Comparison of ester-linked phospholipid fatty acids and diglyceride fatty acids in Marcellus Shale of different maturity and depositional environments

Abstract No: 265511

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1. ABSTRACT

The Middle Devonian Marcellus Shale occurs at depths of 1.5 to 2.5 km, with formation temperatures of 49˚-60˚C, and is one of the largest gas shale plays in North America. Microbial activity has been detected in subsurface shale environments as deep as 3 km with temperatures as high as 70˚C, suggesting that microbial life may exist in the Marcellus prior to energy development. In this study the distribution of ester-linked phospholipid fatty acids (PLFA and DGFA) in core samples were studied to compare the microbial community structure from a less mature, liquids-prone well in Wetzel County and a more mature, gas-prone well in Monongalia County, West Virginia. Ester-linked phospholipid fatty acids were extracted from samples collected at selected intervals and the total yield and variety of PLFA (proxy for recent, viable microbiota) and DGFA (proxy for non-viable or relic biomass) profiles were examined. A prior comprehensive study of these cores suggests that the sediments in these cores were deposited in different geological settings. A total of 22 different PLFA fatty acids and a total of 20 different DGFA fatty acids in the range of C11 to C24 were detected. They consisted of saturated, branched, monounsaturated, polyunsaturated, hydroxy, epoxy, and cyclopropyl fatty acids, and their variations are presented in their relative proportions (mol %). The yield of PLFA lipid fatty acid profiles were higher in the less mature liquids-prone well compared to the more mature gas-prone well, while the variety of PLFA lipid profiles was the same for both wells. The yield and variety of DGFA lipid profiles were also higher in the less mature liquids-prone well compared the more mature gas prone well. The combination of fatty acids present in both cores showed indications of a potentially diverse assemblage of both aerobic and anaerobic bacteria, stress and toxicity related biomarkers, sulfate reducing bacteria, and microbes indicating terrestrial and marine influence. In the Marcellus, this is a possibility because of the alternating anoxic and oxic depositional environmental conditions and the limited nutrient supply or starvation associated with fine grained deep subsurface shale formations. However, it is important to note that the samples described here do not account for the introduction of microbial cells during drilling, collection, and sample storage as well as present and previous engineering practices used in the well field that could alter lipid profiles and biomass. Currently, a science-driven coring effort is underway to obtain pristine shale core samples from a science well at the Marcellus Shale Energy and Environment Laboratory (MSEEL) at West Virginia University where our analyses will be used to assess the extant microbial life within the shale, prior to energy development along with biologic derivatives of relic communities within the formation.

2. INTRODUCTION

Factors such as (1) Primary Production, (2) Rate of organic matter (OM) Burial, (3) Redox Conditions, (4) OM Source, (5) Bioturbation, (6) Molecular Character, that control rate of marine OM production, cycling and preservation are dependent on microbial activities (Figure 1a, b)

Microbial interaction with these factors therefore play an essential role in marine OM production, cycling, and preservation (Figure 1a, b)

PLFA are prime constituents of microbial cellular membranes, hence are good indicators of microbial biomass, diversity and environmental conditions

Subsurface changes in environmental conditions like decrease in redox potential, organic nutrients and pores sizes of shale could modify the microbial populations and their community

Thermal diagenesis and increase in pressure associated with maturity of sediments can also modify the microbial signatures.

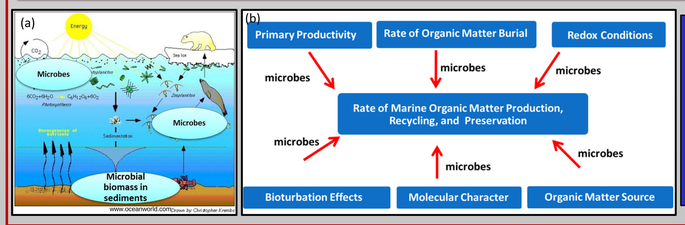


Figure 1: The role of microbes in OM production, cycling and preservation is dependent on past environmental conditions and also controls biogeochemical cycling and the distribution of hydrocarbon resources.

