Biogenic versus Thermogenic H$_2$S Source Determination in Bakken Wells: Considerations for Biocide Application

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Ⓢ *Supporting Information*

ABSTRACT: Hydrocarbon souring represents a significant safety and corrosion challenge to the oil and gas industry. H$_2$S may originate from geochemical or biogenic sources, although its source is rarely discerned. Biocides are sometimes utilized during well operations to prevent or inhibit H$_2$S generation. Here we develop a regional temperature map showing that downhole temperatures in Bakken reservoir wells equal or exceed the upper known temperature limit for microbial life. Attempts to extract microbial DNA from produced water yielded little to no detectable quantities. Stable isotope analysis yielded $^{34}\delta$ values from 4.4 to 9.8‰, suggesting souring had a geochemical origin. Under Bakken reservoir conditions, anhydrite can react with hydrocarbons to form H$_2$S. Anhydrite present near the sour areas studied could be the underlying geochemical source creating this H$_2$S. In cases of geochemical souring, reevaluation of the need for biocide addition may provide significant reductions in both operational costs and overall environmental footprint.
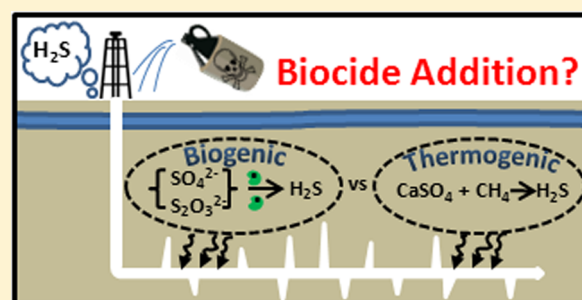
INTRODUCTION

In the shale gas industry, significant financial, environmental, and energy burdens are associated with removing hydrogen sulfide (H$_2$S) from production wells and associated pipelines. Oil and gas companies typically pay a penalty when selling sour gas (defined as having a H$_2$S concentration of >4 ppm),[1] due to safety and corrosion risks to downstream processors and handlers. To mitigate these costs and safety risks, operators install H$_2$S bubble towers at the wellhead that scavenge and reduce H$_2$S levels. Additionally, biocides are commonly added to eradicate H$_2$S-producing microorganisms before the injection water is pumped into the subsurface, where conditions often favor halotolerant sulfidogens.[2,3]

Using the Bakken petroleum system as a natural test lab, we investigate here whether H$_2$S is microbial in origin or is from abiotic processes related to local geochemistry. The Bakken is considered unconventional because of the low porosity and low permeability of the reservoirs that require hydraulic stimulation to recover hydrocarbons. Whereas some microbiology studies have been conducted for unconventional shale plays across North America,[2−16] including one on Bakken hydrocarbon microbiology,[13] the source of H$_2$S is generally unknown. Within the published literature, a variety of sample collection, preparation, and analysis procedures are used, which complicates the interpretation of data.[17] Furthermore, the types and abundance of bacteria within producing oil and gas wells are transient,[2,3] and rarely are wells sampled at similar time points. Most studies report the presence of bacteria in produced water,[2−4,9,12−15] although a number of studies have

found few to no bacteria present.[6,8] Of those studies in which bacteria were found, the Marcellus shale formation shows an eventual dominance by halotolerant sulfidogenic organisms,[2,3] while other shale plays seem to exhibit highly diverse microbial consortia.[4,9,12,13,15]

H$_2$S gas may also arise from geochemical sources[18] and has been shown to originate from the interaction of hydrocarbons with sulfur-bearing minerals such as anhydrite (CaSO$_4$), at 284 °F,[19] via the following reaction:

$$CaSO_4 + CH_{4(g)} \rightarrow CaCO_3 + H_2S_{(g)} + H_2O$$
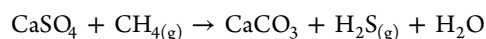
The Khuff shale formation (Abu Dhabi), the Zhongba gas fields (Sichuan Basin, China), the Western Canada basin, and the Bighorn Basin (Wyoming) are examples of the interaction of hydrocarbons and sulfur-containing minerals in the appropriate thermal and geochemical settings resulting in significant H$_2$S generation.[19−21] In some instances, thermogenic H$_2$S comprises >50% total by mass of the gas well effluent stream composition.[22]

