

# Environmental, Exploration and Production

## Applications of Shale Gas Analyses



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## Summary

This document presents an overview of some of the basic science and operational risk involved in the process of drilling deep wells into the subsurface for the purpose of producing hydrocarbons.

In the first two sections of the paper I have briefly described how hydrocarbons are generated as the result of increased temperature and pressure at depth and then shared with you some of my experiences with how some of these hydrocarbons may get to the surface to cause problems and concerns.

In the next part of the document I have described how one might investigate the source of these hydrocarbons: are they natural or anthropogenic and if the latter are they related to the operational aspects of drilling or production.

Finally, I have presented several examples of the uses of hydrocarbon analyses related to exploration and production.

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## Introduction

Until the last decade, organic rich shales have been viewed as source rocks of petroleum and not as petroleum reservoirs, while the more porous and permeable sandstones and carbonates have been the more traditional reservoirs. With the development of hydraulic fracturing methodology coupled with horizontal drilling, organic rich shales are now sought as both source and reservoir. Depending on the type organic material in the shale formation and its temperature history throughout geologic time, shales may produce products ranging from oil to dry gas.

As the inventory of viable shale formations is assessed worldwide, their potential to reverse world dependence on the more traditional oil and gas reserves has prompted widespread speculation. Even the more practical of those assessments need to be tempered in the fact that decades of development with regard to infrastructure such as pipelines, LNG terminals, refineries and ships will be required. Fleets of vehicles and hundreds of power plants will also need to be produced, not to speak of an LNG pump installed at most or all services stations. So the realization of energy independence based on production from shale basins will be a marathon, not a sprint.

That being said, however, the marathon has begun and even in these early miles we have already begun to develop a few blisters from our brand new track shoes. There are many facets of these early consternations, however I would like to focus this discussion on environmental, exploration and production issues and how the analysis of the produced shale gas and some of its close kin may assist in relieving some of the anxieties, both real and perceived.

First, I would like to briefly discuss the geology and geochemistry of shales as source rocks and reservoirs so that we have an understanding of how they function as we later consider analytical tools to facilitate the protection of environmental health and safety and exploration production (EP) issues.

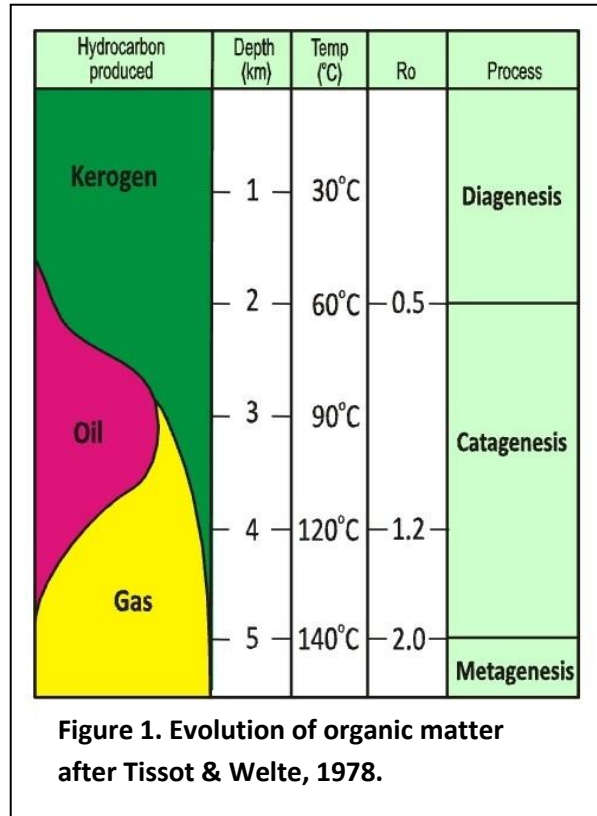
Second, I would like to present several examples of how hydrocarbons produced in a source rock at depth and stored in either a conventional or unconventional

reservoir may find their way toward the surface. We will consider production well bores themselves, abandoned wells, faults and fractures as conduits through which the hydrocarbons may travel.

Finally, I will discuss the analytical tools which may be used to characterize both the produced gases and hydrocarbons which may pose an environmental risk, particularly to near surface drinking water aquifers.

## Shales as a Source Rock and Reservoir of Oil and Gas

Before examining the environmental and EP aspects of shale gas, I think it would be useful to explore how shales are formed and why they may have properties as sources and unconventional reservoirs of oil and gas. The formations known and discussed here as shales are deposited in either marine or lacustrine (oceans or lakes) environments as fine grained deposits, e.g. muds or clays. This deposition occurs in water well away from the high energy shoreline where the water is calm enough that, in addition to the fine grained sediments, organic materials such as the remains of land plants, algae and other marine organic matter may also be deposited. Good source rocks contain more than ~ 1% organic carbon and depending on the type of organic matter deposited may have the potential to produce oil or gas, or both. As deposition continues, the shale is covered by younger sediments and subsides to greater and greater depths. As the shale reaches greater depths over millions of years it experiences increases in temperature and pressure. A world average geothermal gradient is about 25 °C per kilometer (7.6 °C / 1000 ft) (Tissot & Welte, 1978 ), so at a depth of several thousand feet, temperatures in the buried shale may reach 100 °C or more.



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The maturation of the organic matter as it experiences increased temperatures is a product not only of the temperature, but also the time over which it is experienced. One of the useful means of characterizing the integration of time and temperature is derived from the measurement of the reflectance,  $R_o$ , of small particles in the organic matter called vitrinite, which are a component of land plants.

The processes of maturation are described in Figure 1. The early process of maturation is known as diagenesis and occurs at mild temperatures up to  $\sim 50^{\circ}\text{C}$  and includes the subprocesses of biochemical degradation, polycondensation, insolubilization and the formation of a geopolymer known as kerogen (Tissot & Welte, 1978). Next, the process known as catagenesis, thermally alters the kerogen forming oil. This process occurs in the temperature range of  $\sim 50 - 140^{\circ}\text{C}$  vitrinite reflectance range of  $R_o \sim 0.5 - 2.0\%$ . A rock with  $R_o \sim 1.35\%$  is said to be mature and will generate gas associated with the oil (OAG)(Peters & Cassa, 1994). The main gas forming process is known as metagenesis and begins at  $R_o \sim 2.0\%$  (Tissot & Welte, 1978) and begins to form gas which is not associated with oil sometimes called NAG. OAG and NAG will be discussed more thoroughly latter.

At the same time that temperature increases as a result of increased burial depth, pressure also increases. For shales this means compaction and expulsion of fluids, mostly water at shallow depths, but may include matured organic matter in the form of oil or gas as depths and pressures increase. With compaction, there also develop decreases in porosity and permeability. Thus, as the organic material experiences catagenesis and metagenesis, larger molecules are broken down and are increasingly converted into more and more smaller molecules. The increasing amount of organic materials which form may also cause increased internal pressures which may cause natural fracturing to relieve the pressure. These natural fractures in addition to the remaining, but reduced, porosity and permeability, enable the escape of organic fluids which then migrate away from the shale source into more permeable formations. Conventional reservoirs of oil and gas are a direct result of these processes.

Shales are unconventional reservoirs of oil and gas since only a small part of the organic fluids generated escape to conventional reservoirs. Geoscientists have recognized the potential of these unconventional reservoirs for many decades and attempts to increase porosity and permeability through fracturing date at least to 1946 (Nicklen, C. O., 1946). Early fracturing attempts used explosives such as TNT or nitroglycerin in vertical boreholes with varying, but largely non-commercial results. The 1946 example cited above used 5000 qts of nitroglycerin in a borehole filled with marbles. Oil flow was not increased and no further

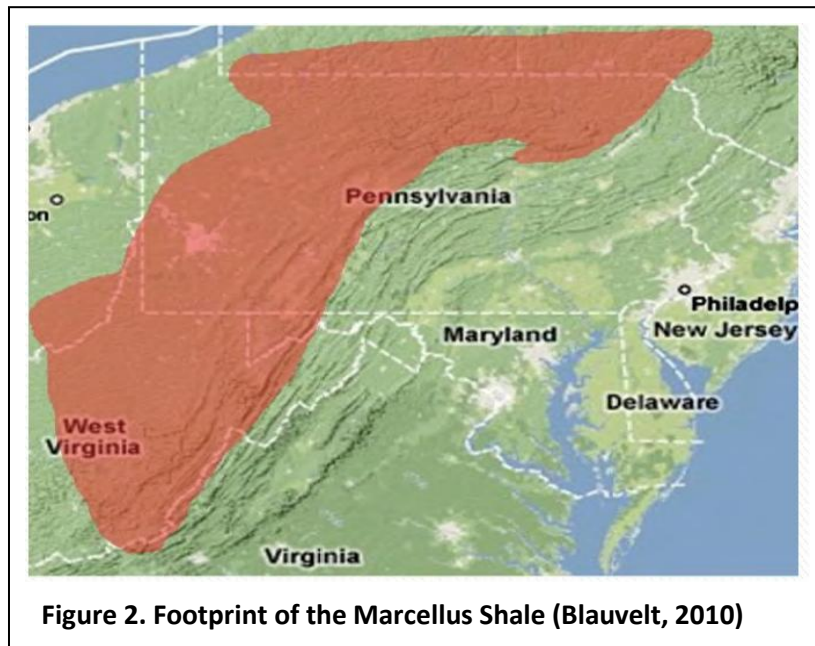
“fracking” was attempted (Miller and Johansen, 1976). Only in the last 20 years, with the development of hydraulic fracturing in horizontal boreholes has shale, as an unconventional reservoir, developed into a commercial potential.

