Diagnostic Environmental Parameters for Differentiating Sources of Water and Gases

Gulf States Energy Retreat
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Houston, Texas

"Truth is so obscure in these times, and falsehood so established, that, unless we love the truth, we cannot know it."

-- Blaise Pascal, 1623-1662, French Mathematician

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“I never give them hell. I just tell the truth and they think it’s hell.”

-- Harry S. Truman, 33^{rd} President

Dimock, Pennsylvania- It's Not Just Methane

"Inorganic hazardous substances are present in four home wells ***<u>at levels that present a public health concern</u>***"

"…this action is ***<u>predominantly</u>*** based upon ***<u>inorganic</u>*** data at the four homes"

USEPA, 1-19-12, Action Memorandum

- Arsenic
- Barium
- Manganese
- Sodium

NEWSFLASH!!!

- 3-15-12 EPA releases data for 11 wells
- 4-6-12 EPA releases data for 20 more wells
- 4-20-12 EPA releases data for 16 more wells
- 5-11-12 EPA releases data for 12 wells

Comments on Results

- "…did not show levels of contaminants that would give EPA reason to take immediate action," EPA spokesman Roy Seneca

- "The affected families want the ***truth***, not more smoke and mirrors: why is Region 3 implying that water full of toxic chemicals and methane poses no health threat?"

  - Water Defense Director

-

Pavillion, Wyoming- Methane? What Methane?

- EPA relied heavily on two parameters
- Extremely high pH- values between 11.2 and 12.0
- Potassium

EPA Phase IV Results & Issues

- EPA's claim that pH values above 11 S.U. are too high for cement is simply not true
- Oneacre & Figueras (1996)- pH values of 12+ in wells
- Cherry, et al (1983)- pH values as high as 11 or 12
- EPA's own document from 1991 (EPA/600/4-89/034) lists the pH of neat cement between 10 and 12 (p. 100)
- USGS publication from 1997 (Water –Resources Investigation Report 96-1233) states that cement has a pH range from 10 to 12

Vagarious Vermont

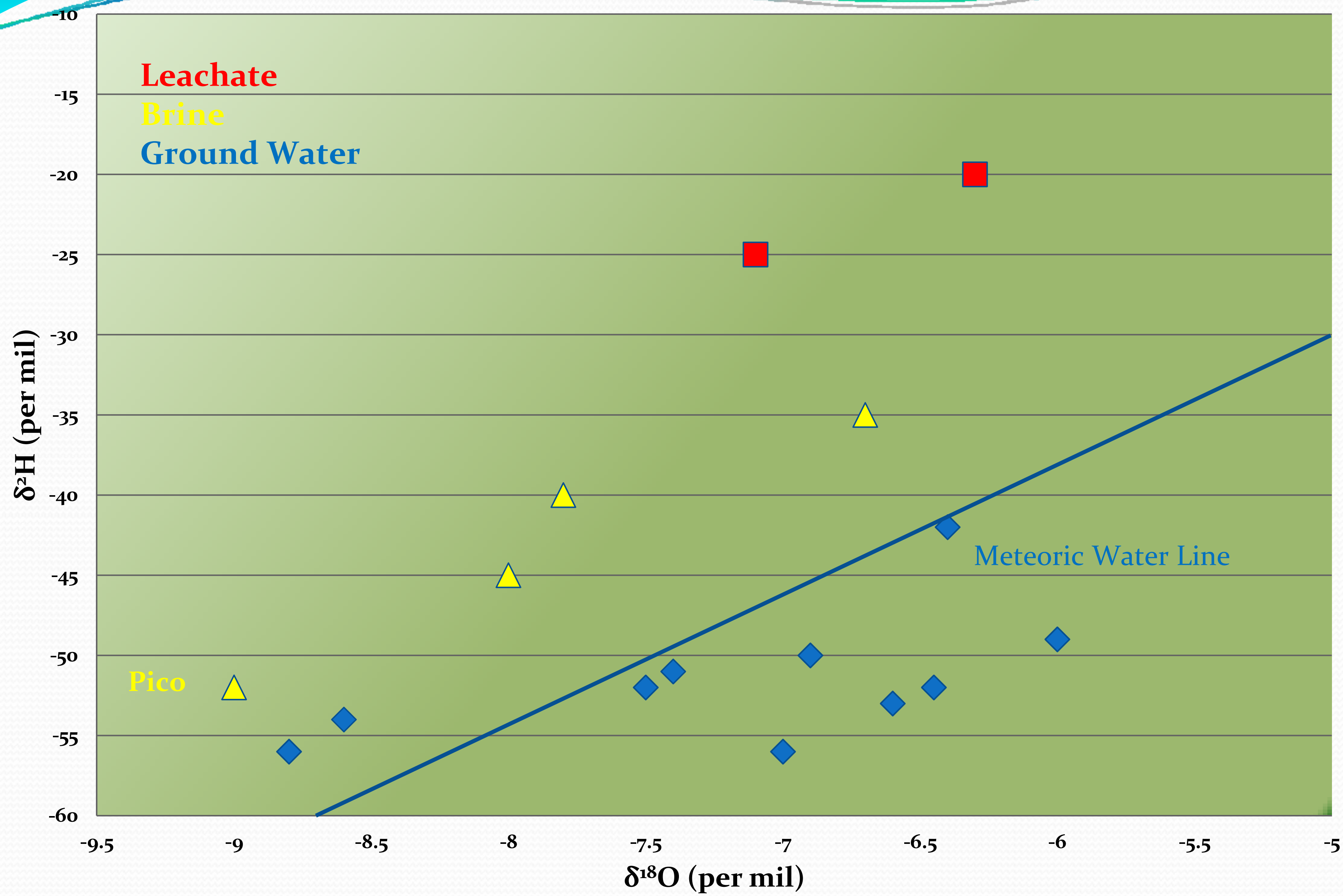
- Vagarious- marked by erratic, irresponsible, impetuous behavior

- "We don't want to be shooting chemicals into our groundwater in pursuit of gas that does not exist," - Vt. Governor Shumlin
- "There have been over 1,000 instances of … water contamination at sites in close proximity to fracking wells between 2008 and 2012 in the United States…" – Vt. State Senator Ginny Lyon
- "Fracking has caused enormous problems with underground water contamination and aboveground waste disposal , entire streams have been destroyed," -author and climate change activist Bill McKibben

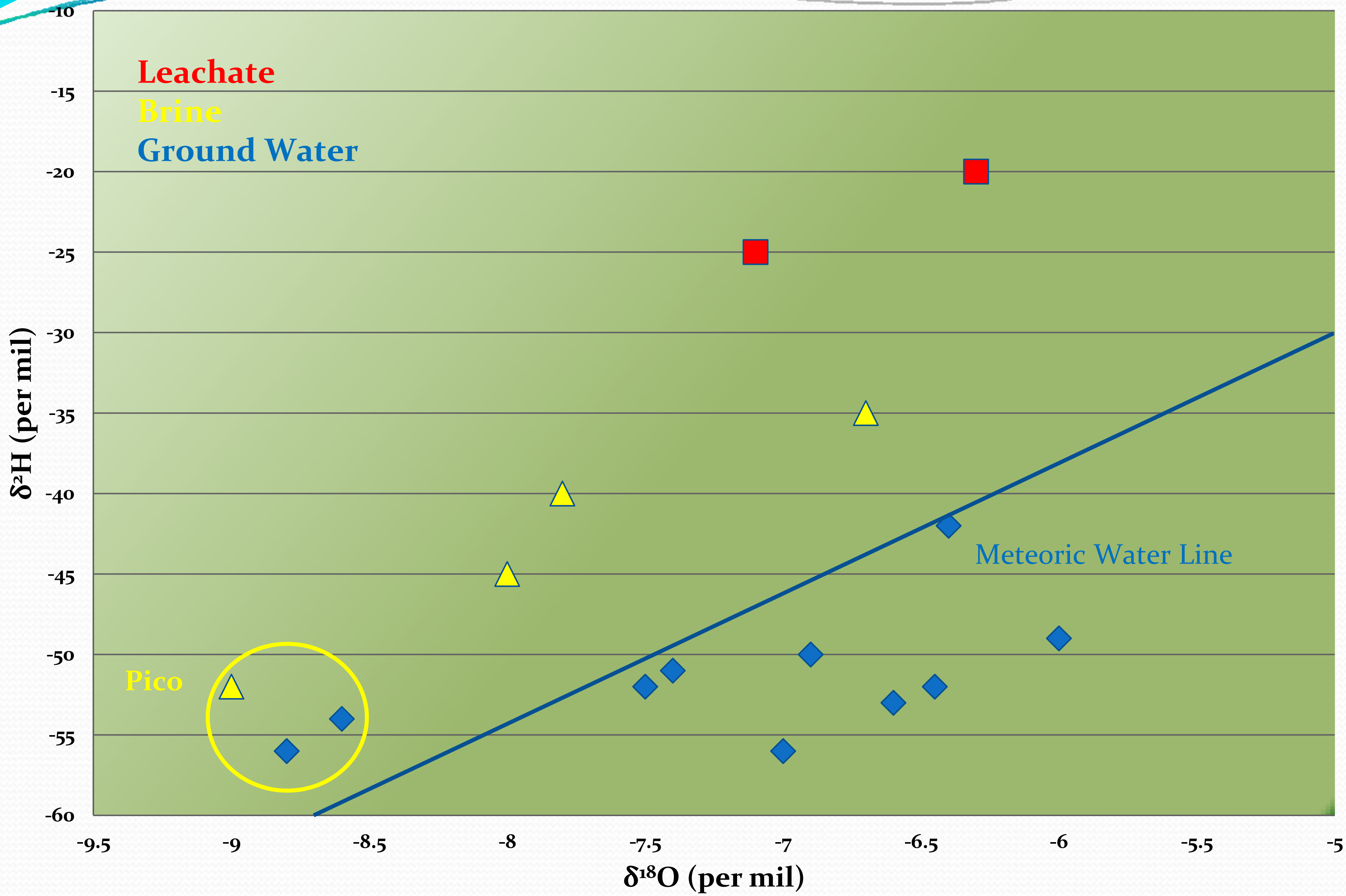
High Chloride Case

- Quaternary alluvial aquifer
- High concentrations of chloride in ground water
- Large MSW landfill adjacent to aquifer
- State agency orders study at landfill to determine leachate migration pathway to aquifer
- State requires landfill company to install a ground water interceptor trench and treatment plant
- Oil companies have producing field on opposite side of aquifer
- Oil companies are not under investigation as a responsible party for the chloride impact to ground water

