

The origin of some natural gases in Permian  
through Devonian Age Systems in the  
Appalachian Basin & the relationship to incidents  
of stray gas migration

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prepared for

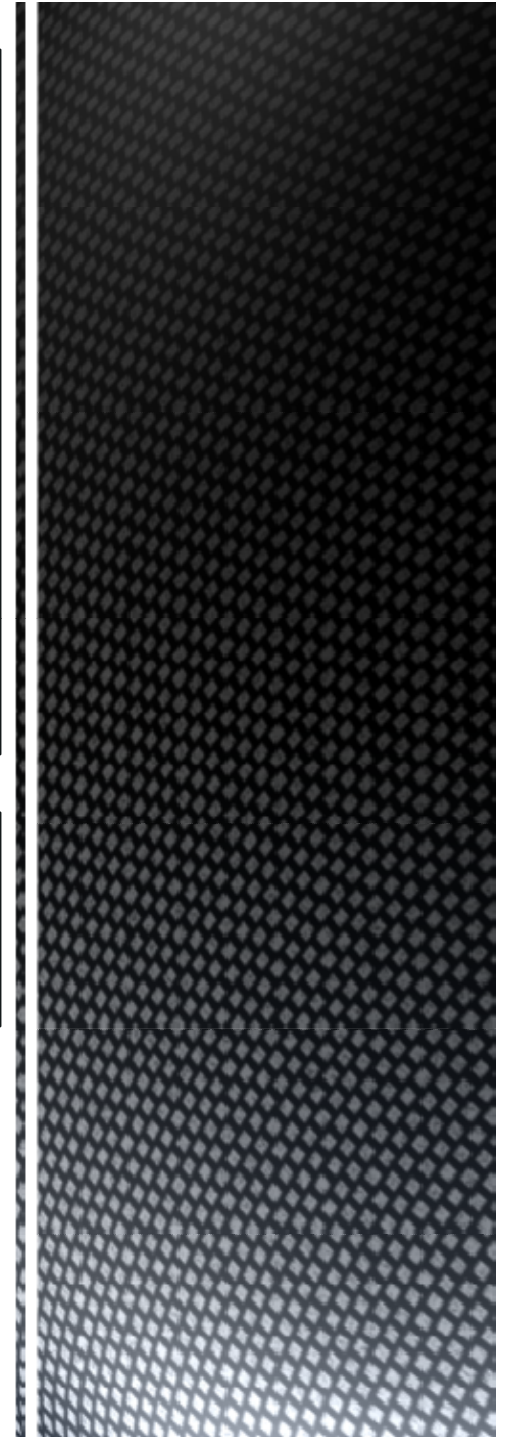


Technical Workshops for Hydraulic Fracturing Study  
Chemical & Analytical Methods  
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The molecular composition and isotope geochemistry for natural gases of Permian through Devonian age system rocks across the Central & Northern Appalachian Basin reveal gases are:

- 1) microbial, thermogenic, and mixed microbial/thermogenic in shallow systems,
- 2) thermogenic gases of different thermal maturities in commercially productive formations

Methane is the Principal Hydrocarbon found in Permian through Devonian age strata and in all stray gas investigations



# STRAY GAS INCIDENTS



- As the allegations of hydraulic fracturing causing contamination of groundwater supplies received the attention of various media outlets, the link to stray natural gas contamination of aquifer systems created by hydraulic fracturing was simultaneously made, inexplicably...
- **Investigations of stray natural gas incidents in Pennsylvania reveal that NO incidents of stray gas migration were caused by hydraulic fracturing of the Marcellus shale.**

## Methane in gas phase

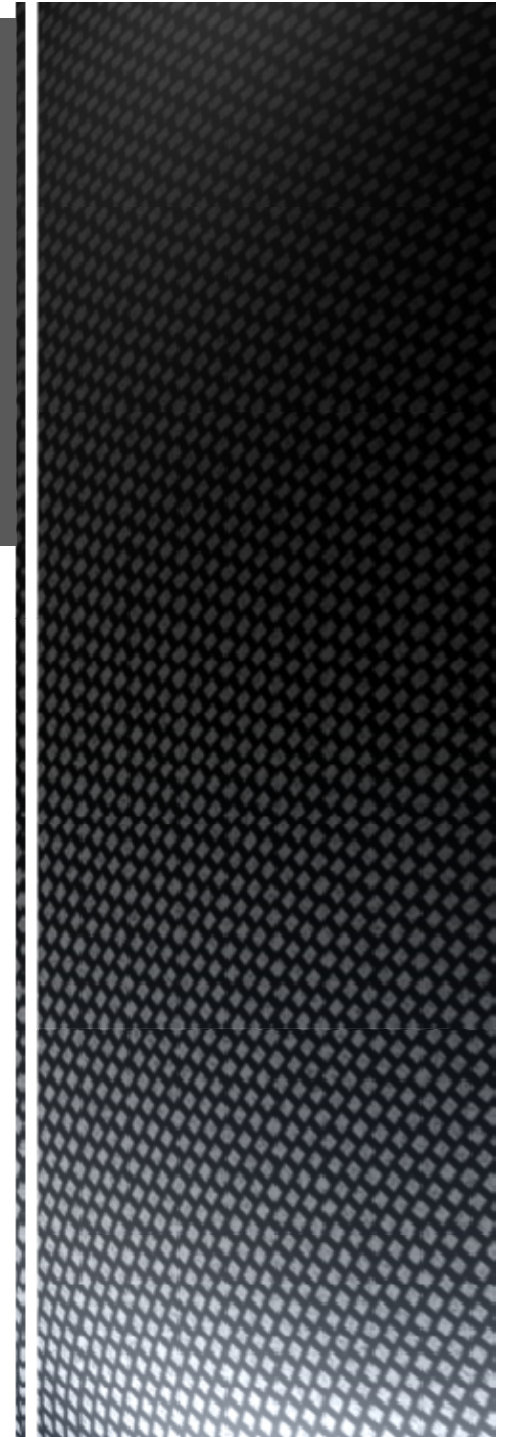
Gas migration in the subsurface occurs principally by advective transport from areas of high pressure to areas of low pressure and is influenced by temporal changes in:

- Barometric pressure
- Soil/bedrock porosity, permeability
- Precipitation - Pore water

## Methane dissolved in water

Methane dissolved in groundwater in the shallow aquifer system is not uncommon in certain areas of the Appalachian Basin...*generally, it does not represent the same threat as gas phase methane, and should not be evaluated the same as methane gas in or around a building.*

Solubility ~ 26-32 mg/l at atmospheric pressure, however, solubility in water is proportional to pressure. Every foot of water exerts .43 psi or 2.31 feet of water is under 1 psi. With increased hydrostatic pressures, dissolved methane concentrations in the groundwater can greatly exceed its solubility, and may represent a threat to indoor air spaces.



# Incidents of stray combustible gas are not recent occurrences.

## Potential Sources Include:

- Naturally occurring gas seeps
- Abandoned, recently drilled & operating gas wells
- Abandoned & operating coal mines
- CBM wells
- Natural gas storage fields
- Natural gas pipelines
- Abandoned & operating landfills
- Naturally occurring shallow formations/aquifers
- Buried organic matter
- Drift gas

Defining the source of natural gas migration requires the investigation & synthesis of different data types, notably gas geochemistry and mechanism of migration.

\* Geochemical evidence reveals that microbial and early thermogenic gases occur naturally in some shallow aquifer systems in areas of Pennsylvania.

\* A thorough definition of background groundwater quality is fundamental to define pre-existing conditions in areas of drilling activity.

\* Interpretations of gas migration incidents should be supported by geochemistry & evidence documenting a mechanism of migration



# Genetic Characterization

Isotope Geochemistry provides the highest level of geochemical characterization of natural gases

Thermogenic: C<sub>1</sub> – C<sub>6</sub> hydrocarbons generated. Formed during the thermal alteration of organic materials.

- Associated & non-associated
- Type I (lacustrine), II (marine), & III (woody) kerogen
  - Early mature
  - Mature
  - Late Mature
  - Overmature

Microbial: C<sub>1</sub> – C<sub>3</sub> hydrocarbons generated. Formed by the bacterial decomposition of organic matter.

