Natural Gas Geochemistry of the Hanson 31-5054z Water Well and Select Upper Jurassic – Lower Cretaceous Oil and Gas Wells, Northwest Louisiana

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Appendix 1 is attached as a separate pdf. file.

Executive Summary

- Six natural gas samples were collected from five producing oil and gas wells and one water "relief" well in DeSoto Parish in northwestern Louisiana to aid the Louisiana Department of Natural Resources in determining the origin of the stray gas in the Hanson 31-5054z water well.
- The Hanson 31-5054z well produces potable water from the Eocene Wilcox Formation.
- The five produced gas samples are from wells completed in the Cretaceous Fredericksburg, Paluxy, Rodessa, and Hosston Formations, and in the Jurassic Cotton Valley Formation. The five produced gas samples contain thermally post mature to overmature thermogenic hydrocarbons generated in deeper petroleum source rocks (Haynesville, Bossier, Cotton Valley, and/or Smackover Formations). Most of the hydrocarbon gases formed through cracking of residual oil in the deep source rocks. The produced gases also contain a minor component of hydrocarbons cracked from post mature refractory organic matter. Gas migration and accumulation in the different Cretaceous reservoirs was iterative resulting in a complex stratigraphic distribution of post mature to overmature hydrocarbons produced from thermally immature to early/peak mature subsurface intervals on the flanks of the Sabine uplift.
- Four of the five produced gas samples appear to contain varying mixtures of microbial methane. Measurement of carbon isotopes of co-produced carbon dioxide could confirm this interpretation.
- Three of the gas samples – Sampson Est. 33 #1, L. A. Smith #2, and Mary Belle Smith 28 #2 Alt - are readily discriminated from one another on various gas isotope cross plots.
- Two of the gas samples (J. B. Barr 28 #2 and Wanamaker #1) are nearly identical in terms of carbon isotope compositions.
- The produced gas from the Wanamaker #1 well contains 2.75% hydrogen. The hydrogen in the Wannamaker #1 may be a product of hydrolysis reactions associated with corrosion in the in the well casing.
- Groundwater and stray gas collected from the Hanson Relief water well (SN 169060) are produced from the Eocene Wilcox Formation. Wilcox strata are thermally immature (VR_o ~ 0.25 to 0.3%) in the study area, yet the stray gas collected from this well is overmature (VR_e ~ 2.5%). The Hanson Relief well gas contains a microbial methane component mixed with predominately thermogenic hydrocarbon components, and has been altered by biodegradation which resulted in loss of propane in the sample. These secondary mixing and alteration effects obscure a precise correlation of the Hanson Relief well gas to the other production gases collected in the study area, but the Hanson gas appears most closely related to the overmature gas produced from the Sampson Est 33 #1 well.

Introduction

In April, 2017, the Hanson 31-5054z water well located approximately 20 miles south of Shreveport, Louisiana (Figure 1) reportedly began to vent natural gas and water (Corey Shircliff, Geologist, Injection and Mining Division, Louisiana Department of Natural Resources, personal communication, November 2017). The wellhead blew off of this water well by August, 2017 and a column of water was reportedly expelled up to 100 feet into the air. The Hanson 31-5054z water well is screened in a freshwater channel sand aquifer (Eocene Wilcox Formation) at 360 feet. A different nearby water well, the Hanson 31-5055z, was noted to have gas bubbling at the surface at the same time. The Hanson 31-5055z well produces fresh water from the same Wilcox aquifer, but from a different channel sand at 460 feet. The Hanson 31-5055z well was plugged, so the stray gas was presumed to be migrating upward behind the casing (PVC casing). The Louisiana Department of Natural Resources initiated mitigation efforts which included performing natural gas geochemical analyses to help determine the origin of the stray gas in the water wells. The wells are located in an active petroleum producing basin making nearby oil and gas wells possible sources of the stray gas (Figure 1). This report provides the results of geochemical analyses of natural gases produced from five oil and gas wells located near the Hanson water wells and a comparison of those results with the stray gas contaminating the water wells. The latter sample was collected from the Hanson Relief water well (SN #169060).

Samples, Location, and Geologic Setting

Six natural gas samples were collected from five producing oil and gas wells and one water "relief" well (Appendix 1) in DeSoto Parish in northwestern Louisiana to aid the Louisiana Department of Natural Resources in determining the origin of the stray gas in the Hanson 31-5054z water well (Figure 1). All six gas samples were collected by Approach Environmental of Shreveport, Louisiana for the Louisiana Department of Natural Resources. Table 1 is a list of the gas samples collected for this investigation. Figure 2 shows the three geologic cross sections indicated on the map in Figure 1.

All six of the wells sampled for this investigation were drilled in the so-called north-central Gulf Coast basin region as defined by Schenk and Viger (1996). DeSoto Parish is located on the south-southeast flank of the Sabine uplift, a broad, low-relief, basement-cored arch which separates the East Texas and North Louisiana Salt Basins (Bartberger and others, 2002, p. 11). The Sabine arch has been a structurally high area for the past 60 m.y. and thus a focus for hydrocarbon migration in the northern Gulf basin during that time (Bartberger and others, 2002). Hood and others (2001) related the distribution of petroleum generated from Mesozoic – Lower Paleogene source rocks in the northern Gulf of Mexico to Paleogene overburden thickness and associated thermal maturation of organic matter. Table 1 and Figures 2 and 3 provide the stratigraphic framework for the six gas samples.

Figure 1. Map of gas sample locations in DeSoto Parish, Louisiana (courtesy of Corey Shircliff, Louisiana Department of Natural Resources). See Table 1 and Figure 2 for well names.

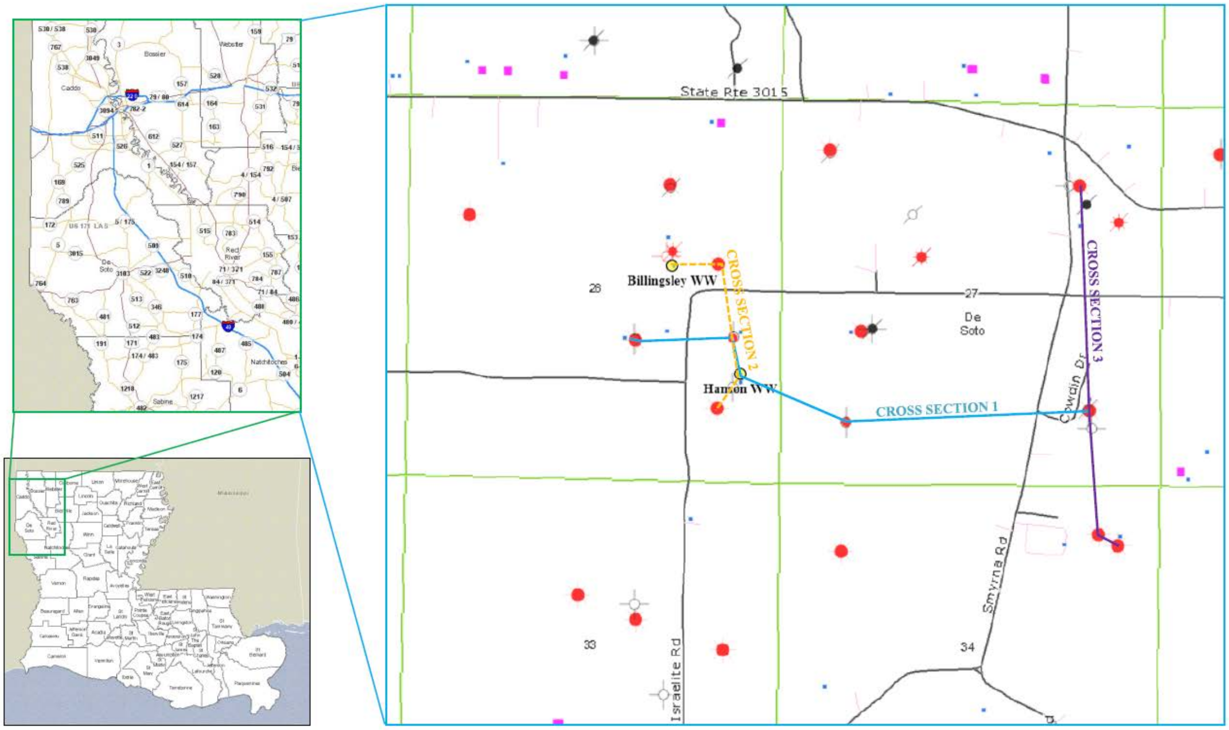


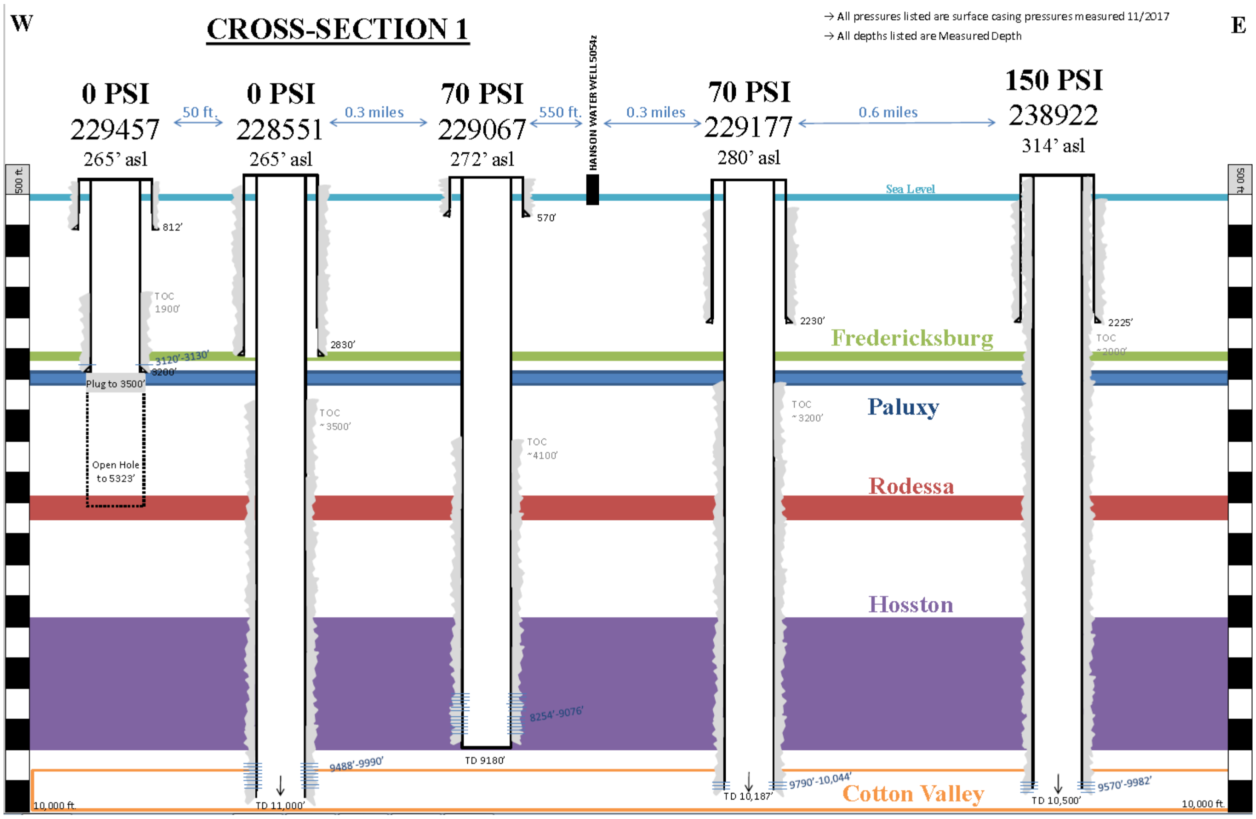
Table 1. Natural gas samples collected from five producing oil and gas wells and the Hanson Relief water well (SN #169060) in DeSoto Parish, Louisiana.

