CONTROLS ON BIOGENIC METHANE FORMATION IN CHEROKEE BASIN COALBEDS, KANSAS

by

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Approved by:
Major Professor
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Abstract

The Cherokee basin in southeastern Kansas is a declining coalbed methane (CBM) field where little is known about how the CBM formed, the extent to which it continues to form, and what factors influence its formation. An understanding of methanogenic processes and geochemistry could lead to potential enhancement of methane formation in the basin. The objectives of this project are to (1) determine the pathway of methane formation and (2) determine whether geochemistry has influenced gas formation. In order to reach the objectives, we analyzed formation water geochemistry, production history, and gas composition and isotopes. Post Rock Energy Corporation gave us access to 16 wells for sampling purposes. We collected gas samples in Isotubes® for compositional and isotopic analyses at a commercial laboratory. We analyzed major ion chemistry from formation water using standard methods. Co-produced water samples we collected are Na-Cl type with total dissolved solids content ranging from 35,367 to 91,565 mg/L. TDS tended to be highest in samples collected from wells with greater total depth. The pH and temperature of sampled water averaged 7.0 and 19°C with an alkalinity ranging from 3.33 to 8.59. Gas dryness and δ\(^{13}\)C CH\(_4\) range from 196 to 4531 and -69.95 to -56.5, respectively, which indicate that methane is being produced biologically. Comparing the δ\(^{13}\)C CH\(_4\) to the δD CH\(_4\), which ranges from -228.2 to -217.2, suggest that the primary pathway of methanogenesis is H\(_2\)/CO\(_2\) reduction. We calculated Δ (the difference between δ values) in order to correlate isotope data to produced water chemistry. Samples ΔD and Δ\(^{13}\)C values range from -189.1 to -168.7 and 61.52 to 69.99. Calculated ΔD\(_{CH4-H2O}\) and Δ\(^{13}\)C\(_{CO2-CH4}\) values approach the range for the acetate/methyl pathways as Cl\(^{-}\) concentration increases, potentially indicating a slight shift in methanogenic pathway in deeper, more saline
portions of the basin. The culturing results revealed that living methanogens are still able to utilize H₂, acetate, and methanol present in co-produced formation water from all tested wells.
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Chapter 1 - Introduction

Natural gas is very important for the United States’ future energy program. Using natural gas as a fuel source has the potential to lead to lower greenhouse gas emissions. Combustion of natural gas produces half the CO$_2$ of coal per energy generated. The domestic quantity of producible natural gas is growing. Production technology and drilling advancements have allowed reserves in the United States to increase from 322.7 to 354 tcf (trillion cubic feet) (U.S. Energy Information Administration, 2014).

Natural gas can form in the subsurface from two different processes: (1) thermocatalytic reactions and (2) microbiological reactions. Natural gas forms via thermocatalytic reactions when organic matter is buried deep in the subsurface and heated (Fig. 1). The second process is from microbial degradation (biogenic) of organic matter. Biogenic gas formation requires a consortium of microorganisms. Bacteria degrade complex organic matter and produce simple substrates that methanogenic archaea use to make natural gas. Substrates used by archaea fall into three categories: H$_2$/CO$_2$ reduction, acetate fermentation, and from methylated compounds (Table 1).

Table 1. Chemical reactions representing the three biogenic methane pathways.

<table>
<thead>
<tr>
<th>Pathway</th>
<th>Chemical Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$/CO$_2$ Reduction</td>
<td>H$_2$ + $\frac{1}{4}$ CO$_2$ $\rightarrow$ $\frac{1}{4}$ CH$_4$ + $\frac{1}{2}$ H$_2$O</td>
</tr>
<tr>
<td>Acetate Fermentation</td>
<td>CH$_3$COO$^-$ + H$^+$ $\rightarrow$ CO$_2$ + 2 H$_2$O</td>
</tr>
<tr>
<td>Methylated Compounds</td>
<td>4 CH$_3$OH $\rightarrow$ 3 CH$_4$ + CO$_2$ + 2 H$_2$O</td>
</tr>
</tbody>
</table>
Understanding the controls on biogenic gas formation could offer opportunities to increase commercial gas production and limit environmental impacts. Many natural gas reservoirs could presently have biologic reactions occurring. If the microorganisms are still there, then the addition of food could enhance their production of methane. By using produced water to re-supply the microbes with food, we could cut down on disposal amounts. Enhancing methane formation and subsequent production would decrease the amount of wells necessary to make a field economic. Drilling fewer wells would also decrease the amount of produced water to dispose.

In this study, we aim to determine if biological processes produce methane in the Cherokee basin (CHB), and if so, what controls methane formation. The CHB is a promising field location for geomicrobiological research for multiple reasons. The Cherokee group coals are buried relatively shallow (~400’ - 1200’) and show immature to mature R_o values (0.5% to 0.7%), suggesting that thermogenic gas is unlikely to be the sole source of methane formation (Newell, 2012). Maximum burial depth is calculated to be ~6,000 feet deep by Pennsylvanian and Permian sediments (Barker et al., 1992). Type I and II organic matter buried that deep would just reach the oil generation window and definitely not reach dry gas generation (Fig. 1). The field averaged 20 Mcfd/well with a cumulative production of 165 bcf as of 2008 (Newell, 2010). Because the R_o values are too low for gas generation, it is unlikely that thermal maturity alone could account for that quantity of gas (Newell, 2010). Finally, the CHB is a good location for this research because the field is in decline. By studying gas formation, we may be able to develop strategies to increase the life of the basin’s CBM wells.
Figure 1. Oil, wet gas, and dry gas generation windows relative to coal rank, vitrinite reflectance, weight % carbon in kerogen, pyrolysis, and SCI (Dow & O'Connor, 1982).
Chapter 2 - Hypotheses