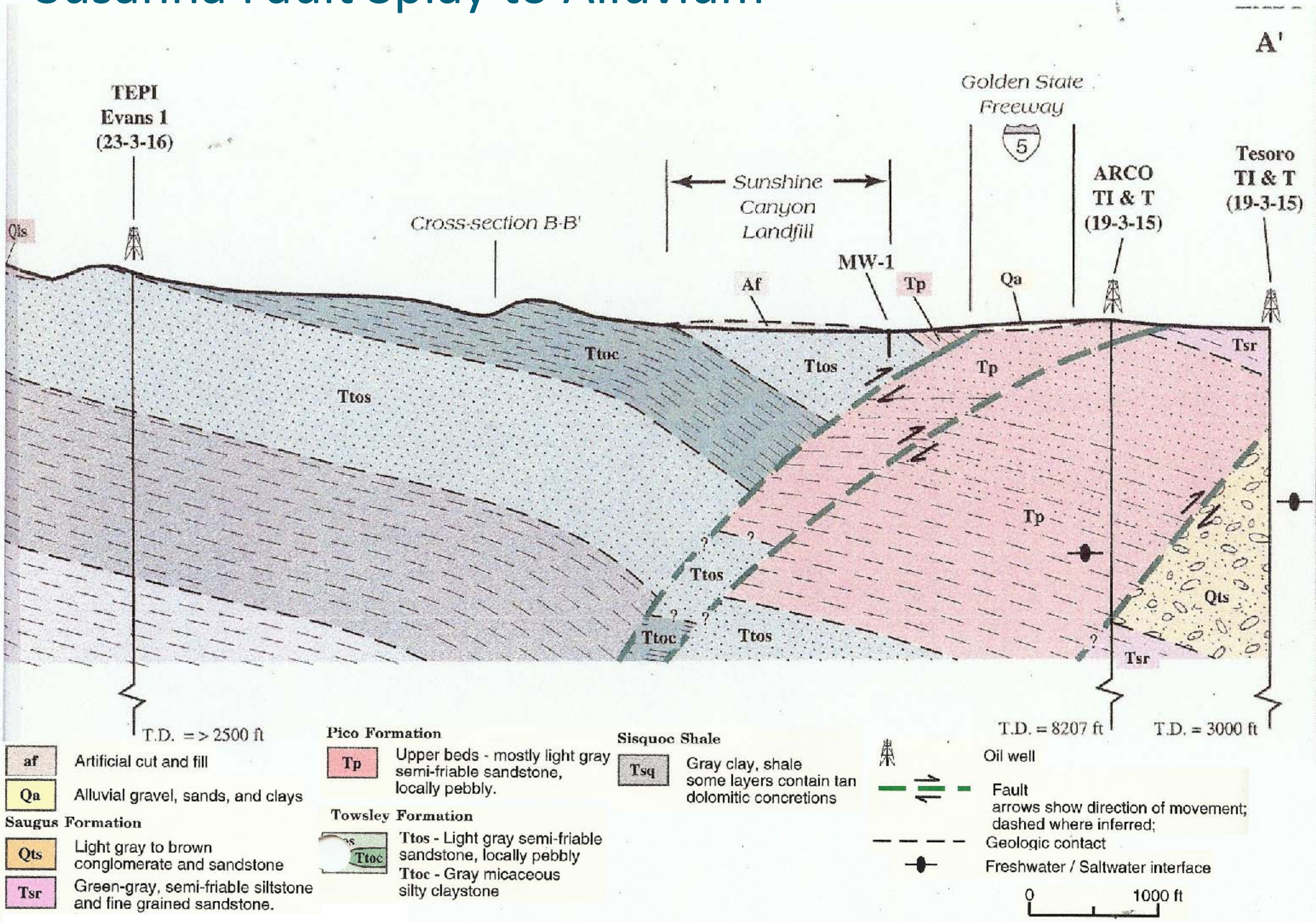
Differentiating Source of High Chlorides in Alluvial Aquifer



Differentiating Source of High Chlorides in Alluvial Aquifer

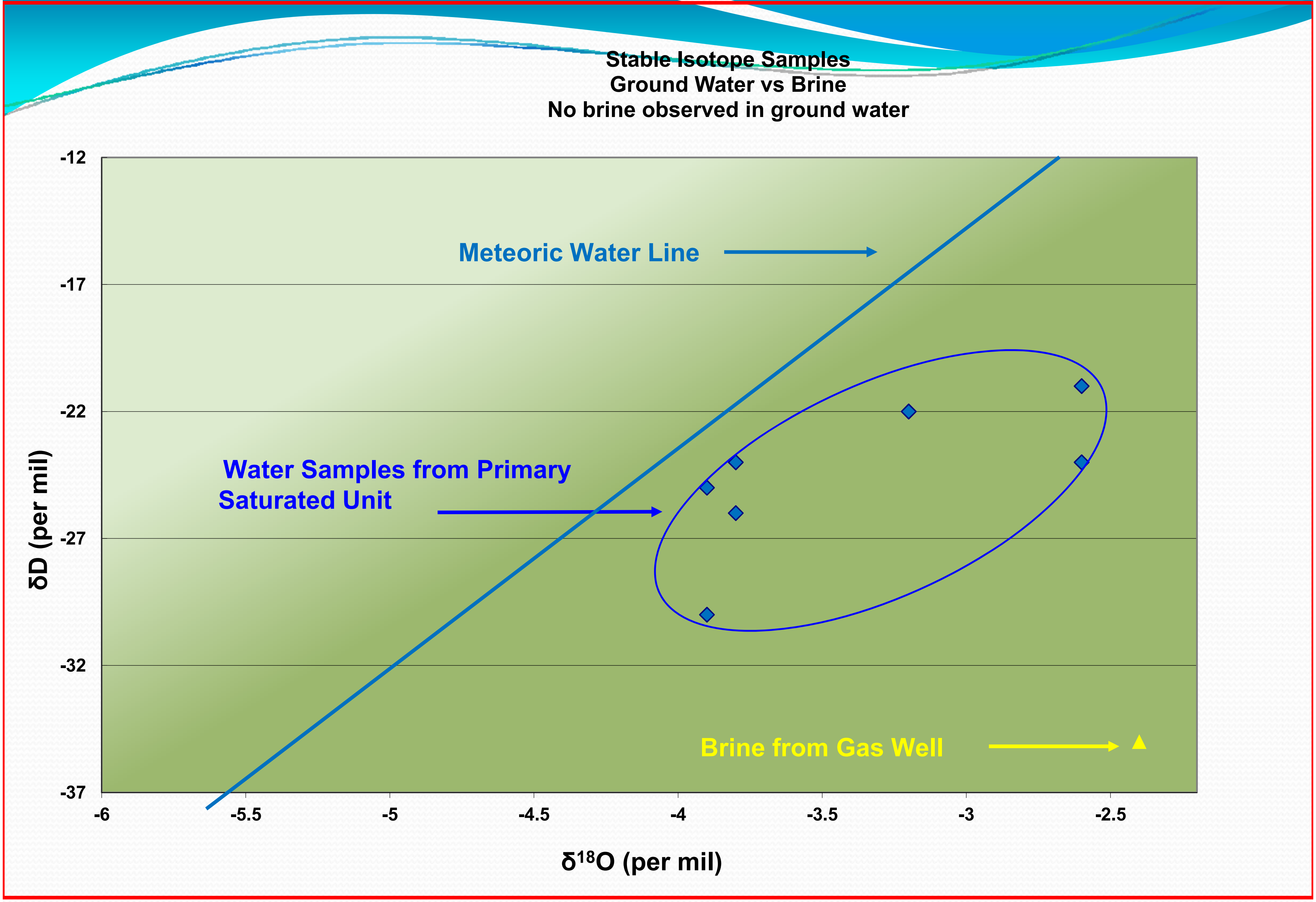


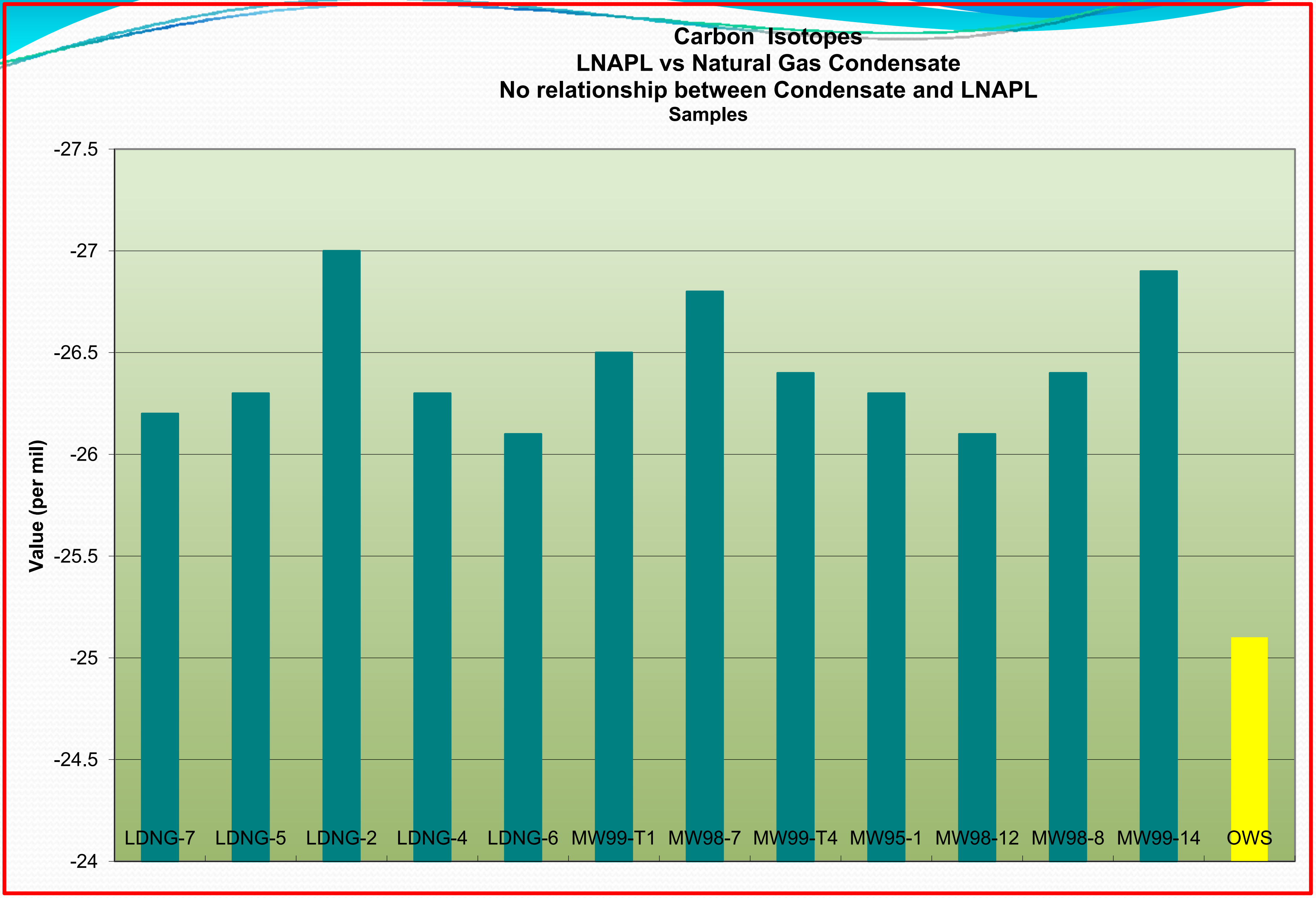
Brine movement from Pico Formation along Santa Susanna Fault Splay to Alluvium



Gas Leak on Residential Gas Line

- Note the gray, discolored soil in front of the backhoe
- Minor leak on 2-inch residential gas line caused discoloration
- Production gas line was not the source of the leak


Stable Isotope Samples
Ground Water vs Brine
No brine observed in ground water
Meteoric Water Line
Water Samples from Primary Saturated Unit
Brine from Gas Well
δD (per mil)
δ18O (per mil)
-12
-17
-22
-27
-32
-37
-6
-5.5
-5
-4.5
-4
-3.5
-3
-2.5


Carbon Isotopes
LNAPL vs Natural Gas Condensate
No relationship between Condensate and LNAPL
Samples
Value (per mil)
-27.5
-27
-26.5
-26
-25.5
-25
-24.5
-24
LDNG-7
LDNG-5
LDNG-2
LDNG-4
LDNG-6
MW99-T1
MW98-7
MW99-T4
MW95-1
MW98-12
MW98-8
MW99-14
OWS

