Biomarkers in the Upper Devonian Lower Huron Shale as Indicators of Biological Source of Organic Matter, Depositional Environment, and Thermal Maturity*

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Abstract

The Lower Huron Shale (Upper Devonian) is considered the largest shale gas reservoir in the Big Sandy Field in Kentucky and West Virginia. The potential for gas shales, such as the Lower Huron, to produce natural gas is a function of type, amount, and thermal maturation of their organic matter. Twenty-one Lower Huron Shale samples from eight wells located in eastern Kentucky and southern West Virginia were analyzed for biomarker content to interpret biological source of organic matter, depositional environment conditions, and thermal maturity. The following biomarkers were identified: n-alkanes (C15 to C35), pristane (Pr), phytane (Ph), steranes (αααR, αααS, ααβR, ααβS isomers of C27 to C30 steranes), and hopanes (C27, C29, C30 and C31 hopanes).

The TAR (terrigenous versus aquatic n-alkanes ratio), n-C17/n-C31, Pr/n-C17, Ph/n-C18, and sterane distribution indicate the source of organic matter in the samples analyzed is predominantly marine algae and bacteria. The most source-specific biomarkers identified in the samples were the C30 steranes indicative of marine brown algae. The Pr/Ph, Pr/n-C17, Ph/n- C18, Ts/Tm ratios and sterane distribution indicate the samples were deposited in a deep water (>100 m) environment with alternating oxic and anoxic conditions. These results and paleogeographic information support depositional models involving a seasonally stratified water column.

The C27-20S/(20S+20R), C28-20S/(20S+20R), C29-20S/(20S+20R), C28-αββ/(αββ+ααα), C29- αββ/(αββ+ααα), Ts/(Ts+Tm), and 22S/(22S+22R) ratio values indicate thermal maturities within the early to peak oil generation stages. Contour maps of the biomarker ratio values indicate increasing thermal maturities toward the southeast within the study area, which corresponds to the direction of increasing maximum burial depth. Biomarker data suggest that gas produced from the Lower Huron Shale in the Big Sandy Field is biogenic or that thermogenic gas has migrated to the Big Sandy Field from more thermally mature areas to the east.

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September 27th, 2011

CLEMSON UNIVERSITY

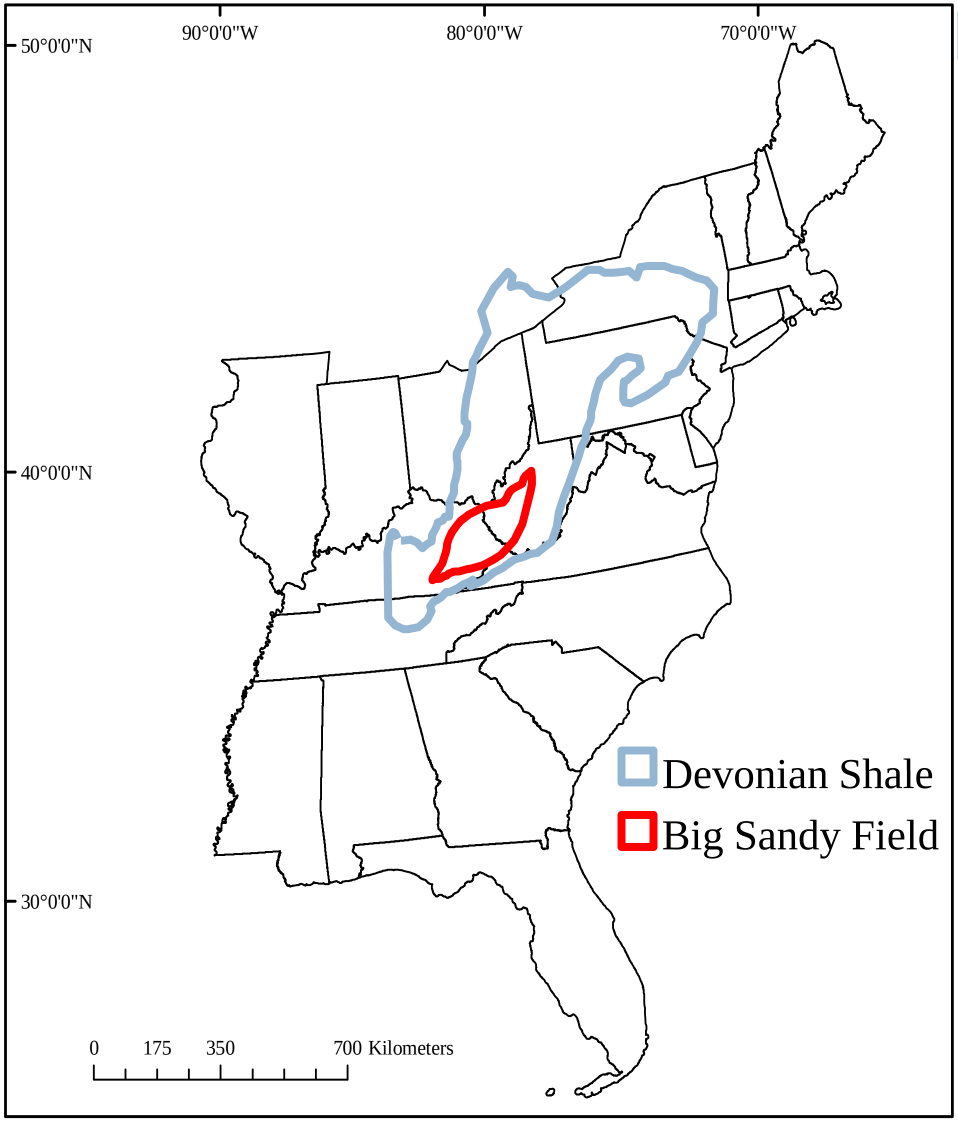
Objectives

- Identify biomarkers in samples of the Upper Devonian Lower Huron Shale from the Appalachian Basin
- Interpret biological origin of the biomarkers identified
- Use the biomarkers to interpret environmental conditions represented by the samples analyzed
- Use the biomarkers to interpret thermal maturity of the samples

Biomarkers

- Preserved remnants of molecules originally synthesized by organisms
  - Distinctive chemical structures closely related to the biological precursor molecule
  - Biological precursors molecules are common in certain organisms that may have been abundant and widespread
  - Are chemically stable during sedimentation and early burial

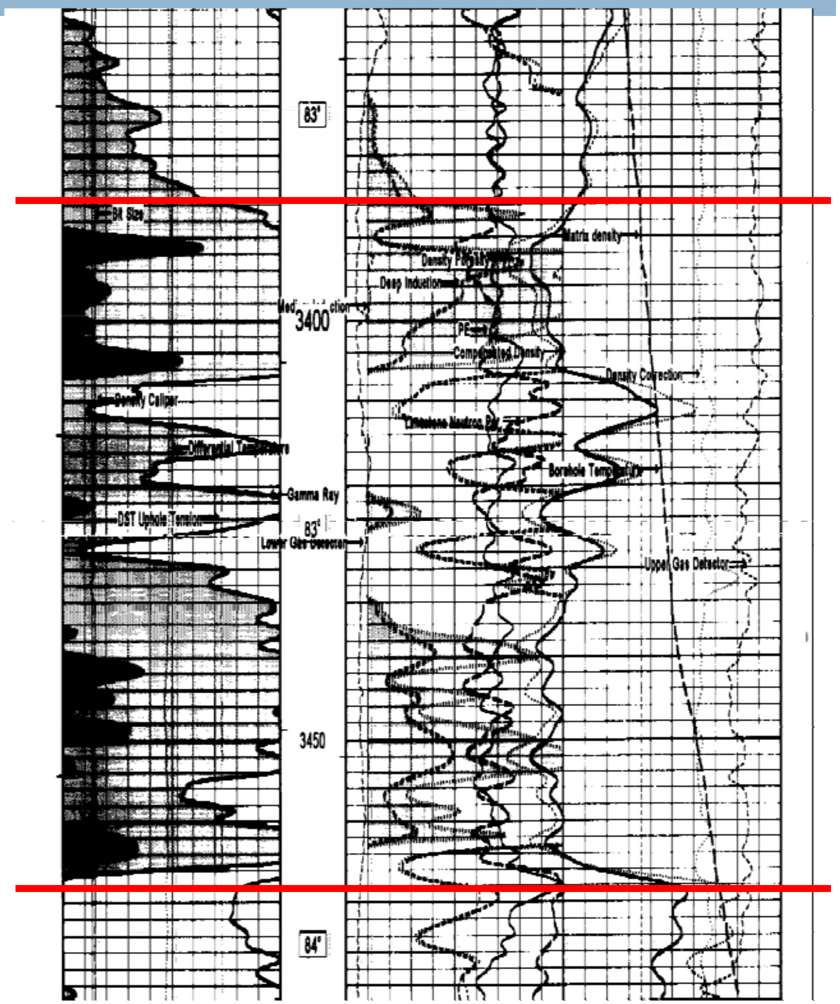
Devonian Black Shales



- Big Sandy Field
  - 2.5 Tcf of gas has been produced from gas shales
  - 6 Tcf undiscovered recoverable reserves
- Lower Huron Shale is the primary reservoir

