Covariation of carbon and hydrogen isotopic compositions in natural gas: separating biogenic, thermogenic, and abiotic (inorganic CO_2 reduction) sources

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“I believe in natural gas as a clean, cheap alternative to fossil fuels.”

“Natural gas is cheap, abundant and clean compared to fossil fuels.”

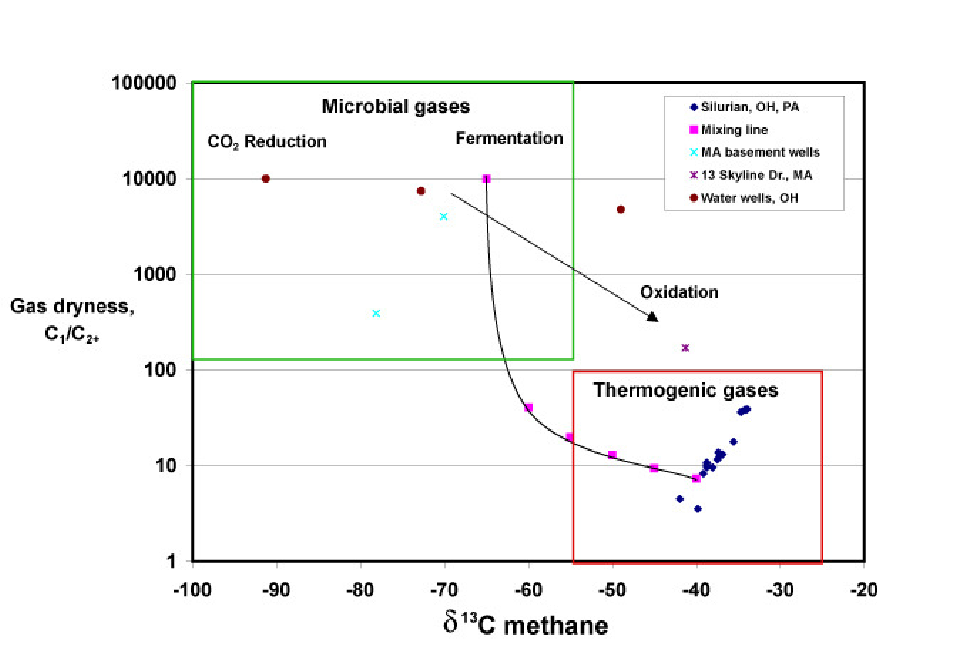
- Nancy Pelosi on Meet the Press, August 2009

Correlating natural gases in groundwater, shows, and seeps to subsurface accumulations or to possible source rocks can be difficult:

- A range of processes affect gas composition
- A limited number of variables were used to characterize gas in the past

Stable isotopes of carbon and hydrogen:

- C1 – C5
- Provide maximum possible information on:
  - Origin
  - Mixing
  - alteration



Goals

- Distinguish gas sources
  - Thermogenic
  - Biogenic (microbial)
  - Abiotic CO_2 reduction, Fischer - Tropsch reactions
- Identify alteration processes
  - Mixing
  - Raleigh fractionation
- Consistency with theoretical kinetic models
- Use all possible measurements

Outline

- Basics
  - Gas generation processes
  - Isotope fractionation in hydrocarbons (HC)
- Standard displays of HC isotope data
  - Bernard plot
  - Schoell plot
  - Chung's natural gas plot (NGP)
- Examples of source, mixing, alteration
  - North Slope, Appalachians, New England
- Conclusion: ^{13}C and ^{2}H on all HC gases yield more information, and therefore stronger interpretations

Nomenclature

$$\delta = \left(\frac{R_x - R_{std}}{R_{std}} \right) \times 1000$$

δ units: parts per thousand, per mil or ‰

Where:

R_x = $^{13}C/^{12}C$ or $^{2}H/^{1}H$ (also D/H) in sample

and

R_{std} = ratio in standard: $^{13}C/^{12}C$, PDB; $^{2}H/^{1}H$, VSMOW

$$\alpha_{A\text{-}B} = \frac{R_A}{R_B}$$

$$\alpha_{A\text{-}B} = K^{1/n}$$

Where K is the equilibrium constant for the exchange reaction for n atoms exchanged

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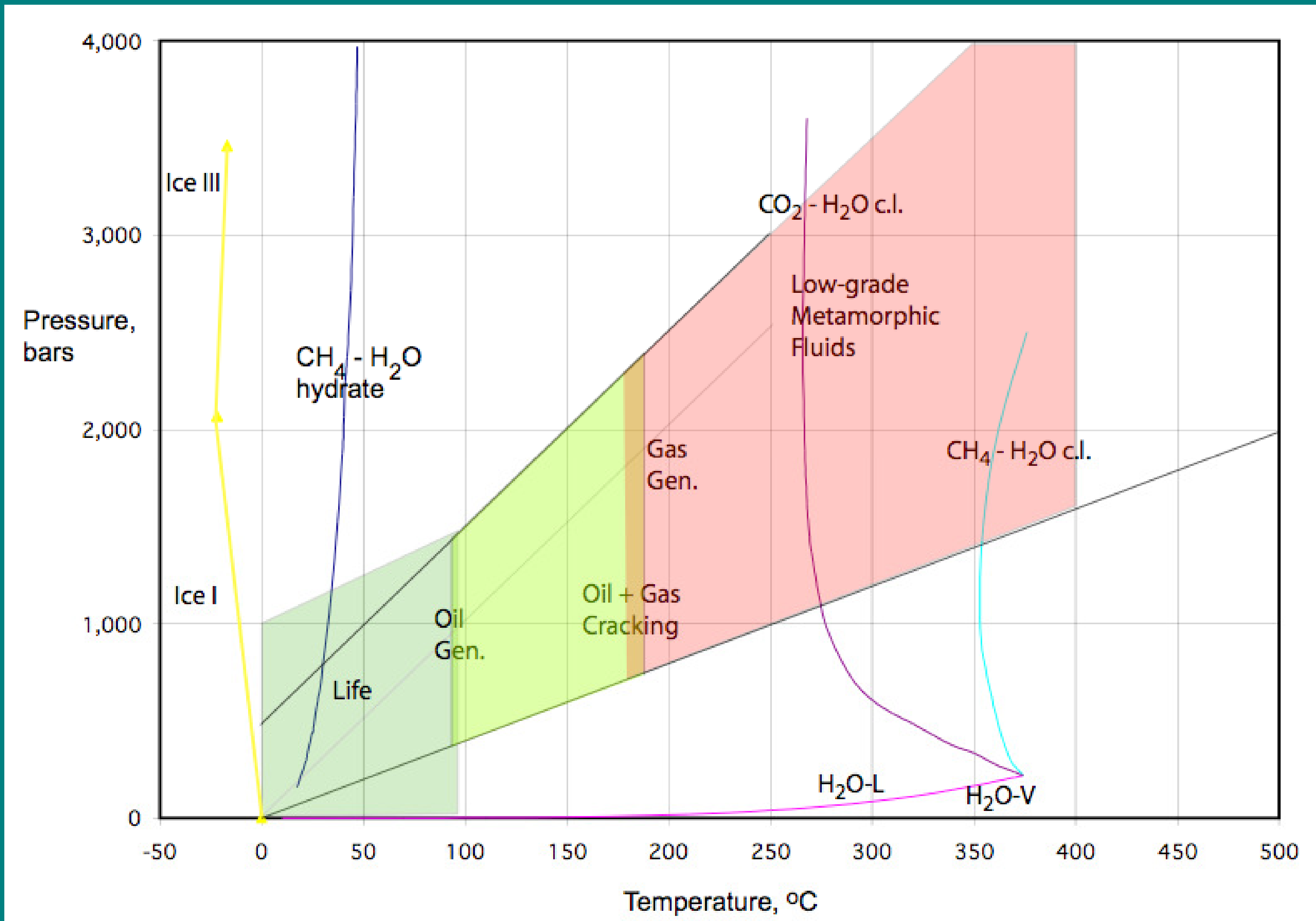
Organic Reaction Facies



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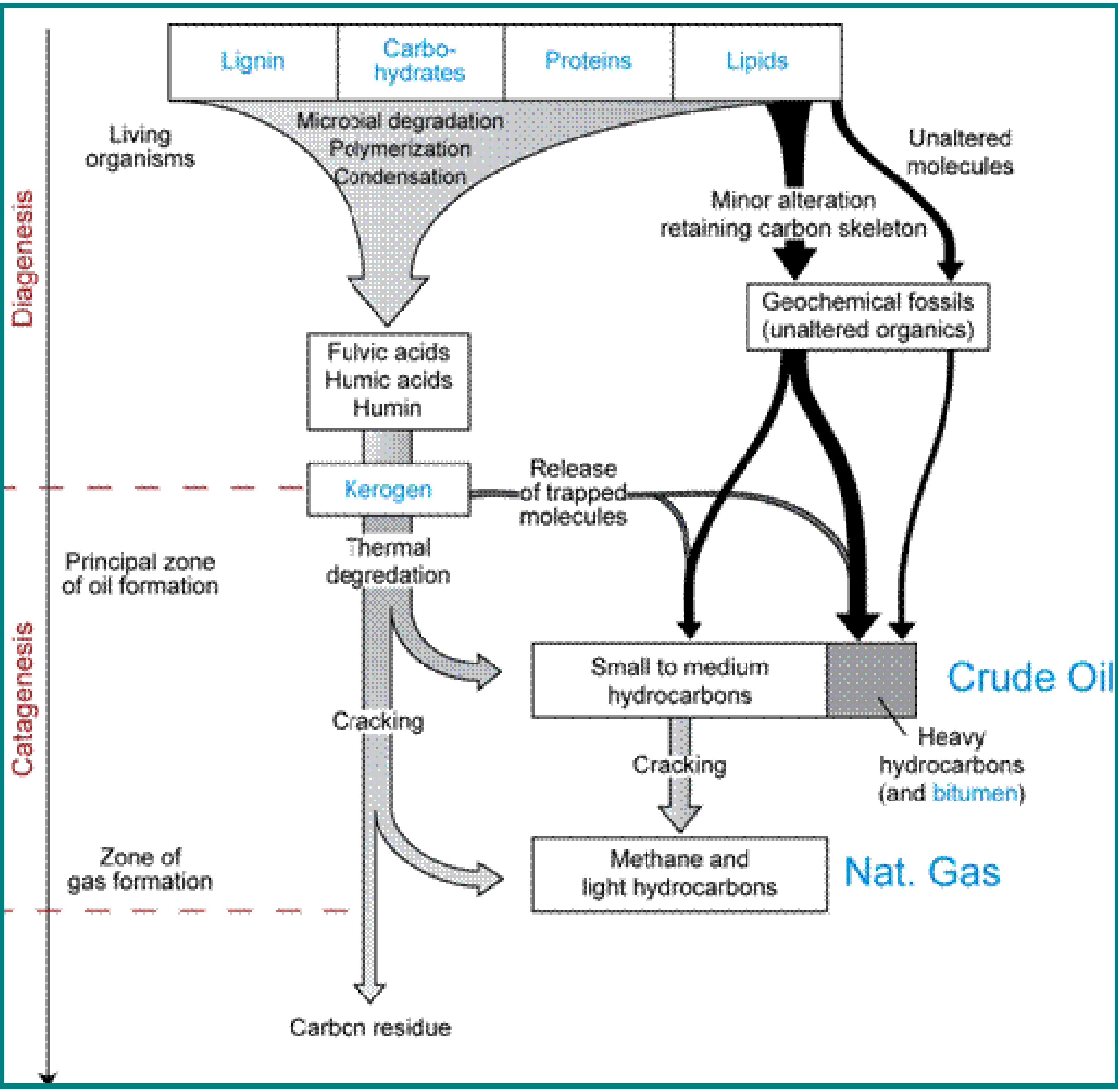
THE MAJOR SOURCES OF HYDROCARBON NATURAL GASES:

- Methanogenic bacteria
- All types of kerogen
- Coal
- Oil in source and reservoir rocks

