

# **Correlating Oils in Turonian-Cenomanian Source Rocks Using Hydrous Pyrolysis and Organic Sulfur Compounds\***

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## **Abstract**

Oils of the Pearsall and Giddings fields in Austin Chalk reservoirs are considered to be derived from Turonian-Cenomanian-age source rocks in the Eagle Ford Group and Boquillas Formation. Reservoir oils in the Austin Chalk Formation of Giddings Field, northeast of San Marcos Arch, may be sourced from the Eagle Ford Group, and those in the large Pearsall Field, southwest of San Marcos Arch may represent a facies change within the Boquillas Formation. Pearsall Field oils in the 30 to 40 API gravity range have lower pristane/phytane ratios, higher C35/C34 terpane ratios, and moderately higher sulfur contents than Giddings Field oils in the same API gravity range. However, oils from both fields contain similar extended tricyclic terpane distributions and stable carbon isotope signatures characteristic of Turonian-Cenomanian source rocks of the Gulf Coast. The interpretive issue is whether the oils from these two large fields are from different organic facies in the Boquillas Formation and Eagle Ford Group, or are they the result of mixing with high-sulfur oils generated by source rocks in the deeper Smackover Formation.

The Boquillas and Eagle Ford formations have total organic carbon contents (TOC) ranging from 0.7-8.1%. Both formations contain Type II kerogen, but have different organic sulfur concentrations. Hydrous pyrolysis experiments were used to produce crude oil from the Eagle Ford/Boquillas Formation at 310, 330, 355° C for 72 h. Bitumen extracts of the pyrolyzed source rock and their expelled oils were analyzed for specific biomarkers including thiophenes. API gravities of the expelled oils were also similar and ranged from 23 to 44 API, but the samples from Boquillas Formation produced tar plugs during experiments at 310° C and 330° C. C27-diasteranes/C27-

steranes ratio values in clastic-rich samples ranged from 0.11-0.19, and in clay-rich and carbonate-rich lithologies ranged from 0.02-0.09. Boquillas lithologies also showed a greater C35/C34-hopane ratios compared to samples from the Eagle Ford.

Dibenzothiophenes showed a greater relative abundance in Boquillas lithologies than in Eagle Ford lithologies. However, the ratios of n-methyl-dibenzothiophenes/total dibenzothiophenes in both lithologies were similar. Preliminary biomarker data indicate facies changes within the formations is responsible for oil-compositional differences in the two fields.

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# CORRELATING OILS IN TURONIAN-CENOMANIAN SOURCE ROCKS USING HYDROUS PYROLYSIS AND ORGANIC SULFUR COMPOUNDS

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Michael Lewan, USGS

## Hypotheses:

- *The Boquillas Formation is responsible for the moderate sulfur oils in Pearsall Field*
- *The Eagle Ford Group is responsible for the low sulfur oils in Giddings Field*

**Gulf Coast  
Petroleum Systems\***

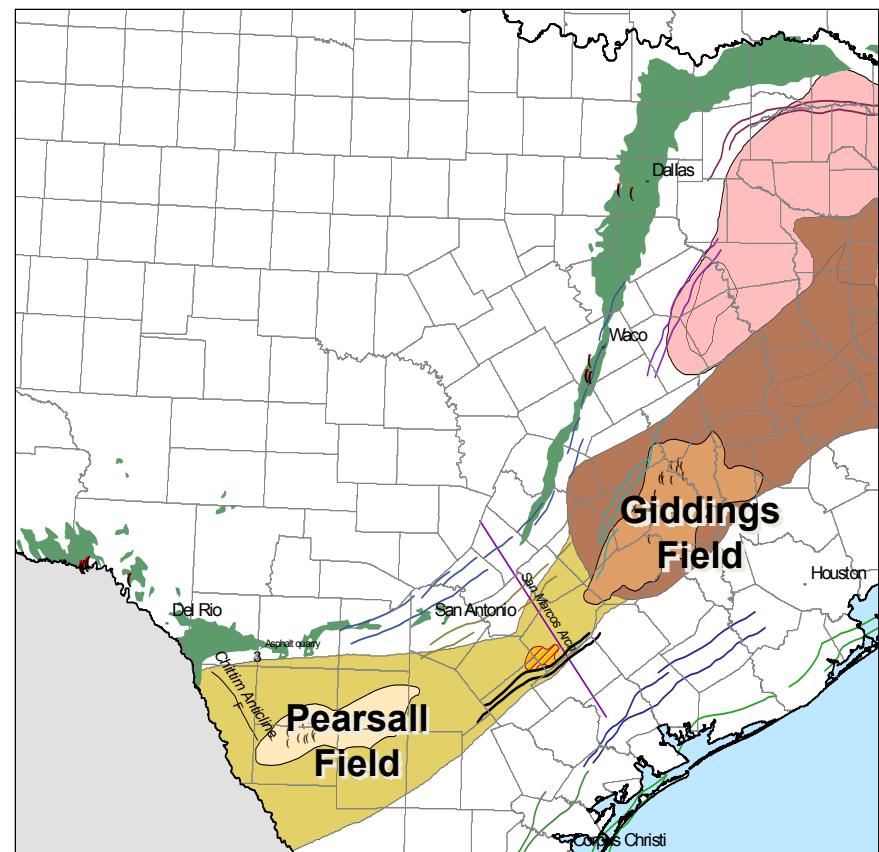
**Smackover Sourced Oils**

- High Sulfur

**Eagle Ford Sourced Oils**

- Med. Sulfur
- Low Sulfur

\*after Wenger et al. (1994)



# Issues and Implications

Why does oil in Austin Chalk Trend go from low- to medium-sulfur (NE to SW)?

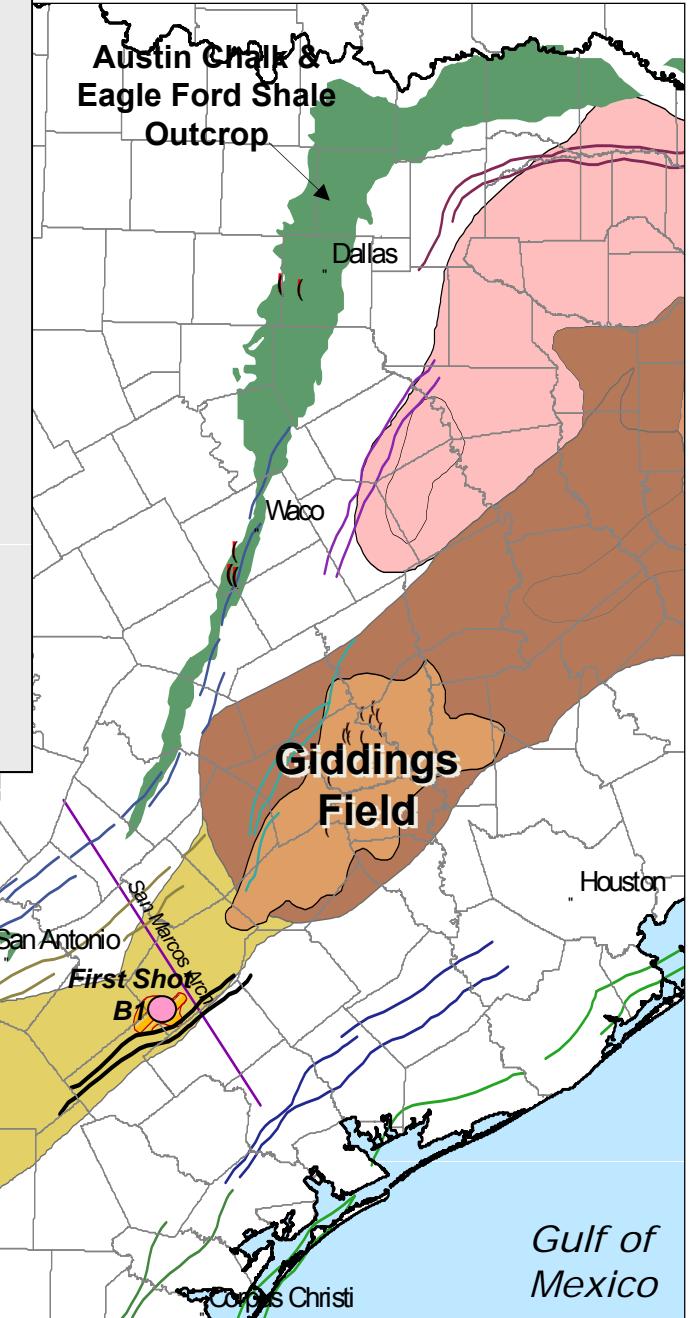
Facies change in the Eagle Ford?

*Change in maturity level for oil generation with facies*

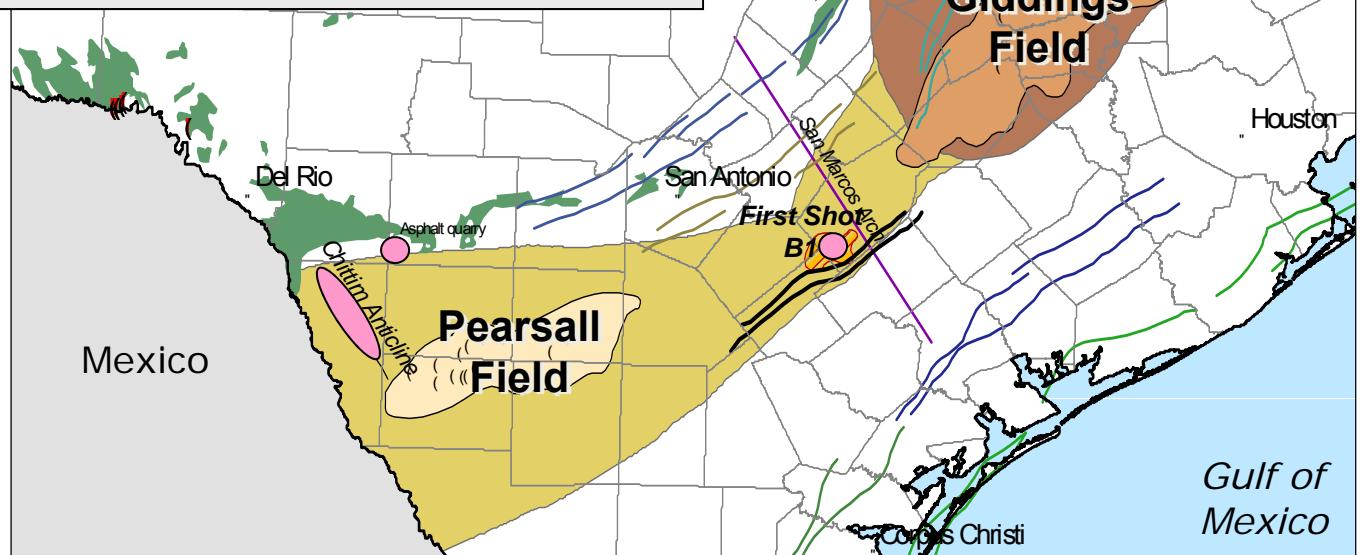
or

Mixing with high-sulfur Smackover oils?

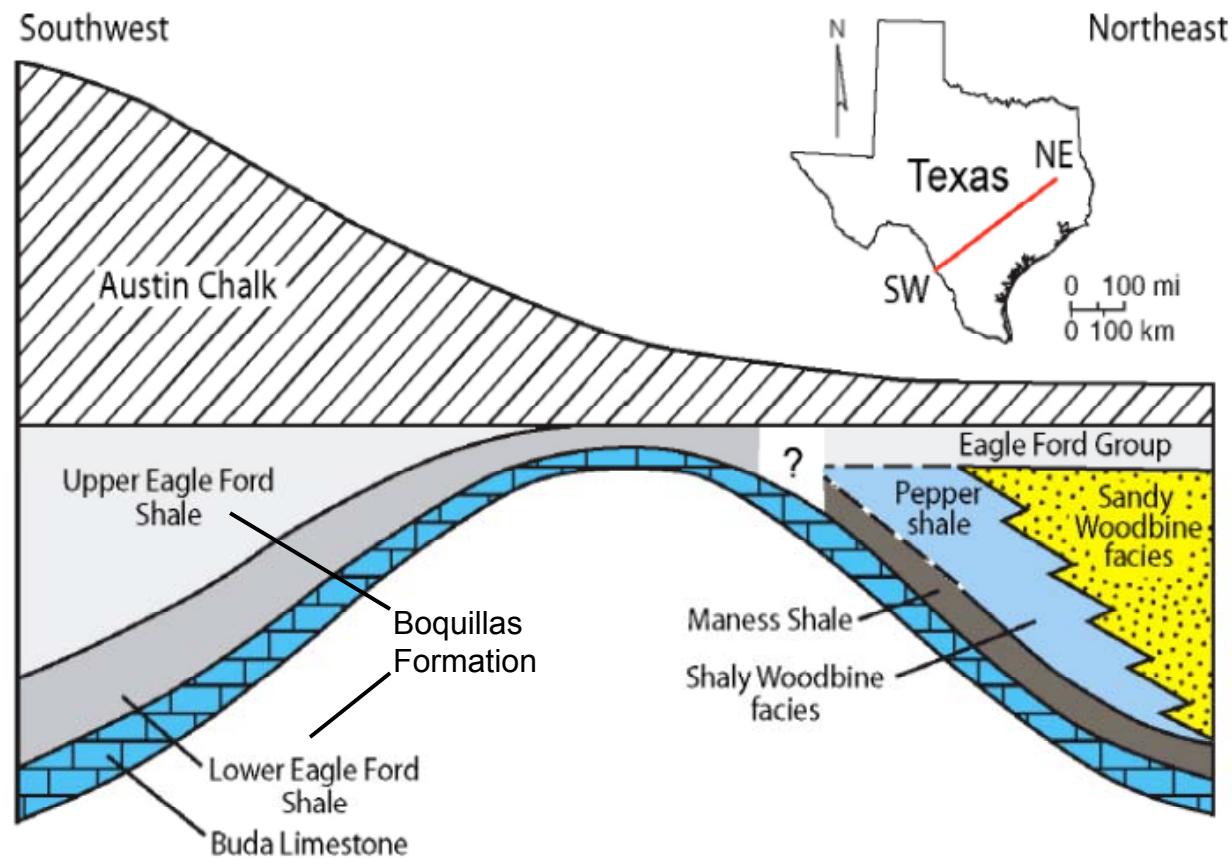
*Large volumes of gas from cracked Smackover oil at depth*