The research objective of this study is to test the following hypotheses: (1) a portion of the natural gas in Cherokee Basin coalbeds was formed biologically and (2) that formation water geochemistry influenced natural gas formation. In order to test these hypotheses, we performed a field study that integrated formation water geochemistry, gas composition, production data, and lab experiments. Specific questions that we aimed to answer are as follows:

1. How did gas in the coalbeds form?
2. Are living cells capable of forming methane present in the coalbeds?
3. How does formation water geochemistry vary across the basin?
4. Are there relationships between water chemistry and gas composition with production?
Chapter 3 - Geologic Setting

3.1 Eastern Kansas Structural Geometry

There are five structural features that are important in describing the subsurface in Eastern Kansas. The Forest City basin is located in the northeast corner of Kansas and is separated from the CHB to the south by the Bourbon arch. Both basins are bound to the west by the Nemaha ridge that starts at the border of Oklahoma and continues north into Nebraska (Lange, 2003) (Fig. 2). The Ozark dome in southwestern Missouri creates the eastern flank of the CHB. To the south, the CHB deepens into the Arkoma basin of Oklahoma and Arkansas.

Figure 2. Map of eastern Kansas showing regional structural features. Red circle is around field study location which coincides with the primary location of current CBM production in the CHB.

During Cherokee deposition, eastern Kansas was located on a shelf that represented the northern extension of the foreland Arkoma basin in eastern Oklahoma and western Arkansas.
The Arkoma basin was formed due to continental collision and the subsequent Ouachita Orogeny (Sutherland, 1988). By the end of the Mississippian, the Ozark dome in western Missouri had been completely developed (Merriam, 1962), which created a slight 0.5° dip to the west until the Cherokee Group reaches the Humboldt fault zone and associated Nemaha ridge (Fig. 2) (Lange, 2003). The Nemaha Ridge was formed pre-Pennsylvanian due to normal faulting in the Humboldt fault zone (Walton, 1996).

3.2 Cherokee Group Stratigraphy

Natural gas wells sampled in this study are completed in the Cherokee Group of Pennsylvanian age. Pennsylvanian rocks in Kansas are predominantly limestones, but the Cherokee Group in the CHB consists of sandstones, shales, and coals (Woody, 1982-1985). Pennsylvanian rocks in this area lay disconformably on Mississippian limestones due to karst topography at the end of Mississippian times (Lange, 2003). Cherokee group sediments thicken as the basin deepens to the south into the Arkoma basin.

Deposition of Cherokee Group sediments was diverse and complicated. Sandstones in the CHB are interpreted to be fluvio-deltaic channels, reworked deltaic sands (Brenner, 1989), and valley fill successions (Walton, 1996). Coals were deposited in fluvial floodbasins, coastal plains, estuarine systems, at the end of rapid marine transgressions, and from mires that developed in Mississippian karsts (Lange, 2003).

The Cherokee group is made up of the older Krebs formation and younger Cabaniss formation that contain anywhere from 6 to 9 coals that can be seen in the subsurface and in outcrop (Woody, 1982-1985; Lange, 2003; Zeller, 1968). The Weir-Pittsburg and Riverton coals of the Cherokee group are considered to be economically important (Newell, 2012). Coals in the Cherokee group are ~400’ to 1200’ deep and differ in maturity and lateral extent (Woody,
1982-1985). Thickness varies from 1-5 feet with vitrinite reflectance ranging from 0.5-0.7% within the Pennsylvanian group (Barker, 1992; Newell, 2012; Woody, 1982-1985).
Chapter 4 - Methods

4.1 Well Selection

Post Rock Energy Corporation provided data and access to commercial coalbed methane wells for our study. They supplied a master list of wells, a location map, and a brief summary of current water and gas production. From that list we calculated an average daily gas production and an average daily water production. We selected wells that cover a wide area spatially and had varying gas and water production characteristics (Fig. 3). My study area is located in Wilson, Neosho, Montgomery, and Labette counties (Fig. 2).

![Well locations marked in purple with well ID’s next to each marker. Satellite image taken from Google Earth.](image)

4.2 Well Production Data

Post Rock Energy supplied detailed production data for each well that was sampled. The production data was specific to each well and not from a group of wells that fed one meter. We
summed daily production numbers for the life of the well and converted from mcf (thousand cubic feet) to mmcf (million cubic feet). Because each well produces from multiple coal zones, we were not able to constrain which coals are more prolific.

4.3 Field Methods

We collected samples during November 11-13, 2013. The same data were collected at each site except for one well that was not currently producing water and one well that was producing oil with the water. Temperature, pH, and conductivity were measured in the field with an Oakton® PC300 handheld meter. Gas samples were collected in Isotubes® (Isotech Laboratories, INC.) at the well location after the produced fluid travelled through a gas separator. The gas samples were taken for compositional and isotopic analyses. Water samples were collected directly from the wellhead in sterile bottles of varying sizes for major ion chemistry and isotopic analyses. We filtered and acidified (with HCl) samples for cation analysis.

