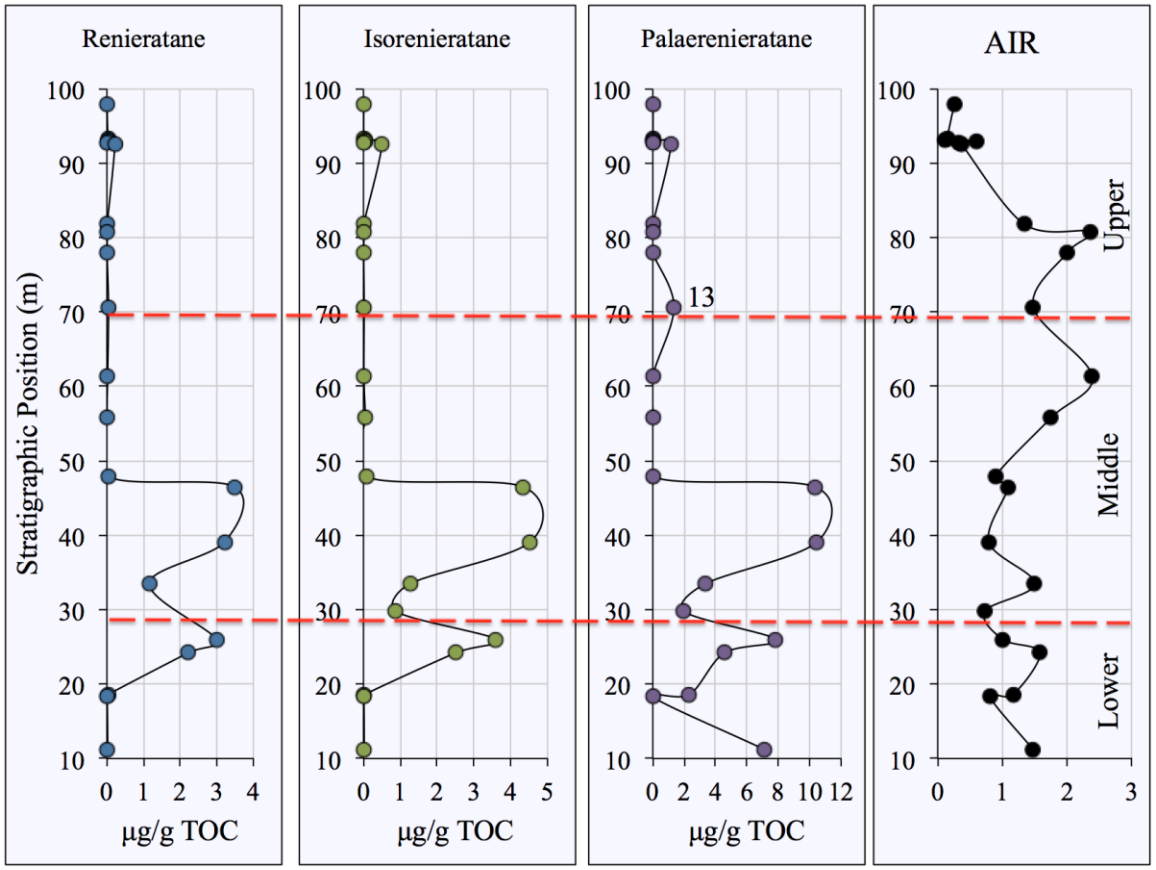
m/z = 133, 134

Sample 5



Aryl Isoprenoids

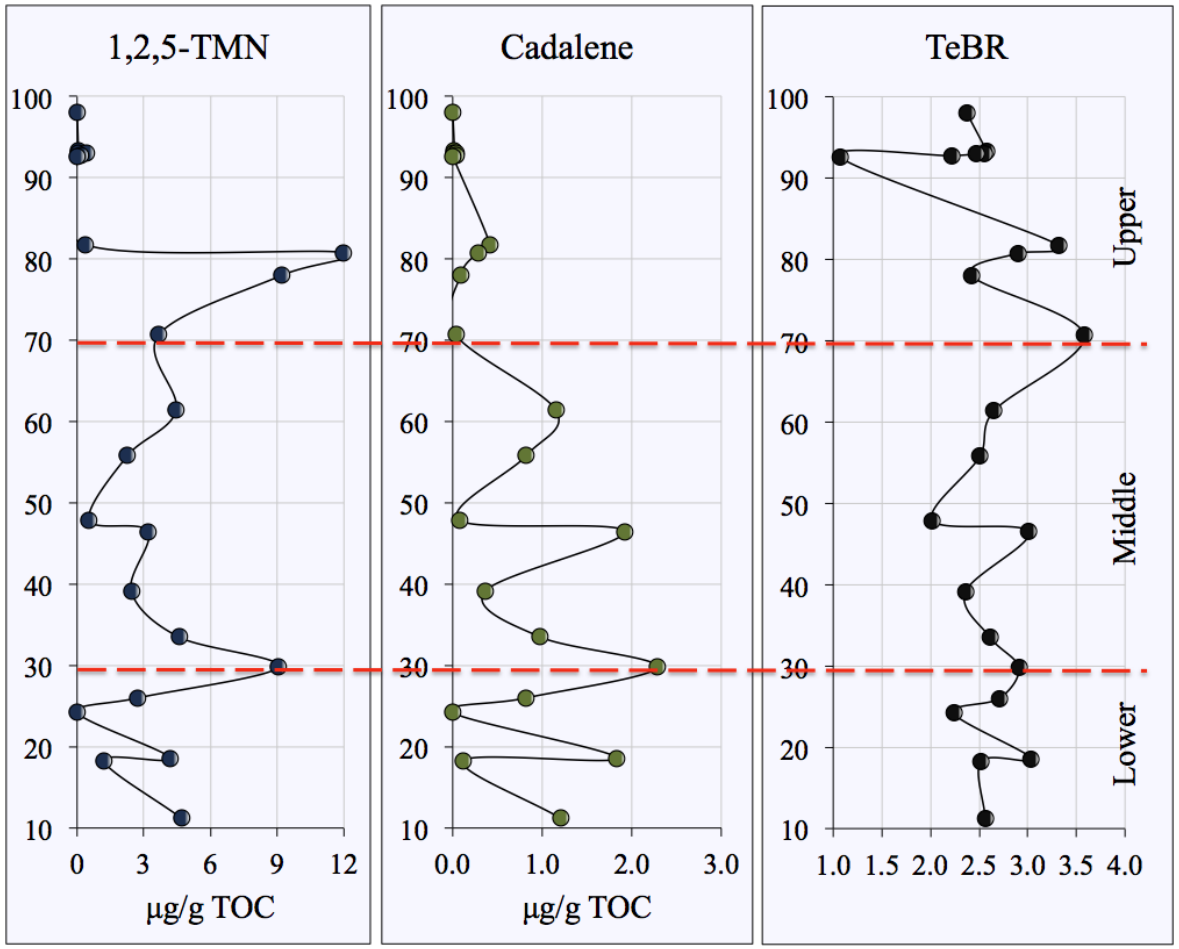
AIR = ($C_{13\text{-}17}/C_{18\text{-}22}$) 2,3,6-trimethyl aryl isoprenoids



- Aromatic carotenoids show two periods of abundance
- AIR fluctuates throughout Lower-Middle member, declines in Upper
- Low AIR values may indicate persistent PZA