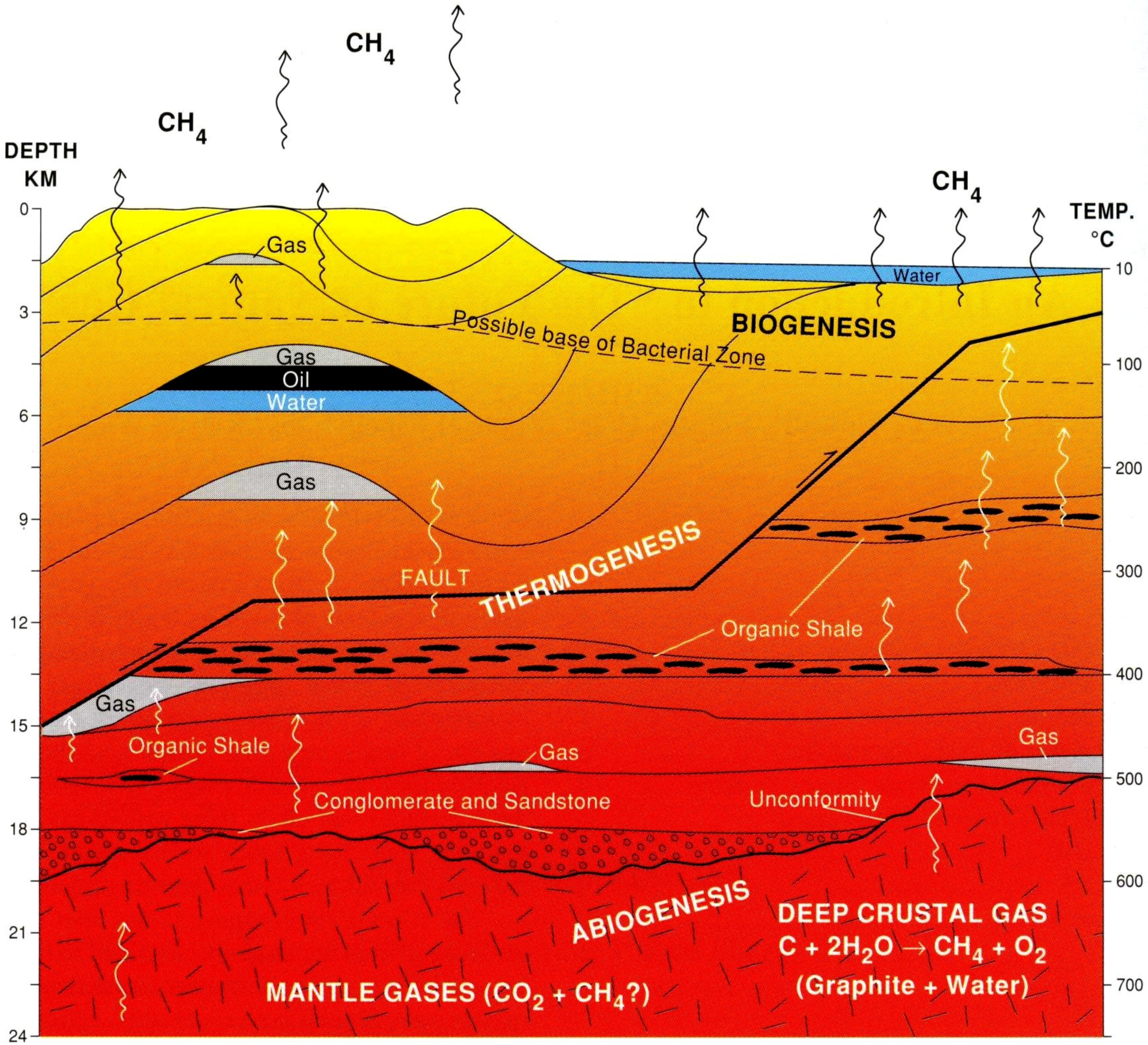
Sources of natural gas:

- The major nonhydrocarbon gases - CO_2, H_2S, and N_2 – are formed by both organic and inorganic processes. Associated He and Ar originate in both the crust and mantle.
- All known commercial hydrocarbon gas accumulations are biogenic in origin:
  - Decomposition of organic matter in the earth's crust
  - No known commercial abiogenic methane accumulations exist based on stable isotope measurements.



Lignin
Carbo-hydrates
Proteins
Lipids
Living organisms
Microbial degradation
Polymerization
Condensation
Unaltered molecules
Minor alteration retaining carbon skeleton
Geochemical fossils (unaltered organics)
Diagenesis
Fulvic acids
Humic acids
Humin
Kerogen
Release of trapped molecules
Thermal degradation
Principal zone of oil formation
Catagenesis
Small to medium hydrocarbons
Crude Oil
Cracking
Heavy hydrocarbons (and bitumen)
Cracking
Zone of gas formation
Methane and light hydrocarbons
Nat. Gas
Carbon residue

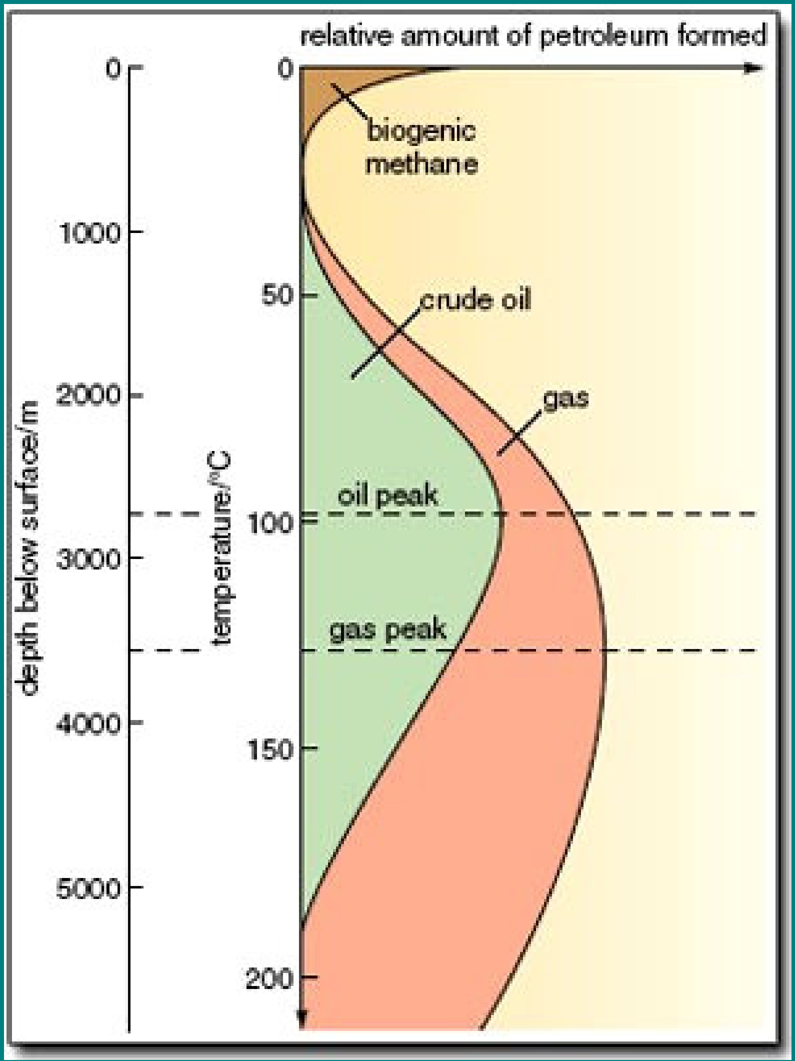
1984)



-Howell and others, 1993

Generation of gases from organic matter with increasing temperature:

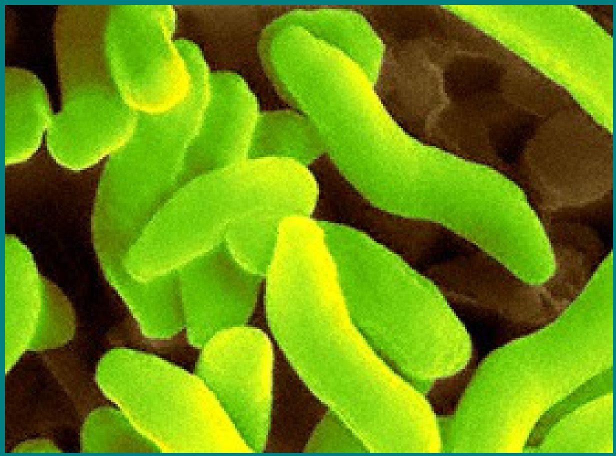
- Diagenesis:
  - microbial methane generation up to ~ 50° C
  - ~ 20% methane in conventional reservoirs
  - Important in some shale reservoirs in the Michigan and Illinois basins
- Primary cracking:
  - thermal cracking of kerogen and coal to generate methane
  - ~25% to 40% of gases
- Secondary cracking:
  - thermal cracking of oil
  - ~40% to 55% of gases
- Metagenesis?



- Hunt, 1996

Microbial Gas Generation

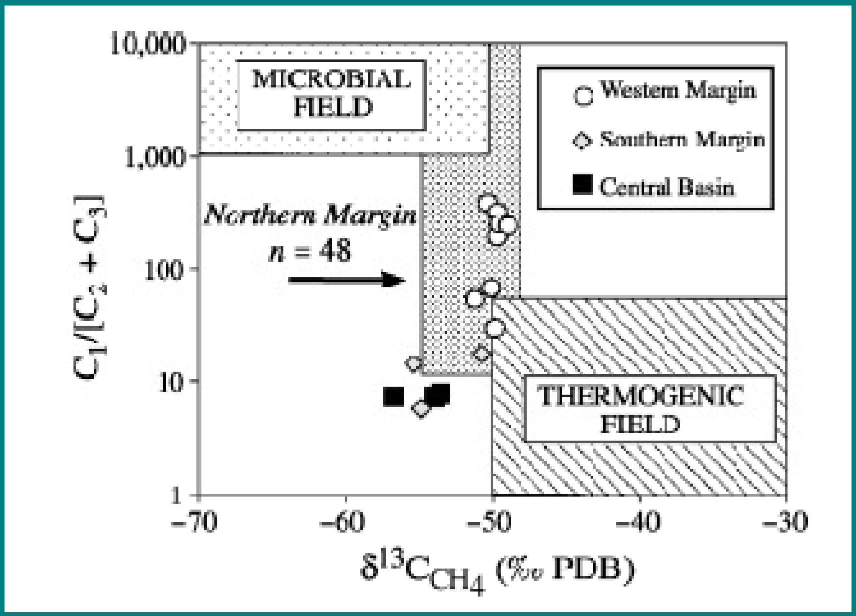
- *Biogenic* vs. *microbial* or *bacterial* gas
- $C_1/(C_2 + C_3) >> 100$
- $\delta^{13}C_1 < 60$ permil
- $\delta DC_1 < 150$ permil
- Covariance of δD values of formation water and CH_4
- Alkalinity of associated formation water (> 10 meq/kg)
- Positive $\delta^{13}C$ of DIC (> 10 permil)
- Microbial fermentation
- CO_2 reduction



Microbial Gas Generation

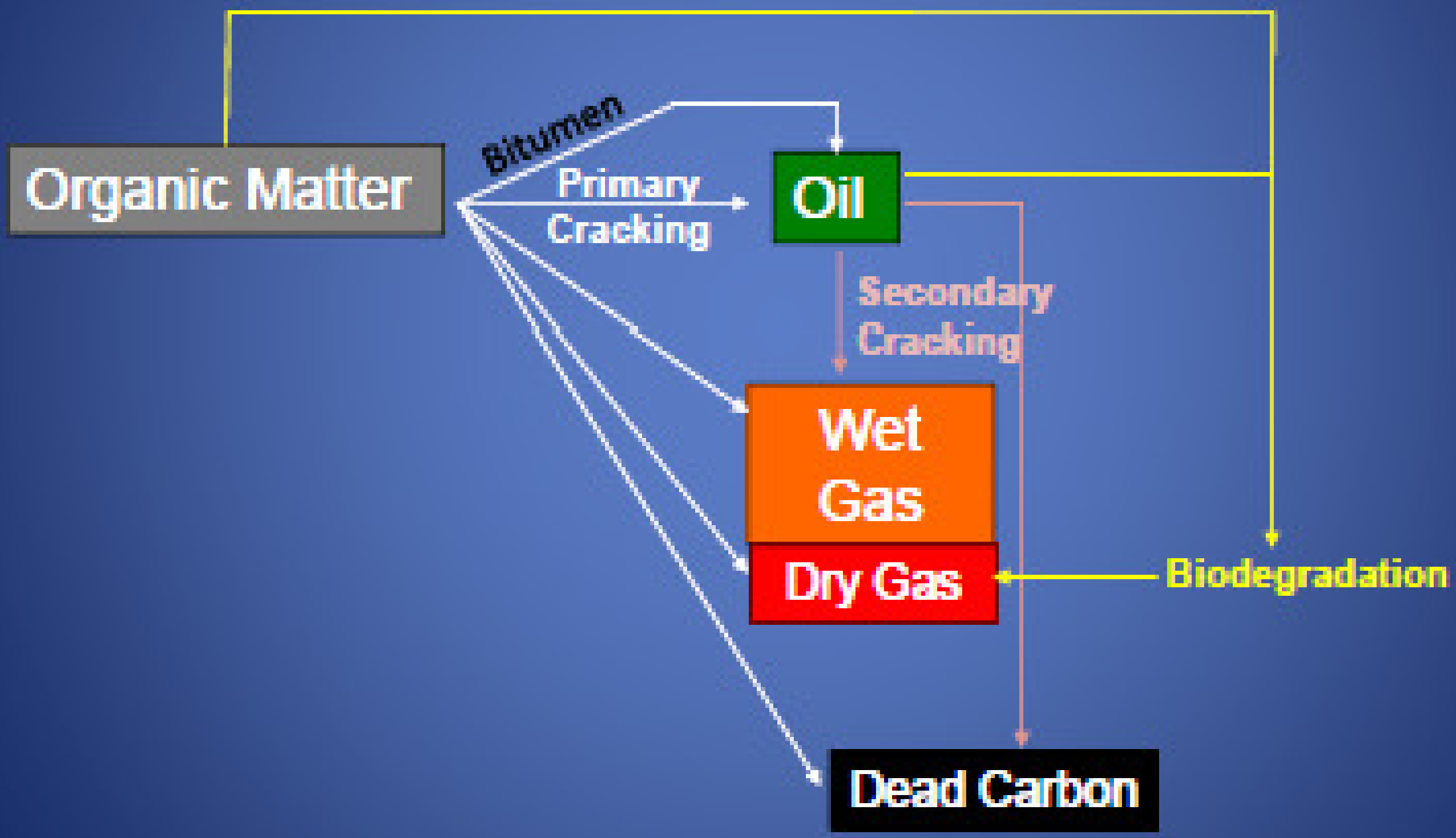
acetate fermentation : $CH_3COOH \rightarrow CH_4 + CO_2$ (reaction 1)

CO_2 reduction : $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$ (reaction 2)



Schematic of Oil and Gas Generation:

why is there more gas at higher thermal maturity?