Development of methods to discern the source of H$_2$S is critical, given that 40% of the world's proven gas reserves are sour.[23] If H$_2$S is from abiotic processes, then biocide addition strictly to control H$_2$S is not warranted. The ramifications of this are significant. Biocide elimination would offer significant
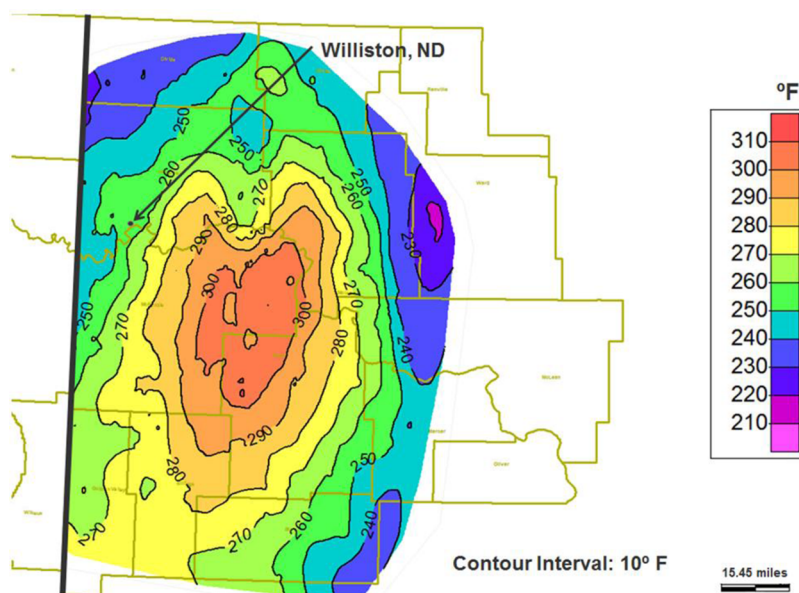
Figure 1. Bakken downhole temperature map. The solid black line represents the North Dakota/Montana border.

savings to shale gas companies.[24] Eliminating biocide injection in cases of thermogenic H$_2$S would also result in a smaller overall environmental footprint: lessening the production and consumption of reagents, as well as their introduction into the environment, where exposure of microorganisms to sublethal biocide concentrations has been shown to increase the development of biocide resistance.[15,25−27] In this paper, we use a combination of sulfur isotope analysis, downhole temperature mapping, and microbial isolation to show H$_2$S in Bakken wells is of geochemical origins. We then provide core sample analysis and discussion concerning possible geological sources of H$_2$S generation.

■ EXPERIMENTAL SECTION

Produced water (PW) was collected from eight wells (two nonsour and six sour) in Mountrail County, ND. All wells had been in operation and producing for >100 days. Glutaraldehyde was added to injection water just before hydraulic fracturing for each well studied. No further biocide addition or microbial control practices occurred after fracturing of any well included in this study. PW samples were collected at the wellhead, before the three-phase (oil, water, and gas) separator. Samples were collected in 2 L polypropylene bottles and filled without headspace to prevent oxygen intrusion. Bottles were immediately placed on ice and held at 4 °C during overnight shipping. Upon arrival at the lab, PW samples were passed through a separatory funnel to separate the oil layer from the aqueous portion. The remaining PW was then filtered through a 0.2 μm filter to capture all biomass and sediment. Water chemistry analysis of the filter effluent was performed by Precision Analysis (Riverton, WY) following EPA guidelines. Filters were frozen at −80 °C until they were processed further; 250 mg of biomass from each filter was scraped, and DNA was isolated using a MoBio PowerSoil DNA extraction kit. Isolated DNA was quantified using a Nanodrop spectrophotometer. DNA purity was assessed by measuring the absorbance at 260 and 280 nm and calculating the A_{260}/A_{280} ratio, which provides an indicator of protein and/or solvent contamination. For wells in which low concentrations (<3 ng/μL) of DNA or low-purity DNA (A_{260}/A_{280} < 1.8) were observed after initial extraction, a

Zymo Research DNA Clean and Concentrator kit was utilized. In all such cases, total DNA yield postclean and concentrate was still significantly below (<4 ng/μL and <20 ng of DNA total) the nominal concentration and total DNA amount (20 ng/μL and 400 ng of DNA total, respectively) for Illumina analysis. Furthermore, A_{260}/A_{280} ratios for all wells were uniformly low (A_{260}/A_{280} < 1.2), suggesting poor quality DNA and discouraging further downstream processing. A positive control soil sample run in parallel with well samples yielded significant DNA of high quality (92.1 ng/μL, 4600 ng of DNA total, A_{260}/A_{280} = 1.83). When no DNA was found using the methods described above, a second sample of PW from well 1 was sampled as described above and overnighted to Rice University; 500 mL of unfiltered PW from well 1 was centrifuged at 6000g for 30 min to pellet any sediment and possible biomass, and 250 mg of this pellet was utilized to repeat the MoBio PowerSoil DNA extraction. Light microscopy of unfiltered PW from well 1 was performed using an oil-immersion lens at 1000-fold magnification.

