

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

**OilTracers Updated Report No. 18-2422**

**Isotech Laboratories Projects 37965 and 37966**

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*Prepared for*

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## Executive Summary

- Ten natural gas samples were collected from nine 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 nine produced gas samples are from wells completed in the Cretaceous Fredericksburg, Paluxy, Rodessa, and Hosston Formations, the Jurassic Cotton Valley Formation and the Upper Jurassic Haynesville Formation. The nine 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 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.
- Six of the nine produced gas samples appear to contain varying mixtures of microbial methane. Measurement of carbon isotopes of co-produced carbon dioxide and dissolved inorganic carbon in groundwater could confirm this interpretation.
- Four of the produced gas samples (J. B. Barr 28 #2, Wanamaker #1, Ford 1, and Jones 1-D) are identical in terms of carbon isotope compositions.
- The other five produced gas samples are readily discriminated from one another on various gas isotope cross plots.
- 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 ( $VR_o \sim 0.25$  to  $0.3\%$ ) in the study area, yet the stray gas collected from this well is overmature ( $VR_e \sim 2.5\%$ ). 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; Figure 1). The wellhead blew off of this water well by August, 2017 and a column of water purportedly was 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 nine 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). A comparison of the natural gas geochemistry of five of these producing wells and the Hanson water well was provided to the Louisiana Department of Natural Resources in February, 2018 (Laughrey, 2018). Geochemical analyses of four additional producing well samples were obtained by the Louisiana Department of Natural Resources in April, 2018 (Table 1). This report provides an update of the earlier investigation utilizing the geochemical data obtained from the four additional wells recently added to the database. The four new analyses were integrated with the working data files developed for the previous investigation and the report was revised to include the new results within the original context of the January, 2018 report. This report supplants the earlier report OT 18-2370 (Laughrey, 2018).

## **Samples, Location, and Geologic Setting**

Ten natural gas samples were collected from nine producing oil and gas wells and one water “relief” well (Table 1 and 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). Six of the gas samples were collected in November and December of 2017 by Approach Environmental of Shreveport, Louisiana for the Louisiana Department of Natural Resources. Additional gas samples, including the four new samples added to this new report data set were collected in April 2018 by Elm Spring Inc. of Magnolia,

Arkansas for the Louisiana Department of Natural Resources. Table 1 is a list of all the gas samples collected for this investigation. Figure 2 shows the three geologic cross sections indicated on the map in Figure 1.

All ten 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 ten gas samples.

**Table 1.** Natural gas samples collected from nine producing oil and gas wells and the Hanson Relief water well (SN #169060) in DeSoto Parish, Louisiana. The four shaded columns with bold text denote the four new gas sample collected in April, 2018 and added to this report’s updated database in September, 2018.

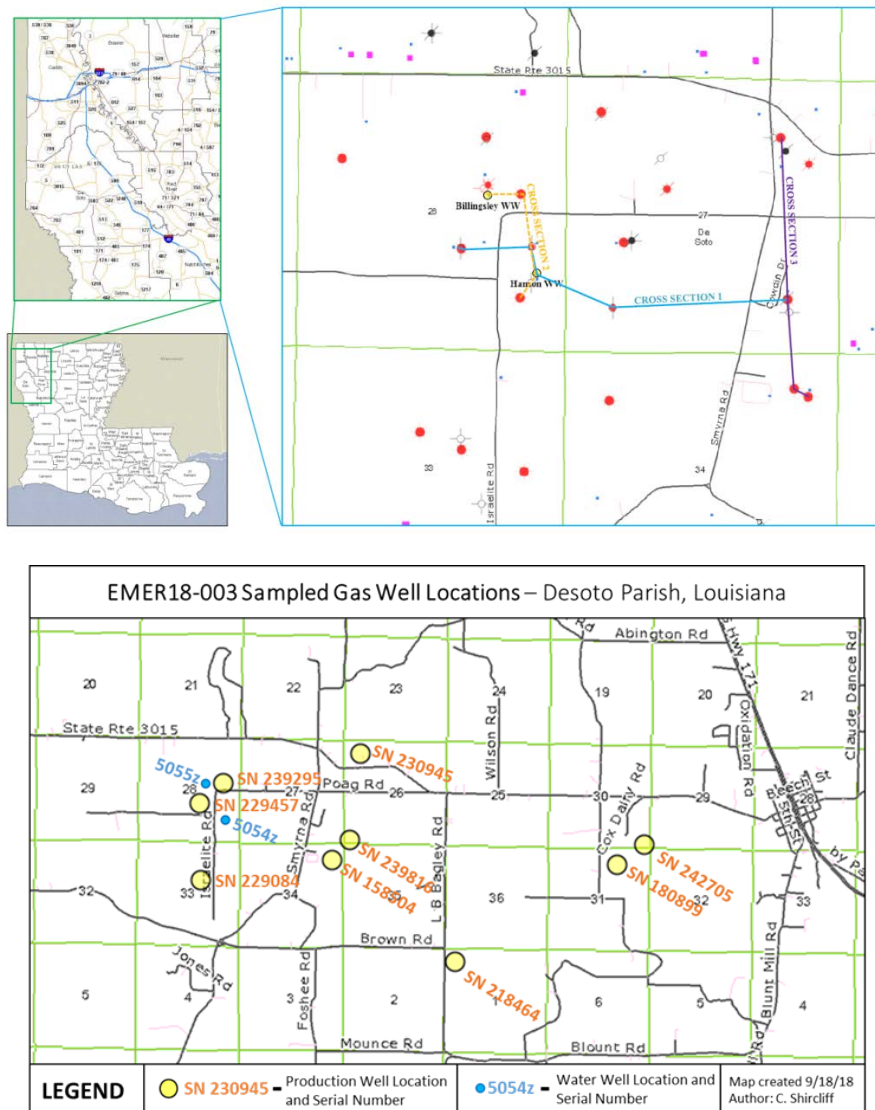
Well Name	Gas Sample Type	Sample Date	Isotech Sample #	Age	Reservoir/Aquifer
Hanson Relief Well	Water Well	12/29/2017	644540	Eocene	Wilcox Formation
L. A. Smith #2	Production	11/29/2017	641272	L Cretaceous	Fredericksburg Formation
J. B. Barr 28 #2	Production	11/9/2017	637782	L Cretaceous	Paluxy Formation
Wanamaker #1	Production	11/9/2017	637783	L Cretaceous	Rodessa Formation
<b>Ford 1</b>	<b>Production</b>	<b>4/5/2018</b>	<b>659673</b>	<b>L Cretaceous</b>	<b>Rodessa Formation</b>
Sampson Est. 33 #1	Production	11/9/2017	637781	L Cretaceous	Hosston Formation
<b>Jones 1-D</b>	<b>Production</b>	<b>4/2/2018</b>	<b>659676</b>	<b>L Cretaceous</b>	<b>Hosston Formation</b>
Mary Belle Smith 28 #2	Production	11/9/2017	637780	L Cretaceous/Jurassic	Cotton Valley Formation
<b>Evans 26H-1</b>	<b>Production</b>	<b>4/5/2018</b>	<b>659674</b>	<b>U Jurassic</b>	<b>Haynesville Formation</b>
<b>Ford 31H-1</b>	<b>Production</b>	<b>4/5/2018</b>	<b>659675</b>	<b>U Jurassic</b>	<b>Haynesville Formation</b>

## Methods

The nine produced gas samples were collected in steel high-pressure gas cylinders or in Isotubes® at the well sites. Analyses were performed at Weatherford’s 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

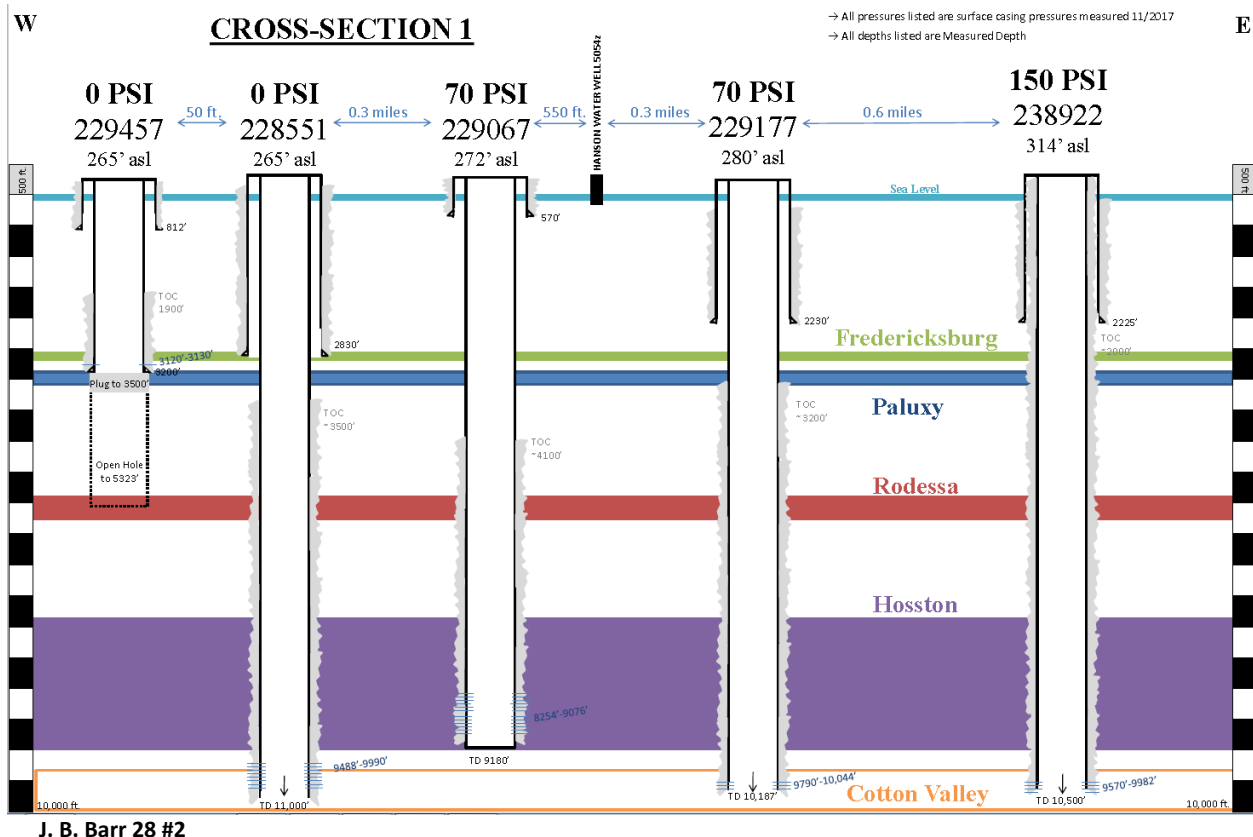
into its individual components in a SRI GC, and then each hydrocarbon was oxidized to CO<sub>2</sub> (for carbon isotopes) and/or H<sub>2</sub>O (for hydrogen isotopes). The latter was further reacted to hydrogen gas by reacting the combustion water with zinc turnings and then measuring the isotope ratio of the hydrogen using a Thermo Delta V Plus IRMS system. The CO<sub>2</sub> 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  $\pm 0.1\%$  (one sigma).

