

# Organic Matter Variations Within the Bakken Shales of Saskatchewan: With Implications Upon Origin and Timing of Hydrocarbon Generation\*

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## Abstract

This study presents a detailed temporal and spatial geochemical analysis of the Upper and Lower Bakken shales within the northern part of the Williston Basin. Analyses show a significant variation in TOC, S1, S2 and HI exists both depth-wise within the Upper and Lower Bakken shales, and in wells across the study area. This depth-wise pattern is mirrored in the yield of extractable organic matter (EOM), proportion of saturate, aromatic and NSO compounds as well as total sulphur. High proportion of NSO compounds in the EOM may reflect the incorporation of high proportion of sulphur into the kerogen during diagenesis. This later interpretation is supported by the relatively high abundance of aryl isoprenoids, likely derived from green sulphur bacteria Chlorobiaceae.

Analysis reveals that the Type II kerogen within the Upper and Lower Bakken are maceral assemblages and not single organic matter types as defined by bulk pyrolysis. This study has identified key molecular 'fingerprints' and the existence of significant variation in biomarkers within the Upper and Lower Bakken shales, indicating existence of green sulfur bacteria Chlorobiaceae and the presence of anaerobic Bacterivorous Ciliates during the deposition of the Upper and Lower Bakken. This indicates that the amorphous organic matter within the Bakken (identified as Bituminite) represents the bacterial reworking of primary organic matter by Bacterivorous Ciliates.

Using conventional maturity parameters, the Type II kerogen would be considered relatively immature, however  $T_{max}$  shows a strong inverse relationship with total sulphur. The implication being that the presence of sulphur may influence the early generation of hydrocarbon at relatively low levels of thermal maturity. Some of the broader implication from this study includes support for a paleo-water depth during the Upper and Lower Bakken that is at least 100 m (thereby accommodating the photic zone and euxinic bottom water), a mechanism and process that explains the origin and composition of the amorphous organic matter within the Upper and Lower Bakken, an explanation for the presence of high amounts of sulphur and pyrite within the shale and presents a challenge to the established notion that precursor organic matter is

extensively reworked, and hence transformed into amorphous kerogen, exclusively within the sediment.

## **Introduction**

The Bakken Formation is generally sub-divided into Upper, Middle and Lower members based upon their respective lithological characteristics, within which the Upper and Lower Bakken members are composed of non-calcareous, fissile, pyritic organic-rich shale that exhibit an apparent degree of lithological uniformity throughout the Williston Basin (e.g. Christopher, 1961). The black shales of the Upper and Lower Bakken have been the focus of a number of previous geochemical and petrographically-based studies that generally conclude that the organic-rich Upper and Lower Bakken are both primarily composed of a marine-derived amorphous kerogen (characterized as Type II-kerogen with an associated Hydrogen Index (HI) of 615 mg hydrocarbon/gTOC) (Osadetz et al., 1992; Osadetz and Snowdon, 1995), contains remnants of Tasmanites (Christopher, 1961; Stasiuk et al., 1990), is generally considered immature with respect to the generation of hydrocarbon and perhaps inappropriately described as a 'flooding surface'. However, several questions remain unresolved; firstly why does the amount of organic matter, expressed as wt.% TOC, vary from about 32.0 wt.% to 1.0 wt.% TOC within a 'flooding surface'; secondly what is the exact character of the organic matter within the Upper and Lower Bakken since Tasmanites is not a Type II kerogen and lastly, why a stratigraphically shallower formation (i.e. Lodgepole Formation) appears to have a higher level of thermal maturity (cf. Jiang et al., 2001).

This project is part of a large integrated assessment of the Phanerozoic fluid and petroleum systems of the southern Saskatchewan portion of the Williston Basin conducted at the Universities of Alberta and Regina. Using high-resolution core sampling, the overall goal of this particular study is to conduct a regional geochemical analysis of the Upper and Lower Bakken and to plausibly explain the apparent spatial and temporal variation in organic matter, source characteristics and hydrocarbon potential. Also provide an understanding of those conditions that led to the formation, accumulation and occurrence of organic matter within the Bakken shale. This study also seeks to identify and understand those processes and conditions that controlled the formation, preservation, alteration and ultimately the geochemical characteristics of the organic matter within the Bakken shale.

