Petroleum Geochemistry of the Mississippian Limestone Play, Northern Oklahoma, USA: Evidence of Two Different Charging Mechanisms East and West of the Nemaha Uplift*

Ibrahim Al Atwah[1], Jim Puckette[1], and Tracy Quan[1]

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Abstract

The Mississippian limestone in northern Oklahoma and southern Kansas is a major oil play within the southern Midcontinent region. Mississippian carbonate reservoirs are known for their heterogeneity with respect to reservoir quality and produced fluids. Oil and gas from the Mississippian reservoirs are chemically heterogeneous, and cannot be explained solely by a single Woodford Shale source-rock model. New molecular geochemical data from east and west of the Nemaha uplift in north-central Oklahoma provides a new insight into the source of hydrocarbons in the Mississippian play, and attempts to provide a plausible scenario of the hydrocarbon charge history.

Organic-rich zones within the Mississippian carbonate section were sampled and screened for total organic carbon (TOC), organic petrography, Rock-Eval pyrolysis and geochemical markers. Additionally, twelve oil samples were analyzed from Mississippian and Woodford producing wells. Rock extracts and oil samples were analyzed using gas-chromatography and gas-chromatography mass-spectrometry techniques for quantitative analysis of diamondoids, saturate and aromatic biomarkers. Results indicate that the Mississippian source-rock has good generation potential (average 2% TOC) and reached the early oil window (average vitrinite reflectance of 0.72% Ro). Extracted bitumen from Mississippian rocks and related oils show unique biomarker signatures; these include the presence of extended tricyclic terpane, high gammacerane index, and high C23 tricyclic terpane relative to hopane, high input of C27 relative to C28 and C29 in regular and rearranged steranes, together with high C27 monoaromatic steroids relative to their C28 and C29 homologues. Moreover, on the basis of diamondoid compound class, the Mississippian samples showed abundance of 4,8- and 4,9-dimethyl dimantanes relative to the 3,4- isomer. The extent of cracking - as measured by diamondoids - reveal a dramatic change in diamondoids concentration over the areas east and west of the Nemaha uplift. A high concentration of diamondoids was observed west of the Nemaha uplift, thus indicating episodic hydrocarbon charge of uncracked followed by cracked oils migrating out of the Anadarko Basin, which supports a long-distance migration model. In contrast, the Mississippian samples from east of the Nemaha uplift are depleted in diamondoids, suggesting a short migration and localized hydrocarbon kitchen under lower thermal stress.

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Evidence of Two Different Charging Mechanisms East and West of the Nemaha Uplift

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OUTLINE

- Introduction
- Study Objectives
- Samples and Methods
- Results
- Major Findings

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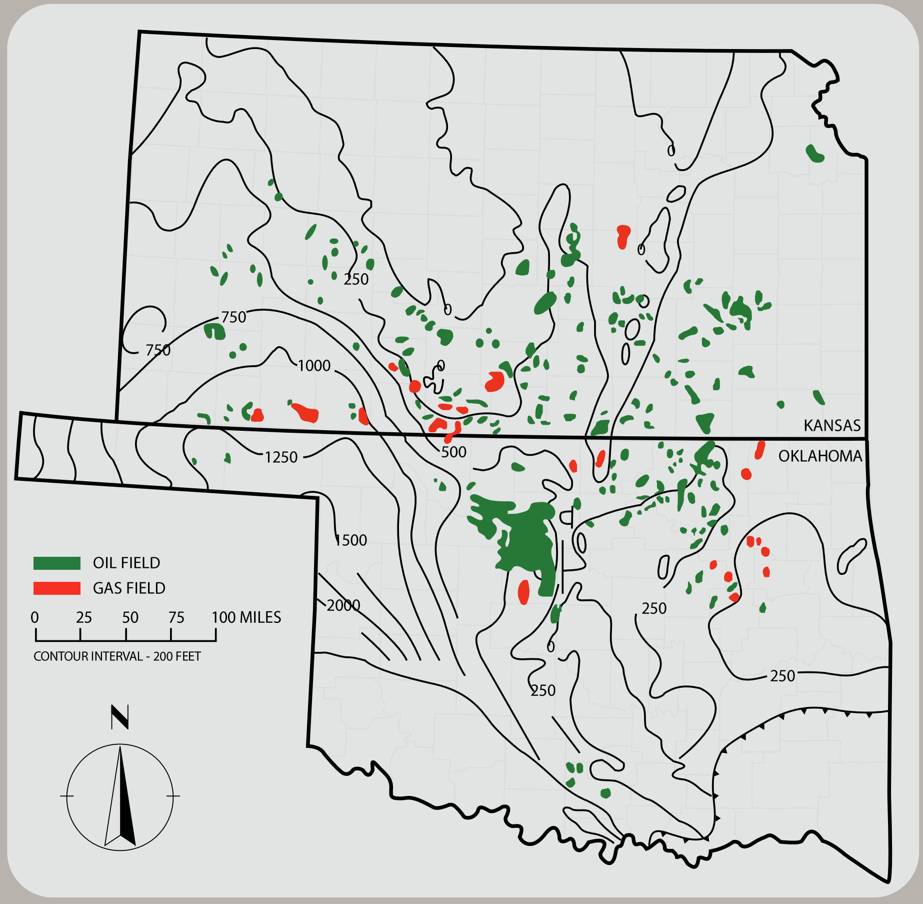
1

INTRODUCTION

The Mississippian Limestone Play

- Produced hydrocarbons in the early 1900's from vertical wells
- Extends across northern Oklahoma and southern Kansas
- Relatively shallow reservoir depths ranging between 3,000ft to 6,000ft

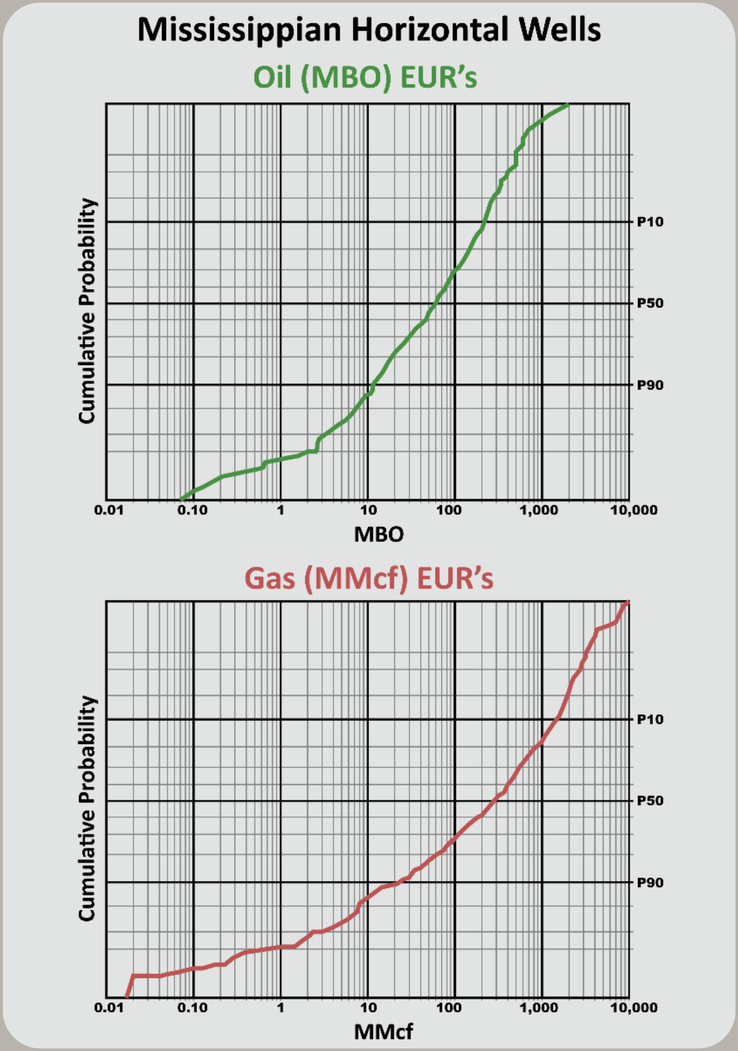


Modified from Adler et al. (1971)

INTRODUCTION

The Mississippian Limestone Play

- Conventional reservoir target is the cherty upper Mississippian carbonates "Miss Chat" with porosity up to 30% and permeability between 0.1 to 50 (mD)
- Oil and Gas EUR's show great amount of hydrocarbons contained within the Mississippian Limestone Play with Average EUR's of 90.8 MBO & 793.4 MMcf



Modified from Dick (2012)

OUTLINE

- Introduction
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- Major Findings

STUDY OBJECTIVES

1) Can the dark colored beds of Mississippian carbonate generate hydrocarbons?

2) Are Mississippian oils chemically different from Woodford Shale oils?

3) How does the Nemaha Uplift influence the Mississippian oil composition?