Well Name	Gas Sample Type	Sample Date	Age	Reservoir/Aquifer
Hanson Relief Well	Water Well	12/29/2017	Eocene	Wilcox Formation
L. A. Smith #2	Production	11/29/2017	Lower Cretaceous	Fredericksburg Formation
J. B. Barr 28 #2	Production	11/9/2017	Lower Cretaceous	Paluxy Formation
Wanamaker #1	Production	11/9/2017	Lower Cretaceous	Rodessa Formation
Sampson Est. 33 #1	Production	11/9/2017	Lower Cretaceous	Hosston Formation
Mary Belle Smith 28 #2	Production	11/9/2017	Lower Cretaceous/Jurassic	Cotton Valley Formation

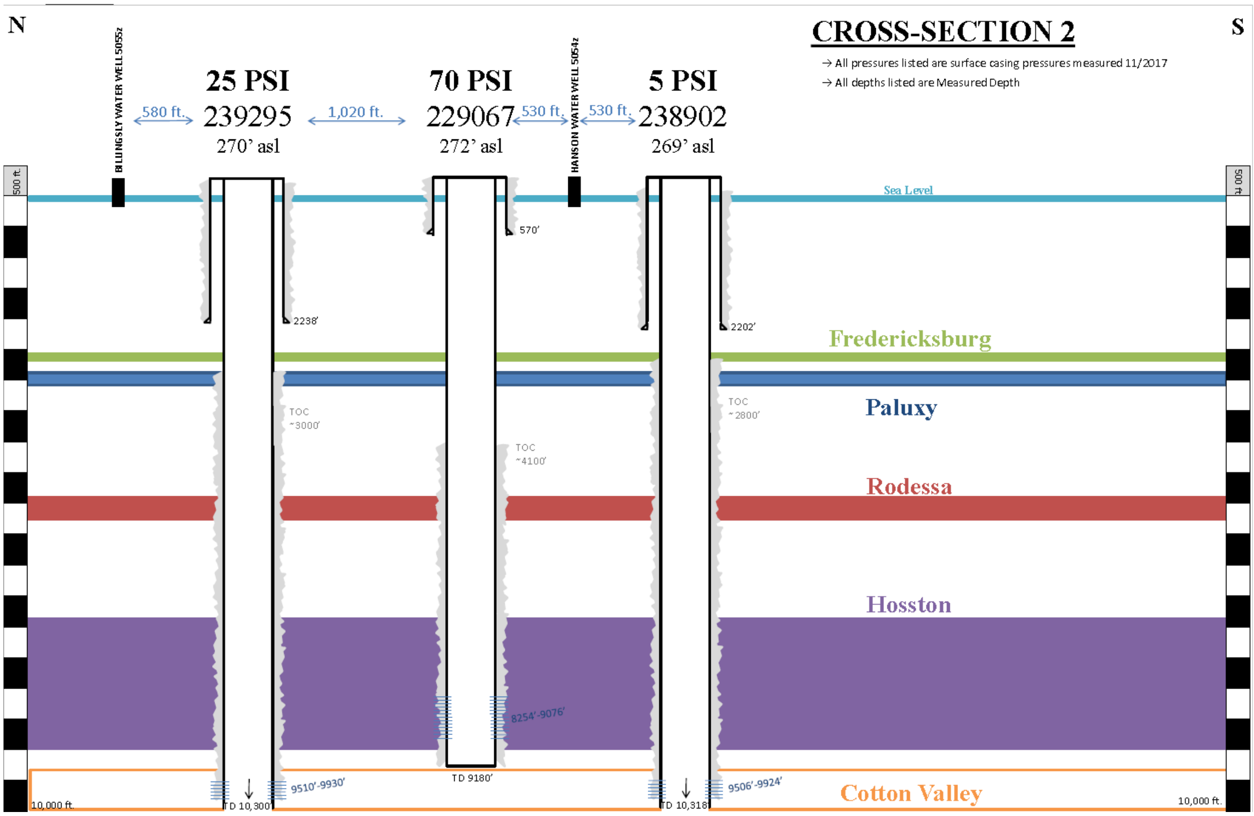
Methods

The five produced gas samples were collected in steel high-pressure gas cylinders at the well sites. Analyses were performed at Isotech Laboratories in Champaign, Illinois and included molecular composition, methane carbon and hydrogen stable isotopes, and ethane and propane stable carbon isotopic compositions. The sample chemical compositions were measured by Shimadzu 2010 GC systems equipped with FID and TCD detectors. Stable isotope compositions were determined off-line. Each sample was separated into its individual components in a SRI GC, and then each hydrocarbon was oxidized to CO_2 (for carbon isotopes) and/or H_2O (for hydrogen isotopes). The latter was further reacted to hydrogen gas by reacting the combustion water with zinc turnings and then measuring the isotope ratio of the hydrogen using a Thermo Delta V Plus IRMS system. The CO_2 combustion products were then introduced to a dual-inlet mass spectrometer for carbon isotope ratio measurements: multiple instruments include Finnigan Delta S, Thermo Finnigan Delta Plus XL, and Thermo Delta V Plus systems. Precision for the carbon isotopic measurement by the off-line methodology is ±0.1‰ (one sigma).

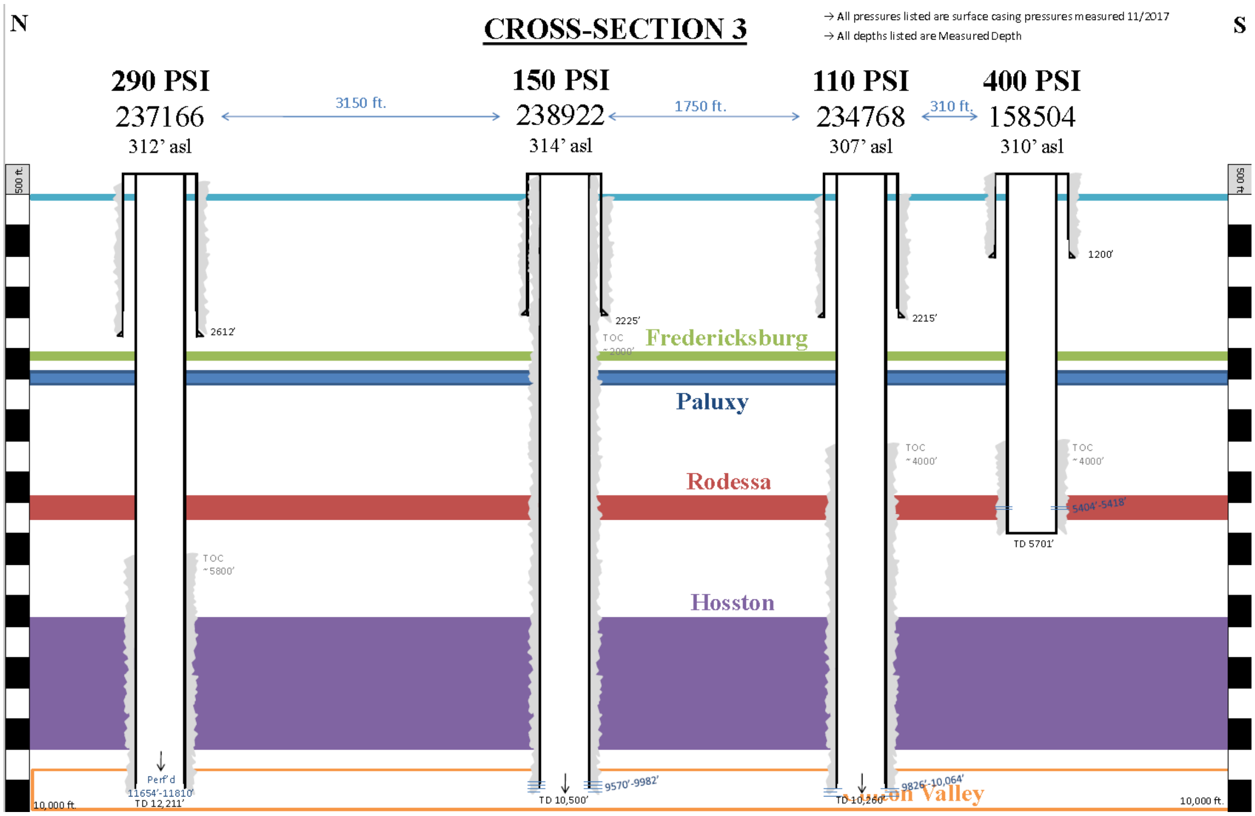
Figure 2. Geologic cross sections 1, 2, and 3 as indicated in Figure 1 (courtesy of Corey Shircliff, Louisiana Department of Natural Resources).



J. B. Barr 28 #2

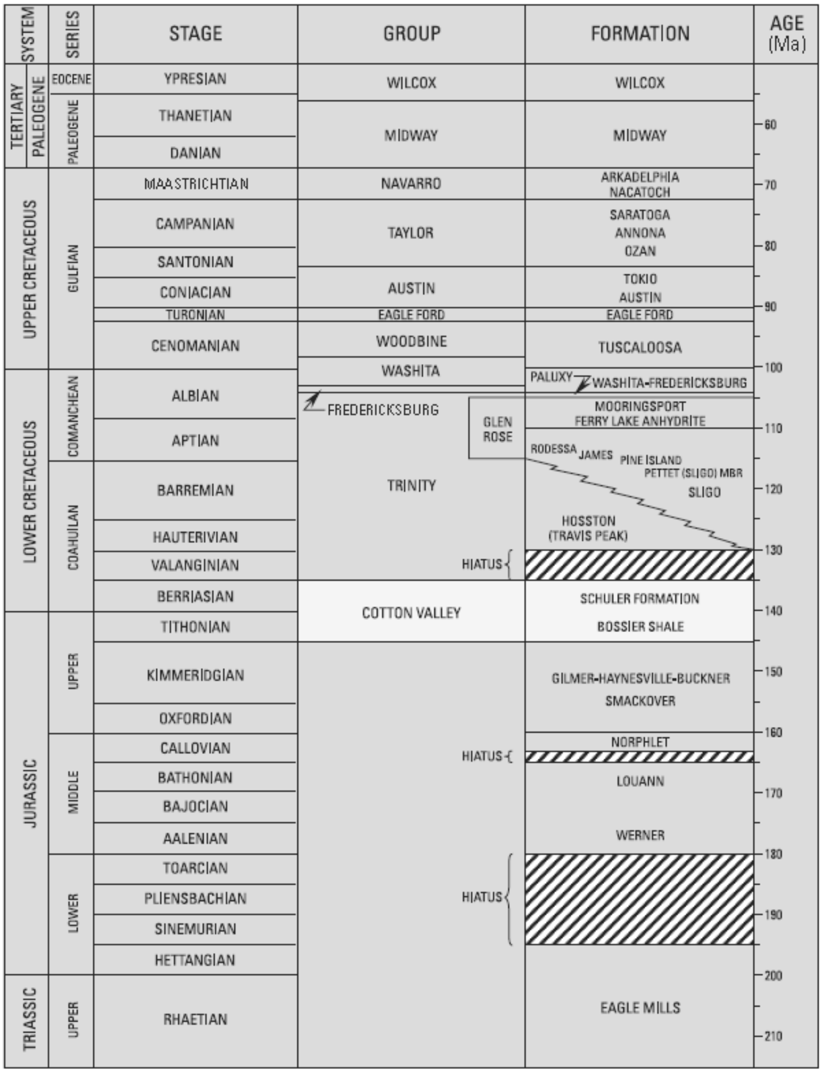


**Mary Belle
Smith 28 #2**



Wanamaker #1

Figure 3. Chronostratigraphic section of northern Louisiana showing the intervals of interest discussed in this report (from Dyman and Condon, 2006, Figure 4, p. 9).



Geochemistry of Produced Gas Samples

Table 2 shows the chemical composition of the five produced gas samples. All of the gas samples are dominated by methane (C_1) which comprises 91.80 to 95.81 mol % of the gross composition. Ethane (C_2) and propane (C_3) make up 0.410 to 3.80 mol % and 0.0325 to 0.927 mol % of the gas composition, respectively. The higher hydrocarbon gases butane through hexanes+ occur as minor constituents.

Table 2. Chemical composition of the five produced gas samples analyzed for this investigation. All values are reported as mol %.