## **Method**

Drill core from 28 wells were selected for analysis based upon core availability, core recovery, the location of wells and the association with areas of proven hydrocarbon generation. High-resolution sampling was achieved by obtaining 20 to 25 g of sample from up to 30 sample sites throughout the Upper and Lower Bakken cored intervals within each well. Weathered material was initially removed from each sample, and the cleaned samples were subsequently pulverized for 10 seconds using a Tema mill to less than 105  $\mu\text{m}$ , homogenized and split into a number of sub-samples for analysis.

The evaluation of hydrocarbon potential and thermal maturity was achieved using Rock-Eval VI pyrolysis. Source extraction, to remove the extractable organic matter (i.e. bitumen), was carried out using the Soxhlet/soxtec extraction method and the extract fraction subsequently fractionated using column chromatography into hydrocarbon (saturate and aromatic) and non-hydrocarbon (e.g. nitrogen-, sulphur- and oxygen-bearing compounds) fractions. Further analysis was conducted using gas chromatography and gas chromatographic-mass spectrometry to investigate the distribution of molecular markers (biomarker) and other hydrocarbon compounds in the aliphatic and aromatic fractions. As

part of a source screening, an examination of the amount of total sulphur present in the sample was also examined using LECO Elemental Analyzer.

## Results and Discussion

The total organic carbon (wt% TOC) content for the Upper and Lower Bakken Formation is not constant throughout the cored intervals, but rather exhibits an extreme degree of variability with depth and across southern Saskatchewan. Results from this study clearly show a depth-wise and spatial variation in TOC that reflects the depth-wise and spatial variations in 'bitumen content' (S1), the amount of kerogen (as S2), associated Hydrogen Index, pyrite and total sulphur content within both the Upper and Lower Bakken shales ([Figure 1](#)). For example, within a given borehole the TOC can vary from ~24 wt.% to 1 wt.%.

This depth-wise pattern is mirrored in the yield of extractable organic matter (EOM), which is in agreement with the values for S1, showing a temporal variation in the proportion of saturate, aromatic and nitrogen-, sulphur-, and oxygen-bearing (NSO) compounds.

The relatively high proportion of NSO compounds within the EOM is consistent with the determined thermal maturation state, but may also reflect the incorporation of sulphur into the kerogen during diagenesis. This later interpretation is supported by the relatively high abundance of aryl isoprenoids, which are likely derived from the green sulphur bacteria Chlorobiaceae.

There is also a depth-wise variation in total sulphur, ranging from 1.3 wt% to 8.1 wt% for the Upper Bakken, and from ~0.25 wt% to typically 6.5 wt% for the Lower Bakken, with two samples showing a high total sulphur content of 13.0 wt%. Using conventional maturity parameters, the Type II kerogen would be considered relatively immature, however  $T_{max}$  shows a strong inverse relationship with total sulphur. The implication being that the presence of sulphur may influence the early generation of hydrocarbon at relatively low levels of thermal maturity (Orr, 1986).

A number of molecular fingerprints within the Upper and Lower Bakken were identified using saturate and aromatic biomarkers; Bacterivorous Ciliates synthesize tetrahymanol, which is the precursor compound of the biomarker gammacerane, and therefore a concentration of gammacerane within a given sample indicates the presence of anaerobic Bacterivorous Ciliates within, or just below the chemocline within the paleo-water column. In addition, the presence of abundant products of isorenieratene; 2,3,6-trimethyl aryl- and diaryl-isoprenoids, which are likely derived from green sulfur bacteria Chlorobiaceae, points towards a significant contribution of organic matter from anoxygenic, sulphide oxidizing phototrophic bacteria. Anoxygenic, sulphide oxidizing phototrophic bacteria exist both within the photic zone and below the chemocline, within the anoxic (euxinic) zone, as shown in [Figure 2](#).