OUTLINE

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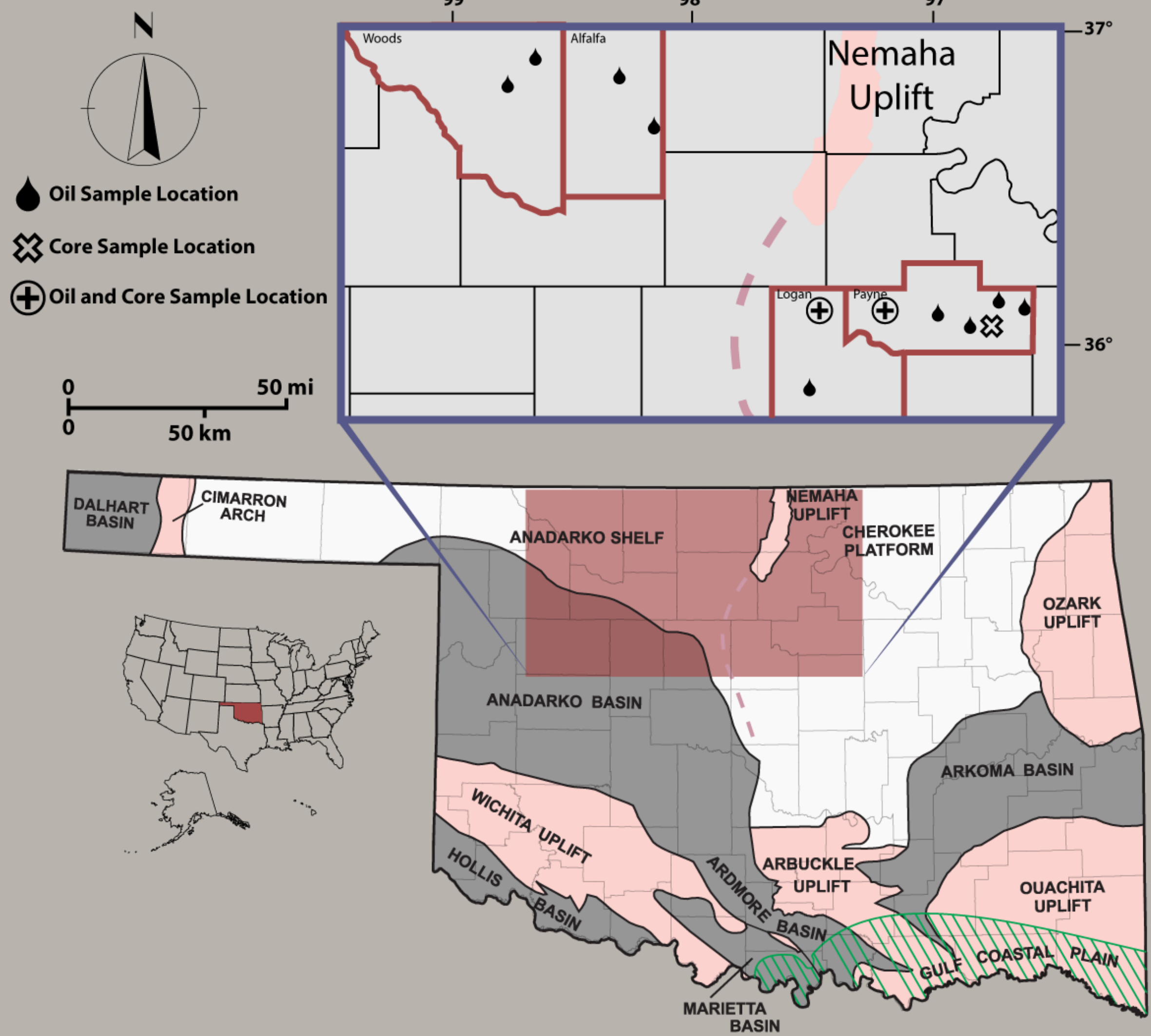
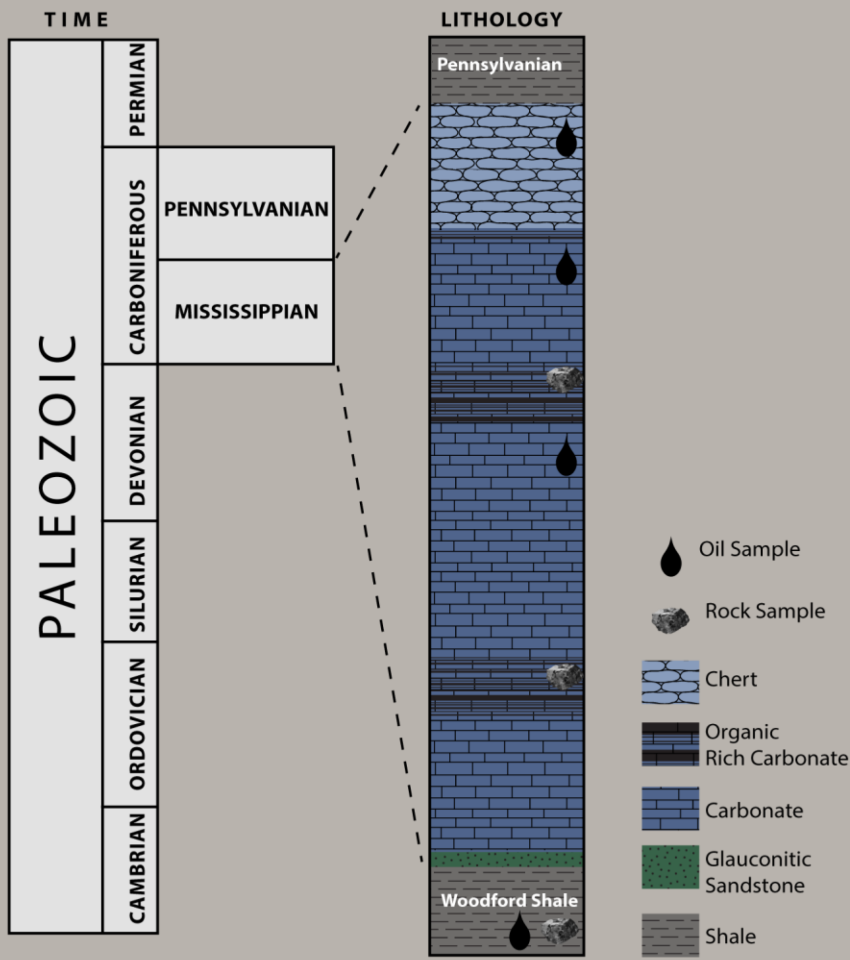
STUDY AREA


N
Oil Sample Location
Core Sample Location
Oil and Core Sample Location
0
50 mi
0
50 km
99°
98°
97°
37°
36°
Woods
Alfalfa
Logan
Payne
Nemaha Uplift
DALHART BASIN
CIMARRON ARCH
ANADARKO SHELF
NEMAHA UPLIFT
CHEROKEE PLATFORM
OZARK UPLIFT
ANADARKO BASIN
ARKOMA BASIN
WICHITA UPLIFT
HOLLIS BASIN
ARDMORE BASIN
ARBUCKLE UPLIFT
OUACHITA UPLIFT
GULF COASTAL PLAIN
MARIETTA BASIN

5 SAMPLING INTERVAL

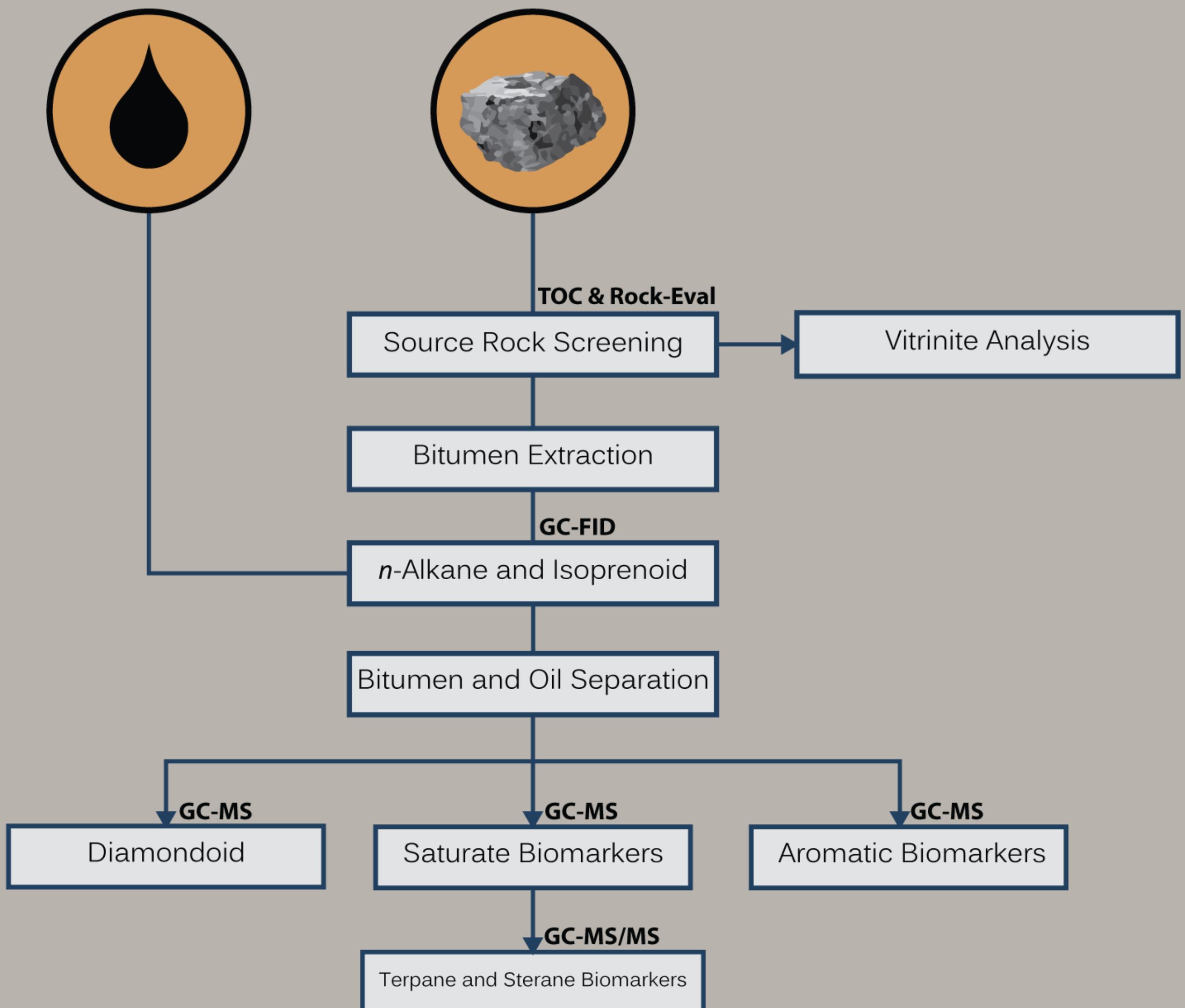
Rock Samples (total 60): from organic-rich Mississippian carbonates, and Woodford Shale.

