# BIOMARKER STRATIGRAPHY AND RELATED MACERALS IN DEVONIAN-MISSISSIPPIAN SHALES, CENTRAL OKLAHOMA, USA.

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## Introduction

Woodford Shale overlying by Mississippian Limestone (Meramec) constitute one of the prolific unconventional hydrocarbon targets in Central and Northern Oklahoma. In recent years, with the advantage of horizontal drilling technology Devonian and Mississippian shales became of great interest for research to understand the petroleum system fundamentals including sources of hydrocarbon in these unconventional reservoirs (Boyd, 2008; Al Atwah et. al., 2015). In this study we investigate 28 core samples located in Lincoln County in Central Oklahoma. This core feature a complete section covering the Mississippian Meramec mudstones and Woodford Shale sections. Rock samples were tested for hydrocarbon generation potential using Rock-Eval 6. Organic petrography and maceral analysis was performed using reflected-light microscopy under incident-white light and UV. Bitumen was extracted from the rock samples using accelerated solvent extractor. Bitumen then was fractionated to saturate and aromatic hydrocarbon fractions. Both saturate and aromatic fractions were analysed using gas chromatography–mass spectrometry (GC-MS) technique for biomarker analysis. Furthermore, detailed biomarker investigation was performed on the saturate fraction using gas chromatography–triple quadrupole mass spectrometry (GC-MS-QQQ).

## Result

Organic-rich intervals within the Mississippian Limestone formation can be divided into three main members (i.e. upper, middle and lower). This division is based on organic-richness together with variation in maceral and biomarker distributions (Fig1). Within the Mississippian mudrocks the upper and lower members are richer in TOC% than the middle member. Moreover, the middle member exhibits an increase in regular C27 sterane relative to regular C29 sterane, together with a moderate abundance of extended tricyclic terpanes. In contrast, upper and lower Mississippian members contain higher concentration of extended tricyclic terpane biomarkers. Most notably, all Mississippian members showed trace amount of tricyclic diterpanes (i.e. rimuane, pimarane, rosane and isopimarane) and tetracyclic diterpanes (i.e.beyerane, phyllocladane, atisane and kurane), which coincide with the presence of spore-like structure organics that could indicate a close link between marine and/or terrestrial spores and diterpanes biomarkers. In contrast, Woodford Shale samples lacked extended tricyclic terpane biomarkers, as well as tricyclic and tetracyclic diterpanes (Fig1). Stratigraphically, the overall trend of decrease in tricyclic and tetracyclic diterpanes with increase in depth could suggest a more distal depositional environment during Late Devonian to Early Mississippian followed by relatively less distal depositional settings.

Organic matter structures and maceral distribution varied across the core section. Overall, Mississippian organics exhibit abundance of amorphous organic matter (AOM), which is

infused into the groundmass of the rock mineral matrix, and exhibiting very weak light-yellow fluorescence. Also, telalginite was observed within the Mississippian members, showing circular spore-like structure (*Dictyotriletes?*). In contrast, Woodford Shale maceral showed abundance of both lamalginite and telalginite macerals. More specifically, the Woodford Shale samples are enriched in *Tasmanites* which increased in radius dimensions with increasing depth.
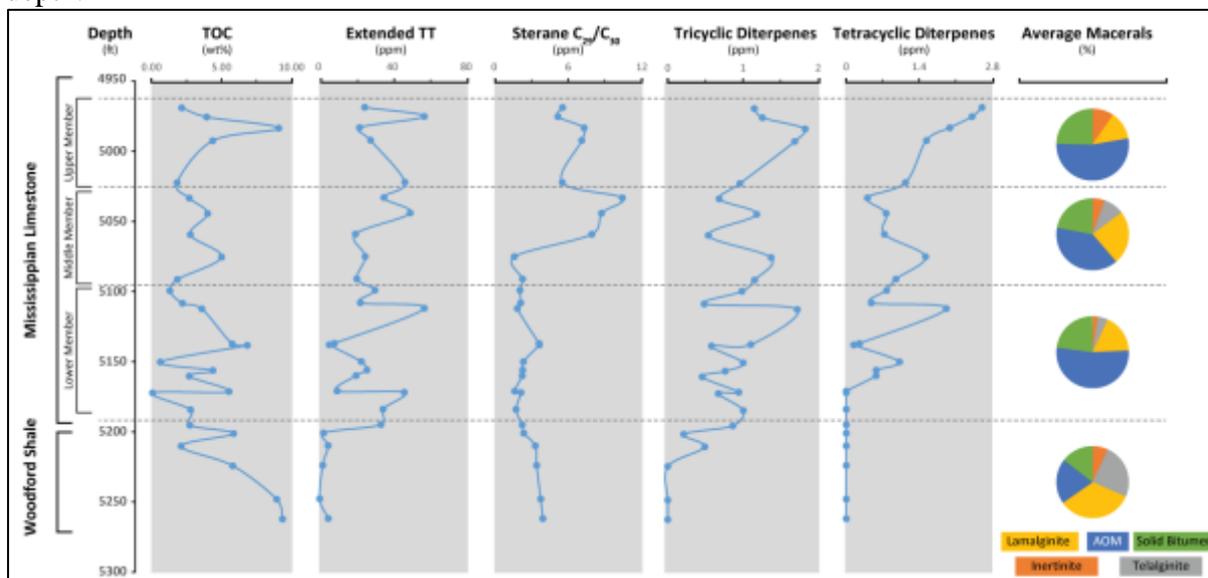


*Figure 1 Vertical profile of rock samples from the Mississippian Limestone and Woodford Shale comparing TOC, average macerals distribution, and selected key biomarker ratios (Extended TT: the sum of absolute concentration of C30-39 extended tricyclic terpanes, Sterane C29/C27: C29 ααα 20R/ C27 ααα 20R, Tricyclic Diterpanes: sum of absolute concentration of tricyclic diterpanes, Tetracyclic Diterpanes: sum of absolute concentration of tetracyclic diterpanes).*

**Conclusion**

Organic-rich Mississippian (Meramec) and Woodford Shales are characterized based on organic richness, macerals distribution and biomarkers composition. Based on the mentioned characteristics the Mississippian Formation contain three main organic-rich members. Most notably, the Mississippian members contained extended tricyclic terpenes together with tricyclic and tetracyclic diterpanes. In contrast, those biomarkers were absent in Woodford Shale samples. These variation in biomarker and maceral across the Devonian-Mississippian are interpreted to represent a change in the depositional environment. Above all, presented biomarker characterization can provide a baseline fingerprint to identify crude-oil source and degree of mixing of hydrocarbon produced from the Woodford and Meramec reservoirs.

**References**

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