One of the larger developing plays is the Marcellus shale with a footprint of over 95,000 square miles (Blauvelt, 2010) in portions of the states of New York, Pennsylvania, Ohio and West Virginia as shown on Figure 2. The Marcellus shale was deposited in a deep basin formed during the build-up of the Acadian Mountains to the east during middle Devonian time (385 million years ago).

Today the formation is found at a depth of ~ 1.3 miles although, based on its maturity and other factors, it may have been buried much deeper in the past. Its thickness varies from 50 – 300 feet.

As these mountains formed, they were being continuously eroded, filling with basin with sediments and organic

matter composed of land plants, algae and other marine organic matter. Kerogen in the Marcellus has been found to be gas prone (Type III) over much of the basin. Total organic carbon ranges from 2 – 14% so it is extremely rich in organic carbon. Vitrinite reflectance ranges from 0.6 – 3.0 % indicative of a mature to post mature source rock with the capacity to produce large amounts of gas (Blauvelt, 2010). Indeed the Marcellus has no doubt sourced several of the conventional reservoirs which have produced gas in the region for decades. Based on its present high organic content it is well on its way to becoming a prolific unconventional reservoir as well. Its composition has a relatively high silica and low swelling clay content which makes the Marcellus brittle, extremely “frackable” and favorable to unconventional productivity. The Marcellus is bounded above and below by



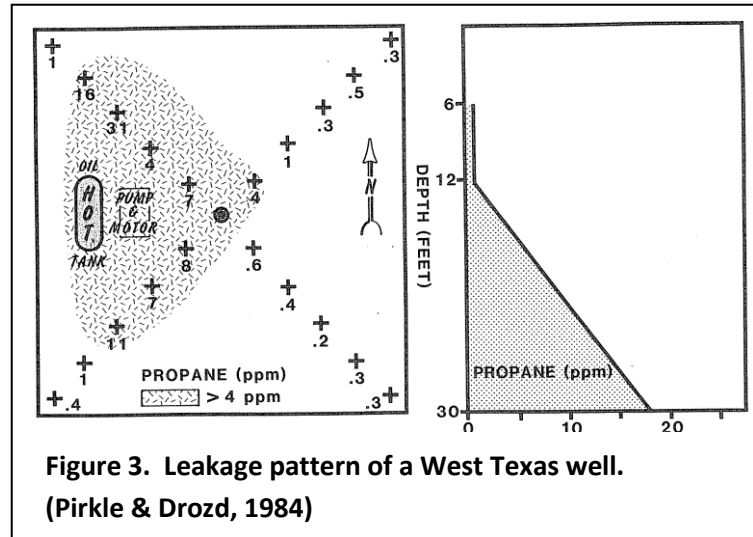
the Tully and Onondaga limestones which act as upper and lower frack barriers. (Blauvelt, 2010) This means that induced fractures from horizontal wells rarely penetrate these limestone barriers and thus minimizes the potential for fluid to escape from the shale itself. During production, the horizontal wellbore is the low pressure point in the formation which induces migration of fluids toward the wellbore rather than toward the boundaries of the shale.

### **Leaks and Seeps**

I would like to spend a bit of time here to relate to you several examples which illustrate how deep subsurface hydrocarbon fluids may get to the surface. The most obvious potential for leakage are well bores themselves, including those which have been abandoned and are of unknown location. Second, faults or series of faults which extend from depth to the surface are often conduits of hydrocarbon migration. Using modern technology many of these conduits can be identified and all must be considered, evaluated and taken into account.

In order to take advantage of oil and gas reservoirs of petroleum, at a minimum one must drill a well into the reservoir at the optimum location to maximize production, while at the same time taking care to insure that environmental health and safety are protected. In modern wells this latter requirement often means that 2 and sometimes 3 strings of casing separated by cement are put in place to depths below the depth of drinking water aquifers. Well investigations, usually called well logs, are run to positively determine the presence of viable cement sealing the annulus between each set of casing. Even with all of these precautions however, one must consider the wellbore as a potential conduit to the surface. The following examples illustrate patterns attributable to well bore leakage.

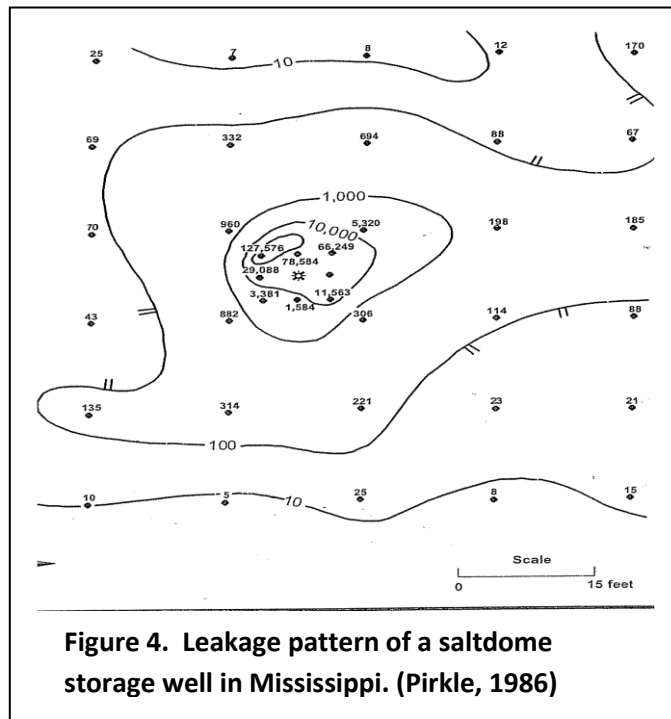
While conducting a geochemical exploration survey in West Texas, a well was monitored which had been found to leak at a depth of approximately 7600 feet (Pirkle and Drozd, 1984). It was felt that due to a bad cement job, there was the potential for communication to the surface. Results of the



**Figure 3. Leakage pattern of a West Texas well. (Pirkle & Drozd, 1984)**

monitoring are shown in Figure 3, in which, on the left, propane in soil gas is shown at a depth of ~12 feet. Propane was chosen to insure that we were not monitoring biogenic gas. The affected area is very near the well bore, although the pattern is not symmetrical. In the depth profile, on the right, increasing concentration with depth, suggests that the source is at depth rather than due to a spill at the surface.

A salt dome storage well in Mississippi was suspected of leakage of natural gas because of measured pressure drops in the well. The cause of this leak was later determined to be corrosion of the casing. Samples were taken at a grid spacing of 15 feet and a depth of 3 feet. The hydrocarbon magnitude around the well within the grid is shown in Figure 4 (Pirkle, 1986). The leakage is largely contained within 20 to 30 feet of the well bore. Both the molecular and isotopic composition of the



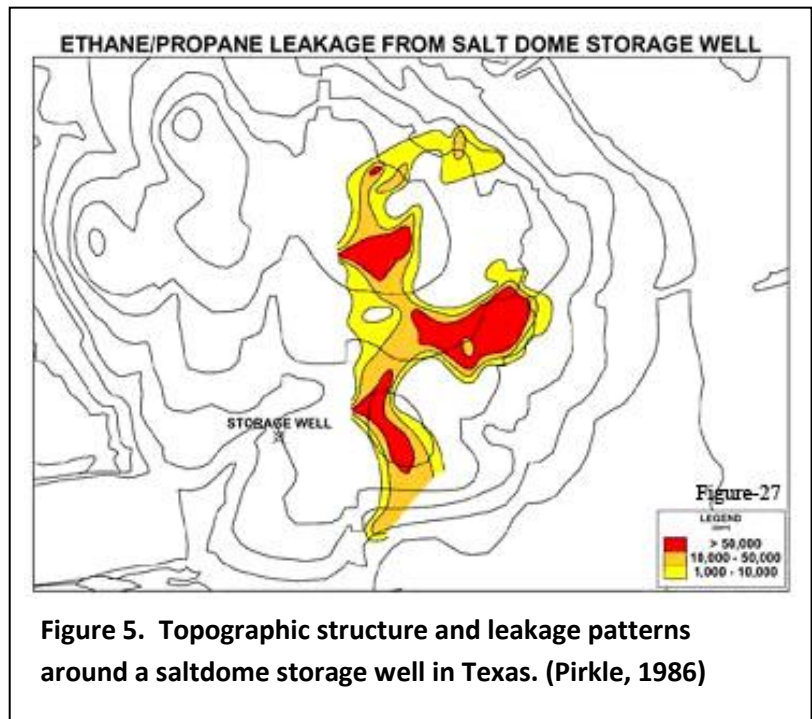
**Figure 4. Leakage pattern of a salt dome storage well in Mississippi. (Pirkle, 1986)**

near surface gases were compared to the stored product in order to ascertain that they were indeed the same and that indeed the source of the surficial hydrocarbons was the stored product in the well.

The two examples presented above in Figures 3 and 4 illustrate our belief that when a well leaks, the evidence of this leakage is usually first manifested around the well bore itself. This may be due to corrosion of the casing in the case of older wells or to bad cement jobs in more recent wells, or both. This should underscore the necessity of insuring that casing cement logs be run on every well and that regular monitoring around the well bore itself be adopted as standard protocol. This applies equally to both vertical and horizontal wells.

