[PS]Inorganic Elemental Analysis of Woodford and Mississippian Mudrocks: Implication for Petroleum Systems Analysis*

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Abstract

The Woodford Shale and the overlying Mississippian Limestone constitute one of the major oil and gas producing intervals across the Anadarko Basin and adjacent shelves. Known for its organic-richness and generation potential, the Woodford Shale has long been recognized as a major source rock for produced oils from the Mississippian Limestone. However, variations in crude-oil composition, together with the presence of secondary organic-rich mudrocks within the Mississippian Limestone, provide another hydrocarbon charge source. Recent organic geochemical studies showed evidence for a contribution to the produced oils from Mississippian mudrocks, in addition to the Woodford Shale. Here, we use inorganic elemental analyses as an additional tool for unraveling source rock depositional settings and secondary processes associated with hydrocarbon generation and migration. In this study, a collection of oil samples, together with core samples from Logan County in north-central Oklahoma, was examined using inductively-coupled plasma mass spectrometry (ICP-MS). Additionally, rock samples were analyzed using Rock-Eval for hydrocarbon generation potential assessment, and oil samples were processed for overall n-alkane profiles using GC-FID. Based on TOC and elemental composition signatures, samples from the organic-rich beds within the Mississippian section were divided into three intervals, and compared with the Woodford Shale samples. Average TOC values for organic-rich Mississippian rocks increase down section with an average of 5.8%, while TOC values for the Woodford Shale average 7.1%. The depth profile trend of major and trace elements such as Mg, Al, Fe, V, Ni etc. were compared with Rock-Eval and GC-FID data to evaluate organic matter type, preservation and redox condition, and hydrocarbon generation potential. Additionally, an inorganic elemental fingerprint was developed for the rocks and compared with that of the crude-oil samples, with the aim to understand the use of elemental fingerprinting as a tool for oil-source correlation and/or secondary alteration processes as a function of hydrocarbon migration.

References Cited

Al Atwah, I., J. Puckette, and T. Quan, 2015, Petroleum Geochemistry of the Mississippian Limestone Play, Northern Oklahoma, USA:

Evidence of Two Different Charging Mechanisms East and West of the Nemaha Uplift: AAPG Annual Convention & Exhibition, Denver, Colorado, May 31-June 3, 2015, Search and Discovery Article #10773 (2015). Website accessed May 2017.

Tribovillard, N., T.J. Algeo, T. Lyons, and A. Riboulleau, 2006, Trace Metals as Paleoredox and Paleoproductivity Proxies: An Update: Chemical Geology, v. 232/1, p. 12-32. doi:10.1016/j.chemgeo.2006.02.012

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ABSTRACT

The Woodford Shale and the overlying Mississippian Limestone constitute one of the major oil and gas producing intervals across the Anadarko basin and adjacent shelves. Known for its organic-richness and generation potential, the Woodford Shale has long been recognized as a major source rock for produced oils from the Mississippian Limestone. However, variations in crude-oil composition, together with the presence of secondary organic-rich mudrocks within the Mississippian Limestone, provide another hydrocarbon charge source. Recent organic geochemical studies showed evidence for a contribution to the produced oils from Mississippian mudrocks, in addition to the Woodford Shale. Here, we use inorganic elemental analyses as an additional tool for unraveling source rock depositional settings and secondary processes associated with hydrocarbon generation and migration. In this study, a collection of oil samples, together with core samples from Logan County in north-central Oklahoma, was examined using inductively-coupled plasma mass spectrometry (ICP-MS). Additionally, rock samples were analyzed using Rock-Eval for hydrocarbon generation potential assessment, and oil samples were processed for overall n-alkane profiles using GC-FID. Based on TOC and elemental composition signatures, samples from the organic-rich beds within the Mississippian section were divided into three intervals, and compared with the Woodford Shale samples. Average TOC values for organic-rich Mississippian rocks increase down section with an average of 5.8%, while TOC values for the Woodford Shale average 7.1%. The depth profile trend of major and trace elements such as Mg, Al, Fe, V, Ni etc. were compared with Rock-Eval and GC-FID data to evaluate organic matter type, preservation and redox condition, and hydrocarbon generation potential. Additionally, an inorganic elemental fingerprint was developed for the rocks and compared with that of the crude-oil samples, with the aim to understand the use of elemental fingerprinting as a tool for oil source correlation and/or secondary alteration processes as a function of hydrocarbon migration.