- Eagle Ford/  
Boquillas  
sample outcrops



# STRATIGRAPHY



*Modified from Hentz and Ruppel, 2010*

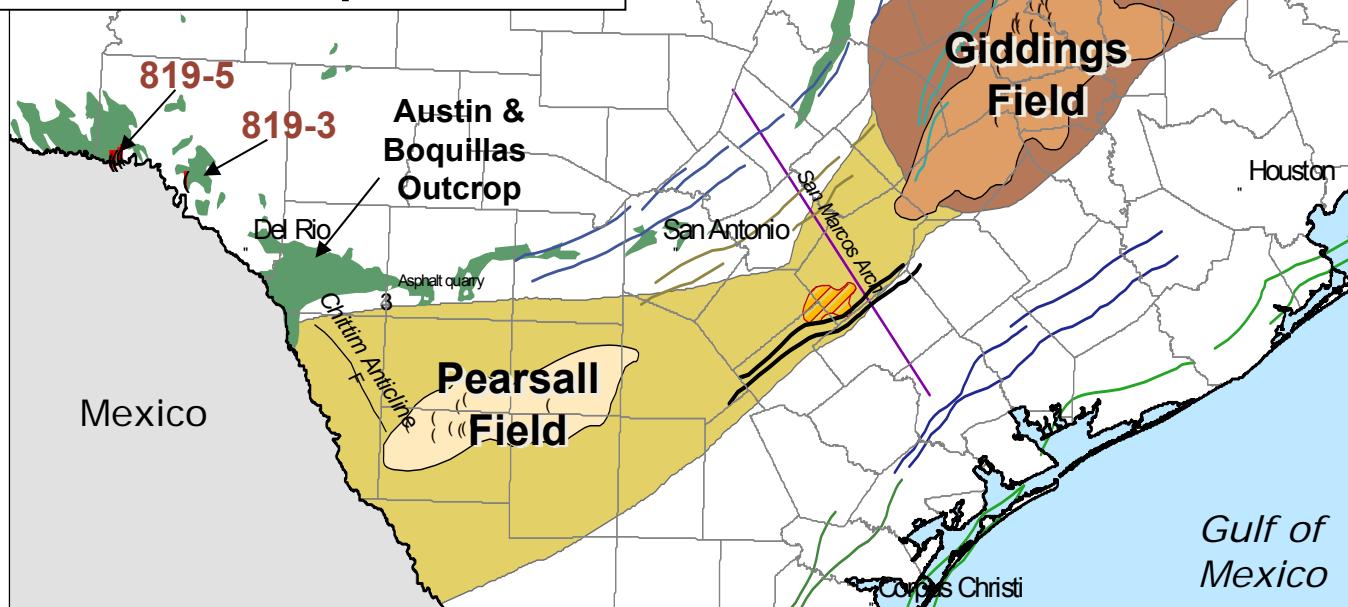
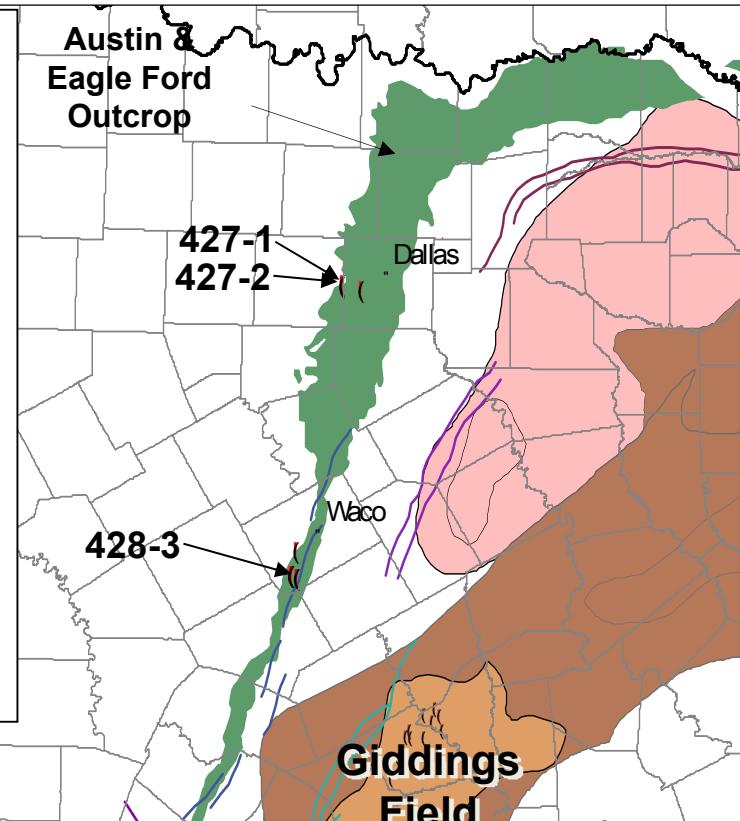
# Eagle Ford/Boquillas Lithofacies

**Chalky Marlstone Eagle Ford  
(427-1)**

**Calcareous Marlstone EF  
(427-2)**

**Chalky Marlstone w/Ist. beds  
(428-3)**

**Dense Marlstone Boquillas  
(819-3 & 819-5)**



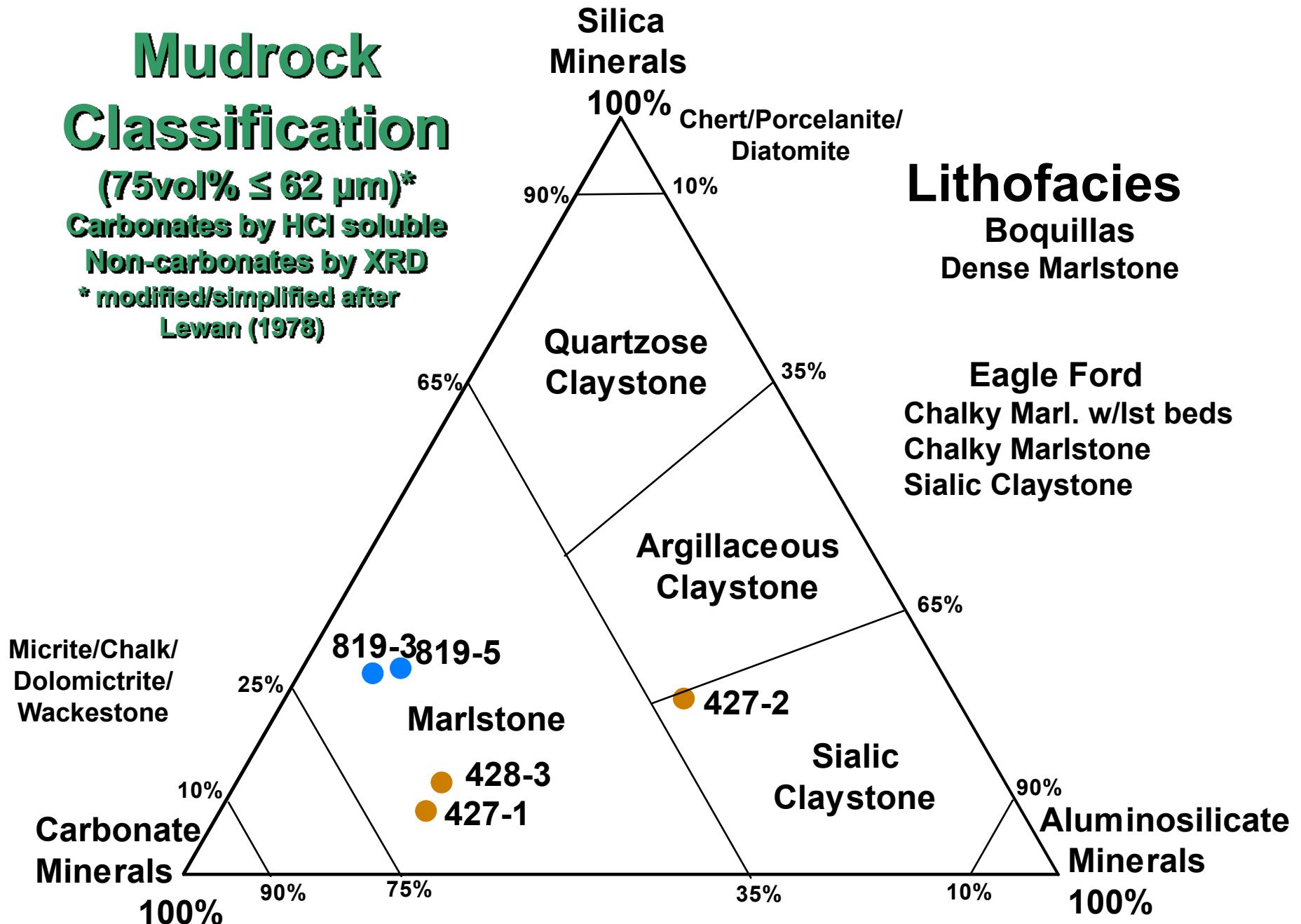
# Mudrock Classification

(75vol% ≤ 62 µm)\*

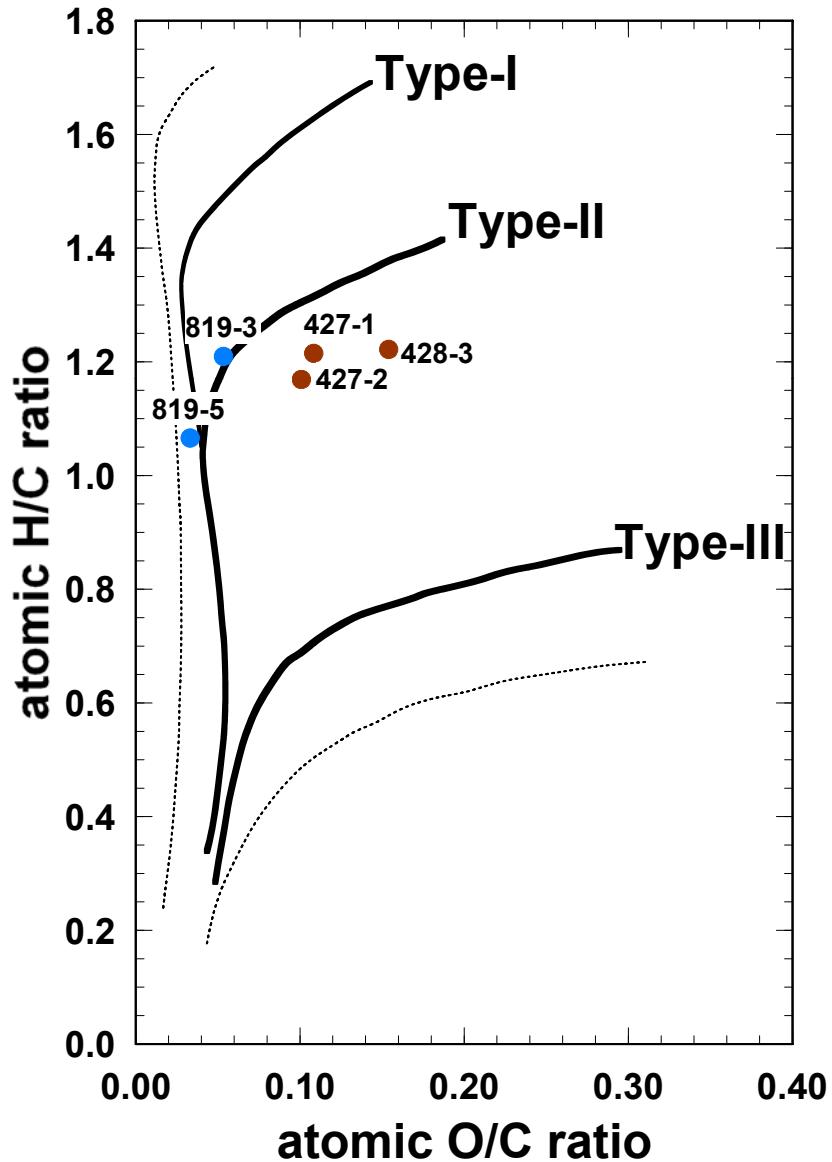
Carbonates by HCl soluble

Non-carbonates by XRD

\* modified/simplified after  
Lewan (1978)



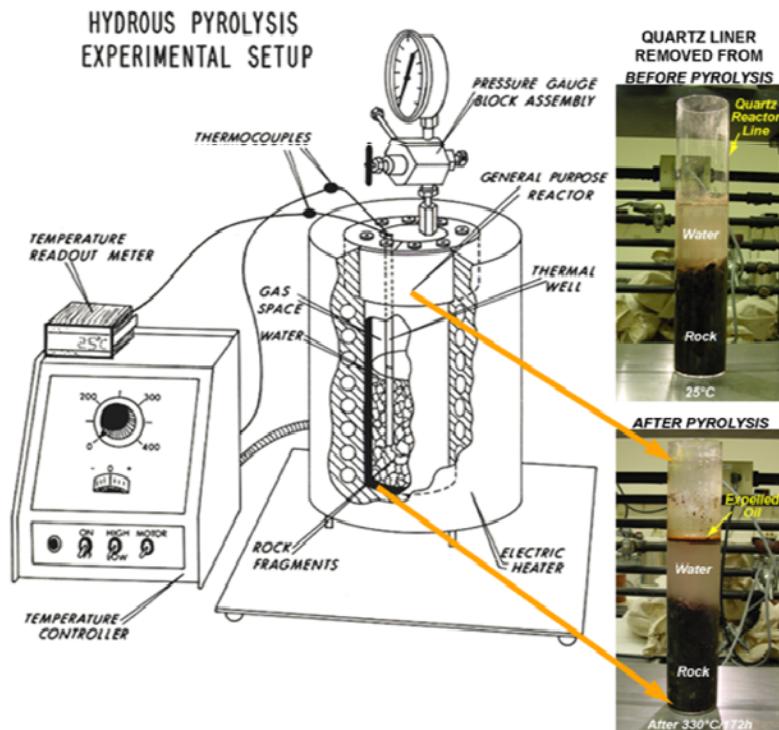
# KEROGEN TYPE



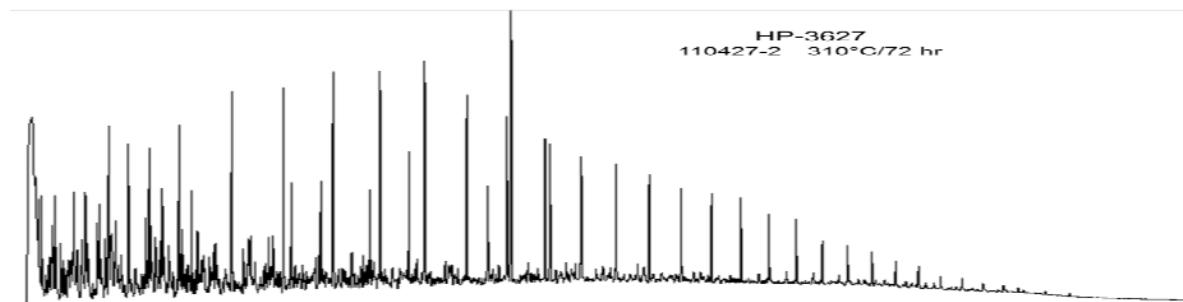
Average $S_{org}/C$ atomic	
100819-3	<b>0.045</b>
100819-5	<b>0.029</b>
110427-1	<b>0.022</b>
110427-2	<b>0.022</b>
110428-3	<b>0.031</b>