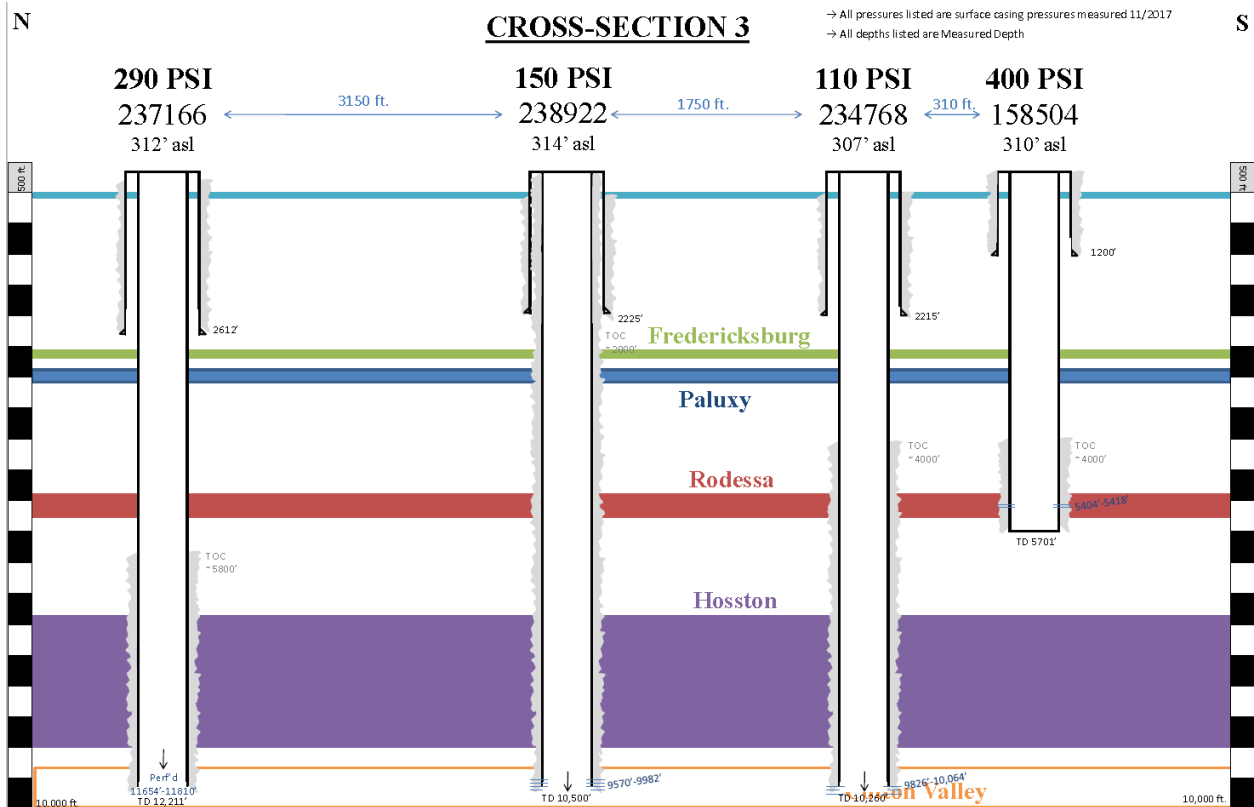
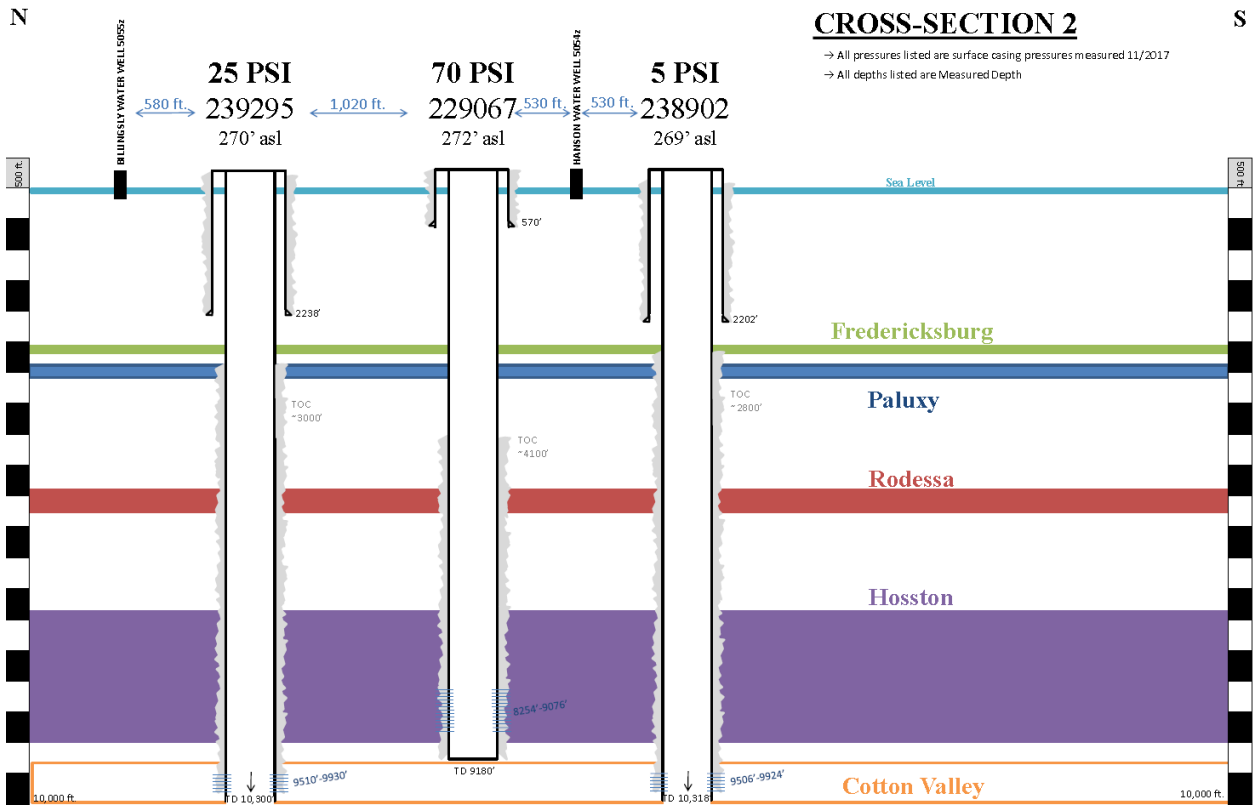
**Figure 1. Top:** Original map of gas sample locations in DeSoto Parish, Louisiana collected for Weatherford OilTracer Report OT-18-2370 (courtesy of Corey Shircliff, Louisiana Department of Natural Resources). **Bottom:** Updated location map (September 2018) for all wells discussed in this report. See Table 1 and Figure 2 for well names.



The stray gas sample collected from the Hanson relief well was collected by IsoFlask®. The IsoFlask® provides a unique closed system design constructed for quantifying dissolved gas concentrations below or above saturation limits. One of two online systems, each consisting of an Agilent 6890 GC, a combustion unit, and a mass spectrometer (Finnigan Delta+ or Finnigan Delta V plus), was used to analyze the carbon isotopic value of hydrocarbon components in this sample. The hydrocarbon components were separated by the GC, and each individual component slated for isotopic analysis was combusted. The resultant CO<sub>2</sub> was introduced directly into the mass spectrometer and Finnigan's Isodat software was utilized for peak detection and quantification. The precision of the carbon isotope data is  $\pm 0.3\%$ .

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







**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).

SYSTEM		SERIES	STAGE	GROUP	FORMATION	AGE (Ma)		
TERTIARY	PALEOGENE	EOCENE	YPRESIAN	WILCOX	WILCOX	80		
			THANETIAN	MIDWAY	MIDWAY			
		DANIAN						
UPPER CRETACEOUS	GULFIAN		MAASTRICHTIAN	NAVARRO	ARKADELPHIA NACATCOCH	70		
			CAMPANIAN	TAYLOR	SARATOGA ANNONA OZAN	80		
			SANTONIAN	AUSTIN	TOKIO AUSTIN	80		
			CONIACIAN		EAGLE FORD			
			TURONIAN		EAGLE FORD			
			CENOMANIAN	WOODBINE	TUSCALOOSA			
				WASHITA	PALUXY WASHITA-FREDERICKSBURG	100		
		LOWER CRETACEOUS	COMANCHEAN		ALBIAN	FREDERICKSBURG	MOORINGSPOINT FERRY LAKE ANHYDRITE	110
					APTIAN	TRINITY	RODESSA JAMES PINE ISLAND PETTET (SLIGO) MBR SLIGO	
			COAHULAN		BARREMIAN		HIATUS	HOSSTON (TRAVIS PEAK)
	HAUTERIVIAN							
	VALANGINIAN							
	BERRIASIAN							
	TITHONIAN			COTTON VALLEY	SCHULER FORMATION BOSSIER SHALE	140		
JURASSIC	UPPER		KIMMERIDGIAN	HIATUS	GILMER-HAYNESVILLE-BUCKNER SMACKOVER	150		
			OXFORDIAN					
			CALLOVIAN		NORPHLET	160		
	MIDDLE		BATHONIAN	HIATUS	LOUANN	170		
			BAJOCIAN					
			AALENIAN		WERNER	180		
			TOARCIAN					
	LOWER		PLIENSCHACHIAN	HIATUS		190		
			SINEMURIAN					
			HETTANGIAN					
TRIASSIC	UPPER		RHAETIAN		EAGLE MILLS	200-210		

### Geochemistry of Produced Gas Samples

Table 2 shows the chemical composition of the nine produced gas samples. All of the gas samples are dominated by methane ( $C_1$ ) which comprises 89.4 to 97.8 mol % of the gross composition. Ethane ( $C_2$ ) and propane ( $C_3$ ) make up 0.311 to 4.1 mol % and 0.0133 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 nine produced gas samples analyzed for this investigation. All values are reported as mol %.

Well Name	He	H <sub>2</sub>	Ar	O <sub>2</sub>	CO <sub>2</sub>	N <sub>2</sub>	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	iC <sub>4</sub>	nC <sub>4</sub>	iC <sub>5</sub>	nC <sub>5</sub>	C <sub>6+</sub>
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
Ford 1	0.0453	nd	0.0131	0.076	1.07	3.57	89.4	4.1	0.887	0.149	0.203	0.0933	0.0751	0.318
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
Jones 1-D	0.0207	0.02	0.0076	0.074	1.56	1.09	91.63	3.64	0.91	0.245	0.27	0.158	0.0991	0.276
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
Evans 26H-1	nd	nd	nd	0.059	2.2	0.2	97.1	0.419	0.0186	0.0016	0.0025	0.0003	0.0002	0.008
Ford 31H-1	nd	nd	nd	0.05	2.49	0.5	96.8	0.31	0.013	0.004	0.002	0.003	0.002	0.009

nd – not detected

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,

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

where C<sub>1</sub> - C<sub>5</sub> are methane through pentane hydrocarbon gases (Haworth and others, 1985). The LHR is calculated as,