CHO Reactions in Crustal Rocks

Cracking of sedimentary OM:

$$[(C_xH_y)\text{-}CH_3\ ]_{Kerogen} \text{--->} CH_4 + C_xH_{(y-1)}$$

$$[(C_xH_y)\text{-}C_2H_5\ ]_{Kerogen} \text{--->} C_2H_6 + C_xH_{(y-1)}$$

Anthracite grade:

$$C_{20}H_4 \text{--->} 19C + CH_4$$

$$C_{20}H_4 + 2H_2O \text{--->} 17C + 2CH_4 + CO_2$$

Graphite buffered, metamorphic fluids:

$$2C + 2H_2O = CH_4 + CO_2$$

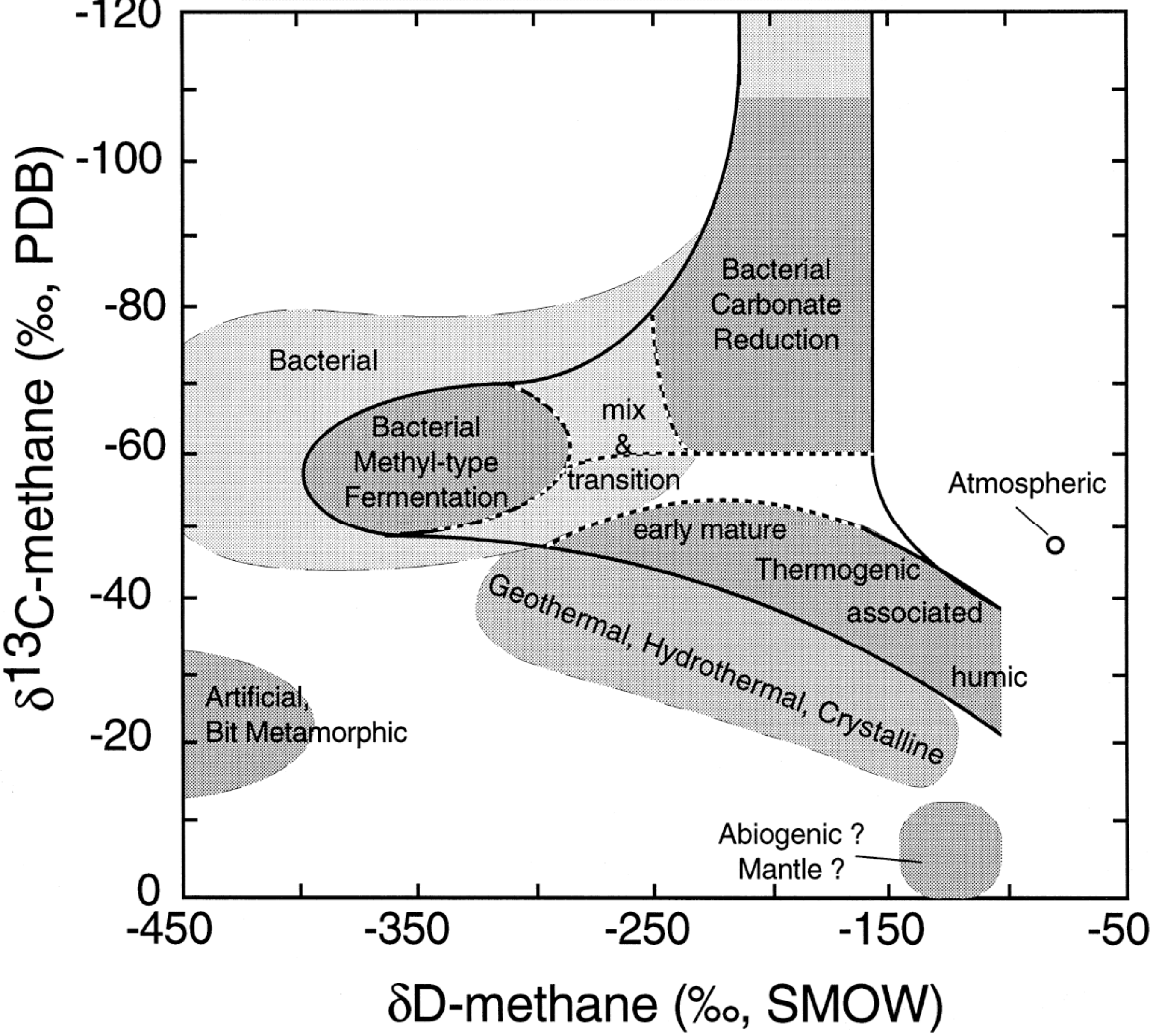
Fischer-Tropsch Type:

$$CO_2 + 4H_2 = CH_4 + 2H_2O$$

$$2CO_2 + 7H_2 = C_2H_6 + 4H_2O$$

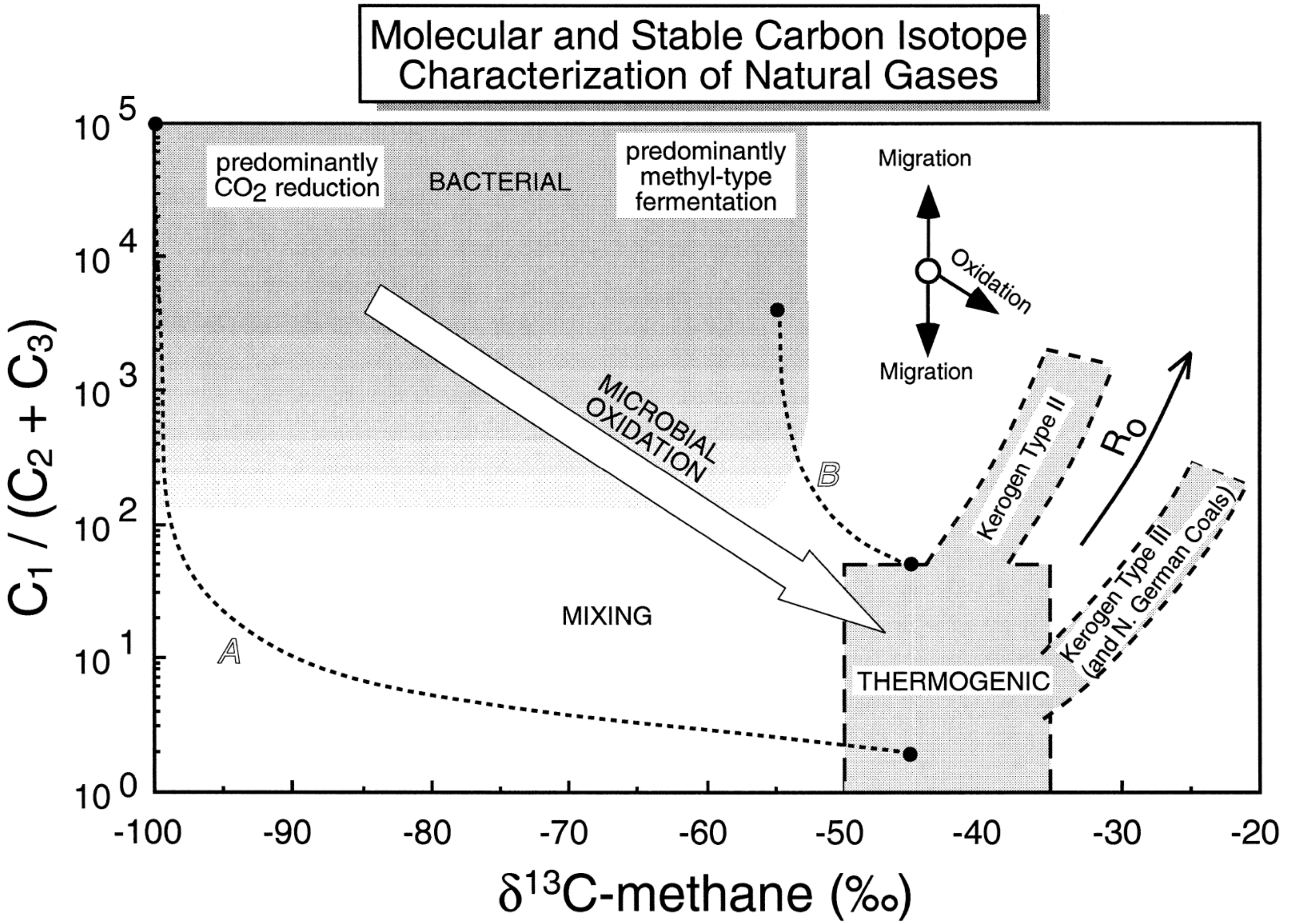
$$nCO_2 + (3n+1)H_2 = C_nH_{2n+2} + 2nH_2O$$