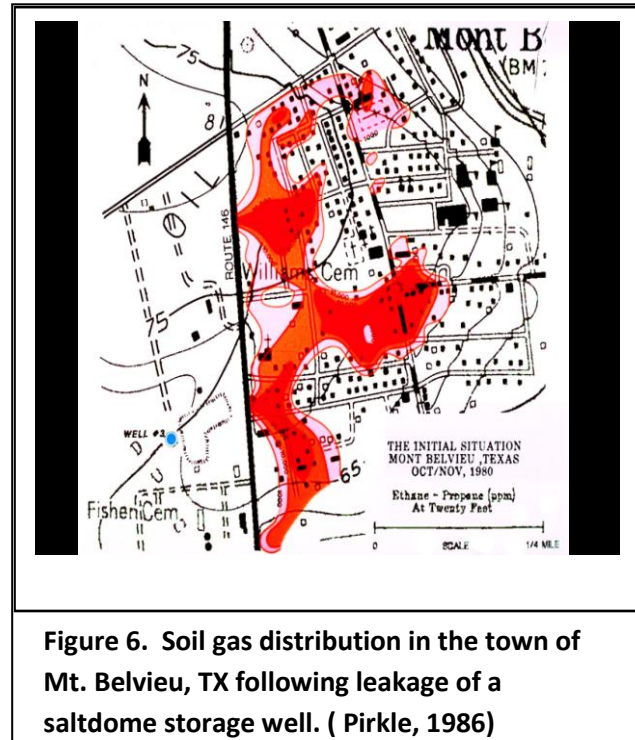
The following example (Pirkle, 1986) is an extreme case where a significant product loss rate was reached which required rapid and extensive remedial action. It occurred at the Barbers Hill Salt Dome as shown on Figure 5. In September 1980, a pressure drop in Storage Well #3 indicated a possible leak of the stored ethane-propane mix in the well. A temperature log revealed an anomaly at the 575 foot level, which was later determined to be the location of the leak. A 2" x 3" hole, apparently caused by corrosion, was eventually found in the casing at this level which is in the caprock over the salt dome. It is noted that this well operated without cathodic protection for a number of years in its early history.

Escaping product into the caprock at the top of the salt is almost certain to have followed an open conduit such as a fault or an abandoned well casing in making



its rapid vertical migration toward the surface. Both avenues were determined to be present. Very little gas was found between 575 feet and 200 feet, suggesting that the several sands in this interval were not exposed to the migrating gases. Sands at the 200 ft level and shallower sands near the surface were, in general charged with the product. During periods of precipitation, bubbles were observed around the Storage Well #3 wellbore as well as a nearby abandoned well.

A soil gas survey of the plant property suggested that the primary direction of migration was to the north and east of the well, to the north presumably following structure, and to the east probably through a fault or zone of weakness observed on aerial photography. Near-surface hydrocarbon soil gas concentrations in this zone increased by a factor of 500 to 1000 as compared to adjacent samples outside the zone. The first of 32 relief wells was drilled to the 200 foot level in this zone. This well produced at a rate of 10 mmcf/d for several days.



**Figure 6. Soil gas distribution in the town of Mt. Belvieu, TX following leakage of a salt dome storage well. ( Pirkle, 1986)**

The product continued its migration to the north and east into the town of Mont Belvieu and was found in a 30 foot aquifer as shown in Figure 6. This delineation of the gas was used to inject nitrogen into the aquifer, effectively purging the ethane-propane gas back to the plant property line.

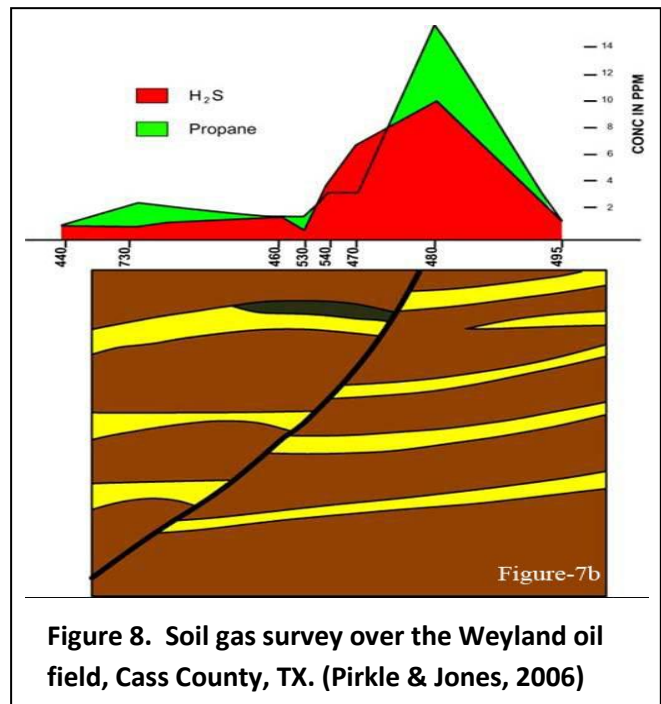
Subsequent to this remedial effort, a preventive monitoring system was installed around the plant boundary and near the casing of each of the 28 storage wells. Monitoring of these ~ 30 foot wells continues to this day as a potential means of early detection of storage well leakage.

While conducting an environmental remediation survey near Los Angeles, CA a macro-seep of petroleum related gas was discovered in the Ballona Channel as shown in Figure 7 (Pirkle & Jones, 2006). We have no knowledge of the presence of abandoned wells, although they may well be present, however this seepage would appear to be related to gas in a reservoir in the Pico formation at about 2000 feet. The seepage was not obvious until following excavation and rainfall, the bubbles as shown were observed.



**Figure 7. Active seepage in the Ballona Channel near Los Angeles. ( Pirkle & Jones, 2006)**

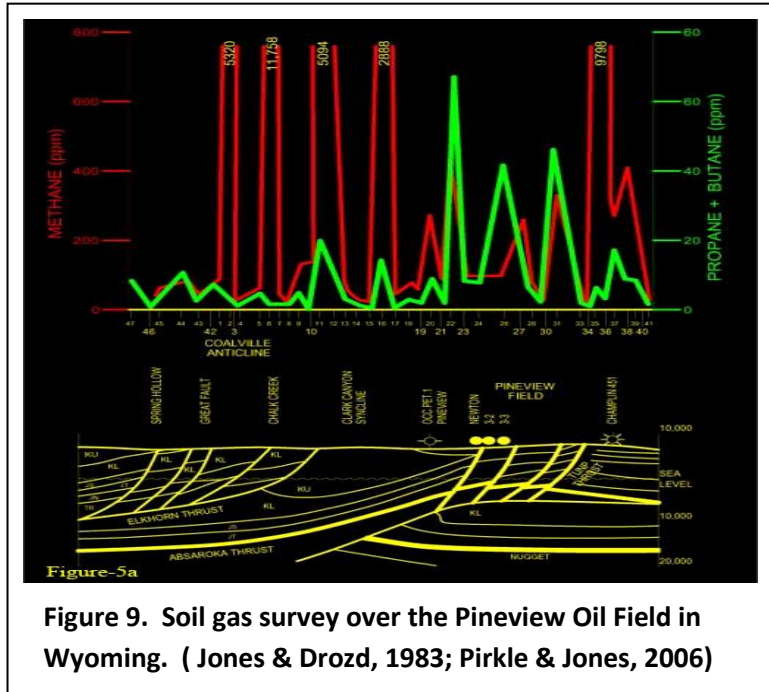
An exploration soil gas survey conducted over the Weyland oil field in Cass County, Texas is shown in Figure 8 (Pirkle & Jones, 2006). Oil reservoir in the Weyland field is of high sulfur content. Hydrogen sulfide in addition to C<sub>1</sub> – C<sub>4</sub> hydrocarbons were found in soil gas in surface samples at a depth of 10 feet. Notice that the soil gas anomaly is deflected somewhat by the bounding growth fault so that it is not observed directly over the reservoir. This fault is no doubt a major conduit for the observed hydrocarbon fluids at the surface. It is also significant that H<sub>2</sub>S, which is much more reactive and soluble than the hydrocarbons, can survive the migration path from reservoir to surface.



**Figure 8. Soil gas survey over the Weyland oil field, Cass County, TX. (Pirkle & Jones, 2006)**

The following soil gas survey was run over the Pineview oil field in Wyoming in 1976, when the field contained only 3 producing wells (Jones & Drozd, 1983, Pirkle & Jones, 2006). This field produces from the Nugget formation at ~ 9000 feet bgs. The data plotted on the profile

shown in Figure 9 were collected on 0.25 mile centers from a depth of 10 feet. Methane is plotted in red and the sum of propane plus butanes is plotted in green. Note that the methane magnitudes, although truncated at 800 ppmv for purposes of illustration, ranged from 2000 to 11,000 ppmv. The data reveal that a significant change in relative

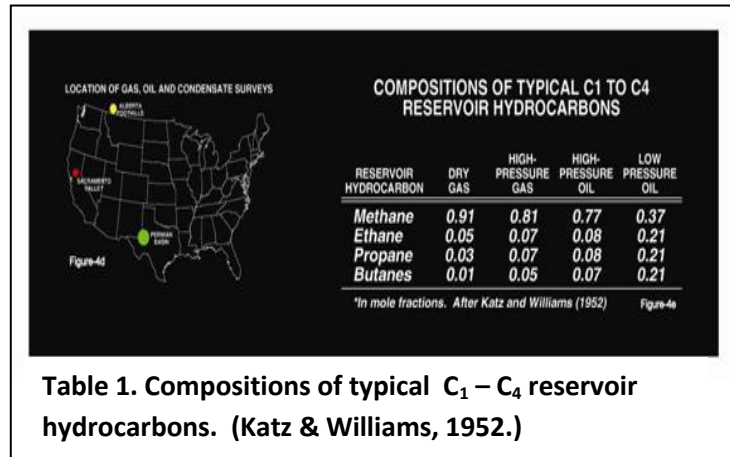


**Figure 9. Soil gas survey over the Pineview Oil Field in Wyoming. ( Jones & Drozd, 1983; Pirkle & Jones, 2006)**

magnitudes of  $C_1$  and  $(C_3 + C_4)$  occurs across the profile and that the wettest gas, i.e. largest  $(C_3+C_4)$  occurs over the oil field and a much dryer gas composition occurs to either side of the field. An idealized cross section of the geologic structure is shown below the data, with the position of the Pineview field indicated. It is also significant to note that the green propane plus butanes profile has its largest values between the Elkhorn thrust on the left to the Tunp thrust on the right. It is very likely that these large thrust faults have been major natural migrational conduits of these hydrocarbon fluids to the surface. The dryer soil gas to the left of the oil field is most likely due to the presence (and leakage) of a gas storage sand which is bounded by the Great fault.