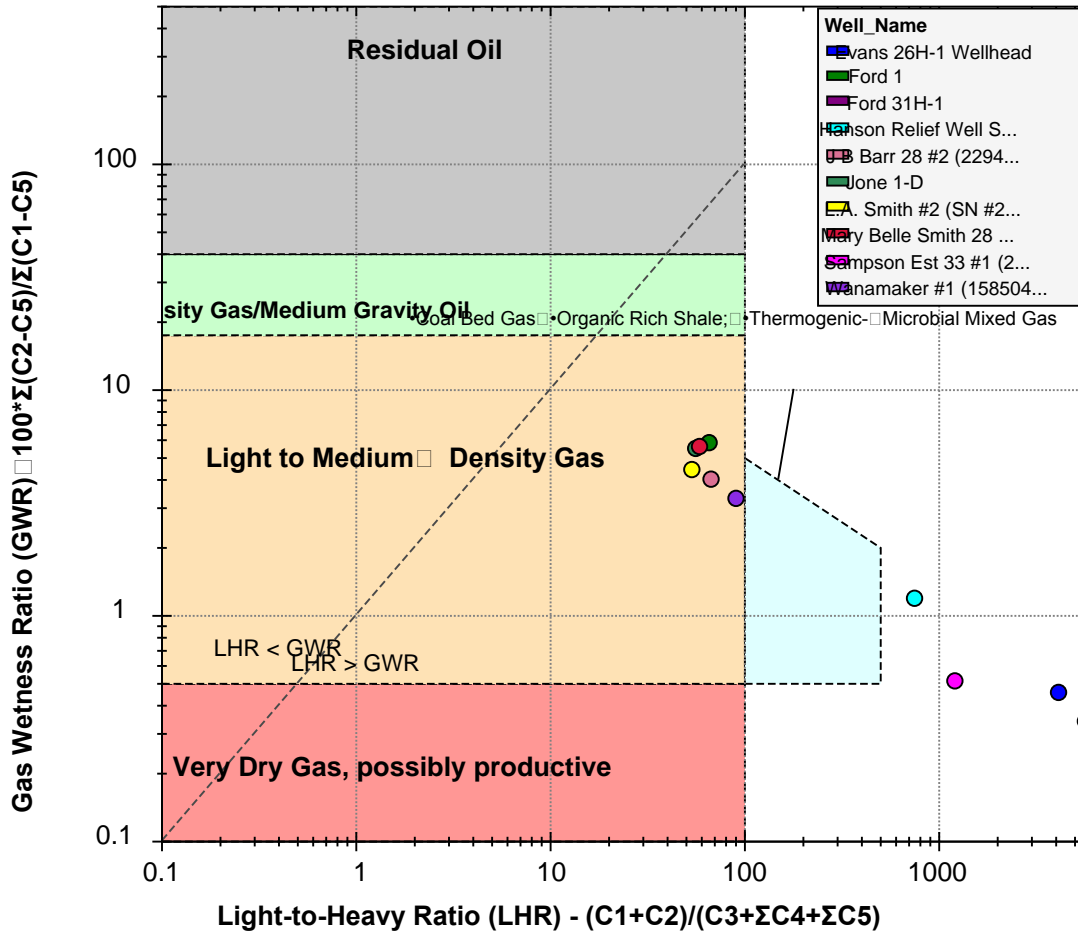
$$(C_1 + C_2)/(C_3 + iC_4 + nC_4 + iC_5 + nC_5),$$

where C<sub>1</sub> – C<sub>5</sub> 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).

Six of the DeSoto Parish produced gas samples plot within the field for light to medium density gas. The Ford 1 gas, produced from the Rodessa Formation, has the highest GWR (5.8%) in the data set; its LHR is 66.4 (Table 3). The Hosston and Cotton Valley Formation gases from the Jones 1-D and Mary Belle Smith 28 #2 wells are very similar. 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). The Haynesville gases collected from the Evans 26H-1 and Ford 31H-1 wells are even dryer with respective GWR of 0.453 and 0.34 (Table 3 and 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.



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 Parish produced gas samples range from 0.2473 to 1.44 (Table 3). Excepting the Sampson Est. 33 #1, Evans 26H-1, and Ford 31H-1 samples, 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**). The Evans 26 H-1 and Ford 31 H-1 samples are very dry gas.

**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
Ford 1	5.8	66.4	0.5867	Wet Gas: condensate; light oil
Sampson Est. 33 #1	0.5081	1213.4	1.44	Mixed Gas: thermogenic/microbial?
Jones 1-D	5.5	56.6	0.8484	Wet Gas: condensate; light oil
Mary Belle Smith 28 #2	5.6	59.2	0.7484	Wet Gas: condensate; light oil
Evans 26H-1	0.4533	4203.4	0.2473	Very dry gas
Ford 31H-1	0.3373	5656.4	0.2932	Very dry gas

**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
$0.5 \leq \text{GWR} < 17.5$	<100	<0.5	Wet Gas: non-associated
$0.5 \leq \text{GWR} < 17.5$	<100	$\geq 0.5$	Wet Gas: condensate; light oil
$17.5 \leq \text{GWR} < 40$	<100	<0.5	Very Wet Gas: non-associated
$17.5 \leq \text{GWR} < 40$	<100	$\geq 0.5$	Very Wet Gas: medium gravity oil
$0.5 \leq \text{GWR} < 17.5$	$\geq 100$	$\geq 0.5$	Mixed Gas: thermogenic/microbial
< 40	$\geq 100$	<0.5	Coal Bed Gas: organic-rich shale-gas
$\text{GWR} > 40$	$\ll 17.5$	$\geq 0.5$	Residual Oil

The gas chemical composition data in conjunction with methane carbon isotope composition indicate that all nine 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 and Appendix 1. The Bernard plot in Figure 5 suggests that all nine gas samples originated as thermogenic hydrocarbons generated from Type II kerogen in marine petroleum source rocks. The Sampson Est. 33 #1, Evans 26H-1, and Ford 31H-1 gases are significantly more thermally mature than the other gas samples. The Mary Belle Smith 28 #2, Jones 1-D, and Ford 1 gases contain the least

thermally mature hydrocarbons in the data set. The Schoell (1983) plot of methane  $\delta^{13}\text{C}$  versus gas wetness shown in Figure 6 supports and refines this interpretation. All nine 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 ( $\delta^{13}\text{C}_1$ ) of -31.68‰. Conversely, the relatively wetter Mary Belle Smith 28 #2 Alt, Jones 1-D, and Ford 1 gas samples plot 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, ‰).

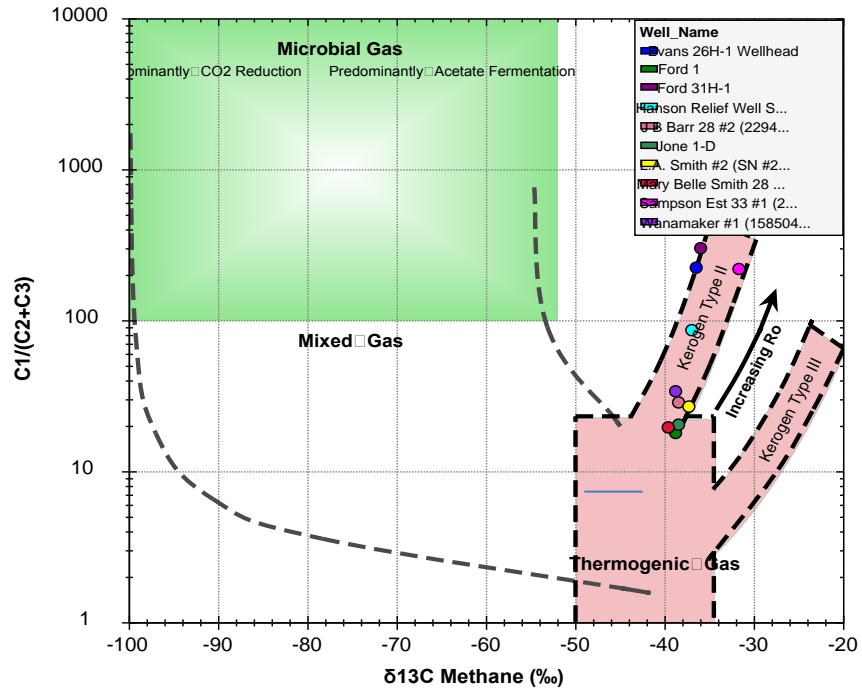
Well Name	Reservoir	$\delta^{13}\text{C}_1$	$\delta\text{D}_{\text{METHANE}}$	$\delta^{13}\text{C}_2$	$\delta^{13}\text{C}_3$
L. A. Smith #2	Fredericksburg Formation	-37.18	-149.0	-25.98	-25.48
J. B. Barr 28 #2	Paluxy Formation	-38.37	-149.7	-25.06	-24.07
Wanamaker #1	Rodessa Formation	-38.74	-155.2	-25.03	-24.23
Ford 1	Rodessa Formation	-38.68	-151.7	-24.86	-24.04
Sampson Est. 33 #1	Hosston Formation	-31.68	-119.3	-23.09	*
Jones 1-D	Hosston Formation	-31.68	-119.3	-23.09	*
Mary Belle Smith 28 #2	Cotton Valley Formation	-39.51	-158.1	-27.12	-24.94
Evans 26H-1	Haynesville Formation	-36.38	-148	-28.29	*
Ford 31H-1	Haynesville Formation	-35.97	-149.6	-28.98	*

- Insufficient concentration for carbon isotopic measurement

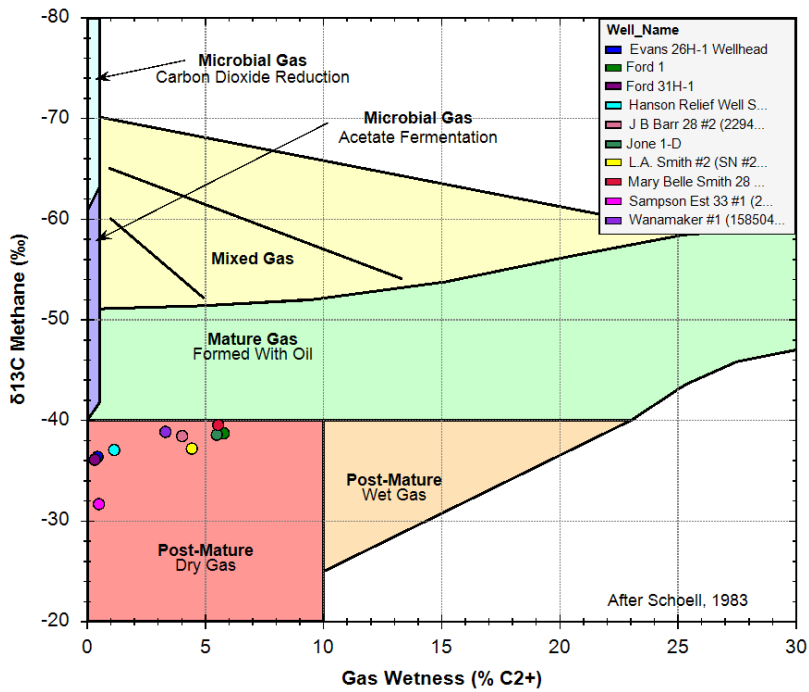
Figure 7 is a plot of methane  $\delta^{13}\text{C}$  versus methane  $\delta\text{D}$  for the DeSoto Parish produced gas samples. The data present the same general thermal maturity trends illustrated in Figures 5 and 6, but the hydrogen isotope results provide better resolution of the genetic interpretive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

Cross plots of ethane  $\delta^{13}\text{C}$  versus propane  $\delta^{13}\text{C}$  (Figure 8) and methane  $\delta^{13}\text{C}$  versus ethane  $\delta^{13}\text{C}$  (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.