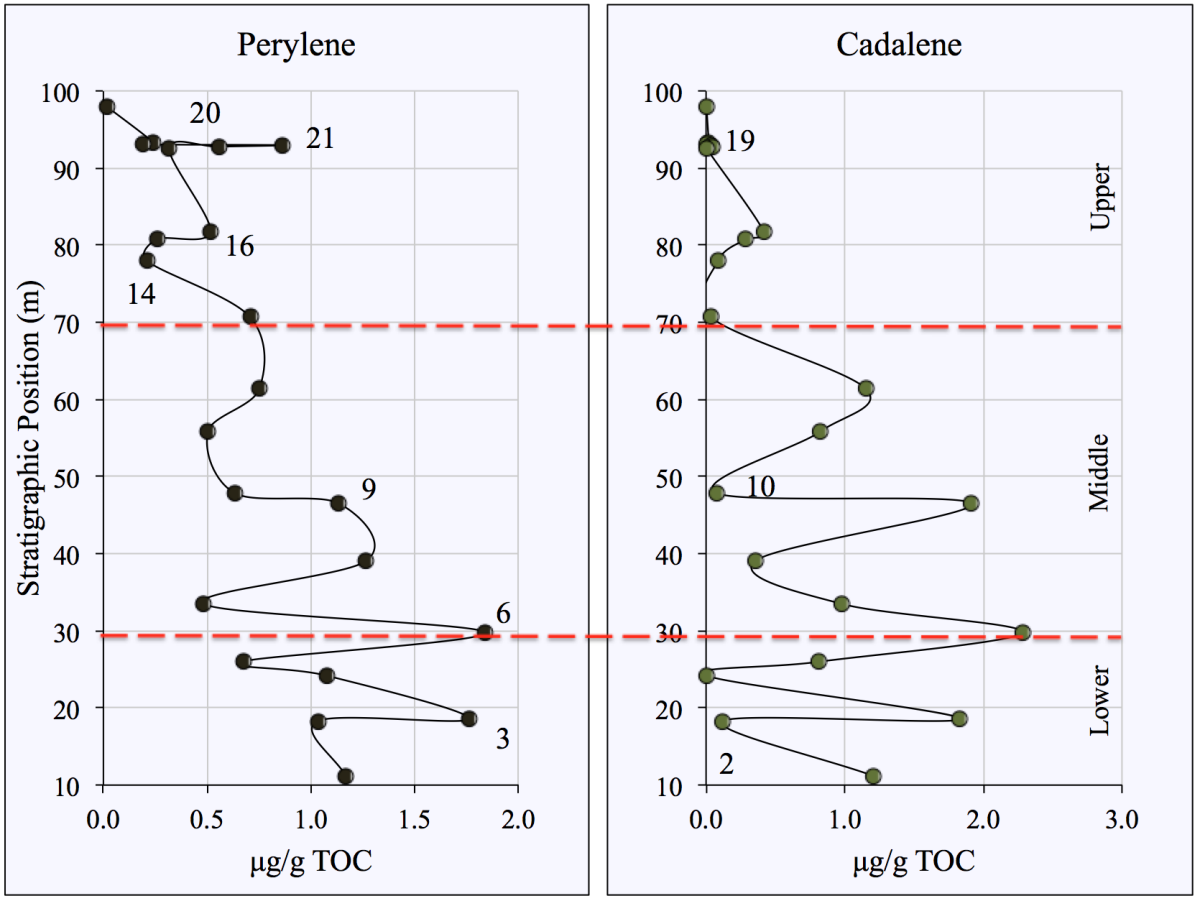
Naphthalenes and Cadalene

TeBR = 1,3,6,7-TeMN/1,3,5,7-TeMN



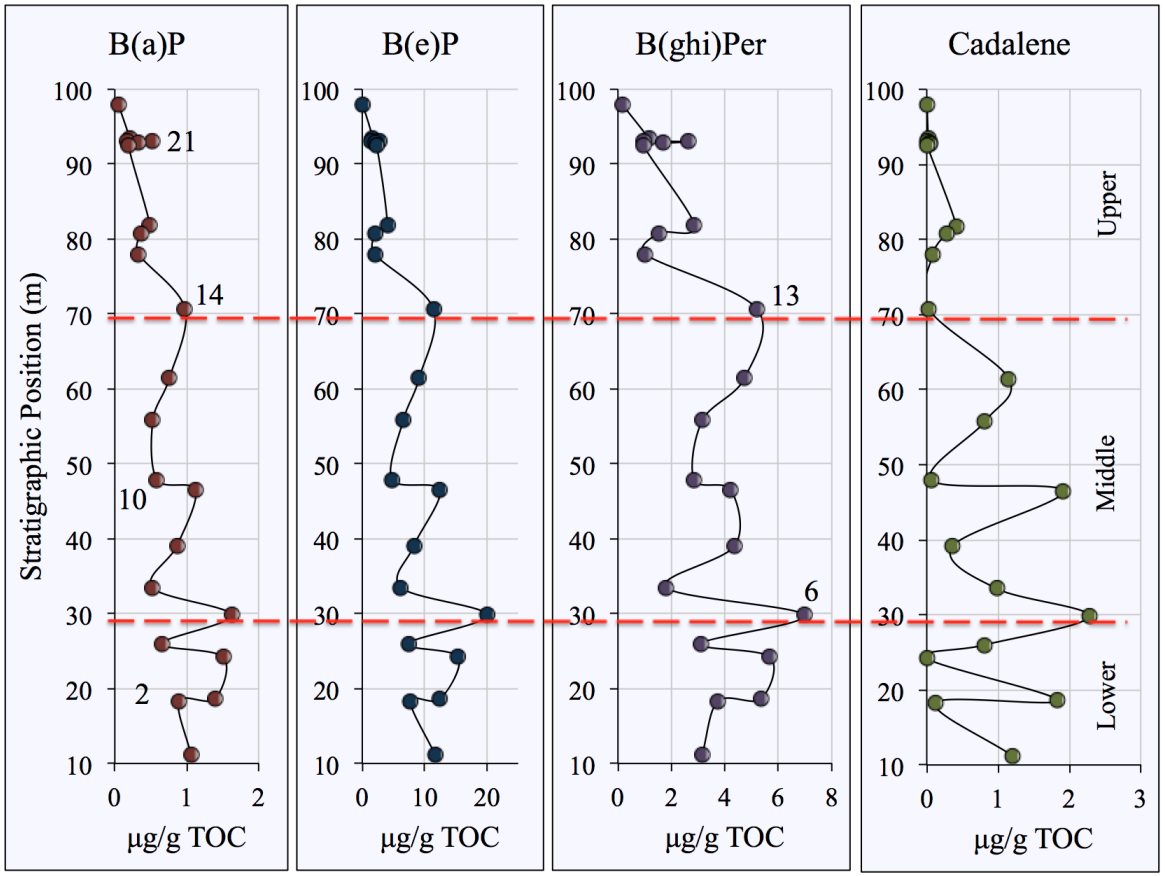
- 1,2,5-TMN and cadalene show Lower-Middle member similarity
- TeBR typically decreases with biodegradation, but follows cadalene in lower section
- Cadalene fluctuation may be suggesting terrigenous input