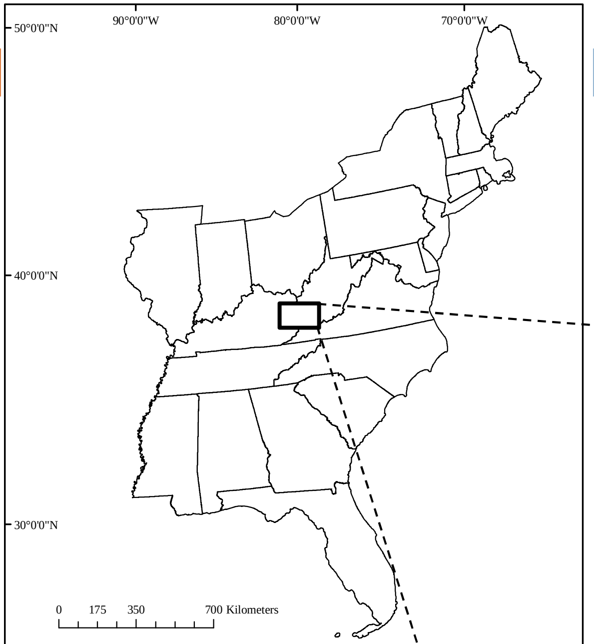
Lower Huron Shale

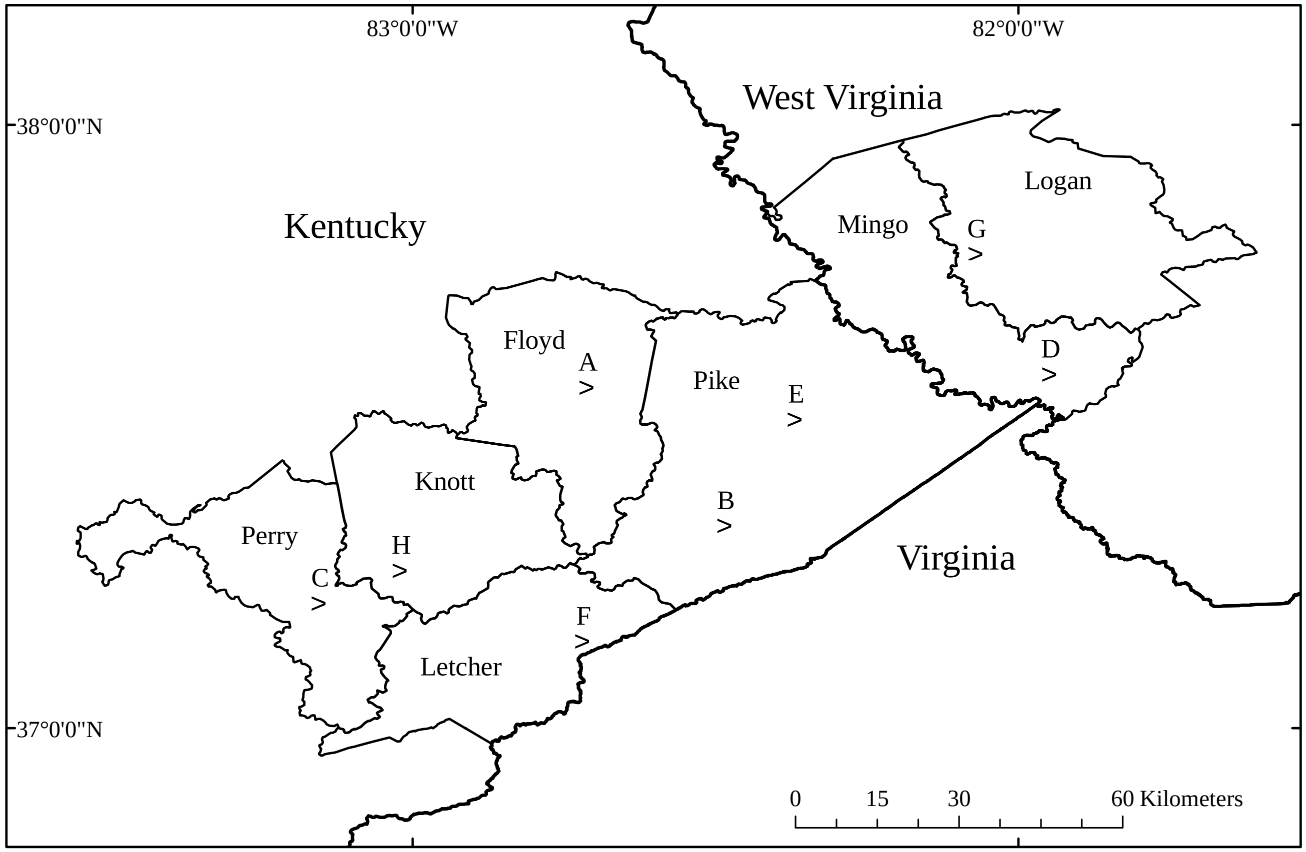
Period	Stage	Age Ma	E. Kentucky	
Mississippian			Sunbury Shale	
		363	Berea Sandstone	
Upper Devonian	Famennian		Cleveland Shale	Ohio Shale
			Three Lick Bed	
			Upper Huron Shale	
			Middle Huron Shale	
			Lower Huron Shale	
	Frasnian	367	Olentangy Shale	
			Rhinestreet Shale	
			Corniferous Formation	
		385		