In addition to chemical analysis, we also collected water samples for culturing analysis in sterilized nitrogen-flushed serum bottles (Fig. 4). During sample collection, we attached the serum bottles directly to the well via rubber tubing and a hypodermic needle to avoid exposing the water to oxygen. Another needle was inserted into the rubber stopper of the serum bottle in order to allow disassociated gas to vent.
4.4 Analytical Methods

We used standard methods for analysis of the major ion chemistry of our samples. We titrated samples with 0.02N H$_2$SO$_4$ to measure bicarbonate alkalinity. Major anion and cation concentrations were collected using a Dionex Corporation ICS 1100 ion chromatography (IC) system. Samples collected for ferrous iron (Fe(II)) concentrations were filtered and acidified in the field. We reduced the samples with hydroxylamine prior to analysis using the ferrozine technique (Stookey, 1970), with a Thermo Scientific Genesys 10S UV-Vis Spectrophotometer.
Gas composition and isotopic samples were collected in Isotubes® and sent to Isotech Laboratories. Gas composition was measured using a gas chromatograph with accuracy of +/- 5% for C$_1$-C$_5$ and +/- 10% for C$_5$-C$_6^+$. Analysis of $\delta^{13}$C and $\delta$D of CH$_4$ and $\delta^{13}$C CO$_2$ was done with dual inlet isotope ratio mass spectrometry (DI-IRMS). Precision of $\delta^{13}$C is 0.1‰ and $\delta$D is 1‰. Water isotope samples were also sent to Isotech for $\delta^{18}$O and $\delta$D of H$_2$O analyses using DI-IRMS. Precision for $\delta$D of H$_2$O is 1‰ and $\delta^{18}$O of H$_2$O is 0.1‰.

In order to determine whether or not correlations are significant we used statistics. Statistical calculations were made using a Spearman’s Rho calculator. For this study, P-values < 0.05 are considered statistically significant correlations.

**4.5 Culturing**

We tested the ability of cells to convert acetate, H$_2$/CO$_2$, and methanol into methane (Fig. 5). These three substrates represent the three major biologic pathways for methanogenesis. Each sample was also used to inoculate two control cultures: a culture that was sterilized following inoculation and a culture that was not amended with any methanogenic substrates. Each culture tube contained 10mL of formation water along with 1 mL of solution containing macronutrients (50 μM NH$_4^+$ and 5 μM PO$_4^{3-}$) and a reducing agent (100 μM Fe $^{2+}$). In the acetate fermentation and methyl-compound cultures, 6.3 mM acetate and 8.4 mM methanol were included as methanogenic substrates, respectively. Compositions of headspace gas in the cultures were 95% N$_2$ and 5% CO$_2$ with the exception of the H$_2$/CO$_2$ reduction cultures. In those cultures the headspace gas was composed 55% N$_2$, 5% CO$_2$, and 40% H$_2$.
The concentrations of these methanogenic substrates were chosen to create an equal final abundance of CH₄ gas in the headspace (9%) if the organisms utilized all available substrate. The cultures incubated in the dark for 107 days at 21ºC. We then analyzed the methane content of the headspace of each culture using a GOW-MAC series 580 gas chromatograph.
Chapter 5 - Results

5.1 Water Chemistry

The pH, water temperature, and conductivity averaged 7.0, 19°C, and 60.9 mS/cm respectively. Alkalinity ranges from 3.33 to 8.59. Water chemistry analyzed using IC resulted in a range of concentrations (Table 2). Sampled water is Na-Cl type. The correlation between Cl⁻ concentration of produced water and longitude is statistically significant (P = 0.022, r = -0.059), meaning Cl⁻ increases westward in the basin (Fig. 6a). Since the basin dips to the west, the total depth of each well also increases to the west in a statistically significant correlation (P = 0.00005, r = -0.88). In contrast, latitude and Cl⁻ do not share a statistically significant correlation (P = 0.16, r = -0.38) (Fig. 6b).

Table 2. Ranges of major ion concentrations and TDS of formation water samples.

<table>
<thead>
<tr>
<th>Component</th>
<th>Min.</th>
<th>Max.</th>
<th>Average</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCO₃⁻</td>
<td>203.2</td>
<td>518.3</td>
<td>300.7</td>
<td>91.6</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>21,300</td>
<td>58,540</td>
<td>34,267</td>
<td>10,493.8</td>
</tr>
<tr>
<td>Mg⁺⁺</td>
<td>346</td>
<td>1,912</td>
<td>874.5</td>
<td>461.2</td>
</tr>
<tr>
<td>Ca⁺⁺</td>
<td>468</td>
<td>2,345</td>
<td>1,274.4</td>
<td>499.6</td>
</tr>
<tr>
<td>K⁺</td>
<td>65</td>
<td>184</td>
<td>100.5</td>
<td>33.3</td>
</tr>
<tr>
<td>Na⁺</td>
<td>12,670</td>
<td>28,050</td>
<td>17,270</td>
<td>4,540.4</td>
</tr>
<tr>
<td>Fe⁺⁺</td>
<td>0.4</td>
<td>84</td>
<td>22.3</td>
<td>24.7</td>
</tr>
<tr>
<td>TDS</td>
<td>35,367</td>
<td>91,565</td>
<td>54,504.6</td>
<td>15,924.3</td>
</tr>
</tbody>
</table>

Water isotopes range from -35.8‰ to -50.6‰ for δD of H₂O and -5.37‰ to -7.39‰ for δ¹⁸O (Appendix C). Water samples with higher δ¹⁸O tend to also have higher Cl⁻ concentration.
(P = 0.044, r = 0.525) (Fig. 7). However, they do not have a significant correlation to longitude (P = 0.15, r = -0.39). The δD H₂O does not vary significantly with Cl⁻ concentration (P = 0.45, r = 0.21).