- CO<sub>2</sub> reduction
- Methyl-type fermentation



# Isotope Geochemistry

## Carbon & Hydrogen Isotopes

Various researchers have determined by examination of stable hydrogen and carbon isotopes of methane that there are common hydrogen and carbon isotopic compositions for thermogenic gas associated with coal and natural gas, drift gas, and other near-surface microbial gases (Craig, 1953; Coleman and others, 1977; Deines, 1980; Schoell, 1980; Rice and Claypool, 1981; Schoell, 1983; Whiticar, 1986; Wiese and Kvenvolden, 1993; Coleman, 1994; Baldassare and Laughrey, 1997; Kaplan and others, 1997; and Rowe and Muehlenbachs, 1999, Osborn and McIntosh, 2010).

- Stable carbon isotope compositions are expressed as the ratio of  $^{12}\text{C}$  to  $^{13}\text{C}$  of the sample compared with that of the international standard ...expressed as per mil (parts per thousand, ‰) and expressed as  $\delta^{13}\text{C}$  values as follows:

$$\delta^{13}\text{C} \text{ ‰} = [(\text{^{13}C/^{12}C}_{\text{sample}} - \text{^{13}C/^{12}C}_{\text{standard}}) / (\text{^{13}C/^{12}C}_{\text{standard}})] * 1000$$

**International standards:**

**carbon: Pee Dee Belemnite (“PDB”)**

**hydrogen: Standard Mean Ocean Water (“SMOW”)**

# Isotopic signatures of methane

In general:

## Microbial methane

acetate fermentation (marsh gas & landfill gas)

- $\delta^{13}\text{C}_1$ : -40 to -62 ‰
- $\delta\text{D}$ : -270 to -350 ‰

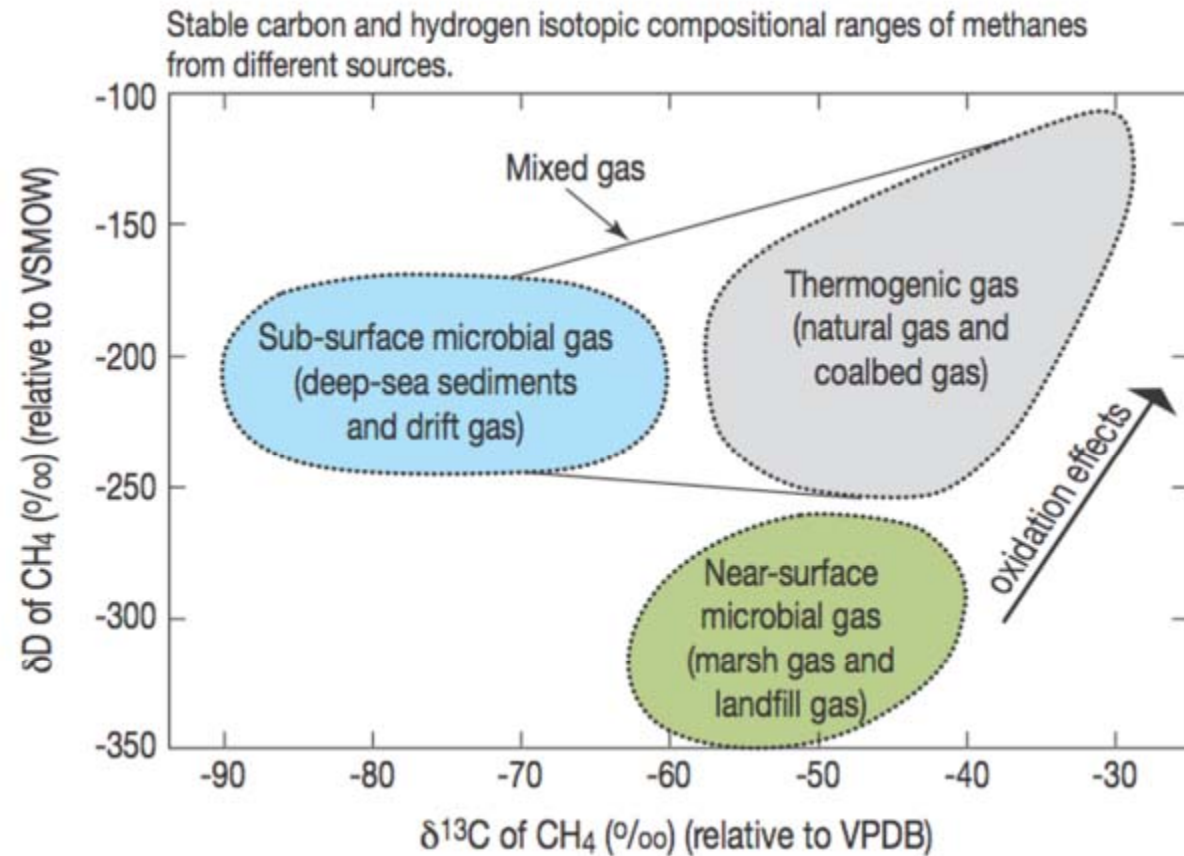
## Microbial methane

$\text{CO}_2$  reduction (drift gas)