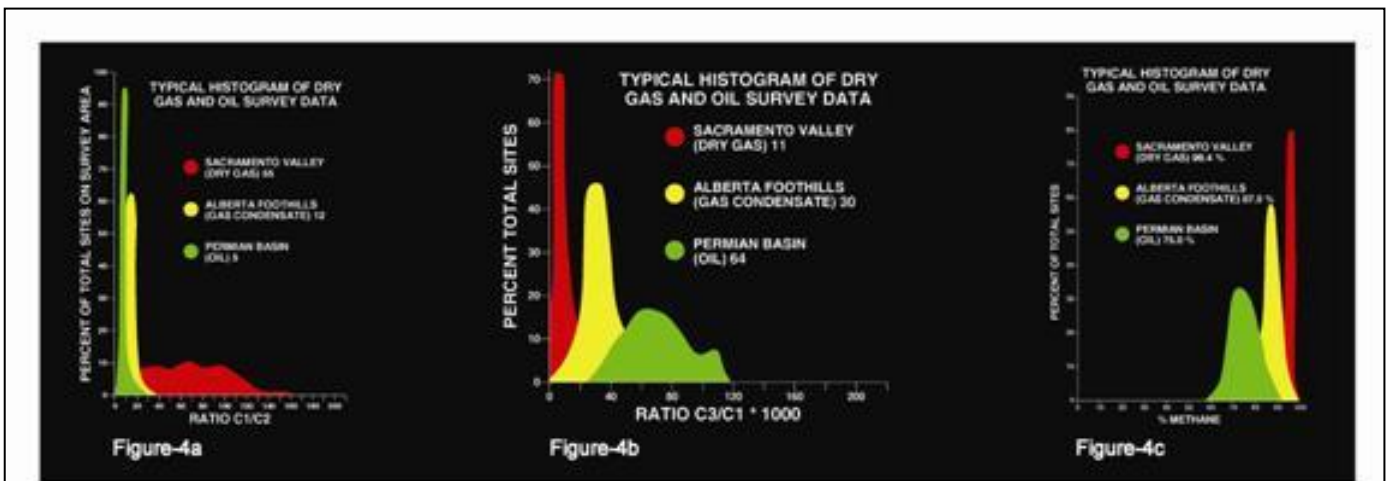
Care should be exercised to avoid “fracking” across a major fault such as shown in the Weyland and Pineview examples, because they can act as conduits for petroleum fluids toward the surface.

Finally, I think it is useful to consider basin wide surveys and their implications for soil gas composition after migration to the surface. First, I would like to consider the typical reservoir hydrocarbon compositions in terms of the C<sub>1</sub> – C<sub>4</sub> hydrocarbons as reported by Katz and Williams, 1952 and presented in Table 1. It is clear that as one considers the range of hydrocarbon fluids from dry gas to low pressure oil, there is a corresponding increase in the C<sub>2</sub>+ hydrocarbon content.



**Table 1. Compositions of typical C<sub>1</sub> – C<sub>4</sub> reservoir hydrocarbons. (Katz & Williams, 1952.)**

The same trend in near surface soil gas compositions have been observed in basin wide surveys and have been discussed by Jones and Drozd (1983), and Pirkle and Jones (2006). Consider the histograms of soil gas composition as presented in Figure 10 over three differing hydrocarbon producing provinces: the Sacramento



**Figure 10. Soil gas composition over three unique hydrocarbon producing provinces. (Jones & Drozd, 1983; Pirkle & Jones, 2006)**

Valley dry gas province; the Alberta Foothills gas condensate province; and the Permian basin oil province. Each survey contained a minimum of 450 soil gas sites with samples taken from a depth of 10 feet. It is clear that the surface soil gas composition of the C<sub>1</sub>–C<sub>4</sub> hydrocarbons changes with great similarity to

changes in reservoir hydrocarbon composition as reported by Katz and Williams, 1952 as presented in Table 1 above. This suggests that thermogenic hydrocarbons may migrate from depth to the near surface without significant change in composition.

I have presented this discussion of Leaks and Seeps to illustrate that there are conduits to the surface for hydrocarbon fluids generated by thermogenic processes at depth. The source of these hydrocarbons may be either reservoirs or source rocks. Some of the conduits are man-made, but many of them are natural. The natural conduits we have little control over, but we can minimize the risk of the man-made conduits with careful planning and execution of field operations. Perhaps the greatest evidence that we can explore hydrocarbons at depth without unacceptable risk to environmental health and safety is the fact that over the last 150+ years since the Drake well was drilled in Pennsylvania, there have been hundreds of thousands of wells drilled to hydrocarbon producing depths and yet we have not succeeded in destroying our drinking water aquifers even though many of those wells in the first 100 years were drilled with little or no concern for the environment and with technology which can only be described as primitive compared with that of today.

### **Biogenic vs Thermogenic Gas**

The overriding environmental concern with regard to shale gas production is contamination of drinking water aquifers near the surface. This concern is not unique to shale gas production, but is of general concern even for traditional vertical well bores. The focus of this document is in regard to hydrocarbons only and does not extend to co-produced water or frack fluids.

Numerous surveys of water wells in Pennsylvania have found that it is not uncommon to find methane and other light hydrocarbons in drinking water aquifers and water wells and while their presence may be due to either shallow or deep wells, they may also occur in the absence of any known manmade cause (Molofsky, et.al., 2011; Baldassare, 2011; Boyer, et.al., 2011; Breen, et.al., 2007; Revesz, et.al., 2010). When such occurrences are of a magnitude to cause concern, the issue to be resolved is source identification. Methane, the most

common and usually the hydrocarbon found in the highest concentration may have several potential sources. First, methane may be formed biogenically by two mechanisms: reduction of carbon dioxide and fermentation of acetate. Second, methane is formed thermogenically from organic matter which is exposed to heat. Thermogenic formation is the mechanism by which methane (and other hydrocarbons) are formed in the Marcellus shale, however as pointed out by Molofsky, et. al.(2011), there are other mature shales between the Marcellus and the surface in which thermogenic hydrocarbons may be formed and act as a source for hydrocarbons in shallow drinking water aquifers. So if we are to judge whether drilling into and fracking the Marcellus shale is responsible for hydrocarbons in drinking water aquifers, we must be able to distinguish thermogenic gases from all other potential sources.

First, let's consider biogenic generation of hydrocarbons. As mentioned above there are two mechanisms of biogenic hydrocarbon generation. Both mechanisms, reduction of carbon dioxide and fermentation of acetate, are thought to produce mainly methane. In gasses where methane is thought to be biogenic, methane to ethane ratios are reported (Taylor, et. al., 2000) to be > 1000. Taylor, et. al. (2000) also found ethane, which based on carbon isotopic composition was suggested to be biogenic, in two near surface aquifers in western Canada. Methane to ethane ratios ranged from 1,000 to 10,000.

A measure of the composition of thermogenic hydrocarbons can be found from the data of Katz and Williams (1952) shown in Table 1, where methane/ethane ratios are found in a range of 1.75 to 18.2 for reservoir oil and gas. In general, several authors, e.g. Burruss and Laughrey, (2010) have suggested that predominantly thermogenic hydrocarbons are characterized by ratios of  $(C_1/C_2+C_3) < 100$  and predominantly biogenic hydrocarbons are characterized by ratios of  $(C_1/C_2+C_3) > 1000$  while ratios between 100 and 1000 are indicative of mixtures of biogenic and thermogenic hydrocarbons. For many years it has also been realized (Schoell, 1980) that biogenic and thermogenic methane can be distinguished using its carbon and hydrogen isotopic signature. Further, methane from the two mechanisms of its formation, reduction of carbon dioxide and acetate fermentation are also distinct. The following figure (After Coleman, et.al.

1993, based on the genetic classification scheme of Schoell, 1980) identifies the range of isotopic composition for each general methane type.

Microbial methane generation in subsurface marine sediments is predominantly due to carbon dioxide reduction. This is because of the generally high concentrations of sulfate in the marine waters, where sulfate reducers out-compete methanogens for acetate and by the time sulfate is depleted, there is little acetate left to ferment. In near surface sediments, where there is relatively little sulfate, methanogenic fermentation of acetate accounts predominantly for methane generation (Whiticar, et. al., 1986). As shown on Figure 11, these two mechanisms produce isotopically distinct signatures of methane.

