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Laboratory Simulations of H_2S Generation in the Bakken Petroleum System

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Abstract

Hydrogen sulfide (H_2S) is an undesired by-product of oil and gas production in both conventional and unconventional plays. Its random occurrences in various locations of Bakken petroleum system (BPS) wells and secular variations in concentrations have been poorly understood by oil producers trying to minimize H_2S in their wells. The goal of this work was to provide insight into one of the potential mechanisms that caused H_2S generation in the BPS. This insight will enable more effective H_2S mitigation and management strategies. Many operators consider the Madison petroleum system as the primary source of H_2S, which is coproduced from the Bakken reservoir as a result of out-of-zone well completions into the Madison reservoirs. This work focuses on quantifying the H_2S generation potential of the Madison Group and Bakken Formation source rocks during the maturation process.

Organic-rich rock samples representing geographical areas with various levels of H_2S concentration in the Williston Basin of western North Dakota (Divide, Mackenzie, Dunn, and Bottineau Counties), stratigraphic units (Bakken and Madison), and a wide range of maturities were collected to investigate cracking of kerogen during source rock maturation as a possible mechanism of H_2S generation in the BPS. Analysis of the sulfur content and type using the Rock-Eval 7S method did not indicate elevated contents of total sulfur and total organic-linked sulfur in organic-rich rocks selected for this study, refuting an initial hypothesis of Type IIS kerogen presence in the BPS or the overlying Upper Lodgepole/Lower Mission Canyon source rock. In particular, the kerogen from the highest H_2S-producing areas of Divide County did not show an elevated total organic sulfur content in the Bakken Formation or Madison Group. However, obvious differences in these source rocks have been found in the 1) distributions of saturate biomarkers, 2) concentration of sulfur-containing benzothiophenes, and

3) contents of carbonate material and pyrite-linked sulfur.

Low- and high-temperature pyrolysis experiments of organic matter proved that the source rocks included in this work have immense potential to generate significant concentrations of H_2S via thermal breakdown. However, $\delta^{34}S$ of the pyrolysis gas did not match those measured in the H_2S in a sizable group of samples collected from producing BPS wells, suggesting that thermal cracking of the organic matter of the source rocks was not the only contributor to H_2S generation in the BPS. It is likely that the current presence of H_2S in the Bakken reservoir is due to other mechanisms of H_2S generation, such as thermochemical sulfate reduction (TSR) or/and chemical reactions triggered by injected well stimulation fluids.

Introduction

Geologic Setting

The Williston Basin's Bakken petroleum system (BPS) comprises the Late Devonian–Early Mississippian Bakken and Three Forks Formations (Figure 1). The Bakken Formation comprises four distinctive geologic rock units. From shallowest to deepest, those units are the Upper Bakken Shale (UBS), Middle Bakken (MB), Lower Bakken Shale (LBS), and Pronghorn Members. The UBS and LBS are the source rocks for the MB reservoir and are made up of black organic-rich, siliciclastic mudstones (shale) deposited within a restricted (reduced oxygen) offshore setting (LeFever et al., 2011; Egenhoff and Fishman, 2013; Borcovsky et al., 2017). The MB reservoir, which is sandwiched between the UBS and LBS, is a mixed carbonate–siliciclastic unit consisting mostly of siltstones. The basal Pronghorn Member ranges from distal mudstones to relatively more coarse-grained, proximal deposits (LeFever et al., 2011). The Three Forks Formation is the other primary oil reservoir in the BPS and consists of interbedded grayish-green dolomitic mudstones, pink to tan silty dolostones, and anhydrite (Bottjer et al., 2011).

Directly overlying the BPS is the Madison Group (Figure 1), a carbonate-dominated Mississippian section subdivided into three formations (in ascending order), the Lodgepole, Mission Canyon, and Charles Formations, which combine to reach a maximum thickness of over 730 m (2400 ft) (Murphy et al., 2009). The Lodgepole Formation comprises shallow to deep marine carbonates that are argillaceous in part (Petty, 2019, 2022).

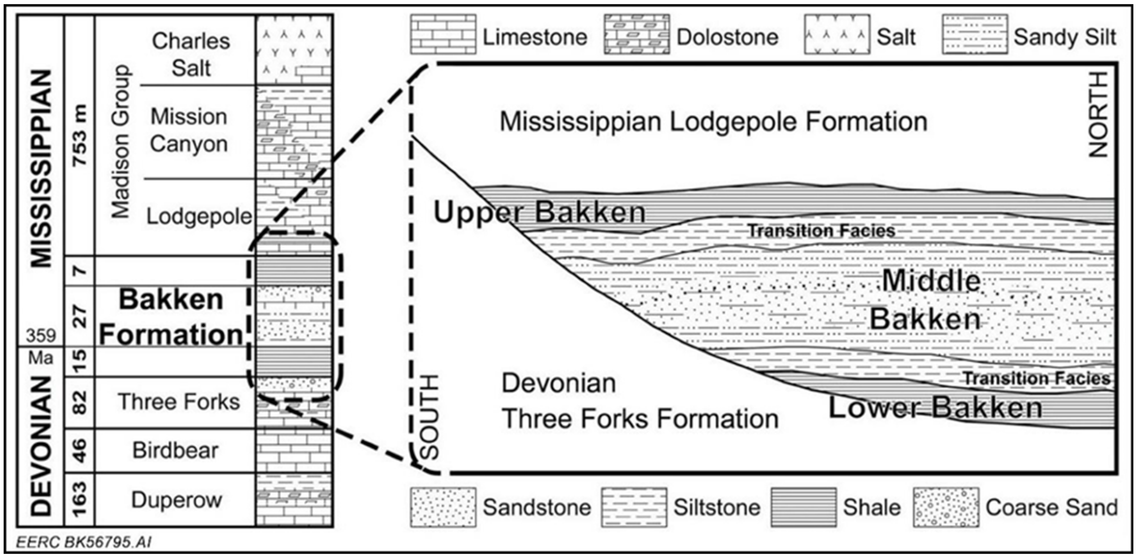

Figure 1. Stratigraphic column of the BPS and adjacent formations (adopted unchanged from Kuhn et al., 2010).

H_2S in Bakken Production

Crude oil produced from the BPS, including the Middle Bakken and Three Forks reservoirs, has historically been light (API gravity of 40º–50°) with low sulfur content (<0.2 wt.%), typically exhibiting nonexistent to low (<<0.1%) concentrations of H_2S in the production stream. However, the frequency of H_2S occurrences in Bakken wells has increased from the time that rapid development of the Bakken oil and gas play began about 12 years ago to the point where H_2S production from wells is becoming increasingly problematic for operators and midstream service providers. H_2S poses health and environmental risks, causes wellbore corrosion, and leads to additional costs related to materials handling and pipeline equipment. The goal of this study was to provide insight into one of the potential mechanisms of H_2S generation in the BPS, thereby enabling more effective H_2S mitigation and management strategies.

Multiple known mechanisms can potentially lead to the occurrence of H_2S in the production stream of oil and gas reservoirs. These mechanisms can be grouped into several broad categories, including thermogenic, biogenic, and geomechanical, related to reservoir stimulation work (Orr, 1986; Worden et al., 1995; Machel et al., 1995; Worden and Smalley, 1996; Mitchell et al., 2017; Badrouchi et al., 2019). Despite previous efforts (Holubnyak et al., 2011; Gaspar et al., 2016; Carvajal-Ortiz et al., 2021), the souring mechanisms in the BPS are poorly understood. Geochemical modeling performed by Holubnyak et al. (2011) showed that the H_2S-generating pyrite oxidation reaction was thermodynamically impossible at Bakken reservoir conditions; however, the methane/anhydrite reaction at a temperature of 120°C could be responsible for generation of H_2S. Based on S isotope composition, thermal regime analysis, and DNA analysis, Gaspar et al. (2016) excluded the bacterial mechanism of souring (BSR, bacterial sulfate reduction) and suggested a geochemical origin of H_2S in the BPS via thermochemical sulfate reduction (TSR). In addition, Carvajal-Ortiz et al. (2021) concluded that a considerable amount of organic sulfur in the Bakken kerogen is available to generate H_2S by aquathermolysis reactions.

Randomness of occurrences, unclear geographical and temporal trends, and the potential link of souring occurrences to recent well stimulation practices add complexity to data interpretation and understanding of H_2S generation mechanisms in the BPS. A common souring in oil and gas operations is caused by BSR. Due to the injection of large volumes of fracking fluid in the reservoir, BSR is considered one of the possible mechanisms of H_2S generation in the Bakken play. However, the biogenic mechanism of souring in a reservoir is questionable in the Bakken because of the high reservoir temperature (110°–150°C) and high salinity of the formation water (TDS > 200,000 mg/L), making bacteria growth difficult. The available evidence indicated that in some instances the higher rates of H_2S concentration appeared to be related to well location and associated geologic setting, although in certain locations, completion type and size of the stimulation job might have affected H_2S occurrences.

The present work was focused on a single geologic mechanism of H_2S generation by source rocks via thermal decomposition of organic matter. A higher content of incorporated S in organic matter (Type II-S kerogen) promotes earlier oil generation and expulsion from the source rock which may be accompanied by generation of significant volumes of H_2S (Orr, 1986, 2001; Baskin and Peters, 1992). It was hypothesized that 1) an elevated level of H_2S in Bakken wells is likely linked to the coproduction of fluids and gases as a result of out-of-zone completion practices connecting Middle Bakken/Three Forks and other overlying or underlying reservoirs, especially in the areas where the Bakken Formation thins and 2) H_2S was generated by the Type II-S kerogen (Orr, 1986) present in the area, with $S/C > 0.04$.