- $\delta^{13}\text{C}_1$ : -62 to -90 ‰
- $\delta\text{D}$ : -180 to -240 ‰

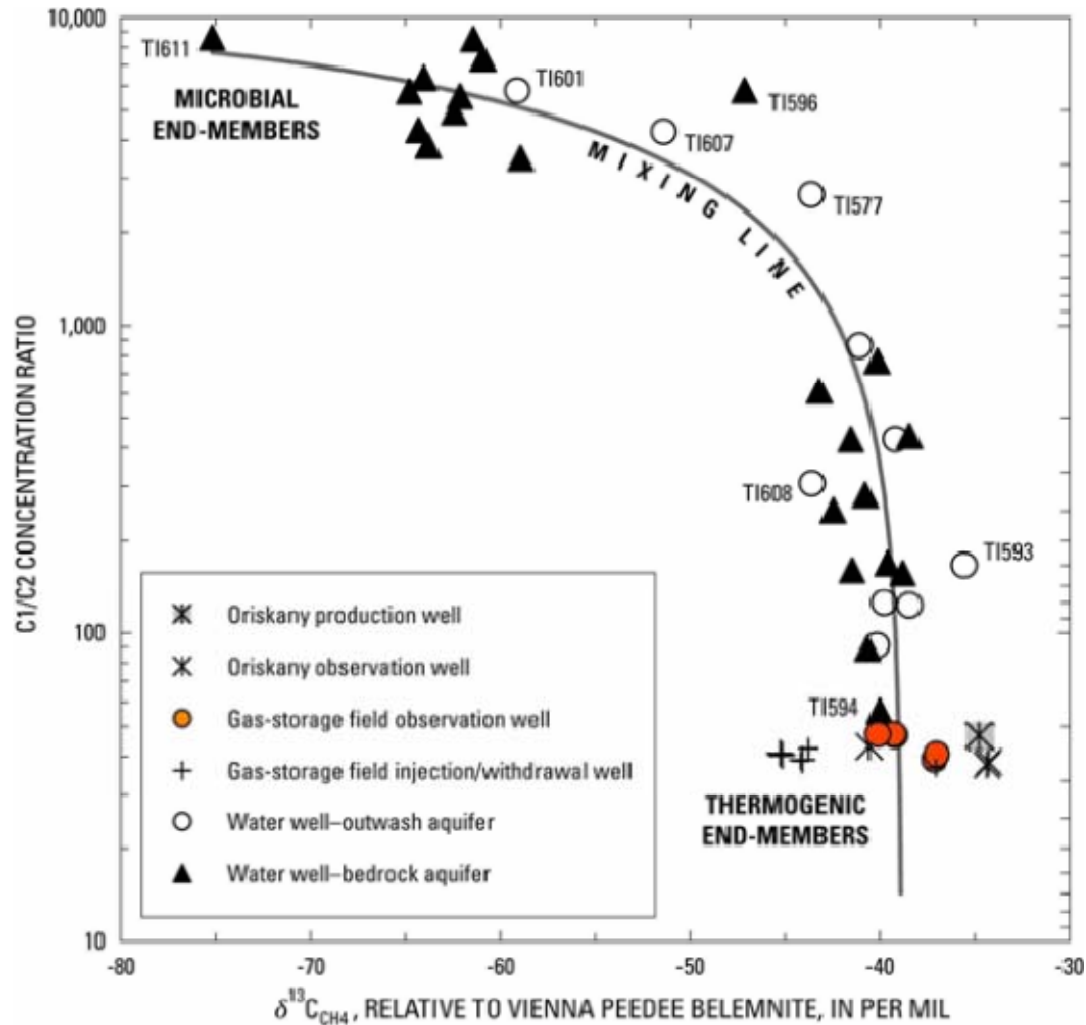
## Thermogenic methane

- $\delta^{13}\text{C}_1$ : -26 to -50 ‰
- $\delta\text{D}$ : -110 to -250 ‰

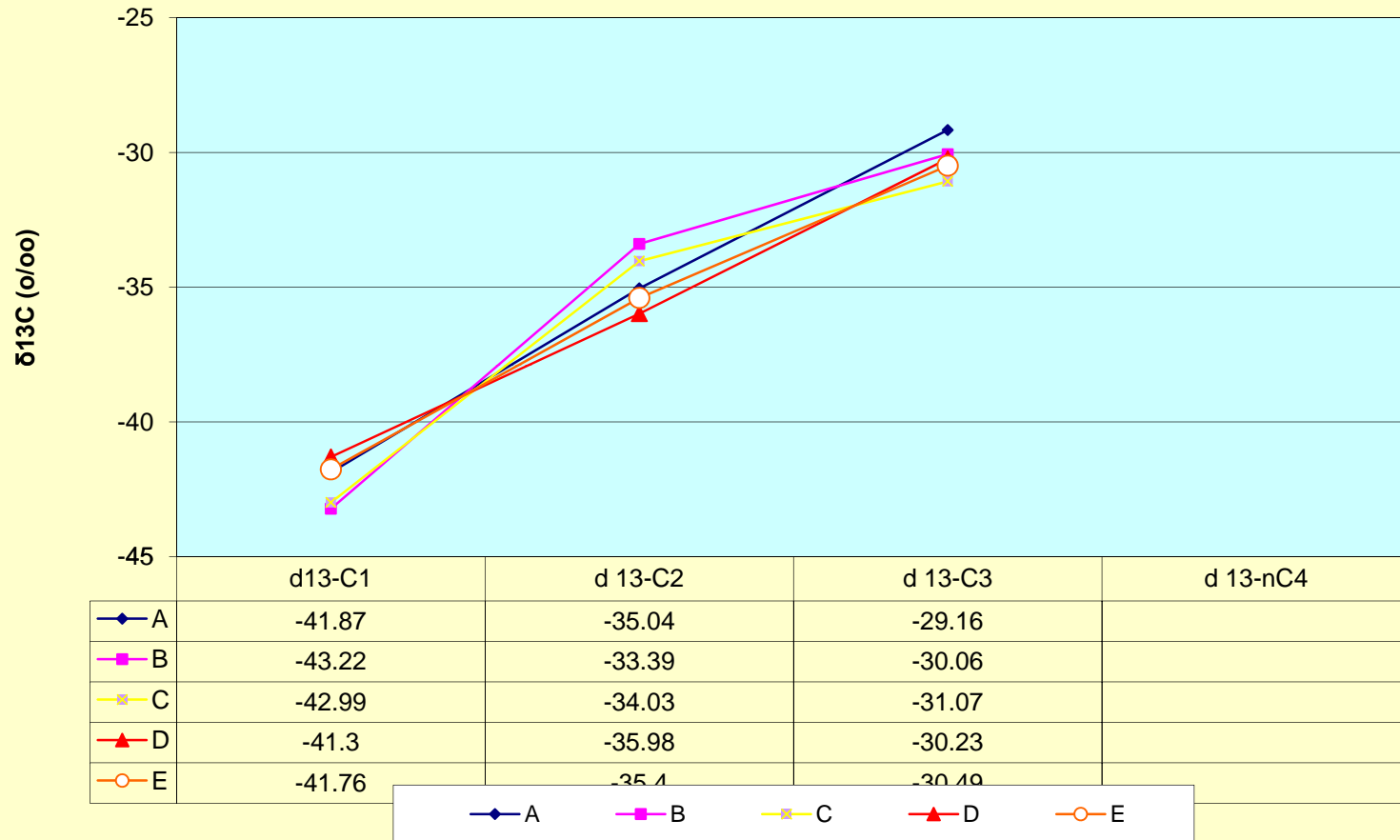


After Coleman and others (1993) based on the data set of Schoell (1980)

# Isotopic mass-balance calculations to determine the fractions of end-member gases can be used to define mixing



## Differentiation of thermogenic gases



$\delta^{13}\text{C}$  for  $\text{C}_1$ ,  $\text{C}_2$ ,  $\text{C}_3$ ,  $\text{C}_4$  can allow discrimination of thermogenic gases from different sources

## DIC: Dissolved inorganic carbon

If we have background groundwater quality for an aquifer, DIC analysis will allow us to determine if methane has been impacted by oxidation or degradation.

Microbial processes such as CH<sub>4</sub> production or CH<sub>4</sub> consumption by oxidation can impart unique isotopic signatures to gases and components of the associated waters. Using a combined gas and water approach is important for constraining the origin of natural gas in water wells.

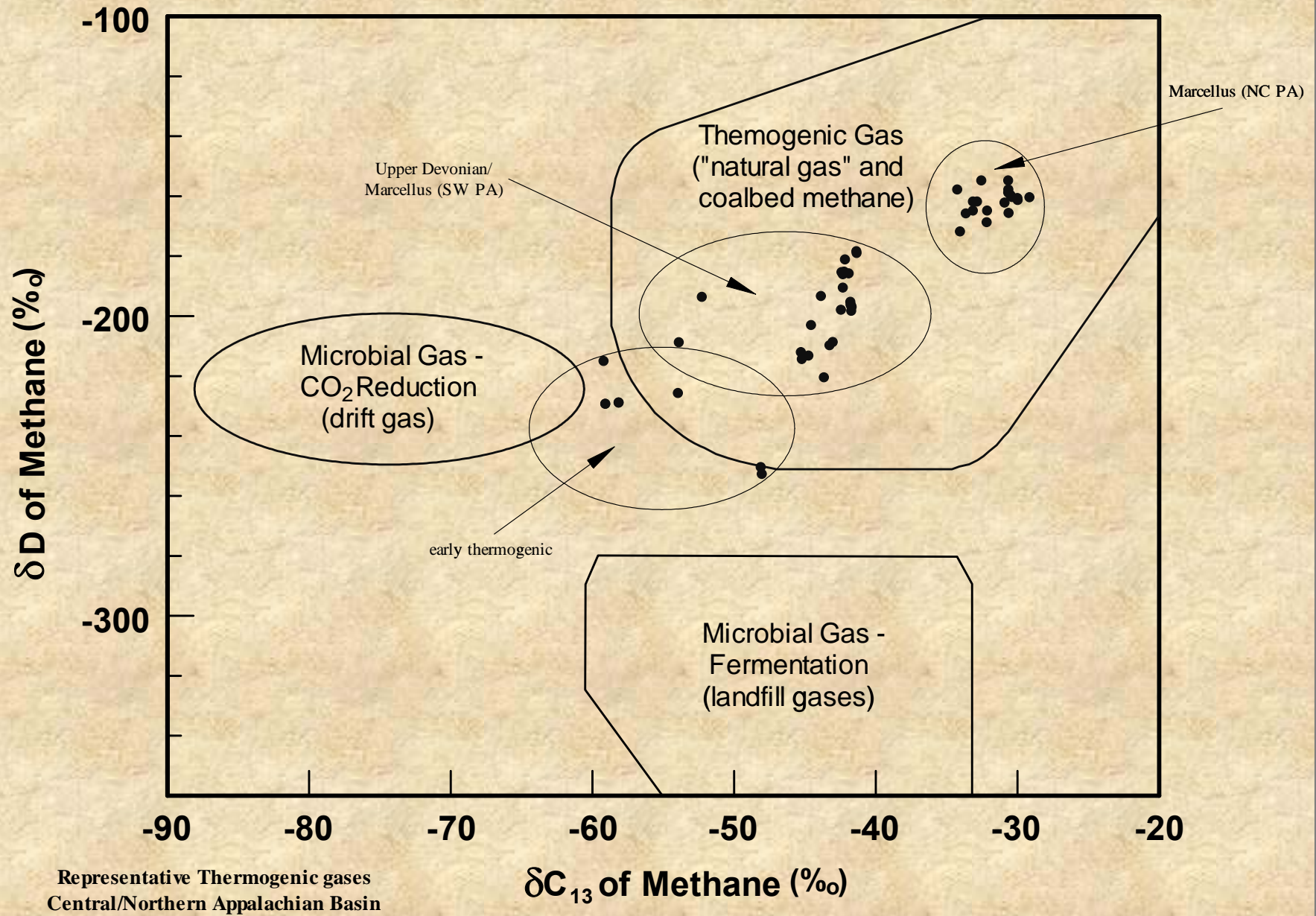
*Whiticar, and Faber, 1986, Revesz, et. al, 2010*