Well Name	He	H_2	Ar	O_2	CO_2	N_2	C_1	C_2	C_3	iC_4	nC_4	iC_5	nC_5	C_{6+}
L. A. Smith #2	0.0253	nd	nd	nd	0.010	1.55	93.68	2.56	0.925	0.247	0.316	0.172	0.137	0.378
J. B. Barr 28 #2	0.0295	nd	0.0060	nd	0.14	2.76	93.06	2.51	0.784	0.225	0.232	0.100	0.0595	0.914
Wanamaker #1	0.0303	2.75	0.0058	nd	0.008	2.16	91.80	2.12	0.601	0.15	0.160	0.0667	0.0420	0.104
Sampson Est. 33 #1	0.0403	nd	0.0074	nd	0.92	2.55	95.81	0.410	0.0325	0.0133	0.0142	0.0069	0.0124	0.188
Mary Belle Smith 28 #2	nd	nd	nd	0.026	2.00	0.14	92.13	3.80	0.927	0.240	0.234	0.145	0.0748	0.288

Figure 4 is a plot of the Gas Wetness Ratio (GWR) versus the Light-to-Heavy Ratio (LHR) of the produced gas samples. The GWR is calculated as,

$$100 \times \sum(C_2\text{-}C_5)/\sum(C_1\text{-}C_5),$$

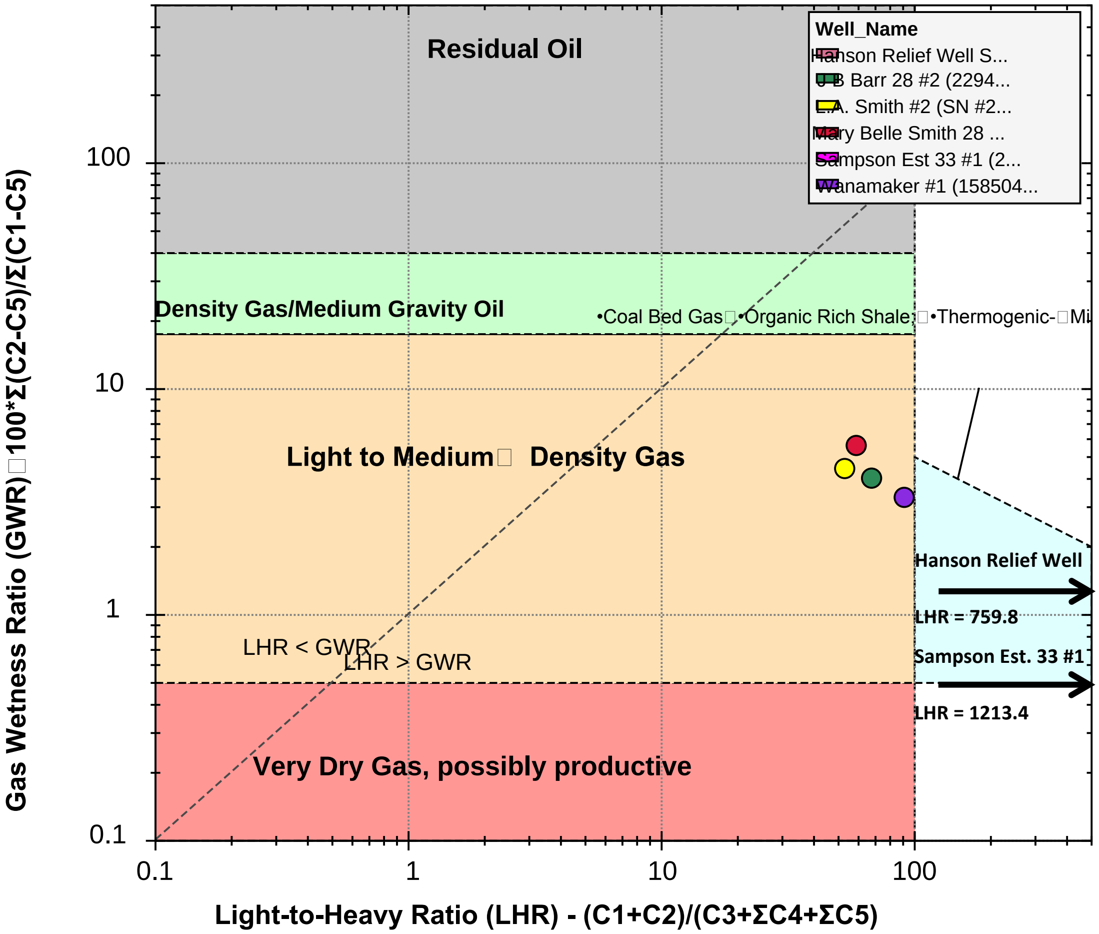
where C_1 - C_5 are methane through pentane hydrocarbon gases (Haworth and others, 1985). The LHR is calculated as,

$$(C_1 + C_2)/(C_3 + iC_4 + nC_4 + iC_5 + nC_5),$$

where C_1 – C_5 again are the methane through pentane hydrocarbons. These parameters are qualitative gas ratios that are useful for interpreting reservoir fluid characteristics (Haworth and others, 1985; Figure 4).

Four of the DeSoto Parish produced gas samples plot within the field for light to medium density gas. The Mary Belle Smith 28 #2 Alt (239295) gas, produced from the Cotton Valley Formation, has the highest GWR (5.6%) in the data set; its LHR is 59.2 (Table 3). The Fredericksburg Formation gas produced from the L. A. Smith #2 (218464) is slightly less wet with a GWR of 4.4% and LHR of 53.5. The Paluxy Formation gas produced from the J. B. Barr 28 #2 (229457) well and the Rodessa Formation gas produced from the Wanamaker #1 (158504) well exhibit decreasing wetness and increasing dryness (Figure 4 and Table 3). The produced Hosston Formation gas collected from the Sampson Est. 33 #1 well (229084) is very different from all of the other gases. The Sampson Est 33 #1 gas is extremely dry with a GWR of only 0.5081 and a LHR of 1213.4 (Table 3). Consequently, this sample falls off of the scale shown in the Haworth and others (1985) plot in Figure 4.

Figure 4. Potential reservoir fluid compositions of the natural gas samples from DeSoto Parish based on the GWR (Gas Wetness Ratio) versus the LHR (Light-to-Heavy Ratio) (Haworth et al., 1985). The liquid associations do not indicate the quantity of liquids, but provide an estimation of the types of liquids encountered in the reservoirs. Note that the Sampson Est. 33 #1 (229084) and Hanson Relief well gases do not appear on the plot because they fall far off of scale (black arrows).



Haworth and others (1985) introduced a third parameter called the oil character ratio (OCR) which is used to refine the interpretation of GWR and LHR values (Table 4). The OCR is calculated as,

$$(iC_4 + nC_4 + C_5)/C_3.$$

The OCR values of the gases in the DeSoto Pariah produced gas samples range from 0.7033 to 1.44 (Table 3). Excepting the Sampson Est. 33 #1 sample, all of the produced gas samples listed in Table 3 are wet gases associated with condensate or light oil. Combined consideration of the GWR, LHR, and OCR suggest that the Sampson Est. 33 #1 sample is mixed thermogenic and microbial gas (Tables 3 and 4). However, other data presented and discussed below conflict with this interpretation (see **Discussion**).

Table 3. Haworth and others (1985) gas composition parameters for the DeSoto Parish produced gas samples. Also see Figure 4 and Table 4.

Well Name	GWR (%)	LHR	OCR	Fluid Type
L. A. Smith #2	4.4	53.5	0.9427	Wet Gas: condensate; light oil
J. B. Barr 28 #2	4.03	68.2	0.7863	Wet Gas: condensate; light oil
Wanamaker #1	3.3	91.7	0.7033	Wet Gas: condensate; light oil
Sampson Est. 33 #1	0.5081	1213.4	1.44	Mixed Gas: thermogenic/microbial?
Mary Belle Smith 28 #2	5.6	59.2	0.7484	Wet Gas: condensate; light oil

Table 4. Summary of the interpretive guidelines for Haworth and others (1985) parameters.

GWR	LHR	OCR	FLUID TYPE
< 0.5	>100	0	Very Dry Gas
0.5 ≤ GWR < 17.5	<100	<0.5	Wet Gas: non-associated
0.5 ≤ GWR < 17.5	<100	≥0.5	Wet Gas: condensate; light oil
17.5 ≤ GWR < 40	<100	<0.5	Very Wet Gas: non-associated
17.5 ≤ GWR < 40	<100	≥0.5	Very Wet Gas: medium gravity oil
0.5 ≤ GWR < 17.5	≥100	≥0.5	Mixed Gas: thermogenic/microbial
< 40	≥100	<0.5	Coal Bed Gas: organic-rich shale-gas
GWR > 40	<<17.5	≥0.5	Residual Oil

The gas chemical composition data in conjunction with methane carbon isotope composition indicate that all five of the produced gas samples are thermogenic in origin (Figures 5 and 6). Stable isotope data for the produced gas samples are provided in Table 5. The Bernard plot in Figure 5 indicates that all five gas samples originated as thermogenic hydrocarbons generated from Type II kerogen in marine petroleum source rocks; the Sampson Est. 33 #1 gas is significantly more thermally mature than the other gas samples. The Mary Belle Smith 28 #2 Alt Cotton Valley Formation gas contains the least thermally mature hydrocarbons. The Schoell (1983) plot of methane δ^{13}C versus gas wetness shown in Figure 6 supports and refines this interpretation. All five produced gas samples plot in the field of post mature dry gas. However, the Sampson Est. 33 #1 gas is significantly more mature than any of the other samples with a gas wetness of only 0.5081% and a methane carbon isotope composition ($\delta^{13}C_1$) of -31.68‰.

Conversely, the relatively wetter Mary Belle Smith 28 #2 Alt gas sample plots on the border between post mature dry gas and mature gas formed with oil.

Table 5. Stable isotope analytical results for the DeSoto Parish produced gas samples. All values are reported in parts per thousand (per mil, ‰)

Well Name	Reservoir	$\delta^{13}C_1$	$\delta D_{METHANE}$	$\delta^{13}C_2$	$\delta^{13}C_3$
L. A. Smith #2	Fredericksburg Formation	-37.18	-149.0	-25.98	-25.48
J. B. Barr 28 #2	Paluxy Formation	-38.37	-149.7	-25.06	-24.07
Wanamaker #1	Rodessa Formation	-38.74	-155.2	-25.03	-24.23
Sampson Est. 33 #1	Hosston Formation	-31.68	-119.3	-23.09	*
Mary Belle Smith 28 #2	Cotton Valley Formation	-39.51	-158.1	-27.12	-24.94

- **Insufficient concentration for carbon isotopic measurement**

Figure 5. Plot of the ratio of methane to ($C_1/(C_2 + C_3)$), versus the carbon isotopic composition of methane ($\delta^{13}C_1$) for the DeSoto Parish natural gas samples (after Bernard and others, 1978). All of the gases plot as thermogenic hydrocarbons. Other data, however, indicate ~ 5 to 12% microbial gas in five of the samples. The brown hypothetical gas mixing lines are from Golding and others (2013) and are discussed in the text. The dashed brown lines represent relative % microbial gas, and the black arrow denotes increasing maturity of thermogenic gas.

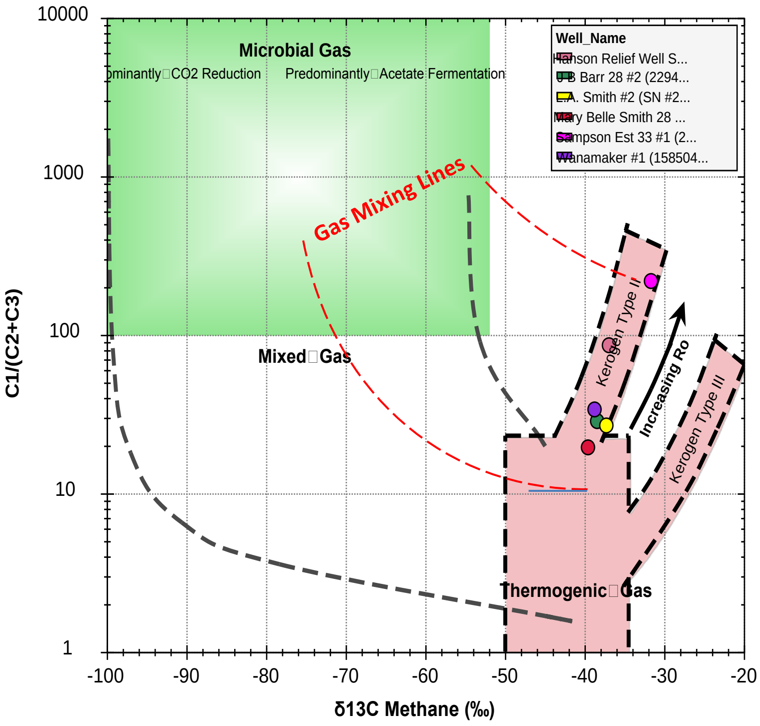


Figure 6. Schoell (1983) plot of $\delta^{13}C_1$ versus gas wetness for the DeSoto Parish natural gas samples.