Oil Samples (total 12): from Mississippian lime reservoirs and siliceous Woodford interval.



Modified from Leblanc and Grammar 2014

METHODS


TOC & Rock-Eval
Source Rock Screening
Vitrinite Analysis
Bitumen Extraction
GC-FID
n-Alkane and Isoprenoid
Bitumen and Oil Separation
GC-MS
Diamondoid
GC-MS
Saturate Biomarkers
GC-MS
Aromatic Biomarkers
GC-MS/MS
Terpane and Sterane Biomarkers

OUTLINE

- Introduction
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RESULTS

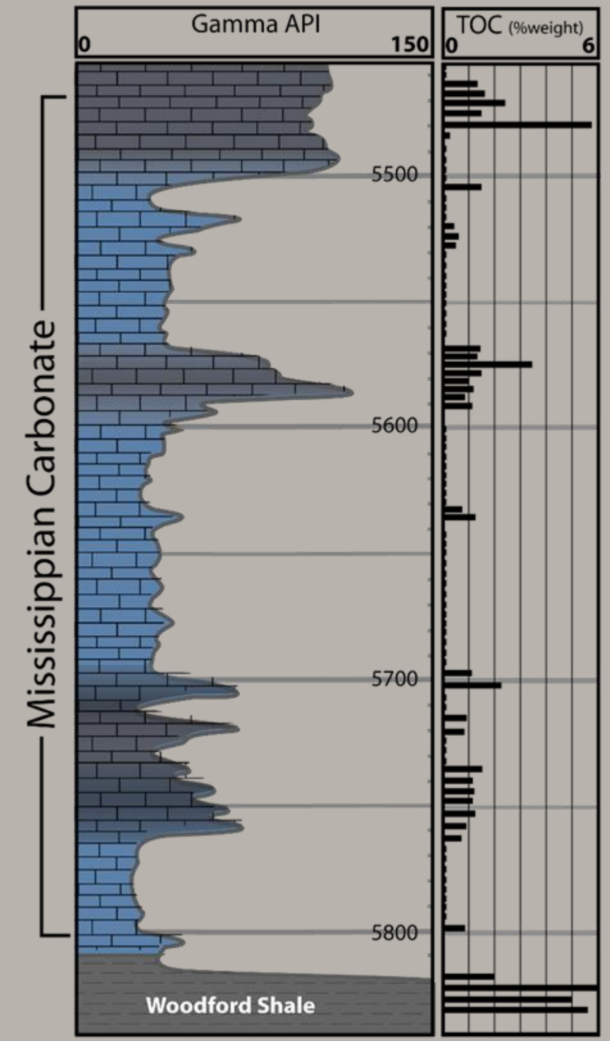
- **Can dark Mississippian beds generate hydrocarbons?**

RESULTS

Source Rock Richness

- **<u>Mississippian</u> : Organic-rich intervals exhibit high Gamma ray, with average TOC of 2%, and reach up to 6%.**

- **<u>Woodford:</u> average TOC of 7%.**

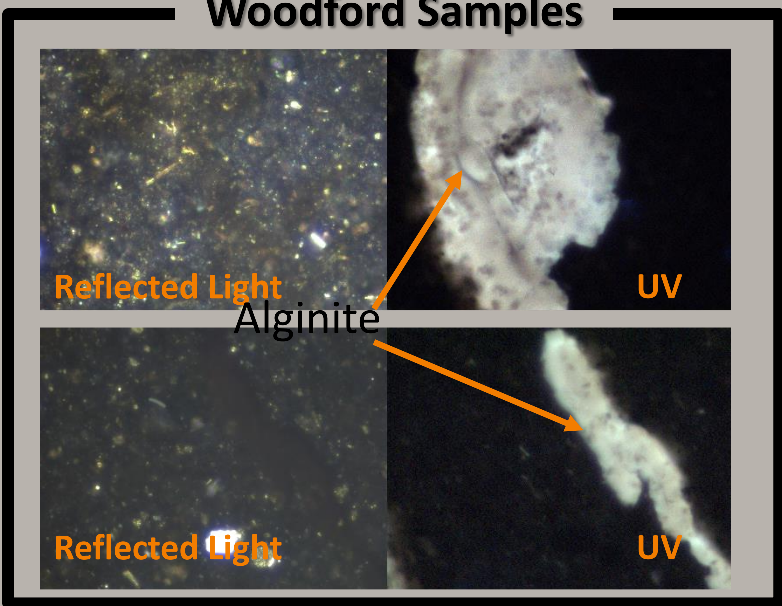


RESULTS

Organic Matter Type (Macerals)

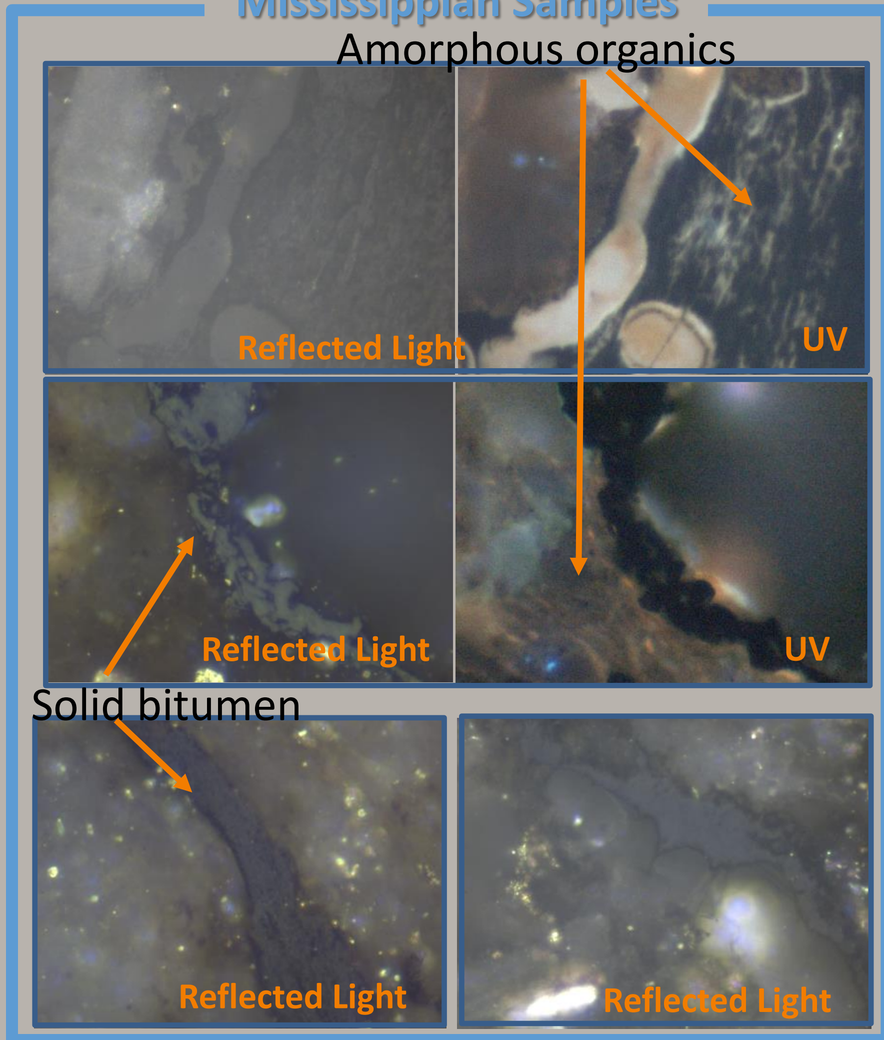
- **Miss: Dominated with amorphous organic matter and solid bitumen.**
- **Wdfd: Dominated with alginite maceral and solid bitumen.**