Hydrogen Stable Isotopes

- Deuterium
- 1 Proton
- 1 Neutron
- Atomic Mass = 2
- 00.015% of H isotopes

- Protium
- 1 Proton
- 0 Neutron
- Atomic Mass = 1
- 99.985% of H isotopes

Stable Isotope Calculation

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

Types of Methane

- Biogenic
- Thermogenic
- Abiogenic and mantle

Biogenic Methane

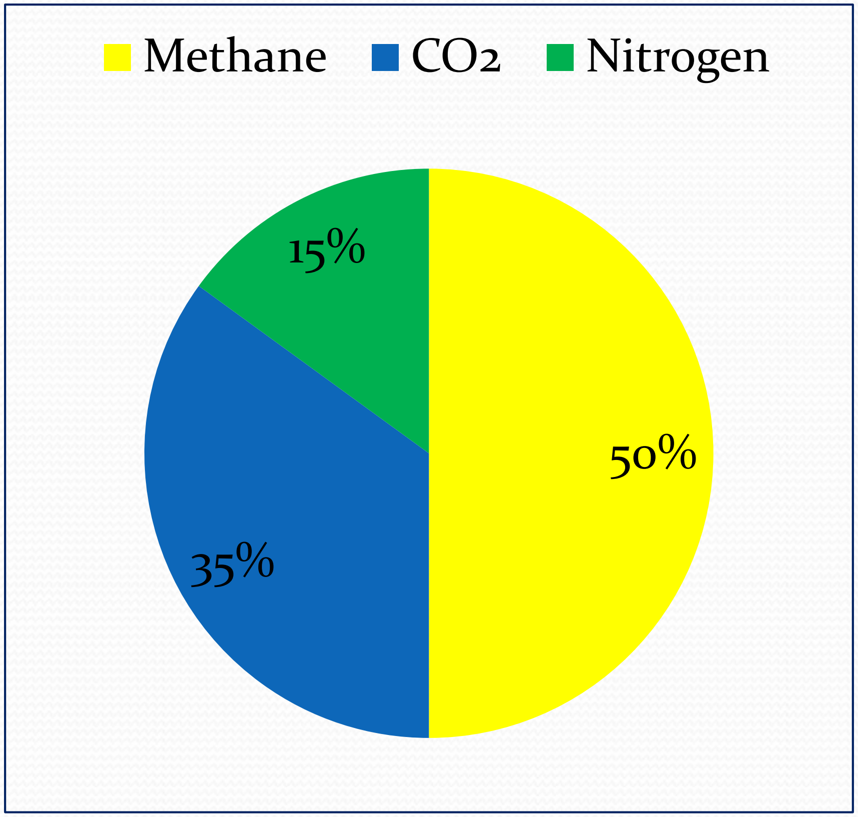
- Most common form in shallow ground water systems
- Formed from bacterial reduction of organic matter
- Requires fully saturated environment without atmospheric oxygen
- Absence of free-energy electron-acceptors such as NO_3 and SO_4

Biogenic Sources

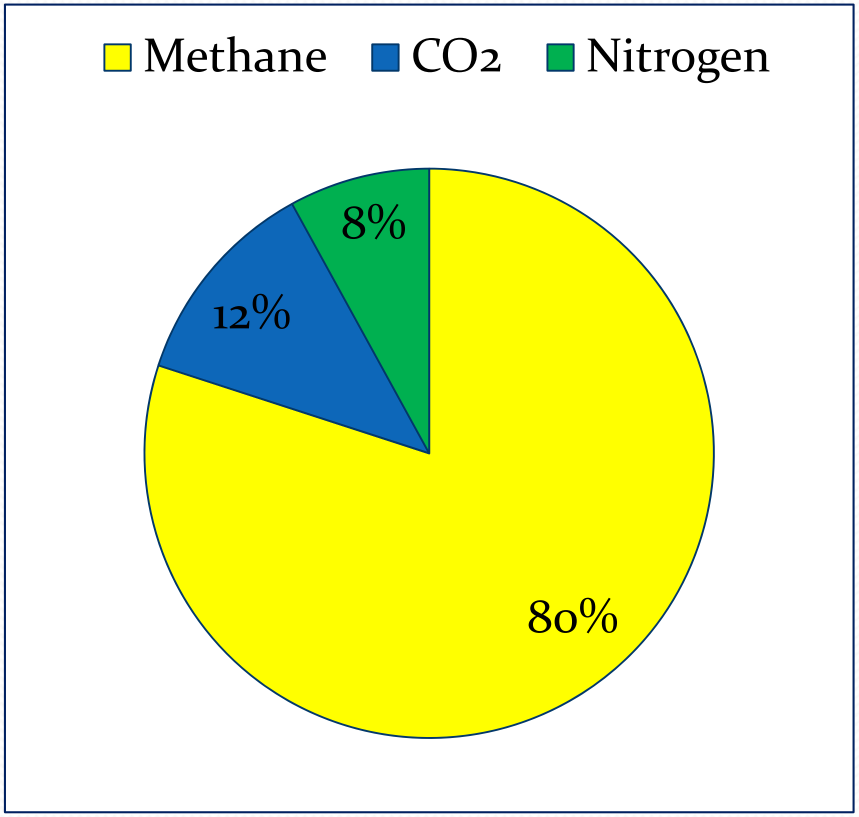
- Lignite to bituminous coal
- Wetlands
- Peat bogs/fens
- Rice Fields
- Landfills
- Marshes
- Glacial Deposits
- Lake Deposits

Biogenic Sources

Marsh & Landfill Gas



Bacterial Source Gas

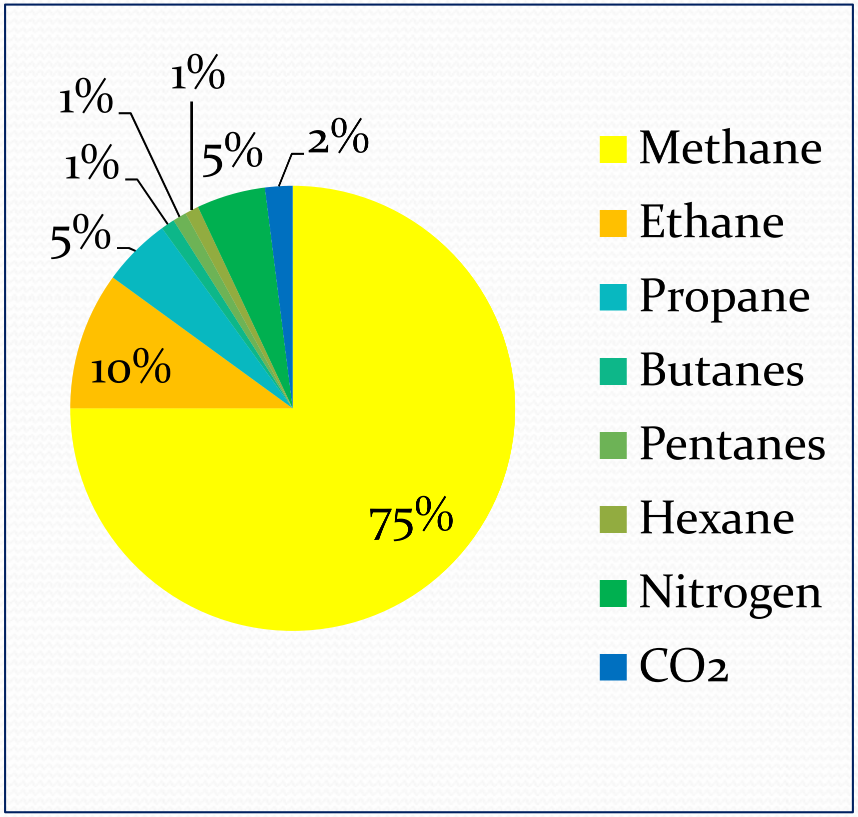


Biogenic Characteristics

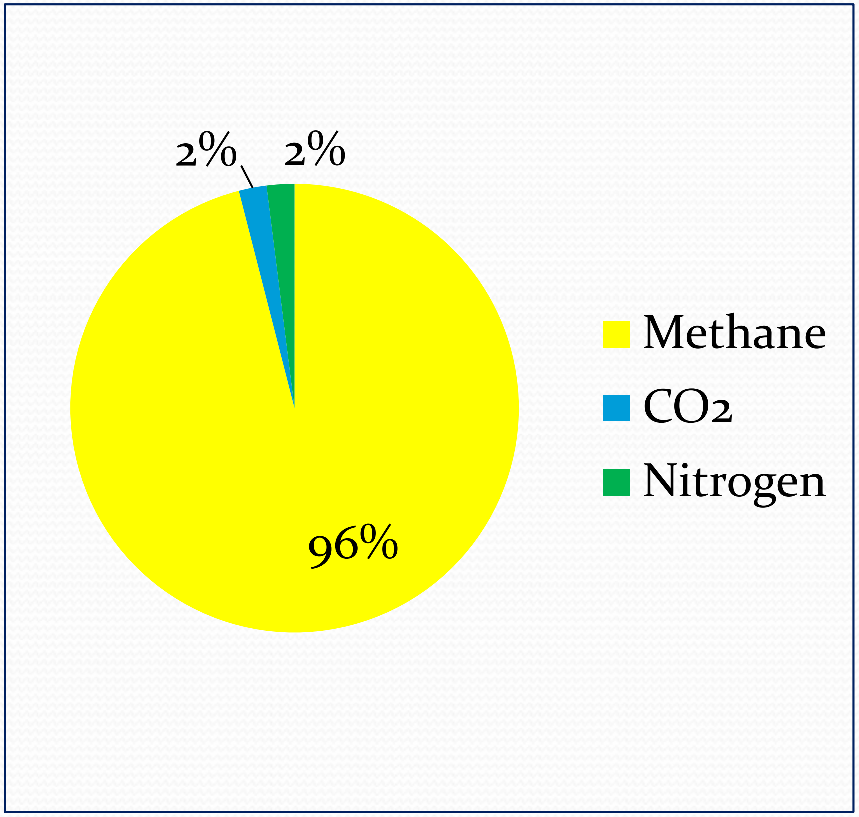
- $\delta\ ^{2}H$ values range from -300 $^{o}/_{oo}$ to -150 $^{o}/_{oo}$
- $\delta\ ^{13}C$ values range from -80 $^{o}/_{oo}$ to -40 $^{o}/_{oo}$
- $\delta\ ^{13}C_{CH4}$ depleted 50 $^{o}/_{oo}$ to 80 $^{o}/_{oo}$ from coexisting $\delta\ ^{13}C_{CO2}$
- Distinguishes biogenic from thermogenic
- Low temperature and pressure
- C2 + hydrocarbons at trace levels or non-detect
- CO2 reduction
- Methyl fermentation

Thermogenic Gas

Wet Gas



Dry Gas



Thermogenic Methane

- Forms by the breaking down of higher mass hydrocarbons
- Elevated temperatures required
- Elevated pressures required
- Represented by natural gas in sedimentary basins
- Enriched in $\delta\ ^{2}H$ and $\delta\ ^{13}C$ compared to biogenic methane
- Can have C_1 through C_6 components