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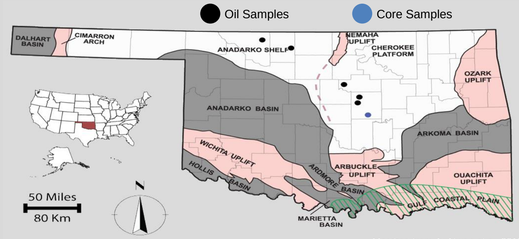
STUDY AREA

Figure 1: Anadarko Basin – North Central Oklahoma



Modified from Al Atwah et al, 2015

SAMPLING INTERVAL

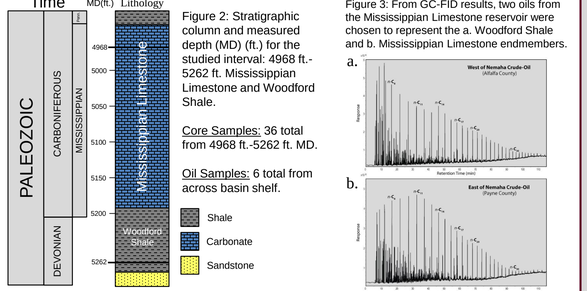


Figure 2: Stratigraphic column and measured depth (MD) (ft.) for the studied interval: 4968 ft.-5262 ft. Mississippian Limestone and Woodford Shale.

Core Samples: 36 total from 4968 ft.-5262 ft. MD.

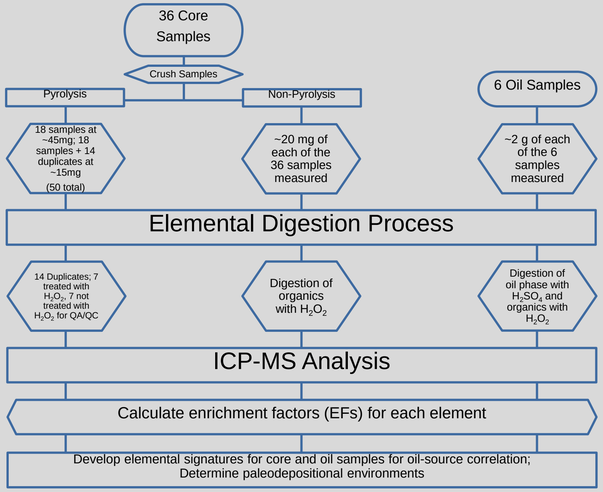
Oil Samples: 6 total from across basin shelf.

Figure 3: From GC-FID results, two oils from the Mississippian Limestone reservoir were chosen to represent the a. Woodford Shale and b. Mississippian Limestone endmembers.