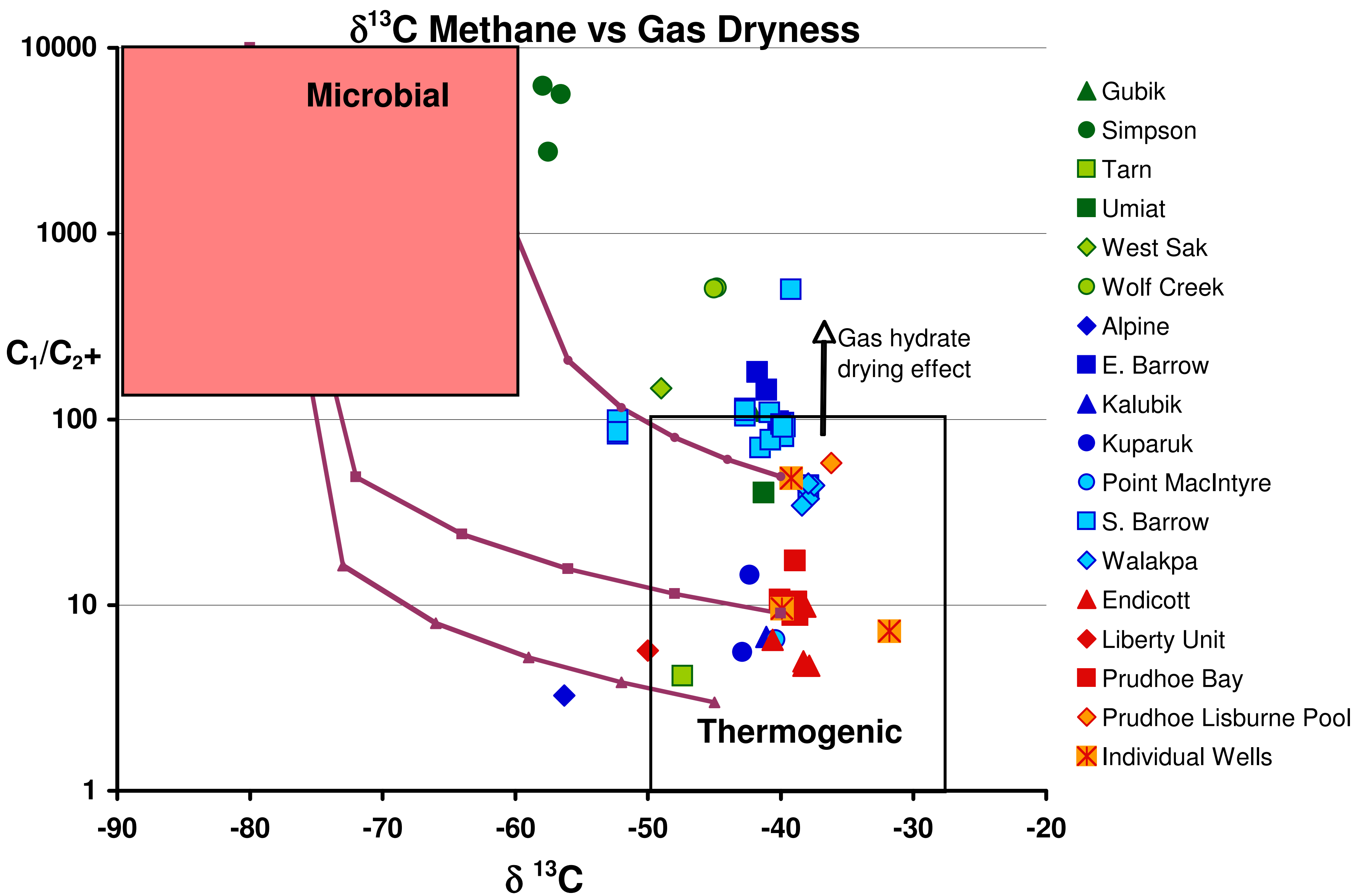
Schoell (Whiticar) diagram



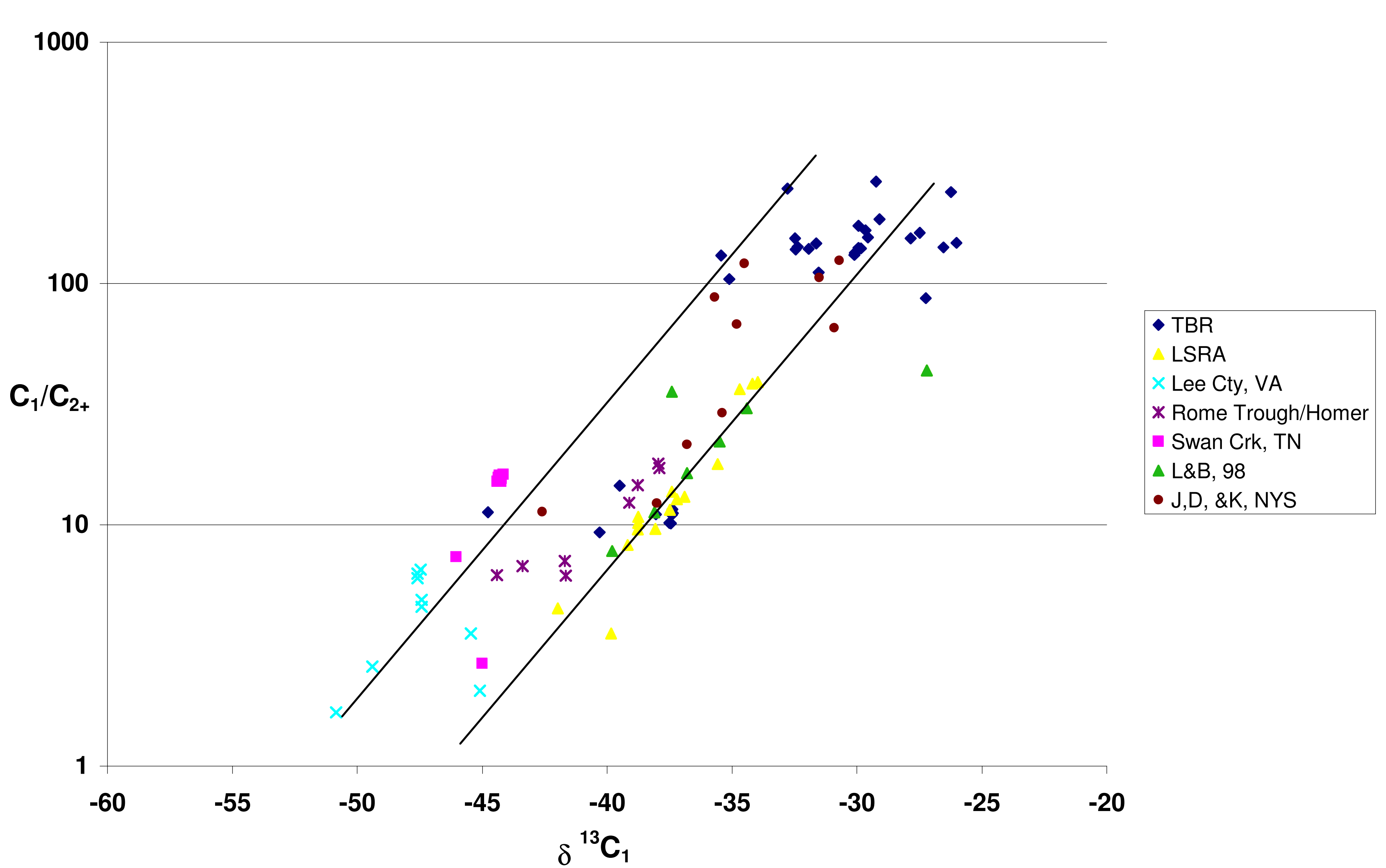
From Whiticar, 1999

Bernard diagram




δ13C Methane vs Gas Dryness
Microbial
Thermogenic
Gas hydrate
drying effect
C1/C2+
δ 13C
10000
1000
100
10
1
-90
-80
-70
-60
-50
-40
-30
-20
Gubik
Simpson
Tarn
Umiat
West Sak
Wolf Creek
Alpine
E. Barrow
Kalubik
Kuparuk
Point MacIntyre
S. Barrow
Walakpa
Endicott
Liberty Unit
Prudhoe Bay
Prudhoe Lisburne Pool
Individual Wells

Bernard plot



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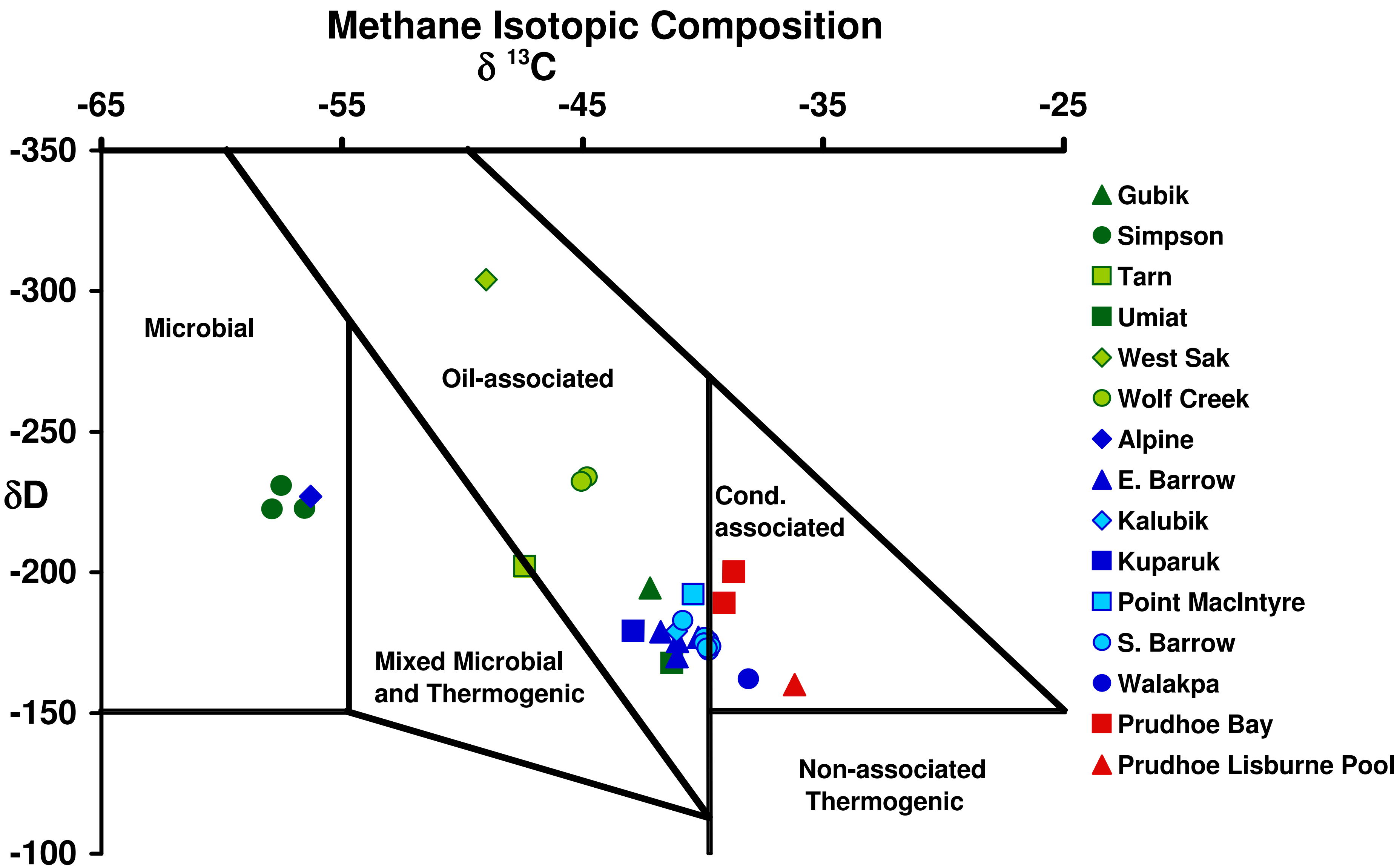

Methane Isotopic Composition
δ 13C
-65
-55
-45
-35
-25
-350
-300
-250
-200
-150
-100
δD
Microbial
Oil-associated
Cond. associated
Mixed Microbial and Thermogenic
Non-associated Thermogenic
Gubik
Simpson
Tarn
Umiat
West Sak
Wolf Creek
Alpine
E. Barrow
Kalubik
Kuparuk
Point MacIntyre
S. Barrow
Walakpa
Prudhoe Bay
Prudhoe Lisburne Pool