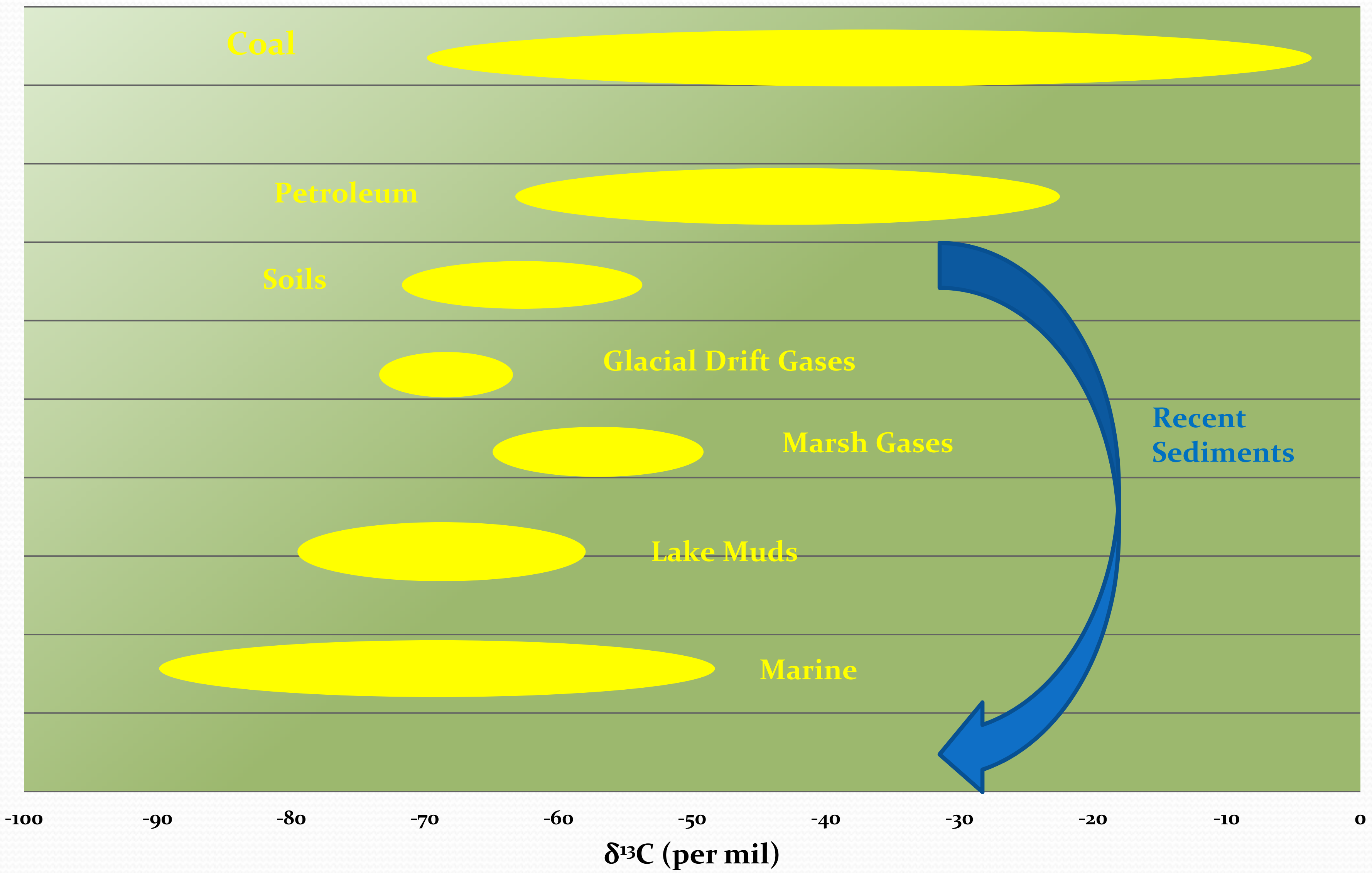
Thermogenic Methane

- Isotope fractionation is suppressed
- $\delta\ ^{13}C$ seldom below -50 $^{o}/_{oo}$
- $\delta\ ^{2}D$ typically between -250 $^{o}/_{oo}$ and -110 $^{o}/_{oo}$
- Ratio of methane to ethane and propane < than biogenic
- $C_1/(C_2 + C_3)$ can be less than 10 for thermogenic

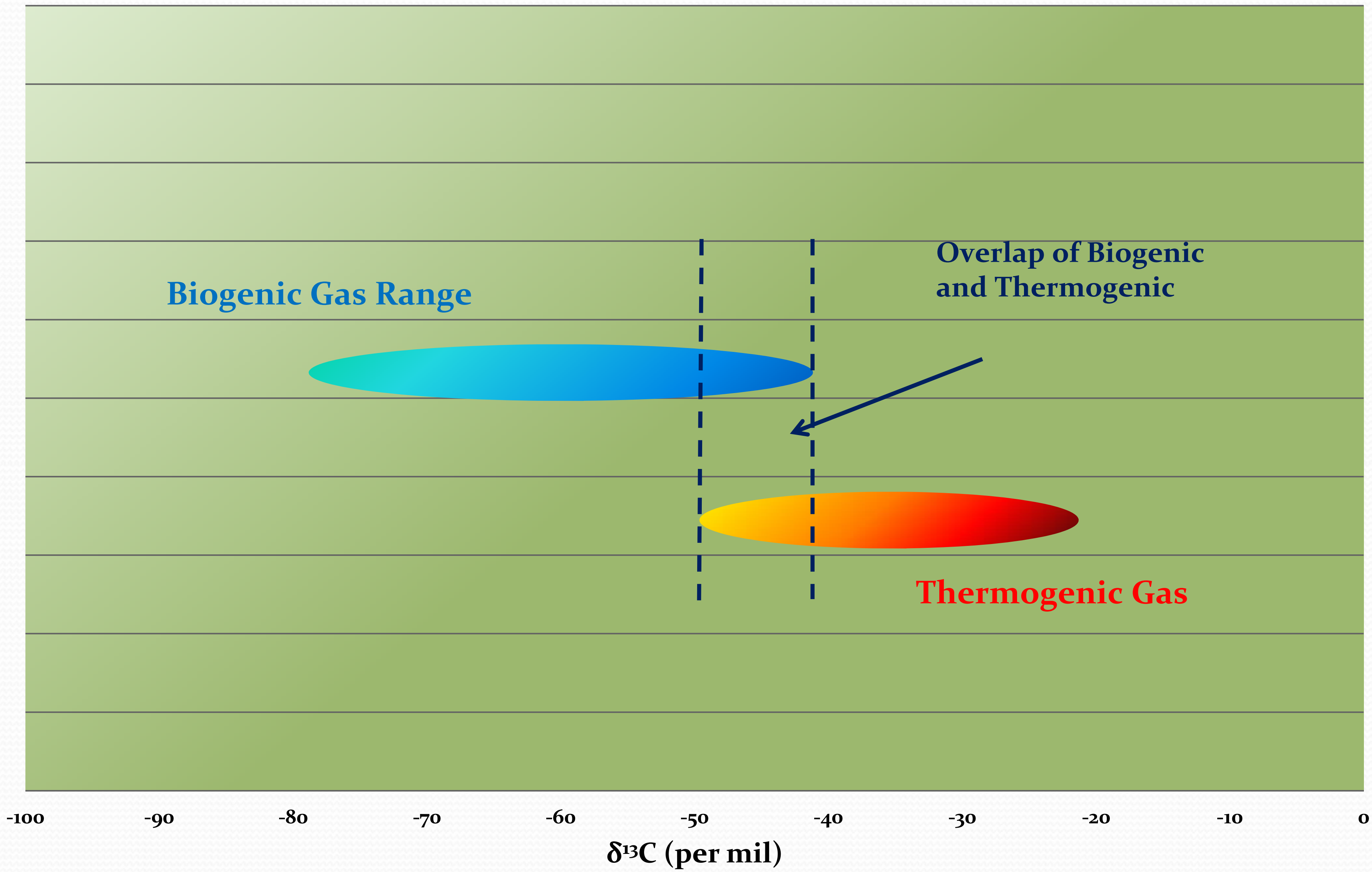
Thermogenic Gas

- Shallow gas does not necessarily mean biogenic gas
- The first gas well drilled (c. 1825) in Fredonia, NY was in Upper/Middle Devonian Shale at a depth of 27 feet.
- Devonian Catskill and Lock Haven Formations can have shallow thermogenic gas within a few hundred feet of surface

Carbon Isotope Ranges of Methane
Various Sources



Carbon Isotope Ranges of Methane
Biogenic vs Thermogenic



Naturally Occurring Methane

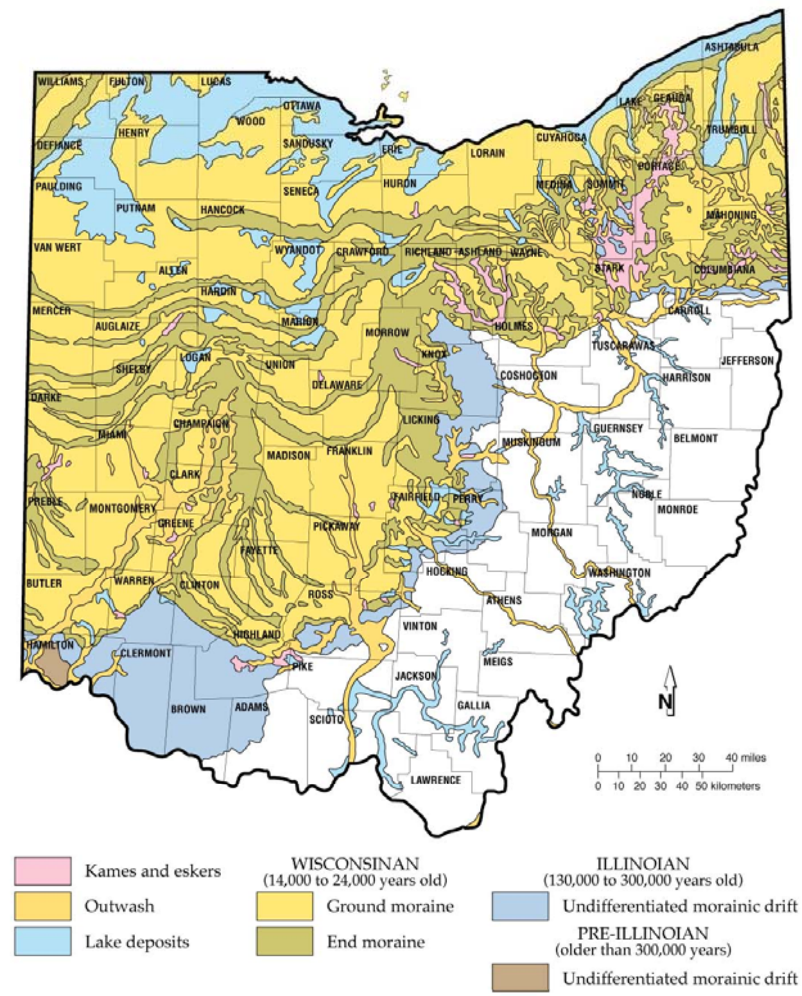
Examples of Naturally Occurring Methane in Ground Water in Different Sedimentary Basins

Naturally Occurring Methane Studies

- Alberta, Canada - ~ 60% of water wells had NOM
- West Virginia- ~ 77% of water wells tested had NOM
- San Juan Basin- ~ 33% of wells had NOM
- Pennsylvania- ~40% of wells estimated to have some gas; Cabot found that 80% of wells in 60 mi^2 area had measurable NOM
- Illinois- State found NOM in glacial moraines
- Louisiana- State found NOM from CBM in water wells
- Texas- NOM associated with major aquifer

Various Potential Sources of Methane in Glaciated Ares of Ohio

- Terminal Moraine
- Ground Moraine
- Till
- Outwash Deposits
- Bogs/Peat Bogs/Fens
- Marshes/Wetlands
- Kettle Lakes
- Coal Beds
- Abandoned Underground Mines
- Strip Mines
- Old Oil and Gas Plays
- Landfills
- Gas Lines
- Sewer Systems



Methods to differentiate methane

- Methane/ethane + ratio
- Thermogenic can have a ratio of 10 or lower
- Mole fractions of numerous gases
- CO_2, N, O, CH_4, C_2H_6, C_3-C_6, Ar, He, H_2S
- Isotopes of C and H
- Ratios such as Ar/O, N_2/C_1, C_1/C_2, C_2/C_3
- Other isotopes
- Gas Wetness Fraction (C_1/C_1-C_5)
- Possible other noble gases- Ne, Xe, Kr

Noble Gases as Markers

- Helium-formed by radioactive decay of thorium & uranium
- Helium may be present or absent in natural gas deposits
- Argon is formed by radioactive decay of Potassium 40
- Thus, Argon concentration is function of original amount of Potassium 40 in formation
- Argon/Oxygen can help distinguish different sources of methane

Field Indicators of Potential Presence of CH_4

- Low Dissolved Oxygen
- Low Oxidation-Reduction Potential (ORP)
- Presence of H_2S
- $SO4^{2-} + CH_4 \longrightarrow HS^- + HCO_3^- + H_2O$ + energy
- H_2S (aq) = $HS^- + H^-$
- Above indicate reduced (anaerobic) ground water conditions
- Hem (1985)- ***“Methane is commonly present in ground water in reduced geochemical systems.”***

Ground Water and Brine Parameters
Sample Parameters, Containers, and Holding Times

Parameter	Suggested Method	Units	Container	Preservative	Holding Time
Groundwater Depth	Field	0.01 feet	Field	n/a	n/a
Temperature	Field	°F	Field	n/a	n/a
Specific Conductance	Field	µmhos/cm	Field	n/a	n/a
pH	Field	pH units	Field	n/a	n/a
Dissolved Oxygen	Field	mg/L	Field	n/a	n/a
Oxidation-Reduction Potential	Field	mV	Field	n/a	n/a
Turbidity	Field	NTU	Field	n/a	n/a
Total Dissolved Solids	2540C	mg/L	1-L plastic	None	7 days
Chloride	300.0	mg/L	1-L plastic	None	28 days
Bicarbonate	300.0	mg/L	1-L plastic	None	14 days
Sulfate	300.0	mg/L	1-L plastic	None	28 days
Sulfide	4500SD	mg/L	1-L plastic	ZnAC + NaOH to pH >9	7 days
Calcium	6010	mg/L	1-L plastic	HNO_3 to pH <2	6 months
Magnesium	6010	mg/L	1-L plastic	HNO_3 to pH <2	6 months
Potassium	6010	mg/L	1-L plastic	HNO_3 to pH <2	6 months
Sodium	6010	mg/L	1-L plastic	HNO_3 to pH <2	6 months
Metals	6010	mg/L	500 mL	HNO_3 to pH <2	6 months
VOCs (Subtitle D Appendix I)	8260B	µg/L	Three 40-mL glass vials	HCl to pH <2	14 days
Oxygen Isotopes (δ18O/16O)	Mass Spec	per mil	1-500 ml plastic	None	None
Hydrogen Isotopes (δ2H/1H)	Mass Spec	per mil	1-500 ml plastic	None	None
Boron	212.3	mg/l	1-L plastic	None	6 months
Bromide	300.0	mg/l	1-L plastic	None	28 days
TPH	8015	mg/l	Three 40-mil glass vials	HCL to pH <2	14 days

µg/L denotes micrograms per liter.