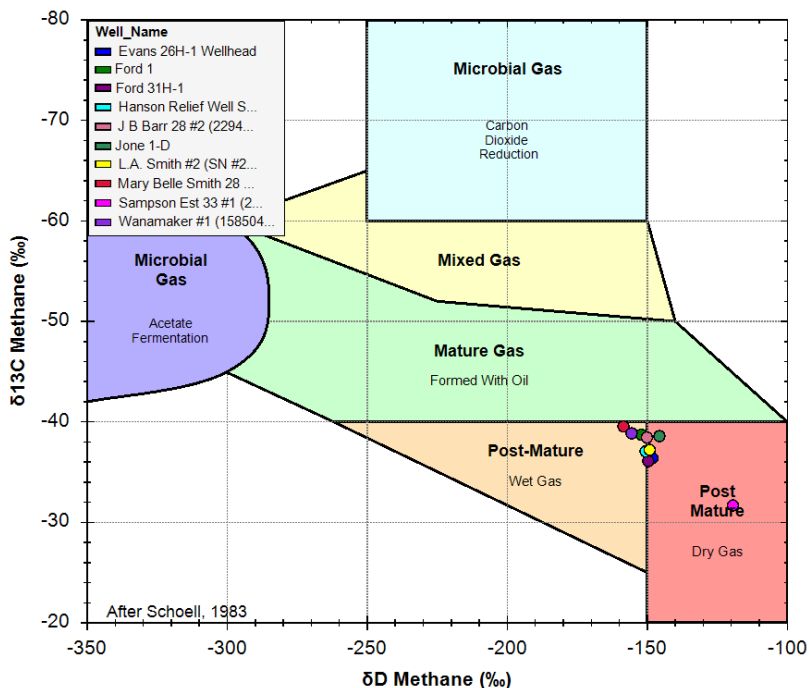
**Figure 5.** Plot of the ratio of  $C_1/(C_2 + C_3)$  versus the carbon isotopic composition of methane ( $\delta^{13}C_1$ ) for the DeSoto Parish natural gas samples (after Bernard and others, 1978). All of the gases plot as thermogenic hydrocarbons. Other data, however, indicate ~ 6 to 15% microbial gas in six of the samples.



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



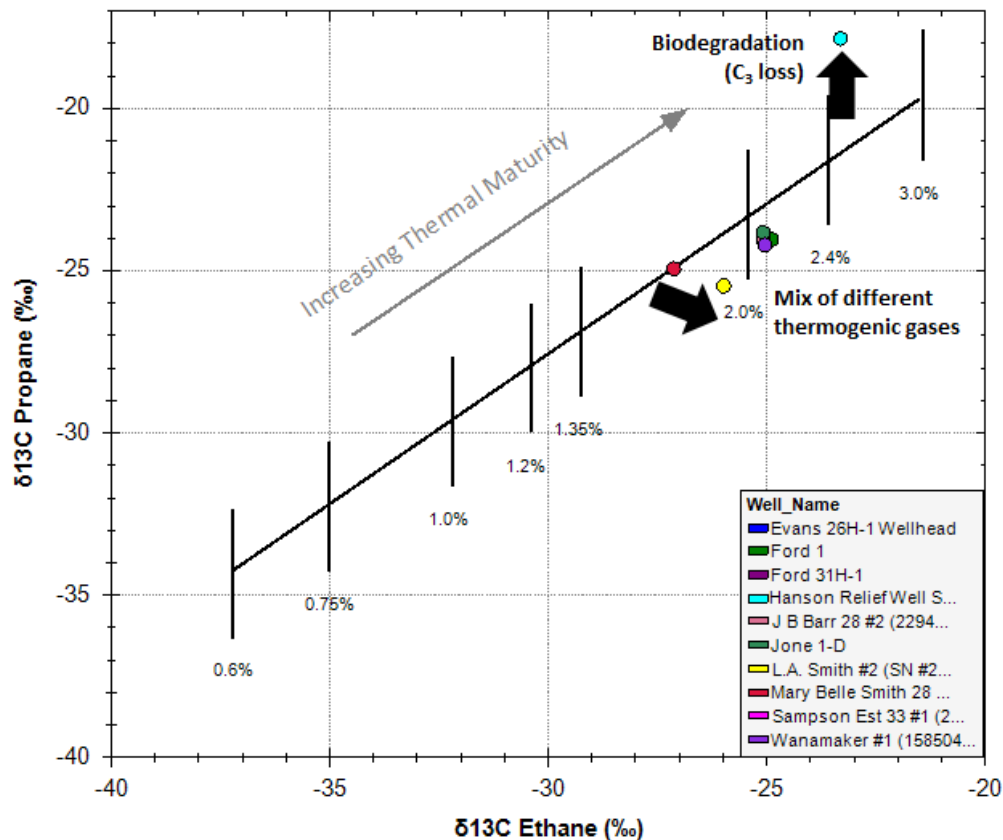
**Figure 7.** Schoell (1983) plot of methane  $\delta^{13}\text{C}$  versus  $\delta\text{D}$  for the DeSoto Parish natural gas samples.



The plot of ethane  $\delta^{13}\text{C}$  versus propane  $\delta^{13}\text{C}$  in Figure 8 provides thermal maturity estimates for six of the produced gas samples as well as for the Hanson Relief well sample (discussed below) in terms of vitrinite reflectance equivalent ( $\text{VR}_e$ ). The Sampson Est. 33 #1, Evans 26H-1, and Ford 31H-1 well samples had 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  $\text{VR}_e \sim 1.7\%$ . 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%  $\text{VR}_e$ . Interestingly, Fredericksburg strata in the study area are thermally immature ( $\text{VR} = 0.25$  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 and Ford 1 wells, the Paluxy Formation hydrocarbons produced from the J. B. Barr 28 #2 well, and the Hosston gas produced from the Jones 1-D well all were generated at a  $\text{VR}_e \sim 2.1\%$ , probably from the same source rock. Note that the L. A. Smith #2, Wanamaker #1, Ford 1, Jones 1-D, and J. B. Barr 28 #2 gas samples all plot slightly downward and off of the ethane  $\delta^{13}\text{C}$  versus propane  $\delta^{13}\text{C}$  correlation trend in Figure 8; 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<sub>e</sub>) and also require a Smackover source for the observed level of hydrocarbon gas maturity shown in Figure 8 (Nunn, 2012).

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

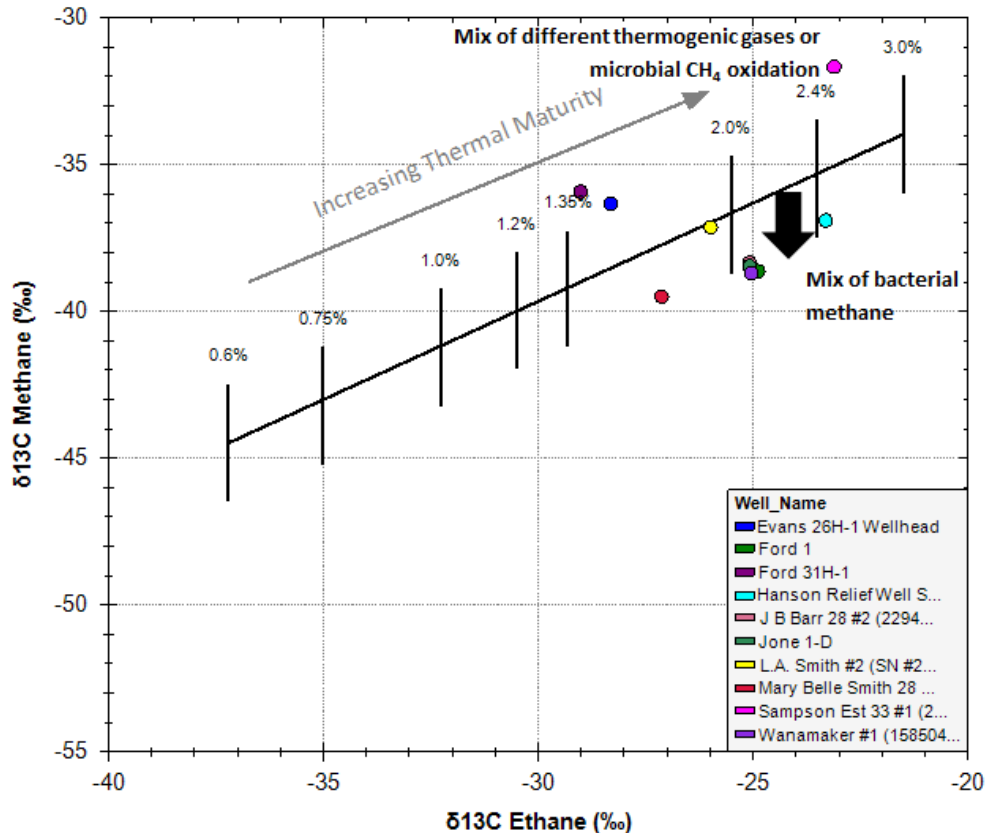


The plot of methane  $\delta^{13}\text{C}$  versus ethane  $\delta^{13}\text{C}$  in Figure 9 yields similar thermal maturity estimates for the six gas samples just discussed as well as for the other three produced gas samples. Maturity of the Hosston Formation gas produced from the Sampson Est. 33 #1 well equates to a VR<sub>e</sub> of ~2.5%. Hosston Formation strata in the study area are in the early (VR<sub>e</sub> = 0.55 to 0.7%) to peak (VR<sub>e</sub> = 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<sub>e</sub> ~ 2.5% interpreted for the Sampson Est. 33 #1 gas produced from the Hosston Formation in this well



indicates that the hydrocarbons were generated in the dry gas window as implied in Figures 6 and 7. Only the Smackover Formation attained this level of thermal maturity in the study area (Nunn, 2012).

**Figure 9.** Plot of  $\delta^{13}\text{C}_1$  versus  $\delta^{13}\text{C}_2$  and relationship to thermal maturity (vitrinite reflectance equivalent) for the DeSoto Parish natural gas samples (after Whiticar, 1994).



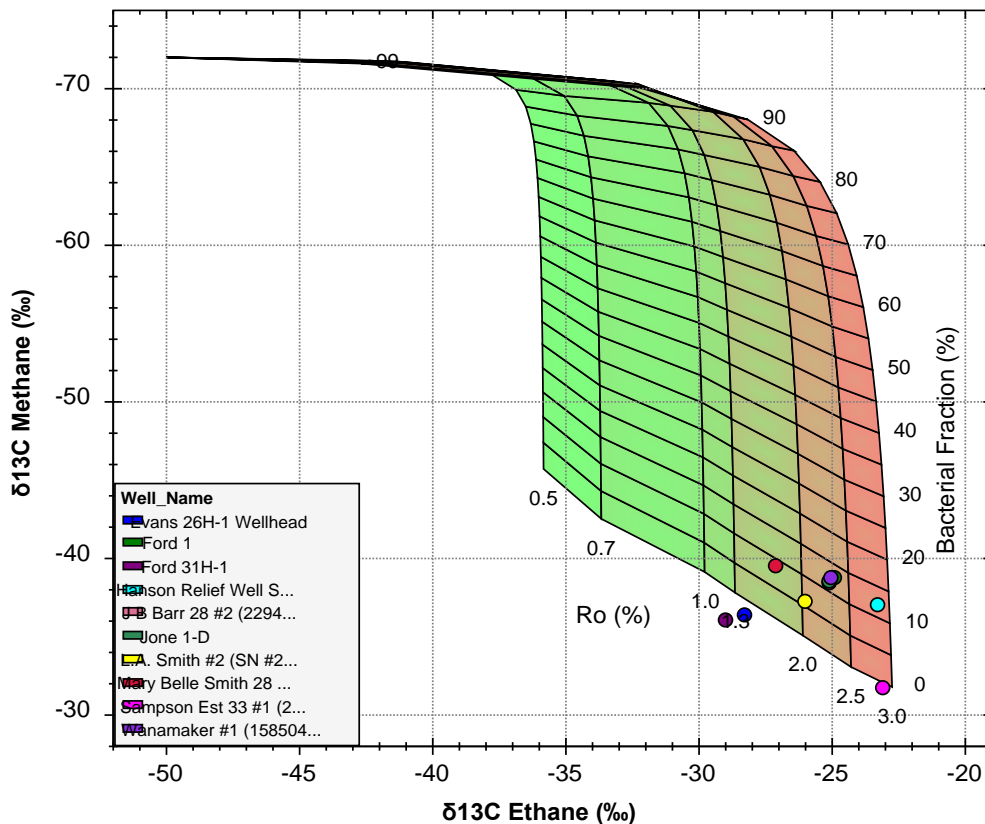
The Haynesville Formation shale-gas samples collected from the Evans 26H-1 and Ford 31H-1 wells exhibit  $\text{VR}_e$  values of  $\sim 1.4$  to  $1.5\%$  in Figure 9. These values are compatible with modelled maturity of the Haynesville published by Nunn (2012).