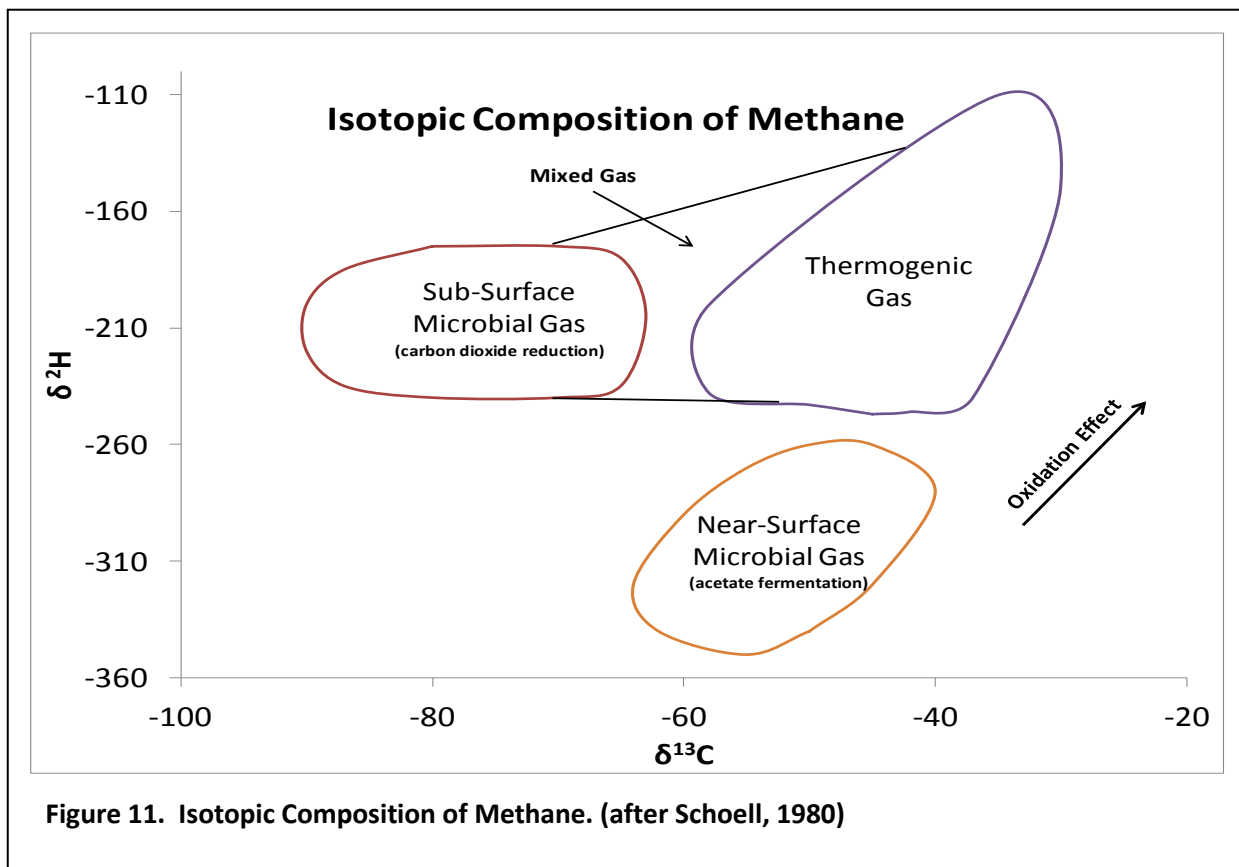


Figure 11. Isotopic Composition of Methane. (after Schoell, 1980)

Thermogenic methane is in general isotopically heavier, both in carbon and hydrogen, than methane from carbon dioxide reduction; and though there is overlap in carbon isotopic composition, its hydrogen isotopic composition is heavier than the isotopic composition of methane from acetate fermentation.

These are general statements and in reality the effects of mixing, oxidation and thermal maturity can impart further distinguishable and often interpretable compositions to the isotopic signature of methane.

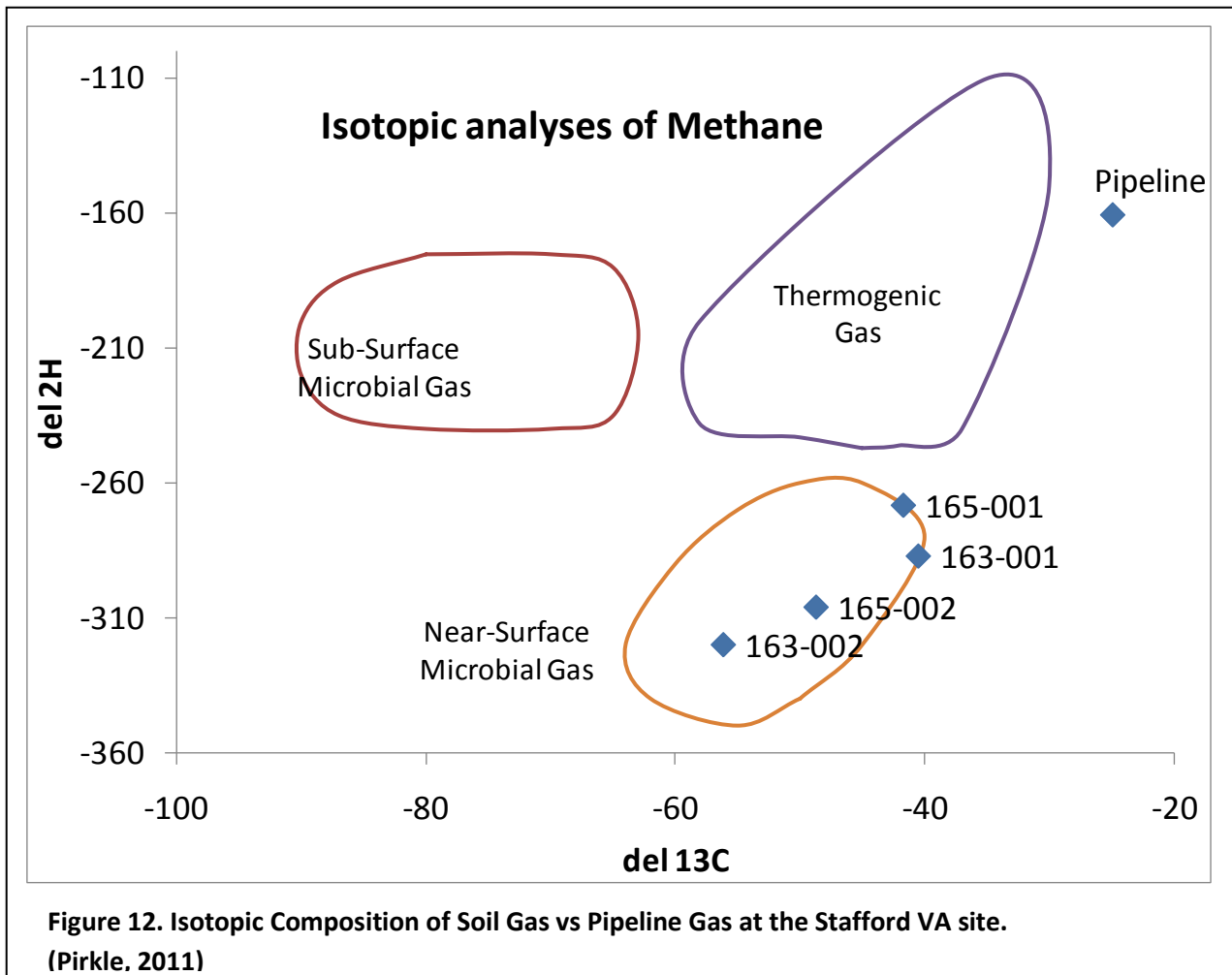
Distinguishing thermogenic and biogenic methane is often required in a variety of environmental investigations. The following example (Pirkle, 2011) required the determination of the source of soil gas methane in a utility trench leading to a residence in Stafford, VA. The natural gas supply line in the trench was one potential source of the methane which was found at > 50 % levels in the soil gas. Samples of the soil gas and the natural gas supply were analyzed for C<sub>1</sub> – C<sub>4</sub> hydrocarbons and the compositional results are shown in Table 2.

Soil Gas Sample Ratios (M = methane; E = ethane; P = propane)				
ID	M/E	E/P	(P/M)x 1000	%M
SG1	13,913	1	0.072	>99.9
SG2	43,206	3	0.009	>99.9
SG3	20,000	2	0.024	>99.9
SG4	46,111	2	0.011	>99.9
NG1	28	8	4.615	95.9

**Table 2. Soil Gas Composition at the Stafford, VA Site. (Pirkle, et. al., 2010)**

The M/E (C<sub>1</sub>/C<sub>2</sub>) ratios of the soil gas samples are all > 10,000 clearly suggesting a biogenic origin, while the M/E ratio for the natural gas sample is 28 which is characteristic of a thermogenic origin. While the compositional results were quite definitive in this case, the isotopic composition of the methane was also determined and the results, shown on Figure 12, confirm the compositional interpretation. The source of the biogenic methane in this case was the surface formation which contained sufficient organic material to be biologically fermented, producing methane.

One of the potential liabilities of gas production is contamination of near surface drinking water aquifers with the produced gas. As we have stated above, the



presence of methane and other hydrocarbons dissolved in near surface aquifers is not uncommon in the Marcellus footprint region. Therefore in order to ascertain whether hydrocarbon presence is attributable to production, it is usual that operators survey drinking water sources within a defined (2500 ft) radius of a planned production well prior to drilling in order to document the presence or absence and composition of dissolved hydrocarbons. These sources may be routinely re-analyzed on an established timetable following well completion or at a point of concern to document the dissolved hydrocarbon content and composition.

Microseeps has and continues to analyze near surface water samples from a number of active exploration basins and typical results are shown in Table 3.