µmhos/cm denotes micromhos per centimeter

L denotes liter

mg/L denotes milligrams per liter

mL denotes milliliter

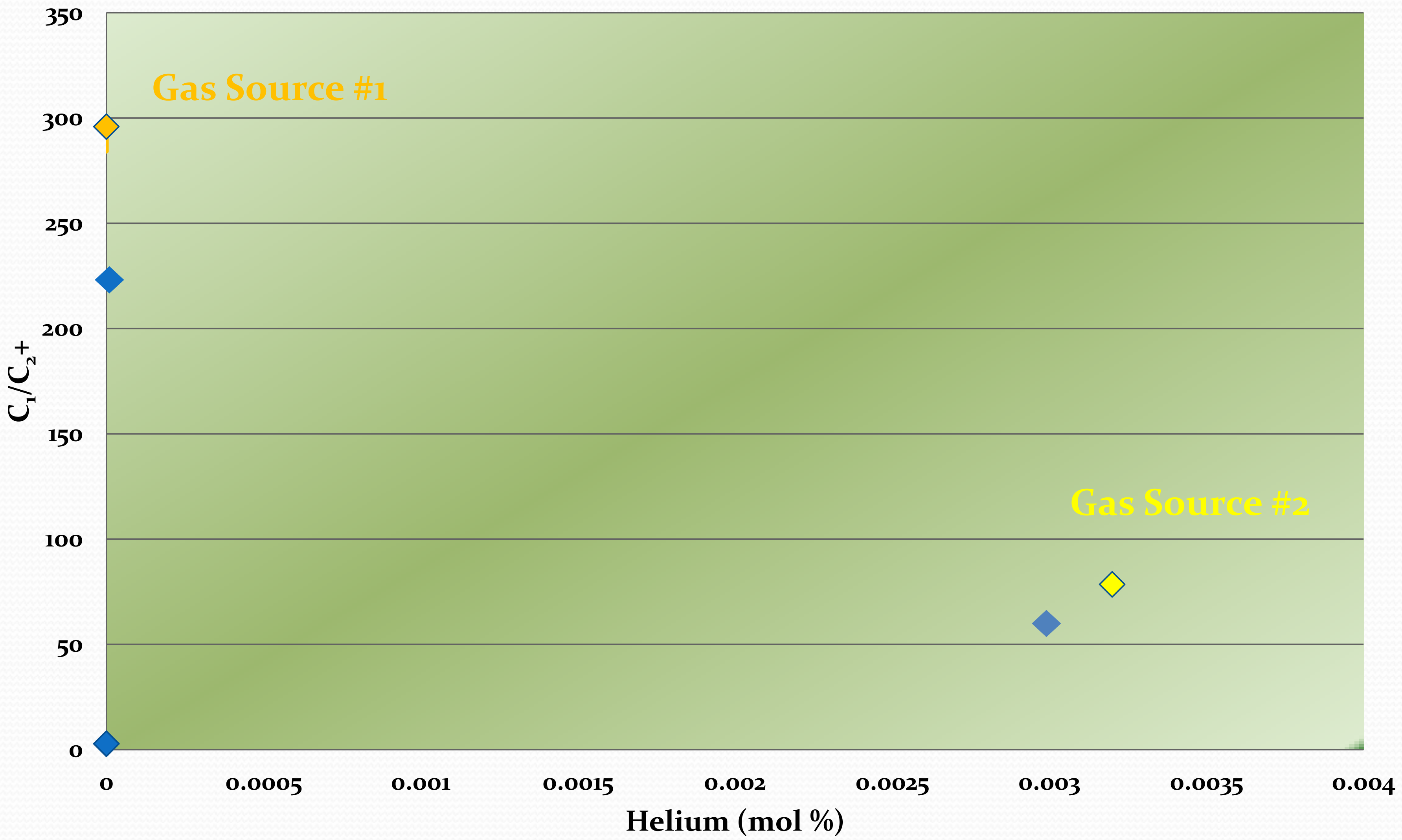
n/a denotes not applicable

NTU denotes Nephelometric Turbidity Units

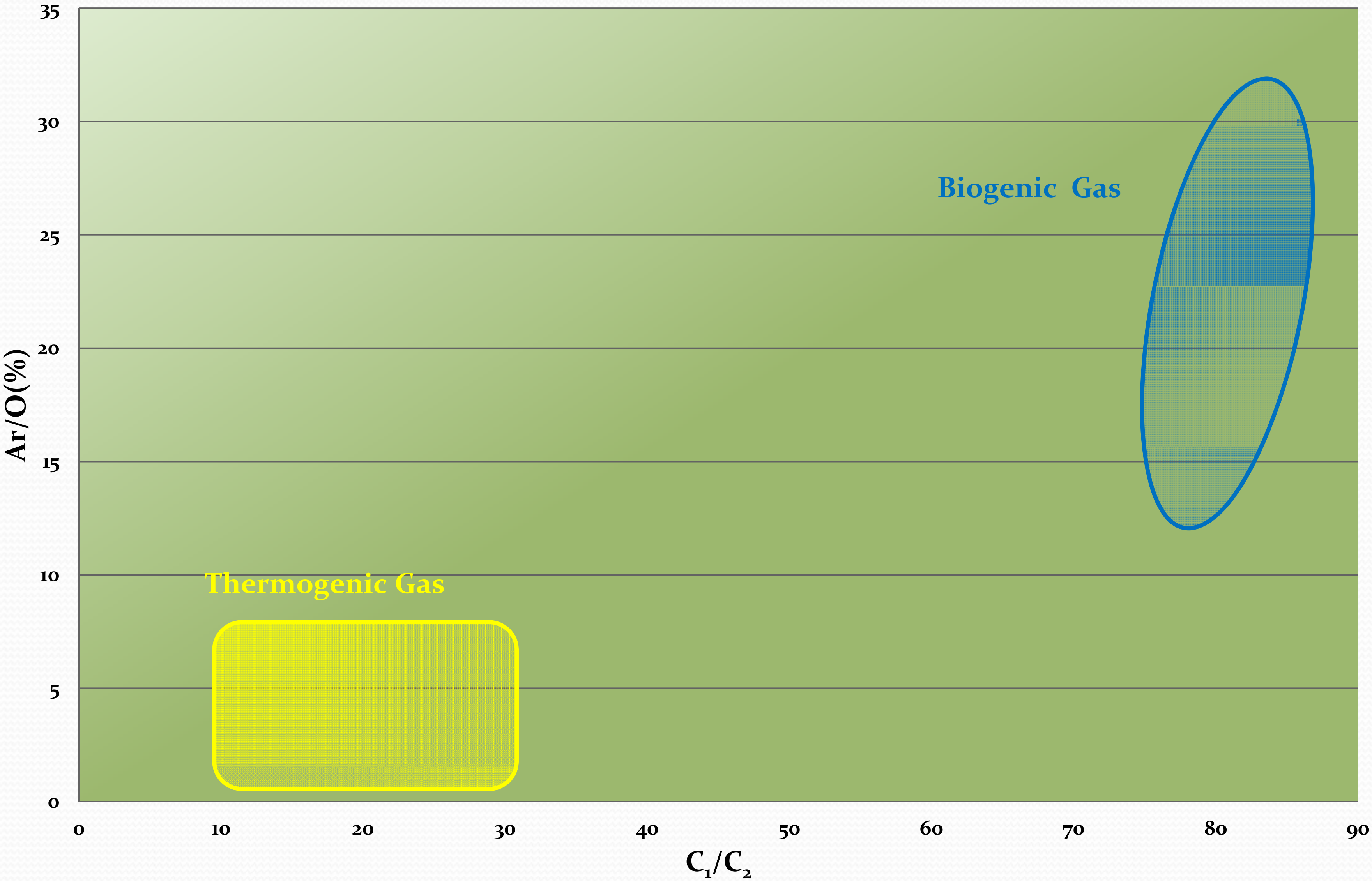
Gas Parameters

Parameter	Unit	Container
Methane	Mol %	Summa canister or equiv.
Ethane	Mol %	Summa canister or equiv.
Propane	Mol %	Summa canister or equiv.
I, N-Butane	Mol %	Summa canister or equiv.
I, N-Pentane	Mol %	Summa canister or equiv.
Hexane	Mol %	Summa canister or equiv.
Oxygen	Mol %	Summa canister or equiv.
Nitrogen	Mol %	Summa canister or equiv.
Hydrogen	Mol %	Summa canister or equiv.
Ethylene	Mol %	Summa canister or equiv.
Carbon Dioxide	Mol %	Summa canister or equiv.
Carbon Monoxide	Mol %	Summa canister or equiv.
Acetylene	Mol %	Summa canister or equiv.
Argon/Oxygen	Mol %	Summa canister or equiv.
Hydrogen Sulfide	ppm	Summa canister or equiv.
Helium	Mol % or ppm	Summa canister or equiv.
Hydrogen Isotopes ($\delta^2H_{C1}/^1H_{C1}$)	per mil	Summa canister or equiv.
Hydrogen Isotopes ($\delta^2H_{C2}/^1H_{C2}$)	per mil	Summa canister or equiv.
Carbon Isotopes ($\delta^{13}C_{C1}/^{12}C_{C1}$)	per mil	Summa canister or equiv.
Carbon Isotopes ($\delta^{13}C_{C2}/^{12}C_{C2}$)	per mil	Summa canister or equiv.
VOC by Method TO-15	ppbv	Summa canister or equiv.
Specific Gravity		
BTU/cu. ft.		