Most of the gas samples plotted in Figure 9 exhibit evidence secondary gas alteration. The over mature ( $\text{VR}_e \sim 2.5\%$ ) dry gas sample from the Sampson Est. 33 #1 well plots upwards off of the  $\delta^{13}\text{C}_1$  versus  $\delta^{13}\text{C}_2$  correlation trend indicating a mix of different thermogenic gases or microbial methane oxidation. The Haynesville shale-gas samples from the Evans 26H-1 and Ford 31H-1 wells also plot upwards away from the linear maturity trend indicating secondary alteration effects. Excepting the L. A. Smith #2 well, all of the remaining samples fall down and away from

the  $\delta^{13}\text{C}_1$  versus  $\delta^{13}\text{C}_2$  correlation trend suggesting a possible mix of thermogenic and microbial gas or other secondary alteration effects.

Figure 10 presents another plot of methane  $\delta^{13}\text{C}$  versus ethane  $\delta^{13}\text{C}$  showing the thermal maturity ( $\text{VR}_e$ ) 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 (Hosston) and the Haynesville gases contain between six and 13% microbial methane.

**Figure 10.** Plot of methane  $\delta^{13}\text{C}$  versus ethane  $\delta^{13}\text{C}$  showing thermal maturity ( $\text{VR}_e$ ) modeled for refractory kerogen<sup>1</sup> and bacterial methane mixing for the DeSoto Parish natural gas samples. Modified from Tang and others, 2000).

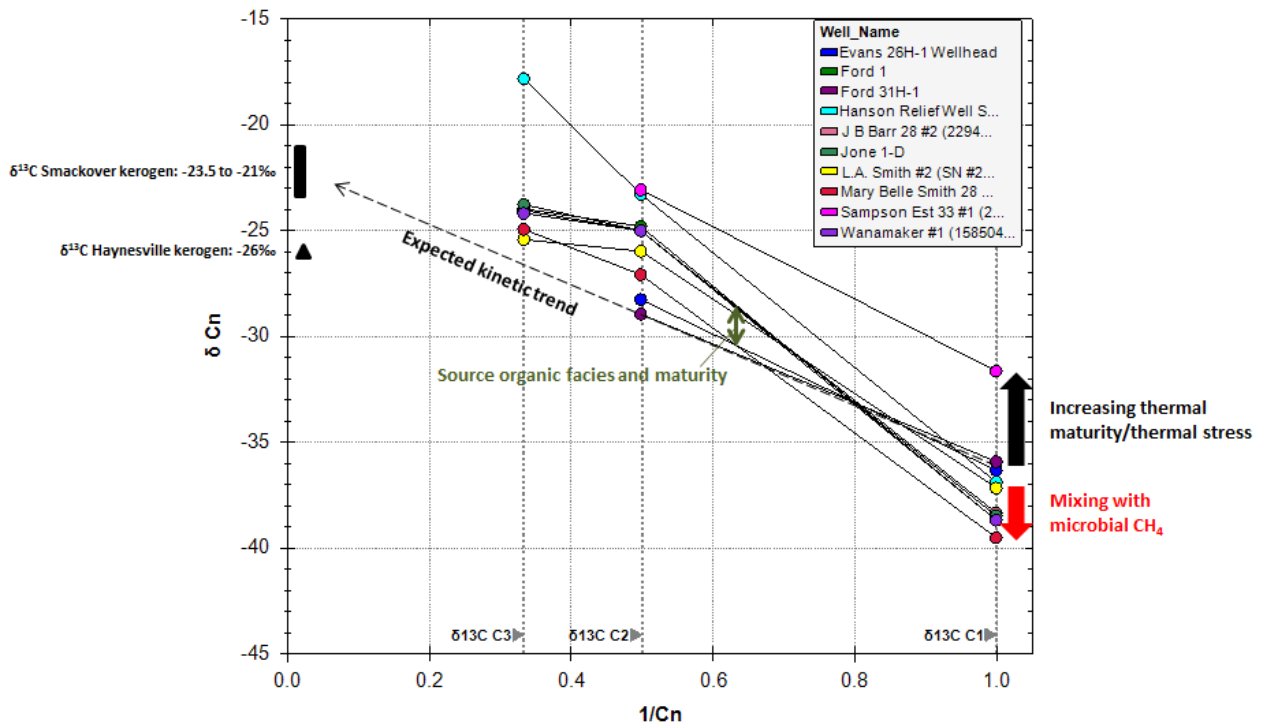


<sup>1</sup>Refractory kerogen is the main lignin-derived component of vitrinite in sedimentary organic matter. It yields methane from either mature Type III kerogen in coal or from post mature to overmature Types I and II kerogen with no remaining oil generation potential.

Figure 11 is a so-called “natural gas plot” or “Chung” plot of  $\delta^{13}\text{C}$  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). 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 is due, in part, to variations in source organic matter and thermal maturity (double arrow in Figure 11).

**Figure 11.** Reciprocal of carbon number ( $1/n$ ) versus  $\delta^{13}C_n$  (Chung and others, 1988) for DeSoto Parish, Louisiana gases.  $\delta^{13}C$  of Haynesville kerogen is from Pernia (2012).  $\delta^{13}C$  of Smackover kerogen is from Oehler (1984).



The two produced Haynesville Shale gas samples from the Evans 26H-1 and Ford 31H-1 wells exhibit a normal natural gas plot straight line trend between  $\delta^{13}C$  of methane and ethane (the samples have insufficient propane for carbon isotopic analysis). The y-intercept of the Haynesville gases trend is isotopically enriched in  $^{13}C$  relative to the reported  $^{13}C$  composition of Haynesville kerogen (Pernia, 2012). It is reasonable to assume that the Haynesville Shale gases were generated in situ in the Haynesville Formation and not migrated from deeper Smackover

sources as the trend in Figure 11 might be construed to show. Therefore the upwards shift of the Chung plot of Haynesville gases from the  $\delta^{13}\text{C}$  Haynesville kerogen value on the y-intercept suggests these hydrocarbons were generated by oil cracking rather than by kerogen cracking (Zou and others, 2007; Golding and others, 2013). The  $^{13}\text{C}$ -enriched methane of these two samples (-35.97 and -36.38‰) is consistent with gas generation from oil breakdown at high thermal stress (Tang and others, 2000; Stolper and others, 2014). The  $^{13}\text{C}$  of both methane and ethane in these Haynesville gas samples suggests generation at burial temperatures of  $\pm 190^\circ\text{C}$  (Rooney and others, 1995), an interpreted estimate in agreement with Nunn's (2012) Haynesville Shale burial and thermal history model. The generation of these gases by oil cracking is explored further in the **Discussion** section of this report below.

The produced Hosston Formation gas collected from the Sampson Est. 33 #1 well also exhibits the expected straight line kinetic relationship on the natural gas plot shown in Figure 11. Bear in mind that, like the two Haynesville samples, the observed trend is incomplete because the Sampson Est. 33 #1 sample had insufficient propane for isotopic analysis. This sample is the most thermally mature produced gas in the data set ( $\text{VR}_e \sim 2.5\%$ ; Figure 9). 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. The interpreted generation temperature for the Hosston Formation gas from the Sampson Est. 33 #1 well is approximately 200 - 210°C (using the Rooney and others, 1995 model). This estimation is compatible with a Smackover source for the gas (Nunn, 2012).

The produced Cotton Valley Formation gas collected from the Mary Belle Smith 28 #2 is post mature ( $\text{VR}_e \sim 1.5$  to 1.7%; Figures 9 - 11). This gas could plausibly be sourced from the Smackover Formation, the Haynesville Shale/Bossier Shale, or source rocks interbedded with Cotton Valley reservoir rocks (see Schenk and Viger, 1996; Peters and others, 2005; Dyman and Condon 2006; Nunn, 2012; Pittman and Rowan, 2012). However,  $\text{VR}_e$  of the Mary Belle Smith 28 #2 hydrocarbons approximates that of the two Haynesville samples from the Evans 26H-1 and Ford 31H-1 wells (Figures 9 - 11). The Haynesville Shale is the likely source of Cotton Valley gas in the Mary Belle Smith 28 #2 well. The natural gas plot for the Cotton Valley sample deviates somewhat from the expected linear trend – a dogleg at  $\text{C}_2$  imparts a slightly convex pattern to the plot (Figure 11). This pattern is most likely due to mixing with residual microbial gas (Figure 11; Golding and others, 2013), although mixing of mature gases derived from Types II and III organic matter or cracking of residual oil are possible as well (Zou and others, 2007).

The produced gases from the Wanamaker #1 (Rodessa reservoir), J. B. Barr 28 #2 (Paluxy reservoir), Ford 1 (Rodessa reservoir), and Jones 1-D (Hosston reservoir) wells have essentially

identical trends on the natural gas plot in Figure 11. Although produced from different reservoirs (Hosston, Rodessa and Paluxy Formations), these four gases appear to share the same source and maturity. These gases have a maturity of  $VR_e \sim 2.1\%$ , a value consistent with Haynesville Shale in the North Louisiana Salt Basin or, possibly, the Smackover Formation source in this area (Nunn, 2012). The gases from these four wells exhibit a distinct convex pattern on the Chung plot in Figure 11 suggesting mixing with residual microbial methane and mixing 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  $VR_e \sim 1.8$  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  $1/n$ . While some mix of residual microbial methane is present (6%, see Figure 10), the strong convexity of the natural gas plot of this sample is mostly due to high thermal maturity (Zou and others, 2007).