3.Location and Study Area

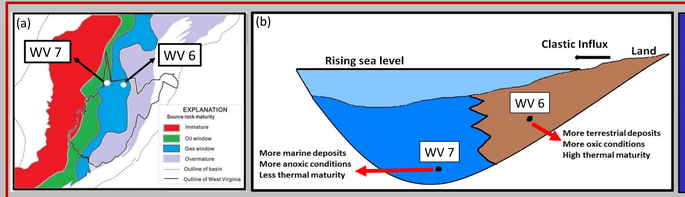
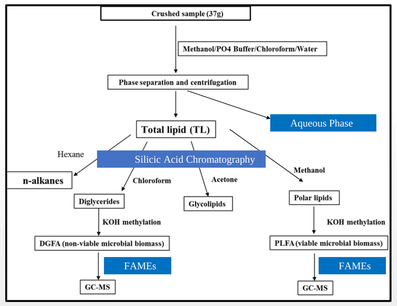


Figure 2: Map of West Virginia showing study sites (a), and a hypothetical depositional model of the Marcellus Shale (b), showing approximate location of WV-6 and WV-7 in the paleo basin. Modified from East et al. (2012)

4. Data and Methods



Sediment samples were collected for lipid analysis from 2 Marcellus cores WV 7 (less mature, liquid prone part of basin) and WV 6 (more mature, gas prone part of basin)

9 samples were collected from each core. To avoid further contamination due to core handling/storage, cores were pared from outside and inner part crushed and homogenized using a sterile mortar and pestle

37g of powdered samples were then extracted using the modified Bligh and Dyer method.

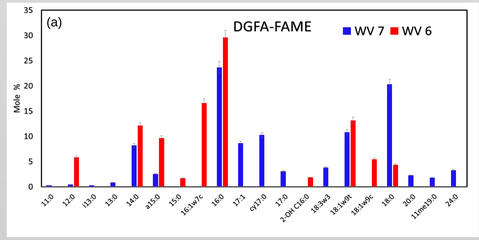
After extraction and separation, the lipids (PLFA and DGFA) were analyzed and quantified as fatty acid methyl esters (FAMEs) using a GC-MS equipped with a Restek RTx-1 column.

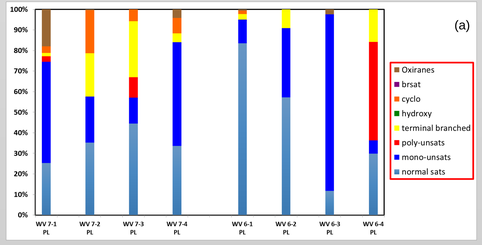
DGFA	WV 7		WV 6	
Functional group totals	mean	S.D	mean	S.D
normal sats	62.09	13.39	53.47	26.81
mono-unsats	19.36	7.86	35.09	21.91
poly-unsats	3.80	6.58	0.00	0.00
terminal branched	2.76	4.79	9.63	11.14
hydroxy	0.00	0.00	1.80	3.61
cyclo	10.24	8.92	0.00	0.00
brsat	1.75	3.03	0.00	0.00
	n=8		n=9	

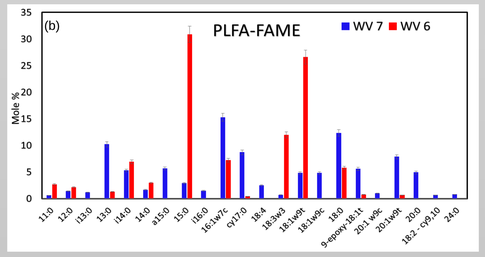
PLFA	WV 7		WV 6	
Functional group totals	mean	S.D	mean	S.D
normal sats	34.66	7.84	41.43	25.30
mono-unsats	33.69	19.05	36.26	34.94
poly-unsats	3.17	4.68	11.97	23.95
terminal branched	13.55	12.58	8.40	6.46
cyclo	9.34	7.92	1.30	2.59
Epoxy	5.59	8.42	0.63	1.13
	n=9		n=9	

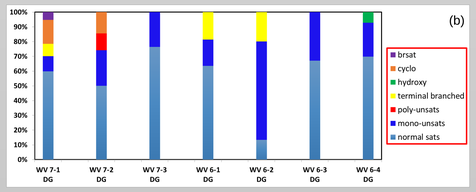
Table 1: Averaged molar percentages of fatty acids functional groups (DGFA and PLFA) recovered from different cores.