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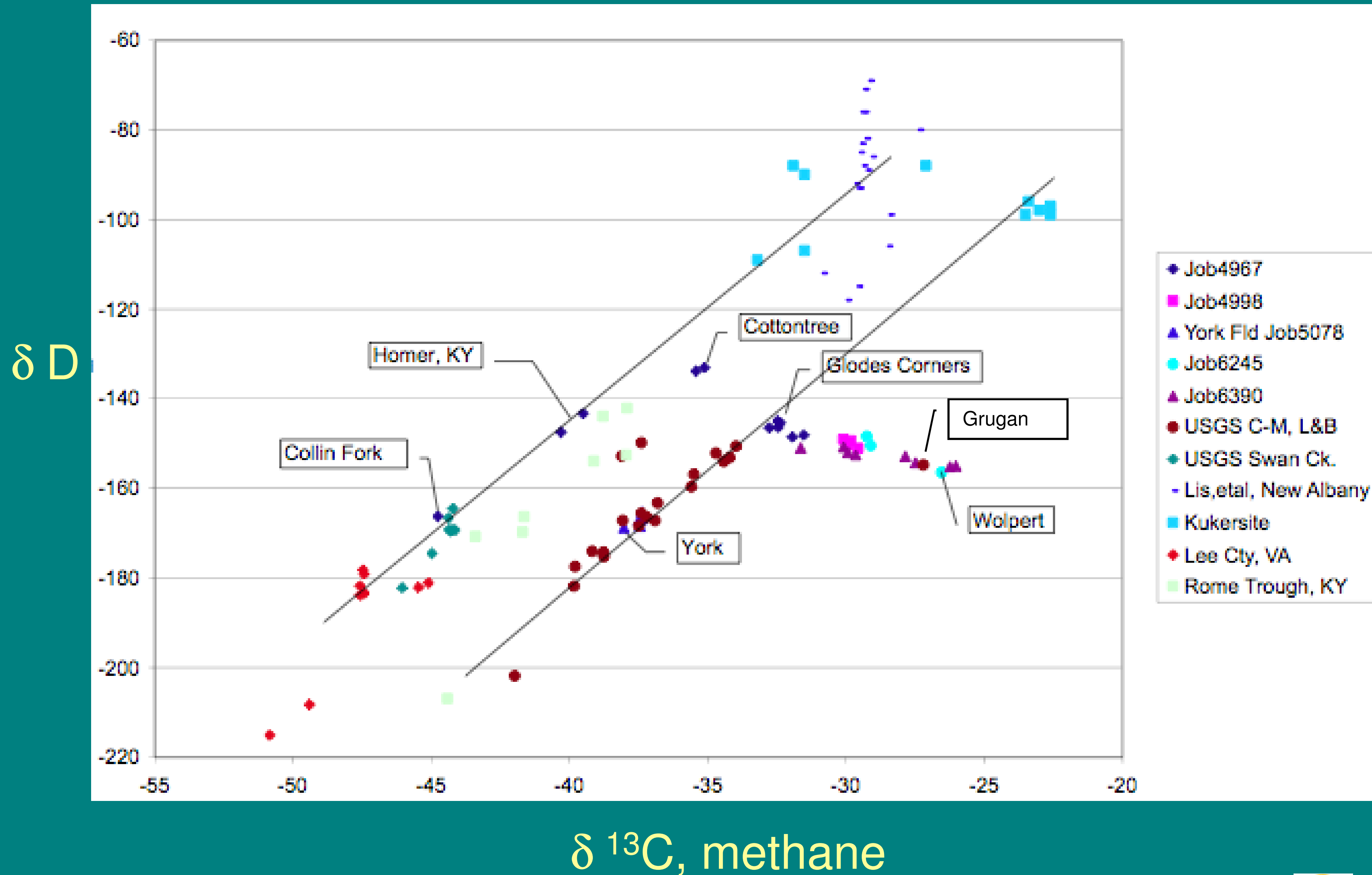
Lower Paleozoic gases compared to sources



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Chung, et al., 1988, cracking model and the natural gas plot (NGP)

- Consider cracking of gases from kerogen with homogeneous isotopic composition, $\delta^{13}C_p$
- All gases form by same reaction mechanism
- Parent molecules (kerogen or oil) are structurally similar
- No condensation reactions form gases

K_R - C
K_R - C - C
K_R - C - C - C
K_R - C - C - C - C
K_R - C - C - C - C - C
K_R - C - C - C - C - C - C
C_m
← C_p →
← C_n →

Isotopic composition of C_n

$$\delta^{13}C_n = [\delta^{13}C_m + (n-1)\ \delta^{13}C_p]/n$$

Rearranging:

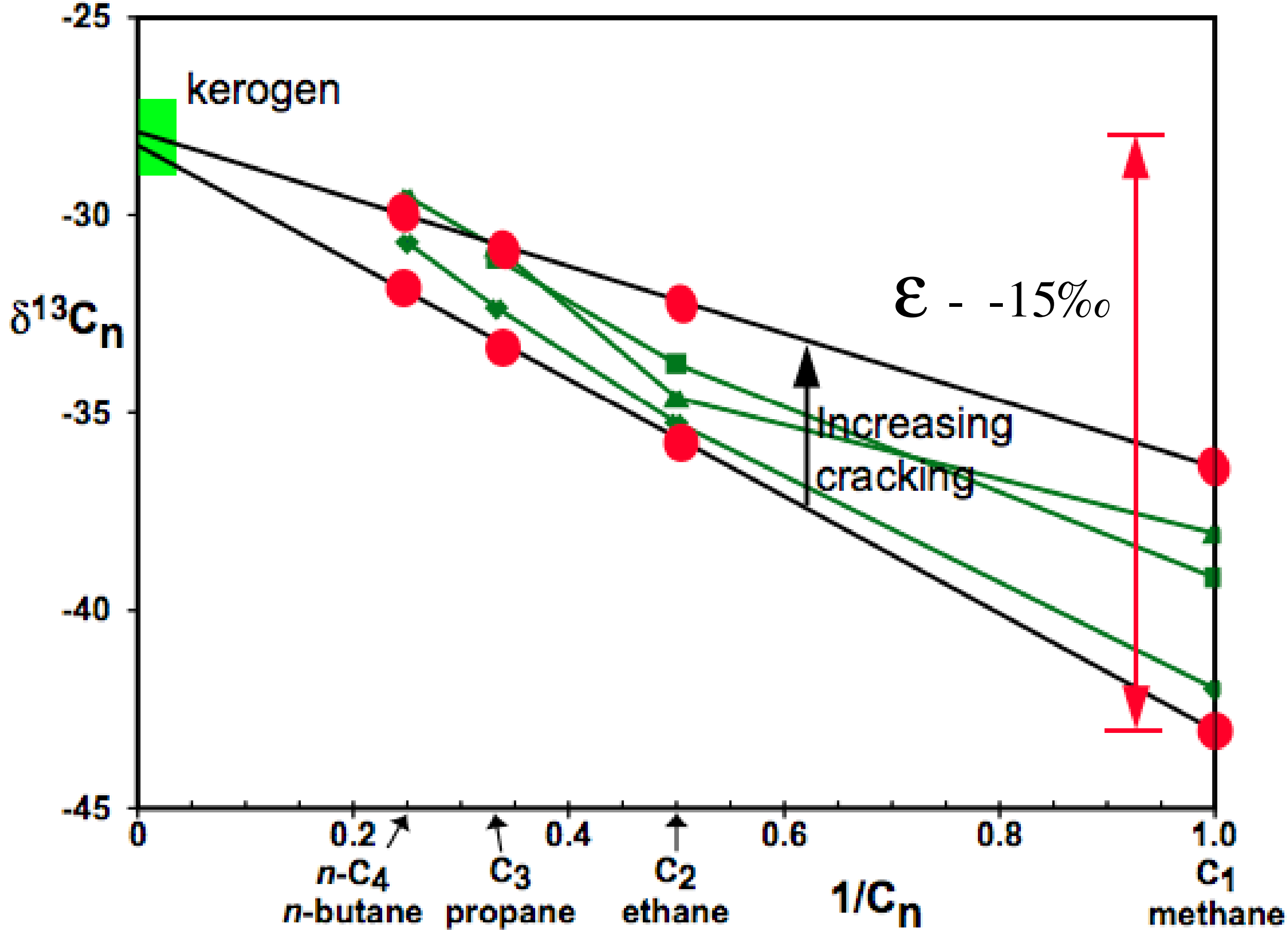
$$\delta C_n = -1/n(\delta C_p - \delta C_m) + \delta C_p$$

Where:
δC_p is $\delta^{13}C$ of parent
δC_m is $\delta^{13}C$ of link C
δC_n is $\delta^{13}C$ of gas molecule

Natural Gas Plot (Chung, et al.)