Type IIS Kerogen has  
 $S_{org}/C$  ratio  **$\geq 0.040$**  (Orr, 1986)

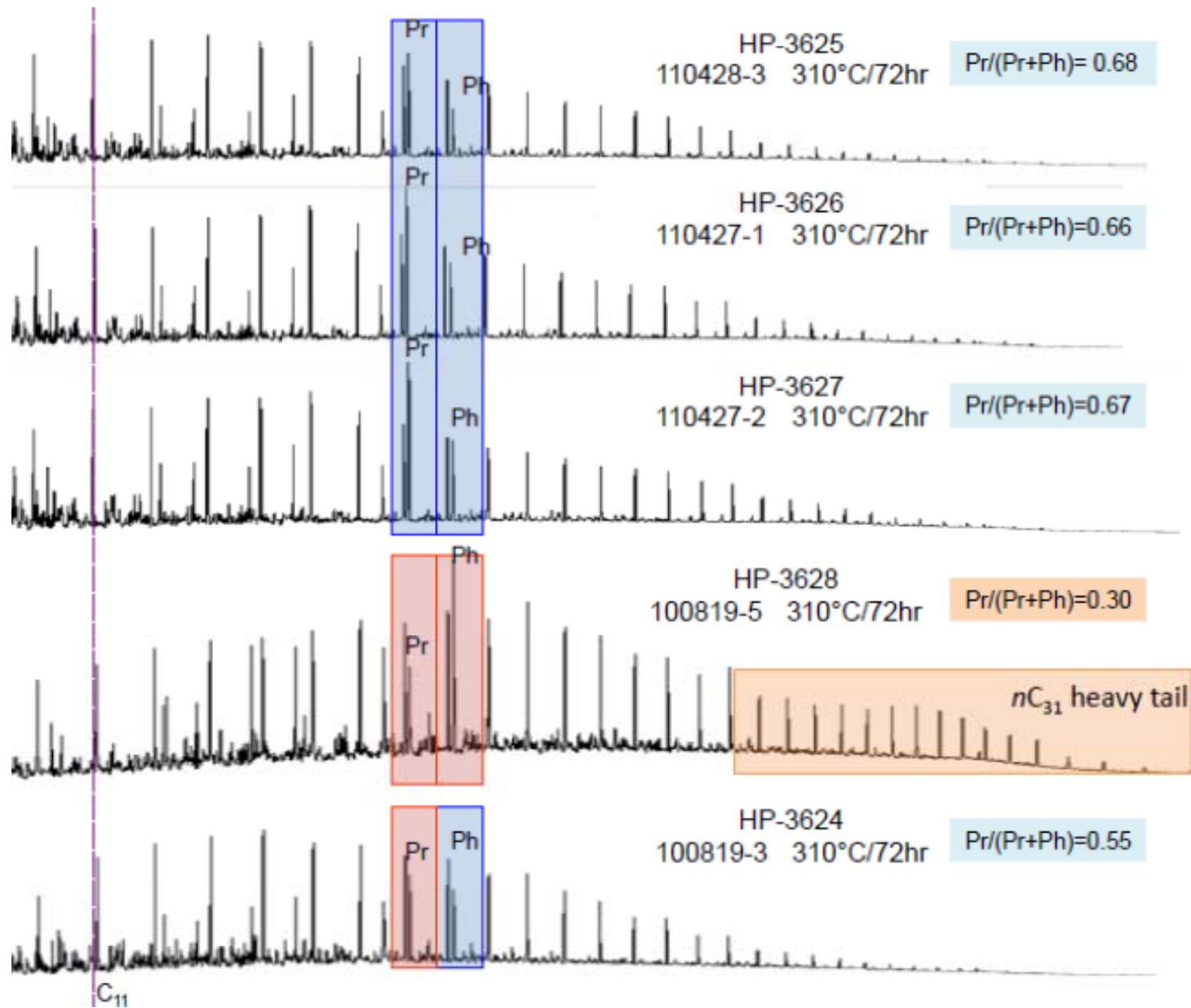
# HYDROUS PYROLYSIS



- Experiments were conducted at 310, 330, 355°C for 72 hrs

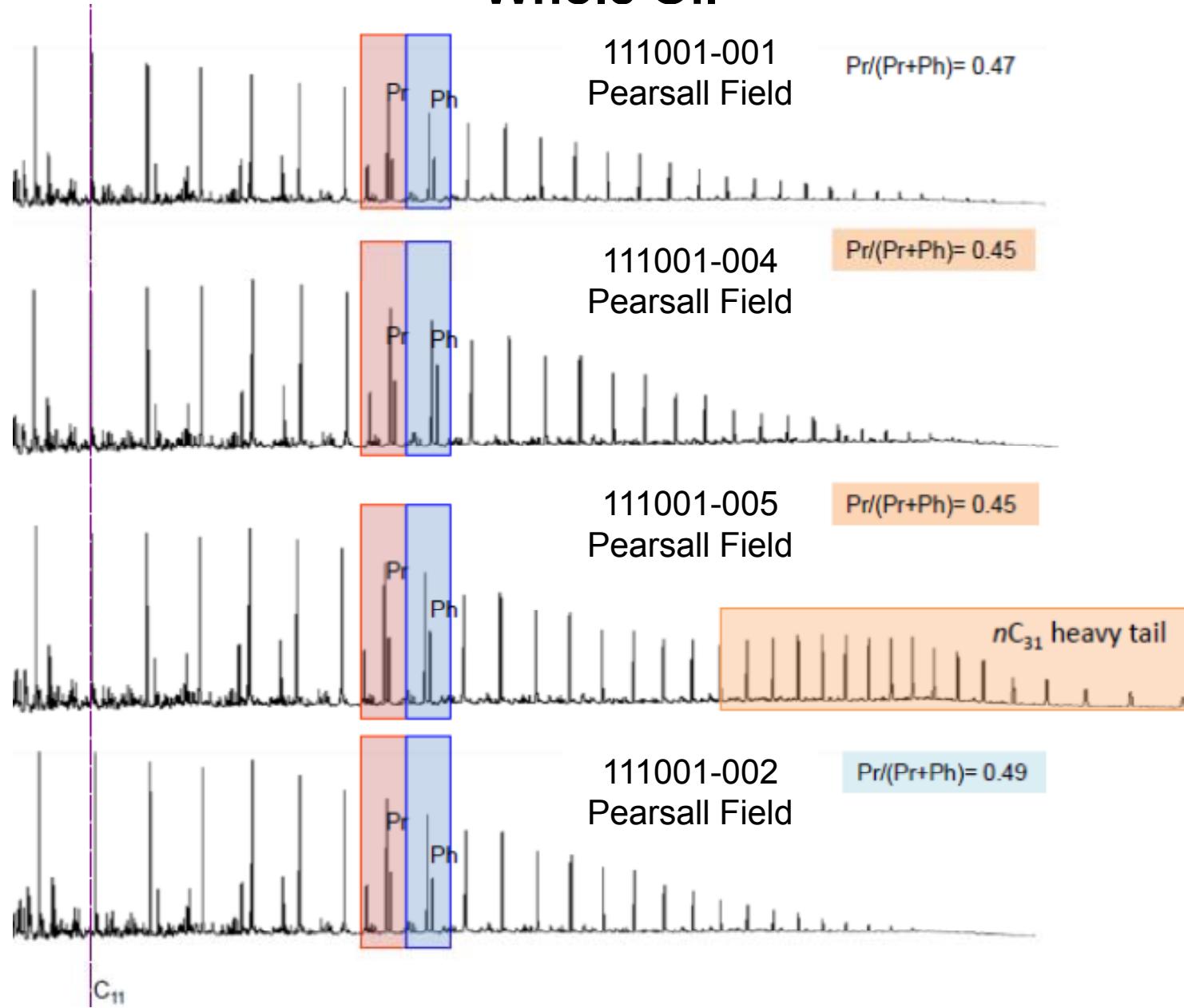


# DATA EVALUATION: HP Expelled Pyrolysates



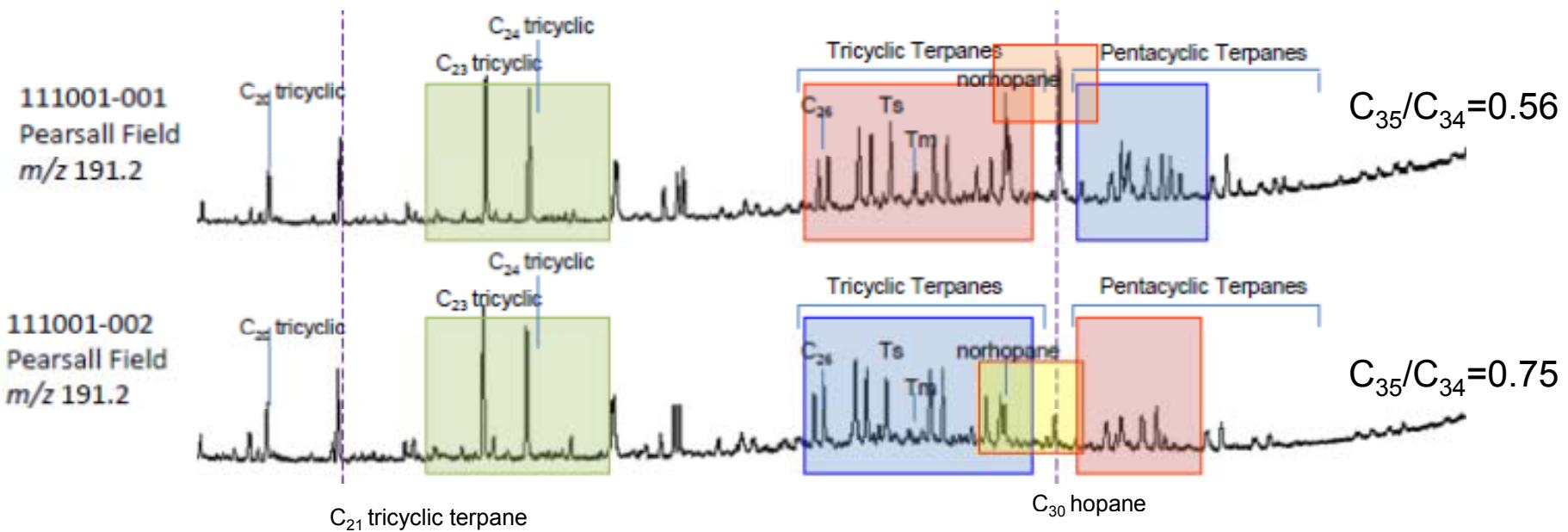
# RESULTS: SOURCE- Pearsall Field Oils

## Whole Oil



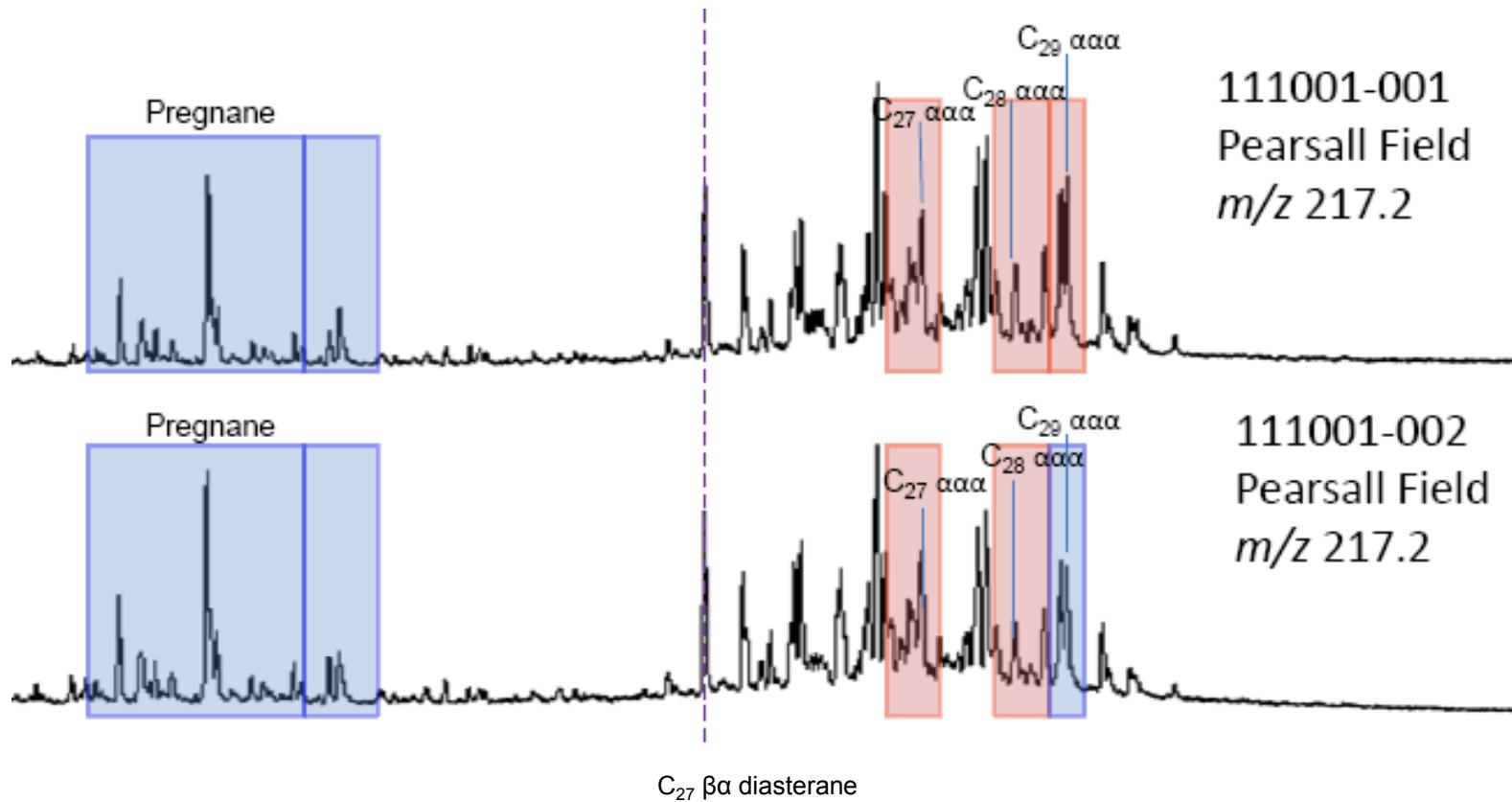
# RESULTS: SOURCE- Pearsall Field Oils

## Hopanes

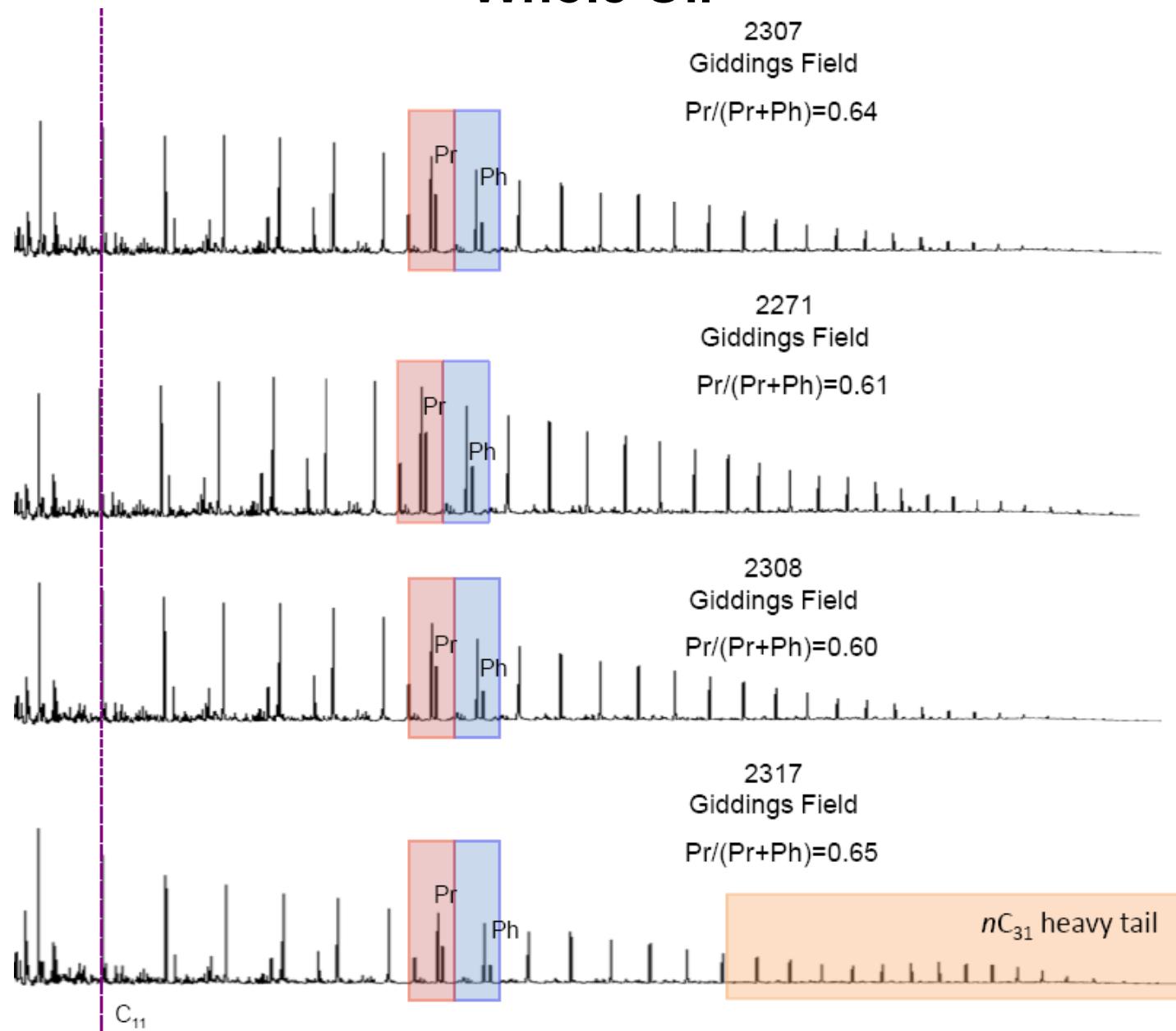


# RESULTS: SOURCE- Pearsall Field Oils

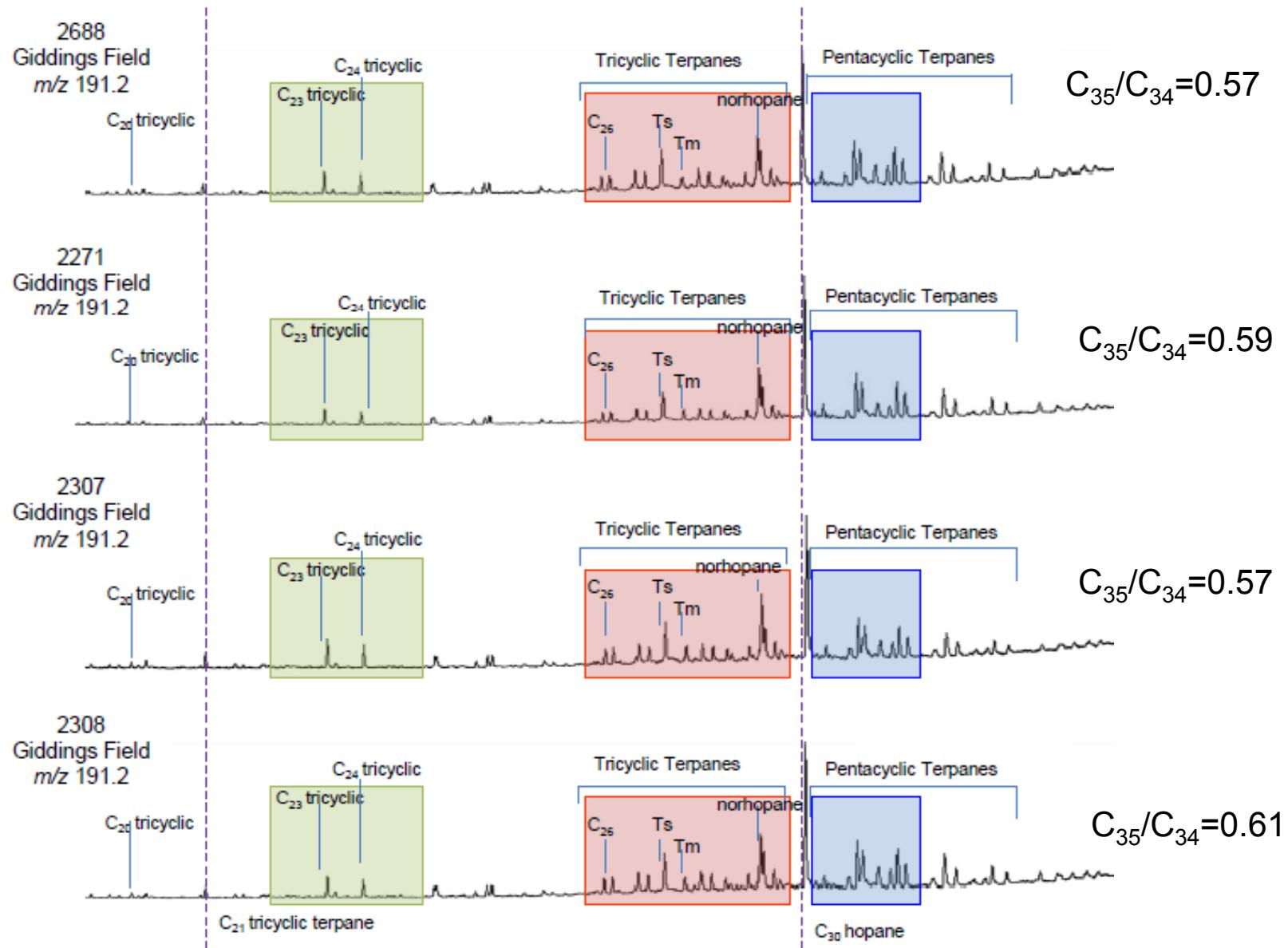
## Steranes



# RESULTS: SOURCE- Giddings Field Oils Whole Oil

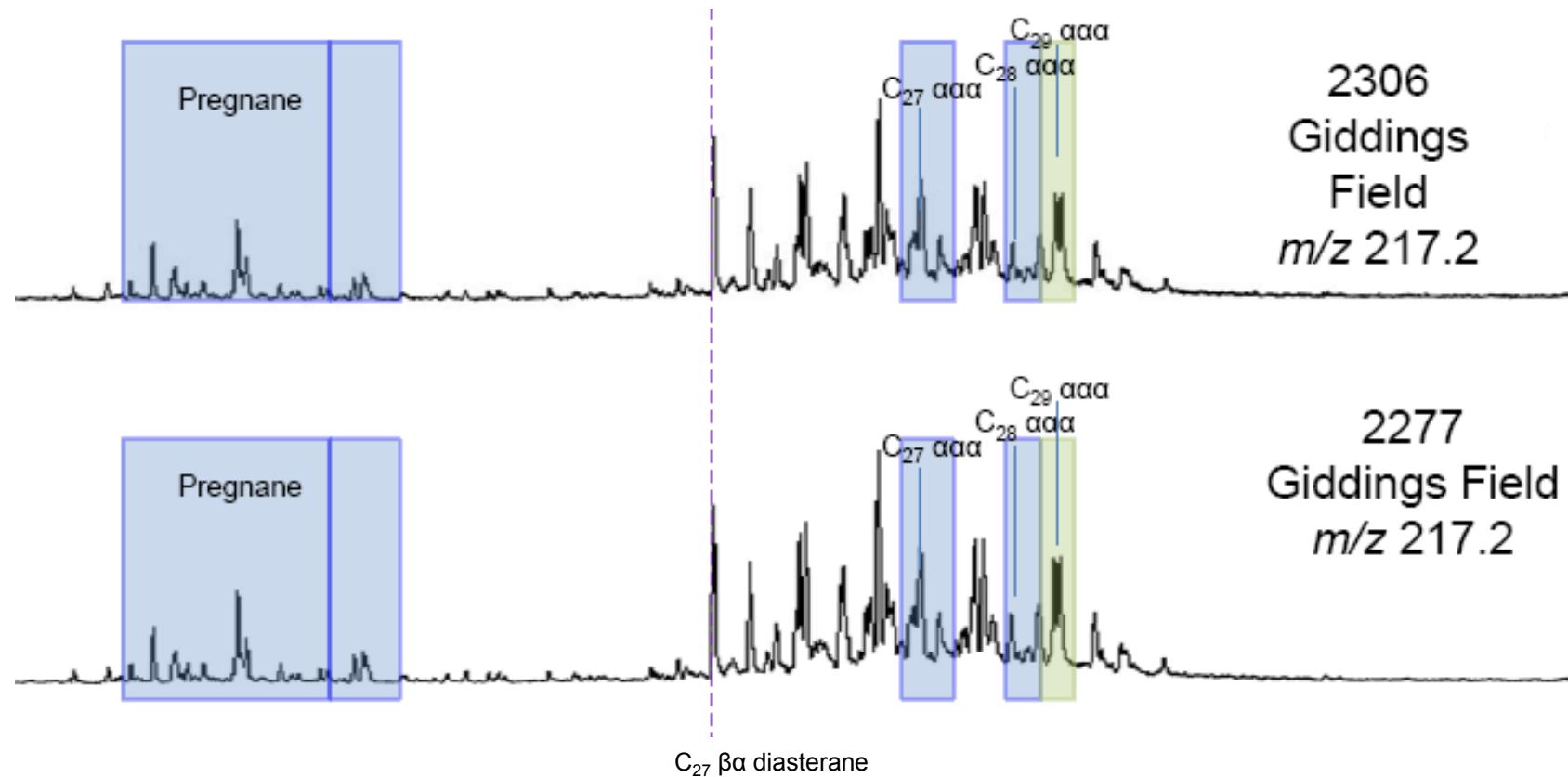


# RESULTS: SOURCE- Giddings Field Oils Hopanes

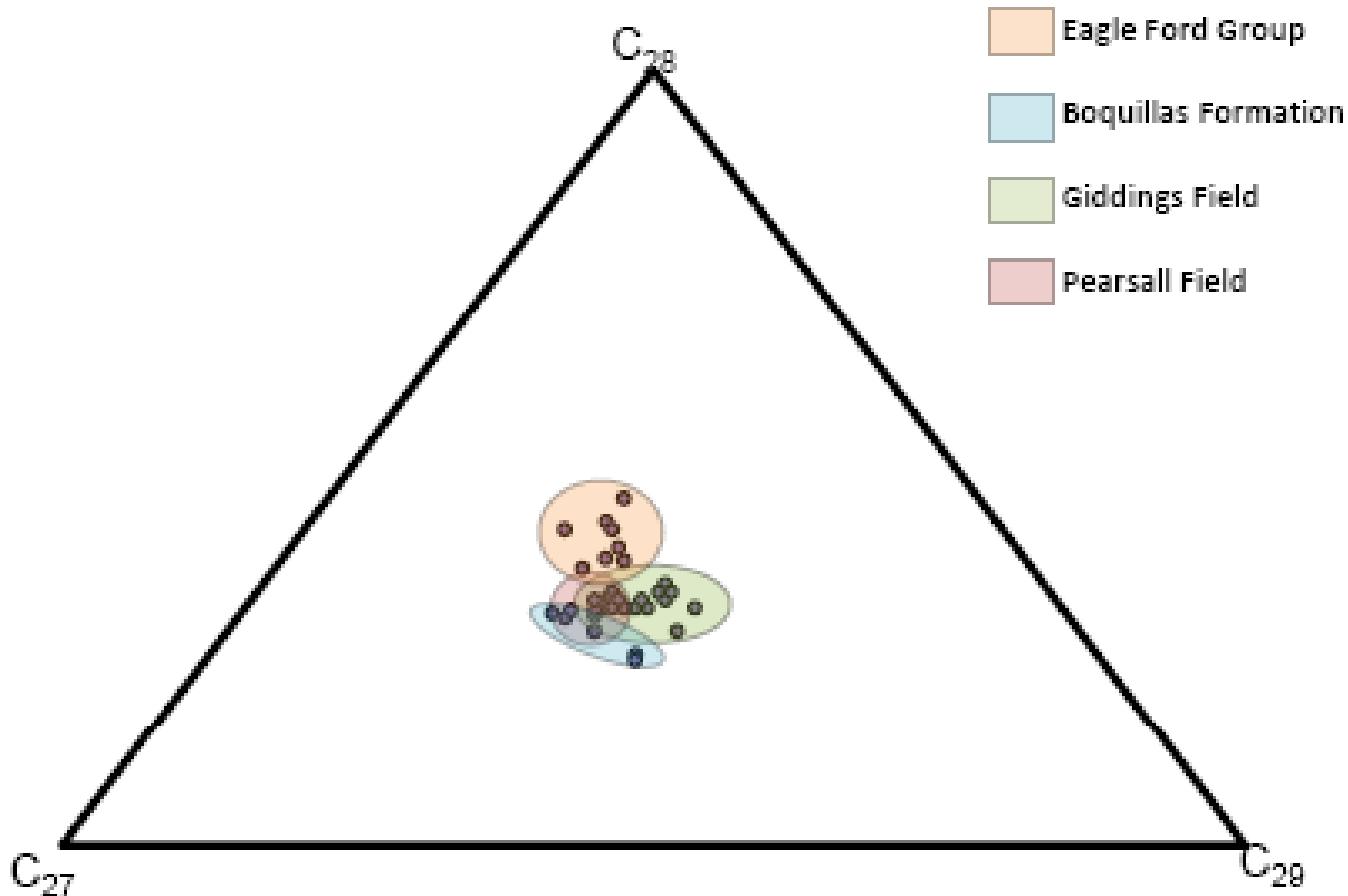