An important question arises about the particular source (organic-rich formation) of H_2S in reservoirs that are thought to be in communication with the Bakken and factors favorable to H_2S generation. Oil generated from the BPS and the corresponding organic matter within the BPS source rocks (i.e., UBS and LBS) were never considered sulfur-rich; therefore, it was assumed that the petroleum system they constitute was less likely to produce significant concentrations of H_2S during oil generation. Underlying the main producing reservoirs of the Middle Bakken and Three Forks Formations is the Devonian-age

Birdbear Formation. Identified organic-rich intervals within the Birdbear are characterized by thermally mature Type II kerogen (Bader et al., 2019; Nwachukwu et al., 2019), which is also low in sulfur content. Unlike oils derived from the BPS, the oils produced from the overlying Madison Group typically have a high sulfur content (Brooks et al., 1987; Osadetz et al., 1992, 1994; Price and LeFever, 1994; Jarvie, 2001; Gaswirth et al., 2010; Lillis, 2012; Nesheim, 2021), which ranges from 0.2 to 3.6 wt%. Furthermore, sulfur-rich oils are found in Mission Canyon reservoirs east of the Nesson Anticline and in the Lodgepole, Mission Canyon, and Charles Formations in the Canadian part of the Williston Basin (Lillis, 2012). These sour oils indicate another source rock facies hypothetically capable of generating significant volumes of H_2S in the Williston Basin. Considering the above characteristics of the Madison Group, it was suggested in this study that in the areas of high H_2S concentration in Bakken production streams, organic-rich intervals overlying the Bakken Formation are characterized by an elevated sulfur content. These source rocks contain Type II-S kerogen capable of generating H_2S that charged the reservoirs above and possibly below.

To evaluate the proposed mechanisms of H_2S generation during maturation of the source rocks, sulfur content in both organic matter and inorganic matrix was measured in the Madison and Bakken Formations using Rock-Eval 7S and compared to published numbers for the typical Type II-S kerogens. Sulfur aromatic compounds (SACs) and saturate biomarker distributions in solvent extracts of the source rocks were analyzed to understand depositional environment, organic matter source, and source rock lithology. Closed system low-temperature and open system high-temperature pyrolysis experiments with Bakken and Madison source rocks were conducted to evaluate their H_2S generation capacity, and S isotope composition was used to correlate pyrolysis and well-produced H_2S.

Samples

A sampling program was developed to achieve two main goals: 1) investigate areas with various levels of souring of oil production and 2) evaluate multiple organic-rich formations representing potential source rocks for Bakken oil production: the UBS and LBS, Lower Lodgepole (LLP), and Mission Canyon (MC), characterized by different lithologies and maturity levels (Figures 1 and 2).

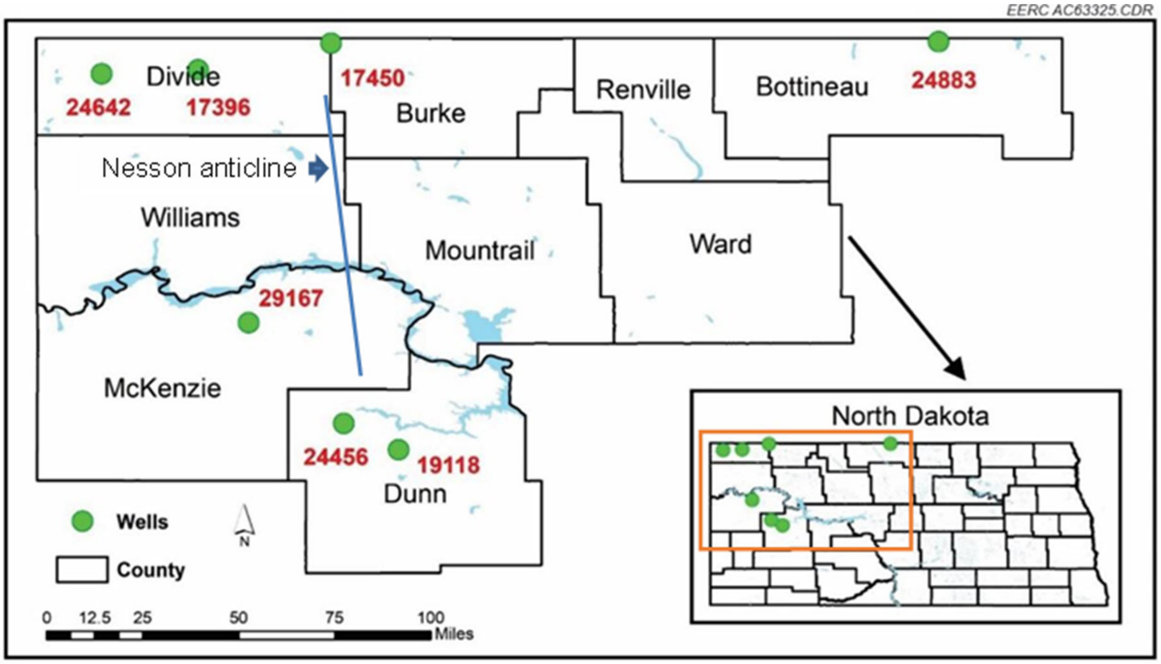

Figure 2. Sample location map of the Williston Basin, North Dakota.

Samples were collected in areas of frequent occurrences and exceedingly high concentrations (>1000 ppm) of H_2S in oil-producing wells such as Divide County in North Dakota. Areas with much lower levels of souring were represented by samples from McKenzie and Dunn Counties. An immature sample of Bakken shale was collected in Bottineau County for low- and high-temperature pyrolysis experiments. In total, thirty-one (31) source rock samples were selected for the purpose of this study and obtained from the Wilson M. Laird Core and Sample Library at the University of North Dakota (Table 1). Additionally, H_2S samples were collected using IsoTraps^{TM} at 30 wellsites at various locations of the Bakken play for sulfur isotope characterization.

Experimental

Sulfur Speciation Work Using Rock-Eval 7S

H_2S generation capacity of source rocks depends on the sulfur content in the organic matter, especially in its reactive part, which can be readily decomposed by thermal stress. To understand sulfur distributions in both organic and inorganic components of the source rocks and evaluate H_2S generation capacity related to kerogen thermal cracking, thirty (30) samples of source rocks representing Divide and non-Divide County locations were characterized geochemically using a Rock-Eval 7S.

Sulfur speciation work was performed using a Rock-Eval 7S analyzer (Vinci Technologies, France), which operates using open-system programmed pyrolysis and oxidation. The basic/total sulfur method was used to measure both organic and inorganic sulfur on 50 mg of crushed rocks described in the publications of Wattripont et al. (2018), Aboussou et al. (2018), and Carvajal-Ortiz et al. (2021). The results of the analysis include standard Rock-Eval parameters characterizing generation potential and maturity of source rocks such as S1, S2, T_{max}, hydrocarbon generation potential (HI), oxygen index (OI), and others. In addition, the method measures total sulfur (TS), total organic sulfur (TOS), and sulfur index (SI) and quantifies pyritic sulfur (FeS_2).

GC–FID and GC–MS of Extracts

An Agilent GC–FID (gas chromatography–flame ionization detector) was used to screen the results of the extraction work and provide detailed C_5–C_{35} hydrocarbon distribution in rock extracts. Injections were performed using the split mode into an Agilent HP-5 60-m × 0.25-mm-i.d. (0.25-µm film thickness) capillary column. The temperature program was 40°C (hold for 10 min) followed by a temperature ramp of 3°C/min to a final temperature of 325°C (hold for 20 min). For the biomarker analysis, the Agilent GC–MS (mass spectrometer) was used to analyze samples in selected ion-monitoring (SIM) mode. Extracts and/or fractions separated on open column were injected in the split mode into an Agilent DB-5 60-m × 0.25-mm-i.d. (0.25-µm film thickness) capillary column. The temperature program was 40°C (hold for 4 min), with a temperature ramp at 4°C/min up to 325°C (hold for 20 min).

Biomarker identification and geochemical ratio interpretations were done based on the guidance and case studies provided in Curiale (1994) and Peters et al. (2005).

Pyrolysis Experiment to Evaluate H_2S Generation Potential

To semiquantitatively evaluate source rock potential to generate H_2S under thermal stress, two separate pyrolysis experiments in open and closed systems were conducted on immature Bakken source rocks. The experimental setups were based on the principles reported in the earlier publications of Tomi et al. (1995), Behar et al. (1995, 1997), and Koopmans et al. (1998) and more recent examples of pyrolysis experiments in combination with ^{34}S isotope measurements of generated H_2S (Amrani et al., 2006, 2019; He et al., 2022). Both simulations of H_2S generation used the immature LBS sample collected