Perylene



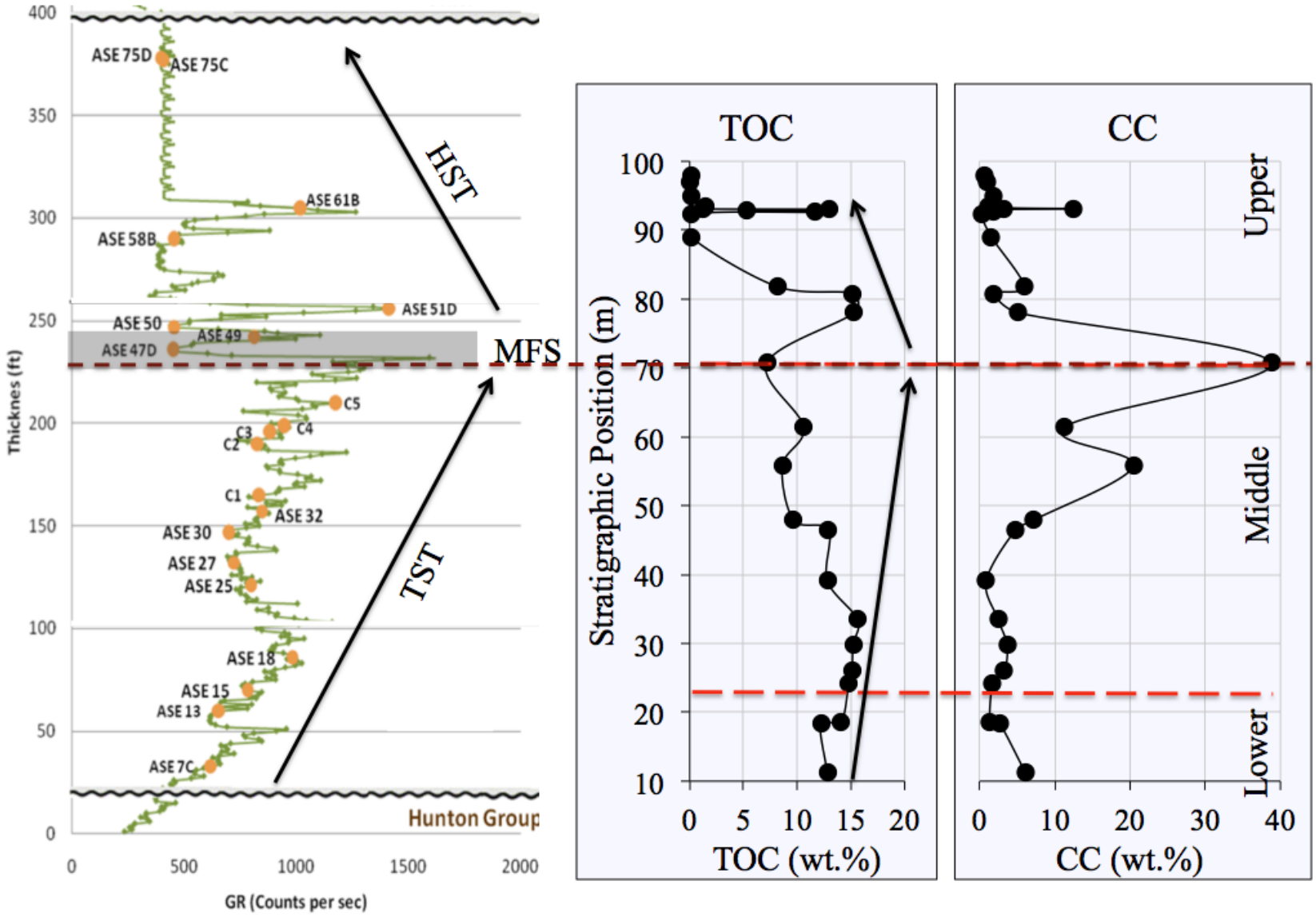
- Perylene and cadalene show similar distribution
- Both are likely from terrigenous source
- Peak abundances may indicate 3rd order HST
- Decreases in Upper member contrast the 2nd order HST