Woodford Samples



25 µm

Mississippian Samples

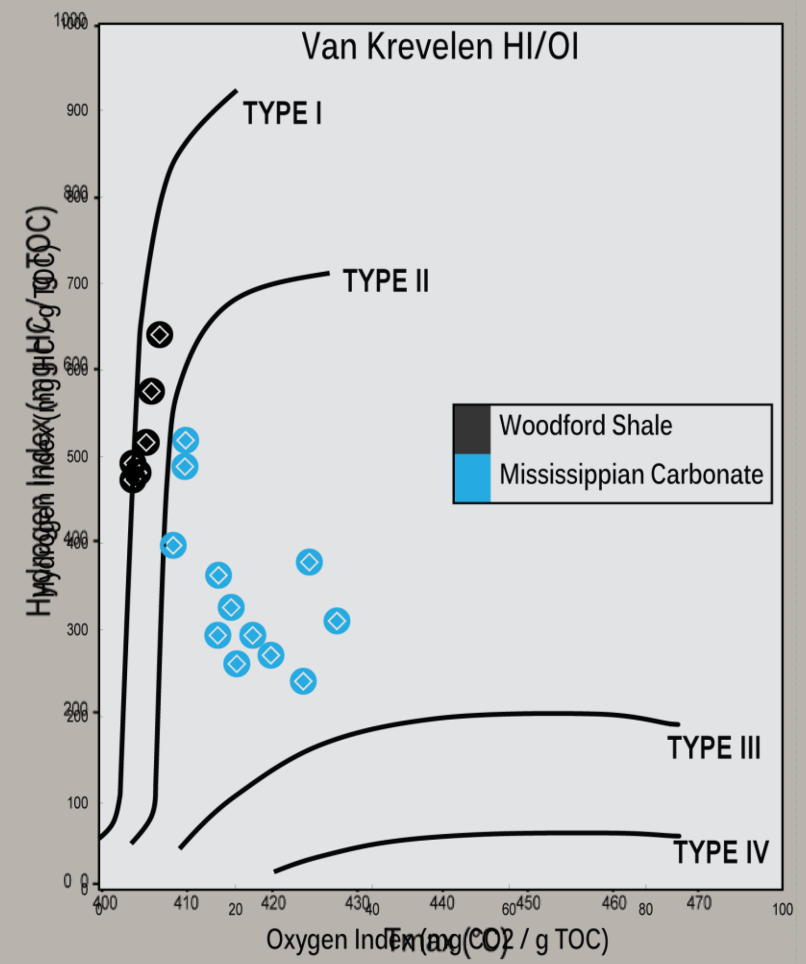


RESULTS

Kerogen Types

- **<u>Mississippian</u> kerogen type is overall type-II, with average hydrogen index values of 315, and oxygen index of 36.**

- **<u>Woodford:</u> kerogen is type-I with average hydrogen index values of 554, and oxygen index of 5.**

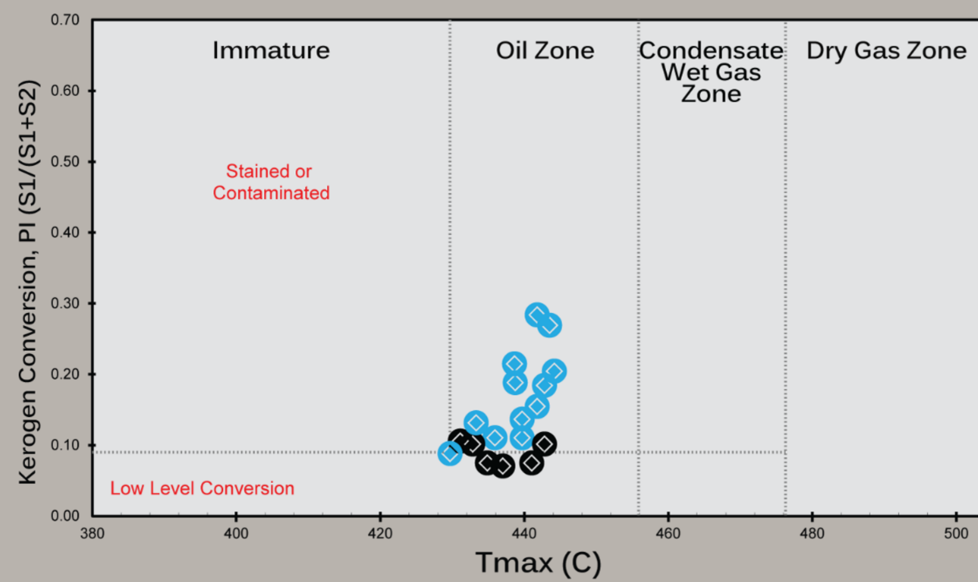


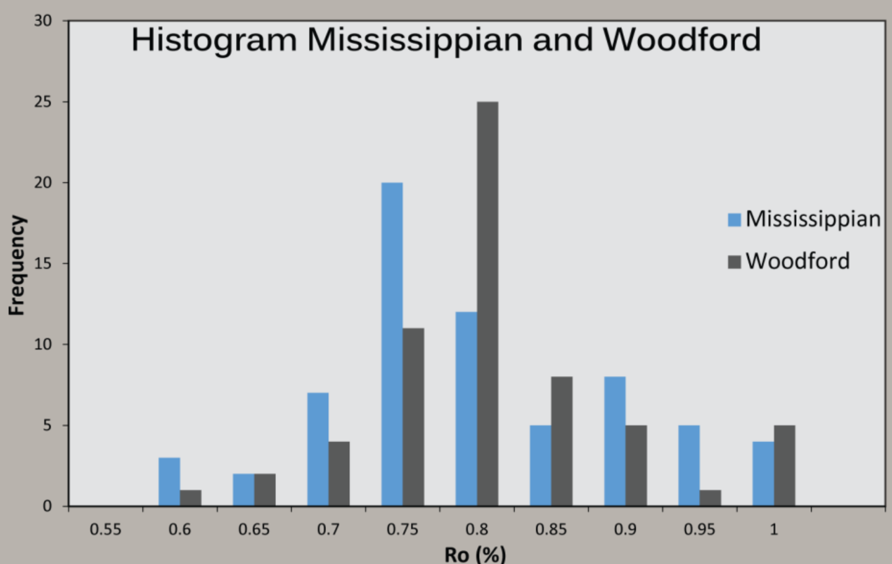
RESULTS

Source Rock Maturity

Mississippian & Woodford: kerogens have reached the early-mid oil window:

- **Average Ro% 0.74 ± 0.08**
- **Average Tmax 440 °C**

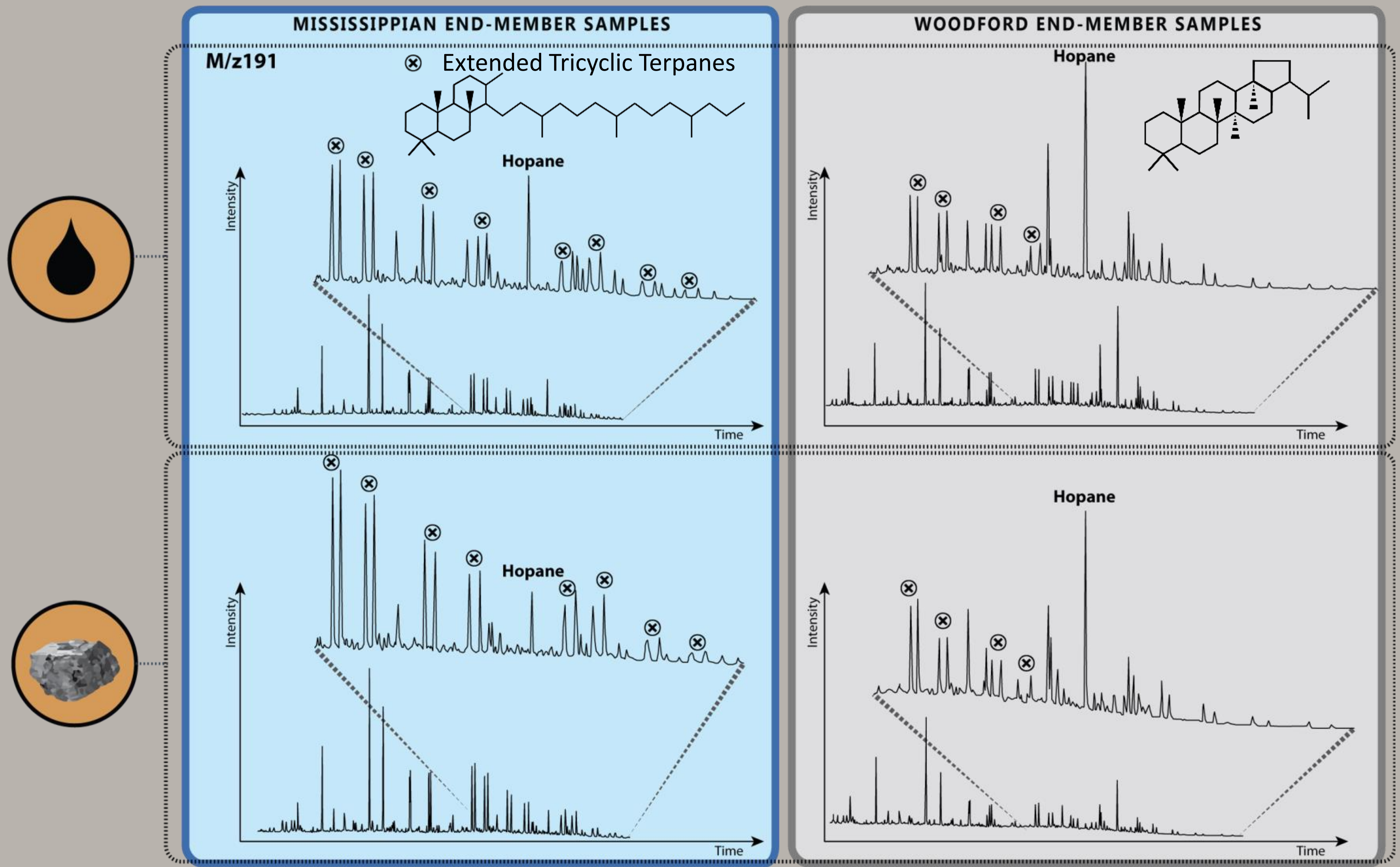




RESULTS

- **Are Mississippian oils chemically different from Woodford oils?**

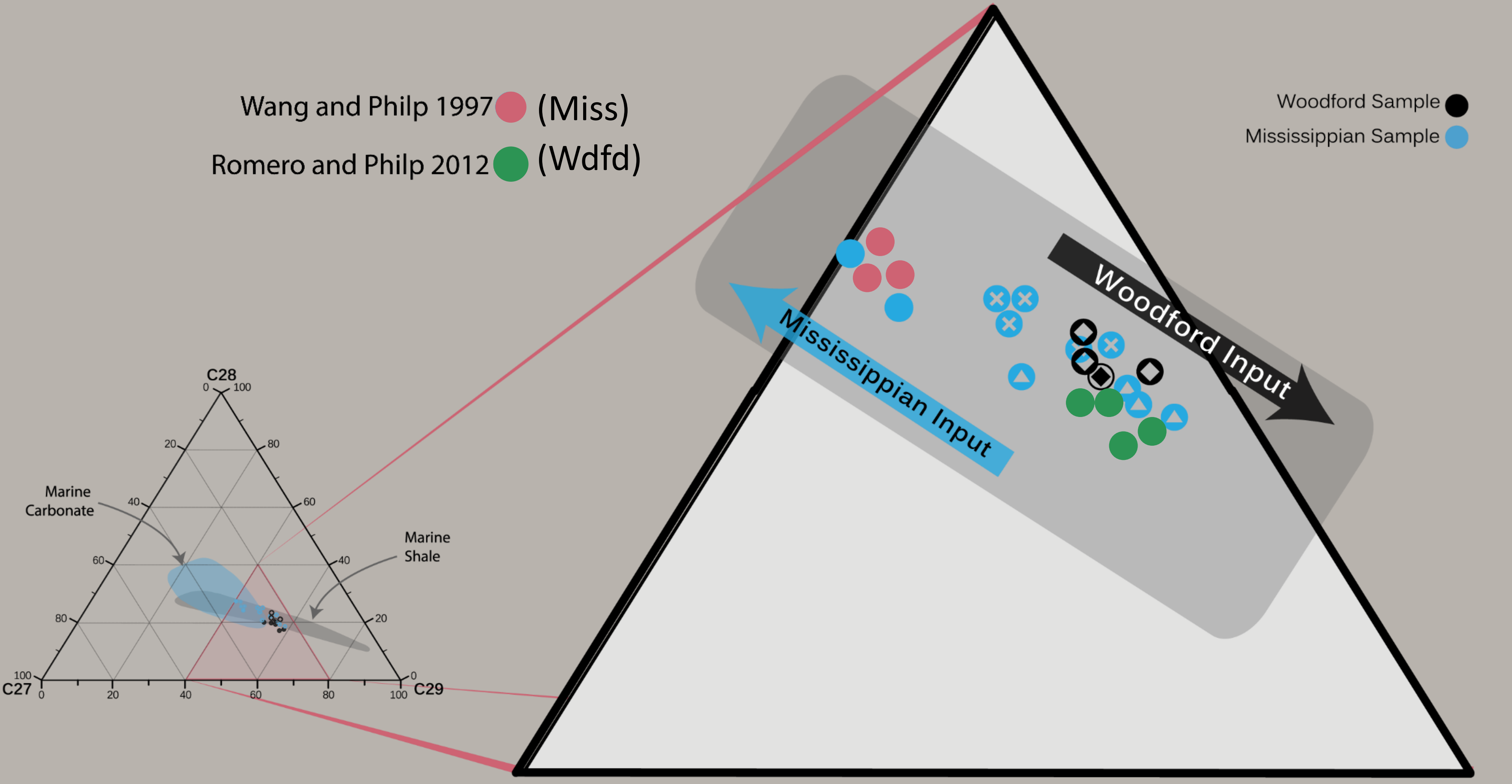
RESULTS



MISSISSIPPIAN END-MEMBER SAMPLES
WOODFORD END-MEMBER SAMPLES
M/z191
Extended Tricyclic Terpanes
Hopane
Intensity
Time