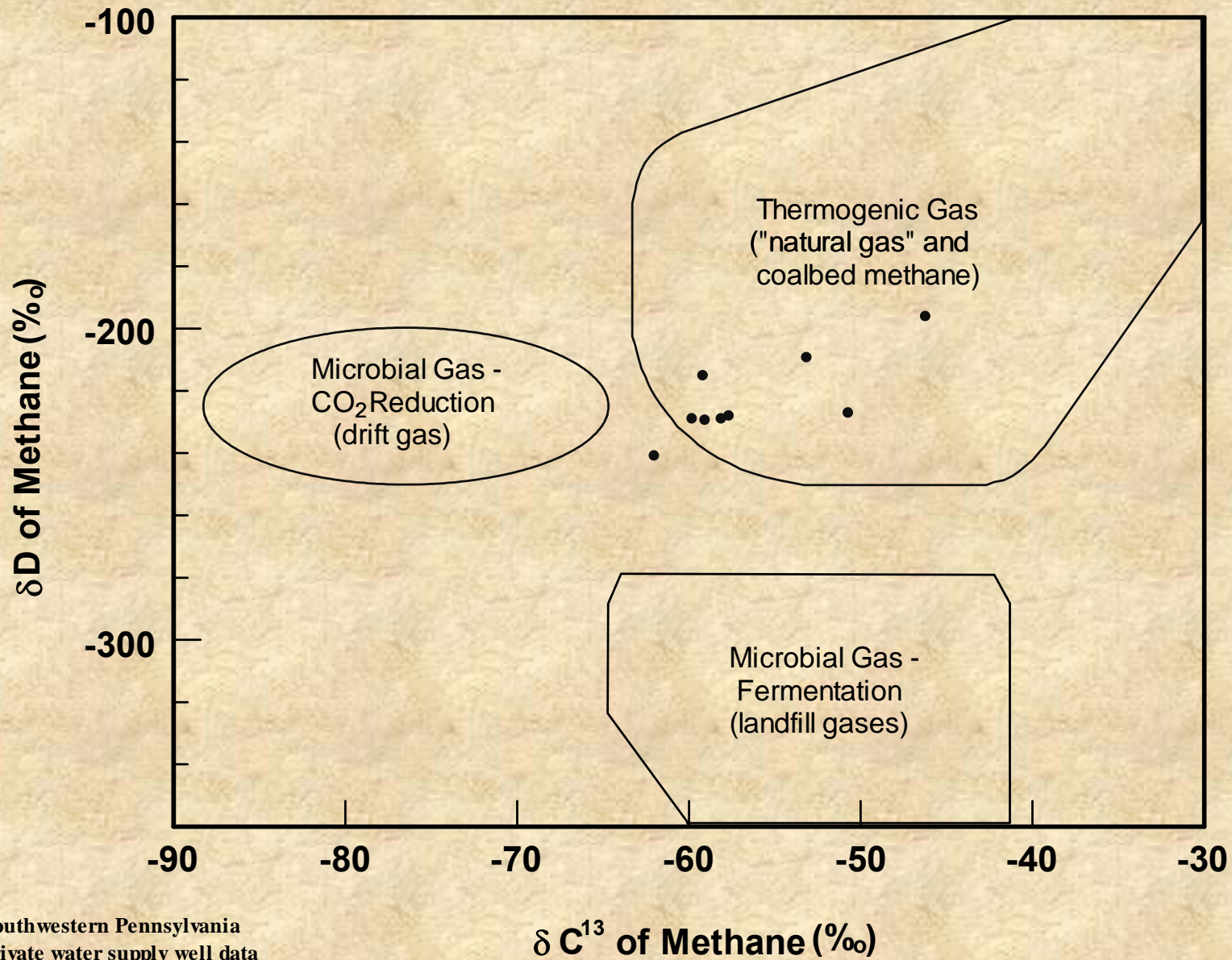
# Central & Northern Appalachian Basin

Representative isotope geochemistry data for thermogenic gases:

# ISOTOPE CROSSPLOT



# ISOTOPE CROSSPLOT

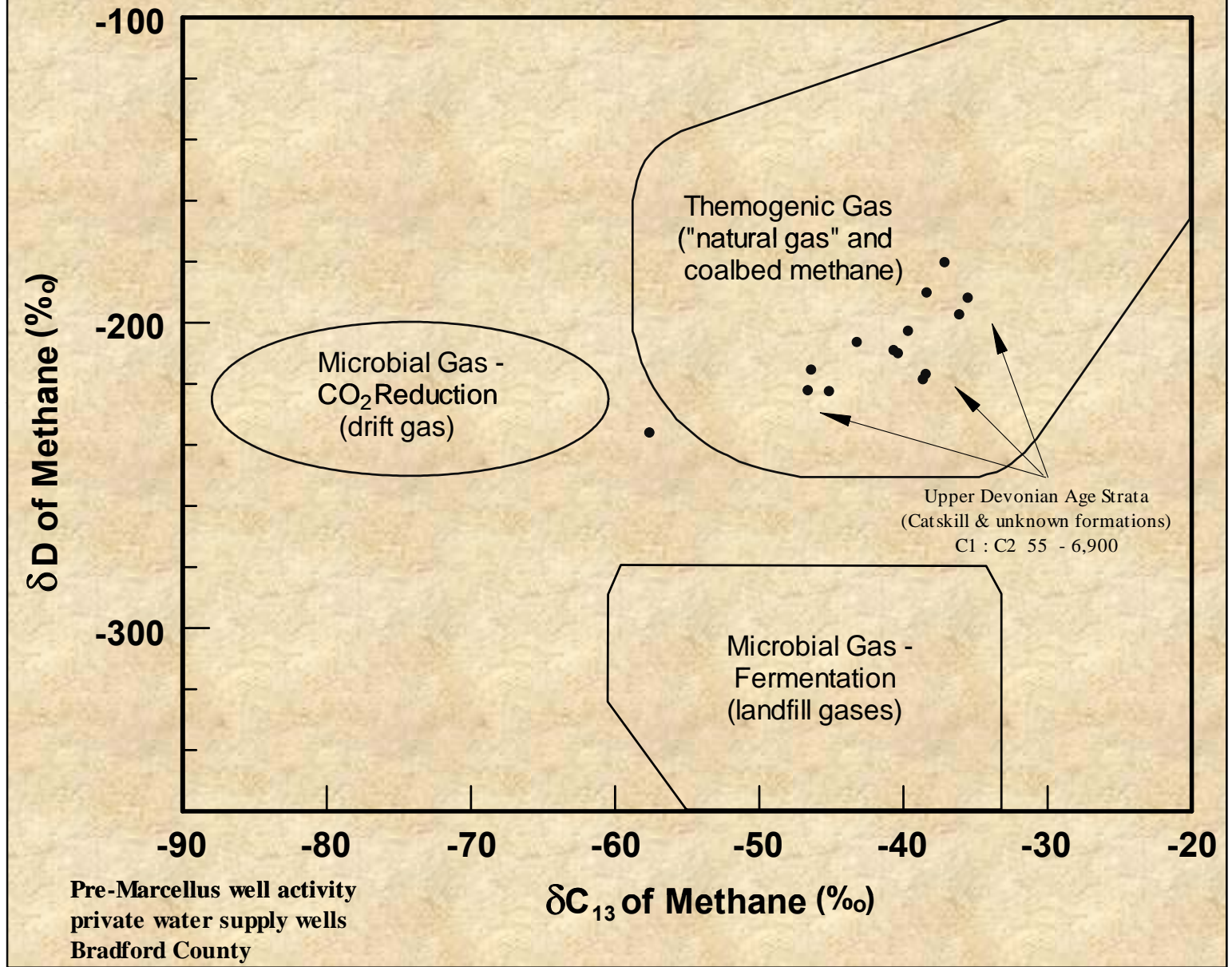


Southwestern Pennsylvania  
Private water supply well data

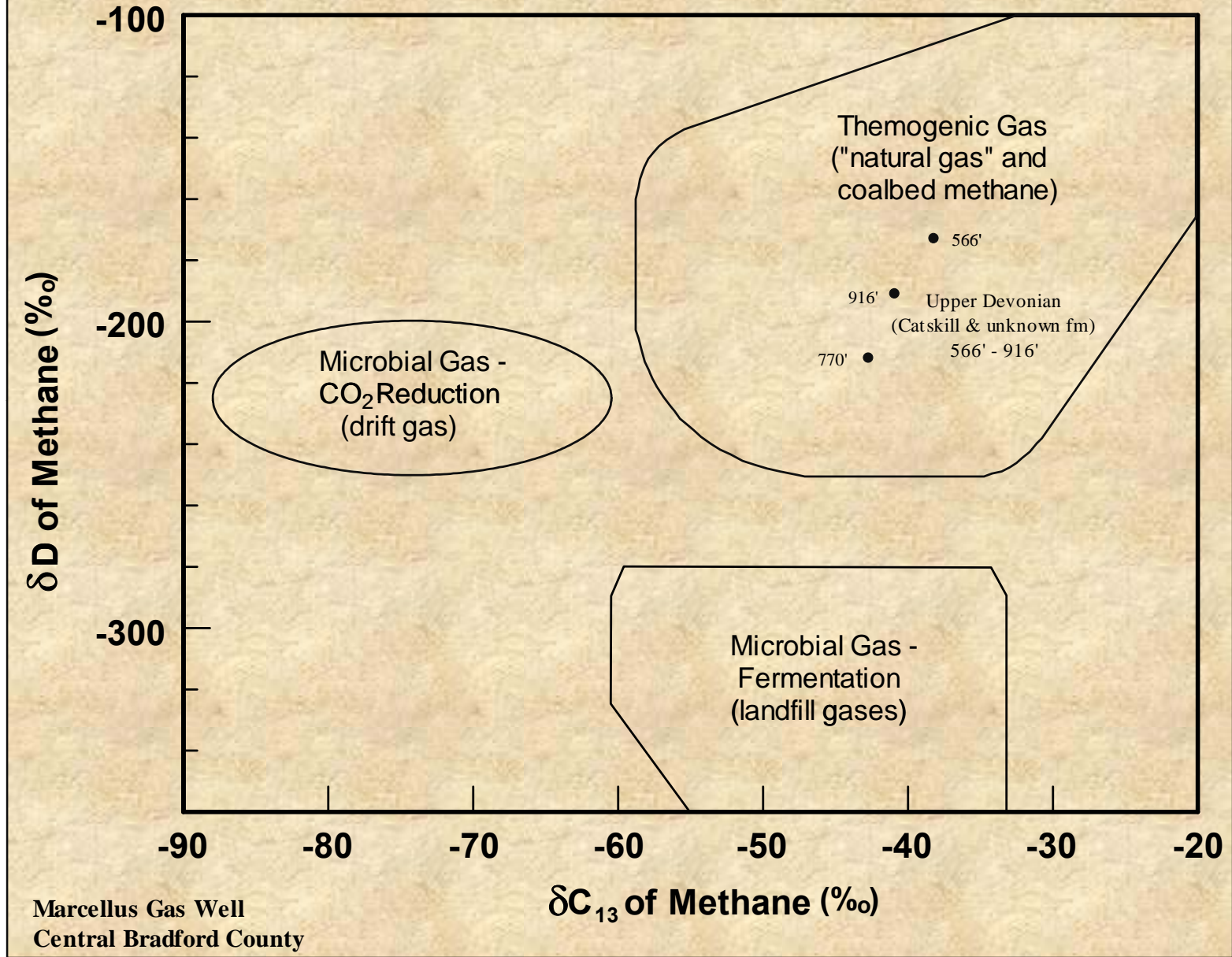
Investigations revealed methane origin as naturally occurring