**Table 3****C<sub>1</sub> - C<sub>4</sub> Hydrocarbons in Drinking Water****(all concentrations in ug/l)**

<b>Sample #</b>	<b>methane</b>	<b>ethane</b>	<b>propane</b>	<b>i-butane</b>	<b>n-butane</b>	<b>ethene</b>	<b>propene</b>	<b>M/E</b>
<b>1</b>	2.2	0.007	<0.050	<0.050	<0.050	0.033	<0.050	589
<b>2</b>	31	0.66	0.017	<0.050	<0.050	0.44	0.013	88
<b>3</b>	8.8	0.13	0.05	<0.050	<0.050	1.8	0.048	127
<b>4</b>	36	0.33	<0.050	<0.050	<0.050	0.89	0.21	205
<b>5</b>	8,101	31	0.51	0.21	<0.050	<0.025	<0.050	490
<b>6</b>	79	0.24	<0.050	<0.050	<0.050	0.66	0.025	617
<b>7</b>	0.55	0.055	<0.050	<0.050	<0.050	0.06	<0.050	19
<b>8</b>	2.01	<0.025	<0.050	<0.050	<0.050	0.017	<0.050	
<b>9</b>	12,950	22	0.39	<0.50	<0.50	<0.025	<0.050	1104
<b>10</b>	4750	7.6	0.029	<0.050	<0.050	<0.025	<0.050	1172
<b>11</b>	3.4	0.006	<0.050	<0.050	<0.050	0.024	<0.050	1063
<b>12</b>	2.15	0.055	<0.050	<0.050	<0.050	0.025	<0.050	73
<b>13</b>	55	0.7	0.021	0.323	<0.050	2.15	0.038	147
<b>14</b>	3902	107	1.65	3.55	0.187	<0.025	<0.050	68
<b>15</b>	0.025	0.006	<0.050	<0.050	<0.050	0.012	<0.050	8
<b>16</b>	4.4	0.045	0.015	<0.050	<0.050	2.6	<0.050	183
<b>17</b>	4.2	0.13	0.46	0.22	0.17	1.9	0.077	61
<b>18</b>	2968	0.12	0.28	0.21	<0.050	3	0.06	46375
<b>19</b>	7732	6.4	0.031	<0.050	<0.050	3.95	0.033	2265
<b>20</b>	165	0.32	0.049	<0.050	0.013	0.008	<0.050	967
<b>21</b>	6,399	1.75	0.22	<0.050	<0.050	1.8	0.04	6856
<b>22</b>	1889	2.8	<0.050	<0.050	<0.050	0.009	0.013	1265
<b>23</b>	48	0.21	0.021	0.043	<0.050	1.9	0.019	429
<b>24</b>	11,986	17.9	0.026	0.022	<0.050	<0.025	0.015	1256
<b>25</b>	8.3	0.006	<0.050	<0.050	<0.050	0.09	<0.050	2594

In the state of Pennsylvania, the PADEP has established a guideline for methane concentrations of 7000 ug/l. Above that concentration, PADEP may ask for the methane source be further identified. Note that in the data in Table 3 only 4 of the 25 samples exceed 7000 ug/l (#'s 5, 9, 19, & 24) and each of those samples has a M/E ratio > 1000. This suggests that the origin of the hydrocarbons in these

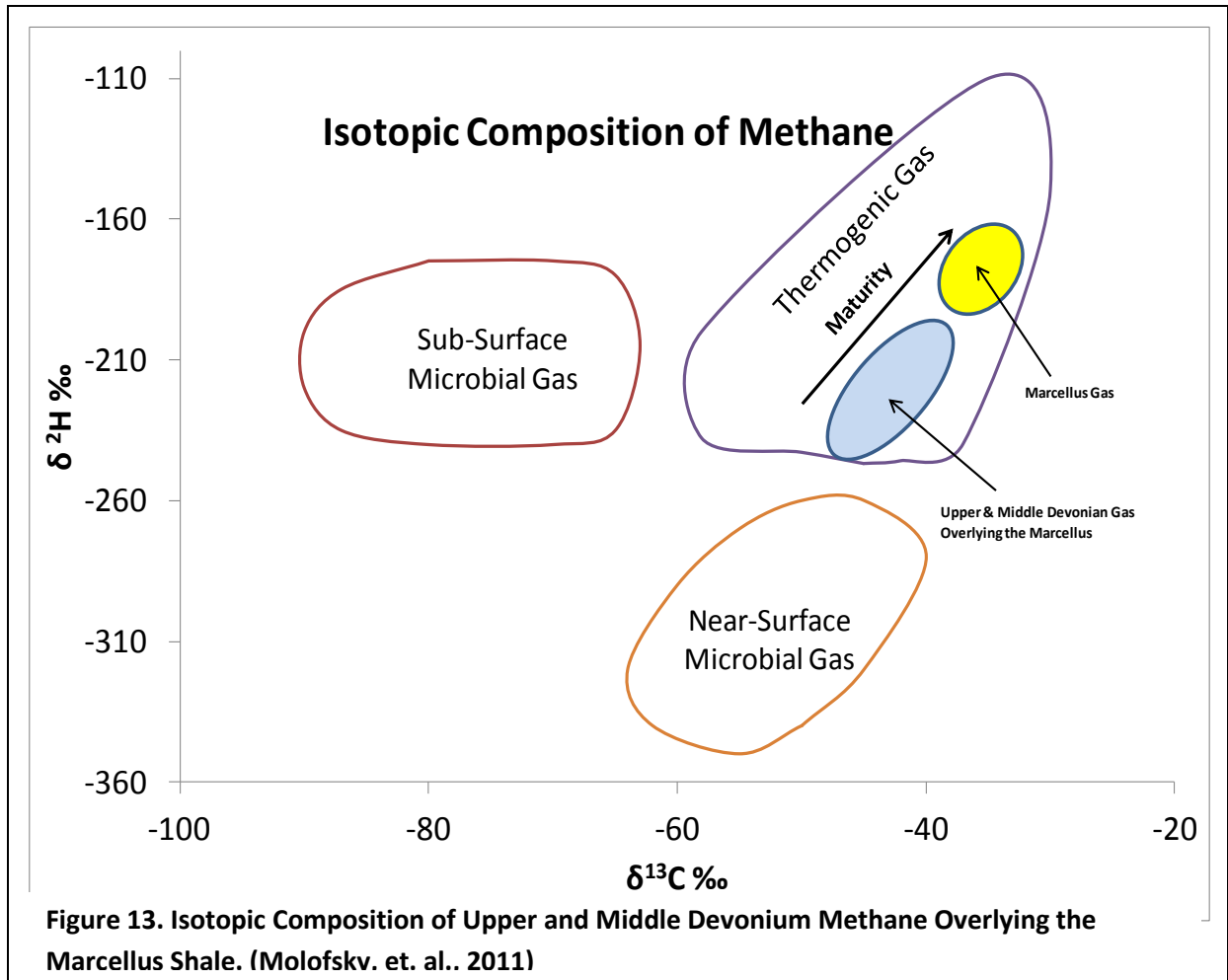
samples is biogenic rather than thermogenic. Of the samples which have M/E < 100, only #14 has dissolved methane > 1000 ug/l.

There is very little uncertainty in interpreting gasses with M/E < 100 as predominantly thermogenic in origin. Many thermogenic gasses, particularly those whose source rock has experienced significant thermal alteration, may be very dry and have M/E ratios which could be misinterpreted as biogenic in origin. Likewise, measured isotopic compositions can be deceiving as the result of mixing or oxidation effects. In cases where it is imperative to have the best interpretation, both compositional and isotopic analyses should be obtained. The interpretative potential of both analyses would seem to be considerably strengthened if the molecular and isotopic composition of the produced gas from the nearby Marcellus shale gas well were also available for comparison.

### **Distinguishing Different Thermogenic Gases**

The isotopic composition of methane, and perhaps higher alkanes, may provide distinction between thermogenic gases which are produced from different sources. This may be due to a difference in the organic material of the source or potentially to differences in thermal alteration of similar sources. Molofsky, et. al. (2011) have pointed out that above the Marcellus shale of Middle Devonian age there are other shales, some of Middle Devonian age and some of Upper Devonian age that have not experienced the extent of thermal alteration of the Marcellus, yet are sufficiently mature to have produced thermogenic hydrocarbons. They have sampled a number of Marcellus wells, some Middle and Upper Devonian formation gases overlying the Marcellus and water wells containing dissolved methane classified as middle/upper Devonian gas by the PADEP. When isotopic composition of methane from this suite of samples is plotted, they fall along a maturation trend line as shown in Figure 13. The methane from formation gases and methane dissolved in water wells which were thought to be sourced from zones above the Marcellus are lighter in both carbon and hydrogen than methane from Marcellus shale gas. This difference in isotopic composition was attributed to increased thermal alteration of the Marcellus gas as compared to its overlying analogs. Further, when data from the recent Duke

University study (Osborn, et al, 2011) are plotted, they are more consistently correlated with these upper/middle Devonian gases that were sourced in formations above the Marcellus. It was pointed out that the differences in isotopic composition of thermogenic gases may not be as distinctive in other parts of the Appalachian basin as in this region, however the use of isotopic composition as a forensic tool for this purpose may be useful in other areas.



Revesz, et.al. (2010) concluded on the basis of molecular and isotopic composition, that gases found in groundwater over the Tioga gas storage reservoir contained both biogenic and thermogenic gases. Gases in wells which were thermogenic in character, based on carbon and hydrogen isotopic composition of methane and ethane, were found to be correlated to storage gas sourced in the Gulf of Mexico rather than native gas from nearby Oriskany sandstone reservoirs.