Pyrogenic PAHs

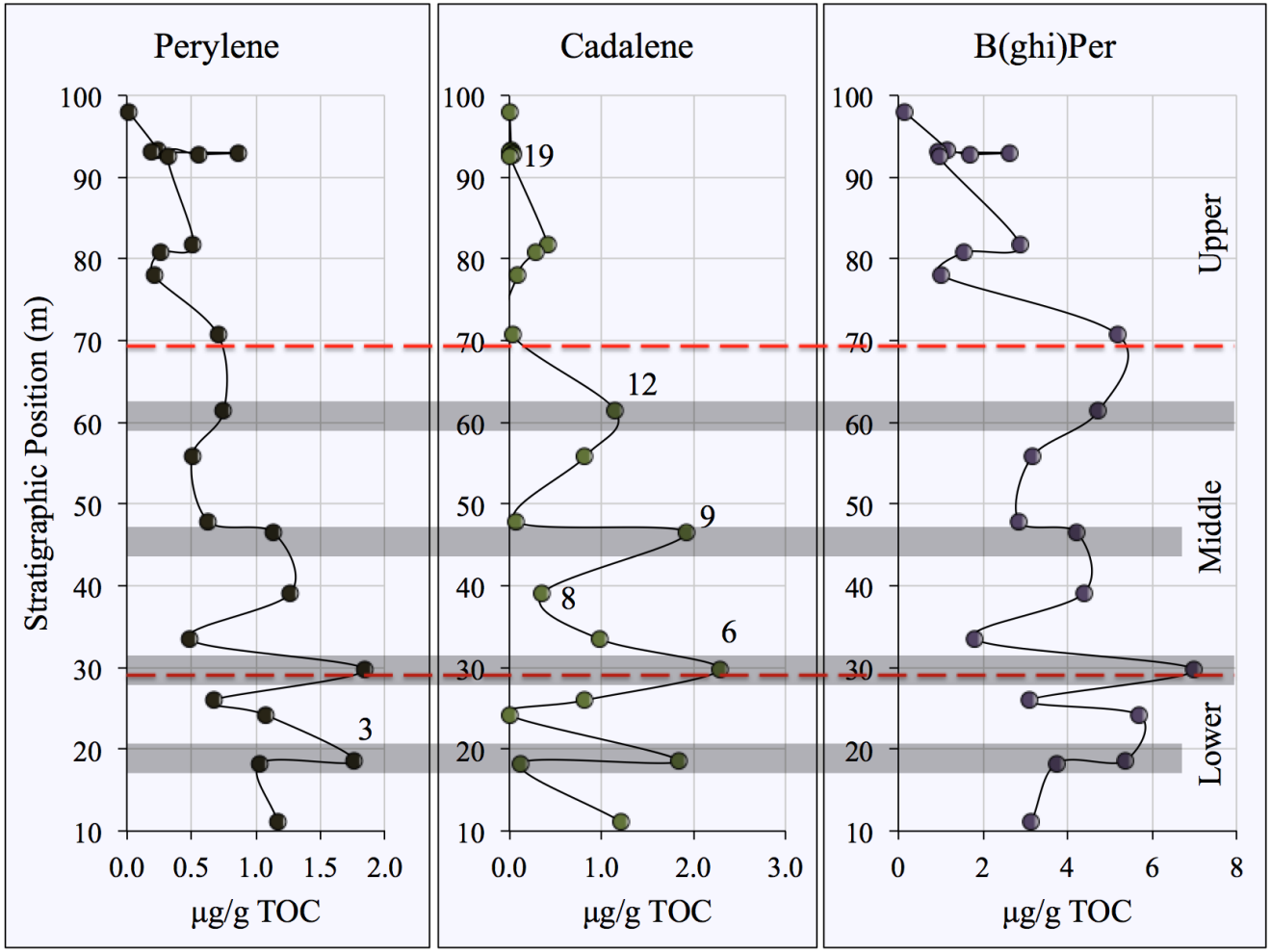


- Pyrogenic compounds correlate to cadalene
- More similar to perylene in Upper member
- Likely from combustion-derived source
- Modern weathering may have a slight effect