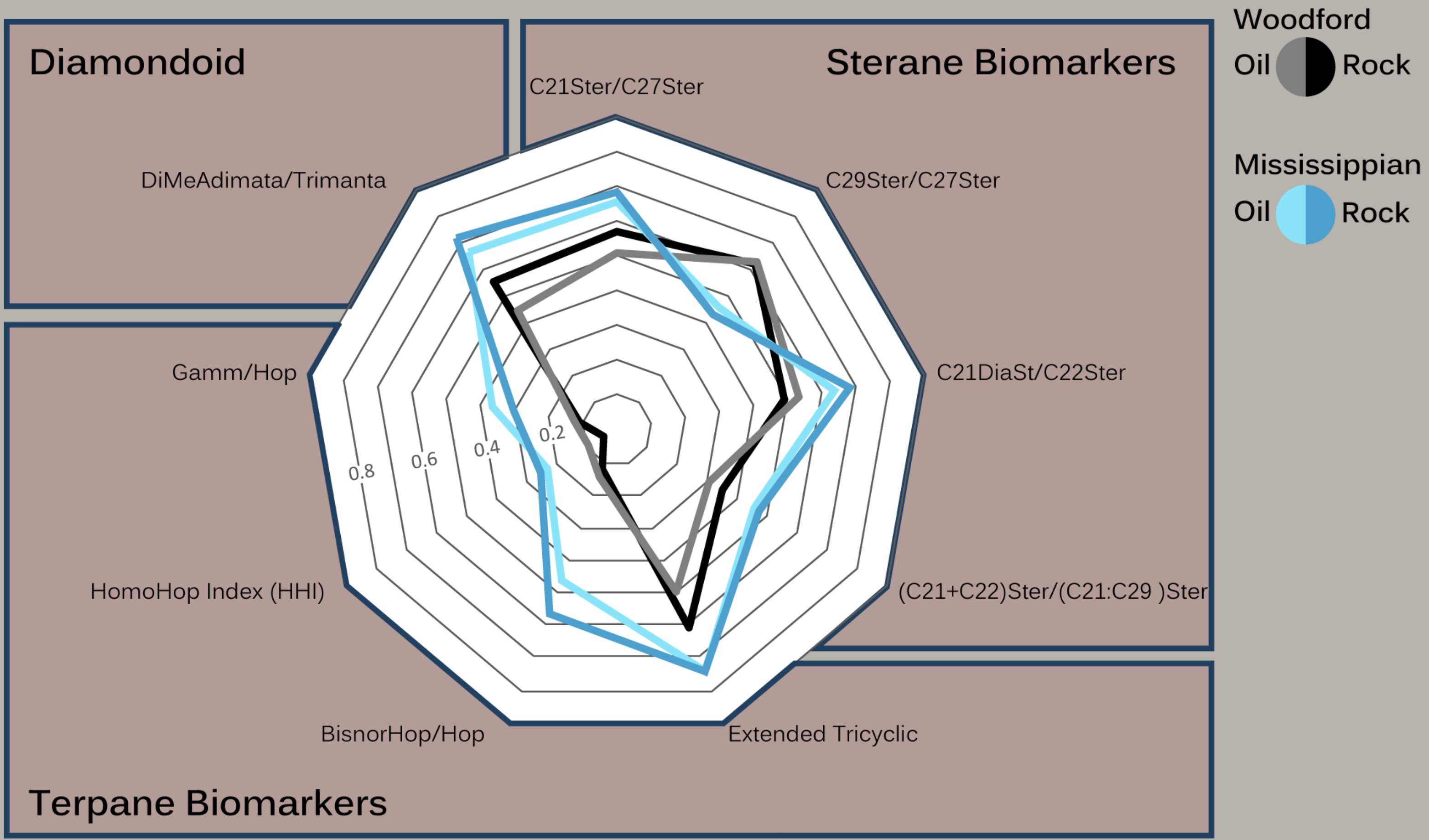
RESULTS

Regular Sterane Biomarkers



RESULTS

Oil-Source Rock Correlation
Mississippian vs. Woodford

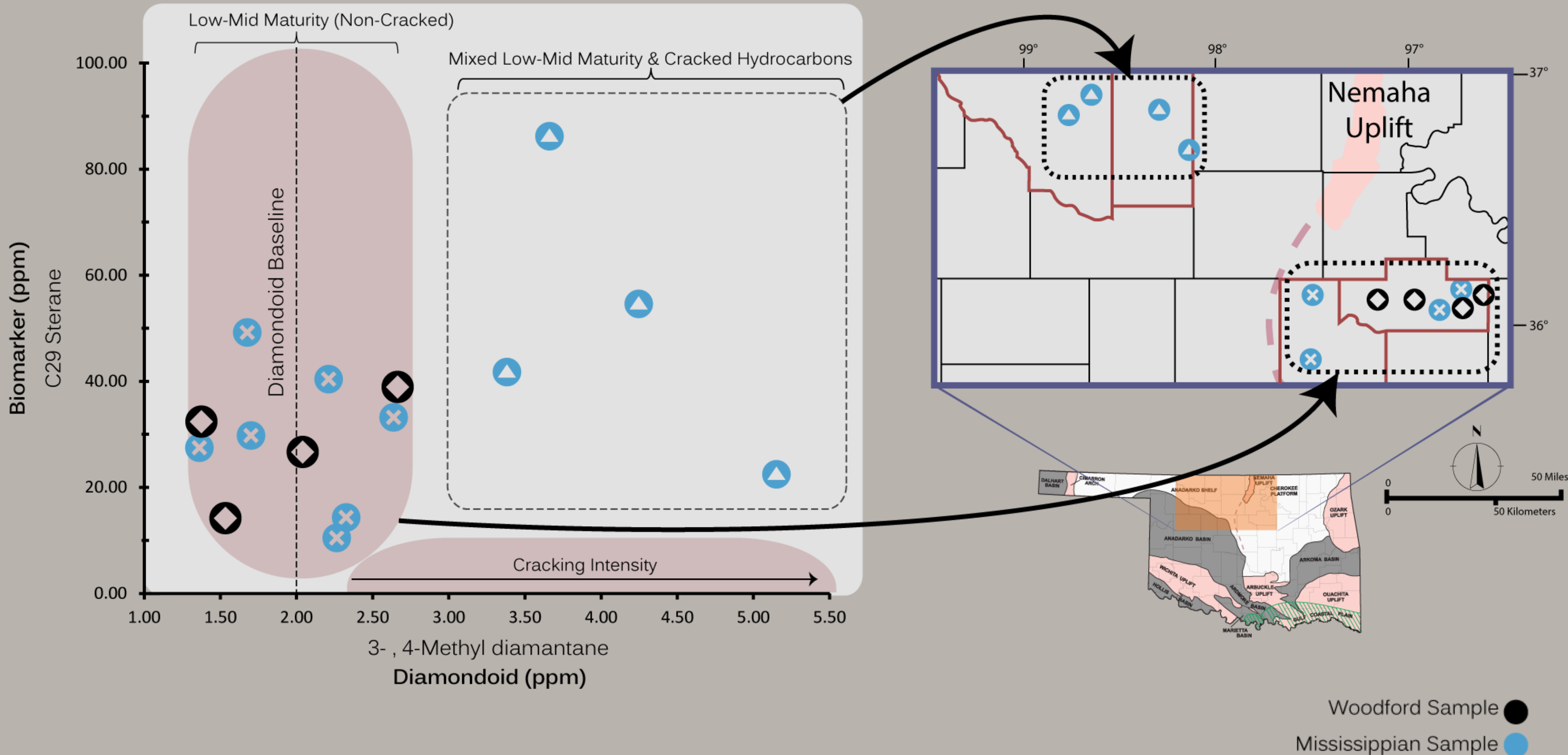


RESULTS

- **How does the Nemaha uplift influence the Mississippian oil composition?**

RESULTS

Extent of Cracking

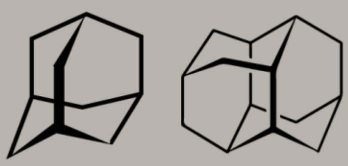


RESULTS

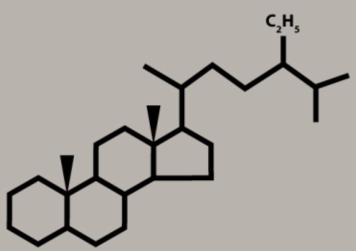
West of Nemaha Uplift

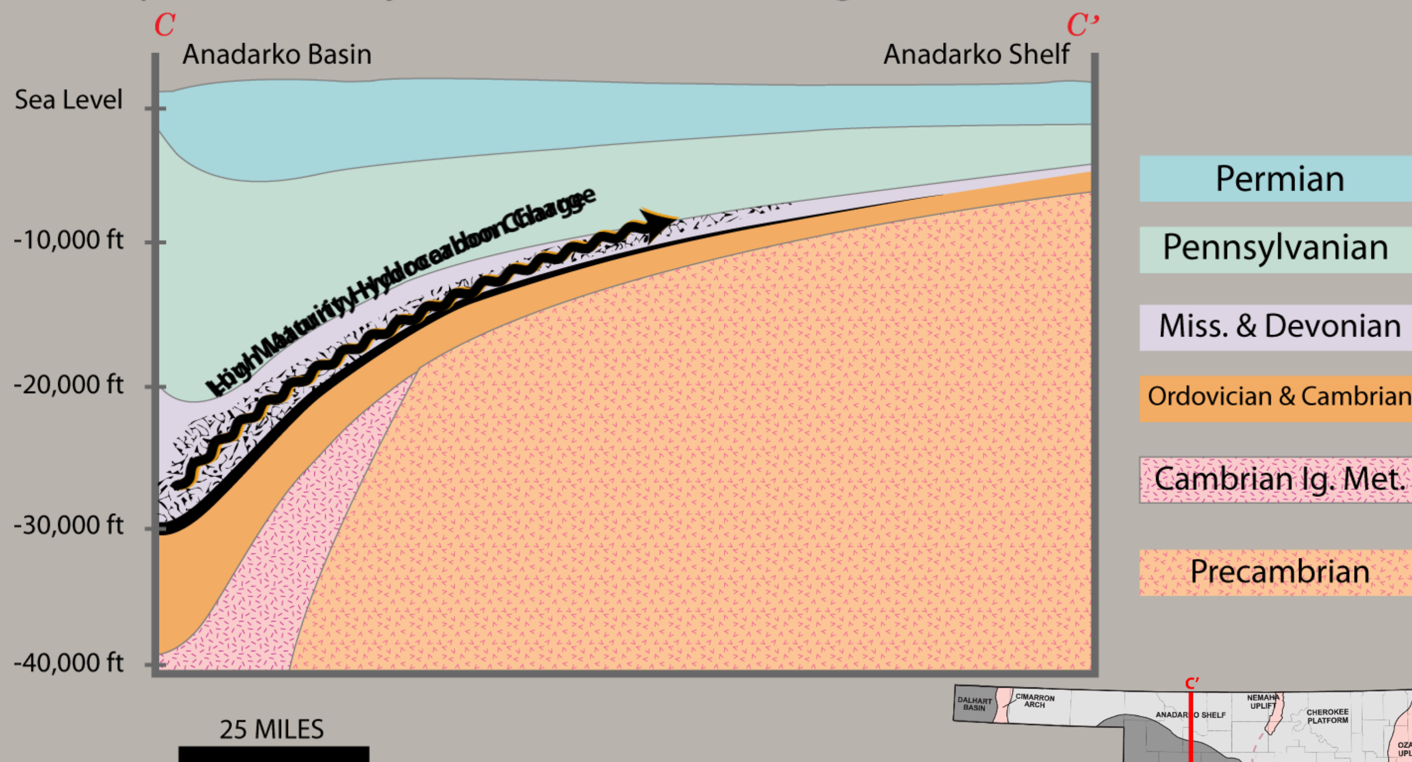
Episodic Hydrocarbon Charge

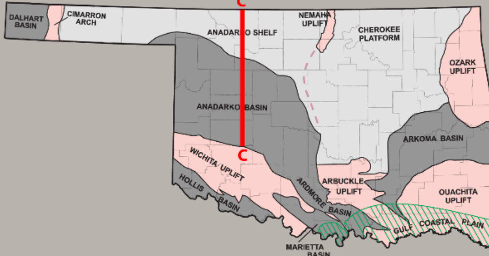
High Diamondoids



High Biomarkers





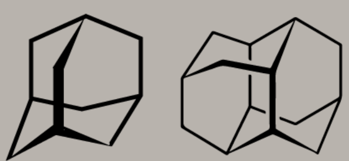


RESULTS

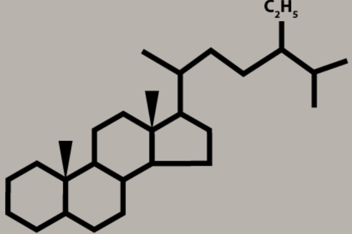
East of Nemaha Uplift

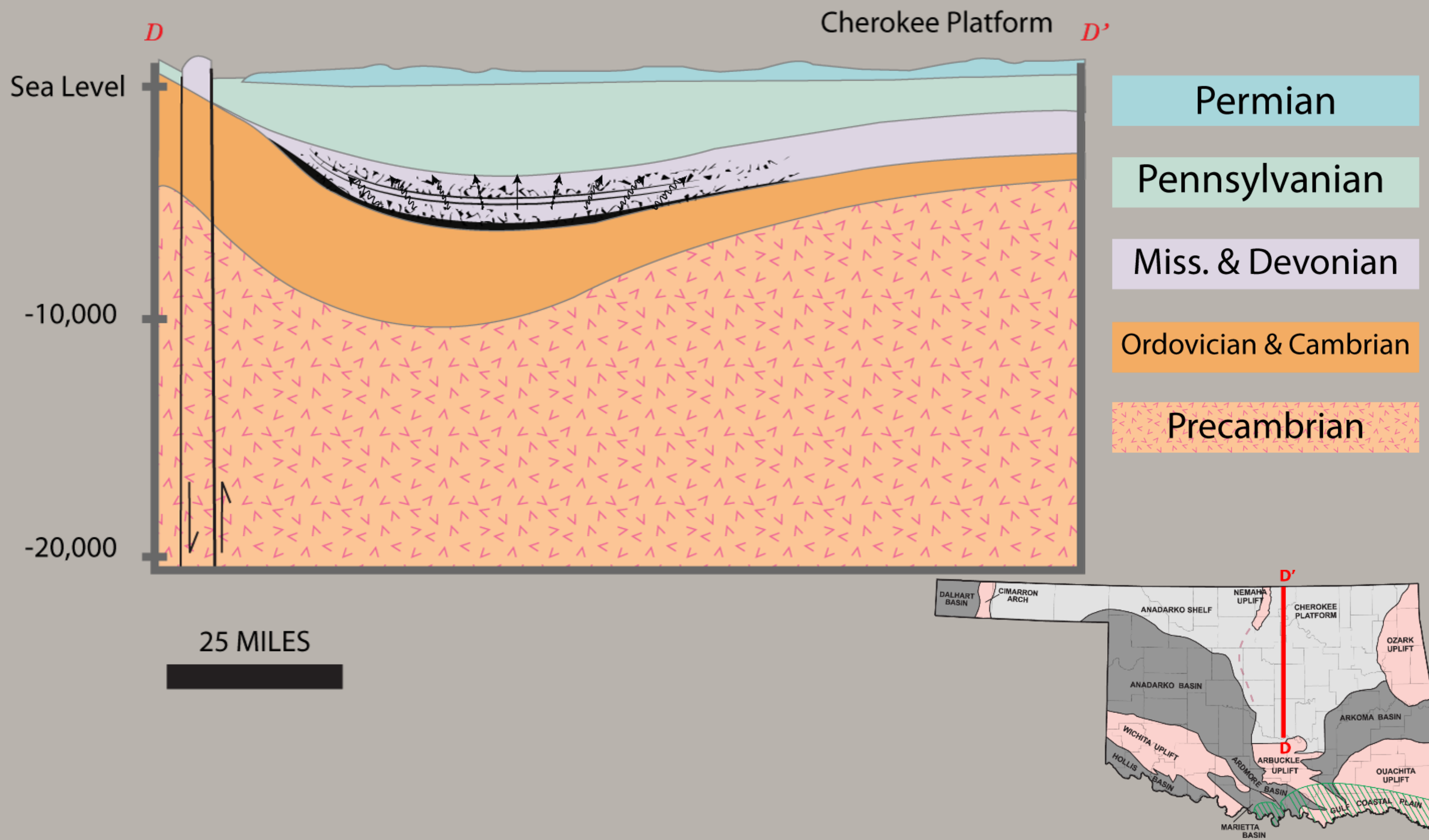
In-situ Hydrocarbon Charge

Low Diamondoids