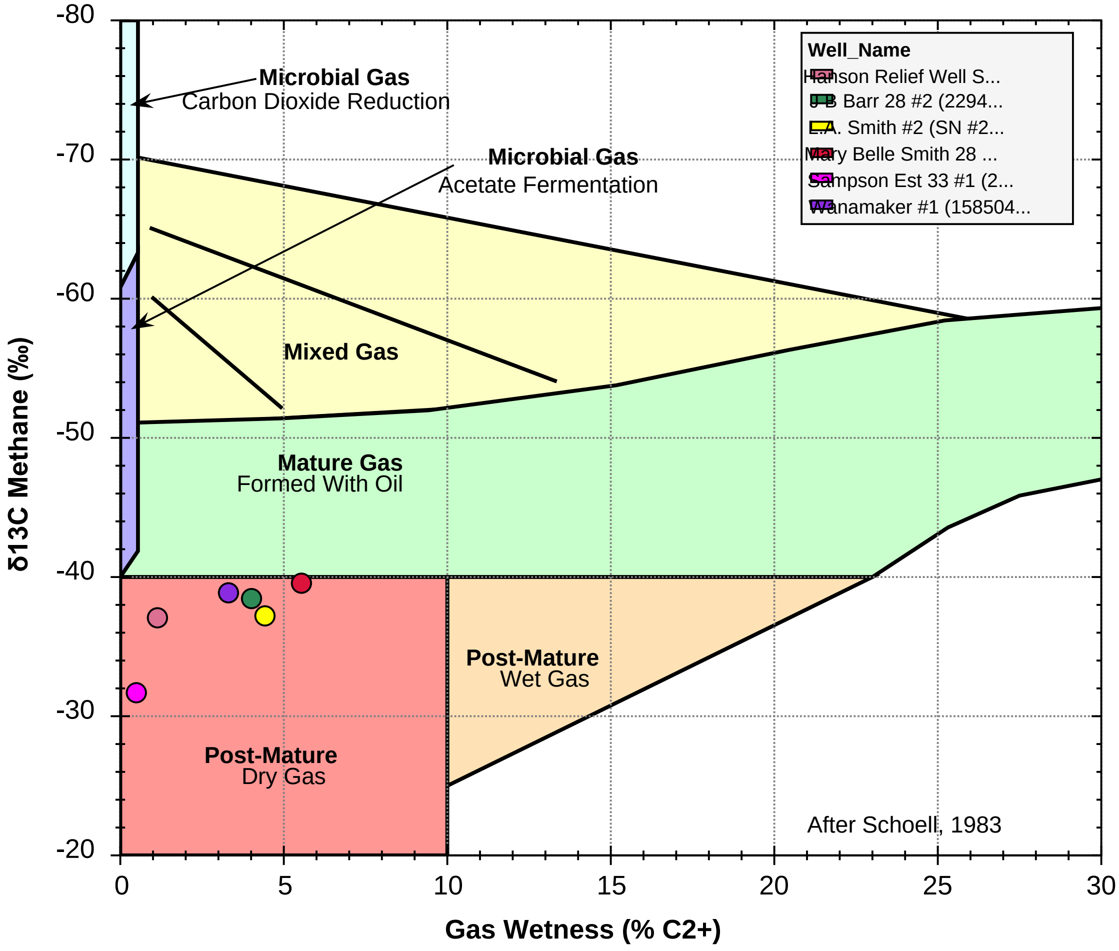
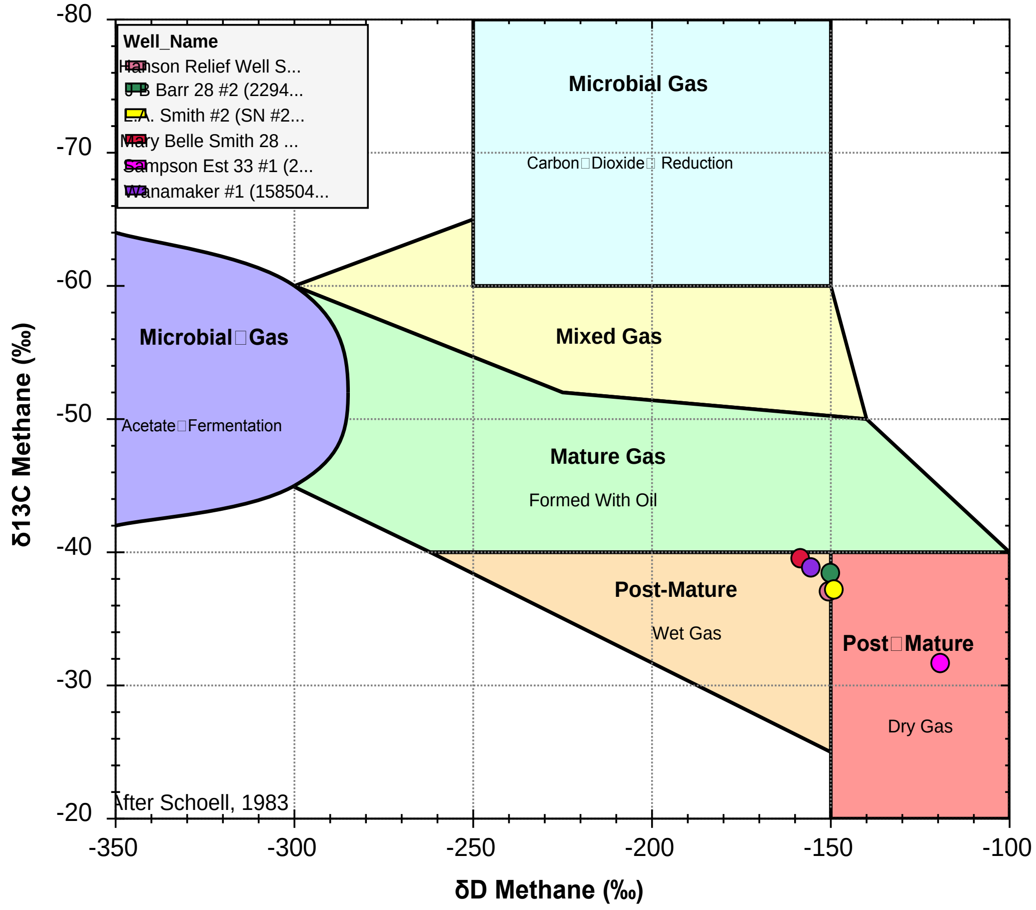


Figure 7 is a plot of methane $\delta^{13}C$ versus methane δD for the DeSoto Parish produced gas samples. The data present the same general thermal maturity trends illustrated in Figures 5 and 6, but the hydrogen isotope results provide better resolution of the genetic interpretive parameters. The Sampson Est. 33 #1 gas contains post mature dry methane. The L. A. Smith #2 and J. B. Barr 28 #2 produced hydrocarbons cluster relatively close together along the boundary between post mature wet and dry gas. The Wanamaker #1 and Mary Belle Smith 28 #2 Alt samples plot together in the field of post mature wet gas.

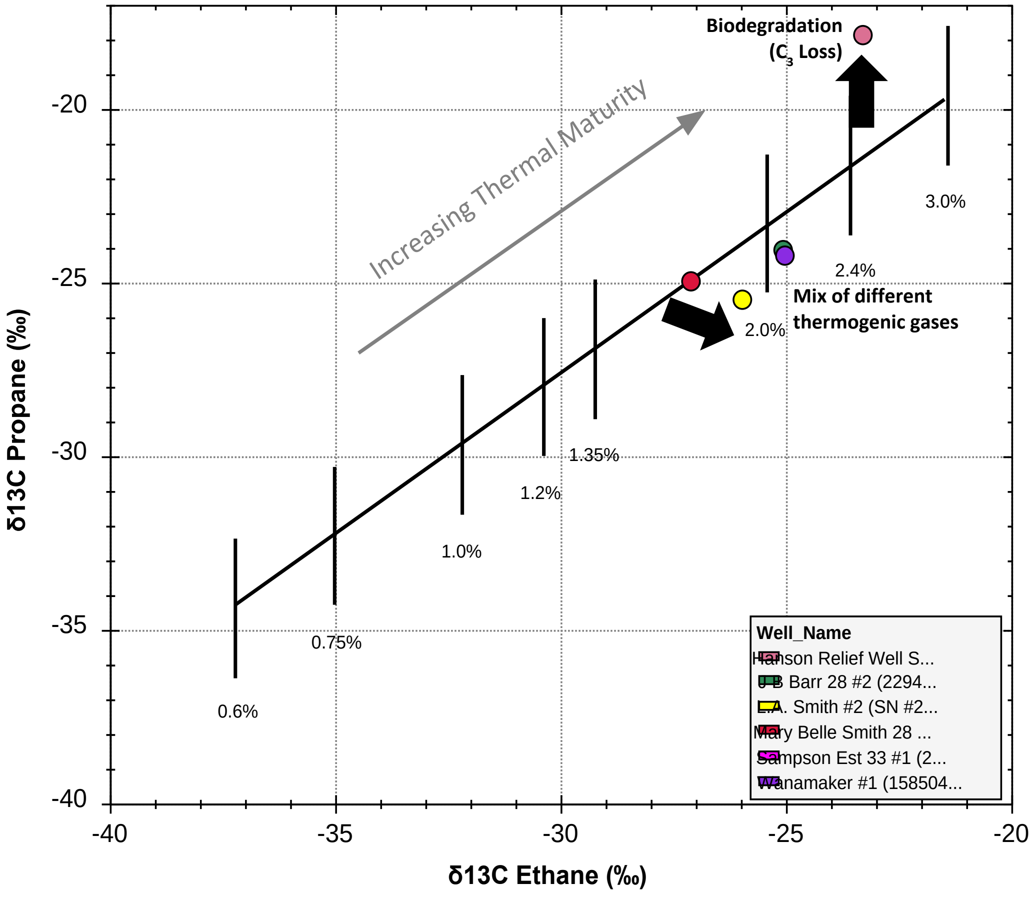
Cross plots of ethane $\delta^{13}C$ versus propane $\delta^{13}C$ (Figure 8) and methane $\delta^{13}C$ versus ethane $\delta^{13}C$ (Figure 9) for the DeSoto Parish produced gases facilitate estimates of the actual thermal maturity of the samples. These plots permit recognition of mixing and secondary alteration effects in the gases as well.

Figure 7. Schoell (1983) plot of methane δ^{13}C versus δD for the DeSoto Parish natural gas samples.



The plot of ethane δ^{13}C versus propane δ^{13}C in Figure 8 provides thermal maturity estimates for four of the produced gas samples as well as for the Hanson Relief well sample (discussed below) in terms of vitrinite reflectance equivalent (VR$_e$). The Sampson Est. 33 #1 well sample has insufficient propane for carbon isotope measurement. The Cotton Valley Formation gas produced from the Mary Belle Smith 28 #2 Alt well was generated in its source rock at a VR$_e$ ~ 1.7%. This estimate agrees with the predicted present day maturation of Haynesville and Bossier Formation source rocks and interbedded Cotton Valley reservoir and source rocks in the study area published by Nunn (2012). The L. A. Smith #2 gas produced from the Fredericksburg Formation is more mature and was generated at approximately 1.8% VR$_e$. Interestingly, Fredericksburg strata in the study area are thermally immature (VR = 0.25 to 0.55%); only Cotton Valley, Bossier, Haynesville and Smackover Formation source rocks attained the level of thermal stress observed in the L. A. Smith #2 gas (Nunn, 2012). The Rodessa Formation hydrocarbons produced from the Wanamaker #1 well and the Paluxy Formation hydrocarbons produced from the J. B. Barr 28 #2 well were generated at a VR$_e$ ~ 2.1%, probably from the same source rock. Note that the L. A. Smith #2, Wanamaker #1, and J. B. Barr 28 #2 gas samples all plot slightly downward and off of the ethane δ^{13}C versus propane δ^{13}C correlation trend; this indicates a mix of different thermogenic gases related to secondary alteration effects (Whiticar, 1994). As is the case described for the Fredericksburg Formation, the Paluxy Formation stratigraphic interval is thermally immature in the study area and only the deeper Smackover interval source rocks reached the level of maturity observed in the J. B. Barr 28 #2 well gas sample (Nunn, 2012). Rodessa Formation strata penetrated in the Wanamaker #1 well are in the early oil window (0.55 to 0.7 VR$_e$) and also require a Smackover source for the observed level of hydrocarbon gas maturity (Nunn, 2012).