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 3.57 mol % of the gross composition (Table 2). The ratio of  $N_2/Ar$  in five of the samples ranges from 143 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 ranges from 0.008 to 2.48 mol % the produced gas samples (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 Wannemaker #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 Wannemaker #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 Wannemaker #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 in an intermediate position between the Ford 31H-1, Evans 26H-1, and Sampson Est. 33 #1 gases and all of the other DeSoto Parish gases on the Bernard plot in Figure 5. It plots near the Ford 31H-1 and Evans 26H-1 gases on the Schoell (1983) plot of  $\delta^{13}\text{C}_1$  versus gas wetness in Figure 6. The Hanson Relief gas resembles that of the L. A. Smith #, Ford 31H-1, and Evans 26H-1 gases on the Schoell (1983) plot of  $\delta^{13}\text{C}_1$  versus  $\delta\text{D}$  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 <sub>2</sub>	Ar	O <sub>2</sub>	CO <sub>2</sub>	N <sub>2</sub>	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	iC <sub>4</sub>	nC <sub>4</sub>	iC <sub>5</sub>	nC <sub>5</sub>	C <sub>6+</sub>
Hanson Relief SN 169060	nd	nd	0.0051	nd	0.74	0.27	97.80	1.05	0.0904	0.00217	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	$\delta^{13}\text{C}_1$	$\delta\text{D}_{\text{METHANE}}$	$\delta^{13}\text{C}_2$	$\delta^{13}\text{C}_3$
Hanson Relief SN 169060	Wilcox Formation	-36.94	-150.2	-23.29	-17.88

The plots of ethane  $\delta^{13}\text{C}$  versus propane  $^{13}\text{C}$  (Figure 8) and methane  $\delta^{13}\text{C}$  versus ethane  $^{13}\text{C}$  (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  $\text{VR}_e$  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  $\delta^{13}\text{C}$  versus ethane  $^{13}\text{C}$  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  $\delta^{13}C_2 = -23.29\text{‰}$ ; the Sampson Est. 33 #1 gas has a  $\delta^{13}C_2 = -23.09\text{‰}$ . 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 ( $-36.94\text{‰}$ ) is significantly lighter than that of the Sampson Est. 33 #1 gas ( $-31.68\text{‰}$ ) 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  $-17.88\text{‰}$ . 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).

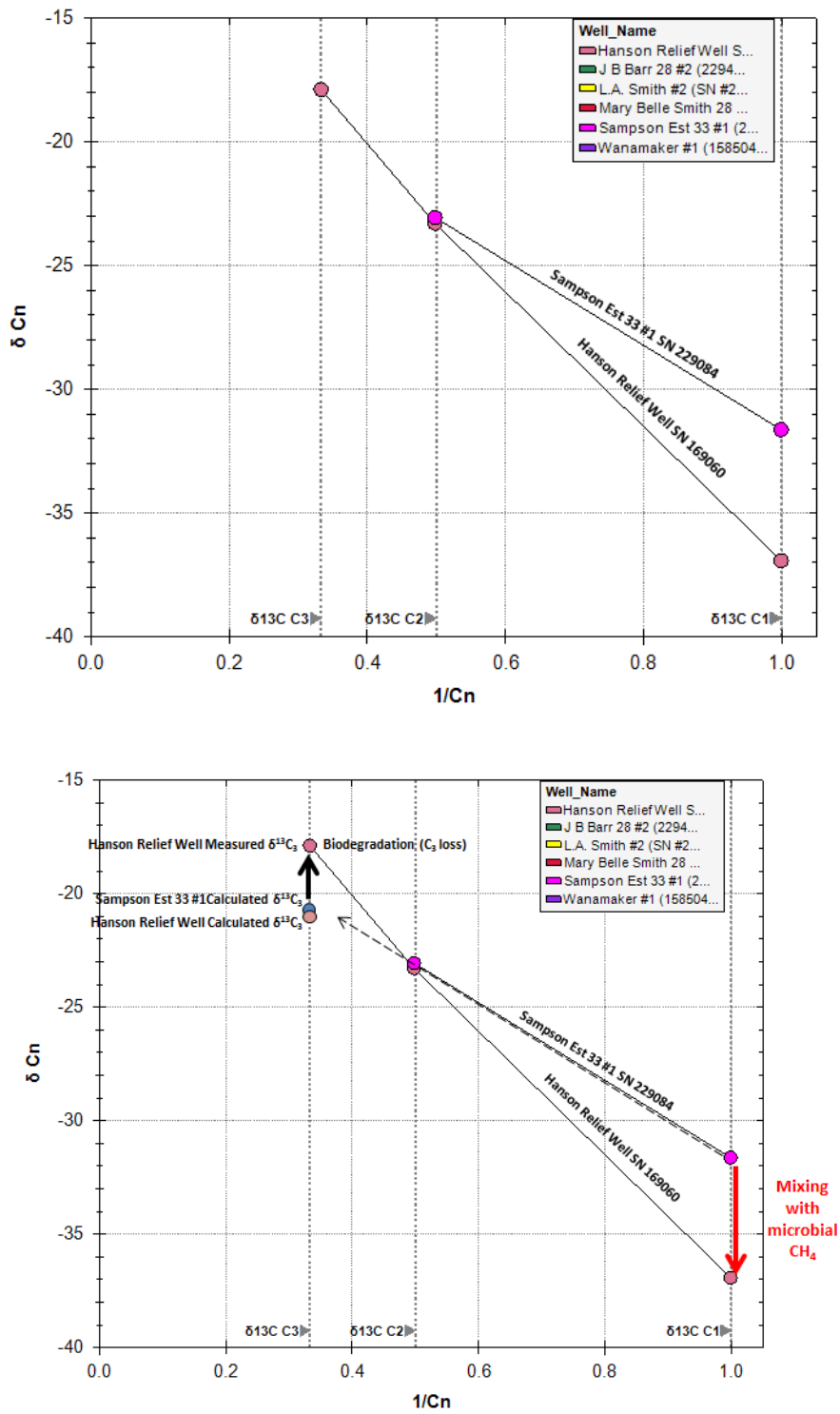
Utilizing the equation developed by Faber (1987) for co-genetic natural gases,

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

the Hanson Relief well gas should have a propane  $\delta^{13}C \sim -21.1\text{‰}$  (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  $-20.9\text{‰}$  (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  $\delta^{13}C_3$  of approximately  $-21.1\text{‰}$  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 ( $VR_e \sim 2.0\%$ ) hydrocarbons generated in marine petroleum source rocks at levels of thermal stress equivalent to  $VR_e$  values between 1.4 and 2.5%. Six of the gases are associated with wet gas or condensate. The Sampson Est. 33 #1, Evans 26H-1, and Ford 31H-1 gases consists of very dry post mature to over 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 and deeper source rocks published by Nunn (2012, Figure 7, p. 91). Higher generation temperatures -  $\sim 200$  to  $210^\circ\text{C}$  – are plausible (Rooney and others, 1995).

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). This includes the Haynesville gases sampled in the Evans 26H-1 and Ford 31H-1 wells (Figure 9). However, the other six produced gas samples have higher thermal maturities: these gases are 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 or from the Haynesville Shale in the Evans 26H-1 and Ford 31H-1 wells. 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).

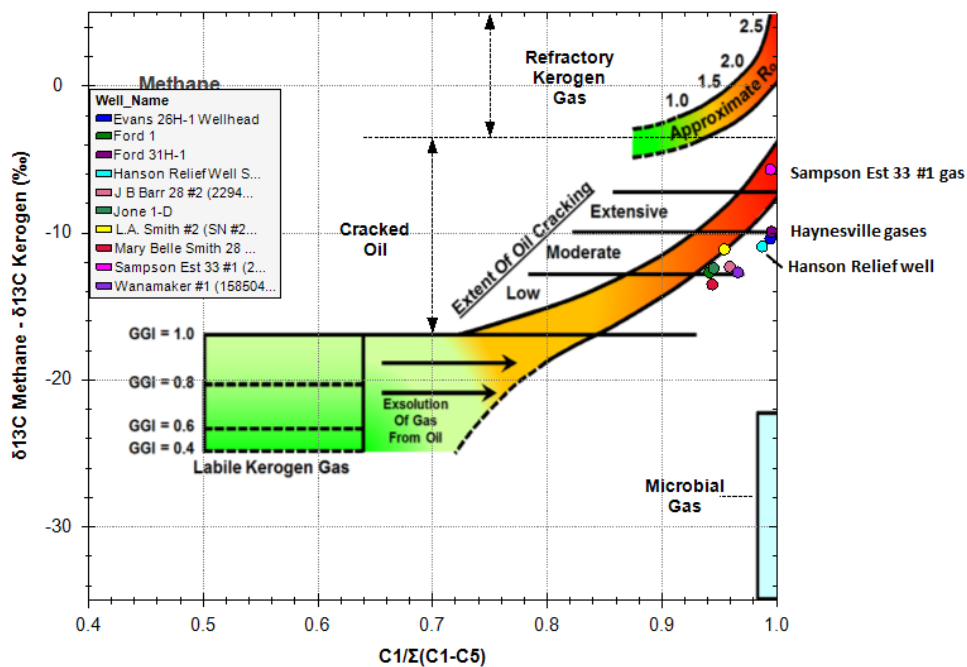
As already noted above, none of the natural gas plot lines in Figure 11 intersect the  $\delta^{13}\text{C}$  of Haynesville or Smackover kerogen as would be expected if the produced gases were generated from these source rock kerogens. This suggests that secondary alteration processes related to high 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. Cracking of refractory kerogen also contributed lesser volumes of gases to the reservoirs. 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  $\delta^{13}\text{C}$  of  $-26.0\text{‰}$  for these plots to calculate the y-axis values based on Haynesville Formation data reported by Pernia (2012). The plots of methane, ethane, and propane  $\delta^{13}\text{C}$  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.

An interesting feature of the Clayton plot in Figure 13 is that six of the produced gas samples 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  $\delta^{13}\text{C}_1$  versus  $\delta^{13}\text{C}_2$  correlation trend in Figure 9 also suggesting a possible mix of thermogenic and residual microbial gas. And these same six samples suggest resolvable microbial gas components in the mixing plot in Figure 10. 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. The fact that the two Haynesville Shale gas samples have no microbial gas admixed with the thermogenic gases makes this interpretation improbable. 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  $\delta^{13}\text{C}$  composition of  $\text{CO}_2$  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.

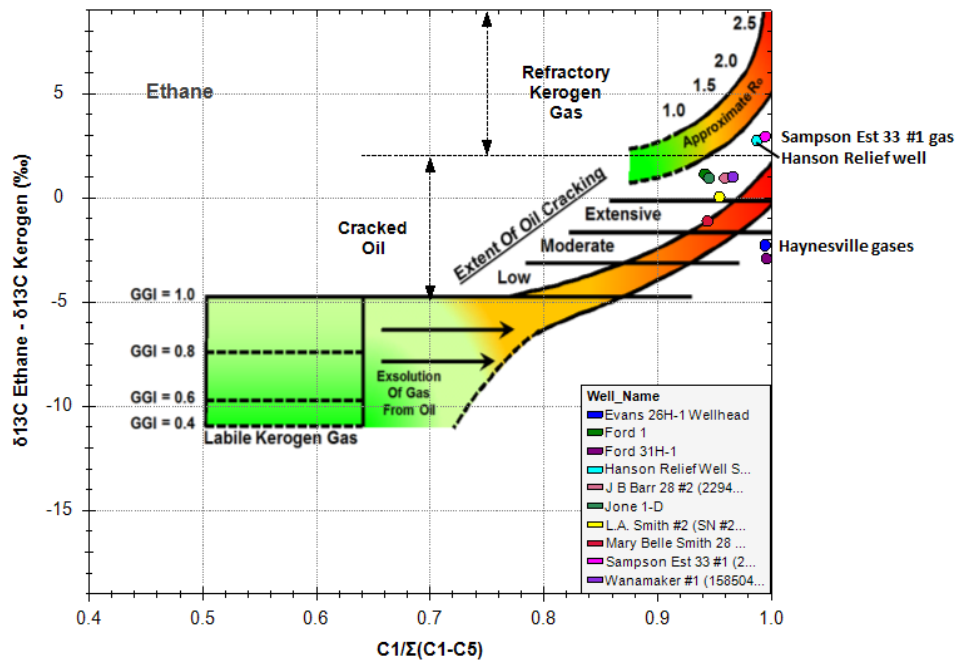
**Figure 13.** Plot of the difference between methane and kerogen  $\delta^{13}\text{C}$  versus gas dryness for the DeSoto Parish produced gases (Clayton, 1991). Solid arrow indicates interpreted mixing with microbial methane.



