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.
References Cited


LeBlanc, S.L., and M. Grammer, 2014, High resolution sequence stratigraphy and reservoir characterization of the Mississippian Lime in Northeastern Oklahoma: AAPG Annual Convention and Exhibition, Houston, TX, April 6-9, 2014. AAPG Datapages Search and Discovery Abstract #90189.

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
Jim Puckette and Tracy Quan

Boone Pickens School of Geology
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
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
- Study Objectives
- Samples and Methods
- Results
- Major Findings
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?
Rock Samples (total 60): from organic-rich Mississippian carbonates, and Woodford Shale.

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

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TOC & Rock-Eval

Source Rock Screening -> Vitrinite Analysis

Bitumen Extraction

n-Alkane and Isoprenoid

GC-FID

Bitumen and Oil Separation

GC-MS

Diamondoid

GC-MS

Saturate Biomarkers

GC-MS

Aromatic Biomarkers

GC-MS/MS

Terpane and Sterane Biomarkers
OUTLINE

- Introduction
- Study Objectives
- Samples and Methods
- Results
- Major Findings
Can dark Mississippian beds generate hydrocarbons?
Source Rock Richness

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

**Woodford**: average TOC of 7%.
Organic Matter Type (Macerals)

**Miss**: Dominated with amorphous organic matter and solid bitumen.

**Wdfd**: Dominated with alginite maceral and solid bitumen.
Kerogen Types

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

**Woodford:** kerogen is type-I with average hydrogen index values of 554, and oxygen index of 5.
Source Rock Maturity

Mississippian & Woodford: kerogens have reached the early-mid oil window:
- Average Ro% 0.74 ± 0.08
- Average Tmax 440 °C
Are Mississippian oils chemically different from Woodford oils?
RESULTS

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

WOODFORD END-MEMBER SAMPLES
Hopane

Intensity vs Time

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RESULTS

Regular Sterane Biomarkers

Wang and Philp 1997 (Miss)
Romero and Philp 2012 (Wdfd)
RESULTS

Oil-Source Rock Correlation
Mississippian vs. Woodford

Diamondoid
DiMeAdimata/Trimanta

Sterane Biomarkers
C21Ster/C27Ster
C29Ster/C27Ster

Terpane Biomarkers
BisnorHop/Hop
Extended Tricyclic

Woodford
Oil Rock
Mississippian
Oil Rock

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How does the Nemaha uplift influence the Mississippian oil composition?
West of Nemaha Uplift
Episodic Hydrocarbon Charge

High Diamondoids

High Biomarkers

Sea Level
-20,000 ft
-30,000 ft
-40,000 ft

25 MILES

Anadarko Basin
Anadarko Shelf

Permian
Pennsylvanian
Miss. & Devonian
Ordovician & Cambrian
Cambrian Ig. Met.
Precambrian
East of Nemaha Uplift
In-situ Hydrocarbon Charge

Low Diamondoids
High Biomarkers

Sea Level
-10,000
-20,000

25 MILES

Permian
Pennsylvanian
Miss. & Devonian
Ordovician & Cambrian
Precambrian

Cherokee Platform
OUTLINE

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


RESULTS

Woodford End-Member

Possible Mix?

Mississipian End-Member
Oils Maturity:

Biomarkers indicate that both Mississippian and Woodford oils are within the early-mid oil window.
C_{27-30} Sterane Biomarkers

**Mississippian Oil (Ad-Lo-2)**

- C_{30} 414 → 217
- C_{29} 386 → 217
- C_{28} 400 → 217
- C_{27} 372 → 217

**Woodford Oil (Me-Py-1)**

- C_{30} 414 → 217
- C_{29} 386 → 217
- C_{28} 400 → 217
- C_{27} 372 → 217

**Peak Table**

<table>
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<tr>
<th>Peak</th>
<th>Compound</th>
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<tr>
<td>1</td>
<td>C_{29} 13β,17β dia 20S</td>
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<tr>
<td>2</td>
<td>C_{30} 13β,17β dia 20R</td>
</tr>
<tr>
<td>3</td>
<td>C_{30} 13α dia 20S</td>
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<tr>
<td>4</td>
<td>C_{29} 13β,17β 20R</td>
</tr>
<tr>
<td>5</td>
<td>C_{29} 13α 20S</td>
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<tr>
<td>6</td>
<td>C_{30} 13α 20R</td>
</tr>
<tr>
<td>7</td>
<td>C_{29} 13β,17α dia 20S (24S + 24R)</td>
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<tr>
<td>8</td>
<td>C_{30} 13β,17α dia 20R (24S + 24R)</td>
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<tr>
<td>9</td>
<td>C_{29} 13β,17α 20R</td>
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