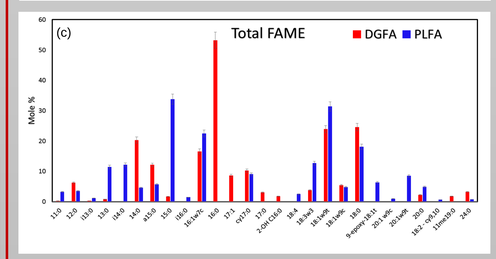
5. Results











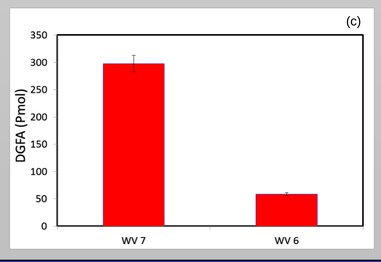


Figure 3. Plot illustrating averaged differences in DGFA profiles (a) PLFA profiles (b), and summed averages for DGFA and PLFA (c) observed within sediment cores.

Figure 4. Plot of average PLFA abundance (a) and average DGFA abundance (b) for individual sediments from WV 7 and WV 6, DGFA abundance in pmol for WV 7 and WV 6 (c).

6. Results

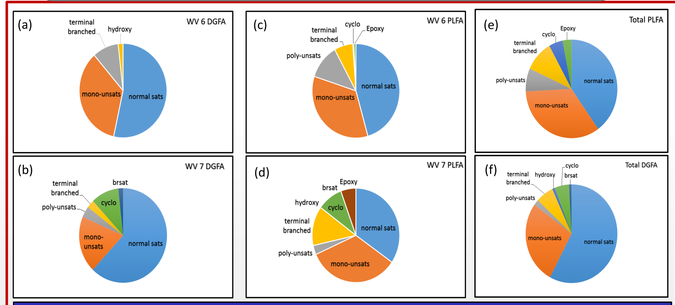


Figure 5. Pie charts showing variety of DGFA lipid functional groups in more mature gas prone well WV 6 (a) and less mature liquid prone well WV 7 (b), PLFA lipid profiles in more mature gas prone well WV 6 (c) and less mature liquid prone well WV 7 (d), total PLFA lipid variety in both wells (e) and total DGFA lipid variety in both wells (f)

7. Discussion

Less mature well (WV 7) had more variety of DGFA and PLFA lipid profiles compared to more mature gas prone well (WV 6) (Figure 3a and b)

Microbial communities represented by the DGFA lipid profiles were different from those represented by the PLFA lipid profiles (Figure 3c)

Most of the individual samples from WV 7 also showed more PLFA and DGFA variety compared to samples from WV 6 (Figure 4a and b)

Less mature, liquid prone core (WV 7) had higher non-viable microbial biomass (DGFA-FAMEs) compared to more mature, gas prone well (WV 6) (Figure 4c)

Total variety of DGFA lipid functional groups were greater in WV 7 than WV 6 (Figure 5a,b)

Total variety of PLFA lipid functional groups are similar in both cores (Figure 5 c and d)

Combined PLFA functional groups in both cores were different from the combined DGFA functional groups (Figure 5 e and f)

Lipids indicative of stress, toxicity and Cl^- exposure like the oxiranes, were only present in the PLFA lipid fraction for both cores.

8. Conclusions

The variety and yield for DGFA and PLFA lipid biomarkers were different for WV 7 and WV 6 cores suggesting potentially different microbial community composition which could be due to differences on depositional environments and thermal maturation.

Trans isomers were detected in both WV 6 and WV 7 cores for the DGFA and PLFA profiles, indicating that microbes in both cores experienced stress due to limited nutrient supply or starvation

Greater yield and variety of lipid biomarkers in less mature WV 7 core could be related to high paleo-productivity during the shale deposition, more marine organic matter contribution, relatively quiescent anoxic marine conditions and low thermal diagenesis

9. Acknowledgements

NSF Early Career instrumentation grant (NSF EAR # 1205596)

NSF Division of Environmental Biology (NSF-DEB # 1342732)