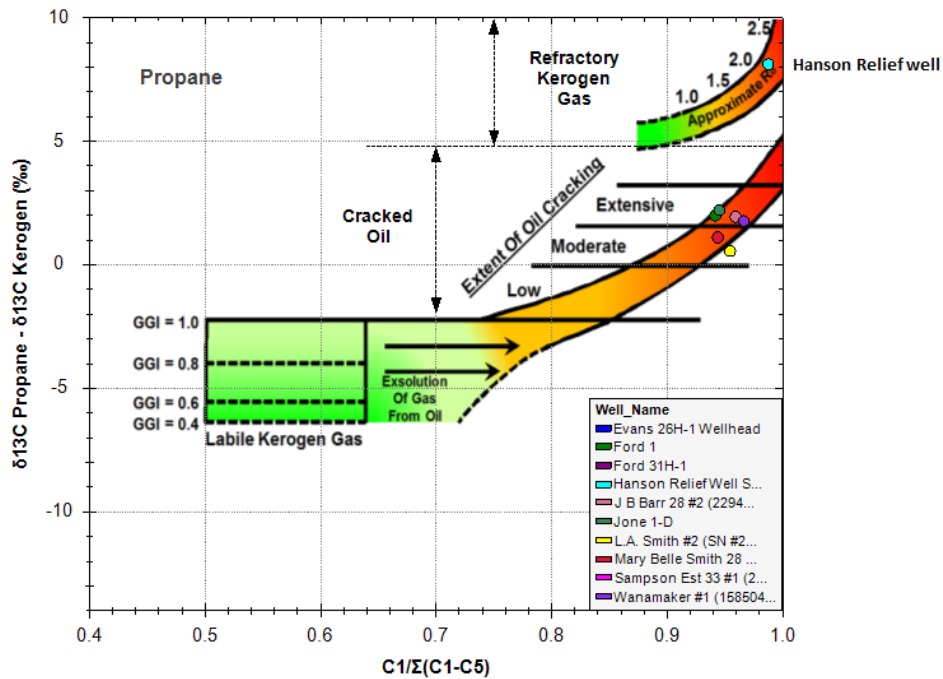
**Hanson Relief Well Gas.** The gas sample collected from the Hanson Relief well consists of predominately post mature ( $VR_e \sim 2.5\%$ ) hydrocarbons mixed with microbially generated methane (Figure 9). The latter contributes approximately 12% methane to the total hydrocarbon gas composition (Figure 10). Biodegradation of the Hanson Relief well gas resulted in propane loss (Figure 8).

The Hanson Relief well methane plots close to the two Haynesville Shale gases collected from the Evans 26H-1, and Ford 31H-1 on the Clayton (1991) plot of the difference between methane and kerogen  $\delta^{13}\text{C}$  versus gas dryness shown in Figure 13. However, this observation does not support a correlation of these three gases because the Hanson Relief gas sample contains an admixture of microbial and thermogenic hydrocarbons. The microbial  $\text{CH}_4$  component pulls the difference between methane  $\delta^{13}\text{C}$  and kerogen  $\delta^{13}\text{C}$  down to a lower value on the y-axis of this plot. The plot of the difference between ethane and kerogen  $\delta^{13}\text{C}$  versus gas dryness shown in Figure 14 shows the strong correlation of the Hanson gas and the Hosston reservoir hydrocarbons produced from the Sampson Est 33 #1 well. The Chung plot in Figure 11 supports this conclusion as well in spite of the different secondary effects obvious in both wells.

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



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



Although these secondary alteration effects somewhat obscure a precise correlation of the Hanson Relief well gas to the other production gases collected in the study area, 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 ( $C1/\sum(C1-C5)$ ): 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  $VR_e \sim 2.5\%$ . 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  $-23.09\text{‰}$  and ethane  $\delta^{13}C$  of the Hanson Relief well gas is  $-23.29\text{‰}$ . Consequently, the two samples plot together in the field of extensive oil cracking.

The gas origin, maturity, and mixing lines published by Tang and others (2000) are shown on the plot in Figure 10. The Sampson Est 33 #1 gas has 0% microbial gas mixed with thermogenic gas. The Hanson Relief well has  $\sim 12\%$  microbial methane mixed with the predominant thermogenic gas. Haynesville shale-gas contains no microbial gas components. Most 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). Additional measurements of the carbon isotope composition of dissolved inorganic carbon (DIC) in the Hanson water well and in produced water from these wells would help to confirm the interpretation of microbial gases in the samples.

As already discussed, The Hanson Relief gas resembles that of several other of the gas samples on the Schoell (1983) plot of  $\delta^{13}C_1$  versus  $\delta D$  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

Ten natural gas samples were collected from nine 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 nine produced gas samples are from wells completed in the Cretaceous Fredericksburg, Paluxy, Rodessa, and Hosston Formations, the Jurassic Cotton Valley Formation, and the Jurassic Haynesville Shale. The nine 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. Most of the gas samples are readily discriminated from one another on various gas isotope cross plots, particularly on the natural gas plot (Figure 11). Four of the gas samples (J. B. Barr 28 #2, Wanamaker #1, Ford 1, and Jones 1-D), 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 ( $VR_o \sim 0.25$  to  $0.3\%$ ) in the study area, yet the stray gas collected from this well is overmature ( $VR_e \sim 2.5\%$ ). 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. Nevertheless, identification of the Sampson Est 33 #1 well as the source of the stray gas in the Hanson 31-5054z water well is 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.

The data discussed in this report clearly demonstrate that methane carbon and hydrogen isotopes are insufficient as stand-alone analyses for determining the source of stray gas in the

study area. The complete chemical composition and isotopic analyses utilized for this study are necessary for characterizing natural gases produced from oil and gas wells and from water wells. Additional geochemical analyses of dissolved gases and DIC in water well samples would refine the interpretations presented in this report.

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## **Appendix 1: Laboratory Data Files**

Lab #: 659674      Job #: 37966      IS-100664      Co. Job#: \_\_\_\_\_  
 Sample Name: Evans 26H-1 Wellhead      Co. Lab#: \_\_\_\_\_  
 Company: XTO Energy  
 API/Well: \_\_\_\_\_  
 Container: IsoTube®  
 Field/Site Name: XTO Jones  
 Location: \_\_\_\_\_  
 Formation: \_\_\_\_\_  
 Sampling Point: \_\_\_\_\_  
 Date Sampled: 4/05/2018 13:08      Date Received: 4/10/2018      Date Reported: 4/27/2018

Component	Chemical mol. %	$\delta^{13}\text{C}$ ‰	$\delta\text{D}$ ‰	$\delta^{15}\text{N}$ ‰
Carbon Monoxide -----	nd			
Helium -----	nd			
Hydrogen -----	nd			
Argon -----	nd			
Oxygen -----	0.059			
Nitrogen -----	0.20			
Carbon Dioxide -----	2.20			
Methane -----	97.10	-36.38	-148.0	
Ethane -----	0.419	-28.29		
Ethylene -----	nd			
Propane -----	0.0186			
Propylene -----	nd			
Iso-butane -----	0.0016			
N-butane -----	0.0025			
Iso-pentane -----	0.0003			
N-pentane -----	0.0002			
Hexanes + -----	0.0008			

Total BTU/cu.ft. dry @ 60deg F & 14.73psia, calculated: 993

Specific gravity, calculated: 0.579

Remarks: Insufficient propane concentration for isotopic analysis.

nd = not detected. na = not analyzed. Isotopic composition of hydrogen is relative to VSMOW. Isotopic composition of carbon is relative to VPDB. All gas component carbon isotope values are reported on a scale defined by a two point calibration of LSVEC and NBS 19. Calculations for BTU and specific gravity per ASTM D3588. Chemical compositions are normalized to 100%. Mol. % is approximately equal to vol. %.

Lab #: 659675 Job #: 37966 IS-100664 Co. Job#: \_\_\_\_\_  
 Sample Name: Ford 31H-1 Co. Lab#: \_\_\_\_\_  
 Company: XTO Energy  
 API/Well: \_\_\_\_\_  
 Container: IsoTube®  
 Field/Site Name: XTO Jones  
 Location: \_\_\_\_\_  
 Formation: \_\_\_\_\_  
 Sampling Point: \_\_\_\_\_  
 Date Sampled: 4/05/2018 11:20 Date Received: 4/10/2018 Date Reported: 4/27/2018

Component	Chemical mol. %	$\delta^{13}\text{C}$ ‰	$\delta\text{D}$ ‰	$\delta^{15}\text{N}$ ‰
Carbon Monoxide -----	nd			
Helium -----	nd			
Hydrogen -----	nd			
Argon -----	nd			
Oxygen -----	0.050			
Nitrogen -----	0.15			
Carbon Dioxide -----	2.49			
Methane -----	96.98	-35.97	-149.6	
Ethane -----	0.311	-28.98		
Ethylene -----	nd			
Propane -----	0.0133			
Propylene -----	nd			
Iso-butane -----	0.0014			
N-butane -----	0.0020			
Iso-pentane -----	0.0003			
N-pentane -----	0.0002			
Hexanes + -----	0.0009			

Total BTU/cu.ft. dry @ 60deg F & 14.73psia, calculated: 989

Specific gravity, calculated: 0.581

Remarks: Insufficient propane concentration for isotopic analysis.

nd = not detected. na = not analyzed. Isotopic composition of hydrogen is relative to VSMOW. Isotopic composition of carbon is relative to VPDB. All gas component carbon isotope values are reported on a scale defined by a two point calibration of LSVEC and NBS 19. Calculations for BTU and specific gravity per ASTM D3588. Chemical compositions are normalized to 100%. Mol. % is approximately equal to vol. %.

Lab #: 659676      Job #: 37966      IS-100664      Co. Job#: \_\_\_\_\_  
 Sample Name: Jone 1-D      Co. Lab#: \_\_\_\_\_  
 Company: XTO Energy  
 API/Well: \_\_\_\_\_  
 Container: IsoTube®  
 Field/Site Name: XTO Jones  
 Location: \_\_\_\_\_  
 Formation: \_\_\_\_\_  
 Sampling Point: \_\_\_\_\_  
 Date Sampled: 4/02/2018 14:00      Date Received: 4/10/2018      Date Reported: 4/27/2018

Component	Chemical mol. %	$\delta^{13}\text{C}$ ‰	$\delta\text{D}$ ‰	$\delta^{15}\text{N}$ ‰
Carbon Monoxide -----	nd			
Helium -----	0.0207			
Hydrogen -----	0.0186			
Argon -----	0.0076			
Oxygen -----	0.074			
Nitrogen -----	1.09			
Carbon Dioxide -----	1.56			
Methane -----	91.63	-38.47	-145.6	
Ethane -----	3.64	-25.07		
Ethylene -----	nd			
Propane -----	0.910	-23.83		
Propylene -----	nd			
Iso-butane -----	0.245			
N-butane -----	0.270			
Iso-pentane -----	0.158			
N-pentane -----	0.0991			
Hexanes + -----	0.276			

Total BTU/cu.ft. dry @ 60deg F & 14.73psia, calculated: 1058

Specific gravity, calculated: 0.619

nd = not detected. na = not analyzed. Isotopic composition of hydrogen is relative to VSMOW. Isotopic composition of carbon is relative to VPDB. All gas component carbon isotope values are reported on a scale defined by a two point calibration of LSVEC and NBS 19. Calculations for BTU and specific gravity per ASTM D3588. Chemical compositions are normalized to 100%. Mol. % is approximately equal to vol. %.