# RESULTS: SOURCE- Giddings Field Oils

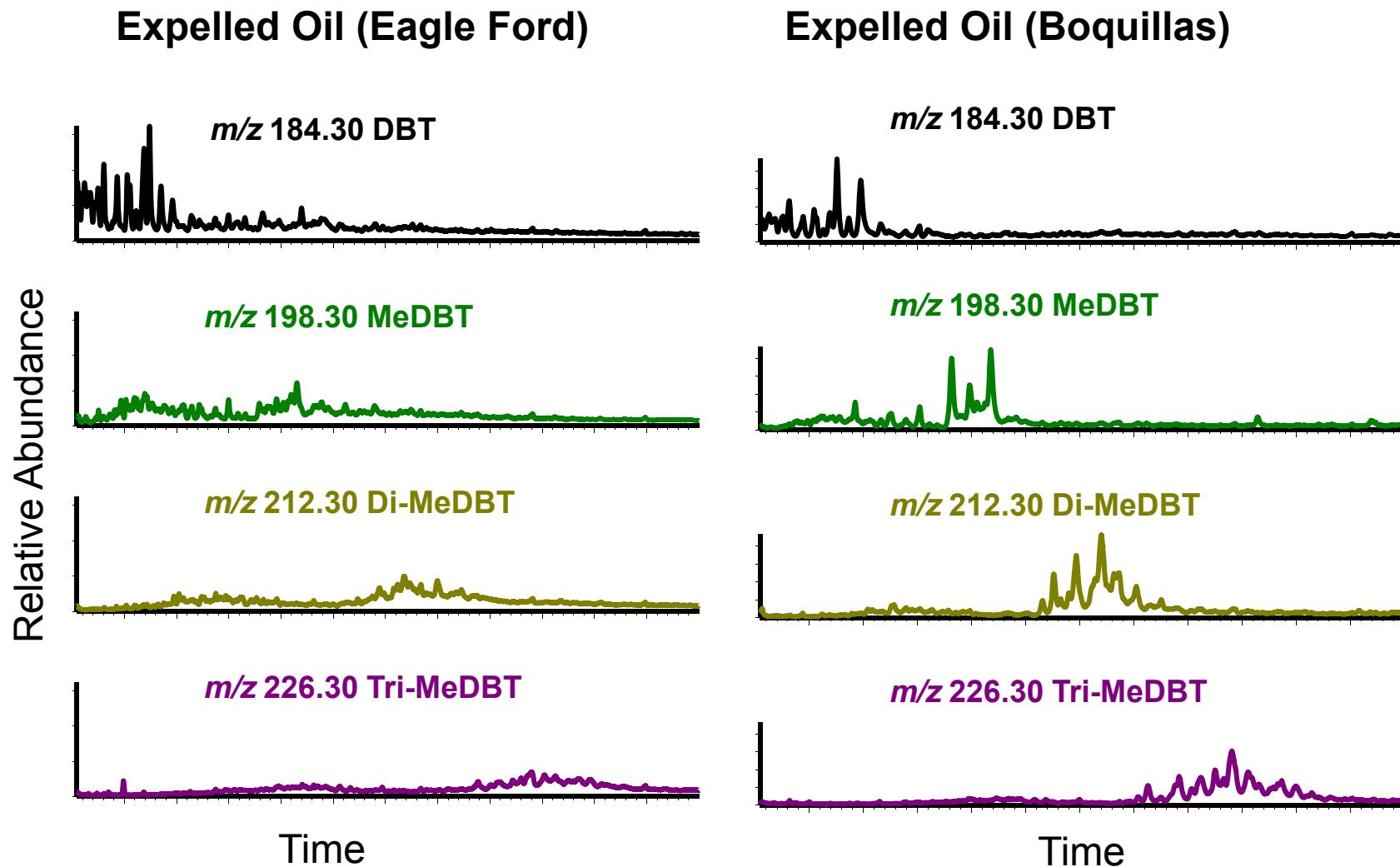
## Steranes



# RESULTS: SOURCE-Giddings Field and Pearsall Field Steranes



# *n*-Methyldibenzothiophene Data



# CONCLUSIONS

- **Giddings Field source:**
  - Eagle Ford Group
    - Tricyclic hopane signatures
  - Boquillas Formation
    - Heavy *n*-alkane tail
    - Sterane signatures
    - Tricyclic and pentacyclic hopane signatures
- **Pearsall Field source:**
  - Boquillas Formation
    - Heavy *n*-alkane tail
    - Sterane signatures
    - Tricyclic and pentacyclic hopane signatures

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**UC Riverside:** Natascha Riedinger

**Baylor University:** Steve Dworkin

**Matador Resources Company:** Bo Henk

**Lamb-Star Engineering, L.P.:** Bill Compton

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# RESULTS: THERMAL Maturity AND DEPOSITIONAL ENVIRONMENT