Study Area and Samples

- 21 cutting samples were analyzed from 8 horizontal wells





Methods: Biomarker Identification

Ultrasonication

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Sulfur Removal

↓

Asphaltene Removal

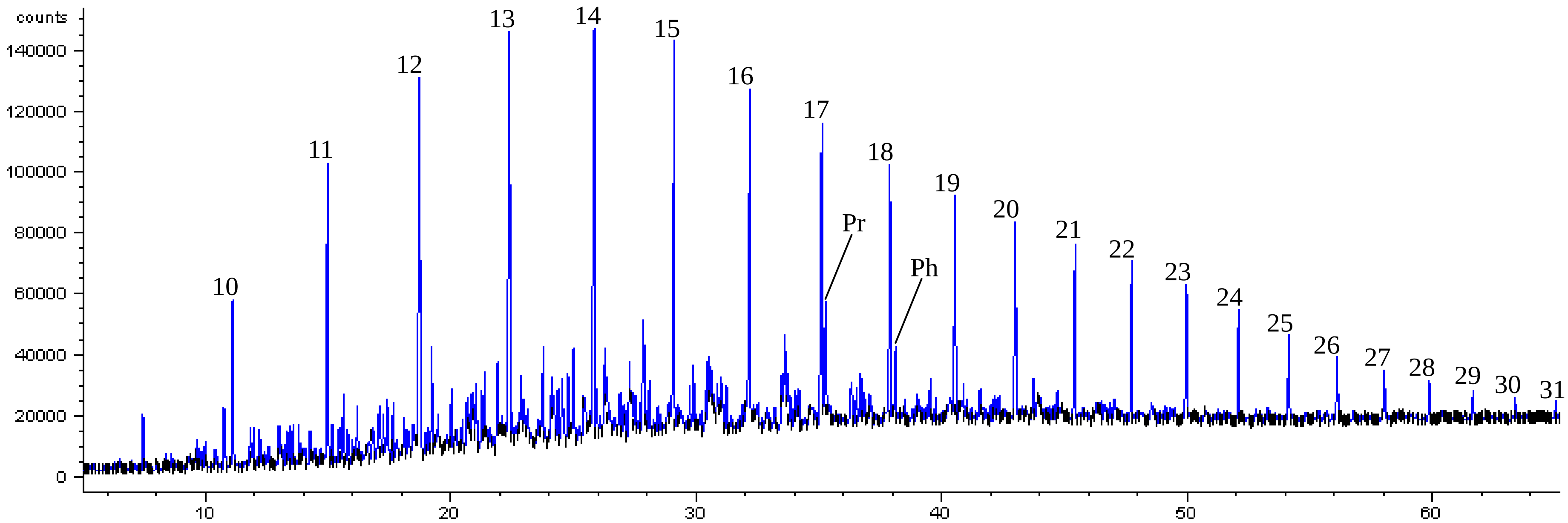
↓

Column Chromatography

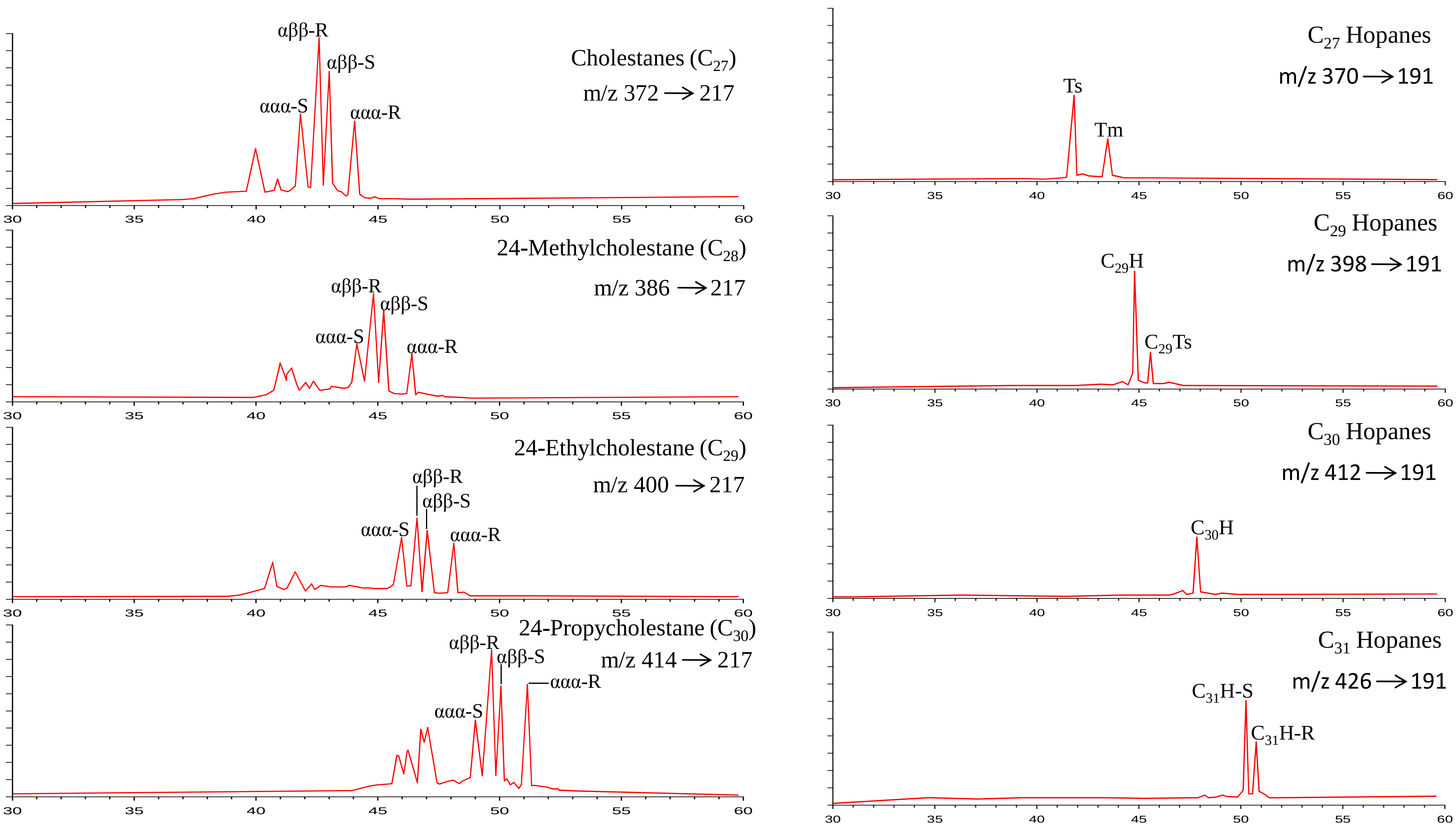
↙ ↘

GC-FID | GC-MS-MS

Identified Biomarkers: GC-FID



Identified Biomarkers: GC-MS-MS



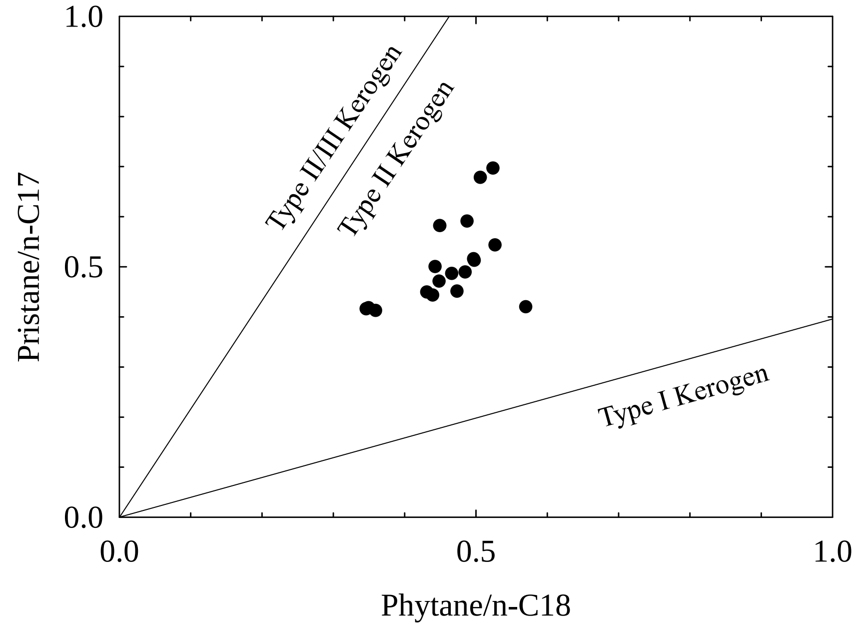
Methods: Biological Source of OM

- N-alkane parameters
  - TAR (Terrigenous vs. aquatic ratio)
  - n-C_{17}/n-C_{31}
- Pr/n-C_{17} vs. Ph/n-C_{18}
- Distribution of C_{27} to C_{30} steranes