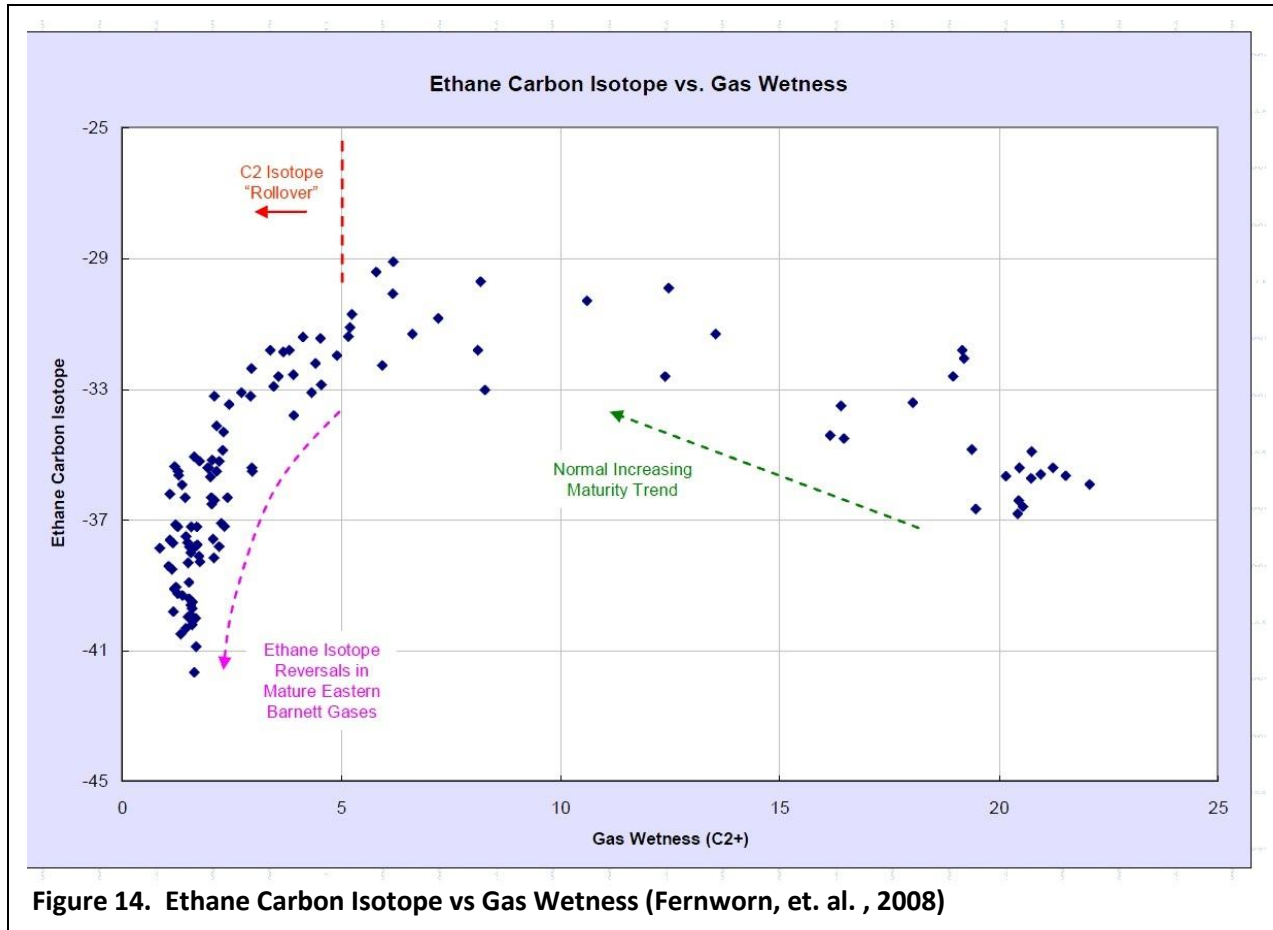
## Exploration and Production Applications

The process of oil and gas formation in source rocks was discussed earlier. When kerogen experiences increased temperatures, it begins to break down and eventually forms what we describe as oil with associated gas, OAG. As thermal alteration increases, the source kerogen is depleted and the generation of liquid components gradually ceases. The liquid components already formed begin to break down with increased temperature and form a gas of much smaller molecules. Eventually, there is no liquid production and the gas at this stage is said to be non-associated gas, NAG. One of the measures of this path of thermal alteration from OAG to NAG is gas wetness or %C<sub>2+</sub>. In OAG, %C<sub>2+</sub> may be > 30% and in NAG, %C<sub>2+</sub> may be in the range of <5%. Isotopic composition of the simple hydrocarbons in the OAG window is almost always:  $\delta^{13}\text{C}_1 < \delta^{13}\text{C}_2 < \delta^{13}\text{C}_3$ . In a number of basins there has been observed what is termed “isotope reversal”,  $\delta^{13}\text{C}_1 > \delta^{13}\text{C}_2 < \delta^{13}\text{C}_3$ . In this case, where only two of the isotopes are reversed, it is called partial isotope reversal; but it may also be complete as  $\delta^{13}\text{C}_1 > \delta^{13}\text{C}_2 > \delta^{13}\text{C}_3$ . At great depth where NAG is being produced, both carbon and hydrogen isotopes of methane and ethane have been observed to be reversed (Burruss and Laughrey, 2010).

Ferworn, et. al. (2008) have shown ethane isotope reversals (also sometimes called isotope rollovers) as a function of gas wetness as documented in Figure 14. They attribute this phenomenon to in-situ cracking of higher hydrocarbons in the liquid petroleum at these increased states of alteration. They also present evidence that wells with both the highest initial production and highest stabilized production are always found in zones of ethane isotope rollover, i.e. in zones where NAG is being produced.

In terms of thermal alteration, the beginning of the ethane rollover may mark the beginning of NAG production. This could be described as the point at which larger molecules are converted into multiple smaller molecules. Envision converting a complex mixture of a crude oil into a gas containing only C<sub>1</sub> – C<sub>4</sub> hydrocarbons. Burruss & Laughrey (2010) describe NAG in which only methane and ethane are present in sufficient concentrations for isotopic determination. In such cases,

there would almost certainly be a significant increase in internal pressure in the shale which would stimulate increased natural internal fracturing. When wells are completed in such a zone, increased productivity would not be surprising and apparently is realized in some cases.



The example presented in Figure 14 is from mature eastern Barnett shale gases, however the ethane rollover phenomenon has been observed in numerous mature shales including the Fayetteville, Woodford, Haynesville, Marcellus, Utica and other shale basins.

Ferworn, et. al. (2008) have also shown that other alterations characterize this zone which is generally characterized where  $C_2+ < 5\%$  as shown in Figure 15. The data in this figure shows that isobutane is degraded faster than n-butane under conditions of advanced alteration, presumably the beginning of NAG generation.