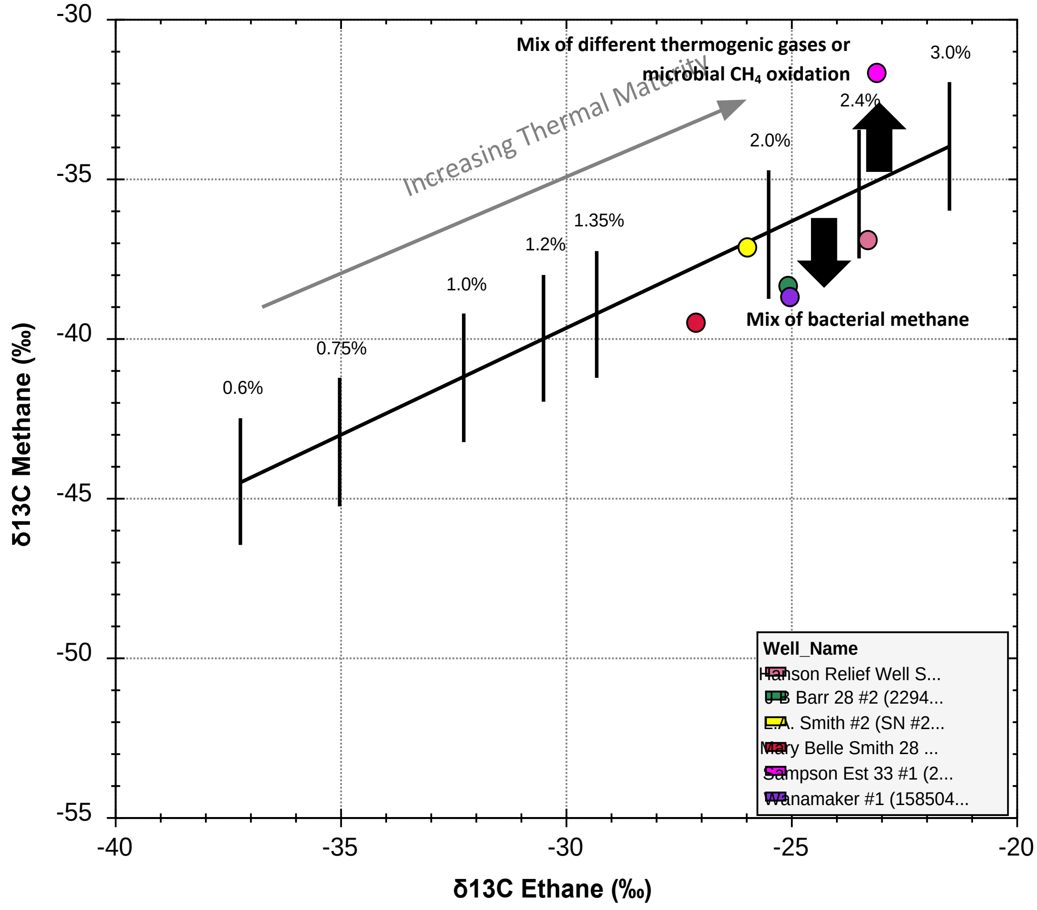
Figure 8. Plot of δ^{13}C$_2$ versus δ^{13}C$_3$ and relationship to thermal maturity (vitrinite reflectance equivalent) for the DeSoto Parish natural gas samples (after Whiticar, 1994).



The plot of methane δ^{13}C versus ethane δ^{13}C in Figure 9 yields similar thermal maturity estimates for the four gas samples just discussed as well as a VR$_e$ of 2.5% for the Hosston

Formation gas produced from the Sampson Est. 33 #1 well. Hosston Formation strata in the study area are in the early (VR_e = 0.55 to 0.7%) to peak (VR_e = 0.7 to 1.0%) oil window, thus the produced gas collected from the Sampson Est. 33 #1 well must have a significantly deeper source. Indeed, the VR_e ~ 2.5% interpreted for the Sampson Est. 33 #1 gas produced from the Hosston Formation in this well was generated in the dry gas window. Only the Smackover Formation attained this level of thermal maturity in the study area (Nunn, 2012).

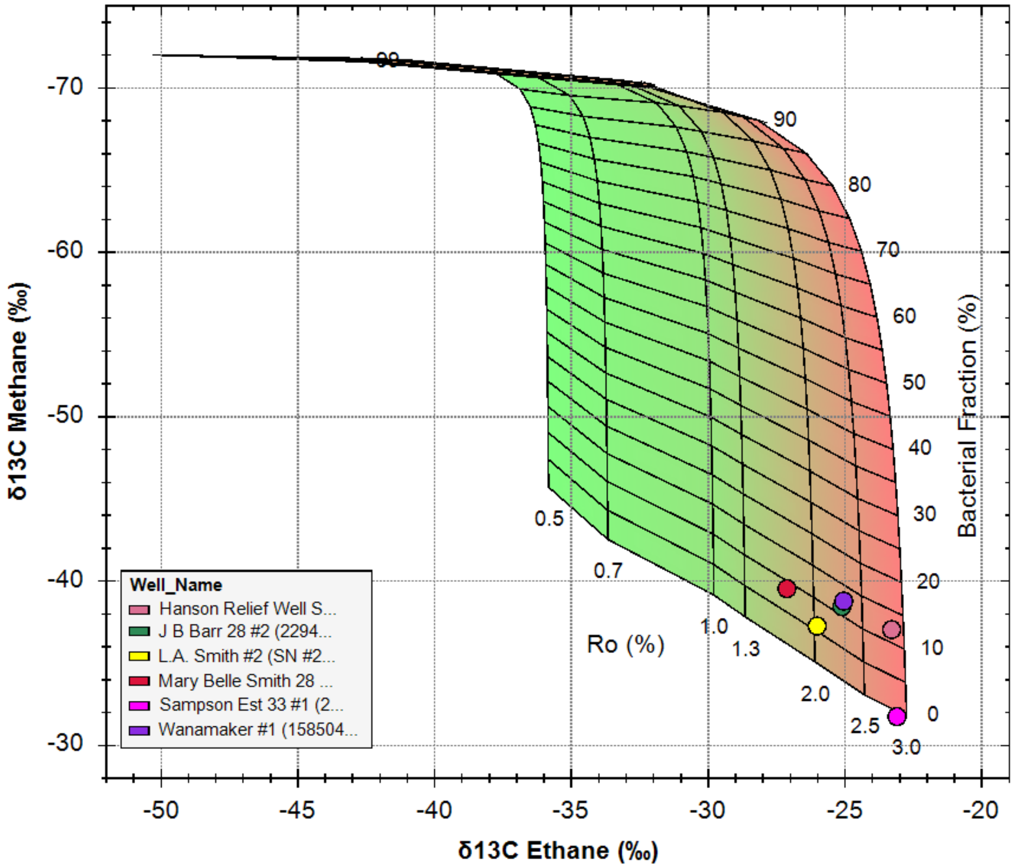
Figure 9. Plot of $\delta^{13}C_1$ versus $\delta^{13}C_2$ and relationship to thermal maturity (vitrinite reflectance equivalent) for the DeSoto Parish natural gas samples (after Whiticar, 1994).



Most of the gas samples plotted in Figure 9 exhibit evidence secondary gas alteration. The post mature dry gas sample from the Sampson Est. 33 #1 well plots upwards off of the $\delta^{13}C_1$ versus $\delta^{13}C_2$ correlation trend indicating a mix of different thermogenic gases or microbial methane oxidation. The Mary Belle Smith 28 #2 Alt, Wanamaker #1, and J. B. Barr 28 #2 well samples fall down and away from the $\delta^{13}C_1$ versus $\delta^{13}C_2$ correlation trend suggesting a possible mix of thermogenic and microbial gas or other secondary alteration effects.

Figure 10 presents another plot of methane $\delta^{13}C$ versus ethane $\delta^{13}C$ showing the thermal maturity (VR_e) of gases generated from refractory kerogen mixed with bacterial methane. The plot suggests that all of the samples except the Sampson Est 33 #1 gas contain between six and 15% microbial methane.

Figure 10. Plot of methane $\delta^{13}C$ versus ethane $\delta^{13}C$ showing thermal maturity (VR_e) modeled for refractory kerogen and bacterial methane mixing for the DeSoto Parish natural gas samples.



[1] **Refractory kerogen is the main lignin-derived component of vitrinite in sedimentary organic matter. It yields methane from either mature Type III kerogen in coal or from post mature to overmature Types I and II kerogen with no remaining oil generation potential.**

Figure 11 is a so-called “natural gas plot” or “Chung” plot of $\delta^{13}C$ against the reciprocal of the carbon number of each hydrocarbon gas in each of the DeSoto Parish natural gas samples. In this model, proposed by Chung and others (1988), a kinetic isotope effect is expressed in methane showing the maximum isotopic fractionation compared to the precursor kerogen. If the wet gas components in the samples were derived from the same source organic material, then there should be a linear relationship between the carbon isotope composition of each hydrocarbon gas component and the reciprocal of their carbon number (Chung and others, 1988; Rooney and others, 1995; straight dashed line in Figure 11, Bottom). If the gases were generated from a single source, then the plot should approximate a straight line, attenuated by increasing thermal maturity reflected by a change in slope (Golding and others, 2012). The vertical spread in the values plotted in Figure 11 (Bottom) is due, in part, to variations in source organic matter and thermal maturity (double arrow).

The produced Hosston Formation gas collected from the Sampson Est. 33 #1 well is the only sample that exhibits the expected straight line kinetic relationship on the natural gas plot shown in Figure 11. Bear in mind that the observed trend is incomplete because the sample had insufficient propane for isotopic analysis. This sample is also the most thermally mature gas in the data set (VR_e ~ 2.5%). This gas is most likely sourced from the Smackover Formation (see **Discussion** below). Note that the y-intercept of the straight line trend of the Sampson Est. 33 #1 gas lays well above (is more positive) the carbon isotope composition of Haynesville and Smackover Formation kerogen. This is because the Hosston gas was mostly generated through oil cracking rather than kerogen cracking as explained in the **Discussion** section below.