N-alkane parameters

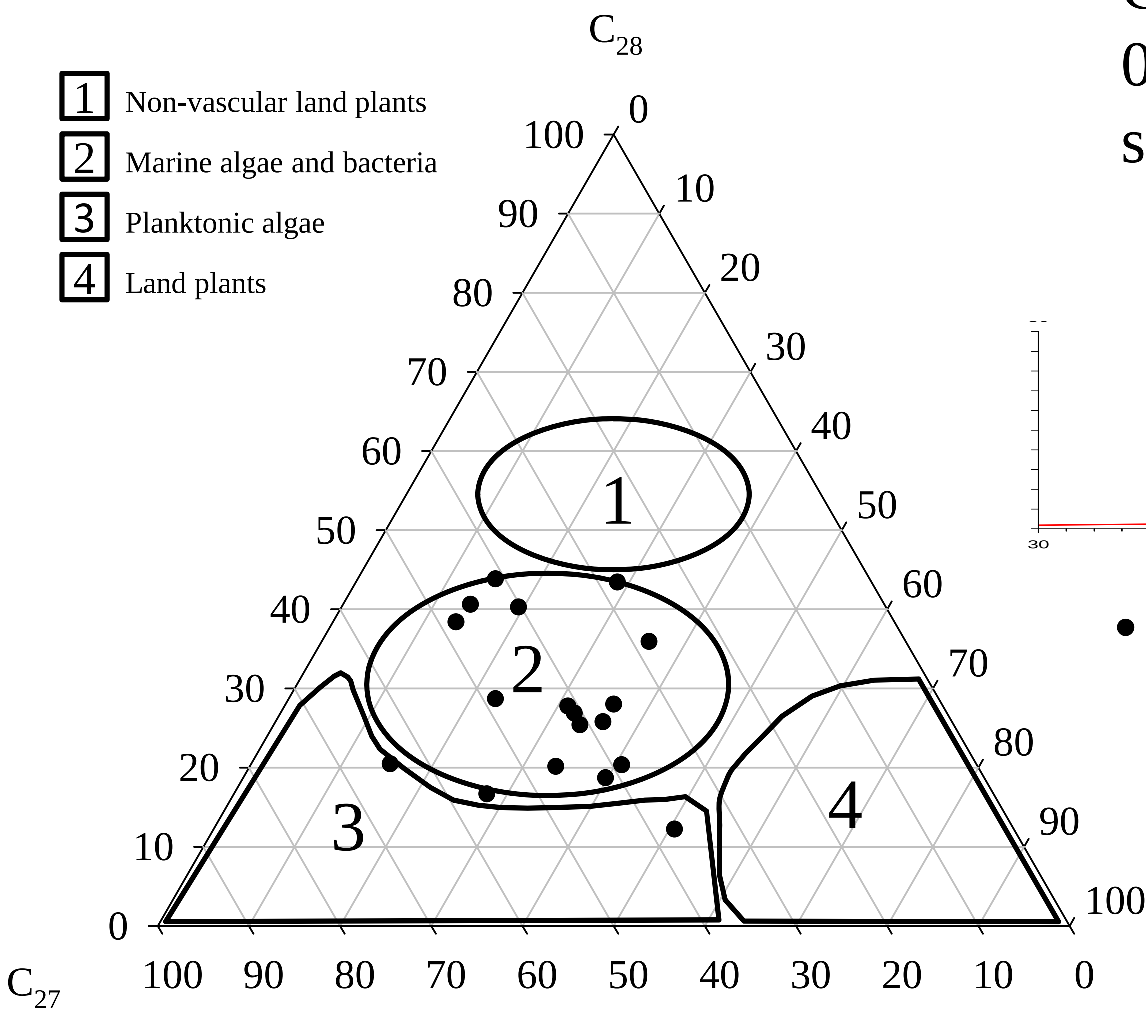
Pr/n-C_{17} vs. Ph/n-C_{18}

- TAR: 0.10 to 0.33 indicate marine algae source of OM
- n-C_{17}/n-C_{31}: 3.30 to 40.0 indicate marine algae source of OM

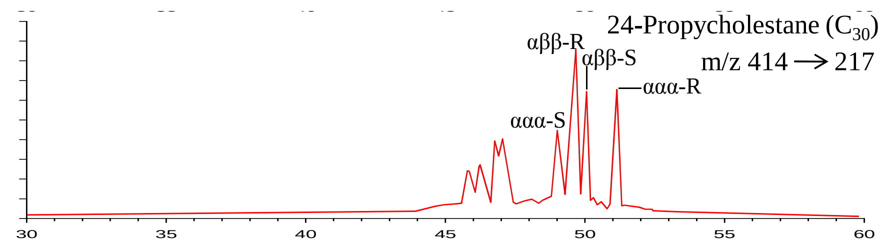


Type II Kerogen – originates from zooplankton, phytoplankton, and bacteria

Sterane Parameters



- C_{29}/C_{27} steranes: 0.13 to 0.88 indicate marine algae source of OM



- C_{30} steranes diagnostic of marine chrysophyte algae

Methods: Depositional Conditions

- Pr/Ph – Redox conditions
- Pr/n-C_{17} vs. Ph/n-C_{18} – Redox conditions
- Ts/Tm – Redox conditions
- Distribution of C_{27} to C_{30} steranes – Depositional environment

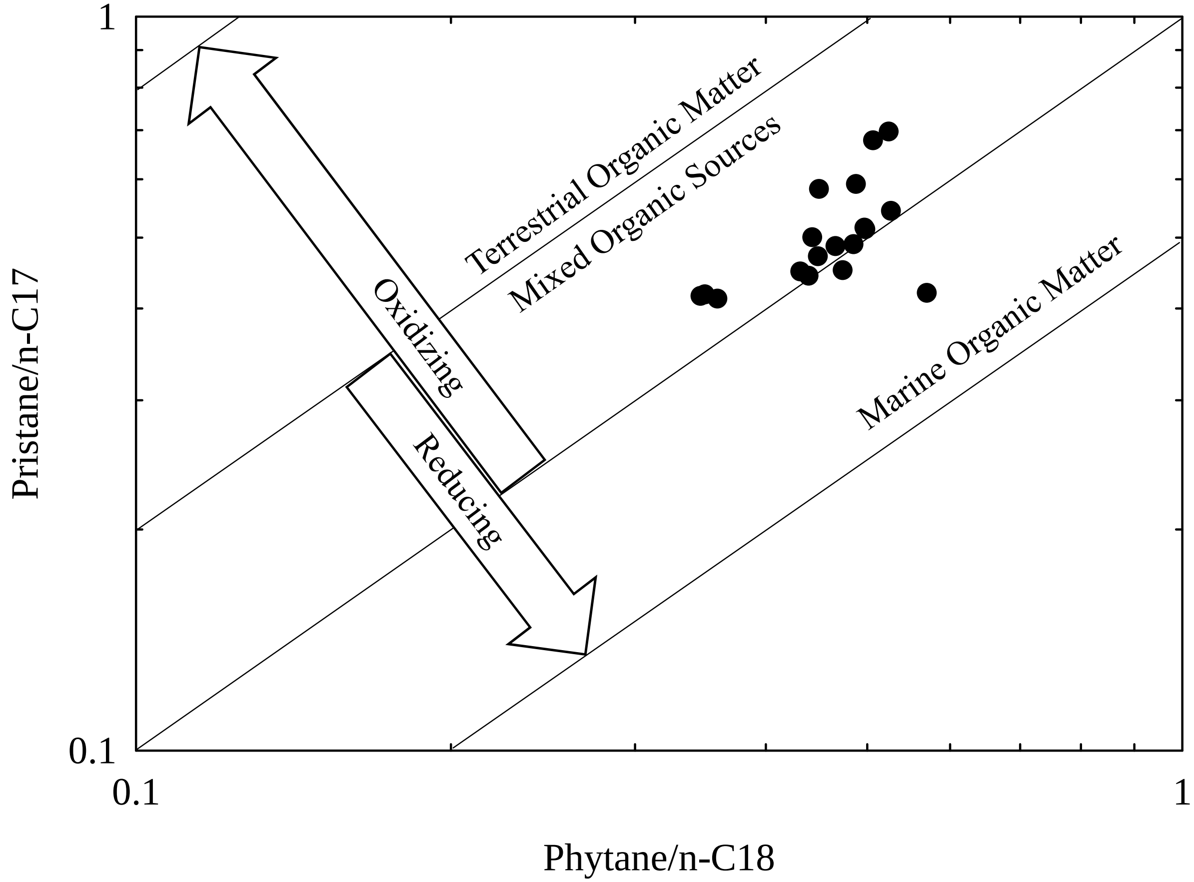
Pr/Ph

- Pr/Ph values range from 1.14 to 1.69 in samples analyzed indicating alternating oxic and anoxic conditions