	Eagle Ford Group	Boquillas Formation	Giddings Field	Pearsall Field	
Pr/Ph	>1	varies	>1	varies	
Pregnane	absent	present	present	present	*indicates stratified water column
$C_{29}/C_{30}$	< 1	varies	< 1	varies	*indicates anoxic carbonate depositional environment
Ts/(Ts+Tm)	0.07	0.19	0.74	0.70	
	0.19				*Waco

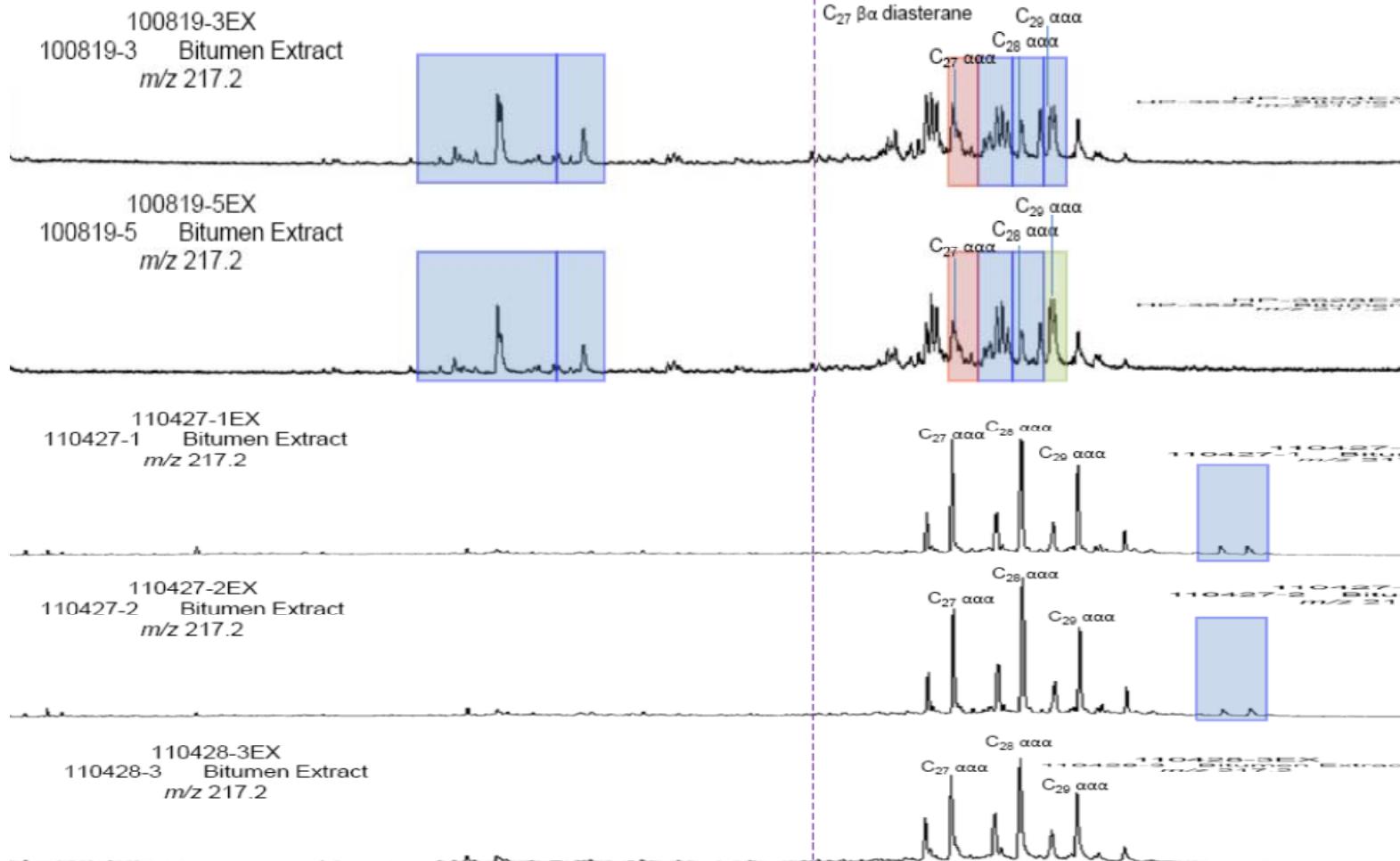
# SUMMARY

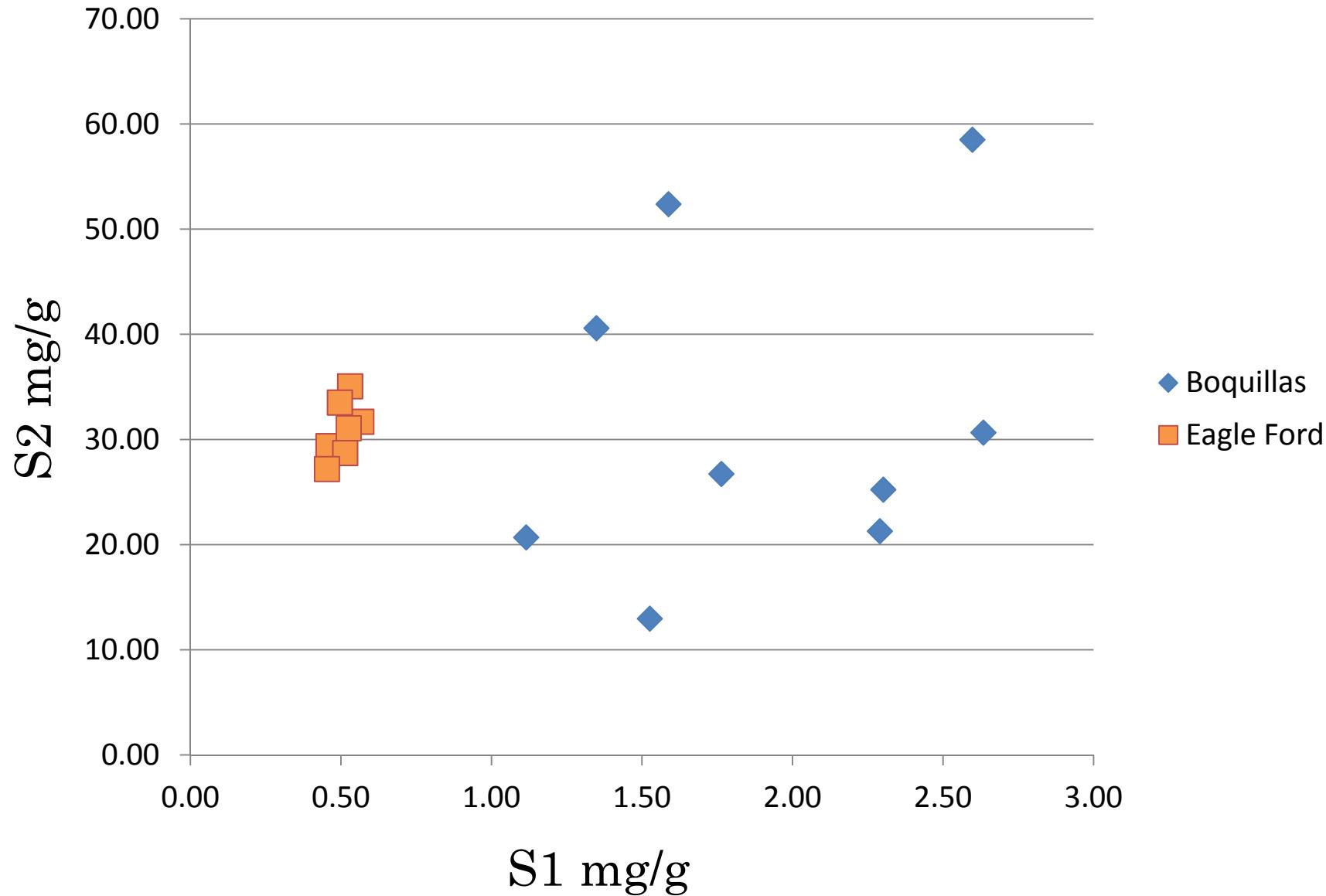
- Source of Pearsall Field:
  - Boquillas Formation
    - 100819-3, 100819-5
- Whole Oil GC:
  - *n*-alkane distributions
    - *nC*<sub>31</sub> alkane heavy tail
  - Pr/Ph signatures
- Hopanes:
  - C<sub>29</sub>/C<sub>30</sub> Hopane
  - Extended hopane signatures
- Steranes:
  - Pregnane, homopregnane