Theoretical kinetic isotope effects during cracking of gases from kerogen:

$$\delta^{13}C_n = -1/n(\varepsilon) + \delta^{13}C_{KER} \quad \text{where} \quad \varepsilon = \delta^{13}C_{KER} - \delta^{13}C_1$$



References:

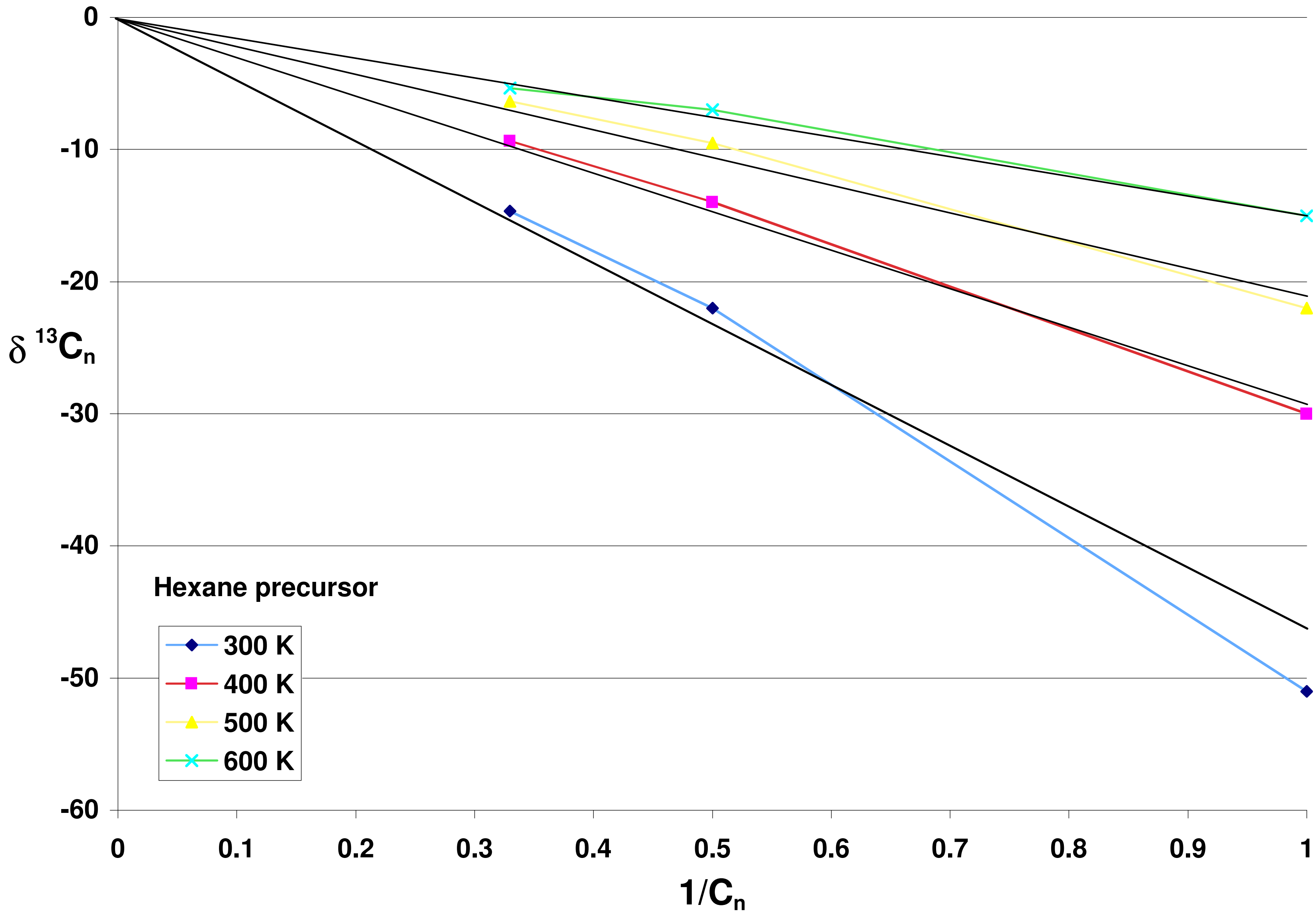
Chung, H. M, et al., 1988, Chem. Geol.

Rooney, M. A., et al., 1995, Chem. Geol.

Support from ab initio calculations:

Tang, et al., 2000, Geochem. Cosmo. Acta

Ab initio calculations, Y. Tang, et al., 2000, GCA, assuming non-cleaved C is 0 per mil



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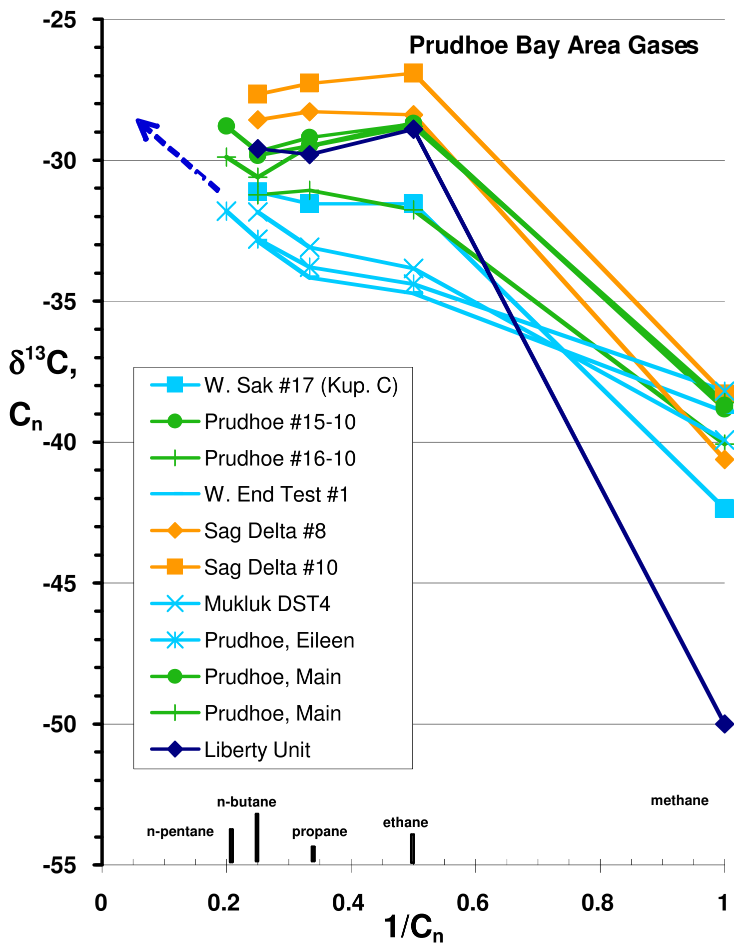
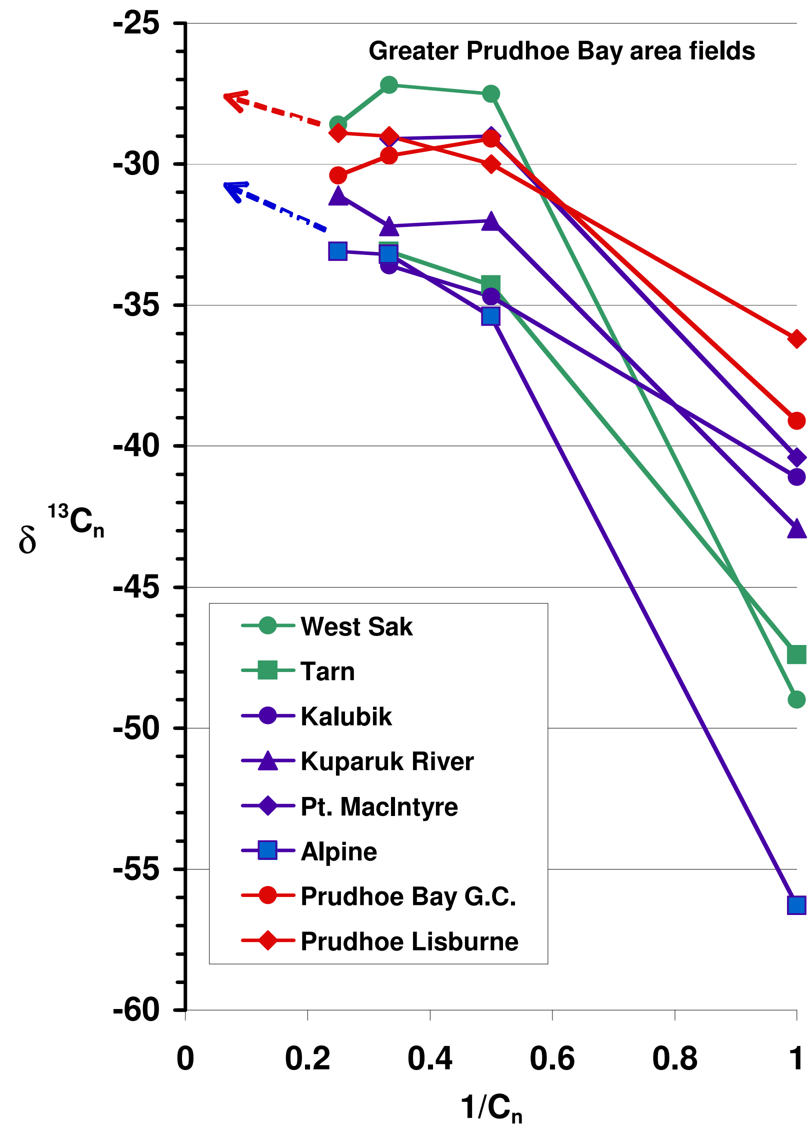
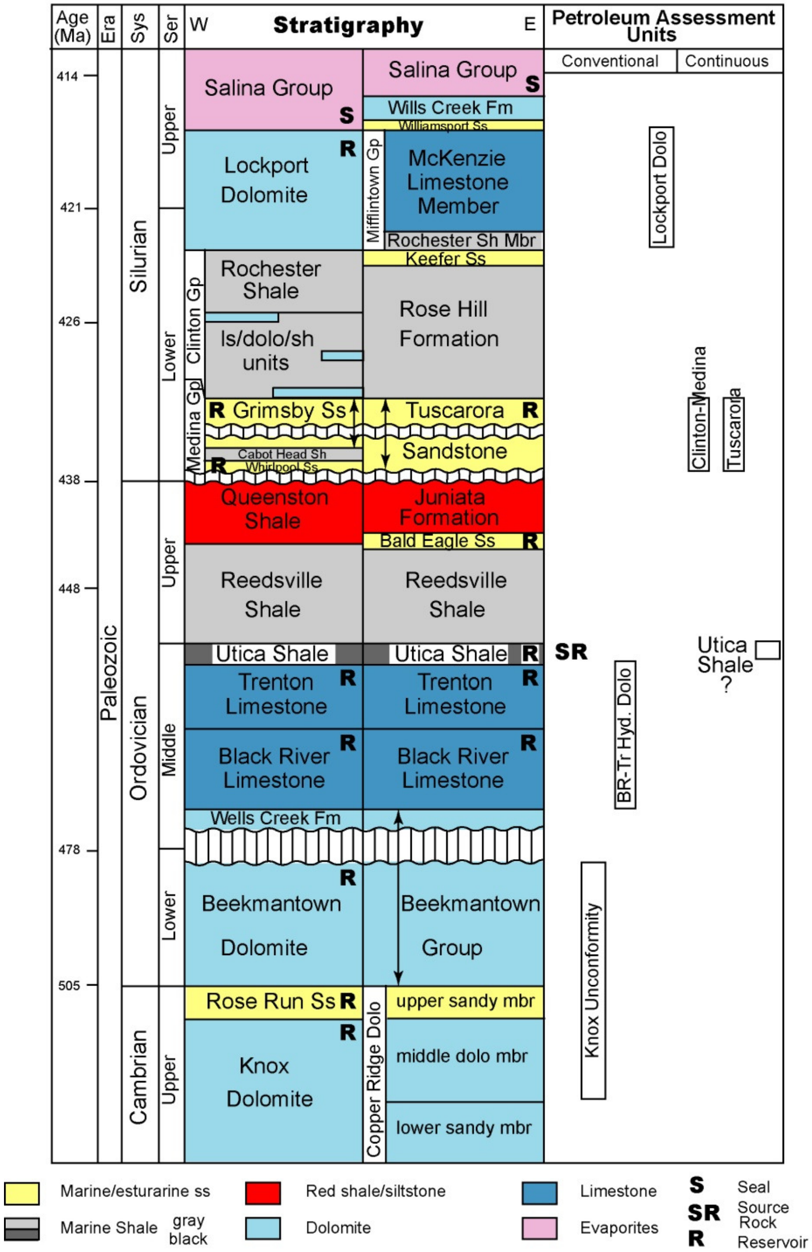
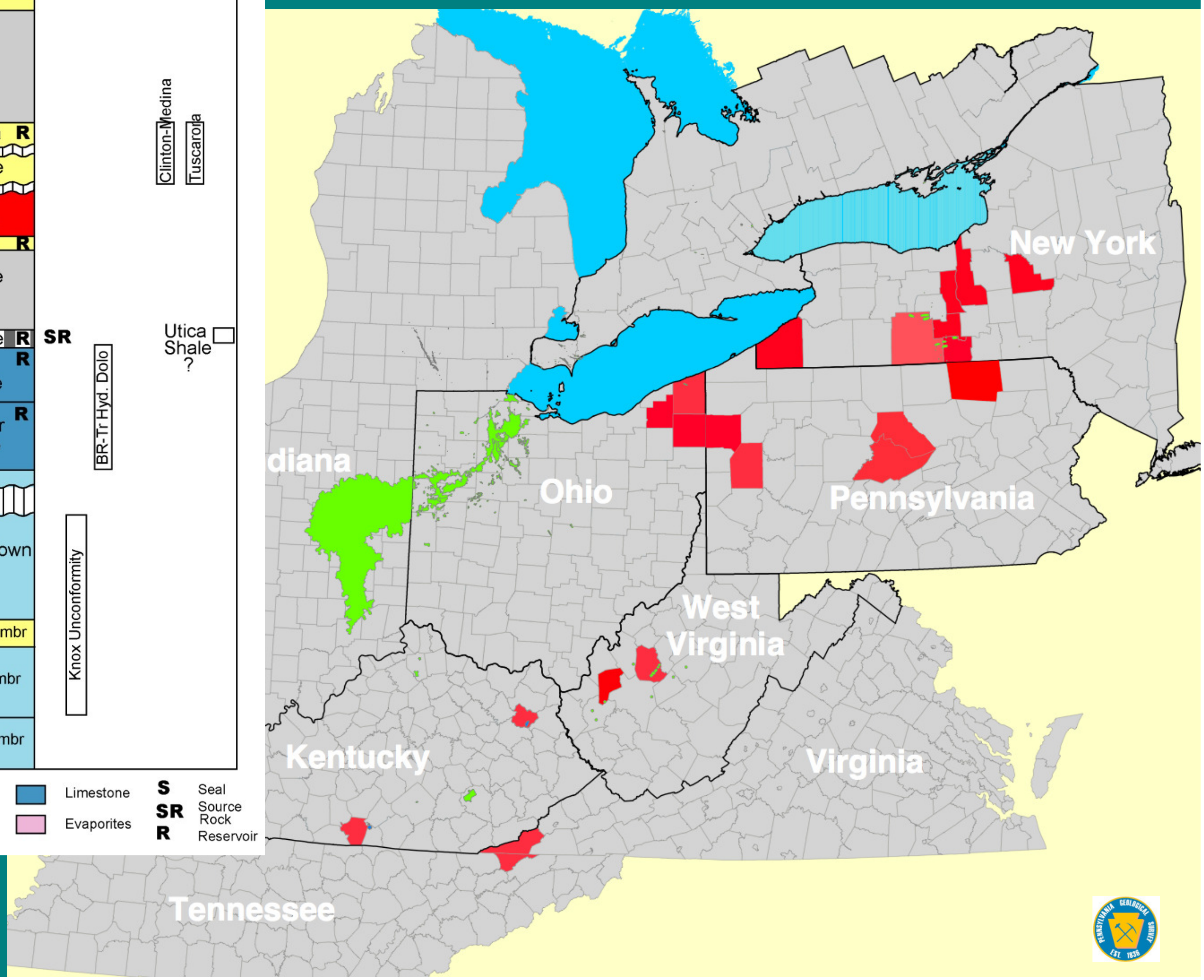
North Slope, Alaska: Selective isotope reversals due to microbial oxidation