To perform $^{34S}\delta$ isotopic analysis, downstream dry gas was collected after the three-phase separator and passed through an IsoTrap, which precipitates H$_2$S gas onto an immobilized catalyst surface. Total gas flow through each IsoTrap varied (between 4 and 50 L) as a function of H$_2$S concentration for each well and was continued until the column indicator changed color upon completion. IsoTrap columns were then shipped to IsoTech Laboratories (Champaign, IL) where the precipitated H$_2$S is liberated as SO$_2$ gas via combustion and subsequently analyzed for $^{34S}\delta$ using isotopic ratio mass spectrometry (IR-MS). As a positive biotic control for isotopic analysis, *Desulfovibrio vulgaris* (which is not necessarily representative of the unknown predominant sulfidogens in the Bakken region but is a prototypical sulfidogen) was grown in triplicate in 500 mL anaerobic Wheaton vials. Produced gas was collected via syringe and bubbled through a 1 M zinc acetate solution to precipitate out sulfide as zinc sulfide. Zinc sulfide was sent for IR-MS $^{34S}\delta$ isotopic analysis. The average positive control $^{34S}\delta$ value was −14‰ with a standard deviation of 0.7‰.

An updated Bakken Formation temperature map was created using Fourier's law of heat conduction (eq 1).

$$T_n = T_o + Q(Z_1/\lambda_1 + Z_2/\lambda_2 + ...Z_n/\lambda_n) \qquad (1)$$

Average surface temperature (T_o), conductive heat flow (Q), unit thickness (Z), and unit thermal conductivity values (λ) were used to calculate Bakken Formation temperatures (T_n) throughout the Williston Basin as previously described.[28] The calculated average surface temperature was 4.44 °C (40 °F), utilizing publically available temperature data ($n_{years} > 100$) recorded at the Sloulin Field weather station in Williston, ND. Updated heat flow values (watts per square meter) were obtained from M. McDonald of the North Dakota Geological Survey.[29] Williston Basin stratigraphy was divided into 18 successive units from the earth's surface to the top of the Nisku Formation based on variable thermal conductivity values (Table S1). Each unit thickness (meters) was determined using in-house well log formation top picks, as well as picks available from the North Dakota Industrial Commission (NDIC).[30] Thermal conductivity values (watts per meter per kelvin) were assigned using previously published data.[31] Several thousand wells basin-wide in North Dakota were utilized in making unit top picks from well logs. Well logs obtained from the NDIC as well as industry sources were utilized for improved coverage. Temperatures were then calculated and imported into the geological analysis software, Petra, and a contour grid was created using minimum curvature to produce an updated Bakken Formation temperature map. The resulting map is a temperature map calculated at the top of the Middle Bakken Formation. The map covers the main extents of the Bakken play in North Dakota and ranges in depth from ~5500 ft true vertical depth below the subsurface (SSTVD) to ~9000 ft SSTVD.

■ RESULTS AND DISCUSSION

Downhole Reservoir Temperatures Are Not Conducive to Microbial Life. The upper known temperature limit of microbial life is 122 °C (252 °F),[32] and that for sulfidogenic metabolism is 120 °C (248 °F).[33] Geochemical production of H_2S is insignificant below temperatures of 100 °C (212 °F).[34,35] Although not a definitive cutoff, temperature may be utilized to indicate whether microorganisms are likely present downhole. An improved temperature map (Figure 1), which corrects for the cooling effects of mud in the borehole environment during drilling, was created for the Williston Basin of North Dakota. Previously published maps utilized uncorrected tool-recorded temperatures that led to calculated temperatures lower than true formation temperature. Seven of the eight wells studied equal or exceed the upper known limit of microbial life (Table 1).

Sulfur Isotope Analysis Indicates Thermogenic H_2S. Next, isotopic analysis of sulfur isolated from H_2S was performed to determine whether H_2S gas is microbial or thermogenic in origin. Well 3 was not tested out of safety concerns because of high H_2S levels. Well 4 was sampled twice to determine assay reliability. All wells yielded positive $^{34S}\delta$ values between 4.4 and 9.8‰ (Table 1). In general, $^{34S}\delta$ values of ≥10‰ are considered solely thermogenic while values between 0 and 10‰ are mixed, but still containing H_2S from predominantly thermogenic origins.[9] A predominantly biogenic well would yield $^{34S}\delta$ values of <0‰. The observed $^{34S}\delta$ values are consistent with the downhole temperature mapping implication of geochemical H_2S.