A parallel petrographic study indicates that the geochemically defined Type II kerogen within the Upper and Lower Bakken shale is an assemblage of macerals generally dominated by the amorphous maceral Bituminite. For example, an Organic Facies dominated by Bituminite 'A' tends to have a relatively high abundance of aryl isoprenoids and Gammacerane although the concentration is variable depending on the chemical reactions taking place within the water column. Thus, indicating not only the presence of green sulphur bacteria Chlorobiaceae and anaerobic Bacterivorous Ciliates, but also clearly indicating that the anaerobic Bacterivorous Ciliates fed upon green sulphur bacteria within

the water column resulting in amorphous kerogen, since the organic matter associated with the sulphide-oxidizing phototrophic bacteria has been further reworked by these ciliates resulting in a structureless amorphous organic matter with no definitive morphology identified by petrographic analysis as Bituminite. The presence of gammacerane thereby acts as an indicator for stratified water column (Sinninghe Damsté et al., 1995) and isorenieratene is an indicator of photic zone anoxia (Summons and Powell, 1987; Koopmans et al., 1996). The presence/absence or variation in these biomarkers indicates either subtle variations in the depth of the photic zone and/or a variation in depth of the hydrogen sulphide (H<sub>2</sub>S) chemocline.

The presence of both isorenieratene, or its derivatives, and gammacerane not only strongly imply the presence of a stratified water column but also indicate that the chemocline occurred within the photic zone, as shown in [Figure 2](#). In contrast, a low concentration or absence of isorenieratene derivatives would signify a change in depth of the chemocline, since the presence of gammacerane alone, without isorenieratene, implies that the top of the euxinic zone (i.e. chemocline) was below the photic zone.

A high bacterial productivity within a stratified water column is also inferred because tetrahymanol is biosynthesized by the ciliates, when their diet is deprived of sterols. This is also consistent with the dominance of bacterially reworked amorphous kerogen within both Upper and Lower Bakken. This study also implies that the bacterial reworking of organic matter took place within the water column, since Bacterivorous Ciliates do not typically live within the sediment.

On the basis of a newly established framework, this study proposed a wide range of geochemical characteristics and molecular proxies within the Upper and Lower Bakken shale, that further enhance our understanding of variations in organic matter (i.e. kerogen) that occurs with the Upper and the Lower Bakken shale, the reconstruction of the paleodepositional setting, the distribution and relative abundance of molecular compounds as well as implications for hydrocarbon generation.

## **Conclusions**

The detailed high-resolution geochemical analysis of Bakken core in this study has shown that the Type II kerogen within the Upper and Lower Bakken is dominated by amorphous kerogen (Bituminite). This study has also identified key molecular ‘fingerprints’ and the existence of significant variation in aliphatic and aromatic biomarkers within the Upper and Lower Bakken shales. This study also documents the compositional differences in the Bakken shales with implication in regional variability in petroleum potential and hydrocarbon generation.

Broader implications of this study include support for a paleo-water depth during the Upper and Lower Bakken that is excess of the photic zone, a mechanism and process that explains the origin and composition of the amorphous organic matter within the Bakken, helps to explain the presence of high amounts of sulphur and pyrite within the shale and presents a challenge to the established notion that precursor organic matter is extensively reworked, and hence transformed into amorphous kerogen, within the sediment by sulphate-reducing bacteria.