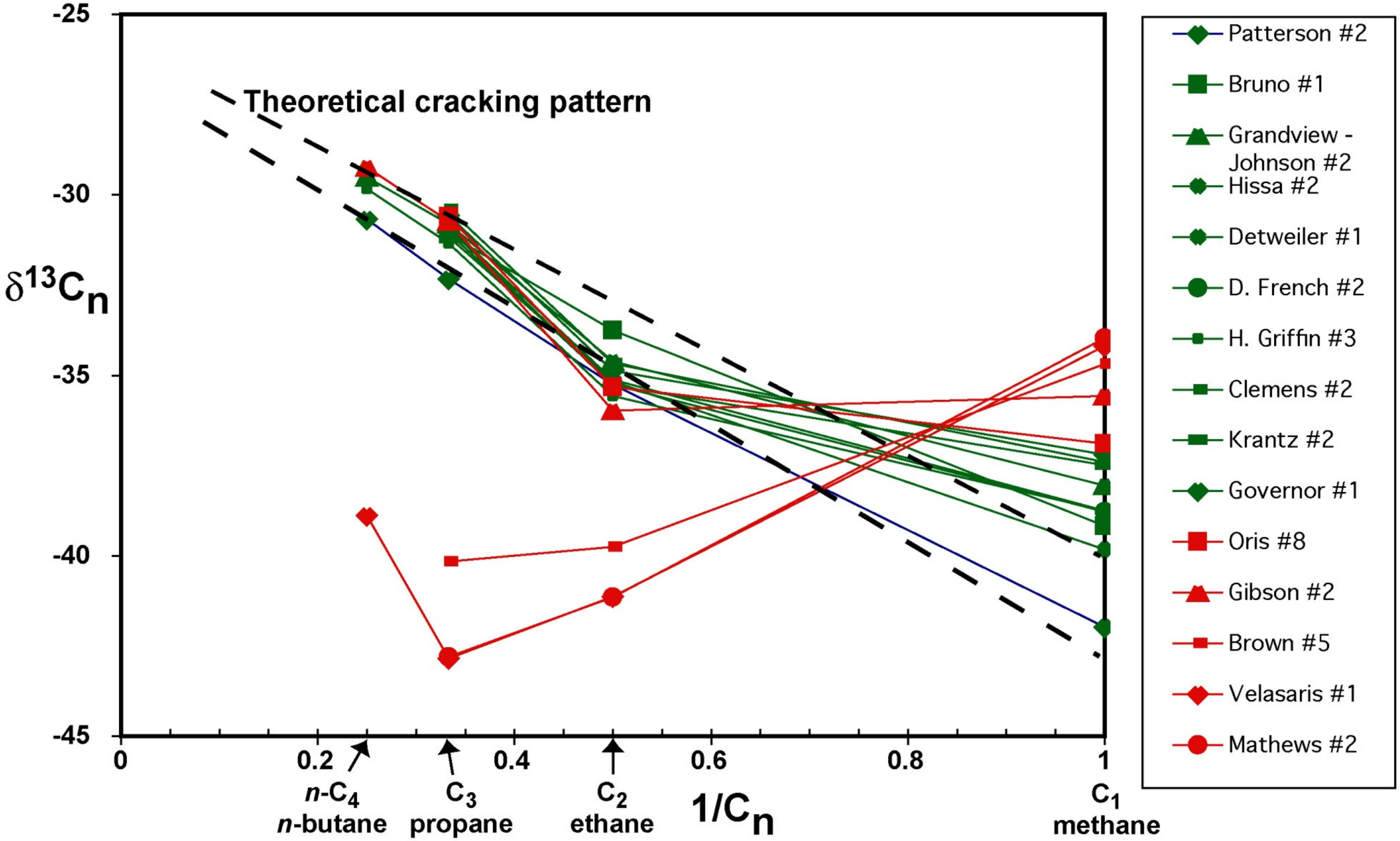


Reservoir intervals and distribution of gas reservoirs

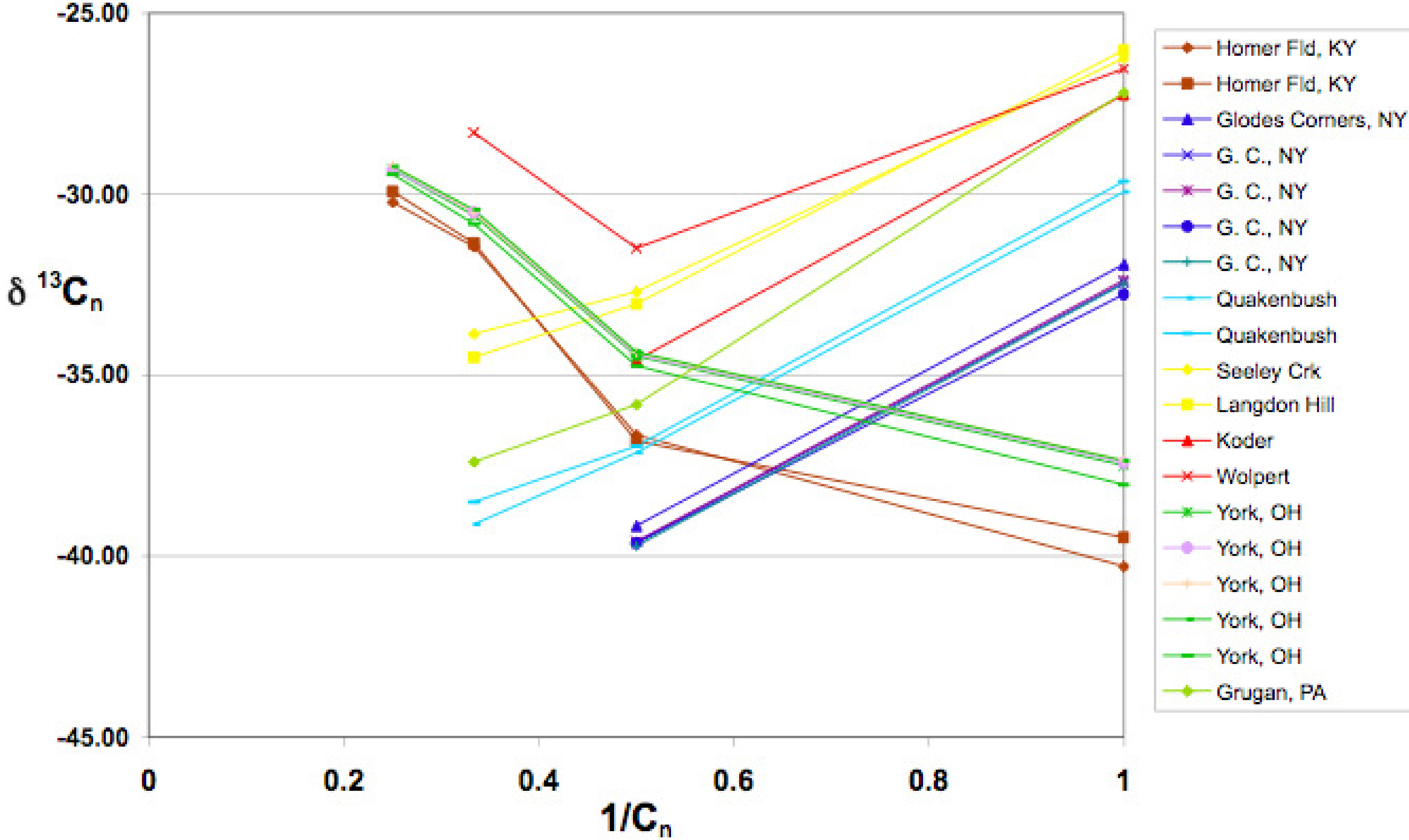




Natural gas plot
samples from basin-center LSRA

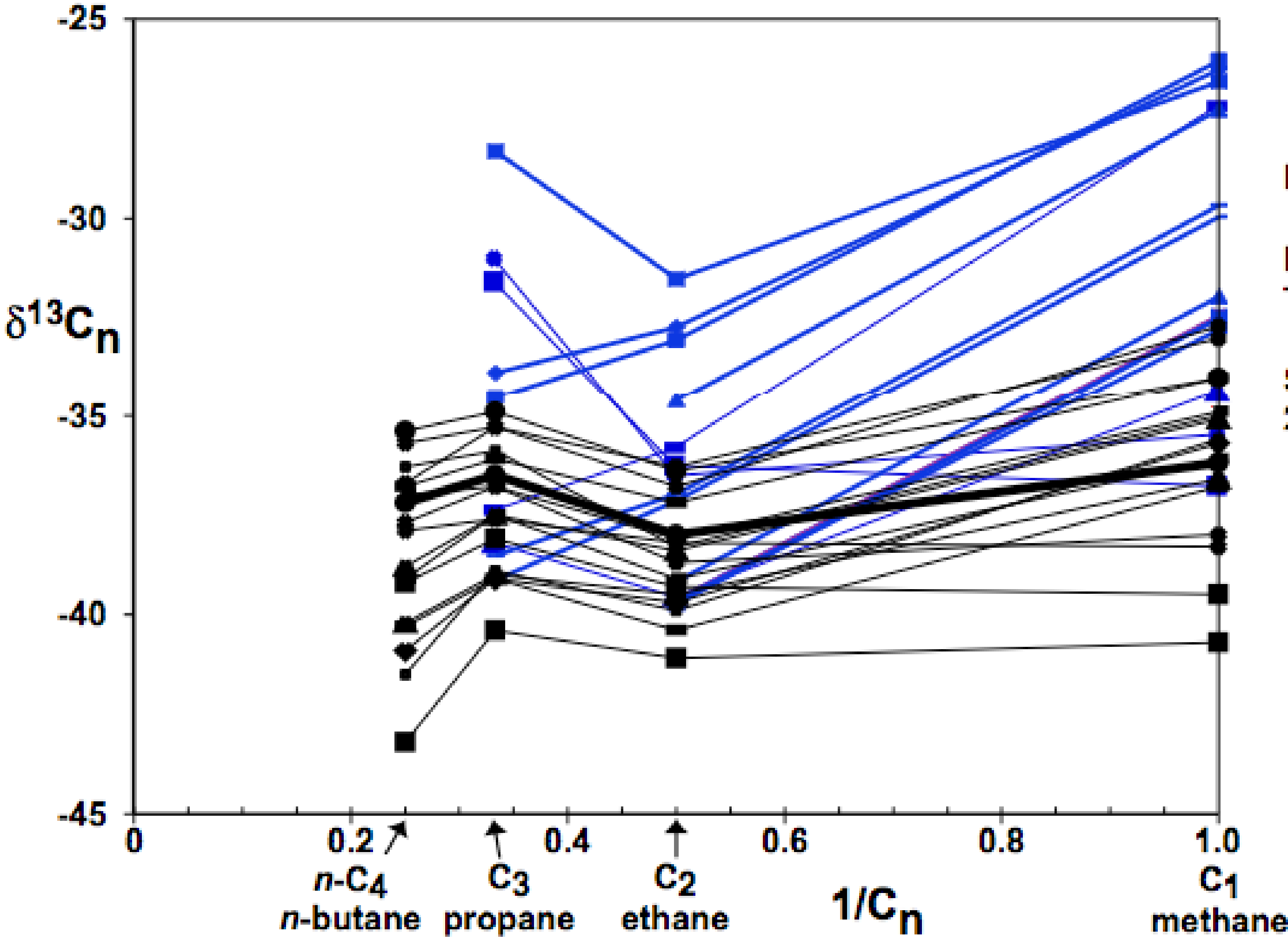


Natural Gas Plot



Natural Gas Plot

Abiogenic, Kidd Creek gases.



Data sources:

Laughrey, et al. 2006, TBR Consortium

Sherwood Lollar, et al. 2002, Nature

Gases generated from two types of organic matter in Middle Ordovician age source rocks, Utica/Antes, Appalachian basin

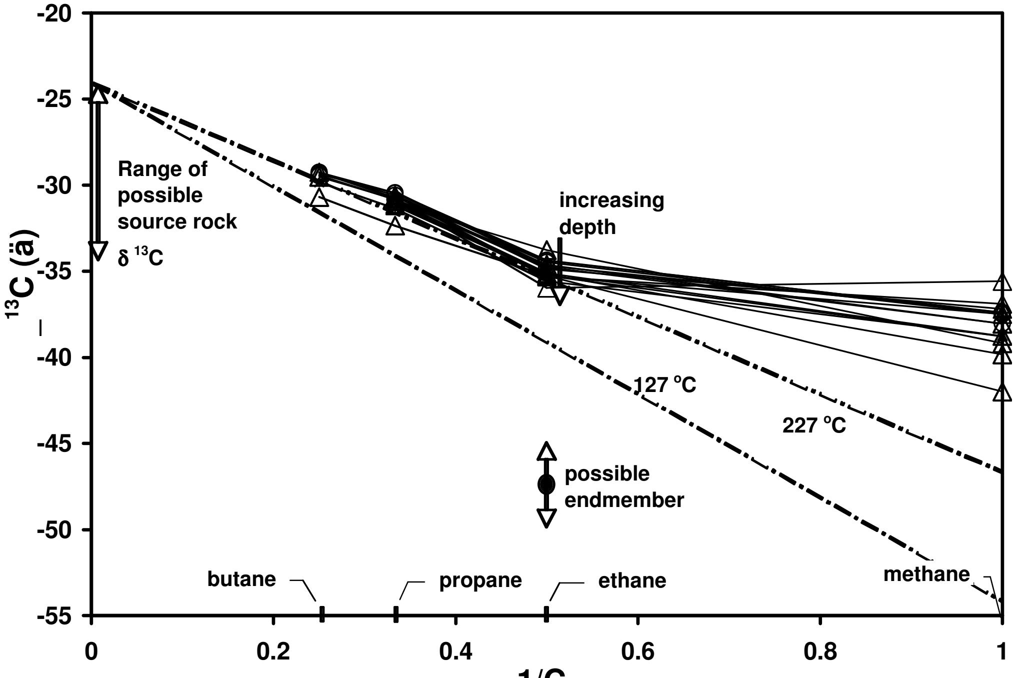


Figure 5a

δ[13]C organic matter range:
-34 to -24 ‰

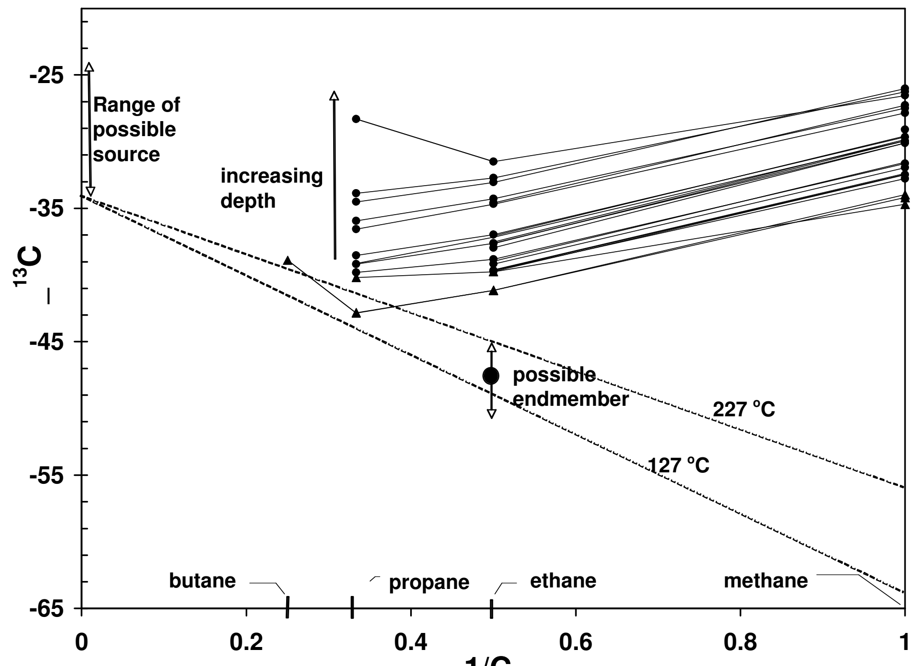
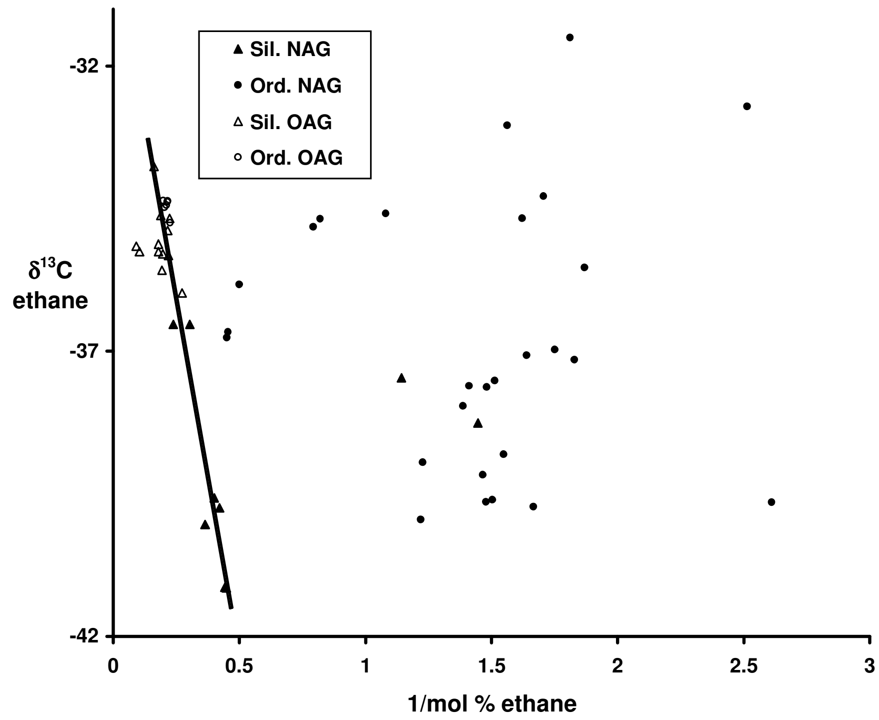
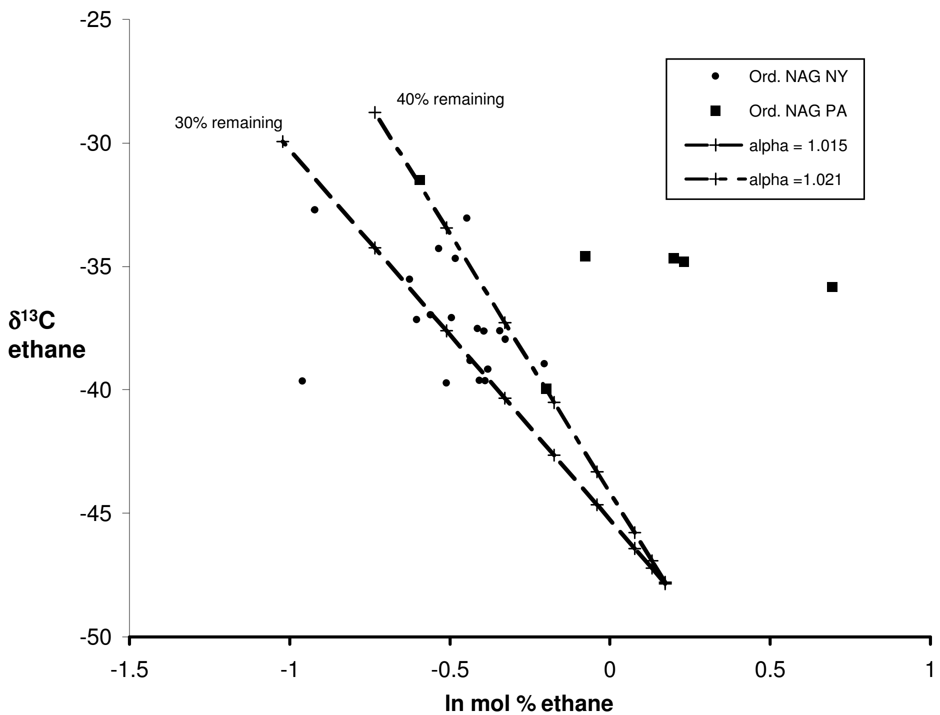