Figure 6. (a) Comparison of Cl⁻ content of produced water samples and total depth of sampled wells with longitude. (b) Cl⁻ and total depth compared to latitude.
Figure 7. Comparison of $\delta^{18}$O and $\delta$D H$_2$O from formation water samples. Data for the Forrest City basin (FCB) is from Cherokee group coal formation water (Mcintosh et al., 2008). Dashed line is the Global Meteoric Water Line (Craig, 1961).

5.2 Gas Isotopes & Composition

Gas samples we collected were predominantly composed of methane, consistent with dry natural gas. On average, methane, ethane, and propane abundance averaged 97.32%, 0.06%, and 0.02%, respectively. Isotopic analyses of $\delta^{13}$C of CH$_4$ and CO$_2$ range from -56.50‰ to -69.95‰ and -0.536‰ to 9.24‰ relative to VPDB (Vienna Pee Dee Belemnite). The $\delta$D of CH$_4$ ranges from -217.2‰ to -228.2‰ relative to VSMOW (Vienna Standard Mean Ocean Water). The analyzed BTU ranges from 970 to 999 (Appendix B).

Comparison of gas isotopes with longitude and latitude shows two different results. There is no significant trend between $\delta^{13}$C CH$_4$ with latitude (Fig. 8a). However, there is a significant correlation ($P = 0.014$) between $\delta^{13}$C CH$_4$ and longitude (Fig. 8b). $\delta^{13}$C CH$_4$ values increase westward in the basin.
Figure 8. Comparison between (a) $\delta^{13}$C CH₄ and longitude and (b) $\delta^{13}$C CH₄ and latitude.

5.3 Culturing

Methane formed in live cultures inoculated with water from each well tested (Fig. 9).

Conversion of hydrogen and methanol to methane was nearly uniform among the samples tested with averages 6.22% and 6.43% and standard deviations 1.15% and 0.85% respectively. By
comparison, the ability to convert acetate to methane was more variable with average 4.91% and standard deviation 3.18%. Raw data from analysis of culture headspace CH₄ is available in Appendix D.

Figure 9. Heatmap depicting the abundance of methane that formed in each culture relative to the maximum amount possible. The maximum amount of CH₄ that could be produced was 9% of the headspace gas in the culture.
Chapter 6 - Discussion

6.1 Water Chemistry

Formation waters in the CHB plot similarly to the Forrest City Basin along the global meteoric water line (GMWL) (Fig. 7). Similar δD H₂O and δ¹⁸O H₂O values imply that similar processes have influenced the water in each basin, consistent with the close proximity and geologic settings. For the most part, water collected from each basin tends to plot slightly to the right of the GMWL. Processes that can move water isotopic composition to the right of the GMWL include evaporation and high temperature water rock interaction. However, the extent to which either process could have influenced composition appears to be minimal considering that the data only plots slightly to the right of the GMWL.

Variation in the isotopic composition of water samples with the solute content of water suggests that variation in water isotopes may reflect mixing between dilute and saline end-members. The Cl⁻ concentration and δ¹⁸O of our samples share a significant positive correlation (P = 0.044, r = 0.525) (Fig. 10). This trend is consistent with dilution of an isotopically heavy saline brine with water that is isotopically lighter and lower in solute content. Similar relationships have been observed in the Illinois Basin where meteoric re-charge reaches the New Albany shale and Pennsylvanian coals to mix with basin brines (Schlegel et al., 2011). In contrast, Cl⁻ negatively correlated with the δ¹⁸O in samples collected by McIntosh et al. (2008) in the FCB. McIntosh et al. suggested that the trend in their samples might reflect climatic shifts and variable residence times. Salinity in our samples have levels lower than those observed in other biogenic gas reservoirs (Waldron et al., 2007)

In addition to the trend between water isotopes and salinity, the trend between Cl⁻ content and total well depth is consistent with results observed in the Illinois and Michigan basin
(Martini, 1998; McIntosh et al., 2002). This relationship may reflect a decrease with depth in the proportion of freshwater recharge that has mixed with basin brine and/or dissolution of evaporite minerals at depth within the basin. Cl/Br ratios of our samples are relatively low, however, suggesting that interaction with evaporate deposits is limited (Appendix C). Hence, an increasing component of brine with depth is a more likely explanation.

Figure 10. Chloride concentrations plotted against δO¹⁸ for the CHB (this study), the FCB (McIntosh et al., 2008), New Albany shale and Pennsylvanian coals from the Illinois basin (Schlegel et al., 2011). Black lines through each dataset are lines of best fit.