# SUMMARY

- Source of Giddings Field:
  - Boquillas Formation
    - 100819-3, 100819-5
  - Eagle Ford Group
    - 110428-3, 110427-1/110427-2
- Whole Oil GC:
  - *n*-alkane distributions
    - *nC*<sub>31</sub> alkane heavy tail
  - Pr/Ph signatures
- Hopanes:
  - Consistent across all samples
  - Extended hopane signatures
  - C<sub>29</sub>/C<sub>30</sub> Hopane
- Steranes:
  - Pregnane, homopregnane

# Results: Depositional Environment

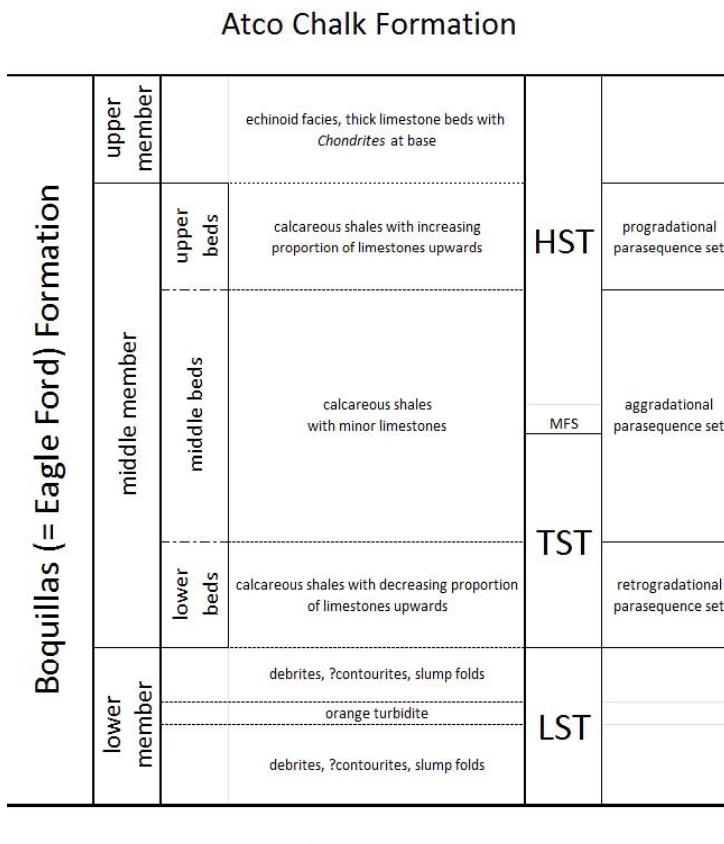




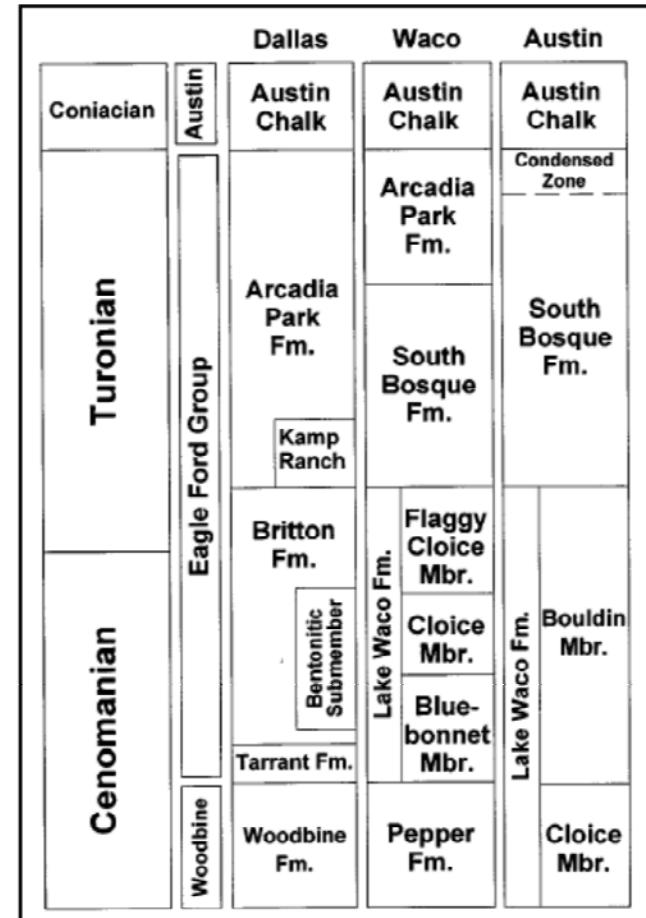
# Sulfur Data

Sample #	S [wt %]	CaCO3 [wt %]	TOC [wt %]	TC_CRS [wt %]	TOS [wt %]
100819-3	1.86	57.76	5.38	3.96	0.52
100819-5	1.59	56.12	4.71	3.12	0.32
110427-1	1.28	62.42	4.67	3.99	0.30
110427-2	2.05	28.60	5.54	4.72	0.34
110428-3	0.82	55.49	6.42	3.41	0.32
100819-3 ex	1.68	54.47	4.94	4.30	0.53
100819-5 ex	1.58	58.06	3.31	2.71	0.42
110427-1 ex	1.56	59.96	4.86	5.80	0.43
110427-2 ex	2.05	27.67	5.40	4.61	0.33
110428-3 ex	0.70	59.48	5.28	3.12	0.28