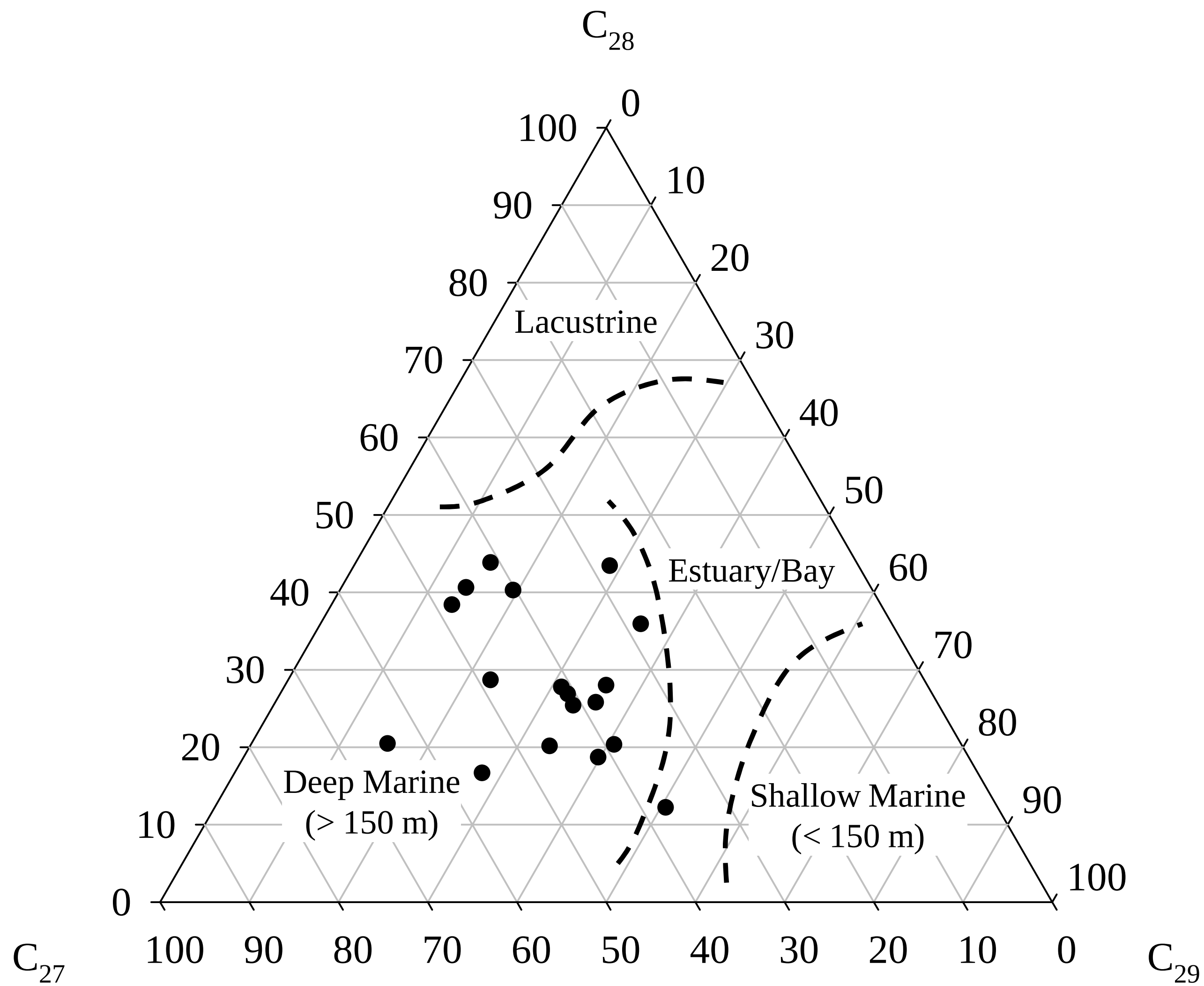
Ts/Tm

- Ts/Tm values range from 1.20 to 3.7 except for a value of 7.40 in one sample
- Ts/Tm value is between 1.0 and 2.0 in 11 of the 18 samples indicating alternating oxic and anoxic conditions

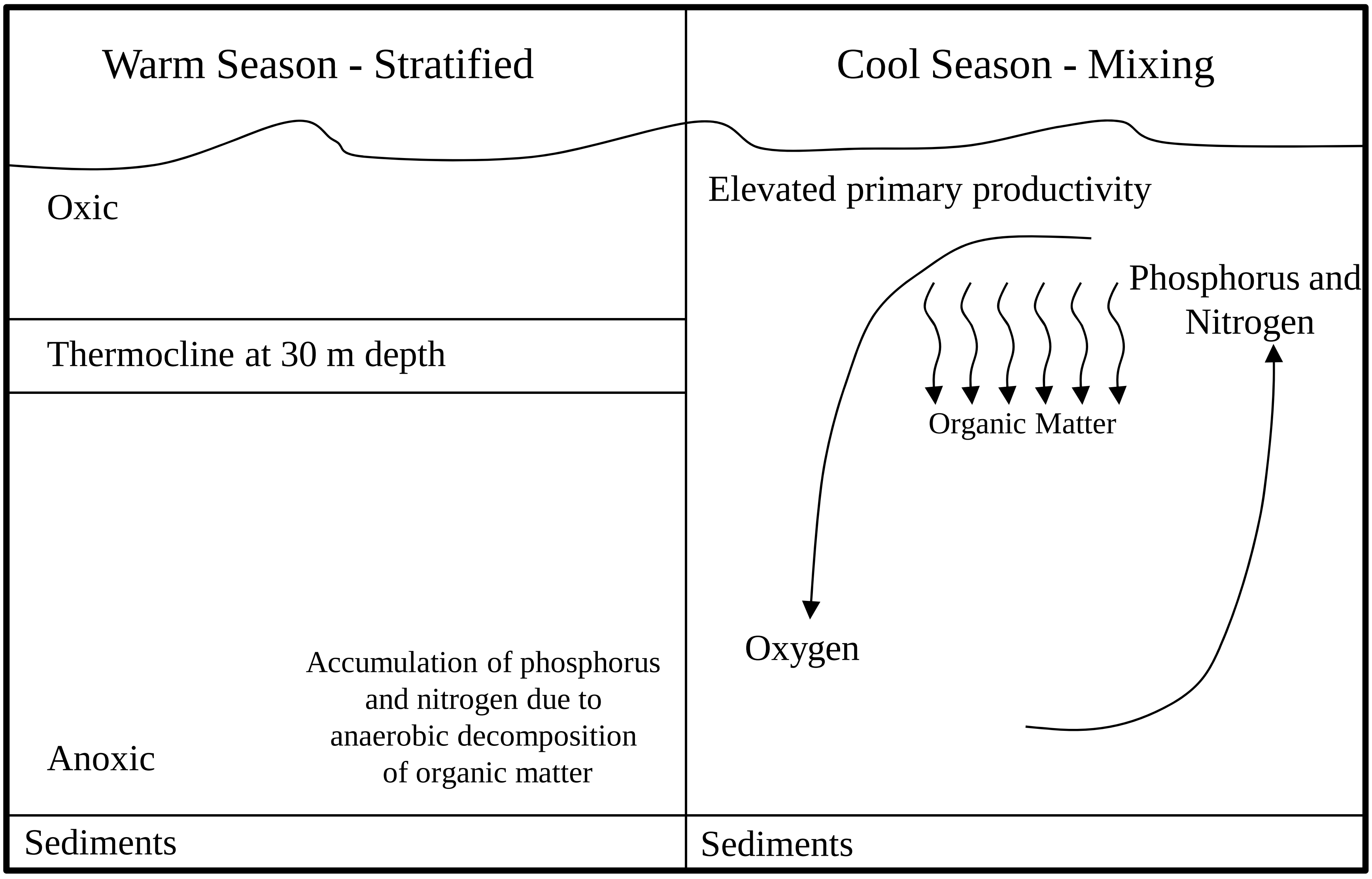
Pr/n-C_{17} vs. Ph/n-C_{18}



Sterane Distribution



Depositional Model



Evidence Supporting Model

Biomarker	Modern Environments
- Pr/Ph, Pr/n-C_{17} vs. Ph/n-C_{18}, and Ts/Tm support alternating oxic and anoxic conditions - Sterane distribution supports a deep water environment - N-alkanes and steranes identifed support an elevation in algal productivity	- Modern subtropical oceans are characterized by a warm season with a thin mixed layer and shallow thermocline and during the cool season the thermocline is broken down (Red Sea) - South China Sea and Arabian Sea algal blooms have been observed in winter due to upwelling of nutrient rich water