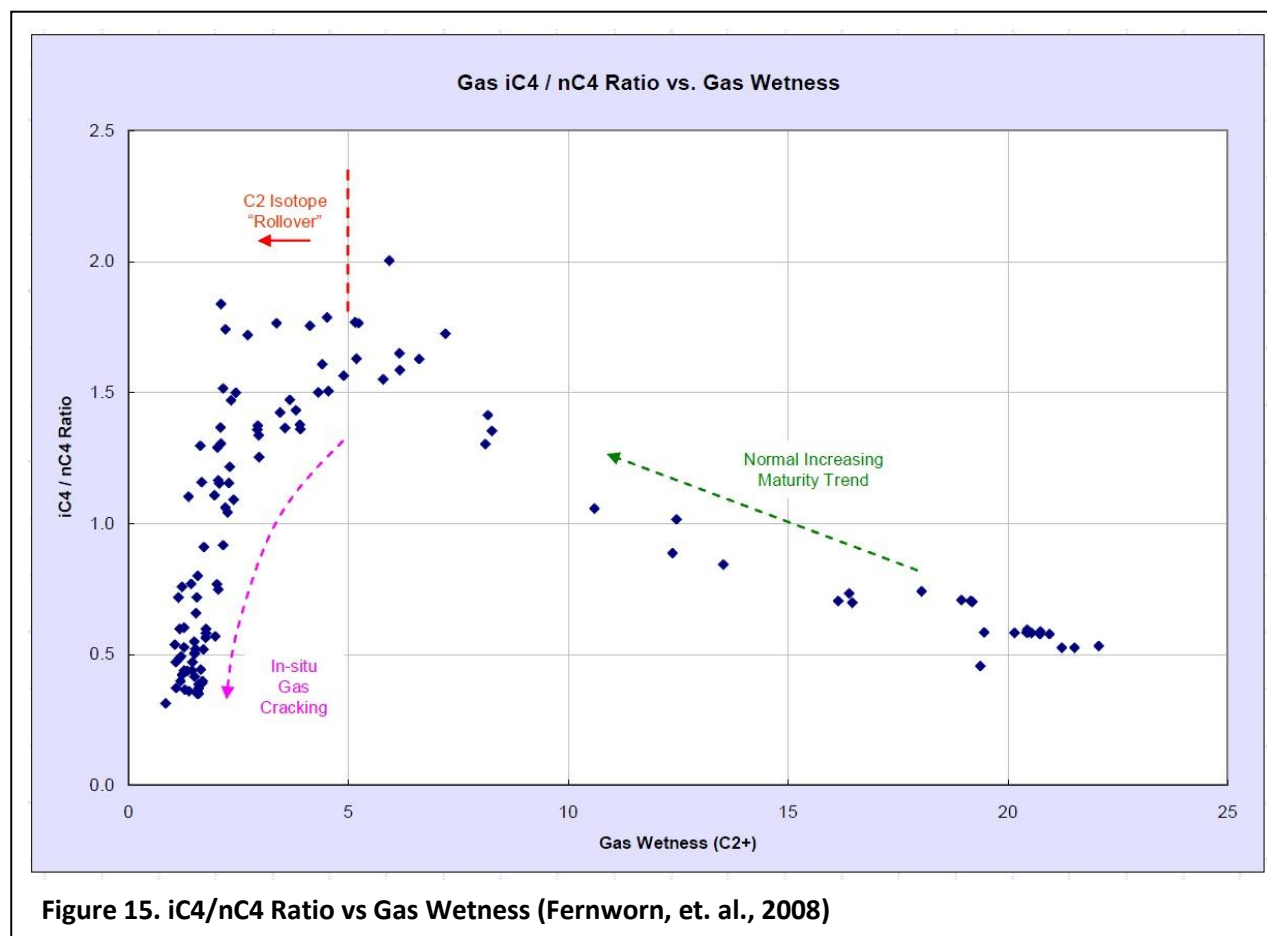
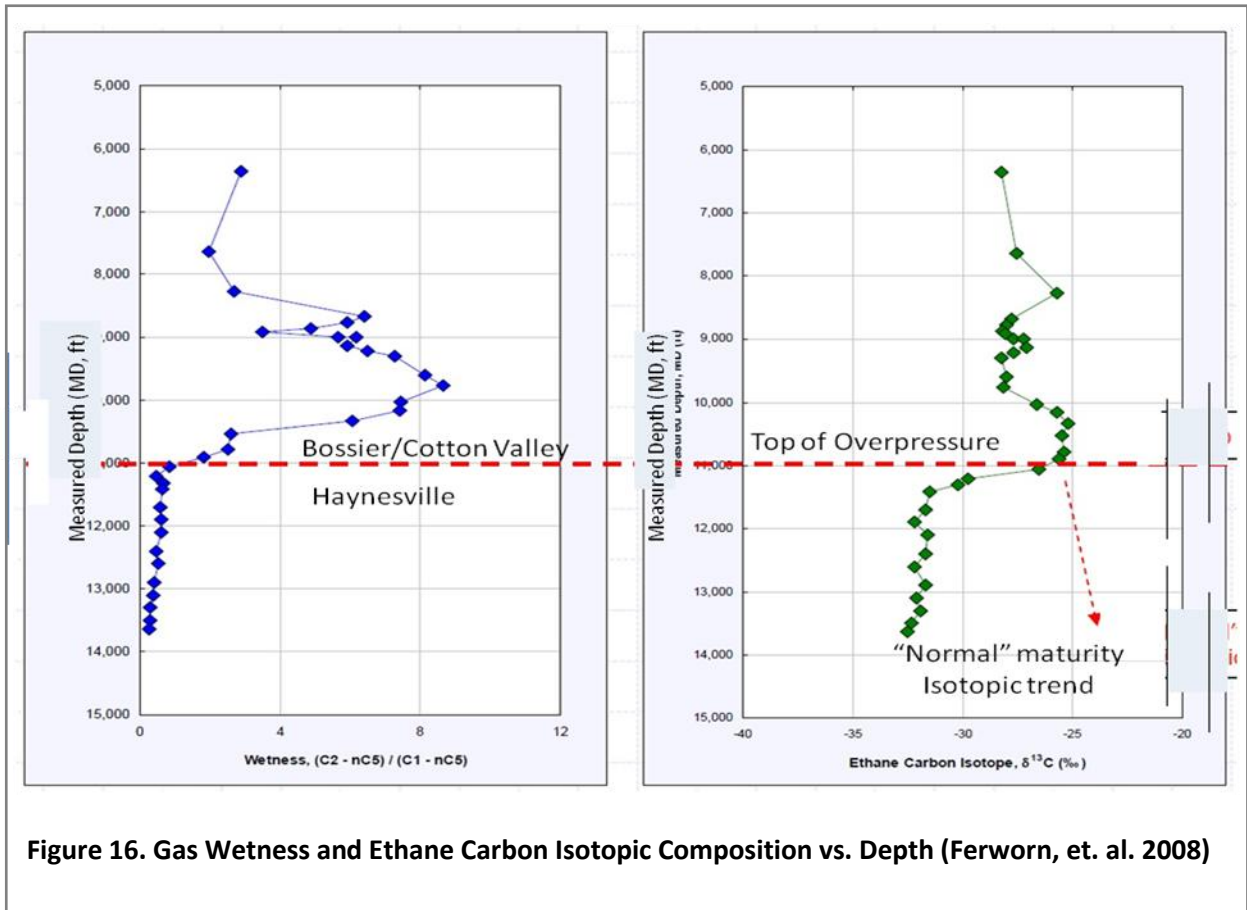


Figure 15. iC4/nC4 Ratio vs Gas Wetness (Fernworn, et. al., 2008)

In comparing the production between comparable wells in the Barnett and Haynesville shales, Ferworn, et.al. (2008) suggest that Haynesville production rates may be 2 to 3 times greater than the Barnett. Both are similar in TOC, source maturity and isotopic reversals, however in the Haynesville there is significant overpressure. They have observed ethane isotope reversals in mud gas as shown on Figure 16. Both the reversal of the isotopic “normal” maturity trend and a significant decrease in gas wetness occur at the top of the overpressured zone. The overpressured zone is most likely in this case the beginning of NAG production which converts large molecules in the liquid phase into multiple small molecules in the gas phase and as we said above creates significant internal pressure increases.

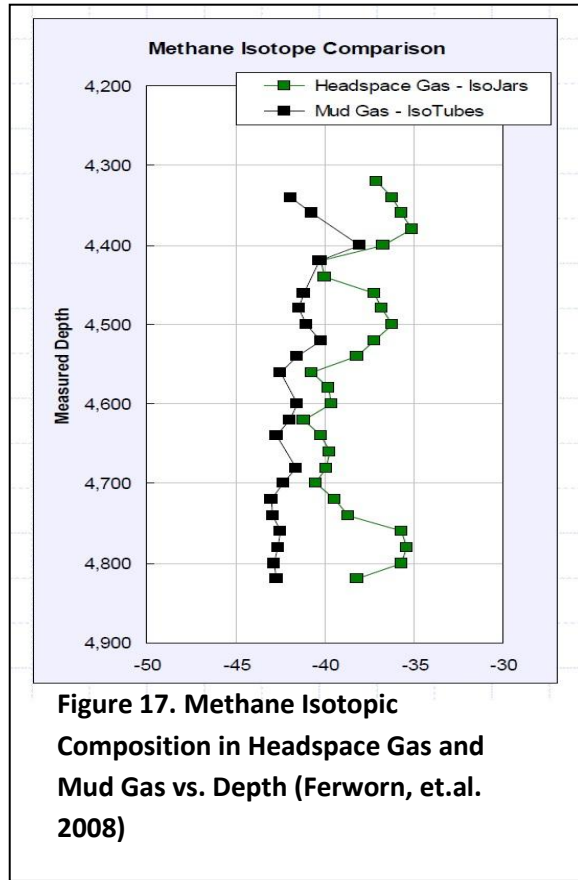
The Haynesville example is perhaps an extreme case of NAG production resulting in overpressure, however documenting the onset of NAG production would seem to be desirable and, as we have illustrated, it has been identified with both

molecular and isotopic analyses. What remains is to determine how to use this in choosing zones of well completion.



Recent research (Ross and Bustin, 2009) has suggested that gas in an organic rich shale is distributed between free gas and adsorbed gas in the nanopores of the organic matrix. Loucks et. al. (2009) has suggested that the pore system in the organic matrix is the main permeable pathway within the unfractured shale and the recent work of Curtis, et. al. (2010) indicates that the pore system in kerogen in organic-rich shales is interconnected throughout the shale.

Several authors (Xia and Tang, 2012, Zumberge et.al., 2009) have noted that there is a difference in  $\delta^{13}\text{C}$  of methane in the gas produced from shale layers (mud gas) and gas released from cuttings (headspace gas). Indeed, Ferworn et. al.(2008) have shown that there are differences in isotopic composition of free mud gas and cuttings headspace gas as shown on Figure 17. They have interpreted zones of separation of the isotopic measurements as zones of increased permeability. If such an interpretation is validated such measurements could be used to choose completion intervals in production wells.



**Figure 17. Methane Isotopic Composition in Headspace Gas and Mud Gas vs. Depth (Ferworn, et.al. 2008)**

## Conclusions

With the development of horizontal drilling techniques and hydraulic fracturing, shales have begun to realize their potential as not only sources of oil and gas, but unconventional reservoirs as well.

Hydrocarbons produced and stored at depth may find their way to the surface in conduits which include leaking well casings, abandoned wells, and faults. If a well leaks, the manifestation is usually observed first around the well casing itself. Routine monitoring around the well casing may reveal leakage before the problem becomes unmanageable.

The molecular and isotopic composition of the light hydrocarbons has been used to identify the source of a gas as either biogenic or thermogenic. Thermogenic gases from different sources may potentially be differentiated using isotopic composition of the light hydrocarbons.

Zones of highest productivity have been associated with the onset of the production of non-associated gas. Both molecular and isotopic compositional data have been used to delineate the beginning of this zone. Differences in isotopic composition of headspace and mud gas may be associated with zones of higher permeability.

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