Table 1. Rock-Eval 7S Data for the Source Rock Samples Used in the Study

NDIC well ID	Formation	EERC Sample ID	Divide County	Depth, ft	TOC, wt%	TS, wt%	TOS, wt%	Fe-S, wt%	Sulfate-S, wt%	TIS, wt%	S2-Sorg, wt%	TIC, wt%	S1, mg HC/g	S2, mg HC/g	S3, mg CO2/g	Tmax, ˚ C	SI, PySorgx1000/TOC	HI, S2x100/TOC	OI, S3x100/TOC	PI, S1/(S1+S2)	OSI, S1x100/TOC	Oil in Rock, bbl oil/ac-ft	H2S, ppm	H2S, µg/g rock	$\delta^{34}S$
17450	Lower Lodgepole	131381	YES	7324.5	13.96	2	1.05	0.44	0.5	0.94	0.34	2.19	3.91	69.19	0.14	436	25	496	1	0	28	86	909	1.5	-11
17450	Lower Lodgepole	131382	YES	7325	11.21	2.01	0.57	0.4	1.04	1.44	0.28	5.44	3.46	59.54	0.17	439	25	531	2	0	31	76	601	0.98	-19.9
17450	Upper Bakken Shale	131384	YES	7337.75	14.35	2.11	0.9	0.86	0.35	1.21	0.2	0.55	4.92	58.85	0.27	433	15	410	2	0	34	108	550	0.91	-23.3
17450	Upper Bakken Shale	131403	YES	7343.75	20.34	3.28	1.68	1.29	0.32	1.61	0.48	0.15	5.82	80.7	0.58	436	24	397	3	0	29	127	2201	3.6	-21.5
17396	Lodgepole/Mission Canyon	131373	YES	7886.25	4.12	1	0	0	0.41	0.41	0.17	8.36	1.82	7.53	0.11	440	0	183	3	0	44	40	297	0.48	-9.4
17396	Lodgepole/Mission Canyon	131370	YES	7897.25	5.69	0.94	0	0	0.4	0.4	0.09	7.98	1.25	10.94	0.38	442	0	192	7	0	22	27	208	0.34	-2.7
17396	Lodgepole/Mission Canyon	131372	YES	7917.75	4.54	1.21	0.26	0.55	0.39	0.94	0.07	7.47	1.43	8.47	0.62	434	18	187	14	0	31	31	1130	1.86	-1.6
17396	Lodgepole/Mission Canyon	131376	YES	7929	3.07	0.84	0	0	0.45	0.45	0.03	10.74	1.81	5.7	0.04	441	0	186	1	0	59	40	129	0.21	2.4
17396	Lodgepole/Mission Canyon	131379	YES	7936.5	5.17	0.89	0.37	0.1	0.42	0.52	0.06	8.92	1.85	10.99	0.11	440	15	213	2	0	36	40	422	0.7	-1.4
17396	Lodgepole/Mission Canyon	131371	YES	7938.5	5.7	0.82	0.42	0.08	0.32	0.4	0.1	8.68	1.73	12.55	0.04	442	14	220	1	0	30	38	261	0.42	3.5
17396	Lodgepole/Mission Canyon	131380	YES	7941.5	12.02	1.24	0.56	0.26	0.42	0.68	0.24	6.51	2.83	32.41	0.08	441	22	270	1	0	24	62	420	0.68	6.4
24642	Lower Lodgepole	131400	YES	8191.75	10.42	2.11	1.04	0.76	0.3	1.06	0.37	3.05	3.17	61.54	0.09	435	36	591	1	0	30	69	1390	2.3	-13.7
24642	Lower Lodgepole	131401	YES	8192	12.77	1.9	0.79	0.48	0.64	1.12	0.13	2.77	0.19	30.95	4.61	430	11	242	36	0	1	4	1008	1.63	-10.5
24642	Lower Bakken Shale	131411	YES	8273.3	16.49	2.4	1.14	1.1	0.16	1.26	0.5	0.21	7.07	90.38	1.31	429	31	548	8	0	43	155	1600	2.66	-22.3
24642	Lower Bakken Shale	131413	YES	8282.5	16.53	2.45	1.26	1.07	0.12	1.19	0.58	0.12	7.87	85.72	0.4	429	36	519	2	0	48	172	1773	2.86	-23.1
24642	Lower Bakken Shale	131414	YES	8292	15.88	2.67	1.39	0.9	0.38	1.28	0.42	0.26	7.63	76.69	0.6	430	27	483	4	0	48	167	1671	2.74	-14
19118	Lower Lodgepole	131387	NO	10796.25	10.08	1.91	0.96	0.79	0.16	0.95	0.1	1.48	3.72	34.28	0.15	443	10	340	1	0	37	81	1027	1.7	-7.4
19118	Lower Lodgepole	131389	NO	10797.5	2.81	1.93	0.15	1.08	0.7	1.78	0.03	3.84	1.38	6.33	0.03	440	11	225	1	0	49	30	224	0.36	-15.5
19118	Upper Bakken Shale	131390	NO	10813.3	10.47	2.94	1.48	0.81	0.66	1.47	0.37	0.22	4.19	31.46	0.21	443	35	300	2	0	40	92	445	0.72	-10.9
19118	Lower Bakken Shale	131404	NO	10875	11.83	2.51	0.95	1.13	0.44	1.57	0.28	0.2	5.32	33.24	0.35	440	25	281	3	0	45	116	1327	2.17	-20.5
19118	Lower Bakken Shale	131406	NO	10886.5	11.69	1.78	0.82	0.65	0.31	0.96	0.2	0.17	4.84	34.6	0.57	440	18	296	5	0	41	106	874	1.42	-17.3
24456	Lower Lodgepole	131392	NO	11056.2	5.36	1.58	0.57	0.8	0.21	1.01	0.08	3.05	2.76	9.84	0.55	445	19	184	10	0	51	60	481	0.78	-3.9
24456	Lower Lodgepole	131394	NO	11059	2.36	1.3	0.17	0.83	0.3	1.13	0.03	0.52	2.43	3.5	0.22	441	17	148	9	0	103	53	669	1.1	-11
24456	Lower Lodgepole	131395	NO	11060	9.56	1.59	0.67	0.76	0.16	0.92	0.1	1.2	4.77	22.25	0.27	445	10	233	3	0	50	104	765	1.26	-7.5
24456	Upper Bakken Shale	131398	NO	11074.25	12.01	2.16	0.83	1.16	0.17	1.33	0.13	0.13	4.84	25.34	0.14	444	12	211	1	0	40	106	1062	1.73	-21.4
24456	Upper Bakken Shale	131399	NO	11075	11.97	2.1	0.89	1.06	0.15	1.21	0.15	0.14	5.11	25.78	0.35	444	13	215	3	0	43	112	1912	3.12	-19.3
24456	Lower Bakken Shale	131409	NO	11136.5	12.06	2.08	0.79	1.01	0.27	1.28	0.14	0.16	5.39	24.48	0.34	445	12	203	3	0	45	118	1412	2.31	-19.4
24456	Lower Bakken Shale	131410	NO	11138.5	14.43	2.13	0.47	1.39	0.27	1.66	0.19	0.09	6.17	29.13	0.43	442	14	202	3	0	43	135	2642	4.37	-23.9
29167	Upper Bakken Shale	128473	NO	11087.8	12.06	1.84	0.76	0.95	0.13	1.08	0.09	0.21	7.06	16.18	0.33	451	8	134	3	0	59	155	584	0.96	-17
29167	Lower Bakken Shale	128482	NO	11156.5	11.5	1.97	0.95	0.88	0.15	1.03	0.08	0.36	4.31	13.3	0.43	454	8	116	4	0	37	94	430	0.7	-22
24883	Lower Bakken Shale	131784	NO	3779	15	4.15	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	414	n/d	618	n/d	n/d	n/d	n/d	3111	5.05	-11.8

Sample location: Inside Divide County – YES, Outside Divide County – NO; TOC – total organic carbon wt%, TS – total sulfur, wt%; TOS – total organic sulfur, wt%; Fe-S – pyrite-linked sulfur, wt%; sulfate-S – sulfate-linked sulfur, wt%; TIC – total inorganic carbon, wt%; S1 – Peak S1, mg of hydrocarbons/g of rock; S2 – Peak S_2, mg of hydrocarbons/g of rock; S3 – Peak S3, mg of CO_2/g of rock; T_{max} – T_{max} of Peak S2, °C; SI – sulfur index, sulfur organic ×1000/TOC; HI – hydrogen index, Peak S2×100/TOC; OI – Peak S3×100/TOC; PI – production index, S1/(S1+S2); OSI – oil saturation index, Peak S1×100/TOC; H_2S, ppm – concentration of H_2S in mixture of gases collected in a plastic bag as a result of high temperature/open system pyrolysis experiment; H_2S mg/g rock – yield of H_2S in microgram per gram of rock in high-temperature pyrolysis experiment, $\delta^{34}S$, ‰ – isotope composition of S in pyrolysis H_2S.

from the 2-Brenden, 9-3 1-M well. In the first experiment, 400 mg of crushed rock was rapidly heated from room temperature to 550°C in inert gas (argon) flow for 14 min. The pyrolysis setup included a quartz pipe with the rock sample trapped inside with the help of glass wool. The pipe with sample was moved inside of the heating element during almost instant pyrolysis. Constant gas (argon) flow through the quartz pipe with the sample 1) transported vaporized products of pyrolysis to the connected in-line portable gaschromatograph measuring the concentration of H_2S in the gas flow in real time or 2) collected vaporized products of pyrolysis in a plastic 1-L bag for measuring the concentration of collected H_2S and other gases on a different GC system or 3) connected them with the IsoTrap tube for the sulfur isotope analysis.

A second pyrolysis test was conducted at a lower temperature but for a longer duration than the first experiment and in the presence of 2 g deionized (DI) water in a closed system. The same Bakken immature shale (1000 mg of crushed rock) was placed in a Hastelloy tube reactor for 48 hr at a temperature of 350°C and a pressure of 1500 psi. After the temperature of the reactors were lowered to 150°C, the gas products of pyrolysis were 1) transferred to a plastic bag for gas compositional analysis using the GC system and 2) pushed through the IsoTrap tube to capture H_2S for the sulfur isotope analysis. A second low-temperature hydrous pyrolysis experiment was conducted to validate high-temperature flash pyrolysis results in terms of total H_2S yield and isotope composition of sulfur.

Sulfur Isotope Analysis by EA–IRMS

IsoTrap tubes with chemically captured H_2S were opened, and the powder containing the reacted H_2S was removed for analysis. Sulfur isotope analysis measuring $^{34}S/^{32}S$ ratio was performed at the Isotech (Stratum Reservoir Company) facility using a Carlo Erba EA1108 elemental analyzer (EA) interfaced with a Thermo Delta V Plus isotope ratio mass spectrometer (IRMS).

Results and Interpretations

Sulfur Speciation in Source Rocks Using Rock-Eval 7S

The details for each sample and Rock-Eval results are shown in Table 1, and their geographic locations are shown in Figure 2. The data for the Bakken and Madison (Lower MC [LMC] and LLP Formations) source rocks plotted in Figure 3 demonstrated a typical marine Type II kerogen trend for the HI relationship with T_{max}. The maturity levels of 30 samples (except one immature Bakken rock) were in the range from upper oil window to peak oil window, as indicated by T_{max} = 429°–455°C. With increasing thermal maturity, the HI dropped from about 600 to 120 mg/g TOC.

All samples selected for this study had a high organic carbon content ranging from 2.4 to 20.3 wt%, with an average value of 10.4 wt%. The highest TOC content was found in UBS rocks (10.5–20.3 wt%) and LBS rocks (11.5–16.5 wt%) followed by LLP rocks (2.4–14.0 wt%), while the upper LP (ULP)/LMC source rocks (3.1–12 wt%) have the lowest TOC values.