2nd Order Sequence

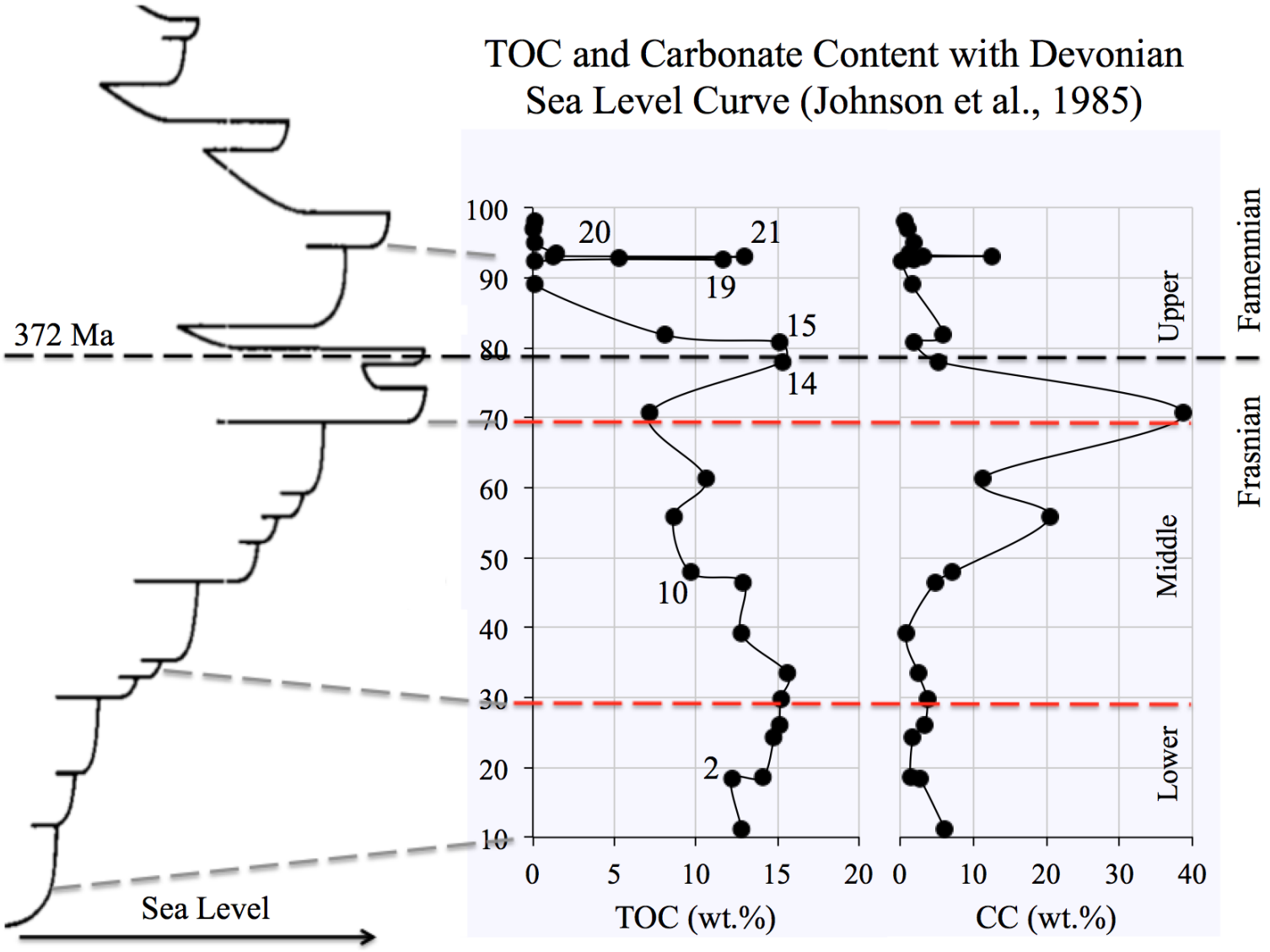


3rd Order Influence



- Correlative peak abundances of terrigenous biomarkers suggest possible 3rd order HST
- Upper Woodford potentially affected by paleoweathering activity

Paleoweathering?



Conclusions