Stable carbon isotopes of HCO₃⁻ (DIC) compared to formation water alkalinity indicates whether or not microbial methanogenesis is altering the values of δ¹³C DIC in the water. Methanogens will selectively use isotopically lighter portions of the formation water, which leaves behind water that is enriched in heavier isotopes. Therefore, a comparison of δ¹³C DIC and alkalinity can show whether microbial methanogenesis has taken place or not (Fig. 11).
FCB has a stronger correlation of increasing alkalinity with increased $\delta^{13}$C DIC than the CHB. Data from the CHB more closely resembles that of the Antrim and New Albany shales of the Michigan and Illinois basins, respectively (Mcintosh et al., 2002; Martini et al., 1998). The Antrim and New Albany shales retain low alkalinities (< 10 meq/L) until $\delta^{13}$C DIC is $> 20\%$, which is similar to the CHB. The $\delta^{13}$C DIC in the CHB gets heavier, which is consistent with $\text{H}_2/\text{CO}_2$ reduction, but not at the same level of alkalinity production as other basins. The important point of this comparison is that the large $\delta^{13}$C DIC in our samples is consistent with microbial methanogenesis. This is not an unreasonable assumption when considering salinity in our samples have levels lower than those observed in other biogenic gas reservoirs, like in Waldron et al., 2007. Indicating that formation water salinity is within the limits for microbial methanogenesis.

Figure 11. Values for the $\delta^{13}$C DIC and alkalinity of waters from the FCB (McIntosh et al., 2008), Antrim Shale Michigan Basin (Martini, 1998), New Albany Shale Illinois Basin (McIntosh et al., 2002), and CHB (this study). Each basin is interpreted to be a biogenic reservoir.
6.2 Pathway of Methanogenesis

Gas chemistry and isotopic composition can be used to evaluate how natural gas formed. We used a Bernard plot (Bernard, 1978), a traditional approach that compares gas dryness index \([C_1/(C_2+C_3)]\) to \(\delta^{13}C\ CH_4\), to determine whether the produced gas was biogenic or thermogenic in origin (Fig. 12). Microbial gas tends to be dry, even though there are microorganisms that can make longer chain hydrocarbons, because microbes that make methane are more abundant in methanogenic communities (Head, 2014). On the other hand, thermocatalytic reactions more readily make longer chain hydrocarbons (i.e. wet gas). The composition of gas samples is consistent with gas that is produced biologically with a small contribution of thermogenic gas mixed into the biogenic gas.

![Bernard Plot](image)

**Figure 12.** Bernard plot used to determine gas origin in the CHB by comparing gas dryness index and \(\delta^{13}C\) of \(CH_4\).

A further evaluation of how microbes formed gas in our samples was done using a Whiticar plot, which compares the \(\delta^{13}C\) and \(\delta D\) of \(CH_4\) (Fig. 13) (Whiticar et al., 1986). Values
from the CHB plot in the H₂/CO₂ reduction zone with a small contribution of thermogenic gas, which is consistent with the Bernard plot.

Previous work had used these traditional plots to evaluate gas origin in CHB coalbeds (Newell and Carr, 2009). Newell and Carr interpreted that some of the gas is thermogenic and assumed that it likely migrated from the Arkoma basin, directly to the south (Newell, 2012). Considering the thermal maturity and presence of black shales in the basin, the small contribution of thermogenic gas could also have originated within the basin.

![Graph showing comparison of δ¹³C and δD CH₄](image)

**Figure 13. Comparison of δ¹³C and δD CH₄ to determine specific methanogenic pathway.**
Gas isotopes can differentiate H₂/CO₂ from acetate/methyl, but it cannot distinguish acetate fermentation from methylotrophic methanogenesis.

Two additional isotopic tracers, which are thought to be more widely applicable, were used to evaluate the origin of the gas (Golding, 2013). The first was to compare the δ¹³C CH₄ to that of δ¹³C CO₂ in the same sample (Fig. 14). This plot was done with calculated fractionation.
factor \( (\alpha_c = (\delta^{13}C\text{ CO}_2 + 1000)/ (\delta^{13}C\text{ CH}_4 + 1000)) \) lines to separate zones for \( \text{H}_2/\text{CO}_2 \) reduction and acetate fermentation (Whiticar et al., 1986). The CHB data plots within the range for \( \text{H}_2/\text{CO}_2 \) reduction, \( \alpha_c > 1.06 \) (Golding, 2013). A line of best fit drawn for the data shows that as \( \delta^{13}C\text{ CH}_4 \) gets heavier it approaches the \( \alpha_c = 1.06 \) line. This means that it is approaching the zone representative of acetate fermentation. While the primary pathway of methanogenesis is \( \text{H}_2/\text{CO}_2 \) reduction, there seems to be some potential contribution of acetate fermentation in the CHB.

![Graph](image)

**Figure 14.** This comparison between \( \delta^{13}C\text{ CH}_4 \) and \( \delta^{13}C\text{ CO}_2 \) for the CHB was plotted with \( \alpha_c \) lines to determine the methanogenic pathway. Red dashed line is the best fit line for CHB samples. Values in purple region are indicative of \( \text{CO}_2 \) reduction and values in red region are indicative of acetate fermentation.

The second tracer for methane origin is the comparison of the \( \delta \text{D} \) of co-produced water with the \( \delta \text{D} \) of \( \text{CH}_4 \). Whiticar (1999) defined a line for \( \text{H}_2/\text{CO}_2 \) reduction:

\[
\delta \text{D}_\text{CH}_4 = \delta \text{D}_\text{H}_2\text{O} - 160\%
\]
The equation for H\textsubscript{2}/CO\textsubscript{2} reduction assumes that 100% of H\textsuperscript{+} ions required for CH\textsubscript{4} formation are sourced from the water where the microbes live. Multiple environments have shown to generate methane roughly 160-180‰ less than the hydrogen isotopes of formation water (Whiticar, 1999). A line for acetoclastic or methylotrophic methanogenesis (acetate/methyl) is defined by the equation:

\[ \delta D_{CH_4} = 0.25 \delta D_{H_2O} - 300\%o \]

It is difficult to determine the difference between acetoclastic or methylotrophic methanogenesis due to the variability of hydrogen isotopes in acetate and methylated compounds. Known δD values for CH\textsubscript{4} formed from acetate or methyl groups are 300‰-377‰ less than δD of formation water (Whiticar, 1999). Acetate/methyl are grouped together when using isotopic tracers, because of the δD\textsubscript{CH4} variability. Sampled wells plot near the H\textsubscript{2}/CO\textsubscript{2} reduction line at lighter δD H\textsubscript{2}O, but move away from the line at heavier δD H\textsubscript{2}O (Fig. 15).