In some source rock samples, TOS showed a positive correlation with total inorganic sulfur (TIS); in others, especially those rich in iron-linked sulfur, the correlation was absent (Figure 4A). TOS varied from very low (undetectable values) to 1.7 wt% and showed a strong positive correlation with TOC (Figure 4B). The average value of the organic sulfur in samples included in this study (0.74 wt%) was lower than that reported for the UBS and LBS (average value of 1.9 wt%) by Carvajal-Ortiz et al. (2021). This result can be explained by the fact that some samples in the Carvajal- Ortiz et al. (2021) study included rocks richer in organic matter content and generation potential, having higher TOC (2.4%–23.4 wt% and average = 13.8 wt%) and HI values (32–946 and average = 396 mg/g TOC). Sulfur index (mg of S/g TOC) was an additional bulk parameter used to characterize organic sulfur distribution in the source rocks selected for this study, which were compared to the source rocks containing Type II-S

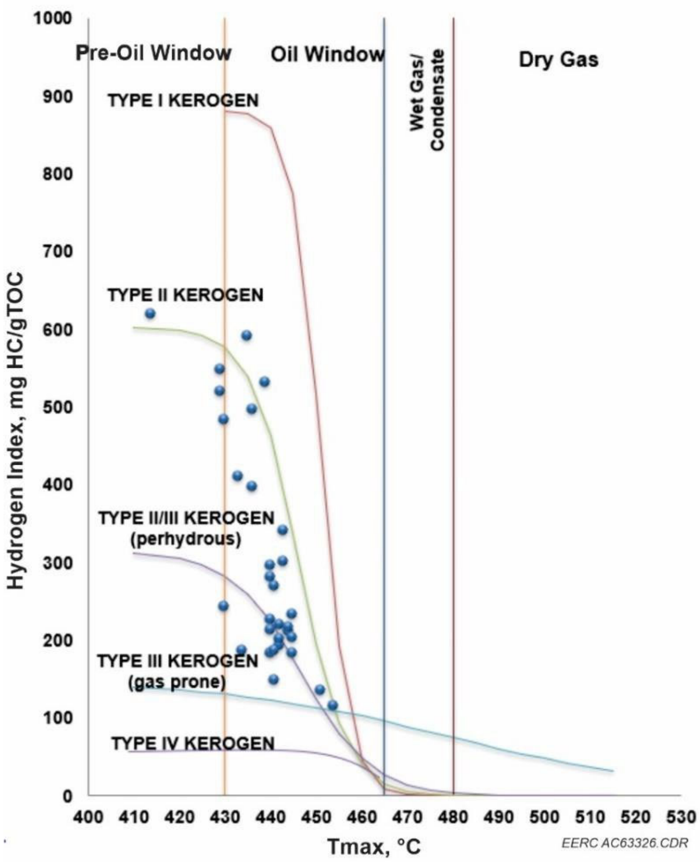

Figure 3. HI vs. T_{max} demonstrating typical trends for marine Type II kerogen in the BPS.

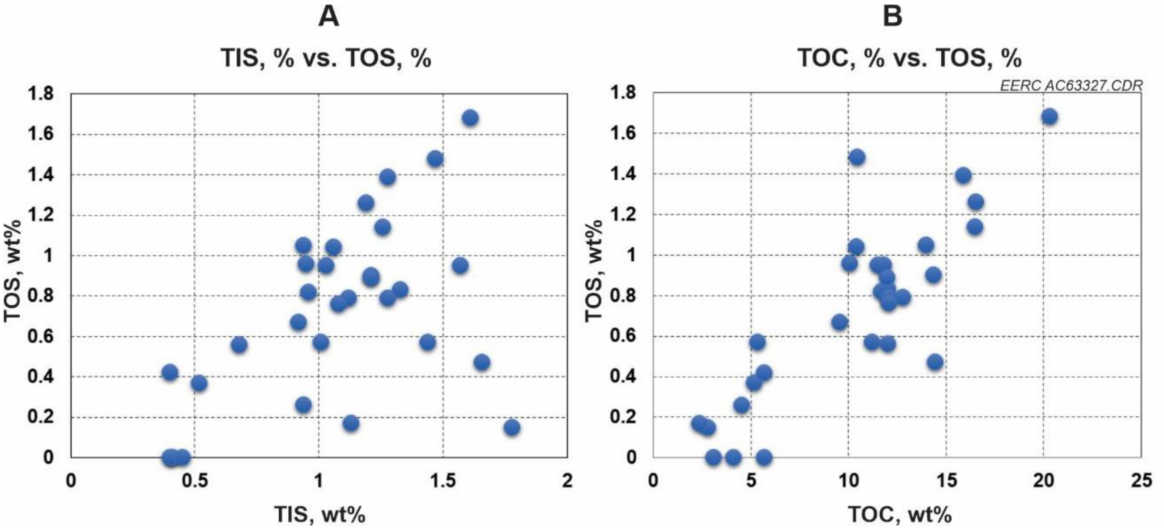

Figure 4. From Rock-Eval 7S tests: A) inconsistent correlation of TOS with TIS and B) TIS correlates with TOC in 30 source rock samples.

kerogen reported in Carvajal-Ortiz et al. (2021) (Figure 5). All organic-rich samples selected for this work had relatively low SI values in the range from 0 to 36, with an average value of 17 (averages: ULP/LMC = 9.8, LLP = 18.2, UBS = 17.8, and LBS = 21.2). These numbers are consistent with the SI values (SI average = 15) in the BPS reported by Carvajal-Ortiz et al. (2021) and are much lower than the threshold

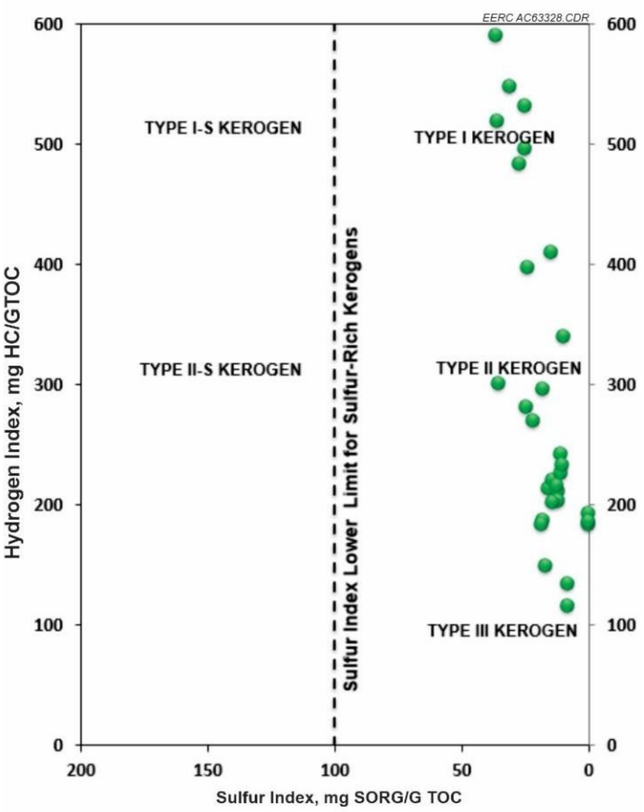

Figure 5. Sulfur index values in organic-rich rock samples selected for this study.

value of the sulfur-rich kerogen (Type I-S and Type II-S). Surprisingly, the samples from Divide County—the county with the greatest H_2S production—did not demonstrate elevated SI values, and the Madison source rocks were consistent with Bakken organic-rich intervals in terms of organic sulfur content evaluated using TOS and SI. These observations did not support our initial hypothesis of existing Type II-S kerogen in the Madison group being responsible for the generation of significant volumes of produced H_2S from Bakken laterals.

Nevertheless, other Rock-Eval 7S parameters revealed interesting results when Bakken and Madison source rocks were compared based on TIC and sulfur linked to pyrite (Fe-S) (Table 1). As expected, clay material-dominated Bakken shales showed very low inorganic carbon (<0.5 wt%), whereas the LLP and Upper Lodgepole (ULP)/LMC intervals had average values of 2.6 wt% and 8.3 wt%, respectively. The Fe-S content was proportionally asymmetric to TIC, with the highest values of Fe-S found in Bakken shales (average = 1 wt%) and the lowest average values of 0.7 wt% and 0.1 wt% in the LLP and ULP/LMC, respectively. Carbonate rocks of the ULP/LMC section are poor in clay material and available iron, which can scavenge sulfur in H_2S to form pyrite. In contrast, clay-rich Bakken source rocks contain abundant iron to scavenge sulfur and form pyrite which was detected by Rock-Eval 7S. X-ray diffraction (XRD) analysis of these rocks might confirm this more rigorously. Because of the mixed lithology and presence of some clay material, the LLP occupies an intermediate position between pyrite-rich Bakken and pyrite-poor ULP/LMC rocks. This negative correlation between carbonate content and the presence of Fe-S can potentially explain the significant concentrations of free H_2S in carbonate-dominated, thermally mature sediments because of the lack of available iron, which can scavenge H_2S-linked sulfur and form pyrite (Tissot and Welte, 1984). Stated differently, the highly reactive H_2S generated in carbonates has a higher chance of being expelled from the source rock and mixed with hydrocarbons because of a lack of available iron in the system to react with the H_2S to form pyrite.

Distribution of Sulfur Aromatic Compounds in Source Rocks

The distribution of SACs in source rock extracts, including dibenzothiophene (DBT) and methyldibenzothiophene (MDBT), sheds additional light on the presence of sulfur in the organic molecules of Bakken and Madison source rocks from different lithologies and geographic locations. The relative concentration of SACs was evaluated using ratios of DBT and phenanthrenes (Phen). Figure 6 shows a ratio–ratio crossplot of DBT/Phen and 4-methylDBT/3-methylPhen in LBS and UBS, LLP, and MC rock extracts grouped by two locations (H_2S-rich Divide County and outside of Divide County). The DBT content within the organic-rich intervals of the two petroleum systems in Divide County was higher than those outside of Divide County, regardless of source rock association. In addition, the MC rocks showed the highest content of SACs, significantly exceeding SAC relative concentrations in the LLP and UBS/LBS. The high content of SACs in Divide County and especially in MC rocks might relate to the prevailing carbonate lithology and potentially highly anoxic depositional environment, which support preservation of sulfur in the petroleum system and incorporation of sulfur in organic molecules during diagenesis (Hughes, 1984; Hughes et al., 1995; Chakhmakhchev and Suzuki, 1995; Jiang and Li, 2002).