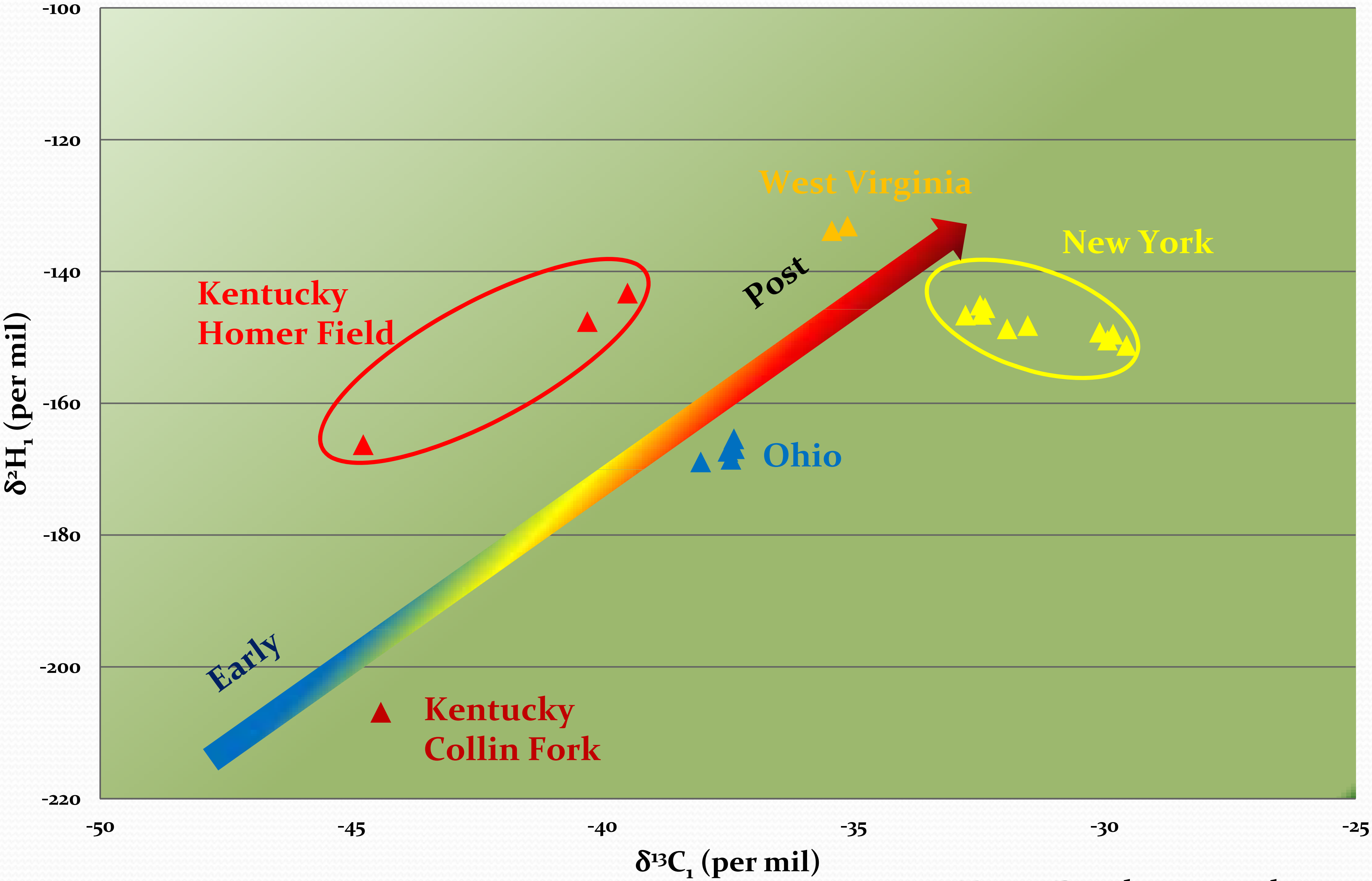
Helium vs Methane/Ethane +



Thermogenic and Biogenic Gas
C_1/C_2 vs Ar/O

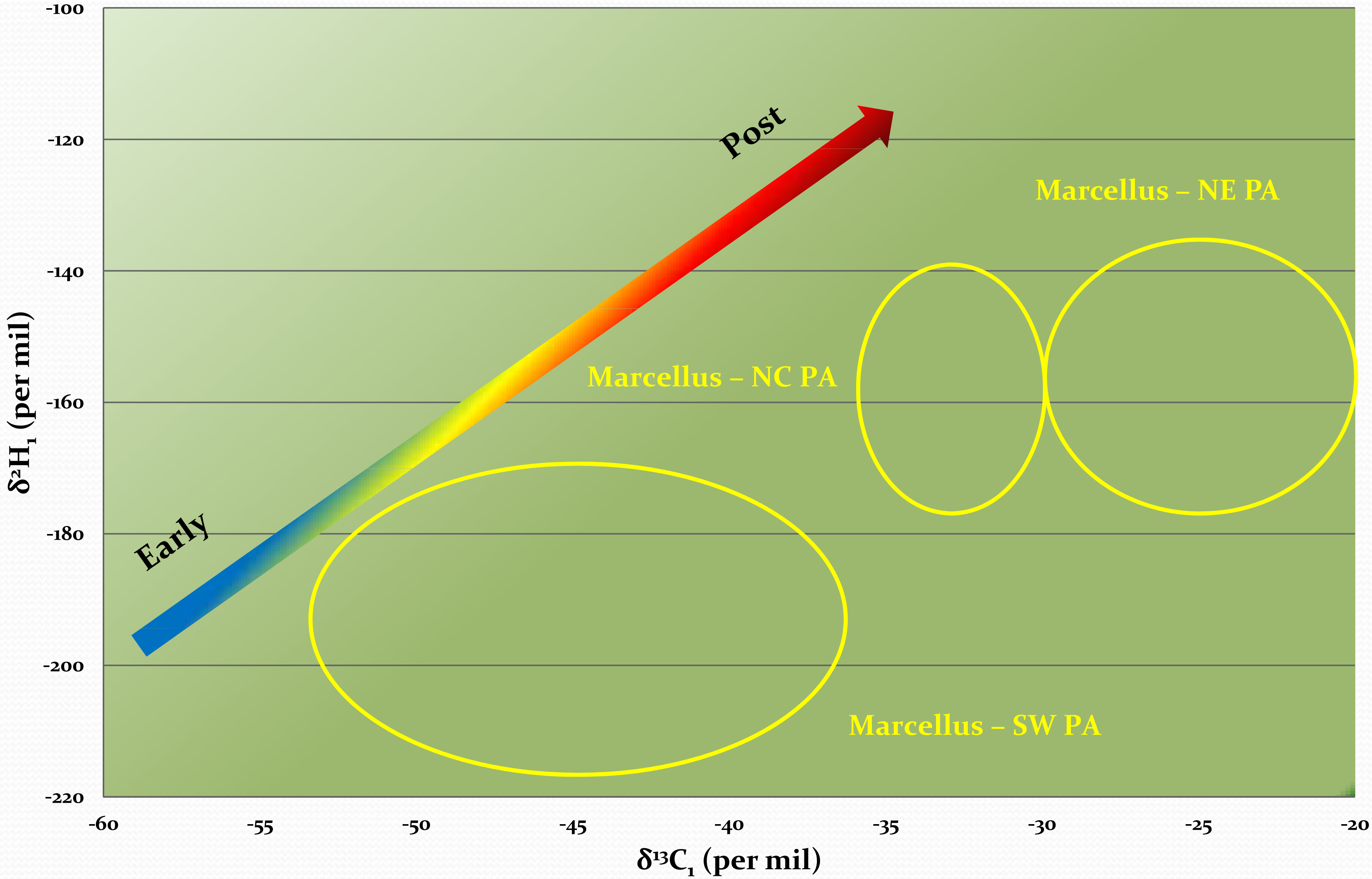


Stable Isotope Signatures/Maturity of Trenton Natural Gases
Appalachian Basin

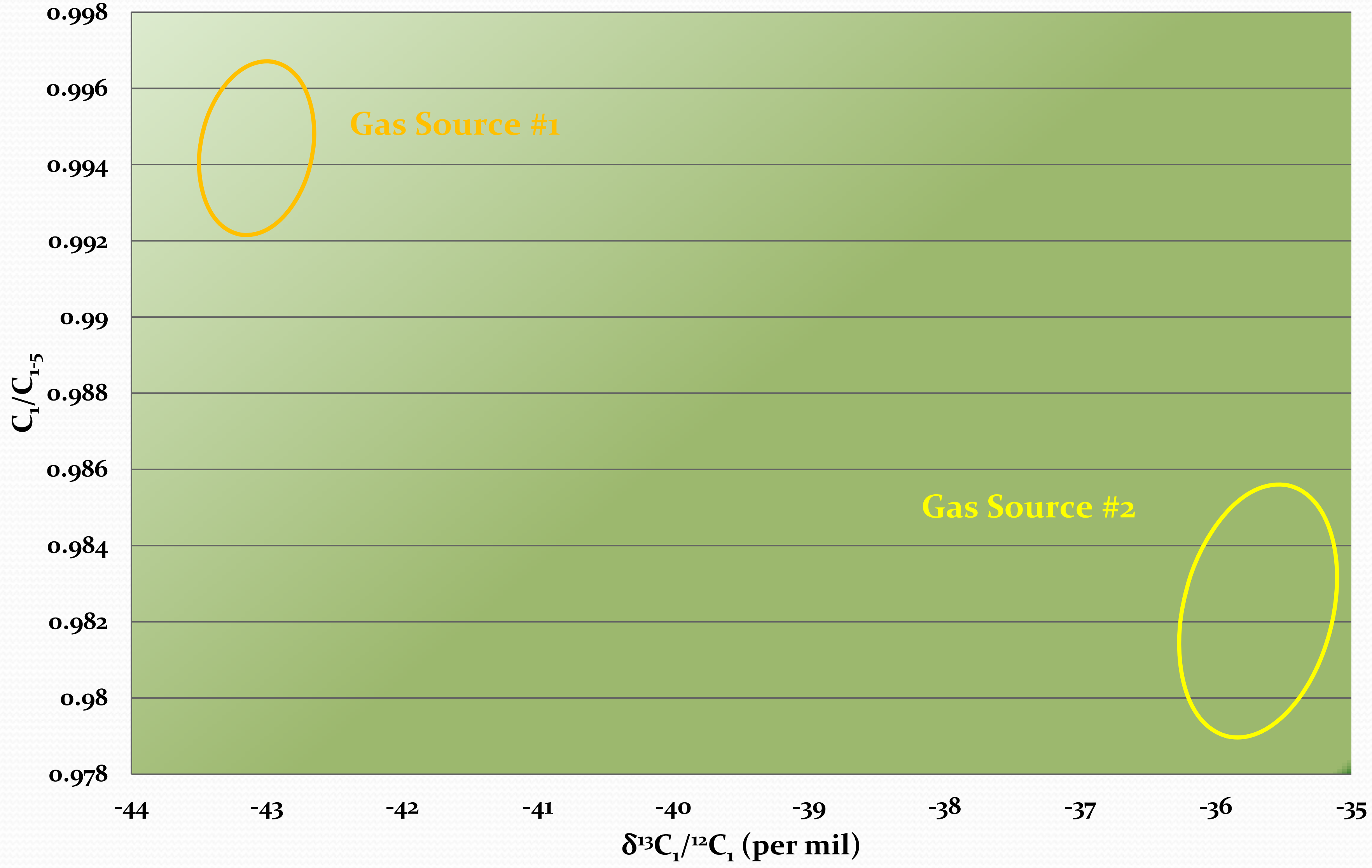


From Patchen, et. al., 2005

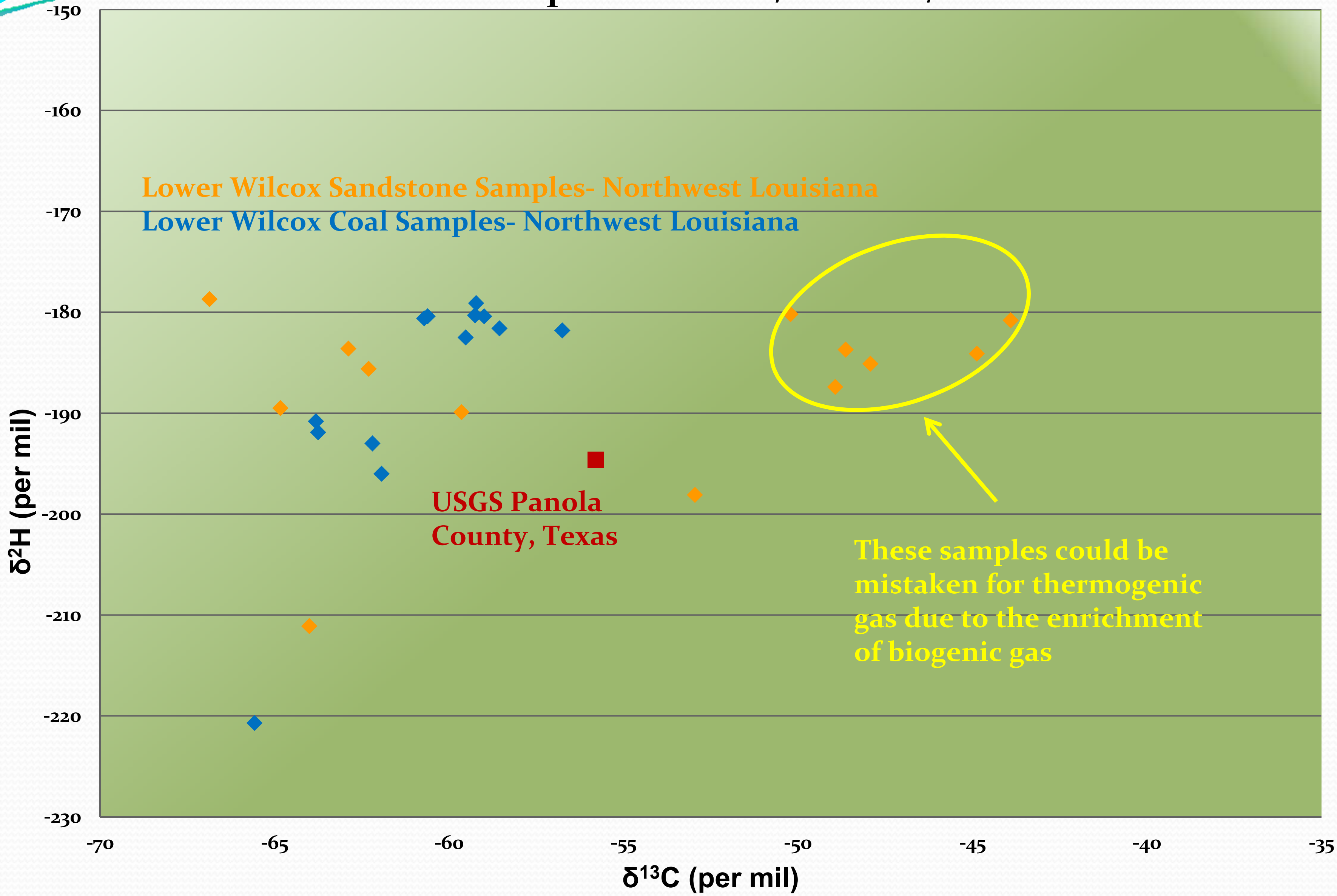
Stable Isotope Signatures of Natural Gases
Appalachian Basin



$\delta^{13}C_1$ vs Gas Wetness Fraction



Lower Wilcox Sandstone and Coal Samples
Stable Isotope Results $^{13}C/^{12}C$ vs $^{2}H/^{1}H$



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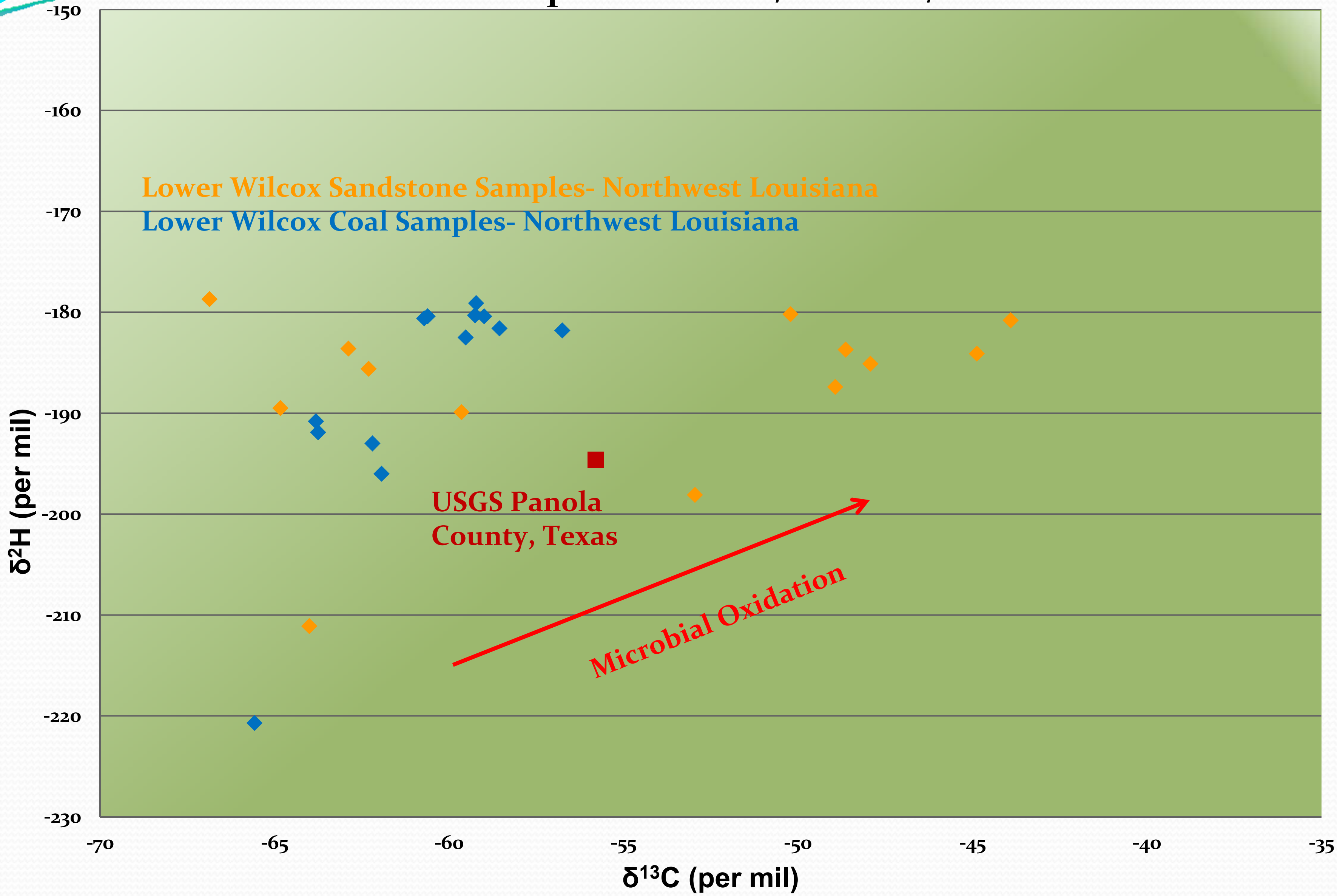