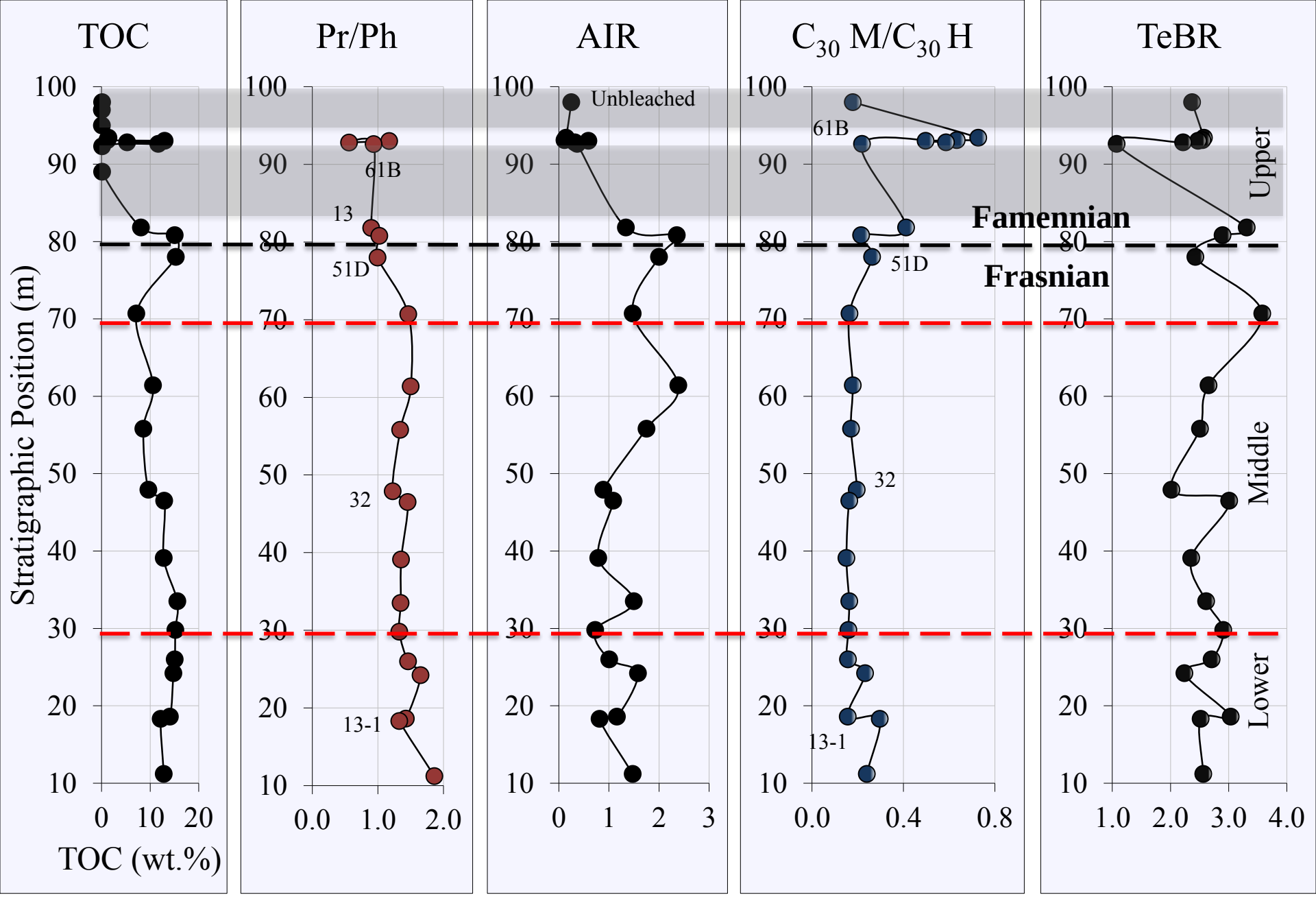
- The Woodford Shale of the McAlister Cemetery Quarry contains the geochemical make-up of a highly productive source rock
  1. TOC ranging 0.07 to 15.6 wt.%
  2. Mostly Type II Kerogen
  3. Immature/Early Maturity Window