High Biomarkers





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KEY FINDINGS

- **Organic-rich intervals within the Mississippian carbonate show good source-rock quality, at the early oil-window (0.74% Ro).**

- **Some of the Mississippian oils exhibit different geochemical markers than the Woodford.**

- **Miss. oils West of Nemaha-uplift are a mixture of cracked and non-cracked hydrocarbons, In contrast, oils from East region are low maturity (non-cracked) hydrocarbons.**

ACKNOWLEDGMENTS

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Saudi Aramco

devon

Chesapeake
ENERGY

BIOMARKER
TECHNOLOGIES
GEOCHEMICAL ANALYSIS

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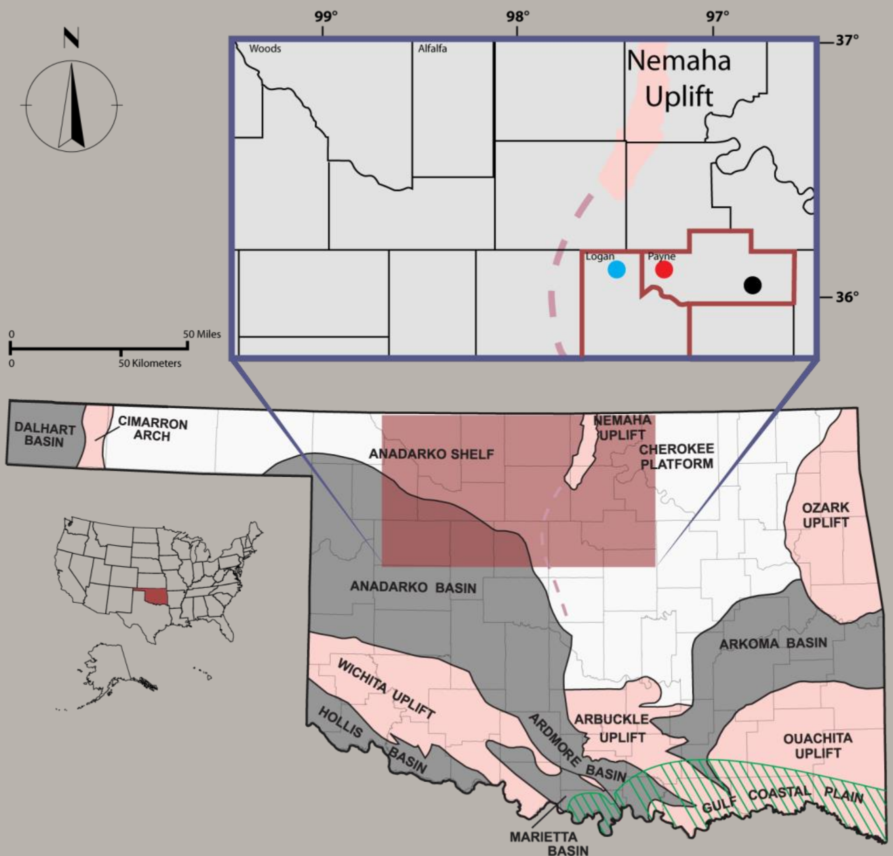
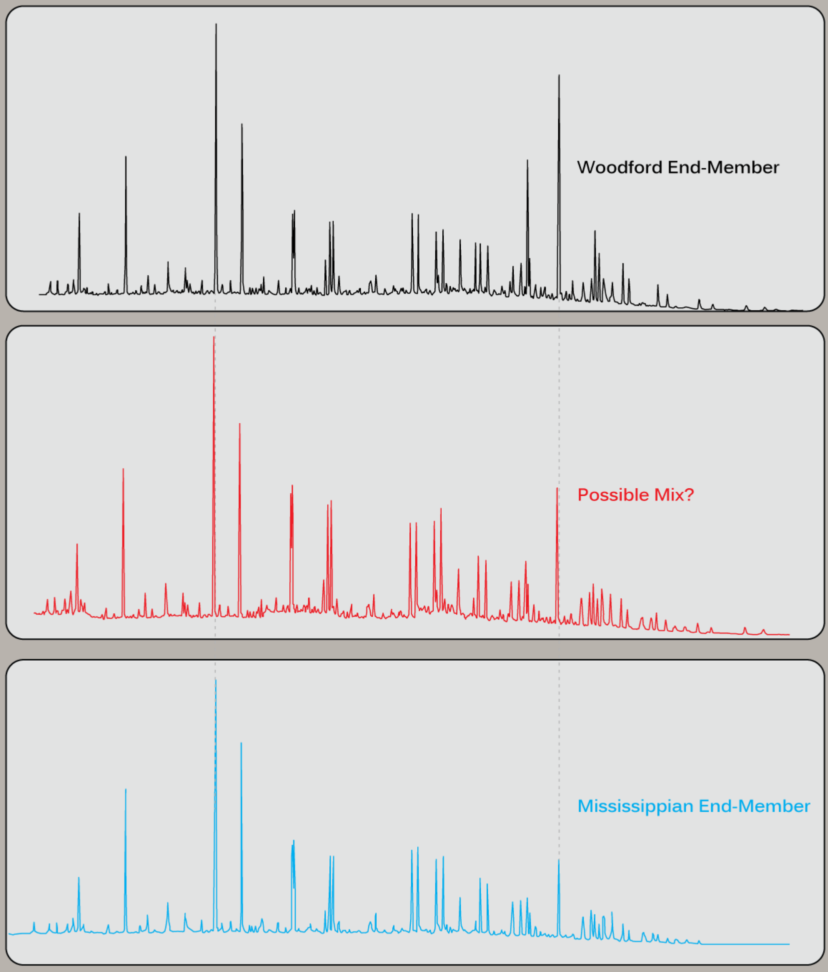
RESULTS