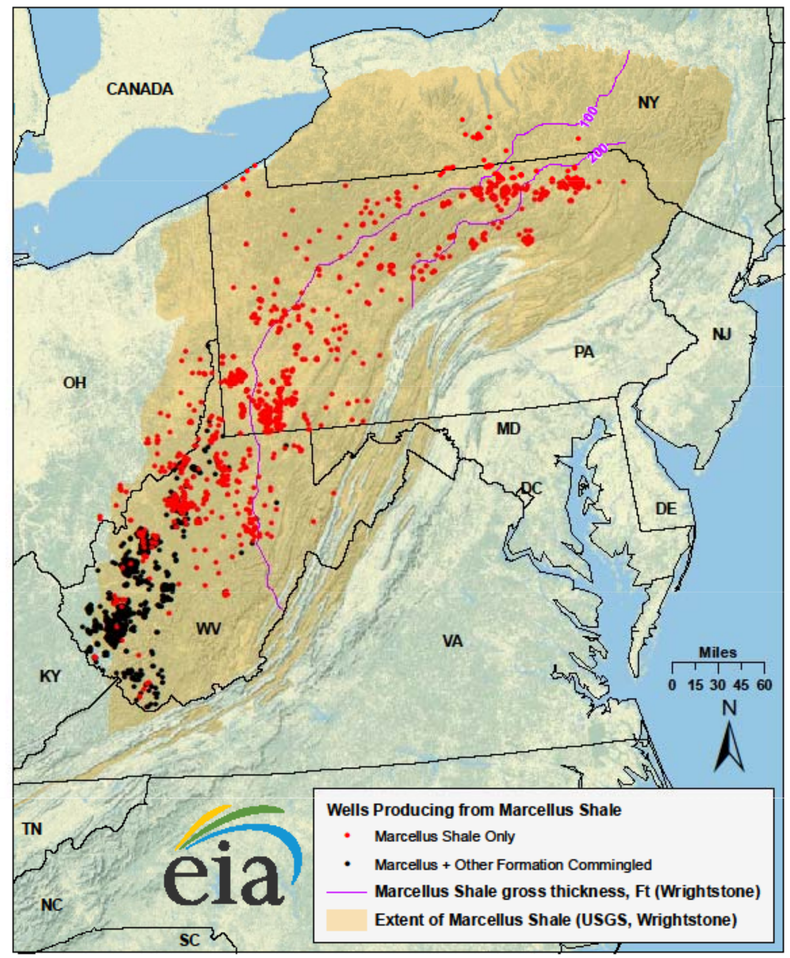
Caution with Isotopes

- Microbial oxidation may change signature
- Signature of source may vary over distance
- Mixing of gases can create interpretation problems
- Isotope “reversal”
- Production signature may change over time
- Failure to identify all potential sources of methane
- Comingling of natural gas from different formations

Mixing of Different Gas Sources

- Note Black Dots
- These represent mixing of natural gas of Marcellus and other gas source in gas wells
- This mixing of different gases could complicate differentiating sources of methane

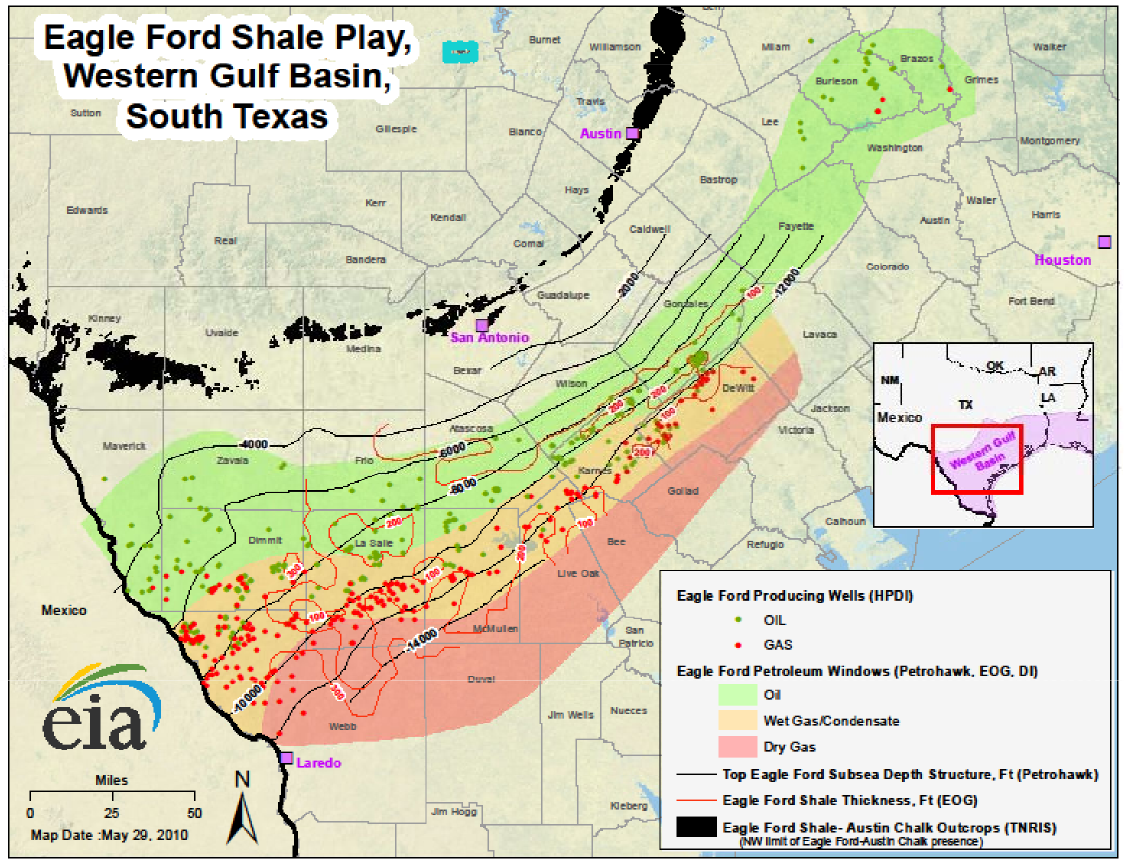
Marcellus Shale Gas Play, Appalachian Basin