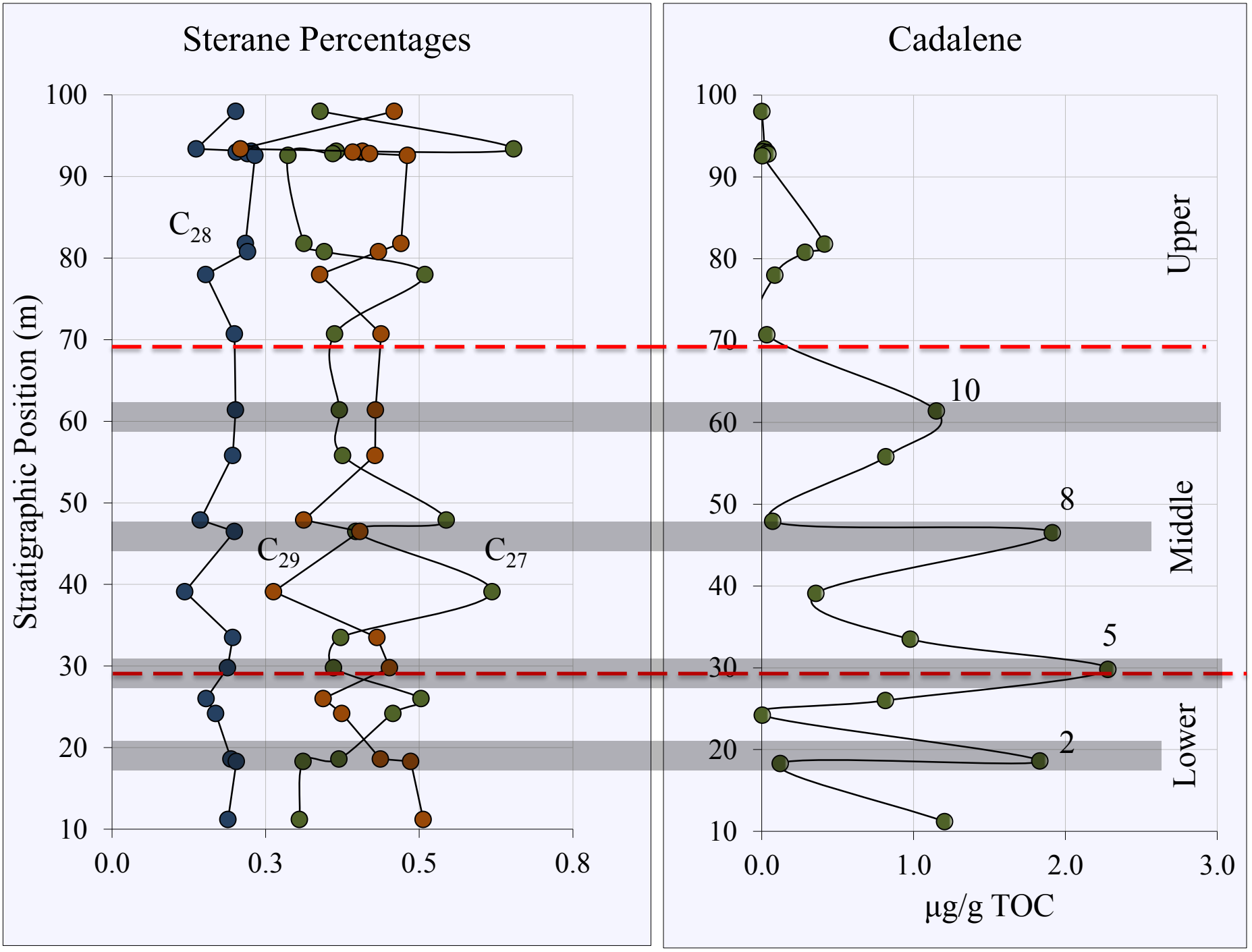
- Modern surface weathering and biodegradation has had a substantial impact on all members of the formation, particularly so in the *n*-alkanes and Serna-Bernal samples