## Acknowledgements

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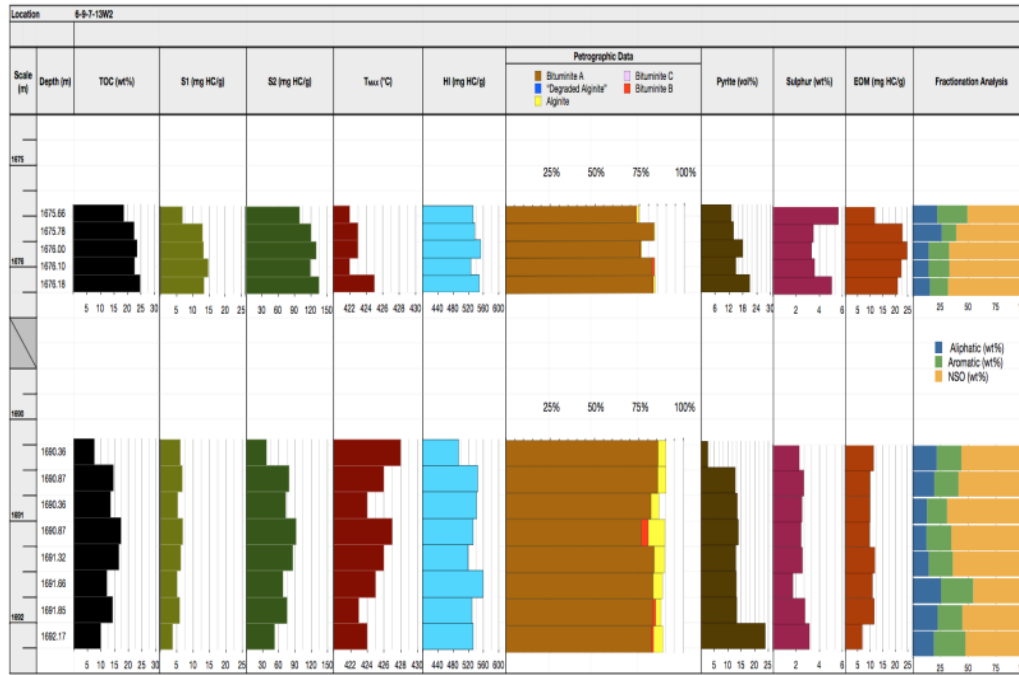
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6-9-7-13W2	Depth [m]	TOC (wt%)	S1 (mg HC/g)	S2 (mg HC/g)	Tmax (°C)	HI (mg HC/g)	Pyrite (wt%)	Sulphur (wt%)	EOM (mg HC/g)	Fractionation Analysis					
UBak	1675.06	12.6%	1.9%	1.4%	6.88	533	18.69	98.63	422	3.64	13.00	11.75	21.89	27.36	53.75
UBak	1675.78	12.6%	3.2%	0.6%	13.94	533	22.33	121.02	423	3.49	14.00	22.79	26.09	13.04	63.87
UBak	1676.02	7.2%	2.2%	0.6%	13.34	533	23.6	130.4	423	3.33	18.00	24.69	14.29	18.49	67.22
UBak	1676.10	11.3%	1.2%	0.4%	14.70	527	22.66	124.48	422	3.59	15.00	22.34	11.14	18.63	67.01
UBak	1676.18	10.2%	3.4%	0.7%	13.3	540	18.7	135.64	425	3.07	12.00	20.31	15.45	16.31	68.23
LBak	1680.30	10.6%	4.4%	0.4%	6.55	495	7.61	37.65	428	2.17	2.00	11.3	21.57	22.33	58.21
LBak	1680.67	10.6%	4.8%	0.4%	6.74	545	14.55	79.24	426	2.65	3.80	9.87	13.33	21.85	58.82
LBak	1681.32	11.6%	4.8%	0.4%	5.33	542	13.5	73.15	424	2.00	3.80	9.85	12.77	18.09	69.14
LBak	1681.66	10.4%	3.8%	0.4%	6.86	535	17.31	52.24	427	2.42	34.00	9.65	13.38	22.28	63.34
LBak	1681.85	10.4%	3.2%	0.2%	6.3	520	18.38	86.14	426	3.54	10.00	11.79	16.4	21.1	64
LBak	1682.17	10.2%	3.4%	0.4%	5.17	539	12.18	68.05	425	1.72	13.20	10.85	15.36	26.98	45.65
LBak	1682.40	12.6%	3.2%	0.2%	5.91	530	14.28	75.73	423	2.8	13.4	11.54	22.35	22.35	55.3
LBak	1682.71	12.2%	3.2%	0.4%	3.78	533	9.88	52.67	426	3.14	24.00	6.74	18.96	28.44	52.6

Figure 1. A depth profile for Valleyview et al. Weyburn 01/06-09-007-13W2M (85A089) showing a depth-wise variation in TOC, various Rock-Eval parameters, pyrite content, sulphur content and extractable organic matter ('bitumen') for the Lower and Upper Bakken. All analyses were conducted on core samples.