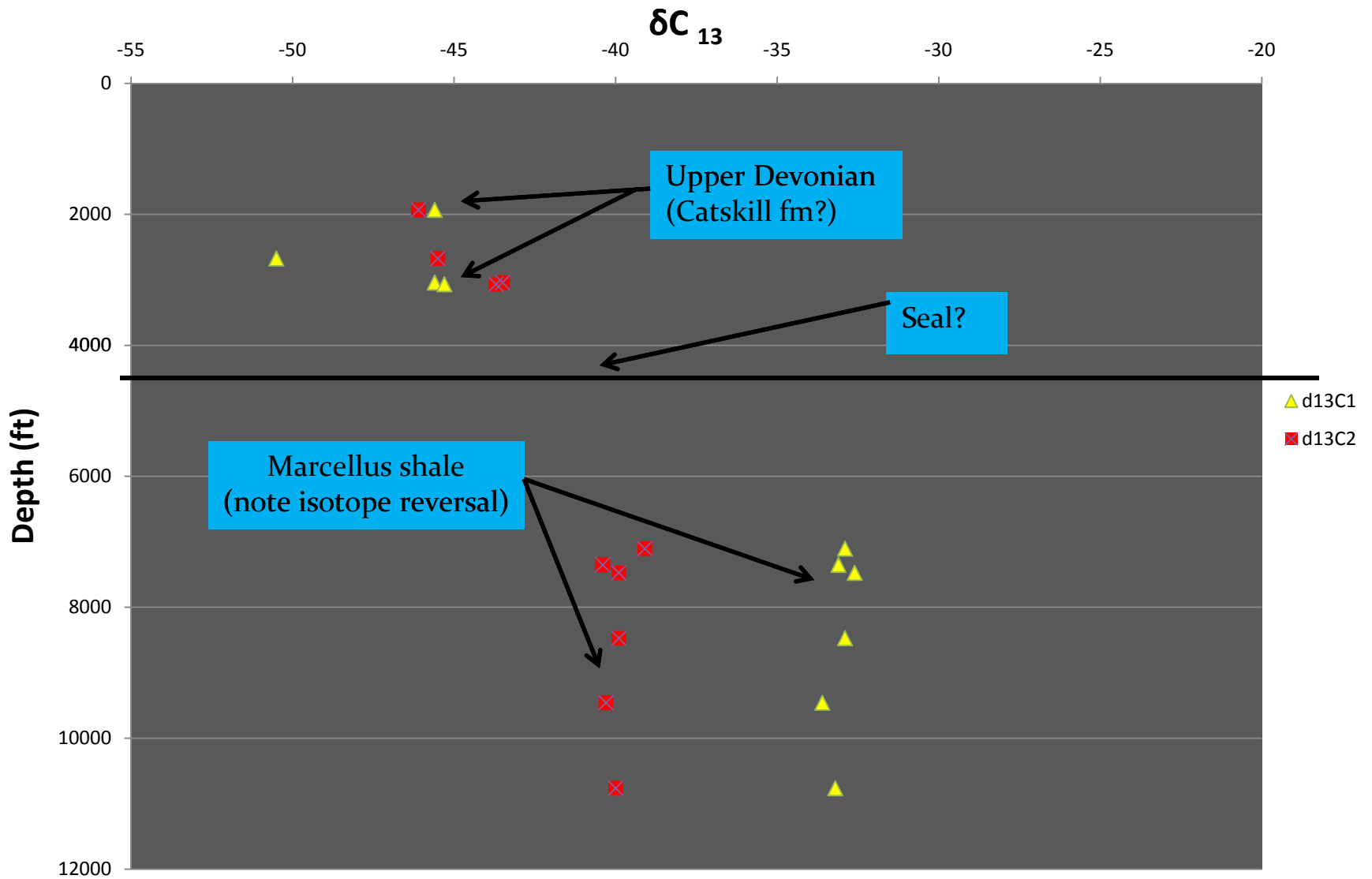
# ISOTOPE CROSSPLOT

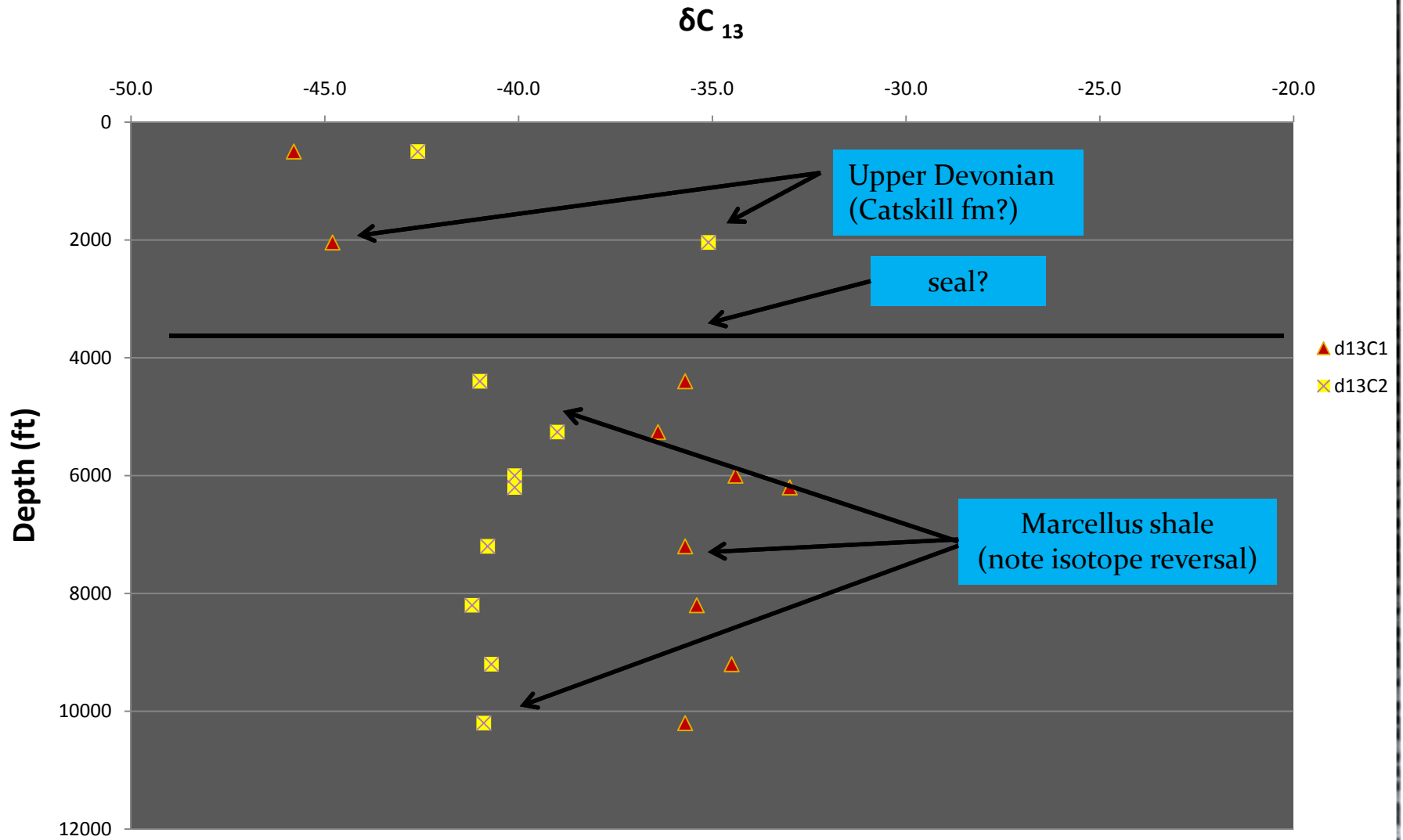


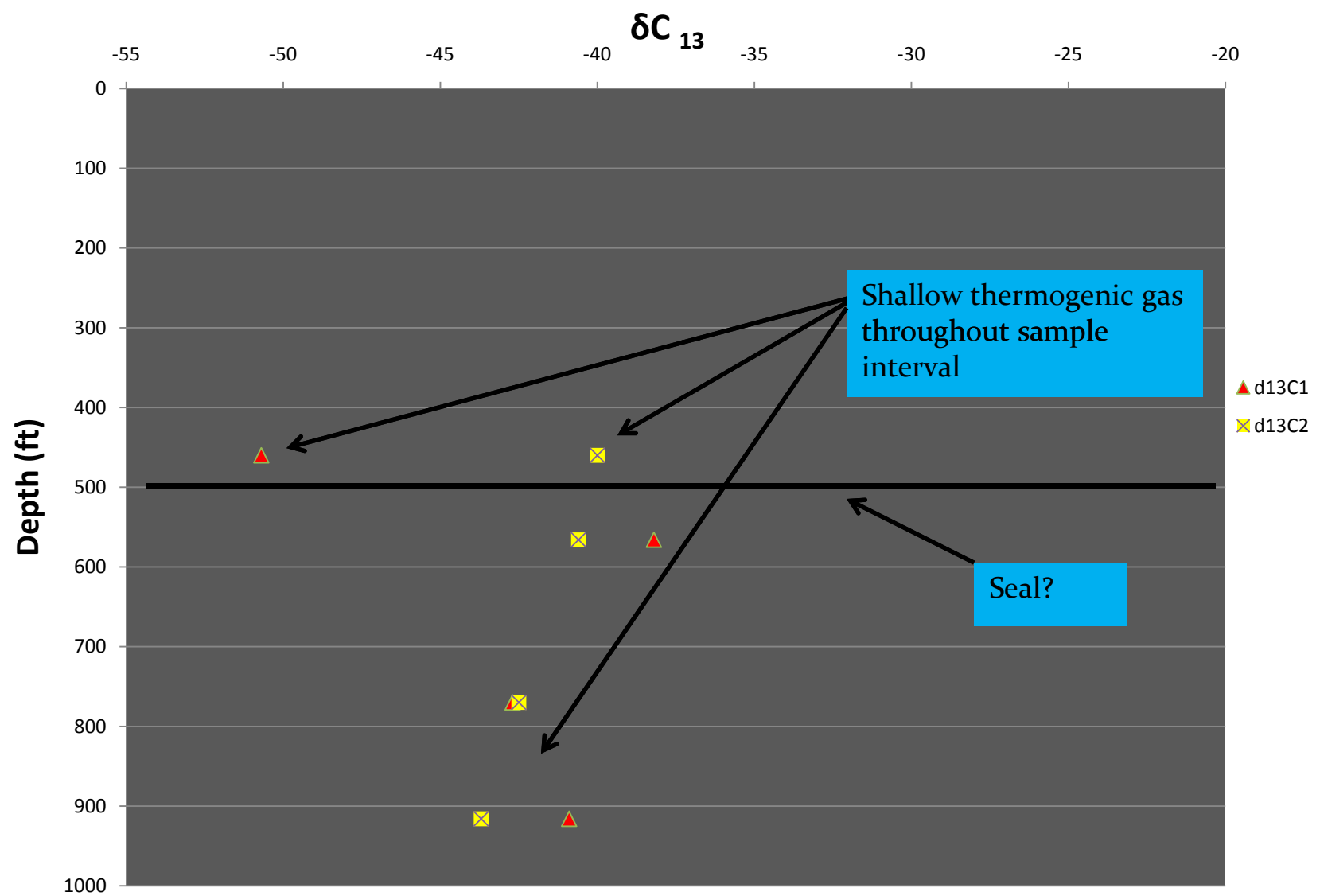
# ISOTOPE CROSSPLOT



Marcellus gas well  
Bradford County, PA







THANK YOU



# **The Origin of Some Natural Gases in Permian through Devonian Age Systems in the Appalachian Basin & the Relationship to Incidents of Stray Gas Migration**

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*The statements made during the workshop do not represent the views or opinions of EPA. The claims made by participants have not been verified or endorsed by EPA.*

## **Introduction**

The molecular composition and isotope geochemistry for natural gases of Permian through Devonian age system rocks across the Central & Northern Appalachian Basin reveal gases are microbial, thermogenic, and mixed microbial/thermogenic in shallow systems, and thermogenic gases of different thermal maturities in commercially productive formations.

Since 2008, the pace of gas well drilling to the Marcellus shale has markedly increased in the Central & Northern Appalachian Basin. This pace is expected to continue as demand for natural gas grows. As drilling activity to the Marcellus shale has increased so have the number of reports of stray natural gas migration to shallow aquifer systems.

As allegations of hydraulic fracturing contaminating groundwater supplies received the attention of various media outlets, the link to stray natural gas contamination of aquifer systems created by hydraulic fracturing was simultaneously made, inexplicably. Pennsylvania leads all states in the number of Marcellus shale gas wells drilled and in production. Investigations of stray natural gas migration incidents in Pennsylvania reveal that not one incident of stray natural gas migration to a shallow aquifer system was caused by hydraulic fracturing of the Marcellus shale.

## **Background**

Methane is the principal hydrocarbon detected in all Permian and Devonian age system rocks across the Appalachian Basin and in all stray gas migration incidents. It is the simplest and most abundant gas hydrocarbon, and is generated by microbial and thermogenic processes. Methane has a specific gravity of .555, and a solubility of 28-32 mg/l in water at standard atmospheric pressure (methane solubility increases with increases in hydrostatic pressure).

Though incidents of stray methane gas and stray methane gas migration have received significant attention as gas well drilling to the Marcellus shale has increased, the occurrence of methane gas, and stray gas migration incidents to shallow aquifer systems have occurred long before the start of the Marcellus shale drilling industry. This is particularly evident in Pennsylvania where there are often multiple potential sources of methane and subsurface methane migration. Potential anthropogenic sources of stray methane migration include

abandoned and operating coal mines, abandoned and operating gas wells, natural gas storage facilities, coalbed methane wells, buried organic matter, and landfills.