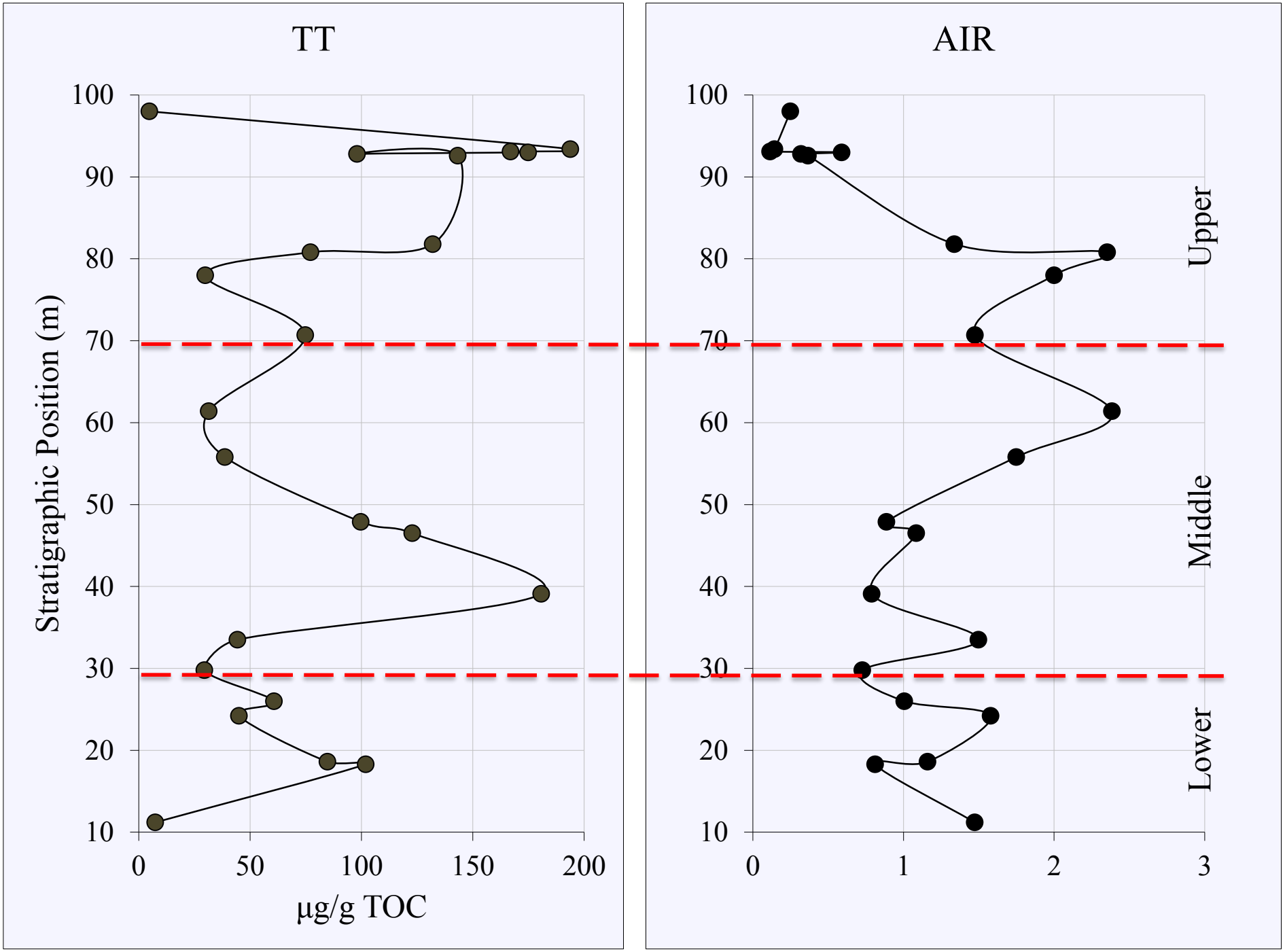
- TOC and other biomarker parameters suggest that 2 intervals within the Upper Woodford were potentially subaerially exposed and paleoweathered.

- Influxes of weathered terrigenous organic matter appear to occur in all sections of the Woodford Shale in this quarry.

- The Woodford Shale represents an overall 2nd order depositional sequence, with several 3rd order parasequences throughout its progression.


TOC
Pr/Ph
AIR
C_{30} M/C_{30} H
TeBR
Stratigraphic Position (m)
TOC (wt.%)
Unbleached
61B
13
51D
32
13-1
Famennian
Frasnian
Upper
Middle
Lower


Sterane Percentages
Cadalene
Stratigraphic Position (m)
100
90
80
70
60
50
40
30
20
10
0.0
0.3
0.5
0.8
C28
C29
C27
Upper
Middle
Lower
10
8
5
2
0.0
1.0
2.0
3.0
µg/g TOC


TT
AIR
Stratigraphic Position (m)
100
90
80
70
60
50
40
30
20
10
0
50
100
150
200
µg/g TOC
0
1
2
3
Upper
Middle
Lower