Distribution of Saturate Biomarkers in Source Rocks

The biomarker analysis completed on source rock extracts demonstrated a strong dependency of sterane and hopane distributions on the lithology of the source rocks. These results are consistent with previous observations of biomarker signatures in petroleum systems of the Madison Group and the Bakken (Williams, 1974; Dow, 1974; Osadetz et al., 1992, 1994; Zumberge, 1983; Price and LeFever, 1992, 1994; Osadetz and Snowdown, 1995; Obermajer et al., 2000; Jarvie, 2001; Jiang and Li, 2002; Stroud and Sonnenberg, 2011; Lillis, 2012; Zumberge et al., 2013; Jarvie et al., 2016; Nesheim, 2021). Rock extracts of the ULP/LMC showed specific markers or indicators of carbonate lithology, including 1) the absence of diasteranes, 2) $C_{29} > C_{30}$ hopane, 3) $C_{35} > C_{34}$ homohopane, 4) abundant C_{24}-tetracyclic terpane, 5) abundant gammacerane, and 6) Pr/Ph < 1 (Table 1). The biomarker distribution in the ULP/LMC indicates the following: 1) a lack of clay materials in source rock lithology; 2) on average, a lower maturity level in comparison to Bakken shales based on sterane 20S/20+20R ratio in the range from 0.43 to 0.51 (upper oil window); 3) a marine algae source of organic matter; and 4) a high level of anoxia in the depositional environment.

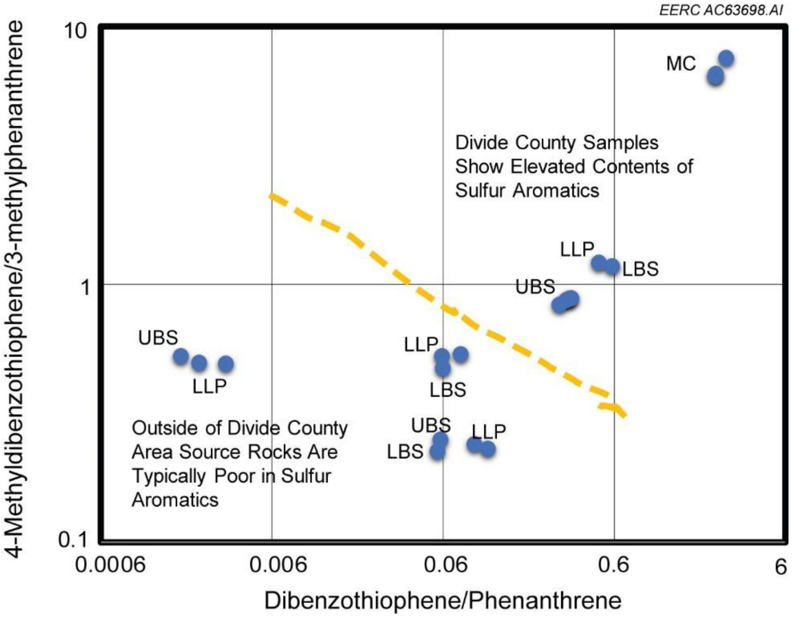

Figure 6. Ratios of sulfur aromatic compounds (DBT) and Phen in LBS and UBS, LLP, and MC showing dependencies on carbonate content in Divide County and other locations.

The source rock of the LLP and UBS/LBS demonstrated similar biomarker distributions, suggesting a predominantly shaley source with abundant clay material. Diasteranes were present, the maturity level varied from an upper oil window to a peak oil window (20S/20 + 20R = 0.45–0.56), and these source rocks were deposited in anoxic conditions ($1 < Pr/Ph < 2$), with predominantly a marine algae organic matter source. As discussed in a previous section, LLP had much lower concentrations of SACs.

Compositionally, the extracts of the LLP and Bakken shales rocks were remarkably similar; however, variable carbonate content in the LLP results in occasional deviations in biomarker distributions toward the ULP/LMC type of signature (Table 1).

Pyrolysis Experiments Evaluating Bakken Source Rock Capacity to Generate H_2S and $\delta^{34}S$ Signature of Pyrolysis H_2S

Two independent semiquantitative pyrolysis experiments were conducted to answer the following questions: Can source rocks in the Williston Basin generate H_2S or, stated differently, can thermal decomposition of the kerogen in a lab simulation produce H_2S? What levels of H_2S concentration can various source rocks produce? and Do experimental conditions such as temperature and duration affect the produced volumes of H_2S or/and sulfur isotope composition?

The results of the first high-temperature, anhydrous in-line pyrolysis of the immature LBS (400 mg) are shown in Figure 7. H_2S generation began almost instantaneously once the sample was moved into the heated zone and exposed to 550°C. Maximum H_2S generation occurred within about a minute, followed by a rapid drop in intensity. The in-line GC system detected a maximum concentration of H_2S in the argon (flow gas) mix of about 1250 ppm H_2S. The actual concentration of the H_2S would be two magnitudes higher once argon is removed from the system. The relative composition of the generated gas mixture is shown in Figure 7. H_2S relative concentration was detected at a level of about 5%, and sulfur isotope composition expressed as $\delta^{34}S$ was measured in duplicate pyrolysis experiments at –10.9‰ and –11.8‰.

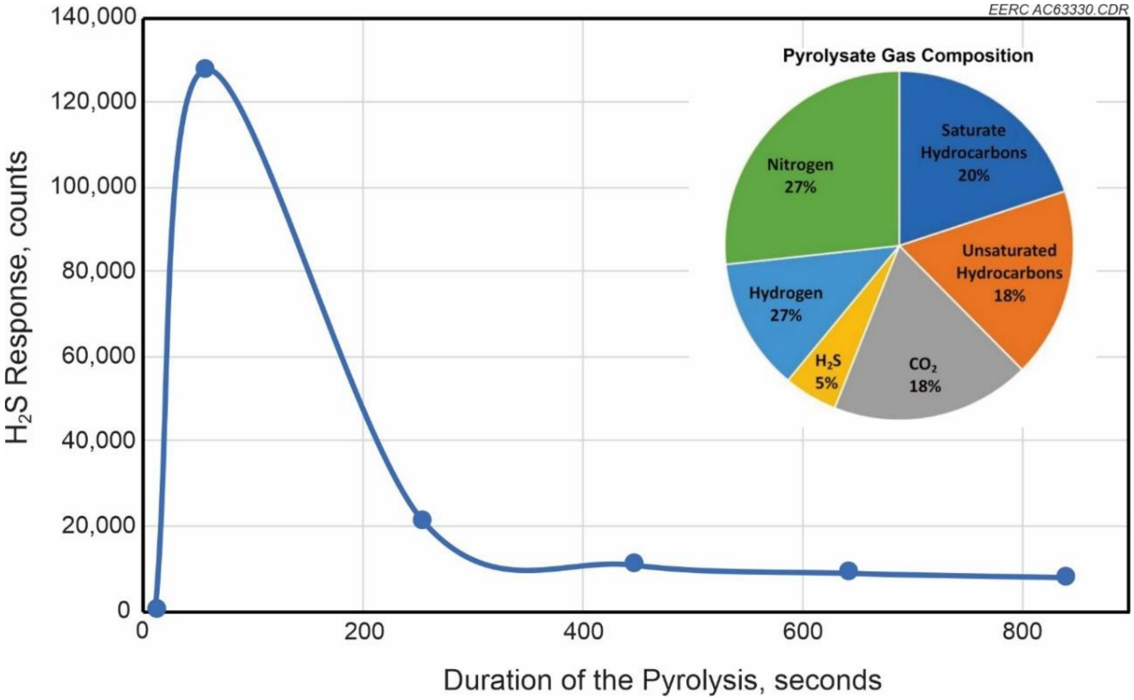

Figure 7. Yield of H_2S during the anhydrous pyrolysis experiment, T = 550°C, 400 mg immature LBS and gas composition of pyrolysate.

The second pyrolysis experiment on the same immature Bakken sample (1000 mg) was conducted at a lower temperature of 350°C with a much longer duration of 48 hr in the pressurized reactor (at 1500 psi) and in the presence of DI water. The generated gas was analyzed using GC to evaluate H_2S concentration and captured for the S isotope analysis. The process of gas transfer from the pyrolysis vessel to the GC inlet port required the use of argon and pyrolysis gas. Because of the dilution with argon, precise measurement of H_2S concentration was not possible. In the argon mixture, the concentration of H_2S was measured at the 2300-ppm level, which is in line with the results of the first high-temperature pyrolysis experiment. Also, $\delta^{34}S$ of H_2S from the low-temperature pyrolysis of immature Bakken shale was measured at –9.7‰, which is close to the –10.9‰ and –11.8‰ values measured in H_2S of the high-temperature duplicate experiments. In summary, both low- and high-temperature pyrolysis experiments on the immature Bakken shale samples generated H_2S in significant concentrations of thousands of ppm (measured semiquantitatively). All further measurements of H_2S generation capacity of various source rocks and isotope composition of S in H_2S were done using high-temperature, open-system pyrolysis with collection of pyrolysate in 1-L Cali5Bond plastic bags or flowing gas through the IsoTrap tubes, as described earlier.

In the high-temperature pyrolysis experiments, H_2S amounts generated by the MC, LLP, and UBS/LBS source rock samples were detected at various concentrations and had distinguishable ranges of isotope signatures ($\delta^{34}S$). This analysis showed that H_2S yields depended on 1) total organic richness of the source rocks (TOC), 2) their hydrocarbon generation potential (HI), and 3) total sulfur content (S, wt%), as shown in Exhibits A, B, and C of Figure 8. The experiments demonstrated that UBS/LBS samples had the highest H_2S generation potential, followed by the LLP and MC (Figures 8, 9).