Al Atwah et al. 2015

APPROACH

Figure 4: Laboratory Workflow for Inorganic Analyses of Core and Oil Samples



RESULTS

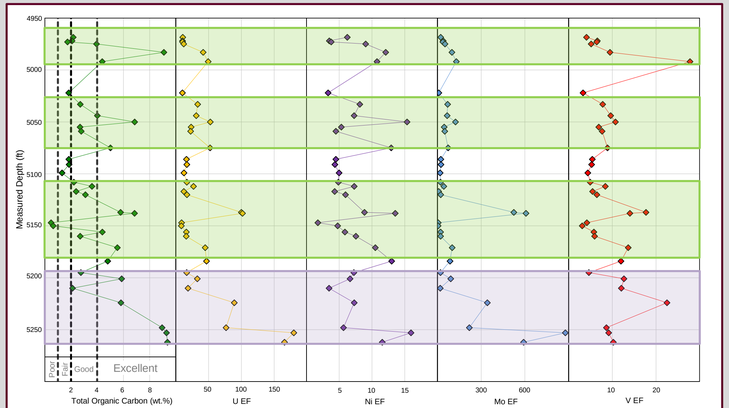
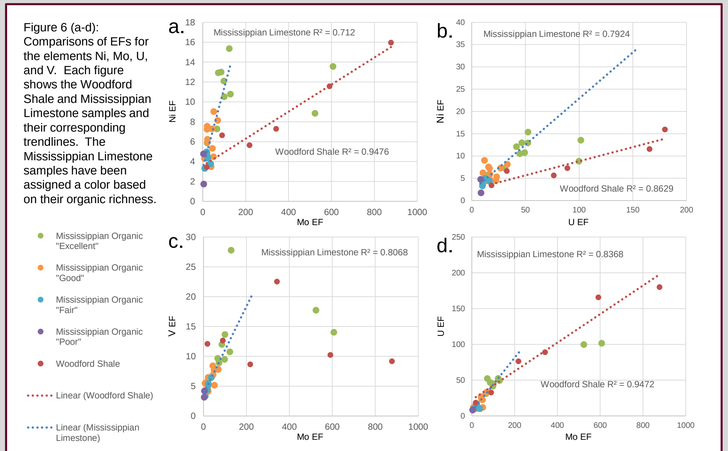


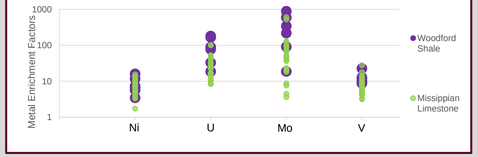
Figure 5: Total organic carbon (TOC) (wt. %) and enrichment factors (EFs) for the elements U, Ni, Mo, and V. Organic rich intervals within the Mississippian Limestone shaded green and the Woodford Shale shaded purple.

Figure 6 (a-d): Comparisons of EFs for the elements Ni, Mo, U, and V. Each figure shows the Woodford Shale and Mississippian Limestone samples and their corresponding trendlines. The Mississippian Limestone samples have been assigned a color based on their organic richness.



RESULTS

Figure 7: The range for the enrichment factors (EFs) for the elements Ni, U, Mo, and V.



DISCUSSION

Comparison of intervals with “excellent” organic preservation (i.e., TOC > 4 wt. %):

- High Ni EFs are likely due to high productivity during deposition (Tribovillard et al., 2006)
- Higher Mo/Ni and U/Ni EF ratios in Woodford shale suggest euxinic (with H_2S) depositional settings along with high productivity and organic matter preservation
- Lower Mo/Ni and U/Ni EF ratios in the Mississippian limestones suggest suboxic/anoxic depositional (without H_2S) settings along with high productivity and organic matter preservation
- Low Mo EFs, coupled with relatively high V and Ni EFs shows periods of H_2S-free anoxia in the Mississippian limestones, allowing for intervals of organic matter preservation to take place
- Mo-Ni EF and U-Ni EF crossplots show that the Mississippian Limestone unit and the Woodford Shale unit have distinct elemental signatures

FUTURE WORK

- Upon digestion and ICP-MS analysis of the produced oils, we will compare the elemental signatures, found in the core samples, with the elemental signatures from the oil samples
  - This will allow us to more accurately track the source of the produced fluids from the Mississippian Limestone reservoir

REFERENCES

Al Atwah, Ibrahim, Jim Puckette, and Tracy Quan. “Petroleum Geochemistry of the Mississippian Limestone Play, Northern Oklahoma, USA: Evidence of Two Different Charging Mechanisms East and West of the Nemaha Uplift.” *AAPG Annual Convention and Exhibition*.

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