Lab #: 641272      Job #: 36848      IS-99404      Co. Job#: \_\_\_\_\_  
 Sample Name: L.A. Smith #2 (SN #218464)      Co. Lab#: \_\_\_\_\_  
 Company: Approach Environmental, LLC      Cylinder: 2017  
 API/Well: \_\_\_\_\_  
 Container: Cylinder  
 Field/Site Name: LDNR Emergency Gas Sampling  
 Location: \_\_\_\_\_  
 Formation: \_\_\_\_\_  
 Sampling Point: \_\_\_\_\_  
 Date Sampled: 11/29/2017 10:45      Date Received: 12/06/2017      Date Reported: 1/18/2018

Component	Chemical mol. %	$\delta^{13}\text{C}$ ‰	$\delta\text{D}$ ‰	$\delta^{15}\text{N}$ ‰
Carbon Monoxide -----	nd			
Helium -----	0.0253			
Hydrogen -----	nd			
Argon -----	nd			
Oxygen -----	nd			
Nitrogen -----	1.55			
Carbon Dioxide -----	0.010			
Methane -----	93.68	-37.18	-149.0	
Ethane -----	2.56	-25.98		
Ethylene -----	nd			
Propane -----	0.925	-25.48		
Propylene -----	nd			
Iso-butane -----	0.247			
N-butane -----	0.316			
Iso-pentane -----	0.172			
N-pentane -----	0.137			
Hexanes + -----	0.378			

Total BTU/cu.ft. dry @ 60deg F & 14.73psia, calculated: 1068

Specific gravity, calculated: 0.605

nd = not detected. na = not analyzed. Isotopic composition of hydrogen is relative to VSMOW. Isotopic composition of carbon is relative to VPDB. All gas component carbon isotope values are reported on a scale defined by a two point calibration of LSVEC and NBS 19. Calculations for BTU and specific gravity per ASTM D3588. Chemical compositions are normalized to 100%. Mol. % is approximately equal to vol. %.

Lab #: 659673      Job #: 37965      IS-100664      Co. Job#: \_\_\_\_\_  
 Sample Name: Ford 1      Co. Lab#: \_\_\_\_\_  
 Company: XTO Energy  
 API/Well: \_\_\_\_\_  
 Container: IsoTube®  
 Field/Site Name: XTO Jones  
 Location: \_\_\_\_\_  
 Formation: \_\_\_\_\_  
 Sampling Point: \_\_\_\_\_  
 Date Sampled: 4/05/2018 10:40      Date Received: 4/10/2018      Date Reported: 4/11/2018

Component	Chemical mol. %	$\delta^{13}\text{C}$ ‰	$\delta\text{D}$ ‰	$\delta^{15}\text{N}$ ‰
Carbon Monoxide -----	nd			
Helium -----	0.0453			
Hydrogen -----	nd			
Argon -----	0.0131			
Oxygen -----	0.076			
Nitrogen -----	3.57			
Carbon Dioxide -----	1.07			
Methane -----	89.40	-38.68	-151.7	
Ethane -----	4.10	-24.86		
Ethylene -----	nd			
Propane -----	0.887	-24.04		
Propylene -----	nd			
Iso-butane -----	0.149			
N-butane -----	0.203			
Iso-pentane -----	0.0933			
N-pentane -----	0.0751			
Hexanes + -----	0.318			

Total BTU/cu.ft. dry @ 60deg F & 14.73psia, calculated: 1035  
 Specific gravity, calculated: 0.624

nd = not detected. na = not analyzed. Isotopic composition of hydrogen is relative to VSMOW. Isotopic composition of carbon is relative to VPDB. All gas component carbon isotope values are reported on a scale defined by a two point calibration of LSVEC and NBS 19. Calculations for BTU and specific gravity per ASTM D3588. Chemical compositions are normalized to 100%. Mol. % is approximately equal to vol. %.

Lab #: 637780      Job #: 36618      IS-99404      Co. Job#: \_\_\_\_\_  
 Sample Name: Mary Belle Smith 28 #2 Alt (239295)      Co. Lab#: \_\_\_\_\_  
 Company: Approach Environmental, LLC      Cylinder: 3043  
 API/Well: \_\_\_\_\_  
 Container: Cylinder  
 Field/Site Name: LDNR Emergency Gas Sampling  
 Location: DeSoto Parish, LA  
 Formation: \_\_\_\_\_  
 Sampling Point: \_\_\_\_\_  
 Date Sampled: 11/09/2017 14:20      Date Received: 11/15/2017      Date Reported: 1/03/2018

Component	Chemical mol. %	$\delta^{13}\text{C}$ ‰	$\delta\text{D}$ ‰	$\delta^{15}\text{N}$ ‰
Carbon Monoxide -----	nd			
Helium -----	nd			
Hydrogen -----	nd			
Argon -----	nd			
Oxygen -----	0.026			
Nitrogen -----	0.14			
Carbon Dioxide -----	2.00			
Methane -----	92.13	-39.51	-158.1	
Ethane -----	3.80	-27.12		
Ethylene -----	nd			
Propane -----	0.927	-24.94		
Propylene -----	nd			
Iso-butane -----	0.240			
N-butane -----	0.234			
Iso-pentane -----	0.145			
N-pentane -----	0.0748			
Hexanes + -----	0.288			

Total BTU/cu.ft. dry @ 60deg F & 14.73psia, calculated: 1064

Specific gravity, calculated: 0.620

nd = not detected. na = not analyzed. Isotopic composition of hydrogen is relative to VSMOW. Isotopic composition of carbon is relative to VPDB. All gas component carbon isotope values are reported on a scale defined by a two point calibration of LSVEC and NBS 19. Calculations for BTU and specific gravity per ASTM D3588. Chemical compositions are normalized to 100%. Mol. % is approximately equal to vol. %.

Lab #: 637781 Job #: 36618 IS-99404 Co. Job#: \_\_\_\_\_  
 Sample Name: Sampson Est 33 #1 (229084) Co. Lab#: \_\_\_\_\_  
 Company: Approach Environmental, LLC Cylinder: 3053  
 API/Well: \_\_\_\_\_  
 Container: Cylinder  
 Field/Site Name: LDNR Emergency Gas Sampling  
 Location: DeSoto Parish, LA  
 Formation: \_\_\_\_\_  
 Sampling Point: \_\_\_\_\_  
 Date Sampled: 11/09/2017 13:55 Date Received: 11/15/2017 Date Reported: 1/03/2018

Component	Chemical mol. %	$\delta^{13}\text{C}$ ‰	$\delta\text{D}$ ‰	$\delta^{15}\text{N}$ ‰
Carbon Monoxide -----	nd			
Helium -----	0.0403			
Hydrogen -----	nd			
Argon -----	0.0074			
Oxygen -----	nd			
Nitrogen -----	2.55			
Carbon Dioxide -----	0.92			
Methane -----	95.81	-31.68	-119.3	
Ethane -----	0.410	-23.09		
Ethylene -----	nd			
Propane -----	0.0325			
Propylene -----	nd			
Iso-butane -----	0.0133			
N-butane -----	0.0142			
Iso-pentane -----	0.0069			
N-pentane -----	0.0124			
Hexanes + -----	0.188			

Total BTU/cu.ft. dry @ 60deg F & 14.73psia, calculated: 990

Specific gravity, calculated: 0.581

nd = not detected. na = not analyzed. Isotopic composition of hydrogen is relative to VSMOW. Isotopic composition of carbon is relative to VPDB. All gas component carbon isotope values are reported on a scale defined by a two point calibration of LSVEC and NBS 19. Calculations for BTU and specific gravity per ASTM D3588. Chemical compositions are normalized to 100%. Mol. % is approximately equal to vol. %.



Lab #: 637782      Job #: 36618      IS-99404      Co. Job#: \_\_\_\_\_  
 Sample Name: J B Barr 28 #2 (229457)      Co. Lab#: \_\_\_\_\_  
 Company: Approach Environmental, LLC      Cylinder: 3063  
 API/Well: \_\_\_\_\_  
 Container: Cylinder  
 Field/Site Name: LDNR Emergency Gas Sampling  
 Location: DeSoto Parish, LA  
 Formation: \_\_\_\_\_  
 Sampling Point: \_\_\_\_\_  
 Date Sampled: 11/09/2017 13:25      Date Received: 11/15/2017      Date Reported: 1/03/2018

Component	Chemical mol. %	$\delta^{13}\text{C}$ ‰	$\delta\text{D}$ ‰	$\delta^{15}\text{N}$ ‰
Carbon Monoxide -----	nd			
Helium -----	0.0295			
Hydrogen -----	nd			
Argon -----	0.0060			
Oxygen -----	nd			
Nitrogen -----	2.76			
Carbon Dioxide -----	0.14			
Methane -----	93.06	-38.37	-149.7	
Ethane -----	2.51	-25.06		
Ethylene -----	nd			
Propane -----	0.784	-24.07		
Propylene -----	nd			
Iso-butane -----	0.225			
N-butane -----	0.232			
Iso-pentane -----	0.100			
N-pentane -----	0.0595			
Hexanes + -----	0.0914			

Total BTU/cu.ft. dry @ 60deg F & 14.73psia, calculated: 1034

Specific gravity, calculated: 0.598

nd = not detected. na = not analyzed. Isotopic composition of hydrogen is relative to VSMOW. Isotopic composition of carbon is relative to VPDB. All gas component carbon isotope values are reported on a scale defined by a two point calibration of LSVEC and NBS 19. Calculations for BTU and specific gravity per ASTM D3588. Chemical compositions are normalized to 100%. Mol. % is approximately equal to vol. %.

Lab #: 637783 Job #: 36618 IS-99404 Co. Job#: \_\_\_\_\_  
 Sample Name: Wanamaker #1 (158504) Co. Lab#: \_\_\_\_\_  
 Company: Approach Environmental, LLC Cylinder: 3073  
 API/Well: \_\_\_\_\_  
 Container: Cylinder  
 Field/Site Name: LDNR Emergency Gas Sampling  
 Location: DeSoto Parish, LA  
 Formation: \_\_\_\_\_  
 Sampling Point: \_\_\_\_\_  
 Date Sampled: 11/09/2017 14:45 Date Received: 11/15/2017 Date Reported: 1/03/2018

Component	Chemical mol. %	$\delta^{13}\text{C}$ ‰	$\delta\text{D}$ ‰	$\delta^{15}\text{N}$ ‰
Carbon Monoxide -----	nd			
Helium -----	0.0303			
Hydrogen -----	2.75			
Argon -----	0.0058			
Oxygen -----	nd			
Nitrogen -----	2.16			
Carbon Dioxide -----	0.008			
Methane -----	91.80	-38.74	-155.2	
Ethane -----	2.12	-25.03		
Ethylene -----	0.0001			
Propane -----	0.601	-24.23		
Propylene -----	nd			
Iso-butane -----	0.154			
N-butane -----	0.160			
Iso-pentane -----	0.0667			
N-pentane -----	0.0420			
Hexanes + -----	0.104			

Total BTU/cu.ft. dry @ 60deg F & 14.73psia, calculated: 1012

Specific gravity, calculated: 0.575

nd = not detected. na = not analyzed. Isotopic composition of hydrogen is relative to VSMOW. Isotopic composition of carbon is relative to VPDB. All gas component carbon isotope values are reported on a scale defined by a two point calibration of LSVEC and NBS 19. Calculations for BTU and specific gravity per ASTM D3588. Chemical compositions are normalized to 100%. Mol. % is approximately equal to vol. %.