Methane is also naturally occurring in some shallow, near surface environments. Microbial methane is generated by bacterial decomposition of organic matter through CO<sub>2</sub> reduction and acetate fermentation pathways. Thermogenic methane also occurs naturally in some aquifer systems in the Central and Northern Appalachian basin. (Laughrey, Baldassare, 1998; Baldassare, Laughrey unpublished data, 1999-2011; Revesez, and others, 2010)

### Genetic Characterization of Natural Gas

Gas-origin/source correlations are determined from geochemical parameters including molecular composition, (relative concentrations of CH<sub>4</sub> to C6 hydrocarbons and non-hydrocarbon gases including He, H, CO<sub>2</sub>, and N<sub>2</sub>), and stable carbon and hydrogen isotope ratios. Analyses of the molecular composition, stable carbon and hydrogen isotopes of C1 – C5 hydrocarbons, and the radioactive isotope of C1 provide the highest level of geochemical evidence to interpret the origin of methane and other hydrocarbons in the subsurface.

Various researchers have determined by examination of stable carbon and hydrogen isotopes of methane that there are common isotopic compositions for thermogenic gas associated with coal and natural gas, drift gas, and other near-surface microbial gases (Coleman and others, 1977; Schoell, 1980; Whiticar, 1986; Baldassare and Laughrey, 1997; Jenden and others, 1993; Kaplan and others, 1997; Rowe and Muehlenbachs, 1999, Revesz, and others, 2010; and Osborn and McIntosh, 2010).

Stable isotope compositions are expressed as

$$\delta = (R_{\text{sample}} - R_{\text{std}}) / R_{\text{std}}$$

$$\delta^i E = \delta(^i E) = \delta(^i E/^j E) = \frac{N(^i E)_B / N(^j E)_B - N(^i E)_{\text{std}} / N(^j E)_{\text{std}}}{N(^i E)_{\text{std}} / N(^j E)_{\text{std}}}$$

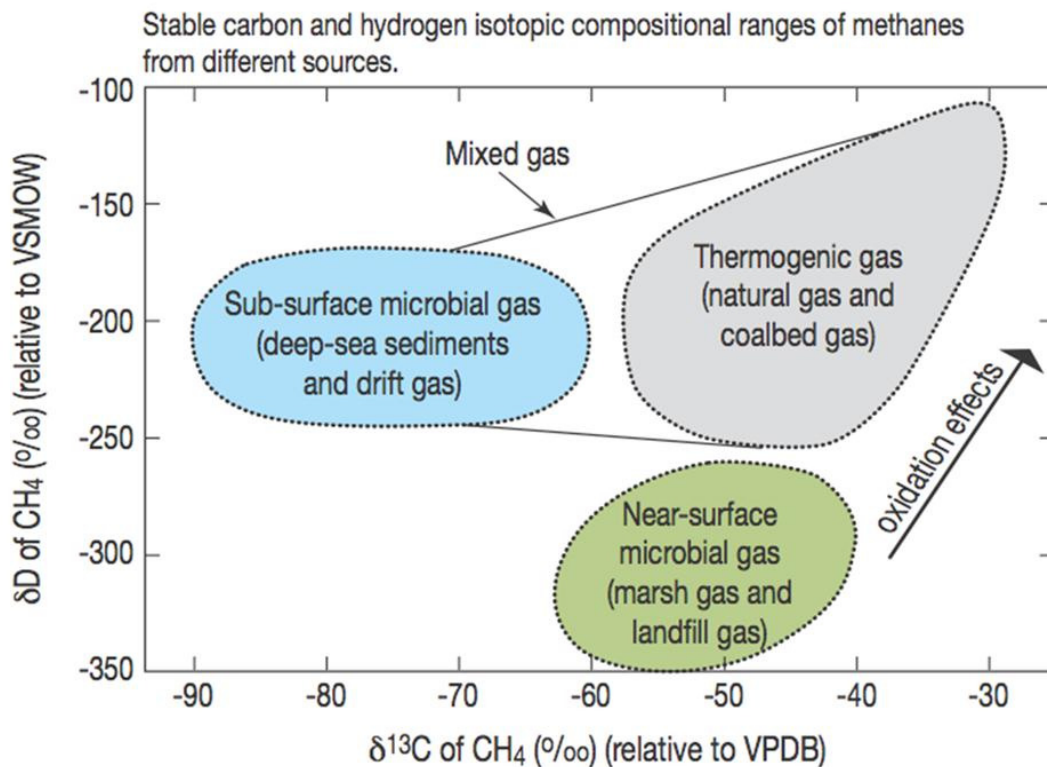
where  $\delta(^i E)$  refers to the delta value of isotope number  $i$  and  $j$  (heavy and light isotopes, respectively) of element E of sample B relative to the same element E in an international measurement standard (std);  $R_{\text{sample}} = N(^i E)_B / N(^j E)_B$  and  $R_{\text{std}} = N(^i E)_{\text{std}} / N(^j E)_{\text{std}}$  are the ratios of the number of isotopes in unknown sample (B) and the international measurement standard. A positive  $\delta(^i E)$  value indicates that the sample is more enriched in the heavy isotope than the international measurement standard. A negative  $\delta(^i E)$  value indicates that the sample is depleted in the heavy isotope relative to the international measurement standard (Revesz, and others, 2010). Stable carbon isotope ratios are relative to Vienna Pee Dee Belemnite (VPDB) standard, and hydrogen isotope ratios are relative to Vienna Standard Mean Ocean Water (VSMOW) standard. (Gat and Gonfiantini, 1981)

In general, microbial methane formed by the acetate fermentation pathway (marsh gas & landfill gas) reveals isotope compositions of  $\delta^{13}\text{C1}$ : -40 to -62 o/oo and  $\delta\text{D}$ : -270 to -350 o/oo.



Microbial methane formed via the CO<sub>2</sub> reduction (drift gas) pathway reveal isotope compositions of δ<sup>13</sup>C<sub>1</sub>: -62 to -90 ‰ and δD: -180 to -240 ‰. Thermogenic methane reveal isotope compositions of δ<sup>13</sup>C<sub>1</sub>: -26 to -50 ‰ and δD: -110 to -250 ‰ as depicted in Figure 9.

Additionally, δ<sup>13</sup>C values of dissolved inorganic C (DIC) compared to the DIC in background groundwater can reveal additional evidence of methane origin in groundwater. Microbial processes such as CH<sub>4</sub> production or CH<sub>4</sub> consumption by oxidation can impart unique isotopic signatures to gases and components of the associated waters. Using a combined gas and water approach is significant to constrain the origin of natural gas in water wells. Microbial CH<sub>4</sub> production by acetate fermentation results in C and H stable isotope signatures in associated waters that are different from microbial CH<sub>4</sub> produced by CO<sub>2</sub> reduction (Whiticar and Faber, 1986; Revesz et. al., 2010; Osborn, McIntosh, 2010).



After Coleman and others (1993) based on the data set of Schoell (1980)

Figure 9. Isotope geochemistry for Marcellus Shale gas have expanded our view to reveal more thermally mature thermogenic methane than fit within the standard isotope crossplot, and that also reveal isotope reversals (C<sub>1</sub>, C<sub>2</sub>) throughout the stratigraphic section. Similarly, stable carbon and hydrogen isotope compositions reveal a broader range for early thermogenic methane.