Source: US Energy Information Administration based on data from WVGES, PA DCNR, OH DGS, NY DEC, VA DMME, USGS, Wrightstone (2009). Only wells completed after 1-1-2003 are shown. Updated June 1, 2011

Different Gas Windows

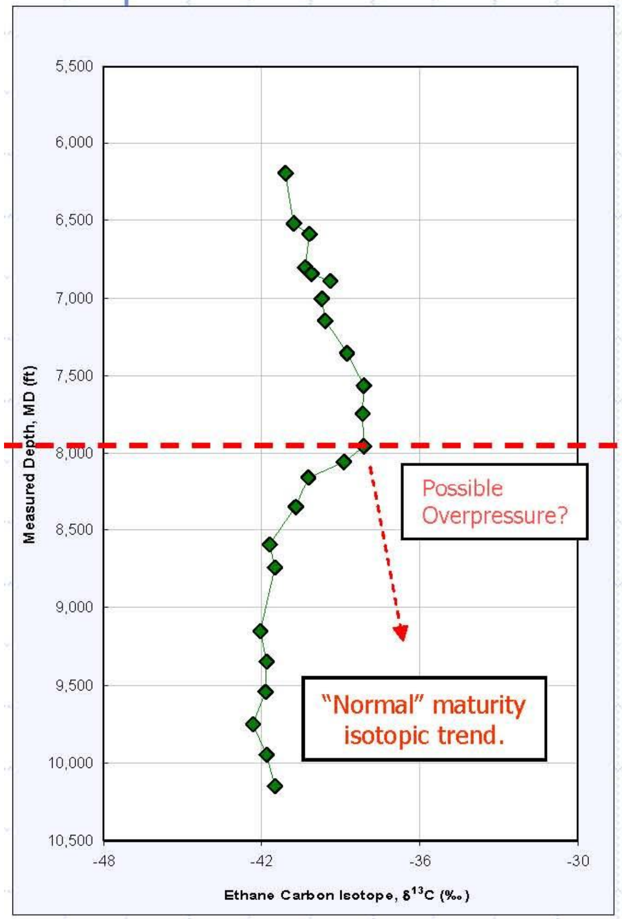
- Gas windows can change over short distances.
- In the Eagle Ford, three windows can occur in the same county.
- Gas associated with oil.
- Gas associated with condensate.
- Unassociated dry gas.
- These windows would be expected to exhibit differences in:
  - Mole fractions
  - Various ratios
  - Noble Gases
  - Thermal Maturity
  - Isotopic Signatures
  - Gas Wetness Fraction

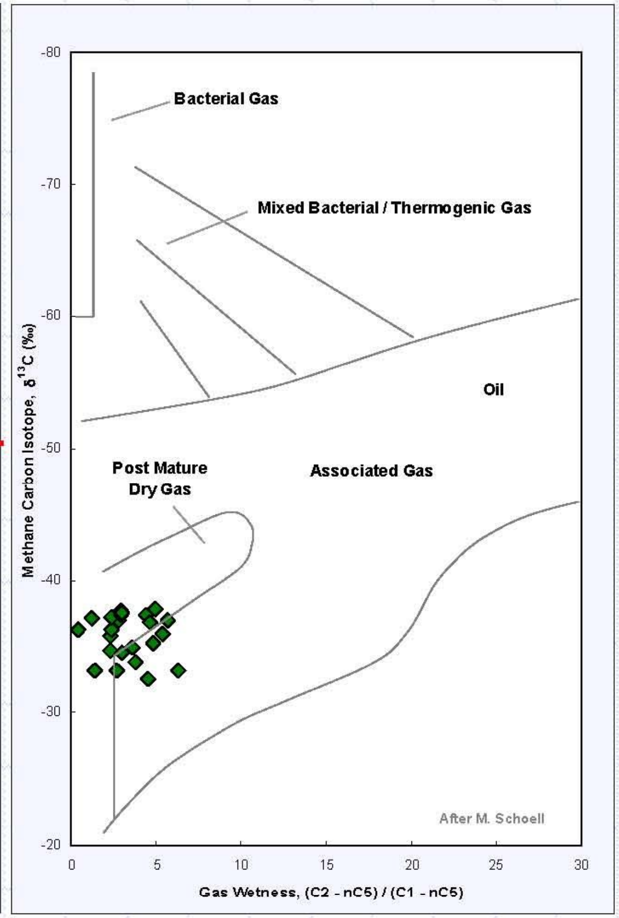


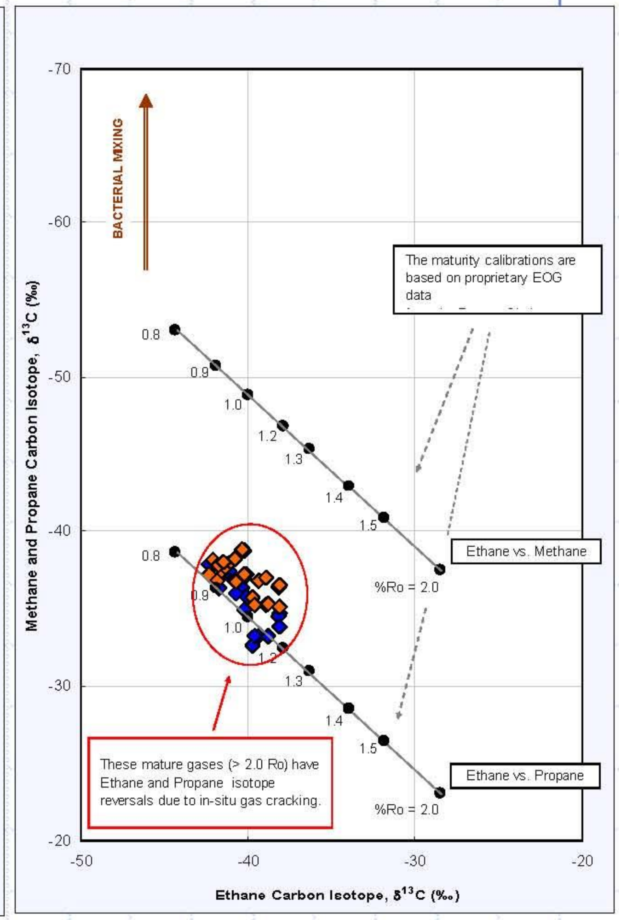
Isotope Reversals

- Isotope reversals are typically noted for C_1 and C_2 isotopes
- Reversals suggest:
- In-situ cracking
- Overpressure
- Little, if any, seepage of deeper gas to shallow layers

Marcellus Example (with Isotopic Reversal)

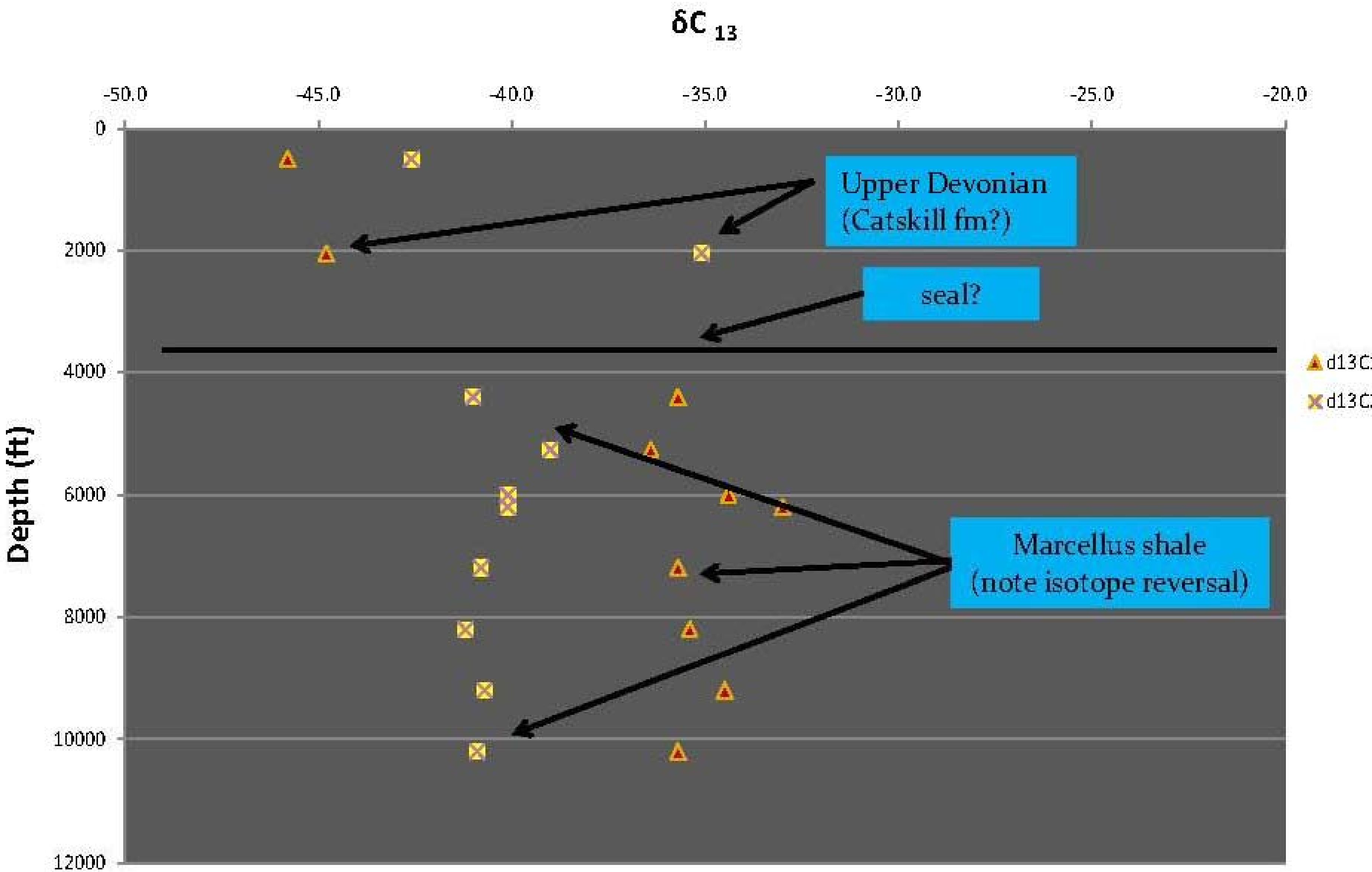






Ferworn, et. al., 2008

Marcellus gas well
Bradford County, PA



Baldassare, 2011

Conclusions

- CH_4 occurs ***naturally*** in many geological environments
- CH_4 occurrence can be natural or anthropogenic related
- Need to thoroughly understand all possible sources of CH_4
- Potential sources can be pipelines, old wells, landfills, swamp gas, glacial material high in organic content, mines, gas storage reservoirs, etc.
- Baseline study is imperative to determine existence of gas
- Baseline study needs to determine the signature of the gas
- Forensic tools include mole fractions, isotopes, and various ratios and relationships
- Without baseline data, it may not be possible to conclusively determine source of gas, especially if mixing of different gases may occur