A calculation of potential contribution was done to help determine what percentage of produced methane was from the different pathways. Assuming that the -300‰ line is 100% acetate/methyl methanogenesis and the -160‰ line is 100% H\textsubscript{2}/CO\textsubscript{2} reduction, a potential percent contribution was determined. The distance between line A and B in δD CH\textsubscript{4} at each samples δD H\textsubscript{2}O value was calculated and then the position of each sample along the line was used to determine the potential influence of the different pathways. Acetate/methyl contribution on average is 18.75% and the contribution of H\textsubscript{2}/CO\textsubscript{2} reduction is 81.25%. Samples with lighter δD H\textsubscript{2}O values have a larger potential contribution of acetate/methyl formation. Both isotopic tracers have shown that the primary methanogenic pathway is H\textsubscript{2}/CO\textsubscript{2} reduction with some contribution of acetate/methyl methanogenesis.
Figure 15. Comparison of $\delta D$ CH$_4$ and H$_2$O with predetermined lines of methanogenic pathways from Whiticar (1999). Line (A) is representative of CO$_2$ reduction with dashed lines indicating 160‰ ± 10‰ and line (B) is representative of acetate/methyl methanogenesis.

The separation of data points from the -160‰ line (Fig. 15) could be interpreted in two ways. The $\delta D$ of CH$_4$ does not vary with the $\delta D$ H$_2$O. Or, as the $\delta D$ of H$_2$O values increase, the data trend begins to shift towards the acetate/methyl line and could be indicative of added acetate/methyl contribution to methanogenesis. The increase in $\delta D$ H$_2$O values alone does not explain the shift away from the H$_2$/CO$_2$ reduction line. A study by Waldron et al. (2007) showed that formation water salinity was a driving factor for microbial community composition in the Antrim Shale of the Michigan Basin. It also showed that some hydrogenotrophic communities adapted to salinities above the previously determined upper limit (Waldron et al., 2007). In the CHB the $\delta D$ H$_2$O values increase with salinity. This relationship between salinity and
community composition could explain why the CHB shifts towards the acetate/methyl line at heavier δD H₂O.

6.3 Formation water geochemistry and methanogenesis

We calculated isotope separation of the carbon isotopes ($\Delta^{13}C_{CO_2-CH_4} = \delta^{13}CO_2 - \delta^{13}CH_4$) and hydrogen isotopes ($\Delta D_{CH_4-H_2O} = \delta D CH_4 - \delta D H_2O$) to evaluate how methanogenic pathways relate to geochemistry. The $\Delta^{13}C$ values range from 61.52‰ to 69.99‰ and the ΔD values range from -168‰ to -189.1‰. Golding (2013) defined ranges of isotope separation for the H₂/CO₂ reduction pathway and the acetate/methyl pathways. The range for the acetate/methyl pathway using ΔD had to be calculated using the equation $\delta D_{CH_4} = 0.25*\delta D_{H_2O} - 300‰$. Using two variations of the equation subtracting 300‰ and 325‰, with multiple $\delta D_{H_2O}$ values across the sample range, we calculated pseudo $\delta D_{CH_4}$ values that correlate to acetate/methyl methanogenesis. We determined a range of isotope fractionation factors for acetate/methyl methanogenesis by averaging the calculated ΔD values.

We plotted the $\Delta^{13}C$ and ΔD values against Cl⁻ to evaluate whether our data are consistent with salinity as a control on methanogenic pathway (Fig. 16 & 17). The $\Delta^{13}C$ values show that H₂/CO₂ reduction is predominate throughout the basin (Fig. 16). Values are located at the lower boundary in the range for H₂/CO₂ reduction and decrease with increasing Cl⁻ concentrations indicating that there could be some acetate/methyl contribution. The ΔD values plot isotopically lighter than the H₂/CO₂ reduction boundaries and decrease with increasing Cl⁻ concentration (Fig. 17). The CHB seems to demonstrate that a community of acetoclastic methanogens could be increasing at salinities above the known upper limit of ~1,000 mM Cl⁻.
Figure 16. Carbon isotope fractionation plotted against CHB Cl- concentration. Grey shaded areas are representative of fractionation ranges that correlate to CO₂ reduction and Acetate/methyl methanogenesis.