Table 1. Summary of Test Wells and Results[a]

well no.	sour	[H_2S] (ppm)	$^{34S}\delta$ ‰	temperature isotherm (°F)
1	no	0	N/A	270−280
2	no	0	N/A	280−290
3	yes	90000	N/A (safety)	240−250
4	yes	600	5.4, 4.4	250−260
5	yes	98	7	250−260
6	yes	105	7.9	280−290
7	yes	50	9.8	280−290
8	yes	30	9.6	270−280

[a]H_2S concentration, sulfur isotope ratio, and calculated downhole temperature (based on Figure 1) for each well.

Microorganisms Were Not Detected in Produced Water. Produced water samples were taken from all eight wells and filtered as described earlier with the original intent of submitting DNA for Illumina analysis. All eight wells yielded no measurable or negligible amounts of DNA (in Figure S1). As a further check, an additional PW sample for well 1 was taken and analyzed using an alternative preparation method.[3] Again, no DNA was observed. Finally, a small aliquot of PW from well 1 was observed at 1000× magnification with light microscopy, and again, no microbes were observed.

Water Chemistry. Total dissolved solids (TDS) and main ion concentrations for all eight wells are relatively high [i.e., 291403 ± 19580 mg/L for TDS, 81325 ± 3917 mg/L Na⁺, and 185025 ± 12400 mg/L for Cl⁻ (Figure 2)]. These TDS concentrations are significantly higher than those for other shale studies reporting active microorganisms.[2,3,12,36] A recent analysis of Marcellus PW that exhibited TDS values similarly
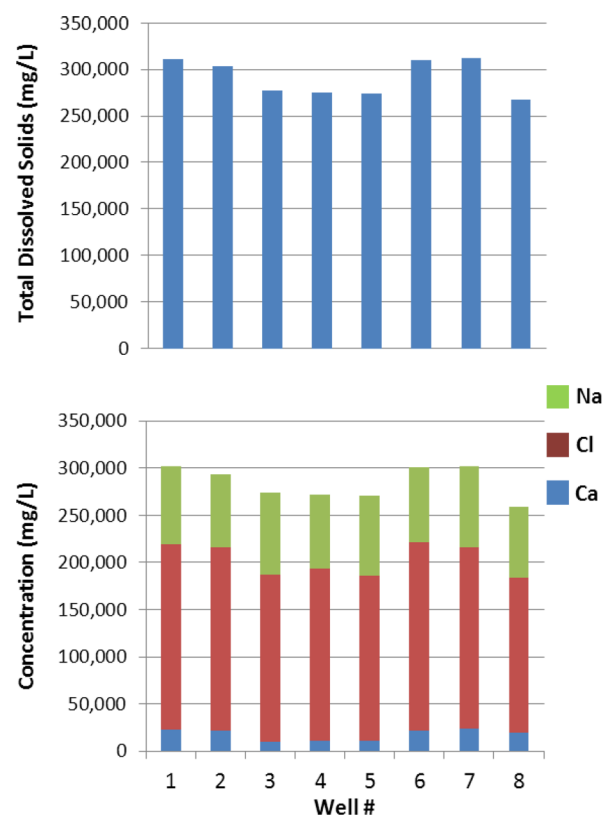

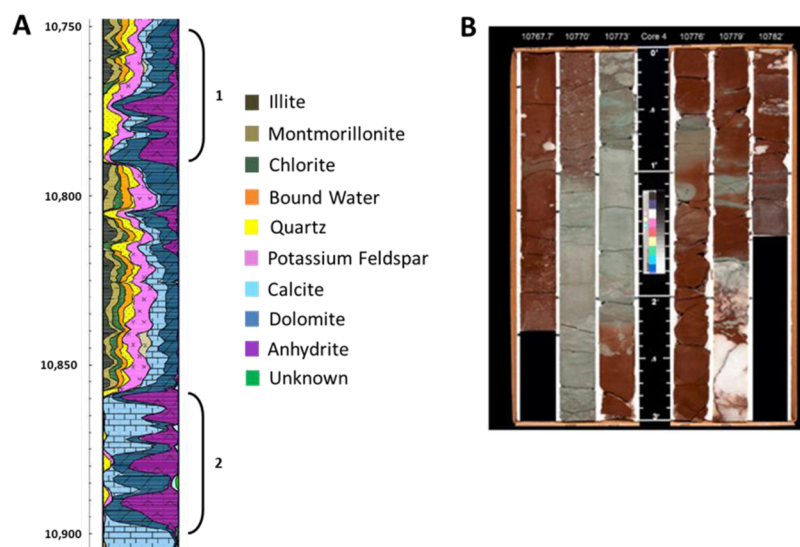**Figure 2.** Selected water chemistry. All values are in milligrams per liter.