# Eagle Ford Group (K 98.9-89.0 Ma)

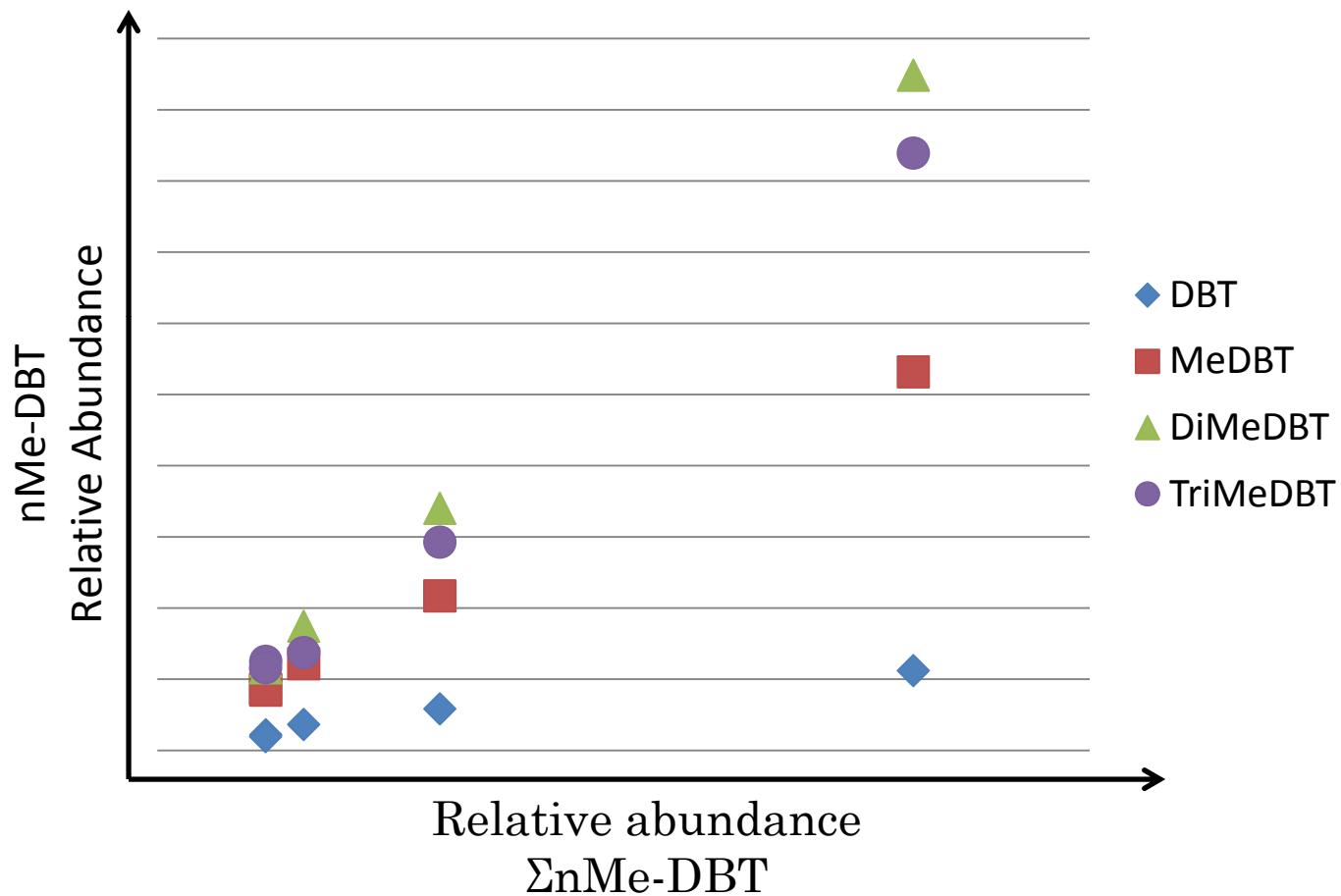


Lock et al., 2010



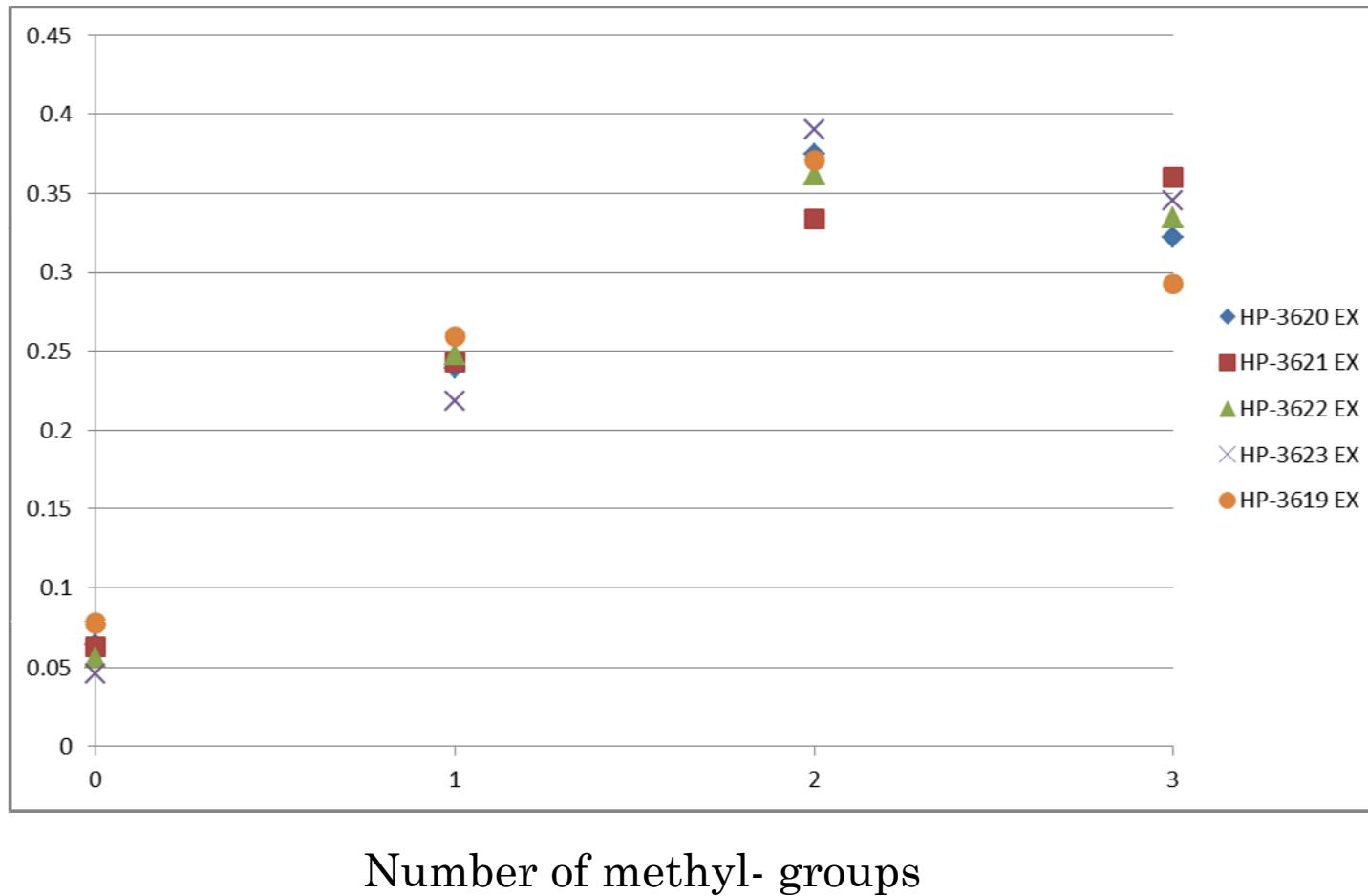
Dawson, 2007

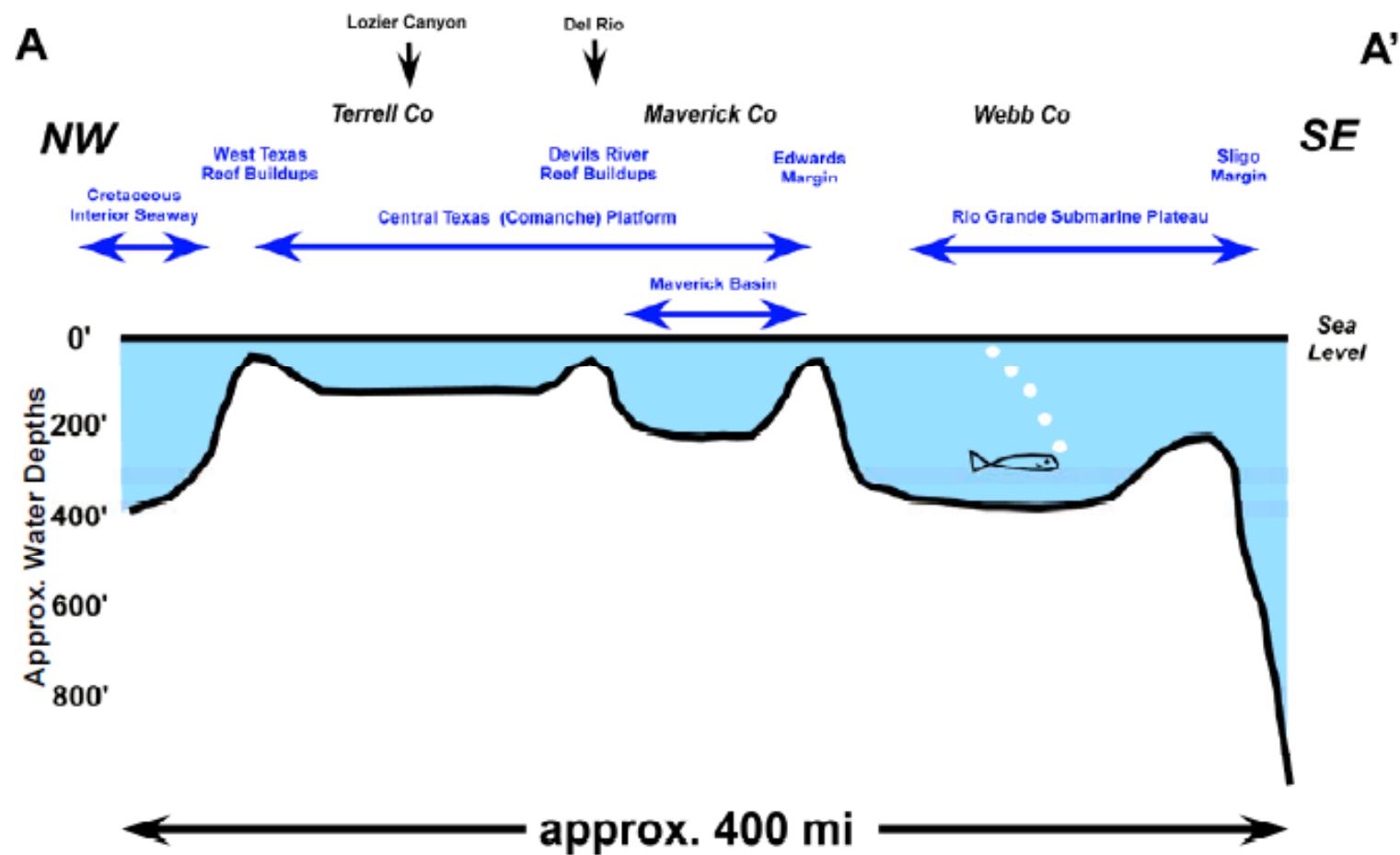
# *n*-Methyl-Dibenzothiophene ratios of bitumen extracts