Figure 17. Hydrogen isotope fractionation plotted against CHB Cl- concentration. Grey shaded areas are representative of fractionation ranges that correlate to CO₂ reduction and Acetate/methyl methanogenesis.
These results are somewhat unexpected. Traditionally, acetate fermentation coincides with freshwater environments and \( \text{H}_2/\text{CO}_2 \) reduction is more common in saline environments. However, in our samples we see an increase in the amount of acetate or methyl contribution with salinity. We know our samples are within salinity limits (~2,000 mM) (Whiticar et al., 1986) for methanogenic bacteria to live so it is not unreasonable to assume that acetoclastic (or methylotrophic) methanogens could be contributing to methanogenesis at higher salinity environments. Therefore, the shift in \( \delta D \) CH\(_4\) towards the acetate/methyl line is likely due to a change in microbial communities with increasing Cl\(^{-}\) concentrations rather than the changes in the isotopic composition of water itself.

The fractionation factor for carbon isotopes (\( \alpha_c \)) was compared to longitude to understand spatial correlations to gas isotopes. Sampled gas \( \alpha_c \) decreases westward in the basin (Fig. 18). While the correlation is not statistically significant (\( p = 0.187 \)), the fractionation factor does seem to decrease towards the acetate/methyl pathway westward in the basin. This is the same trend we see with \( \Delta^{13} \)C and chloride concentrations, further supporting the interpretation that microbial communities are shifting towards acetate/methyl with depth, increased Cl\(^{-}\), and location in the basin.
6.4 Analysis of Production

In order to determine geological controls on production, we compared cumulative production to the total number of feet of coal that were perforated in each well (Fig. 19). This was done to determine if gas production in the CHB is dependent upon coal thickness or not. While there is no statistical correlation between the data, the gas production does seem to decrease with increasing amount of open perforations. This could be due to the presence or lack of prolific coals, the age differences between different wells, or each wells stage in the de-watering process. This negative correlation is evidence that increased thickness of coal perforated in each well does not increase production.
Sodium and chloride are the major contributors to TDS in the CHB and are potentially the controlling factors for microbial communities. Because Cl⁻ is an important chemical constituent, it was compared to cumulative gas production to determine if there is any geochemical control on production (Fig. 20). As Cl⁻ concentration increases, cumulative production decreases. This correlation matches the shift from H₂/CO₂ reduction to acetate/methyl contribution. Potentially, the decreased contribution from H₂/CO₂ reduction also decreases the cumulative production of the well. While this correlation is not very strong, it does seem to exist in the field.

Figure 19. Total open perforations (perfs) compared to cumulative gas production in million cubic feet.
We compared Fe$^{2+}$ to average gas production from two weeks prior to sampling (Fig. 21) in order to determine the redox state of the produced water and how it correlates to gas production. There is a statistically significant ($P = 0.011$) correlation between Fe$^{2+}$ concentration and gas production. In samples with high gas production, there is an increased amount of ferrous iron when compared to samples with lower gas production. The variation in Fe$^{2+}$ concentrations of sampled water could indicate that the water is in a reducing environment. Because larger concentrations of Fe$^{2+}$ correlate to higher gas production, reduction of Fe$^{3+}$ could be important for increased production of gas. The varying quantities of Fe$^{2+}$ could also be indicative of different sources of water. However, different sources of water are unlikely considering the previous correlations found between water chemistry and isotopes in this study.

**Figure 20.** Comparison of Cl$^-$ to cumulative gas production for the CHB. The solid black line is the line of best fit for the samples.
Figure 21. Comparison of average gas production from the two weeks prior to sampling and ferrous iron concentration ($\text{Fe}^{2+}$). Production increases with increasing iron concentration.

More detailed comparisons between production and formation water geochemistry could not be made because of the number of uncontrollable variables in production information; each well produces from multiple or different coal seams, are different ages, and in different stages of de-watering. Because of these reasons, it is difficult to determine specific correlations between geochemistry and production in the CHB.
Chapter 7 - Conclusions

This study aimed to test the research hypotheses that (1) a portion of the gas in Cherokee Basin coalbeds was produced biologically and (2) formation water geochemistry influences gas production. These hypotheses were tested with a field study and lab experiments that utilized formation water, gas samples, and all available production data. The conclusions we reached are as follows:

1. Consistent with the relative low thermal maturity of Cherokee Basin coalbeds, natural gas in the field area is primarily biogenic in origin. Isotopic results indicate that microorganisms formed the gas primarily through CO$_2$ reduction.

2. A small component of gas formed via acetoclastic or methylotrophic methanogenesis. The proportion of gas formed by these alternative pathways appears to increase with the solute content of the water.

3. Culturing results demonstrate that living cells present in the basin are able to make methane.

4. Production does not clearly relate to total coal thickness per well or produced water geochemistry for the most part. Additional research is needed to explore whether those variables may influence production rates.
References


Newell, D.K., 2012. Personal Communication: Personal unpublished writings and ideas were transferred and conveyed through e-mail.


Walton, A.W., 1996. Sequences in the Cherokee Group (Desmoinesian, Middle Pennsylvanian) of southeastern Kansas: *Transactions of the 1995 AAPG Mid-Continent Section Meeting*.