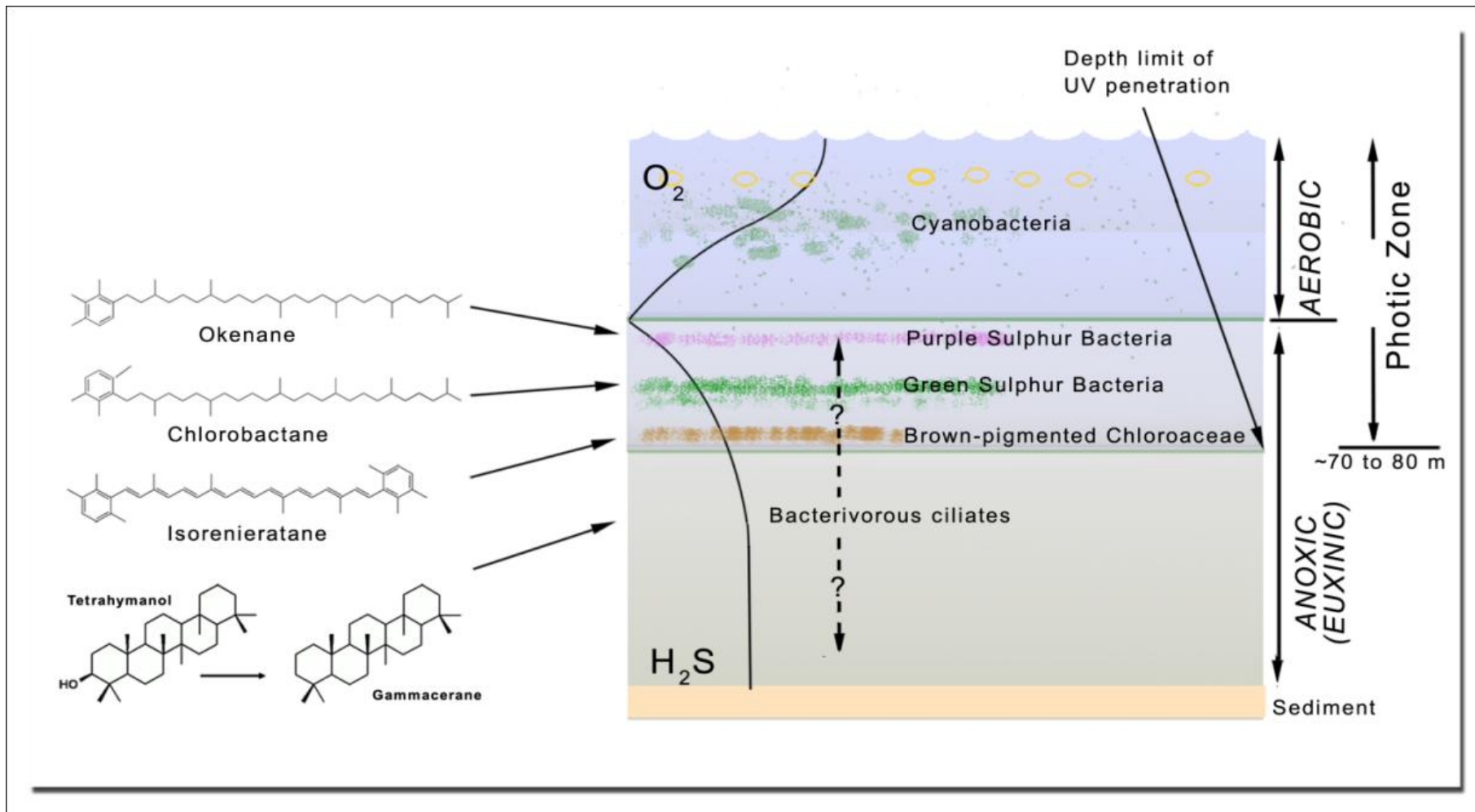


Figure 2. A proposed and generalized paleo-depositional environment for the Upper and Lower Bakken, showing the presence of a chemocline, the existence of euxinic conditions, various biological entities and their associated depth of occurrence and associated biomarkers.