More recent studies by Cai et al. (2010), Hofmann et al. (2017), Bilkiewicz and Kowalski (2020), and Kutuzov et al. (2021) confirmed effectiveness of $\delta^{34}S$ to 1) understand the mechanisms of H_2S generation and to discriminate bacterial thermochemical sulfate reduction processes and thermal decomposition of kerogen and 2) correlate the organic matter of source rocks and oils in various worldwide petroleum systems. Figure 9 shows that $\delta^{34}S$ of H_2S generated in pyrolysis experiments by source rock samples of the MC, LLP, and UBS/LBS had vastly different values. For example, $\delta^{34}S$ values of the UBS/LBS were in the range of –24‰ to –11‰, LLP $\delta^{34}S$ varied from –20‰ to –4‰, and MC generated more ^{34}S, with typical values of $\delta^{34}S$ in the range from –9‰ to +6‰. However, unexpectedly, none of these $\delta^{34}S$ ranges generated by the Bakken shales (UBS and LBS) and LLP samples matched the ^{34}S-dominated H_2S ($\delta^{34}S$ =+2‰ to +19‰ and average $\delta^{34}S$ = +12) collected at about 30 Bakken oil-producing wells. There is a better match of S isotope composition between MC-generated H_2S and well-collected gas.

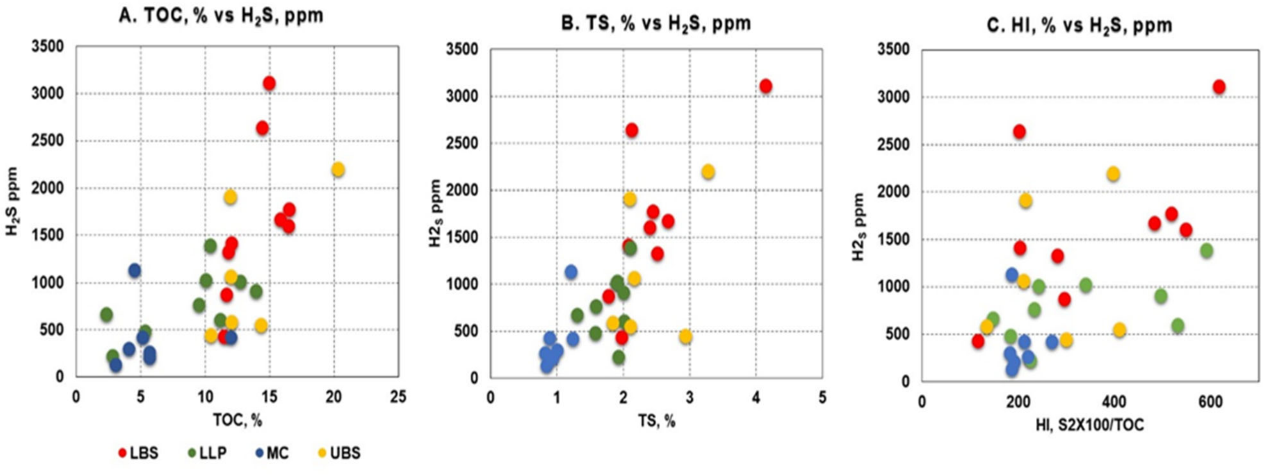

Figure 8. H_2S yields in high-temperature pyrolysis experiments of source rocks showing positive correlations with A) TOC, %, B) HI, and C) TS, %. A few outliers in the three graphs are likely due to analytical errors and linkage of S to inert organic matter which does not breakdown at 550°C and produces very small quantities of H_2S (Carvajal-Ortiz et al., 2021).

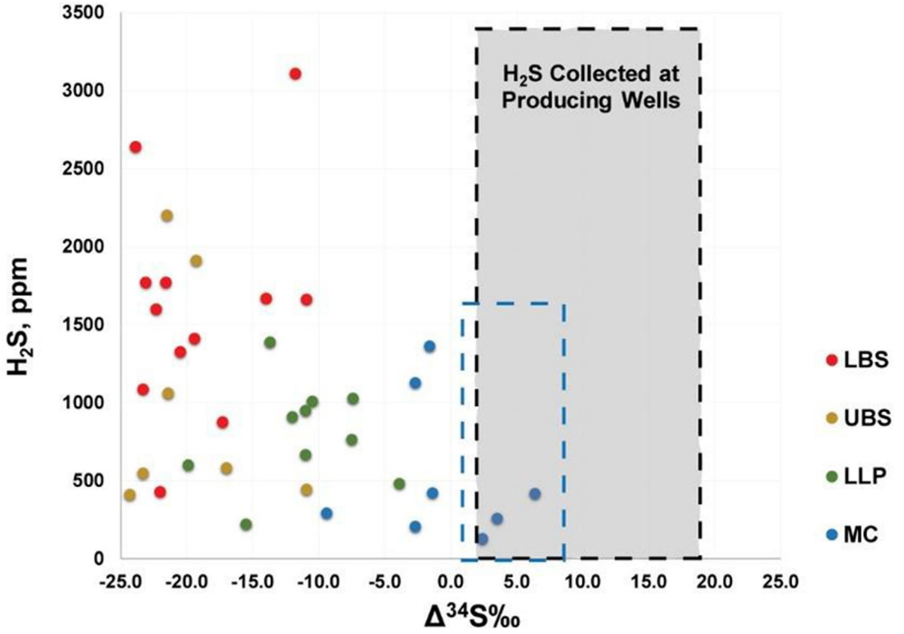

Figure 9. Values $\delta^{34}S$ of source rock pyrolysis and producing wells H_2S. Experiments demonstrated that UBS/LBS samples had the highest H_2S generation potential, followed by LLP and MC. The black rectangle outlines the $\delta^{34}S$ range of H_2S collected at more than 30 oil-producing wells.
The blue rectangle outlines the range on the graph where Mission Canyon $\delta^{34}S$ matches $\delta^{34}S$ of well-produced H_2S.

Discussion

Multiple known mechanisms and their combinations can potentially lead to the occurrence of H_2S in the production stream of oil and gas reservoirs. These mechanisms can be grouped into several broad categories, including thermogenic, source rock-generated, biogenic, and geomechanical effects, related to reservoir stimulation work (Orr, 1986; Worden et al., 1995; Machel et al., 1995; Worden and Smalley, 1996; Mitchell et al., 2017; Badrouchi et al., 2019).

Initially, a biogenic process was considered as a likely mechanism of H_2S generation in Bakken oil production because of 1) the large amounts of injected surface water used during completion operations, 2) increasing H_2S concentrations with production time in some wells, and 3) the initially sweet nature of the Bakken petroleum system. Moreover, a proprietary report indicated a correlation between the size of the stimulation job (volume of injected fluid) and the level of souring. However, the biogenic mechanism of reservoir souring is questionable in the Bakken because of the high reservoir temperatures (110°–150°C) and elevated salinity of the formation water (TDS > 200,000 mg/L) making microbial growth unlikely, especially in the context of the predominance of heavier ^{34}S isotope ($\delta^{34}S$ of +2 to +19‰) in produced H_2S. Operator anecdotal evidence suggests that the higher rates of H_2S concentration appeared to be related to well location and associated geologic setting, although in certain locations, completion type and size of the stimulation job might have affected H_2S occurrences.

TSR is another possible mechanism of H_2S generation in the presence of anhydrites and hydrocarbons at a higher reservoir temperature of 110°–150°C. This process is slow and requires hundreds or thousands of years to occur at high-temperature reservoir conditions and does not necessarily happen in all petroleum provinces. Those heavier isotopic signatures of produced H_2S suggest a thermal process such as TSR. The analytical work measuring $\delta^{34}S$ of SO_4 in produced water and Three Forks anhydrite and laboratory experiments simulating TSR were in progress at the time of this paper submission, and both mechanisms of BSR and TSR were not included in the scope of this publication.

The final major H_2S generation mechanism is the focus of this work: H_2S generation by source rocks via thermal decomposition of organic matter. It was hypothesized that 1) an elevated level of H_2S in Bakken wells is likely linked to the coproduction of fluids and gases as a result of out-of-zone completion practices connecting the Middle Bakken/Three Forks and overlying Madison reservoirs. To evaluate the proposed mechanisms of H_2S generation during maturation of the source rocks, geochemical characterization and simulation experiments have been done on both Bakken and Madison source rock samples.

Our sulfur speciation work based on Rock-Eval 7S analysis demonstrated that all the samples of organic-rich rocks contain relatively low TOS from the LBS/UBS, LLP, and ULP/LMC from very low to 1.7 wt%. These values are lower but comparable to the data reported for the Bakken shales by Carvajal-Ortiz et al. (2021). Both bulk parameters such as organic-linked sulfur value and SI (<100) indicated that the samples included in this study, even with lower maturities and higher remaining generation potential, represent marine Type II kerogen, not Type I-S or II-S (> 5wt% S). In addition, source rock samples from Divide County, where high produced concentrations of H_2S are observed, showed no difference in bulk organic sulfur content, with the source rock samples representing other areas of the BPS. Our initial hypothesis of existing sulfur-rich source rocks (Type II-S kerogen) in the Williston Basin was incorrect, especially in sour production areas of Divide County. Other evidence supports the possibility of an alternative hypothesis: that H_2S generation is possible through maturation of marine Type II kerogen in the basin. In more recent work, Xia and He (2017) suggested that not only can Type I-S and II-S kerogens generate abundant H_2S but also Type II kerogen. They stated that the 1.4 wt% of sulfur in Type II kerogen can generate, via thermal cracking, significant concentrations of H_2S (up to 100,000 ppm, or 10 vol%).

In this study, two independent pyrolysis experiments conducted at different conditions including time, temperature, pressure, and presence of water confirmed the immense potential for Bakken and Madison source rocks to generate significant volumes of H_2S (thousands of ppm) during source rock thermal maturation. The prevailing lithology of the petroleum system controls the further pathway of the generated H_2S, which can be scavenged by the iron in clay minerals to form pyrite or, if iron is not present in the system (carbonates), dissolved in oil, hydrocarbon gas, or/and reservoir water.