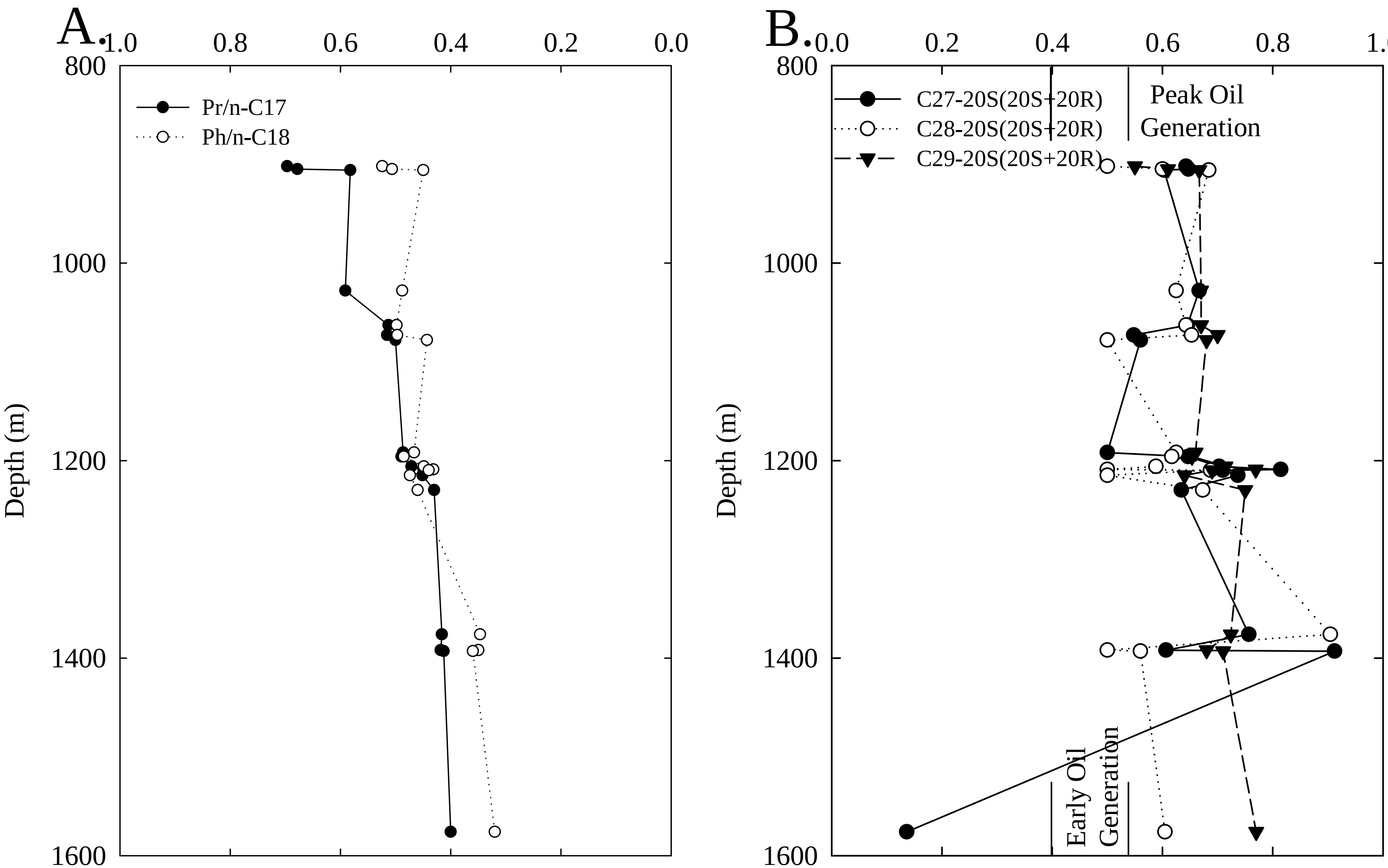
Methods: Thermal Maturity

- Based on the ratio of a complex biologically produced compound to a thermodynamically stable compound produced from alteration of the less stable complex biological compound
  - $Pr/n\text{-}C_{17}$
  - $Ph/n\text{-}C_{18}$
  - C_{27}-20S/(20S+20R)
  - C_{28}-20S/(20S+20R)
  - C_{29}-20S/(20S+20R)
  - C_{28}-αββ/(αββ+ααα)
  - C_{29}- αββ/(αββ+ααα)
  - Ts/(Ts+Tm)
  - 22S/(22S+22R)

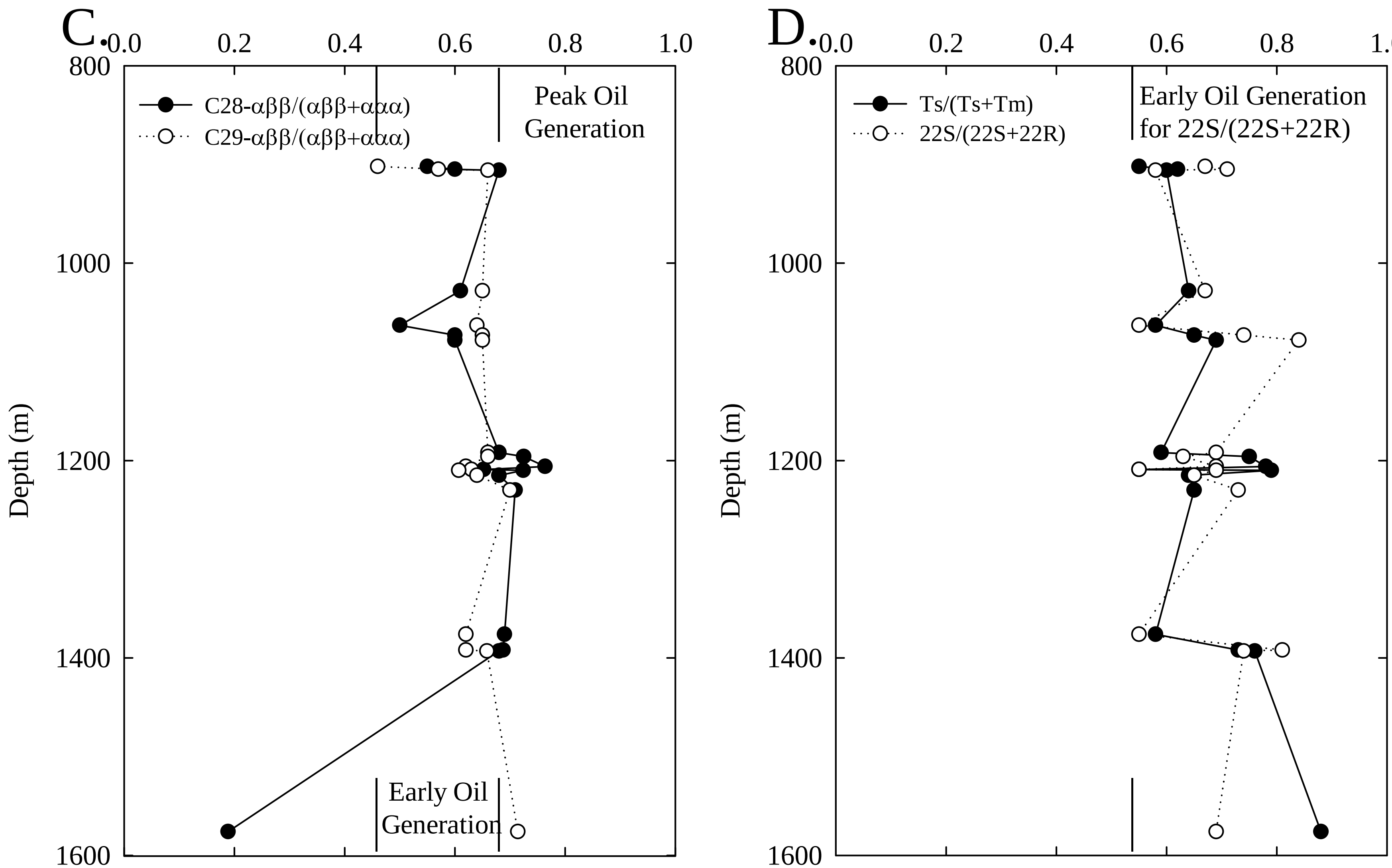
Thermal Maturity Values

Ratio	Values	Thermal Maturity
$Pr/n\text{-}C_{17}$	0.40 – 0.70	
$Ph/n\text{-}C_{18}$	0.32 – 0.52	
C_{27}-20S/(20S+20R)	0.14 – 0.91	At or above peak oil generation
C_{28}-20S/(20S+20R)	0.50 – 0.90	Early to peak oil generation
C_{29}-20S/(20S+20R)	0.55 – 0.77	At or above peak oil generation
C_{28}-αββ/(αββ+ααα)	0.19 – 0.79	Early to peak oil generation
C_{29}- αββ/(αββ+ααα)	0.46 – 0.71	Early to peak oil generation
Ts/(Ts+Tm)	0.55 – 0.88	Early to late oil generation
22S/(22S+22R)	0.55 – 0.84	At or above early oil generation