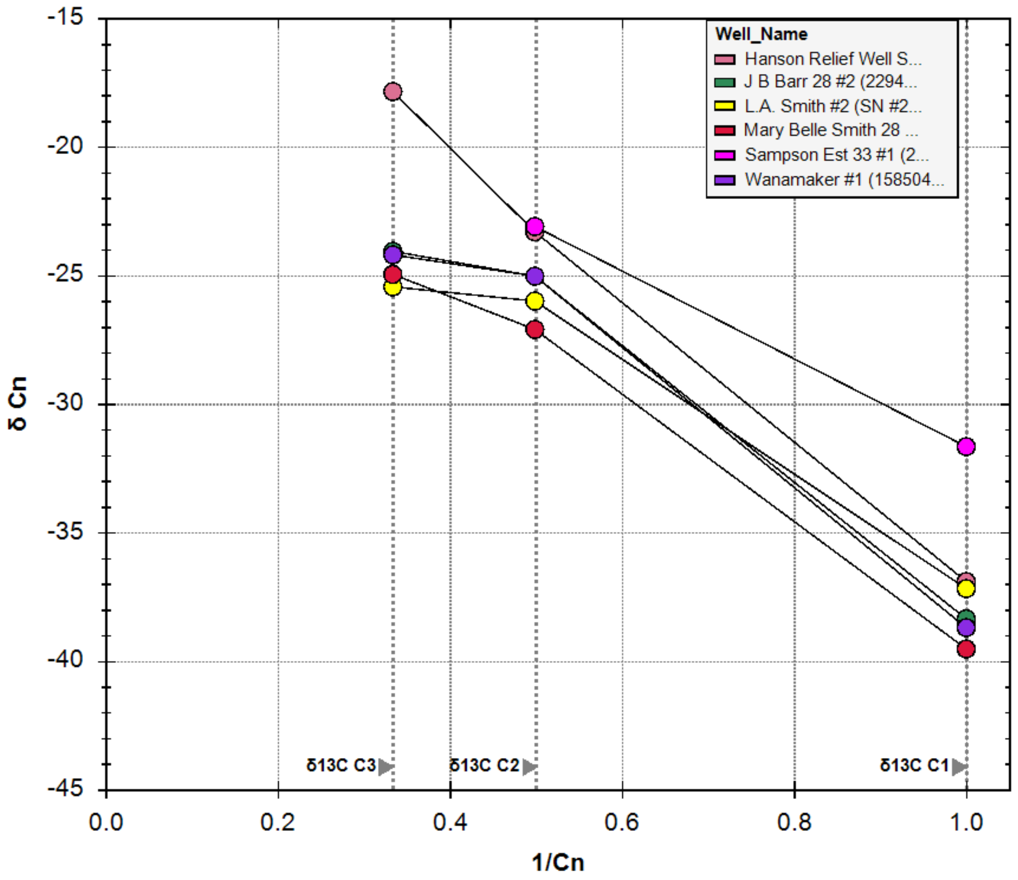
The produced Cotton Valley Formation gas collected from the Mary Belle Smith 28 #2 is the relatively least mature gas in the data set (VR_e ~ 1.5 to 1.7%). This gas is could be sourced from the Smackover Formation, the Haynesville Shale/Bossier Shale, or source rocks interbedded with Cotton Valley reservoir rocks (discussion above and see Schenk and Viger, 1996; Peters and others, 2005; Dyman and Condon 2006; Nunn, 2012; Pittman and Rowan, 2012). The natural gas plot for this sample deviates somewhat from the expected linear trend – a dogleg at C_2 imparts a slightly convex pattern to the plot (Figure 11). This pattern may be related to mixing with residual microbial gas (Golding and others, 2013), to mixing mature gases derived from Types II and III organic matter, and to cracking of residual oil (Zou and others, 2007).

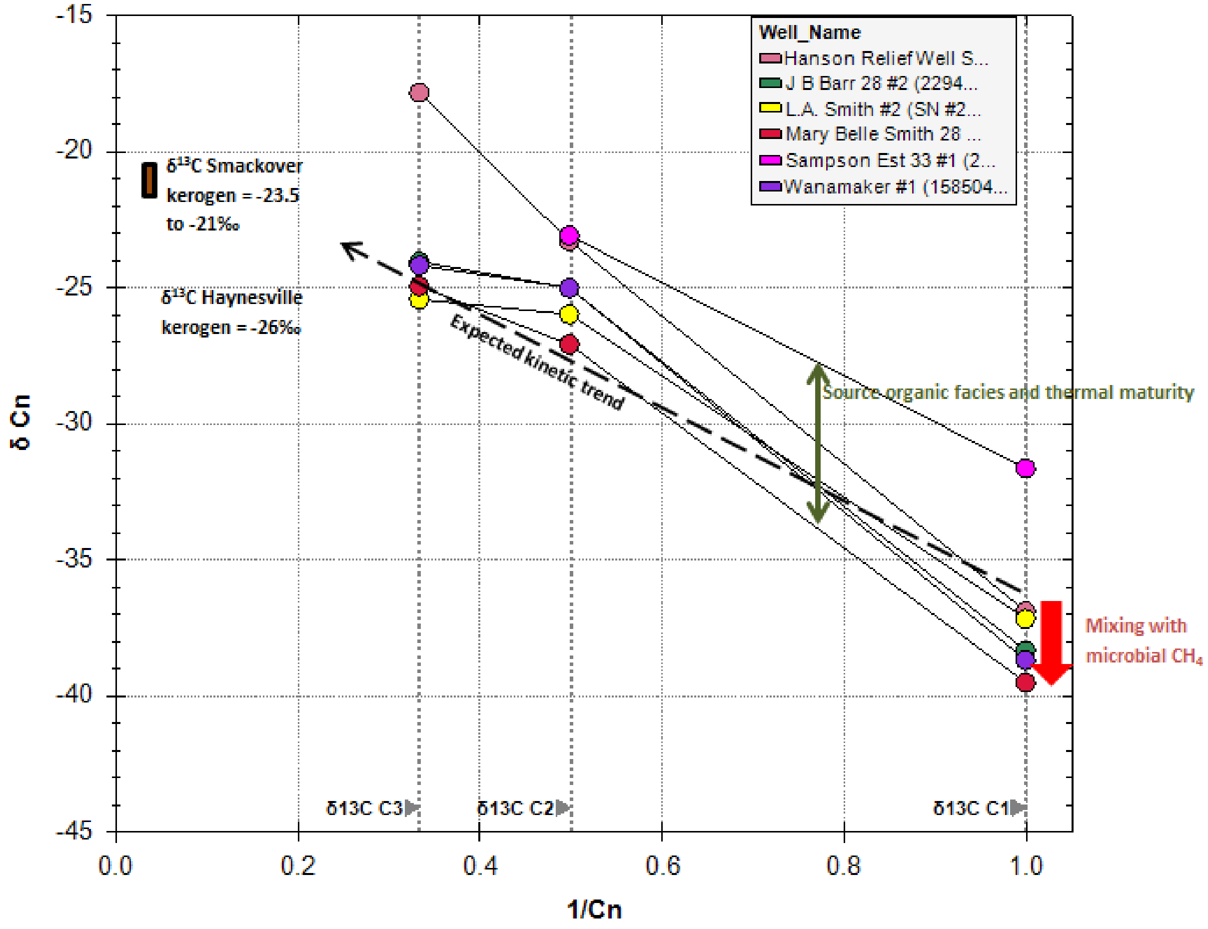
The produced gases from the Wanamaker #1 and the J. B. Barr 28 #2 plot almost identically on the natural gas plot in Figure 11. Although produced from different reservoirs (Rodessa and Paluxy), these two gases appear to share the same source and maturity. These gases have a maturity of VR_e ~ 2.1%, a value consistent with a Haynesville Shale or, more likely, the Smackover Formation source in this area (Nunn, 2012). The gases from both the Wanamaker #1 and the J. B. Barr 28 #2 wells exhibit a distinct convex pattern suggesting either mixing with residual microbial methane or a mixture of mature gases derived from Types II and III kerogen and oil cracking in the original source rock (Zou and others, 2007; Golding and others, 2013).

The produced gas from the Fredericksburg reservoir in the L. A. Smith #2 well is post mature with a VR_e ~ 1.8 to 1.9%. Again, the Haynesville Shale or Smackover Formations are probable source rocks for the gas (Nunn, 2012). The natural gas plot in Figure 11 shows that the L. A. Smith #2 gas exhibits a strongly deviated convex trend of $\delta^{13}C$ versus 1/n.

None of the natural gas plot trends in Figure 11 intersect the $\delta^{13}C$ of Haynesville kerogen at the right side y-axis as would be expected if the produced gases were generated from that particular source rock organic matter. The ethane – propane trends could intercept the $\delta^{13}C$ of Smackover kerogen, but doglegs in the plot and their convex shape obscure this speculation. This is further evidence that secondary alteration processes related to gas mixing and high thermal stress controlled the carbon isotopic compositions of these samples.

Figure 11. Reciprocal of carbon number (1/n) versus $\delta^{13}C_n$ (Chung and others, 1988) for DeSoto Parish, Louisiana gases. **Top:** Chung plot without interpretive annotation. **Bottom:** Annotated Chung plot with interpretive parameters. $\delta^{13}C$ of Haynesville kerogen from Pernia (2012). $\delta^{13}C$ of Smackover kerogen from Oehler (1984).





Non-hydrocarbon gases identified in the DeSoto Parish produced gases include nitrogen, carbon dioxide, helium, argon, and hydrogen. Nitrogen occurs in all of the gas samples and ranges between 0.14 and 2.76 mol % of the gross composition (Table 2). The ratio of N_2/Ar in three of the samples ranges from 344.6 to 460, values considerably in excess of the N_2/Ar ratio in air (83.9). Possible nitrogen sources in the produced gases include various organic and inorganic crustal sources and mantle outgassing. Carbon dioxide is negligible in most of the produced gas samples, but comprises 0.92 mol % of the Sampson Est. 33 #1 sample and 2.00 mol % of the Mary Belle Smith 28 #2 Alt gas sample (Table 2). Possible CO_2 sources include thermal degradation of organic matter and carbonate, bacterial oxidation of CH_4, and magmatic degassing (Hunt, 1996).

The produced gas from the Wanamaker #1 is unusual in that it contains 2.75 mol % hydrogen. Hydrogen is extremely mobile and reactive. For this reason, it is extremely unusual in natural gas. Although plausible, it is unlikely for hydrogen-forming reactions to occur in a petroleum reservoir (Hunt, 1996). It is also unlikely that hydrogen is actively diffusing upwards from deeper sources (Hunt, 1996). The hydrogen in the Wannamaker #1 could be a product of hydrolysis reactions associated with corrosion in the in the well casing (Brondel and others, 1994; Popoola and others, 2013). Conversely, hydrogen might be a result of cathodic protection practices designed to minimize casing corrosion (Zainalabedin and others, 2002). This is less likely in the case of the Wanamaker #1 well because the process is more of a problem with external casing and hydrogen migrating through annular space.

Geochemistry of Stray Gas in the Hanson Relief Water Well

Table 6 lists the chemical composition results for the Hanson Relief well gas sample. Table 7 provides the results of stable isotope analyses of the Hanson Relief well sample. The GWR of the sample is 1.1923 and the LHR is 759.8 (Figure 4). The Haworth parameters suggest that the Hanson Relief well sample is mixed thermogenic and microbial gas. The Hanson Relief well gas plots between the Sampson Est. 33 #1 gas and all of the other DeSoto Parish gases on both the Bernard plot in Figure 5 and on the Schoell (1983) plot of $\delta^{13}C_1$ versus gas wetness in Figure 6. The Hanson Relief gas resembles that of the L. A. Smith #2 gas on the Schoell (1983) plot of $\delta^{13}C_1$ versus δD in Figure 7 due to similar hydrogen isotope values. However, this is the only plot that suggests a possible similarity between these two gas samples. All other plots and interpretations clearly demonstrate that these are distinctly different natural gases.

Table 6. Chemical composition of the Hanson Relief water well gas sample analyzed for this investigation. All values are reported as mol %.

Well Name	He	H_2	Ar	O_2	CO_2	N_2	C_1	C_2	C_3	iC_4	nC_4	iC_5	nC_5	C_{6+}
Hanson Relief SN 169060	nd	nd	0.0051	nd	0.74	0.27	97.80	1.05	0.0904	0.0.0217	0.0118	0.0045	0.0017	0.0049

Table 7. Stable isotope analytical results for the DeSoto Parish produced gas samples. All values are reported in parts per thousand (per mil, ‰)

Well Name	Reservoir	$\delta^{13}C_1$	$\delta D_{METHANE}$	$\delta^{13}C_2$	$\delta^{13}C_3$
Hanson Relief SN 169060	Wilcox Formation	-36.94	-150.2	-23.29	-17.88

The plots of ethane δ^{13}C versus propane ^{13}C (Figure 8) and methane δ^{13}C versus ethane ^{13}C (Figure 9) clearly discriminate the Hanson Relief well gas from all of the other samples. The

Hanson Relief well gas is post mature with a VR_e of just over 2.5%, a value similar to that of the Sampson Est. 33 #1 gas (Figure 9). The two gases, however, have been altered by different secondary processes. The Hanson Relief well sample shifts downward away from the maturity correlation on the plot of methane $\delta^{13}C$ versus ethane ^{13}C in Figure 9 suggesting mixing with bacterial gas (The Hanson Relief well gas appears to contain about 12% bacterial gas, a value similar to all of the DeSoto Parish samples except for the Sampson Est. 33 #1 sample - see Figure 10). Also note that the Hanson Relief well gas is biodegraded which resulted in propane loss (Figure 8). The Sampson Est. 33 #1 gas shifts upward away from the maturity correlation in Figure 9, opposite the position of the Hanson Relief gas, indicating a mix of thermogenic gases or microbial oxidation of methane.