Figure 3. Characterization of Three Forks Formation. (A) X-ray diffraction analysis of the region located <300 ft below typical horizontal drilling and within the theoretical vertical fracturing zone. High-anhydrite areas are marked as 1 and 2. Region 1 lies <150 ft from horizontal drilling. (B) Core sample taken from region 1 (drilling depth of 10767−10783.5 ft). Each vertical slice represents 3 vertical feet of formation. Anhydrite nodules are colored white or gray. Brown areas are dolomite with iron.

high like those in our study also found insignificant levels of microbial DNA for community analysis and significantly reduced levels of culturable bacteria.[5] Such high salt concentrations (8−9-fold the salinity of seawater) are known to exert osmotic stress and hinder microbial growth.[3,37] Free sulfate (SO_4^{2-}) PW concentrations measured ≤0.1% of the TDS, and no correlation with H_2S levels was observed. The PW pH values for all eight wells were between 5.6 and 6.1 (Table S2).

Geological Considerations. Pyrite (FeS_2) and anhydrite ($CaSO_4$) are both sulfur-bearing minerals present in the Bakken petroleum system. Either mineral could be the underlying geochemical source initiating the H_2S generation. To quantify the presence of the two minerals, mineralogical core analysis was performed for the Bakken and entire Three Forks formation one mile west of sour wells 6 and 7. Figure S2 provides a model of this cored well and the associated Bakken petroleum system stratigraphy (Upper Bakken Shale, Middle Bakken, Lower Bakken Shale, and Three Forks) drawn to scale on the basis of petrophysical logs.

Pyrite is found abundantly within the Upper and Lower Bakken Shales,[38−40] and in smaller amounts within the Middle Bakken and Three Forks reservoirs. However, previous geochemistry simulations (with Workbench PHREEQC and CMG GEM) showed that pyrite oxidation reactions are not thermodynamically feasible under Bakken reservoir conditions.[41] Interestingly, anhydrite was also found in significant amounts (1−4 vertical feet) in the third bench of the Three Forks Formation (Figure 3). Direct reaction of anhydrite with methane or other hydrocarbons to form H_2S has been observed in carbonate oil reservoirs.[19,42] Additionally, modeling studies that utilized Bakken reservoir conditions as input parameters have shown production of H_2S from anhydrite reacting with hydrocarbons is thermodynamically feasible at temperatures ranging from 230 to 284 °F (110 to 140 °C, respectively).[41]

Preexisting natural fractures in the middle Bakken,[43−45] lower Bakken,[43,45] and Three Forks formations[39,43] may provide a fracture network allowing reactions to take place and movement of the H_2S into the reservoirs. Alternatively,

H_2S gas could follow flow paths created by hydraulic stimulation. Current drilling is typically performed in the Middle Bakken and the upper Three Forks formations. Vertical separation between the third bench anhydrite layer and typical Three Forks formation horizontal drilling depths is approximately ~150 ft. Recent models demonstrate vertical fracture heights in the Bakken typically range from 100 to 200 ft and in rare instances may reach 400 ft pending the completions technique utilized.[46] On the basis of distance, this precludes the Mission Canyon formation, which is known to harbor sulfur-containing ores,[47] from being a source of H_2S gas. The anhydrite, however, lies within or slightly outside the expected downward propagating fracture lengths offering a possible explanation of the observed H_2S contamination. Further studies comparing the isotopic signature of sour gas with core anhydrite from the same well will be useful in establishing a possible causative link between anhydrite and Bakken reservoir souring.

Environmental Implications. In cases of geochemical souring, a reevaluation of biocide use to control H_2S may be warranted. Biocide application incurs significant operation costs and the potential for environmental impact. Further investigation to increase the extent of characterization of sour wells in various plays could result in play specific maps, which would enhance decisions about biocide injection. Curtailing the use of biocides in cases when the source of souring is abiotic would reduce operation costs and mitigate environmental impacts of unconventional oil and gas production.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.estlett.6b00075.

Thermal conductivity values (Table S1) used to generate Figure 1, raw DNA extraction values (Figure S1), a visual representation of Bakken stratigraphy with a horizontal well included, drawn to scale (Figure S2), and PW pH values for each well studied (Table S2) (PDF)

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Notes

The authors declare no competing financial interest.

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