Ratio Values Vs. Depth



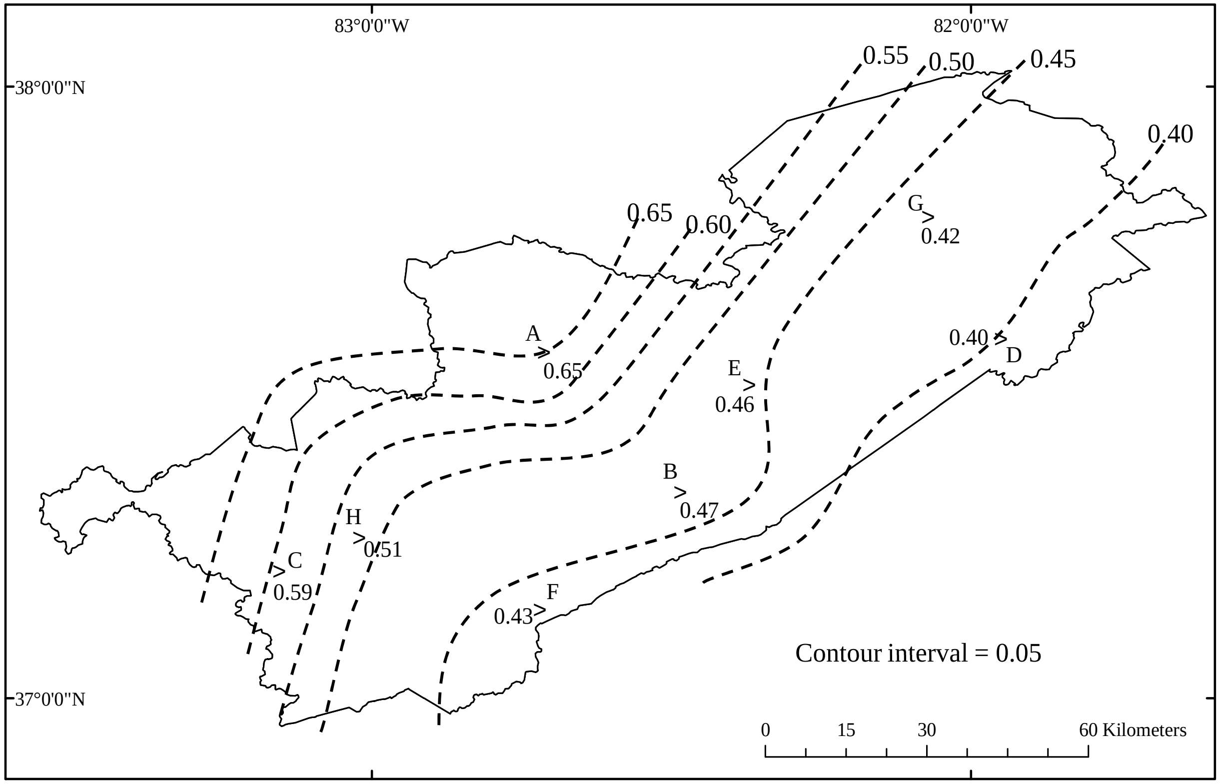
Ratio Values Vs. Depth



Thermal Maturity Contours

- Contours maps of ratio values indicate an increase in thermal maturity toward the southeast within the study area

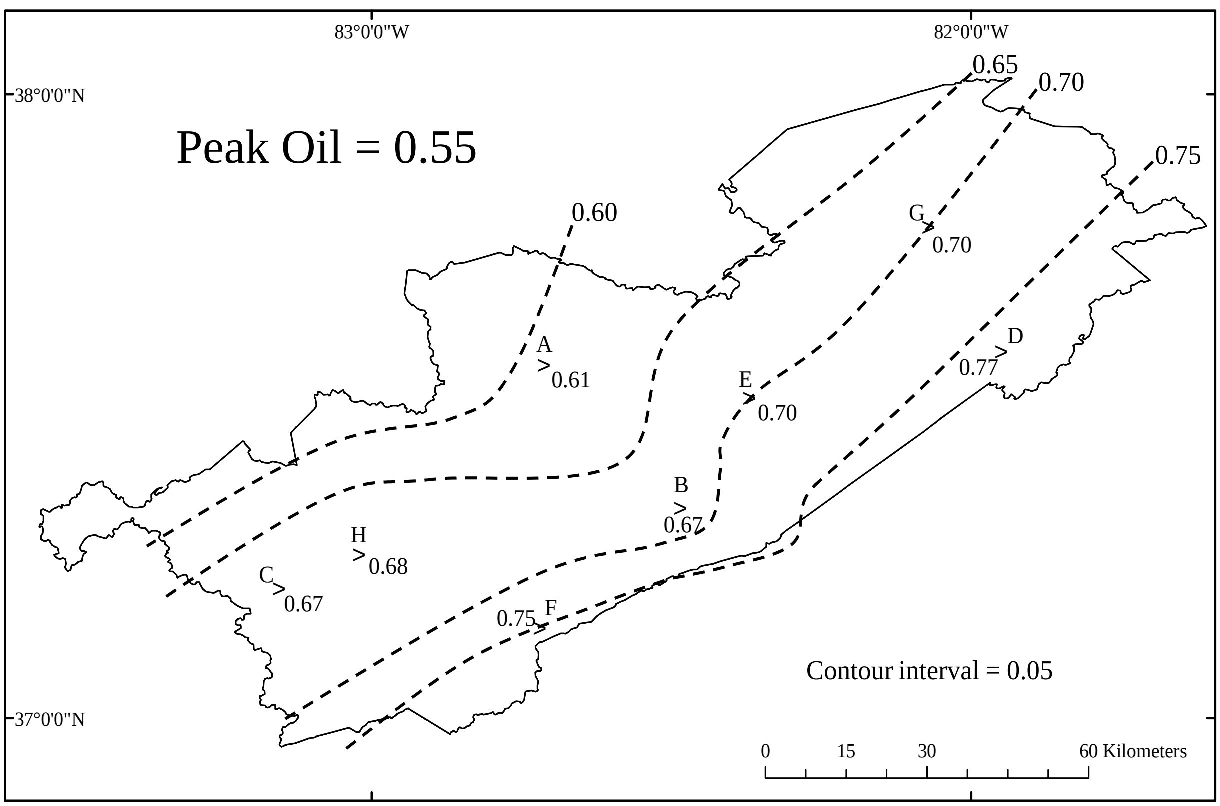
Pr/n-C_{17}



Thermal Maturity Contours

- Contours maps of ratio values indicate an increase in thermal maturity toward the southeast within the study area

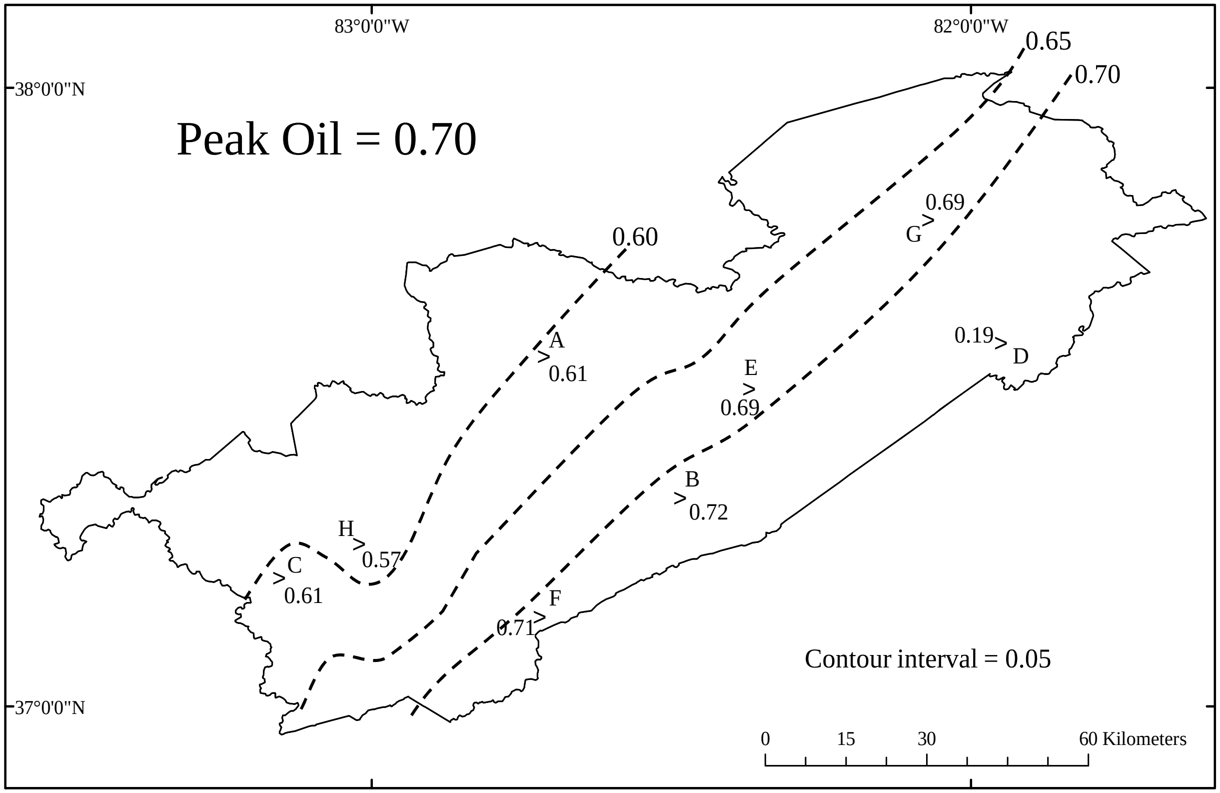
C_{29}-20S/(20S+20R)