Although clearly altered by secondary microbial processes, the Hanson Relief well gas shares several geochemical characteristics with the Sampson Est. 33 #1 gas. As already discussed, both samples have a VR_e of approximately 2.5%. The two gas samples have similar ethane $\delta^{13}C$ values: the Hanson Relief gas has a $\delta^{13}C$ = -23.29‰; the Sampson Est. 33 #1 gas has a $\delta^{13}C$ = -23.09‰. The two samples plot close together on the natural gas plot shown in Figure 11. The Hanson Relief gas, however, does exhibit two significant deviations from the trend of the Sampson Est. 33 #1 gas on the Chung plot (Figure 12):

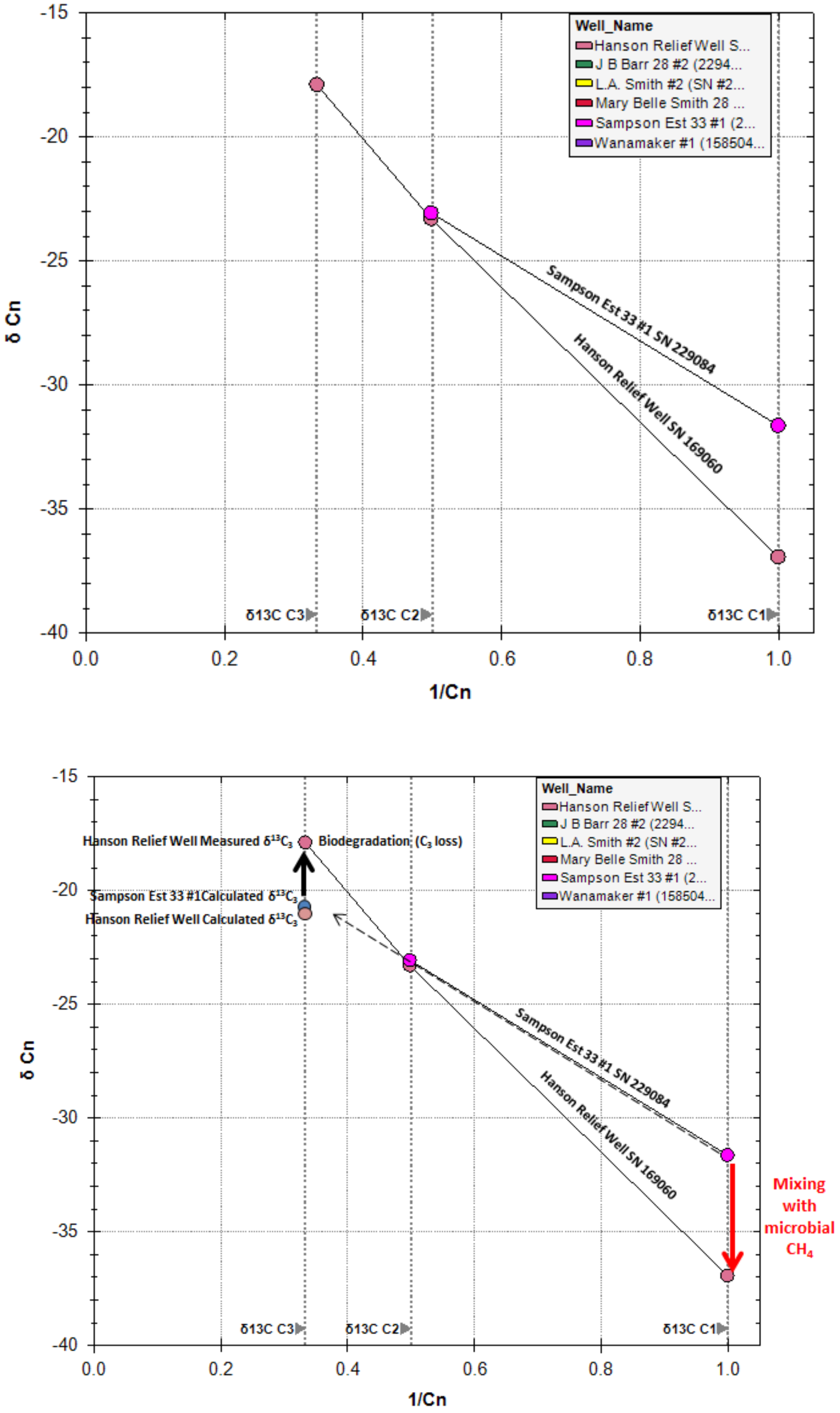
1. Methane $\delta^{13}C$ of the Hanson sample (-36.94‰) is significantly lighter than that of the Sampson Est. 33 #1 gas (-31.68‰) due to secondary microbial gas input, and
2. Biodegradation of propane, which is selective towards the lighter isotope (^{12}C), resulted in residual C_3 enriched in ^{13}C in the Hanson sample. The $\delta^{13}C$ of the Hanson sample propane is -17.88‰. This heavy value imparts a distinctive dogleg to the natural gas plot of the sample resulting in a concave trend indicative of selective propane biodegradation (Figures 11 and 12).

Utilizing the equation developed by Faber (1987) for co-genetic natural gases,

$$\delta^{13}C_{PROPANE}\ (‰) = 0.93\delta^{13}C_{ETHANE}\ (‰) + 0.55,$$

the Hanson Relief well gas should have a propane $\delta^{13}C \sim -21.1‰$ (Whiticar, 1994). Biodegradation of the Hanson Relief well propane resulted in an approximately 3.22‰ depletion in the lighter ^{12}C isotope. Although the Sampson Est. 33 #1 gas lacked sufficient propane for isotopic analysis, the Faber (1987) equation indicates that its propane should have a $\delta^{13}C$ of approximately -20.9‰ (Figure 12). If so, then this value would fall along the expected straight line trend for co-genetic gases for the Sampson Est. 33 #1 sample shown in Figure 12 (Bottom). The Hanson Relief gas has a calculated $\delta^{13}C$ of approximately -21.1‰ and would plot along the same trend if it was not altered by biodegradation accompanied by propane depletion (Figure 12, Bottom).

Figure 12. Reciprocal of carbon number (1/n) versus $\delta^{13}C_n$ (Chung and others, 1988) the Hanson Relief well and the Sampson Est. 33 #1 gas samples (from Figure 11). **Top:** Uninterpreted Chung plot. **Bottom:** Interpreted Chung plot.



Discussion

Produced DeSoto Parish Gases. The results of the stable carbon isotope analyses completed for this study suggest that the produced gas samples collected in DeSoto Parish contain post mature (VR_e =1.2 to 2.0%) to overmature (VR_e >2.0%) hydrocarbons generated in marine petroleum source rocks at levels of thermal stress equivalent to VR_e values between 1.6 and 2.5%. Four of the gases are associated with wet gas or condensate. The Sampson Est. 33 #1 gas consists of dry post mature hydrocarbons. The Cotton Valley, Bossier/Haynesville shales, and Smackover Formation source rocks are the only intervals that reached these levels of thermal maturity in the study area (Nunn, 2012). Numerous workers have published evidence and arguments for a Haynesville and Smackover petroleum source for Cotton Valley Formation hydrocarbons in northwest Louisiana (Dyman and Condon, 2006 and references reported therein).

The methane carbon isotope results reported in this study are consistent with those reported by Stolper and others (2014) for Haynesville gases produced from shale reservoirs with measured vitrinite reflectance (VR_o) between 1.7 and 2.5%. Stolper and others (2014) report that these maturities indicate average gas generation temperatures of approximately 169 to 175°C. These values agree with the predicted temperature and maturation history for the Haynesville Shale published by Nunn (2012, Figure 7, p. 91).

The maturity of the Cotton Valley Formation gas produced from the Mary Belle Smith 28 #2 Alt well is consistent with the maturity of stratigraphically adjacent Haynesville Formation and Smackover Formation source rocks in the study area (Nunn, 2012). However, the other four produced gas samples represent post mature to overmature hydrocarbons that have migrated upwards from the deeper source rocks into thermally immature to early/peak mature stratigraphic intervals. All of the Lower Cretaceous reservoir gases (Fredericksburg, Paluxy, Rodessa, and Hosston Formations) produce hydrocarbons that are significantly more thermally mature than those produced from the Cotton Valley Formation in the Mary Belle Smith 28 #2 Alt well. This observation suggests that the gases produced from the Fredericksburg, Paluxy, Rodessa, and Hosston Formations in the study area have iteratively migrated upwards from deeper areas of the North Louisiana Salt Basin as discussed by Schenk and Viger (1996), Hood and others (2001), Bartberger and others (2002), Dyman and Condon (2006), and Nunn (2012). Fractures associated with Louann Salt tectonics and the Sabine uplift must be a major control on the distributions of hydrocarbons in the Lower Cretaceous reservoirs in DeSoto Parish (Bartberger and others, 2002).

As already noted above, none of the natural gas plot lines in Figure 11 intersect the $\delta^{13}C$ of Haynesville or Smackover kerogen as would be expected if the produced gases were generated from these source rock kerogens. This suggests that secondary alteration processes related to high thermal stress influenced the carbon isotopic compositions of the samples. The Clayton (1991) plots presented in Figures 13, 14, and 15 indicate that moderate to extensive oil cracking is the principal secondary process affecting the carbon isotope composition of the DeSoto Parish produced gases. The Clayton (1991) plots illustrate maturity-related variations in the relative abundance and isotopic composition of methane, ethane, and propane in the gas samples. Maturity of labile (oil prone) kerogen is represented by the degree of gas generation (Gas Generation Index, or GGI). Maturity of refractory kerogen is represented by equivalent vitrinite reflectance. I used a kerogen $\delta^{13}C$ of -26.0‰ for this plot to calculate the y-axis values based on data reported by Pernia (2012). The plots of methane, ethane, and propane $\delta^{13}C$ versus dryness presented in Figures 13, 14, and 15 suggest that all of the produced gas samples are largely secondary and were generated mostly from oil cracking.

Another interesting feature of the Clayton plot in Figure 13 is that the gases produced from the Mary Belle Smith 28 #2 Alt, Wanamaker #1, and J. B. Barr 28 #2 wells fall slightly off of the Rayleigh fractionation curve for oil cracking in the direction of the microbial gas field. Recall that these same samples fall down and away from the $\delta^{13}C_1$ versus $\delta^{13}C_2$ correlation trend in Figure 9 also suggesting a possible mix of thermogenic and residual microbial gas. This interpretation is surprising given the high thermal maturity of the gases. It is plausible, although unlikely, that a minor component of early microbial gas, generated in the source rocks, is mixed with high maturity hydrocarbons. It is also possible that a microbial methane component generated in the reservoir strata intervals is mixed with the high maturity gases that migrated upwards from the Haynesville/Smackover source rocks. This is a more likely scenario. In both cases, the isotopic composition of the produced gas would be *cumulative*, i. e., a weighted average of the isotope compositions of all the gas that accumulated in the reservoir. We could test the hypothesis that microbial methane generated in the reservoir strata intervals mixed with deep-sourced migrated post mature gas by analyzing the $\delta^{13}C$ composition of CO_2 in the samples.

As discussed above, the Haworth and others (1985) parameters in Table 3 suggested that the Hosston Formation gas produced from the Sampson Est. 33 #1 well consists of mixed thermogenic and microbial gas as well. This is a function of the anomalously high OCR of 1.44. This sample, however, plots as a mix of thermogenic gases in Figure 9, and exhibits no evidence of a microbial component in Figure 10. The Hosston Formation gas produced from the Sampson Est. 33 #1 well is a mixed overmature thermogenic gas generated mostly by extensive cracking of residual oil in deeper petroleum source rocks.