Appendix A. Basic well information for dataset. Location, well names, and API numbers were supplied by Post Rock Energy. All other information was taken from well log headers.
Appendix B - Gas composition and isotopes data

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Appendix B. Gas composition and Isotope values for selected Cherokee Basin wells. The result nd means the value was below detection limit.
# Appendix C - Water chemistry and isotopes data

| Sample | Temp °C | pH | HCO₃ mg/L | Alk mg/L | Cl mg/L | SO₄ mg/L | Br mg/L | Na mg/L | K mg/L | Mg mg/L | Ca mg/L | Fe mg/L | Balance mg/L | TDS mg/L | Percent | δ¹⁸O CO₂ ‰ | δ¹³C | δ³⁴S H₂O ‰ | δ¹⁸O H₂O ‰ | Cl/Br |
| 1 | 18 | 7.15 | 345.5 | 284.3 | 35710 | 4.436666667 | 172 | 17650 | 68 | 1013 | 1200 | 83.9 | -5.2 | 56532 | 2.70 | -62.23 | -220.4 | -37.9 | -6.22 | 207.6 |
| 2 | 18 | 6.75 | 440.5 | 361.3 | 48790 | 10.71666667 | 292 | 23620 | 118 | 1912 | 1336 | 30.7 | -5.0 | 76911 | 4.27 | -60.50 | -224.9 | -35.8 | -5.56 | 167.1 |
| 3 | 18 | 6.98 | 234.9 | 192.7 | 28840 | 5.156666667 | 125 | 14920 | 73 | 785 | 966 | 12.2 | -3.5 | 46154 | -5.36 | -69.12 | -220.7 | -38.8 | -6.32 | 230.7 |
| 4 | 19 | 6.73 | 325.2 | 266.9 | 35930 | 4.976666667 | 116 | 17830 | 152 | 795 | 1835 | 21.4 | -4.3 | 57276 | 6.67 | -57.67 | -219.7 | -48.7 | -7.06 | 309.7 |
| 5 | 17 | 6.55 | 215.4 | 176.7 | 58540 | 0.666666667 | 268 | 28050 | 123 | 1830 | 2345 | 16.5 | -5.3 | 91565 | 4.49 | -57.57 | -224.1 | -38.0 | -5.37 | 218.4 |
| 6 | 21 | 6.81 | 317.3 | 260.2 | 29900 | 4.026666667 | 133 | 15560 | 116 | 649 | 1492 | 6.6 | -2.5 | 48410 | 2.87 | -62.75 | -228.2 | -50.6 | -7.39 | 290.3 |
| 7 | 25 | 7.01 | 240.4 | 197.2 | 39890 | 3.866666667 | 132 | 20790 | 184 | 675 | 1591 | 3.1 | -4.0 | 63707 | 5.02 | -56.50 | -217.2 | -48.5 | -6.83 | 302.2 |
| 8 | 9 | 6.99 | 304.4 | 249.7 | 24310 | 3.156666667 | 120 | 13200 | 65 | 501 | 468 | 8.4 | -3.9 | 39320 | 7.60 | -61.48 | -218.2 | -37.4 | -5.85 | 202.6 |
| 9 | 15 | 6.78 | 381.3 | 321.8 | 44080 | 5.336666667 | 174 | 20860 | 95 | 1240 | 1724 | 36.5 | -6.5 | 68909 | 7.65 | -57.26 | -224.9 | -40.1 | -5.71 | 253.3 |
| 10 | 24 | 214.8 | 176.2 | 37130 | 5.556666667 | 143 | 16960 | 83 | 808 | 1439 | n.d. | -9.0 | 56961 | 8.04 | -57.03 | -222.6 | -41.6 | -6.14 | 259.7 |
| 11 | 28 | 6.76 | 518.3 | 425.2 | 21300 | 5.136666667 | 72 | 11900 | 93 | 346 | 707 | 0.4 | -2.2 | 35367 | 5.07 | -59.25 | -224.9 | -47.9 | -7.18 | 295.8 |
| 12 | 17 | 7.54 | 289.2 | 237.2 | 26220 | 6.856666667 | 113 | 13670 | 80 | 695 | 866 | 1.7 | -3.4 | 42179 | 9.24 | -60.75 | -223.2 | -38.8 | -6.17 | 232.0 |
| 13 | 18 | 7.55 | 214.8 | 176.2 | 23440 | 4.966666667 | 95 | 12670 | 79 | 486 | 837 | 3.3 | -2.4 | 38006 | -1.08 | -63.47 | -222.4 | -42.5 | -6.42 | 246.7 |
| 14 | 7.55 | 214.8 | 176.2 | 23440 | 4.966666667 | 95 | 12670 | 79 | 486 | 837 | 3.3 | -2.4 | 38006 | -1.08 | -63.47 | -222.4 | -42.5 | -6.42 | 246.7 |
| 15 | 18 | 7.39 | 263 | 215.5 | 24240 | 2.996666667 | 102 | 13110 | 79 | 523 | 844 | 24.4 | -2.3 | 39044 | 6.40 | -59.29 | -219.2 | -40.5 | -6.27 | 237.6 |
| 16 | 16 | 7.1 | 203.2 | 166.7 | 35680 | 4.656666667 | 151 | 18260 | 99 | 859 | 1466 | 62.6 | -3.5 | 56958 | 6.21 | -59.46 | -223.6 | -39.6 | -5.93 | 236.3 |

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**Appendix C.** Water chemistry and isotope values for selected Cherokee Basin wells.
## Appendix D - Raw culturing results

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<th>Sample #</th>
<th>Control 1 (% CH₄)</th>
<th>Control 2 (% CH₄)</th>
<th>Acetate Culture (% CH₄)</th>
<th>Methanol Culture (% CH₄)</th>
<th>H₂ Culture (% CH₄)</th>
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</table>

**Appendix D.** Raw culturing results from selected wells in the Cherokee Basin. Values are percent of CH₄ headspace gas at the end of culturing experiment. Wells without culture data did not have water collected for culturing, or the amount of water available was limited and was used for other analyses.