Thermal Maturity Contours

- Contours maps of ratio values indicate an increase in thermal maturity toward the southeast within the study area

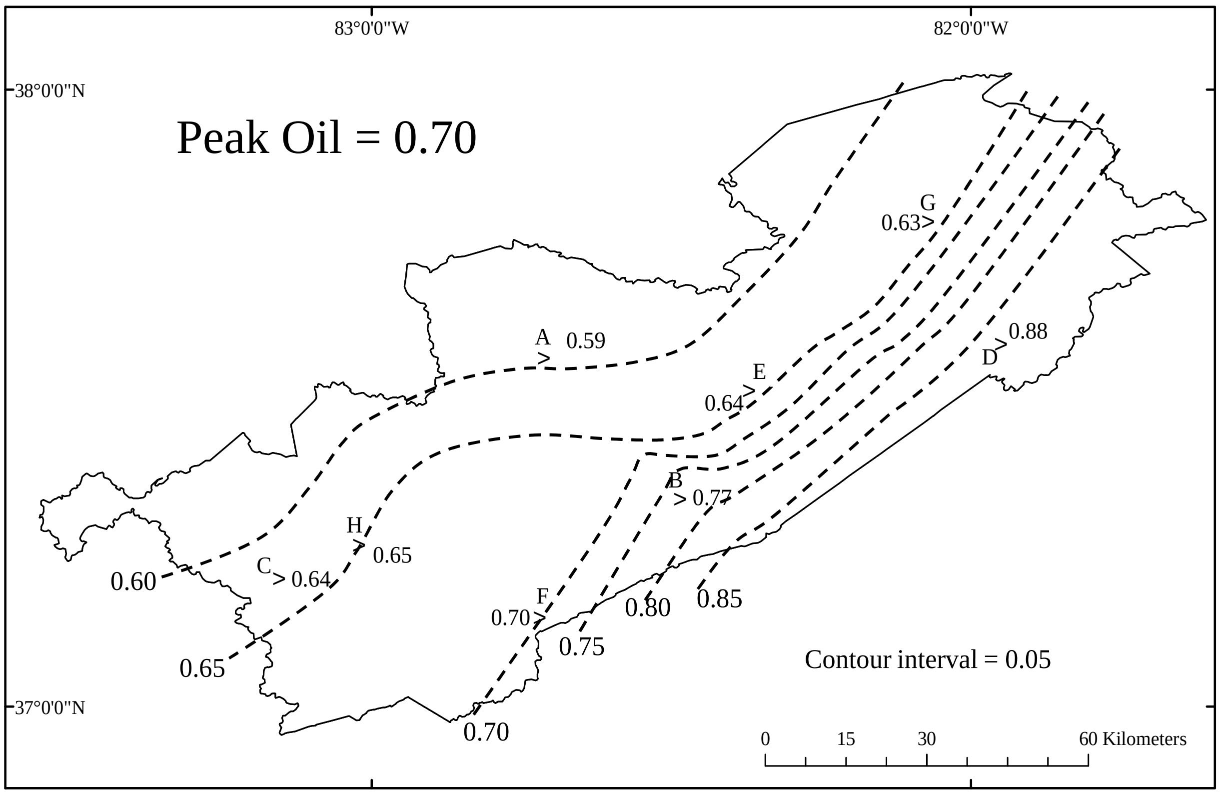
C_{28}-αββ/(αββ+ααα)



Thermal Maturity Contours

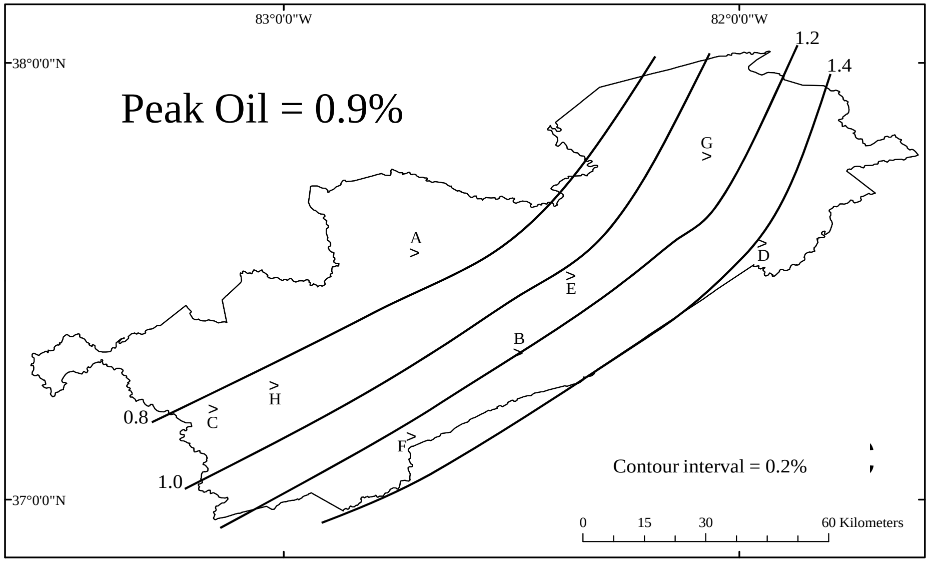
- Contours maps of ratio values indicate an increase in thermal maturity toward the southeast within the study area

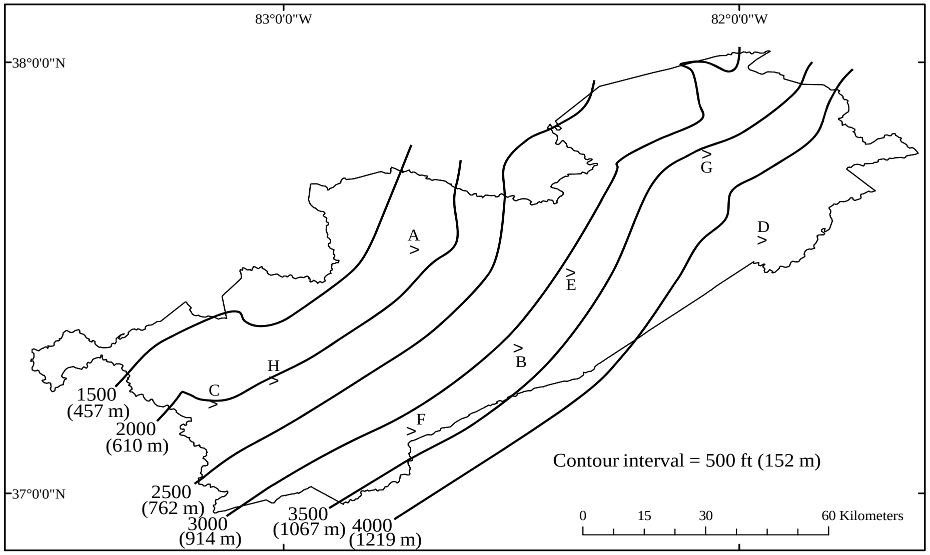
Ts/(Ts+Tm)



Thermal Maturity Contours

- Contours of R_o values indicate increased thermal maturity toward the southeast
- An increase towards the southeast is expected, which corresponds to the direction of increasing maximum burial depth





Conclusions

- Biomarkers indicate the biological source of organic matter in the Lower Huron Shale is marine algae and bacteria
- Biomarker ratios in the samples analyzed indicate the Lower Huron Shale was deposited in alternating oxic and anoxic conditions
- Sterane distributions in the samples analyzed indicate the Lower Huron Shale was deposited in deep waters (> 150 m)

Conclusions

- Biomarker ratios indicate that the samples analyzed have reached the early to late oil generation stages
- Contour maps of the biomarker maturity ratio values indicate increasing thermal maturity toward the southeast within the study area
- Biomarker data suggest that gas produced from the Lower Huron Shale in the south-eastern area of the Big Sandy Field is thermogenic

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