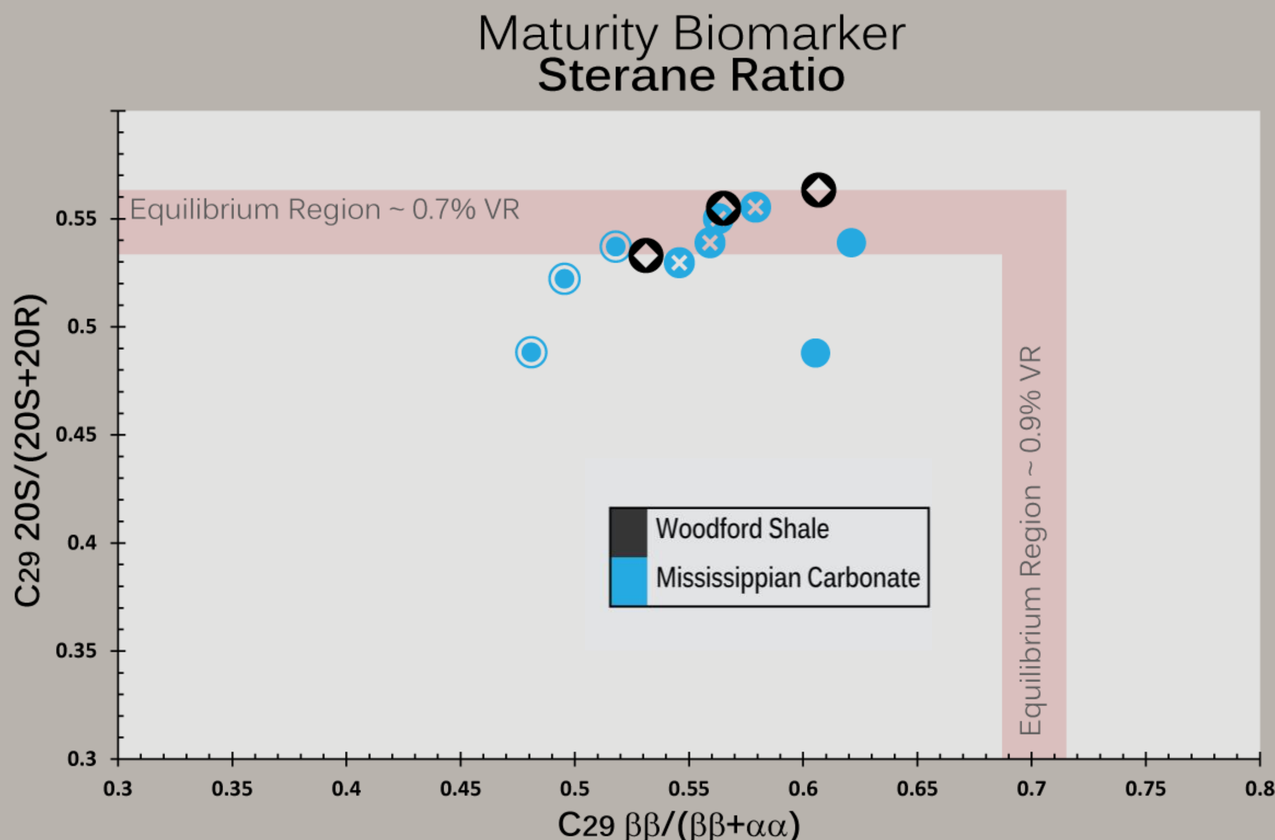

N
99°
98°
97°
37°
36°
Woods
Alfalfa
Nemaha Uplift
Logan
Payne
0
50 Miles
0
50 Kilometers
DALHART BASIN
CIMARRON ARCH
ANADARKO SHELF
NEMAHA UPLIFT
CHEROKEE PLATFORM
OZARK UPLIFT
ANADARKO BASIN
ARKOMA BASIN
WICHITA UPLIFT
HOLLIS BASIN
ARDMORE BASIN
ARBUCKLE UPLIFT
OUACHITA UPLIFT
GULF COASTAL PLAIN
MARIETTA BASIN


Woodford End-Member
Possible Mix?
Mississippian End-Member

RESULTS

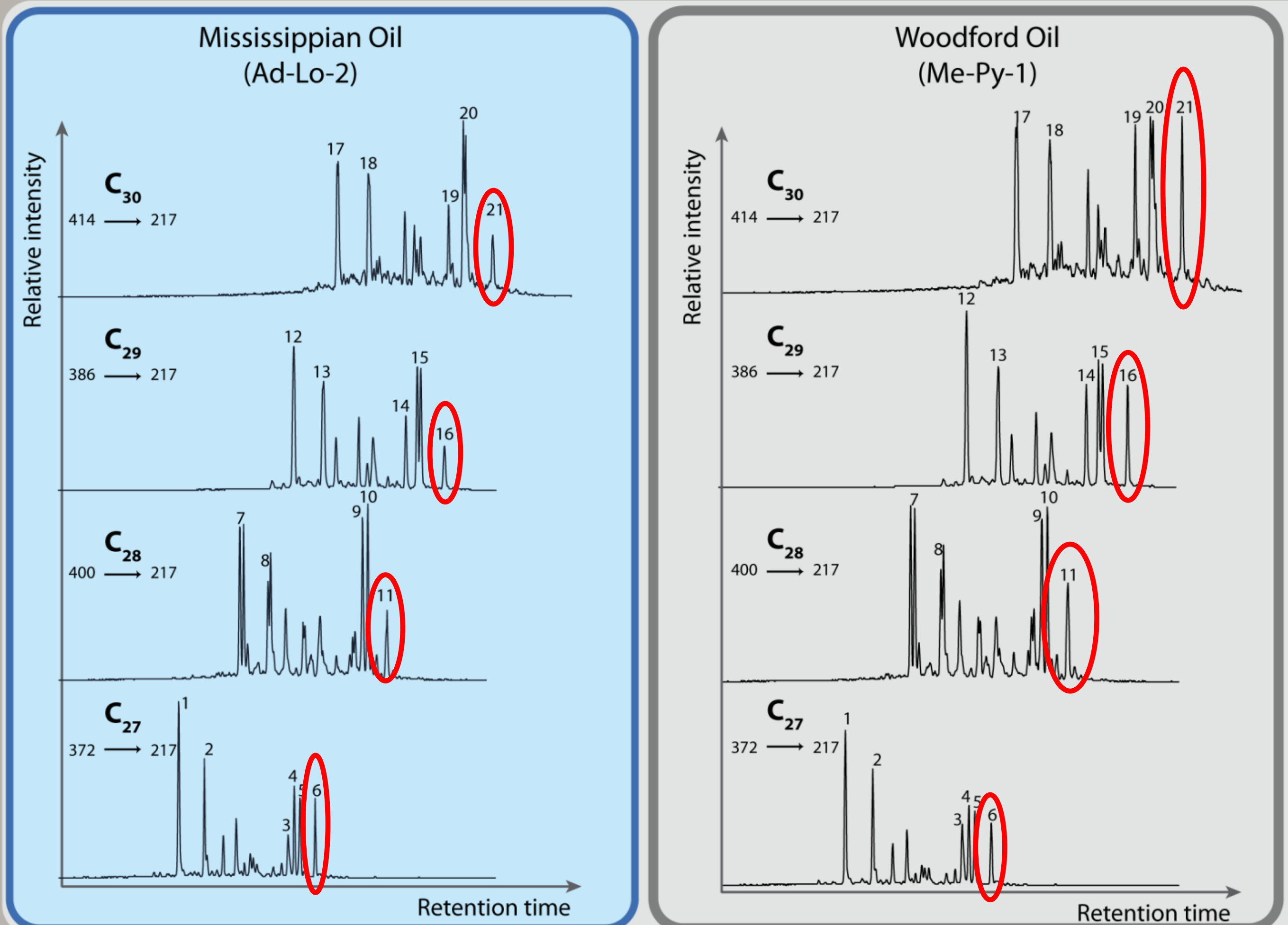
Oils Maturity:

- **Biomarkers maturity ratios indicate that both Mississippian and Woodford oils are within the early-mid oil window**



RESULTS

C_{27-30} Sterane Biomarkers



Peak	Compound
1	C_{27} 13β,17β dia 20S
2	C_{27} 13β,17β dia 20R
3	C_{27} ααα 20S
4	C_{27} αββ 20R
5	C_{27} αββ 20S
6	C_{27} ααα 20R
7	C_{28} 13β,17α dia 20S (24S + 24R)
8	C_{28} 13β,17α dia 20R (24S + 24R)
9	C_{28} αββ 20R
10	C_{28} αββ 20S
11	C_{28} ααα 20R
12	C_{29} 13β,17α dia 20S
13	C_{29} 13β,17α dia 20R
14	C_{29} ααα 20S
15	C_{29} αββ 20R+S
16	C_{29} ααα 20R
17	C_{30} 13β,17α dia 20S
18	C_{30} 13β,17α dia 20R
19	C_{30} ααα 20S
20	C_{30} αββ 20R+S
21	C_{30} ααα 20R