Figure 13. Plot of the difference between methane and kerogen δ^{13}C versus gas dryness for the DeSoto Parish produced gases (Clayton, 1991). Solid arrow indicates interpreted mixing with microbial methane.

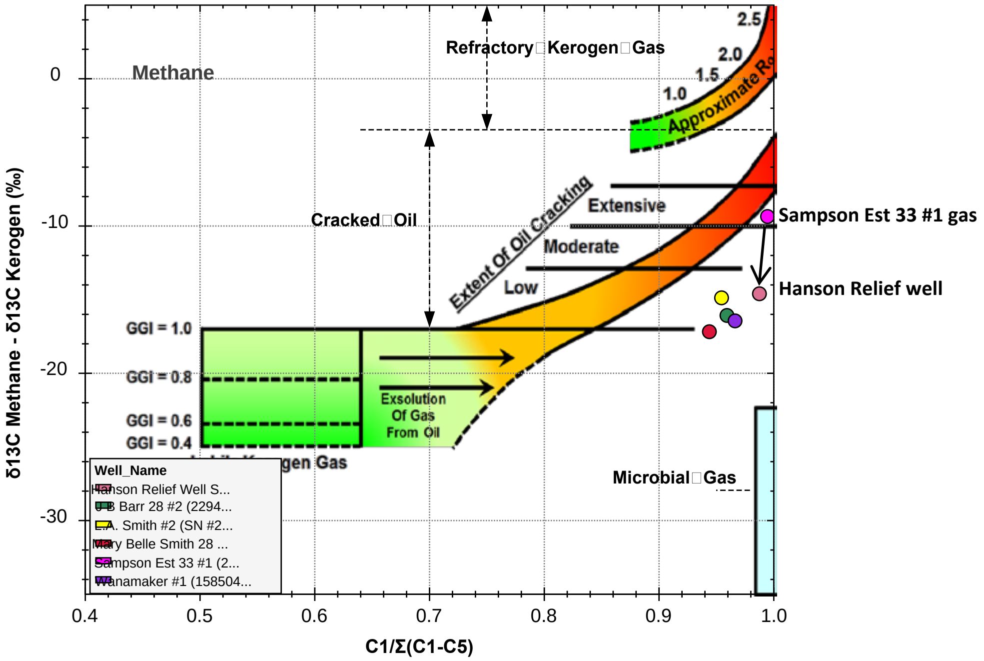


Figure 14. Plot of the difference between ethane and kerogen δ^{13}C versus gas dryness for the DeSoto Parish produced gases (Clayton, 1991).

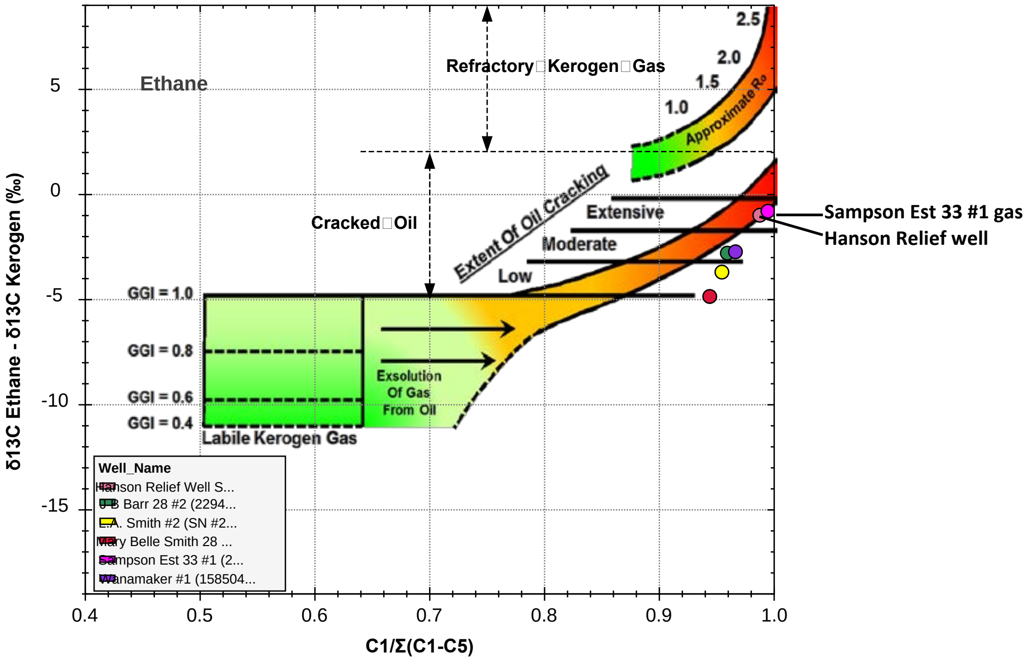
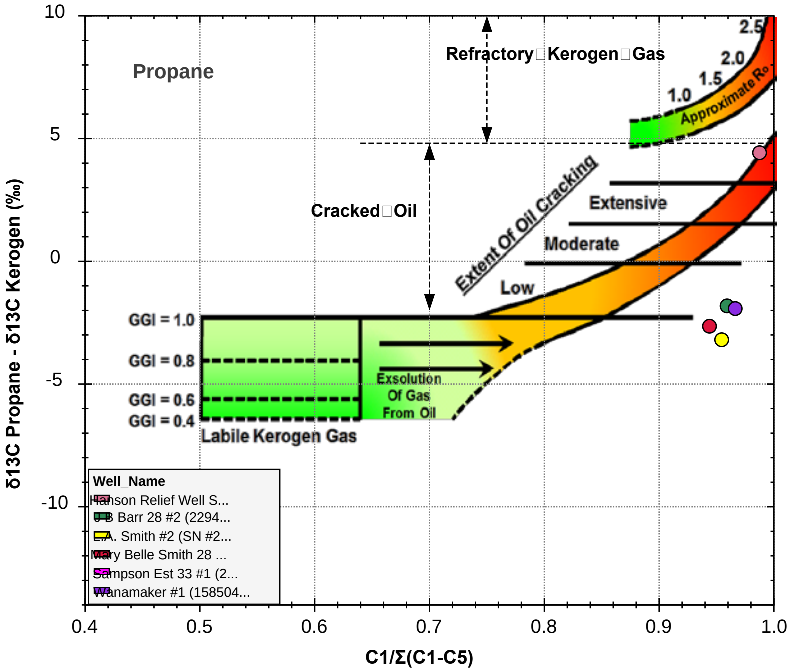


Figure 15. Plot of the difference between propane and kerogen δ^{13}C versus gas dryness for the DeSoto Parish produced gases (Clayton, 1991).



Hanson Relief Well Gas. The gas sample collected from the Hanson Relief well consists of predominately post mature (VR$_e$ ~ 2.5%) hydrocarbons mixed with microbially generated methane (Figure 9). The latter contributes approximately 12% methane to the total hydrocarbon gas composition (Figure 10). Biodegradation of the Hanson Relief well gas resulted in propane loss (Figure 8). These secondary alteration effects obscure a precise correlation of the Hanson Relief well gas to the other production gases collected in the study area, but the Hanson gas appears most closely related to the overmature gas produced from the Sampson Est 33 #1 well (Figures 11 and 12). This interpretation is supported by the Clayton (1991) plots presented in Figures 13 and 14:

- In Figure 13, the Sampson Est 33 #1 and Hanson Relief well gases have similar dryness (C1/∑(C1-C5)): dryness of the Sampson Est 33 #1 gas is 0.9949 and dryness of the Hanson Relief well gas is 0.9881. Thermal maturity of both gas samples is VR$_e$ ~ 2.5%. The Sampson Est 33 #1 gas was mostly generated by extensive cracking of residual oil in deep petroleum source rocks. The overmature Hanson well gas was also generated mostly by cracking of residual oil, but the position of the sample on the Clayton (1991) plot has shifted downward towards the microbial methane field due to mixing with bacterially generated gas within the Wilcox aquifer.

- In Figure 14, the Sampson Est 33 #1 and Hanson Relief well gases have similar dryness as outlined above, and the two gas samples have similar ethane $\delta^{13}C$ values: ethane $\delta^{13}C$ of the Sampson Est 33 #1 gas is -23.09‰ and ethane $\delta^{13}C$ of the Hanson Relief well gas is -23.29‰. Consequently, the two samples plot together in the field of extensive oil cracking.

The gas origin and mixing lines published by Golding and others (2013) are superimposed on the Bernard and others (1978) plot shown in Figure 5 (brown dashed lines). The Sampson Est 33 #1 gas ($C_1/C_2 + C_3 = 216.5$ and $VR_e \sim 2.5\%$) has 0% microbial gas mixed with thermogenic gas. The Hanson Relief well gas ($C_1/C_2 + C_3 = 85.75$ and $VR_e \sim 2.5\%$) has ~ 12% microbial methane mixed with the predominant thermogenic gas. All of the other DeSoto Parish gas samples contain between 6 and 15% microbial methane mixed with thermogenic gas. Measurements of $\delta^{13}CO_2$ would help to confirm and quantify the estimates of microbial methane in the mixed gases as well as further constrain the secondary effects influencing the gas geochemistry of the DeSoto Parish samples (Whiticar, 1994; Baldassare and Laughrey, 1997; Golding and others, 2013).

As already discussed, The Hanson Relief gas resembles that of the L. A. Smith #2 gas on the Schoell (1983) plot of $\delta^{13}C_1$ versus δD in Figure 7 due to similar hydrogen isotope values. However, all of the other plots unequivocally show that these are different natural gases, particularly the thermal maturity trends implied in Figures 4, 5, 6, 11, 14, and 15, and quantified in Figures 8, 9, and 10. While hydrogen isotopes can be diagnostic of a type of gas and its organic source, they never exhibit a clear thermal dependency (Whiticar, 1994, p. 276 – 277).

Conclusions

Six natural gas samples were collected from five producing oil and gas wells and one water “relief” well in DeSoto Parish in northwestern Louisiana to aid the Louisiana Department of Natural Resources in determining the origin of the stray gas in the Hanson 31-5054z water well. The Hanson 31-5054z water well produces from the Eocene Wilcox Formation. The five produced gas samples are from wells completed in the Cretaceous Fredericksburg, Paluxy, Rodessa, and Hosston Formations, and in the Jurassic Cotton Valley Formation. The five produced gas samples contain post mature to overmature thermogenic hydrocarbons generated in deeper petroleum source rocks. Gas migration and accumulation in the different reservoirs was iterative resulting in a complex stratigraphic distribution of highly mature hydrocarbons produced from thermally immature to early/peak mature subsurface intervals on the flanks of the Sabine uplift. Three of the gas samples – Sampson Est. 33 #1, L. A. Smith #2, and Mary Belle Smith 28 #2 Alt - are readily discriminated from one another on various gas isotope cross plots, particularly on the natural gas plot (Figure 11). Two of the gas samples (J. B.

Barr 28 #2 and Wanamaker #1), however, are identical in terms of carbon isotope compositions.

Produced natural gas from the Wanamaker #1 well contains 2.75% hydrogen. The hydrogen in the Wannamaker #1 may be a product of hydrolysis reactions associated with corrosion in the in the well casing.

Groundwater and stray gas collected from the Hanson Relief water well (SN 169060) are produced from the Eocene Wilcox Formation. Wilcox strata are thermally immature (VR_o ~ 0.25 to 0.3%) in the study area, yet the stray gas collected from this well is overmature (VR_e ~ 2.5%). The Hanson Relief well gas contains a microbial methane component mixed with predominately thermogenic hydrocarbon components, and has been altered by biodegradation which resulted in loss of propane in the sample. These secondary mixing and alteration effects obscure a precise correlation of the Hanson Relief well gas to the other production gases collected for this study, but the Hanson gas appears most closely related to the overmature gas produced from the Sampson Est 33 #1 well.

The interpreted correlation of the gases from the Hanson Relief well and the Sampson Est 33 #1 well establishes similar source rocks and thermal maturities for the hydrocarbons in these samples. Identification of the Sampson Est 33 #1 well as the source of the stray gas in the Hanson 31-5054z water well would be circumstantial. The geochemistry of dissolved and free natural gases would have to be established in several water wells in the study area to ascertain the comparative character of the Wilcox aquifer gases and produced gases in DeSoto Parish.

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