Further analysis of S isotope signatures of H_2S generated by Bakken and Madison source rocks and collected at producing oil wells provided more clarity for the hypothesized souring mechanism. The comparison of the S isotope compositions of the pyrolysis and well-sampled H_2S demonstrated a mismatch, especially when ^{34}S-depleted H_2S of Bakken shales ($\delta^{34}S$ = –24‰ to –11‰) was compared to ^{34}S-dominated H_2S collected at oil-producing wells ($\delta^{34}S$ = +2‰ to +19‰) (Figure 9). Unlike Bakken samples, the $\delta^{34}S$ values of the Mission Canyon Formation source rocks closely match some, but not all, H_2S samples collected at the wellsites (Figure 9). This suggests that Mission Canyon organic-rich intervals could be a source of H_2S in a limited number of the Bakken producing wells via communication between reservoirs caused by out-of-zone stimulation work. There is anecdotal evidence to support the Madison/Bakken communication scenario in stimulated wells saying that H_2S was detected at the beginning of flowback at some wells in Divide County. However, it is not uncommon when Bakken production develops an elevated concentration of H_2S after some time (days or weeks) of production or refrac work. In this delayed H_2S scenario, produced oil and gas initially flow from a higher energy area, which is a sweet target zone of the Middle Bakken, then as pressure drops in the Middle Bakken, the hydrocarbon flow extends out to the lower energy areas that are fracture tips in the Madison Formation.

For those wells with the $\delta^{34}S$ in the range from +10‰ to +19‰, TSR would be the plausible mechanism of H_2S generation. The existence of TSR in the Williston Basin is yet to be proved and is currently being investigated by the EERC research team.

The comparison of $\delta^{34}S$ was made using a limited number of data points including 31 source rocks and about 30 H_2S samples captured at oil-producing wells, which do not necessarily represent the heterogeneity of the entire BPS. Therefore, the conclusion made in this paper must be treated with caution because more isotope data from the wellsites and additional laboratory work simulating other mechanisms of souring might completely change current interpretations.

Conclusions

1 Organic-rich samples representing various geographic areas, stratigraphic units, and maturities were collected to investigate one of the possible mechanisms of H_2S generation via thermal decomposition in the BPS. The Rock-Eval 7S method did not indicate elevated contents of total sulfur and total organic-linked sulfur in organic-rich rocks selected for this study, refuting a hypothesis of Type II-S kerogen presence in the Williston Basin. In addition, the highly H_2S-producing areas of Divide County did not show an elevated content of total organic sulfur in source rocks of both the Bakken Formation and Madison Group.

2 Visible differences in source rocks have been identified when sulfur-containing aromatics were measured against other polycyclic aromatic compounds in source rock extracts. Samples from Divide County had a much higher concentration of sulfur-containing benzothiophenes and a higher content of nonorganic carbon from Rock-Eval data, indicating a higher content of carbonate material in the source rocks. The higher carbonate content was accompanied by lower concentrations of the pyrite-linked sulfur, suggesting a lack of reactive iron in the system to scavenge reduced sulfur. Biomarker signatures of the source rock extracts clearly differentiated MC and Bakken/LLP petroleum systems pointing at the carbonate lithology and highly anoxic depositional environment of the marine algae-dominated organic matter source in the MC.

3 Pyrolysis experiments suggest that source rocks in the Williston Basin with moderate to low S contents have the potential to generate significant concentrations of H_2S via thermal decomposition of kerogen. The $\delta^{34}S$ of H_2S generated in pyrolysis experiments of source rock samples representing MC, LLP, and UBS/LBS had vastly different values. A mismatch between ^{34}S-depleted H_2S of Bakken shales and ^{34}S-dominated H_2S of producing wells made Bakken shales a less likely source of H_2S in producing wells. Different from the Bakken samples, the $\delta^{34}S$ values of the MC source rocks closely match some, but not all, H_2S samples collected at the wellsites. This suggests that MC organic-rich intervals could be a source of H_2S for a limited number of the Bakken producing wells via communication between reservoirs caused by out-of-zone stimulation work.

4 For those wells with the $\delta^{34}S$ of H_2S in the range from +10‰ to +19‰, thermal decomposition of the organic matter of the source rocks was not a major contributor to souring in Bakken reservoirs, and other mechanisms might be responsible for H_2S generation. The TSR would be a plausible mechanism of H_2S generation considering the presence of anhydrite and high reservoir temperature in formations underlying Bakken. However, the existence of TSR in the Williston Basin is yet to be proved and is currently being investigated by the EERC research team.

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References

Aboussou, A., Lamoureux-Var, V., Wagner, T., Pillot, D., Kowalewski, I., März, C., Garcia, B., and Doligez, B. 2018. Pyritic Sulphur and Organic Sulphur Quantification in Organic Rich Sediments Using Rock-Eval. Proceedings of the First EAGE/IFPEN Conference on Sulfur Risk Management in

Exploration and Production; Rueil-Malmaison, France, September 18−20. DOI: 10.3997/2214-4609.201802758.

Amrani, A., Rosenberg, Y.O., Meshoulam, A., Said-Ahmad, W., Turich, C., Luu, N., Jacksier, T., Stankiewicz, A., Feinstein, S., and Shurki, A. 2019. Sulfur Isotopic Composition of Gas-Phase Organic Sulfur Compounds Provides Insights into the Thermal Maturation of Organic-Rich Rocks. *Geochimica et Cosmochimica Acta* **259**: 91–108.

Amrani, A., Said-Ahamed, W., Lewan, M.D., and Aizenshtat, Z. 2006. Experiments on δ^{34}S Mixing Between Organic and Inorganic Sulfur Species During Thermal Maturation. *Geochimica et Cosmochimica Acta* **70**: 5146–5161.

Bader, J.W., Nwachukwu, F., and Grader, G.W. 2019. Birdbear and Duperow Formations (Devonian) of the Williston Basin. Williston Basin Core Workshop, October 7–10, 2019, Wilson M. Laird Core and Sample Library, Grand Forks, North Dakota.

Badrouchi, F., Wan, X., Bouchakour, I., Akash, O., Rasouli, V., and Damjanac, B. 2019. Lattice Simulation of Fracture Propagation in the Bakken Formation. 53rd U.S. Rock Mechanics/Geomechanics Symposium, New York, New York, June 23–26.

Baskin, D.K. and Peters, K.E. 1992. Early Generation Characteristics of a Sulfur-Rich Monterey Kerogen. *AAPG Bulletin* **76**: 1−13.

Behar, F., Vanderbroucke, M., Tang Y., Marquis, F., and Espitalie, J. 1997. Thermal Cracking of Kerogen in Open and Closed Systems: Determination of Kinetic Parameters and Stoichiometric Coefficients for Oil and Gas Generation. *Organic Geochemistry* **26**: 321–339.

Behar, F., Vandenbroucke, M., Teermann, S. C., Hatcher, P. G., Leblond, C., and Lerat, O. 1995. Experimental Simulation of Gas Generation from Coals and a Marine Kerogen. *Chemical Geology* **126**: 247–260.

Bilkiewicz, E. and Kowalski, T. 2020. Origin of Hydrocarbon and Non-Hydrocarbon (H_2S, CO_2 and N_2) Components of Natural Gas Accumulated in the Zechstein Main Dolomite (Ca2) Strata in SW Part of the Polish Permian Basin: Stable Isotope and Hydrous Pyrolysis Studies. *Journal of Petroleum Science and Engineering* **192**: 107296.

Borcovsky, D., Egenhoff, S. O., Fishman, N., Maletz, J., Boehlke, A., and Lowers, H. 2017. Sedimentology, Facies Architecture, and Sequence Stratigraphy of a Mississippian Black Mudstone Succession – The Upper Member of the Bakken Formation, North Dakota, USA. *AAPG Bulletin* **101** (10): 1625–1673. DOI:10.1306/01111715183.

Bottjer, R.J., Sterling, R., Grau, A., and Dea, P. 2011. Stratigraphic Relationships and Reservoir Quality at the Three Forks–Bakken Unconformity, Williston Basin, North Dakota, *in* J.W. Robinson, J.A. LeFever, and S.B. Gaswirth, eds., The Bakken–Three Forks Petroleum System in the Williston Basin: Denver, Rocky Mountain Association of Geologists, p. 173–228.

Brooks, P.W., Snowden, L.R., and Osadetz, K.G. 1987. Families of Oils in Southern Eastern Saskatchewan. Proceedings of the Fifth International Williston Basin Symposium, *Saskatchewan Geological Society, Special Publication* **9**: 253–264.

Cai, C., Li, K., Zhu, Y., Xiang, L., Jiang, L., Tenger, Cai, X., and Cai, L. 2010. TSR Origin of Sulfur in Permian and Triassic Reservoir Bitumen, East Sichuan, Basin, China. *Organic Geochemistry* **41**: 871–878.

Carvajal-Ortiz, H., Gentzis, T., and Ostadhassan, M. 2021. Sulfur Differentiation in Organic-Rich Shales and Carbonates via Open-System Programmed Pyrolysis and Oxidation—Insights into Fluid Souring and H_2S Production in the Bakken Shale, United States. *Energy & Fuels* **35** (15): 12030–12044.

Chakhmakhchev, A.V. and Suzuki, N. 1995. Saturate Biomarkers and Aromatic Sulfur Compounds in Oils and Condensates from Different Source Rock Lithologies of Kazakhstan, Japan and Russia. *Organic Geochemistry* **23** (4): 289–299.

Curiale, J.A. 1994. Application of Organic Geochemistry to Petroleum Exploration and Field Development. Unocal Training Course and Material, Japan National Oil Corporation, Chiba, Japan.

Dow, W.G. 1974. Application of Oil-Correlation and Source-Rock Data to Exploration in Williston Basin. *AAPG Bulletin* **58**: 1253–1262.

Egenhoff, S.O. and Fishman, N.S. 2013. Sedimentology of the Upper Bakken Shale Member, North Dakota, USA. *J. Sediment. Res*. **83**: 803–824. DOI: 10.2110/jsr.2013.60.

Gaspar, J., Davis, D., Camacho, C., and Alvarez, P. 2016. Biogenic Versus Thermogenic H_2S Source Determination in Bakken Wells: Considerations for Biocide Application. *Environmental Science & Technology Letters* **3**: 127−132.

Gaswirth, S.B., Lillis, P.G., Pollastro, R.M., and Anna, L.O. 2010. Geology and Undiscovered Oil and Gas Resources in the Madison Group, Williston Basin, North Dakota and Montana. *The Mountain Geologist* **47** (3): 71–90.

He, K., Zhang, S., Wang, X., Ma, Q., Li, Z., Canfield, D.E., Mi, J., Tang, Y., and Guo, J. 2022. Effects of Inorganic Sulfur Species on Hydrocarbon Conversion and 34S Isotope Fractionation During Thermal Maturation of Type II Kerogen. *Organic Geochemistry* **168**: 104420.