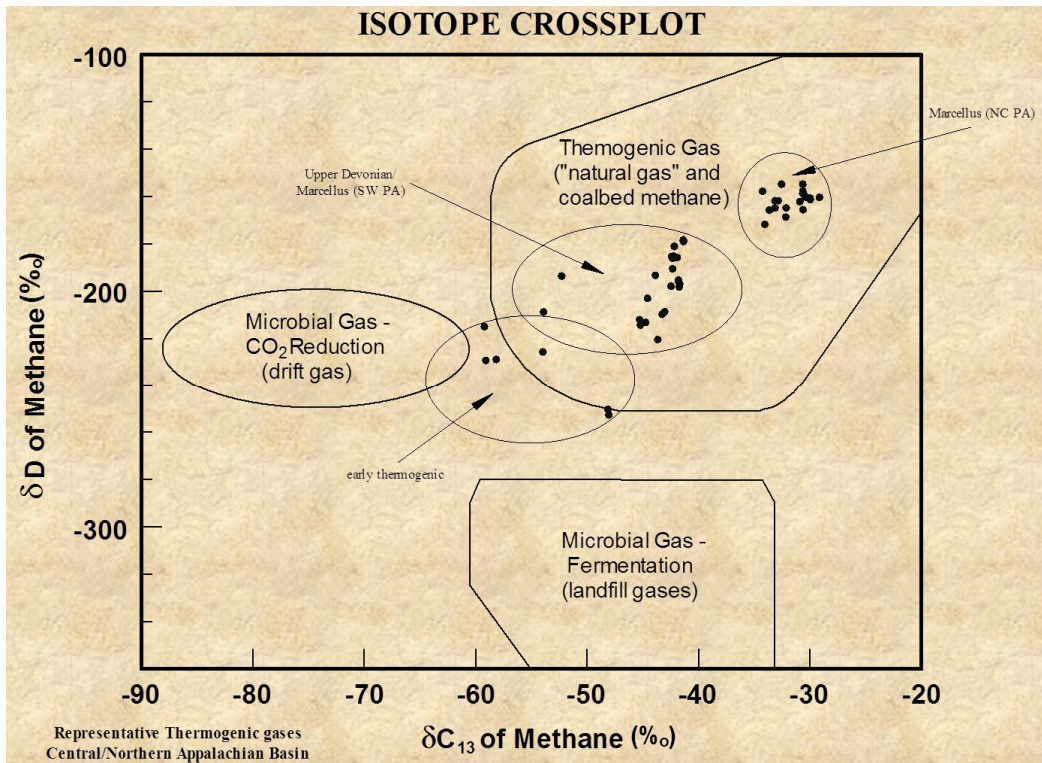


Figure 10 provides a small dataset of a much broader database documenting isotope compositions of thermogenic gases in areas across the Central and Northern Appalachian basin. In addition, recent geochemistry for Marcellus shale gas (unpublished data, Baldassare, 2011) and deeper natural gas resources in areas of the Appalachian basin reveal a complicated thermogenic history that cannot be explained by current hydrocarbon generation models (Burruss, Laughrey, 2010).

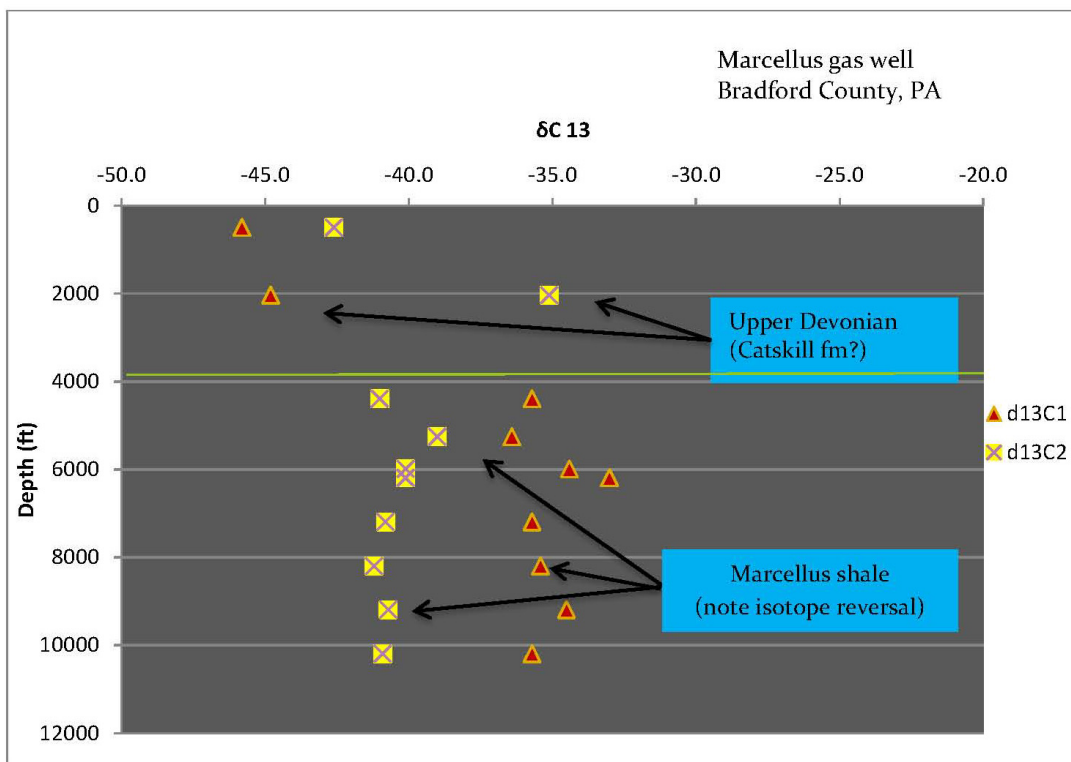


Figure 11 provides a small dataset of a much broader database documenting isotope compositions of thermogenic gases in areas across the Central and Northern Appalachian basin. In addition, recent geochemistry for Marcellus shale gas (unpublished data, Baldassare, 2011) and deeper natural gas resources in areas of the Appalachian basin reveal a complicated thermogenic history that cannot be explained by current hydrocarbon generation models (Burruss, Laughrey, 2010).

## **Conclusions**

Defining the source of natural gas migration requires the investigation and synthesis of different data types, notably gas geochemistry and mechanism of migration. Geochemical evidence reveals that microbial and early thermogenic methane occurs naturally (pre-existing anthropogenic activity) in some shallow aquifer systems in areas of the Appalachian Basin . Water wells drilled to these formations create low pressure zones and potentially a migration point for naturally occurring methane or stray methane from anthropogenic sources. Building structures and other low pressure zones also represent potential migration pathways.

Given the occurrence of multiple potential anthropogenic and naturally occurring stray gas sources, it is essential that a thorough characterization and definition of background groundwater quality is implemented to define pre-existing conditions prior to drilling activity. Stray gas migration incidents should be thoroughly investigated and supported by multiple lines of evidence, principally, geochemistry & analyses documenting a mechanism of migration.

## References

- Baldassare, F.J., Laughrey, C.D., 1997, Identifying the source of stray methane by using geochemical and isotopic fingerprinting: *Environ. Geosc.* 4(2), 85-94.
- Burruss, R.C., Laughrey, C.D., 2010, Carbon and Hydrogen Isotopic Reversals in Deep Basin Gas: Evidence for Limits to the Stability of hydrocarbons, *Organic Geochem.*, 2010; doi: 10.1016/j.orggeochem.
- Coleman, D.D., Meents, W.F., Liu, C.L., Keogh, R.A., 1977. Isotopic identification of leakage gas from underground storage reservoirs—A progress report. *Illinois State Geol. Surv.*, Illinois Petroleum No. 111.
- Gat, J.R., Gonfiantini, R., 1981. Stable isotope hydrology, deuterium and oxygen-18 in the water cycle. International Atomic Energy Agency, Technical Report Series No. 210.
- Jenden, P.D., Drazan, D.J., Kaplan, I.R., 1993. Mixing of thermogenic natural gases in northern Appalachian Basin. *Am. Assoc. Petrol. Geol. Bull.* 77(6), 980-998.
- Laughrey, C.D., Baldassare, F.J., 1998. Geochemistry and origin of some natural gases in the Plateau Province, C. Appalachian Basin, Pennsylvania and Ohio. *Am. Assoc. Petrol. Geol. Bull.* 82(2), 317-335.
- Osborn, S.G., McIntosh, J.C, 2010. Chemical and isotopic tracers of the contribution of microbial gas in Devonian organic-rich shales and reservoir sandstones, northern Appalachian Basin. *Appl. Geochem.* 25, 456-471.
- Révész, K.M., Breen, K.M., Baldassare, A.J., and Burruss, R.C., 2010. Carbon and hydrogen isotopic evidence for the origin of combustible gases in water-supply wells in north-central Pennsylvania. *Appl. Geochem.* 25, 1845-1851
- Rowe, D., Muehlenbachs, K., 1999. Isotopic fingerprints of shallow gases in the Western Canadian sedimentary basin: tools for remediation of leaking heavy oil wells. *Org. Geochem.* 30, 861-871.
- Schoell, M., 1980. The hydrogen and carbon isotopic composition of methane from natural gases of various origins. *Geochem. Cosmochem. Acta* 44(5), 649-661.
- Whiticar, M.J., Faber, E., 1986. Methane oxidation in sediment and water column environments –Isotope evidence. *Org. Geochem.* 10, 759-768.
- Whiticar, M.J., 1999. Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane. *Chem. Geol.* 161, 291-314.