$$\text{DBT Ratio} = \frac{n\text{-MeDBT}}{\Sigma n\text{-MeDBT}}$$

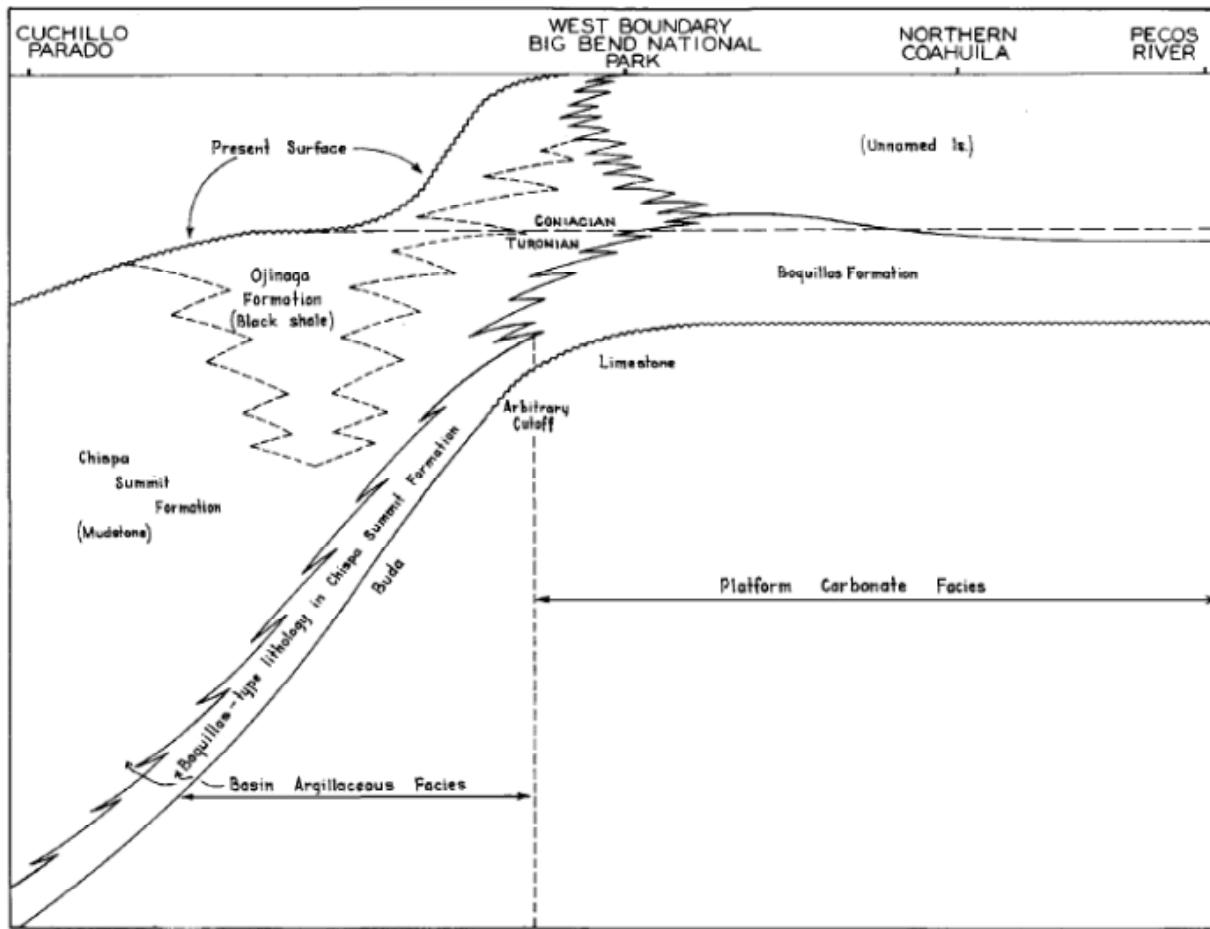
# DBT Ratios of bitumen extracts





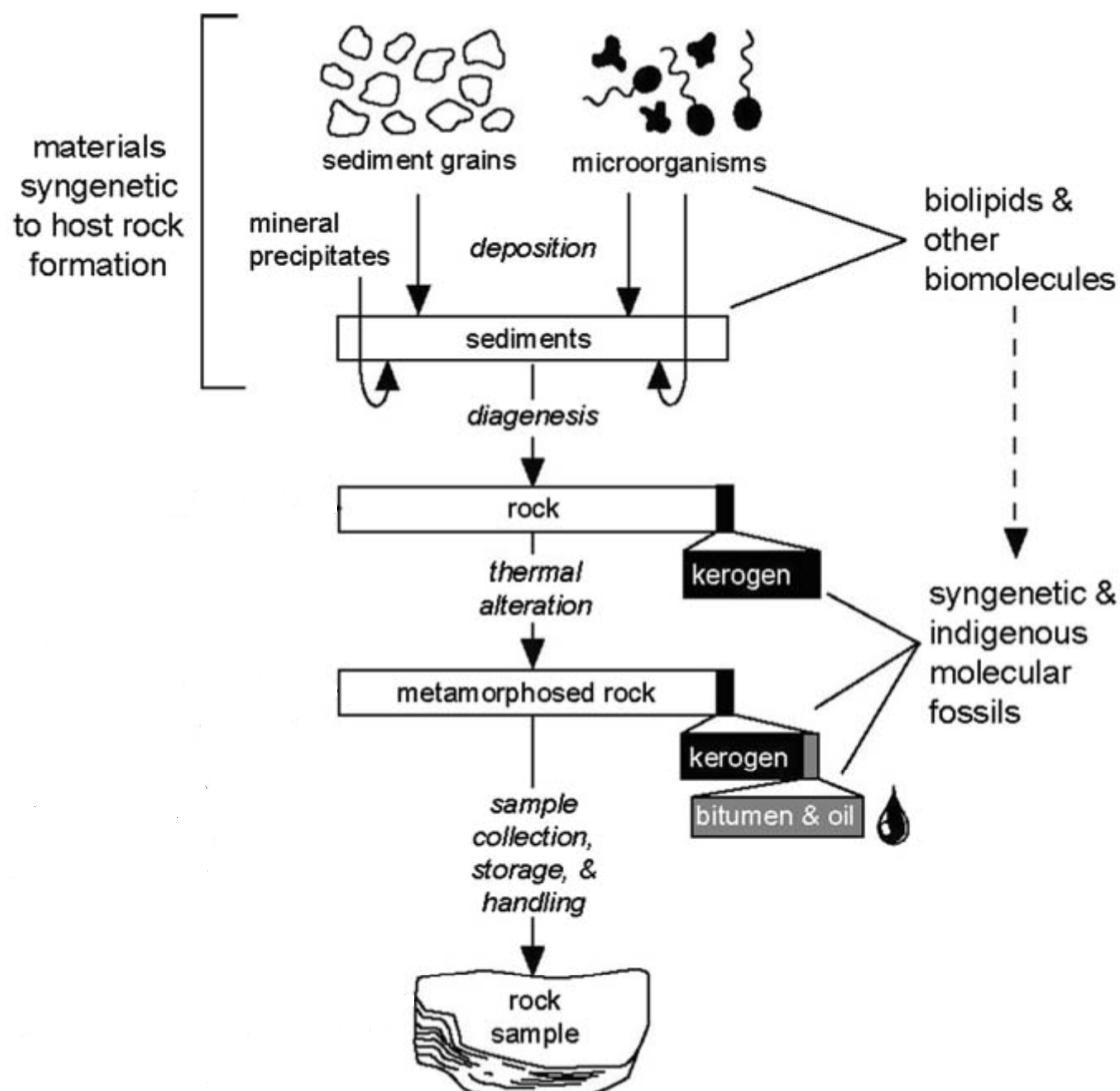
*Donovan and Staerker, 2011*

# Boquillas Facies

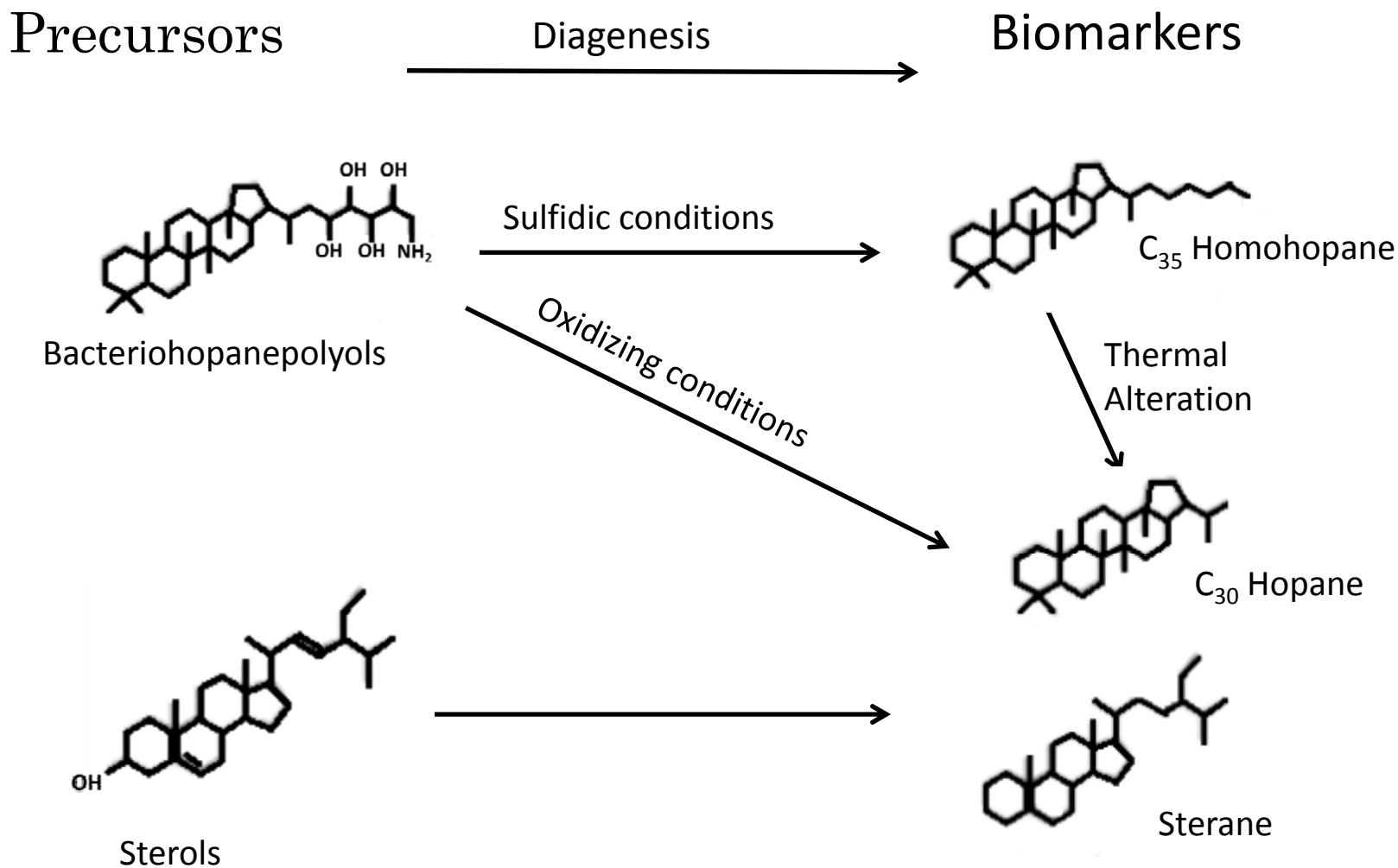


Powell, 1965

# Background

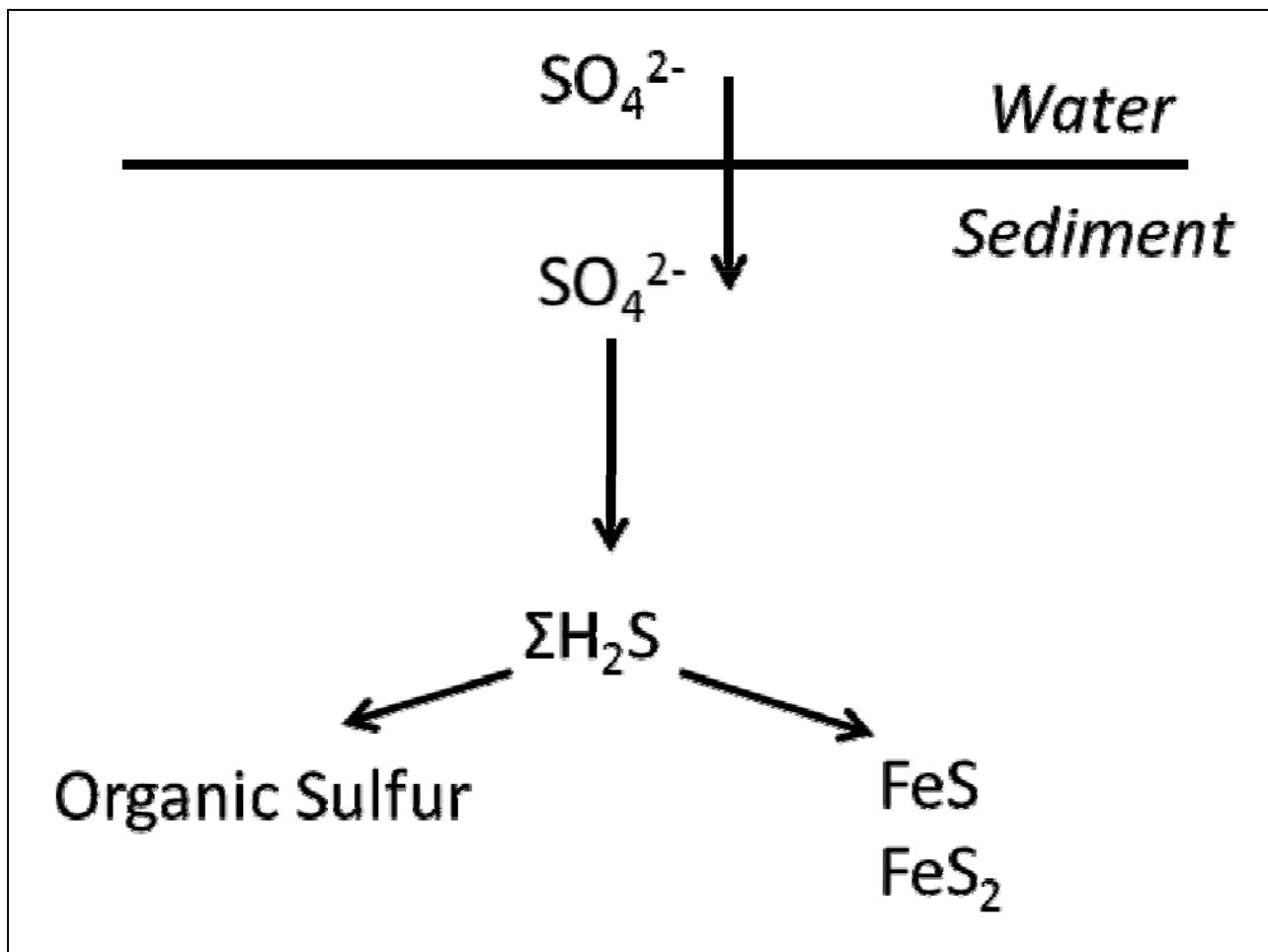


Modified from Eigenbrode, 2007



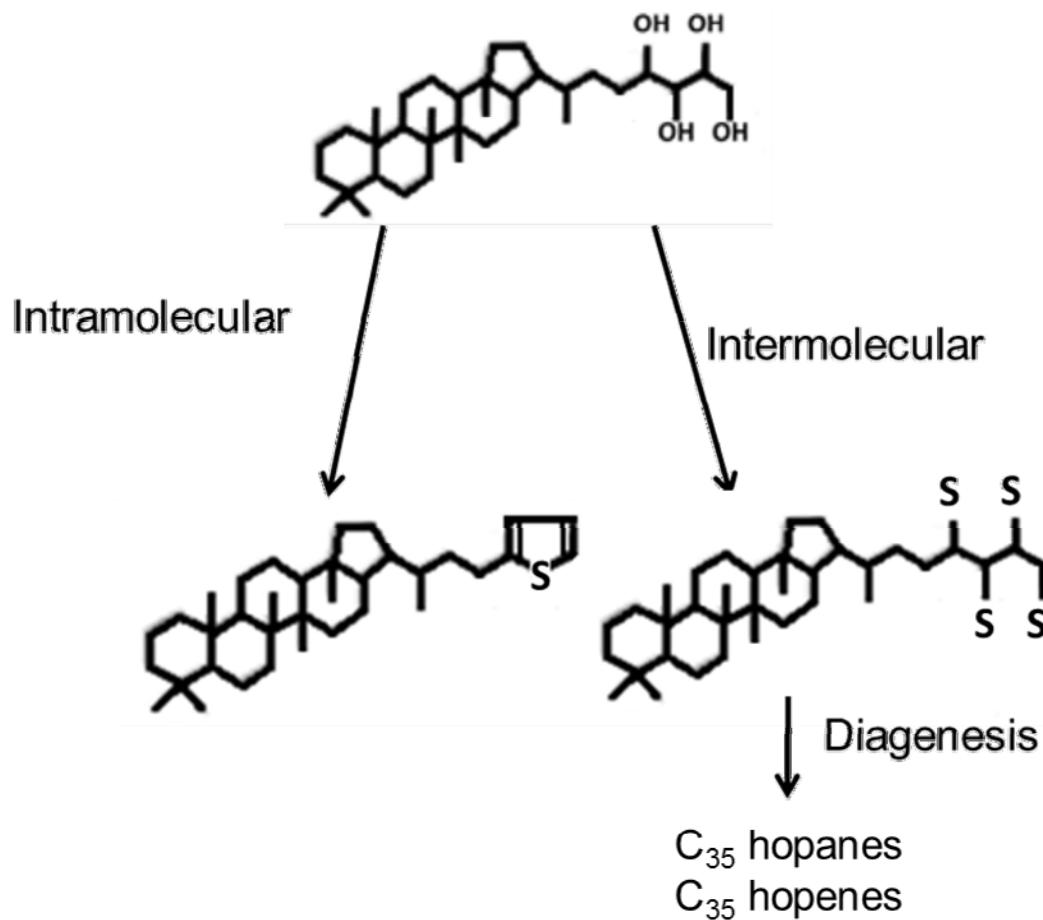
Modified from Eigenbrode, 2007

# Sulfur Geochemistry



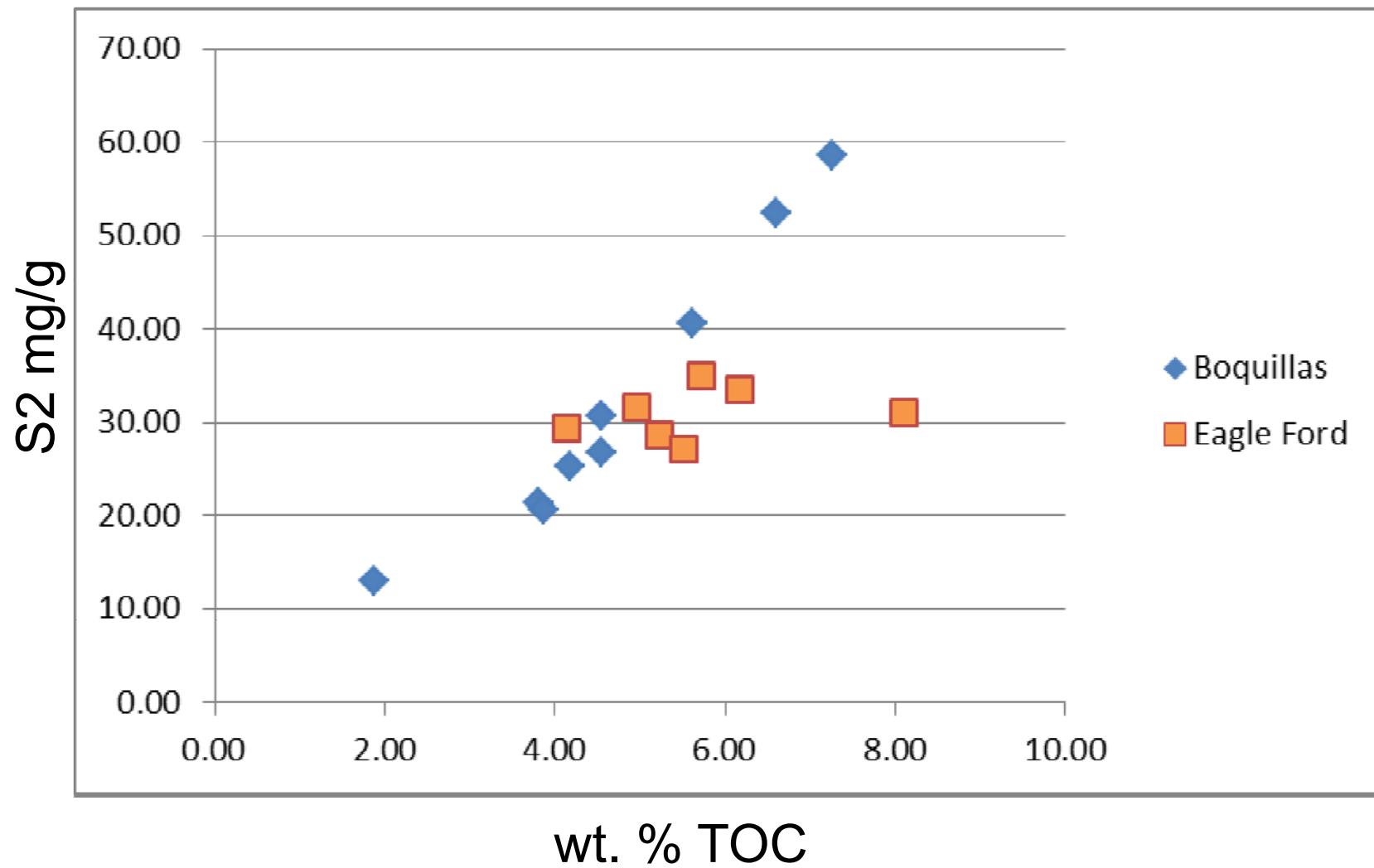
Modified from Werne et al., 2004

# Sulfur Geochemistry

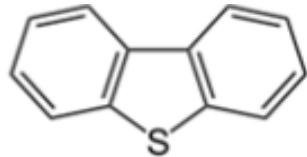


*Modified from Sinninghe Damsté and de Leeuw, 1990*

# RESULTS: ROCKEVAL PYROLYSIS

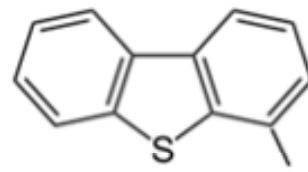


# Target Compounds



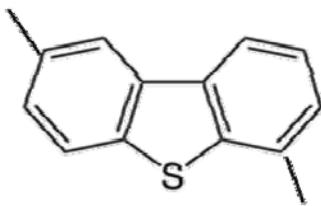
DBT

Dibenzothiophene (*m/z* 184)



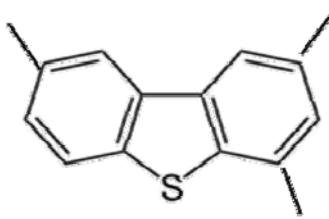
Me-DBT

Methyl-dibenzothiophene (*m/z* 198)



DiMe-DBT

Dimethyl-dibenzothiophene (*m/z* 212)



TriMe-DBT

Trimethyl-dibenzothiophene (*m/z* 226)