Hofmann, A., van Strien, W., and Malekzadeh R. 2017. Improving the Efficiency of H_2S Mitigation in Middle East Oil and Gas Fields. Paper presented at the Abu Dhabi International Petroleum Exhibition and Conference held in Abu Dhabi, UAE, 13–16 November 2017, SPE-188257-MS.

Holubnyak, Y.I., Bremer, J.M., Mibeck, B.A.F., Hamling, J.A., Huffman, B.W., Klapperich, R.J., Smith, S.A., Sorensen, J.A., and Harju, J.A. 2011. Understanding the Souring at Bakken Oil Reservoirs. SPE International Symposium on Oilfield Chemistry, The Woodlands, Texas, April 11–13, 2011, No. SPE 141434-PP.

Hughes, W.B. 1984. Use of Thiophenic Organosulfur Compounds in Characterizing Crude Oils Derived from Carbonate Versus Siliclastic Sources, in Palacas, J.B., ed., Petroleum Geochemistry and Source Rocks Potential of Carbonate Rocks. *AAPG Studies in Geology* **18**: 181–196.

Hughes, W.B., Holba, A.G., and Dzou, L.I.P. 1995. The Ratios of Dibenzothiophene to Phenanthrene and Pristane to Phytane as Indicators of Depositional Environment and Lithology of Petroleum Source Rocks. *Geochimica et Cosmochimica Acta* **59** (17): 3581–3598.

Jarvie, D.M. 2001. Williston Basin Petroleum Systems—Inferences from Oil Geochemistry and Geology. *The Mountain Geologist* **38**: 19–41.

Jarvie, D.M., LeFever, J.A., and Nordeng, S.H. 2016. Madison Group Source Rocks, Williston Basin, USA. Search and Discovery Article #51301 Posted October 10, 2016. Adapted from oral presentation given at AAPG 2016 Annual Convention and Exhibition, Calgary, Alberta, Canada, June 19–22, 2016.

Jiang, C. and Li., M. 2002. Bakken/Madison Petroleum Systems in the Canadian Williston Basin, in Part 3: Geochemical Evidence for Significant Bakken Derived Oil in Madison Group Reservoirs. *Organic Geochemistry* **32**: 1037–1054.

Koopmans, M.P., Carson, F.C., Sinninghe Damstéa, J.S., and Lewanb, M.D. 1998. Biomarker Generation from Type II-S Kerogens in Claystone and Limestone During Hydrous and Anhydrous Pyrolysis. *Org. Geochem*. **29** (5–7): 1395–1402.

Kuhn, P., Di Primio, R., and Horsfield, B. 2010. Bulk Composition and Phase Behavior of Petroleum Sourced by the Bakken Formation of the Williston Basin. *Petroleum Geology Conference Series* **7:** 1065– 1077.

Kutuzov, I, Said-Ahmad, W., Turich, C., Jiang, C., Luu, N., Jacksier, T., and Amrani A. 2021. The Molecular and Sulfur Isotope Distribution of Volatile Compounds in Natural Gases and Condensates from Alberta, Canada. *Organic Geochemistry* **151**: 104129.

LeFever, J.A., LeFever, R.A., and Nordeng, S. 2011. Revised Nomenclature for Bakken Formation (Mississippian-Devonian), North Dakota, in Robinson, L., LeFever, J.A., and Gaswirth, S., eds., Bakken- Three Forks Petroleum System in the Williston Basin. *RMAG Guidebook*, p. 11–26.

Lillis, P.G. 2012. Review of Oil Families and Their Petroleum Systems of the Williston Basin. *The Mountain Geologist* **50** (1): 5–31.

Machel, H.G., Krouse, H.R., and Sassen, R. 1995. Products and Distinguishing Criteria of Bacterial and Thermochemical Sulfate Reduction. *Applied Geochemistry* **10**: 373–389.

Mitchell, A.F., Skjevrak, I., and Waage, J. 2017. A Re-Evaluation of Reservoir Souring Patterns and Effect of Mitigation in a Mature North Sea Field. Paper presented at the SPE International Conference on Oilfield Chemistry, Montgomery, Texas, April 2017. SPE184587-MS.

Murphy, E.C., Nordeng, S.H., Junker, B.J., and Hoganson, J.W. 2009. North Dakota Stratigraphic Column. North Dakota Geological Survey Miscellaneous Series 91, www.dmr.nd.gov/ndgs/documents/ Publication_List/pdf/Strat-column-NDGS-(2009).pdf.

Nesheim, T.O. 2021. Re-Examining the Madison Petroleum System within the Williston Basin. *Outcrop* **70** (8), www.rmag.org.

Nwachukwu, C.F., Nordeng, S.H., and Neshiem, T.O. 2019. Diagenesis and Porosity Development Within the Lower B-Zone Birdbear Formation, McKenzie County, Williston Basin, North America. Williston Basin Core Workshop, October 7–10, 2019, Wilson M. Laird Core and Sample Library, Grand Forks, North Dakota.

Obermajer, M., Osadetz, K.G., Fowler, M.G., and Snowdon, L.R. 2000. Light Hydrocarbon (gasoline range) Parameter Refinement of Biomarker-Based Oil-Oil Correlation Studies—An Example from Williston Basin. *Organic Geochemistry* **31**: 959–976.

Orr, W.L. 1986. Kerogen/Asphaltene/Sulfur Relationships in Sulfur-Rich Monterey Oils. *Organic Geochemistry* **10**: 499−516.

Orr, W.L. 2001. Evaluating Kerogen Sulfur Content from Crude Oil Properties: Cooperative Monterey Organic Geochemistry Study, in Isaacs, C.M., and Rullkötter, J., eds., The Monterey Formation: from Rocks to Molecules. New York, Columbia University Press, p. 348−367.

Osadetz, K.G., Brooks, P.W., and Snowdon, L.R. 1992. Oil Families and Their Sources in Canadian Williston Basin (southeastern Saskatchewan and southwestern Manitoba). *Bulletin of Canadian Petroleum Geology* **40**: 254–273.

Osadetz, K.G. and Snowdon, L.R. 1995. Significant Paleozoic Petroleum Source Rocks in the Canadian Williston Basin—Their Distribution, Richness, and Thermal Maturity (Southeastern Saskatchewan and Southwestern Manitoba). *Geological Survey of Canada Bulletin* **487**: 60.

Osadetz, K.G., Snowdon, L.R., and Brooks, P.W. 1994. Oil Families in Canadian Williston Basin (southwestern Saskatchewan). *Bulletin of Canadian Petroleum Geology* **42**: 155–177.

Peters, K., Walters, C., and Moldowan, J.M. 2005. The Biomarker Guide: Biomarkers and Isotopes in Petroleum Systems and Earth History, 2d ed. Cambridge University Press, Cambridge.

Petty, D.M. 2019. An Alternative Interpretation for the Origin of Black Shale in the Bakken Formation of the Williston Basin. *Bulletin of Canadian Petroleum Geology* **67** (1): 47–70.

Petty, D.M. 2022. Shallow-Water Versus Deep-Water: Stratigraphic Geometries in the Organic-Rich Shale/Mudstone Debate. *GSA Today* **32**: 4–10.

Price, L.C. and LeFever, J.A. 1992. Does Horizontal Bakken Drilling Imply a Huge Oil-Resource in Fractured Shales, in Schmoker, J.W., Coalson, E.B., and Brown, C.A., eds., Geological Studies Relevant to Horizontal Drilling: Examples from Western North America: Denver, Colorado, RMAG, pp. 199–224.

Price, L. C. and LeFever, J. 1994. Dysfunctionalism in the Williston Basin—The Bakken/Mid-Madison Petroleum System. *Bulletin of Canadian Petroleum Geology* **42**: 187–218.

Stroud J. and Sonnenberg, S. A. 2011. The role of the Lodgepole Formation in the Bakken petroleum system, Billings Nose, North Dakota, in Robinson, J., LeFever, J. A., Gaswirth, S. B., eds., The Bakken-Three Forks Petroleum System in the Williston Basin: Denver, Colorado, Rocky Mountain Association of Geologists.

Tissot, B.P. and Welte, D.H. 1984. Petroleum Formation and Occurrence. Springer-Verlag, New York.

Tomi, J., Behar, F., Vandenbroucke, M., and Tang, Y. 1995. Artificial Maturation of Monterey Kerogen (Type II-S) in a Closed system and Comparison with Type II Kerogen: Implications on the Fate of Sulfur. *Org. Geochem.* **23** (7): 647–560.

Wattripont, A., Bouton, N., Espitalié, J., and Antonas, R. 2018. Rock-Eval Sulfur and GEOWORKS Software. Proceedings of the First EAGE/IFPEN Conference on Sulfur Risk Management in Exploration and Production, Rueil-Malmaison, France, September 18−20. DOI: 10.3997/2214- 4609.201802756.

Williams, J.A. 1974. Characterization of Oil Types in Williston Basin. *AAPG Bulletin* **58**: 1243–1252.

Worden, R.H., Smalley, P.C., and Oxtoby, N.H. 1995. Gas Souring by Thermochemical Sulfate Reduction at 140 Degrees C. *American Association Petroleum Geology Bulletin* **79**: 854–863.

Worden, R.H. and Smalley, P.S. 1996. H_2S-Producing Reactions in Deep Carbonate Gas Reservoirs—Khuff Formation, Abu Dhabi. *Chemical Geology* **133:** 157–171.

Xia, D. and He, Z. 2017. Hydrogen Sulfide (H_2S) in the Permian Basin. Proceedings of the AAPG 2017 Annual Convention and Exhibition, Houston, Texas, April 2−5, Article 10950.

Zumberge, J.E. 1983. Tricyclic Diterpane Distributions in the Correlation of Paleozoic Crude Oils from the Williston Basin, in Bjorøy, M., ed., *Advances in Organic Geochemistry 1981*: New York, John Wiley, p. 738–745.

Zumberge, J.E., Curtis, J.B., and Rocher, D. 2013. Identification of Three Williston Basin Oil Families Derived from Mississippian Carbonate Source Rocks. Presented at the Unconventional Resources Technology Conference held in Denver, Colorado, USA, 12–14 August. URTeC 1580243.