Figure 5b

Mixing between OAG and Sil. NAG



Raleigh fractionation in Ord. NAG



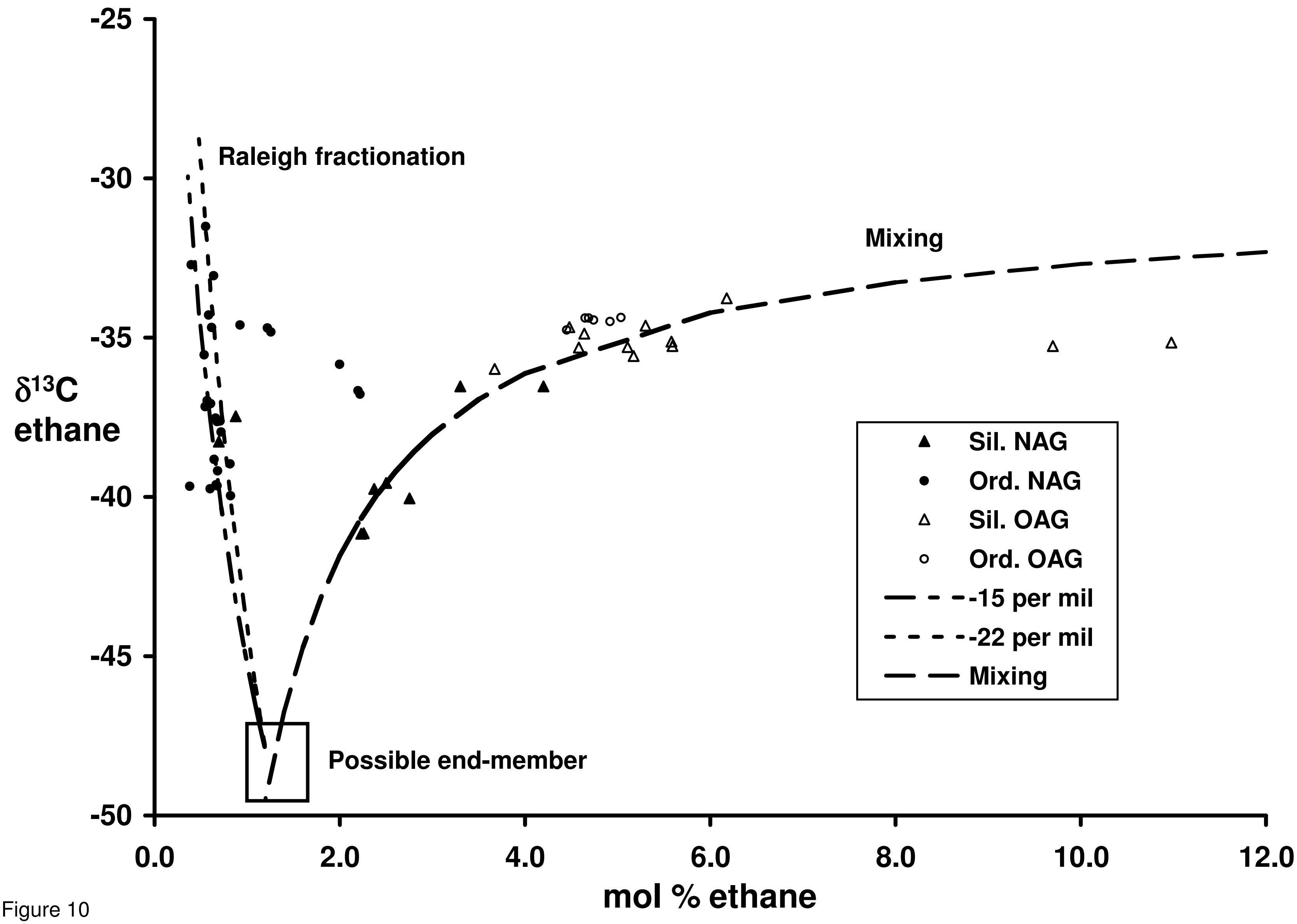
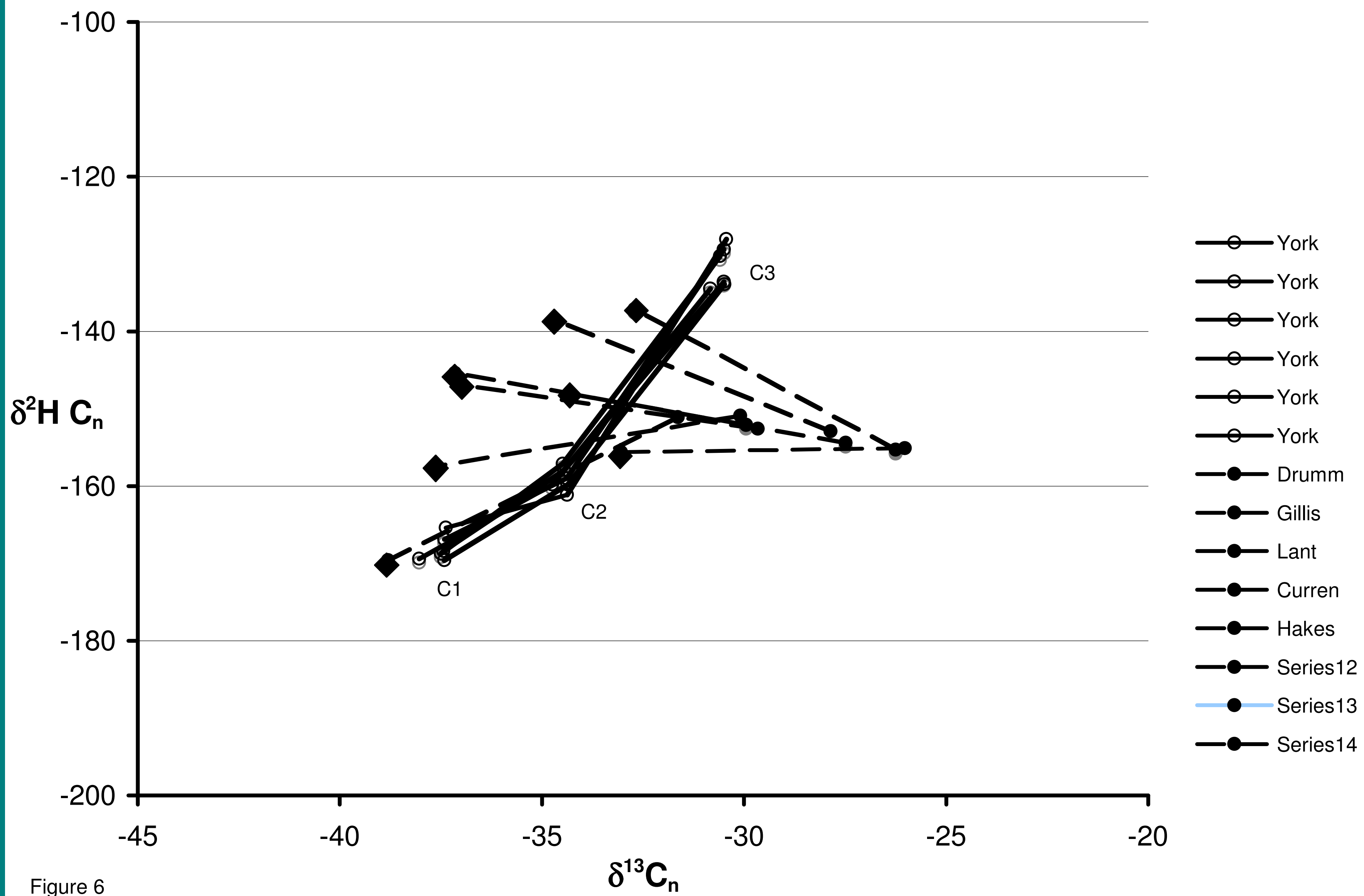

-25
-30
-35
-40
-45
-50
δ13C
ethane
Raleigh fractionation
Mixing
Possible end-member
Sil. NAG
Ord. NAG
Sil. OAG
Ord. OAG
-15 per mil
-22 per mil
Mixing
0.0
2.0
4.0
6.0
8.0
10.0
12.0
mol % ethane

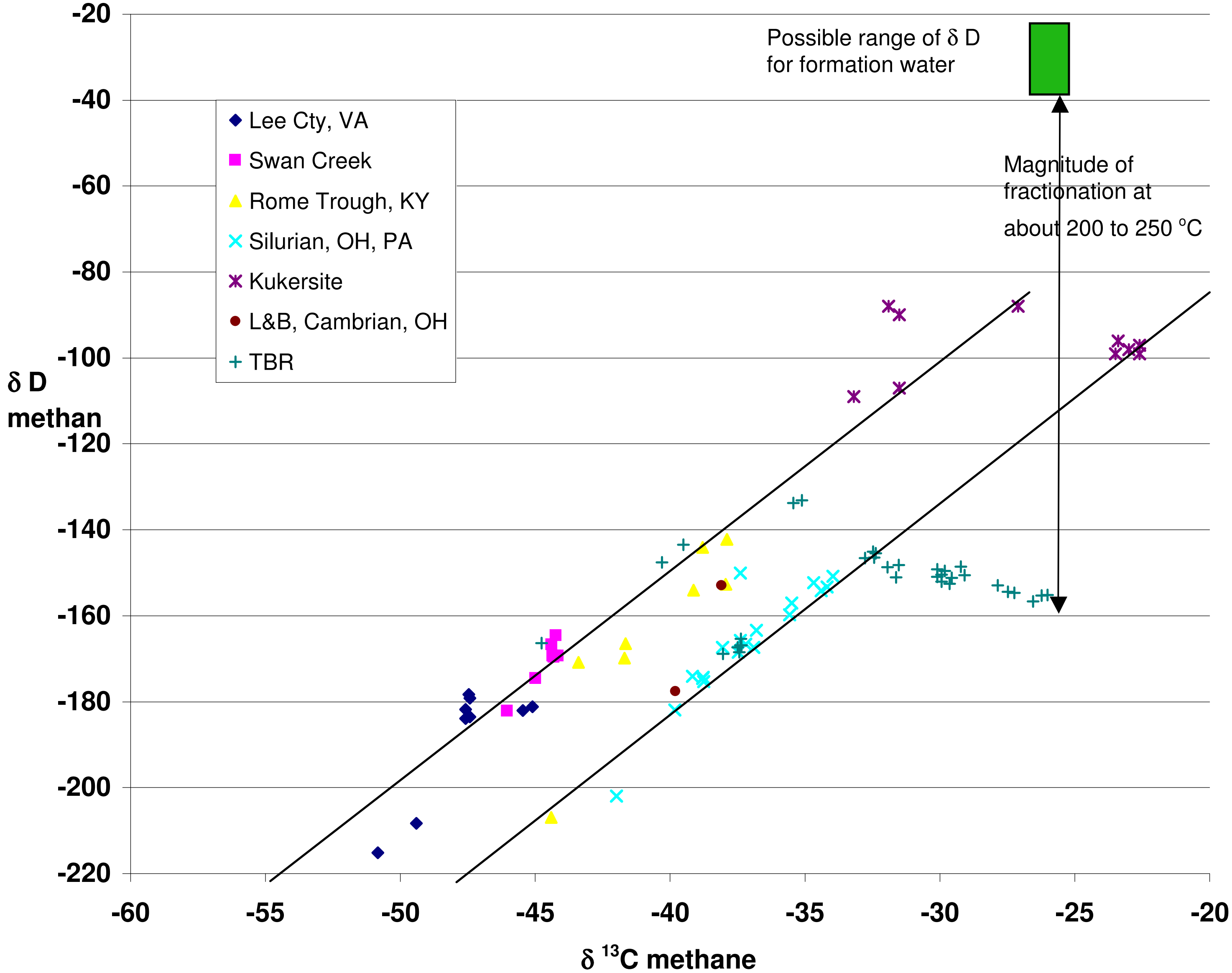
Figure 10



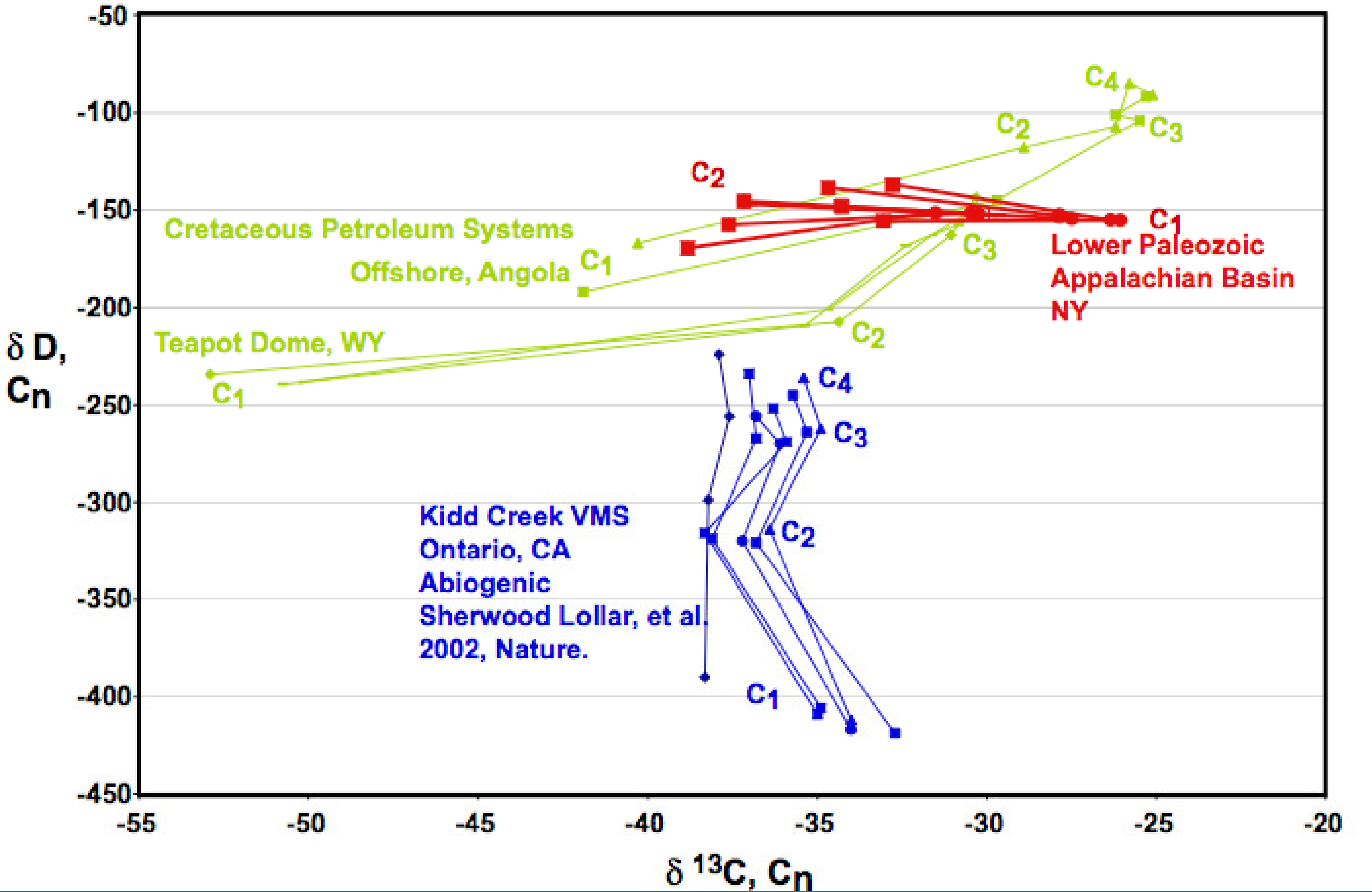
-100
-120
-140
-160
-180
-200
δ²H Cn
-45
-40
-35
-30
-25
-20
δ¹³Cn
C1
C2
C3
York
York
York
York
York
York
Drumm
Gillis
Lant
Curren
Hakes
Series12
Series13
Series14

Figure 6

Possible H/D exchange between CH_4 and H_2O



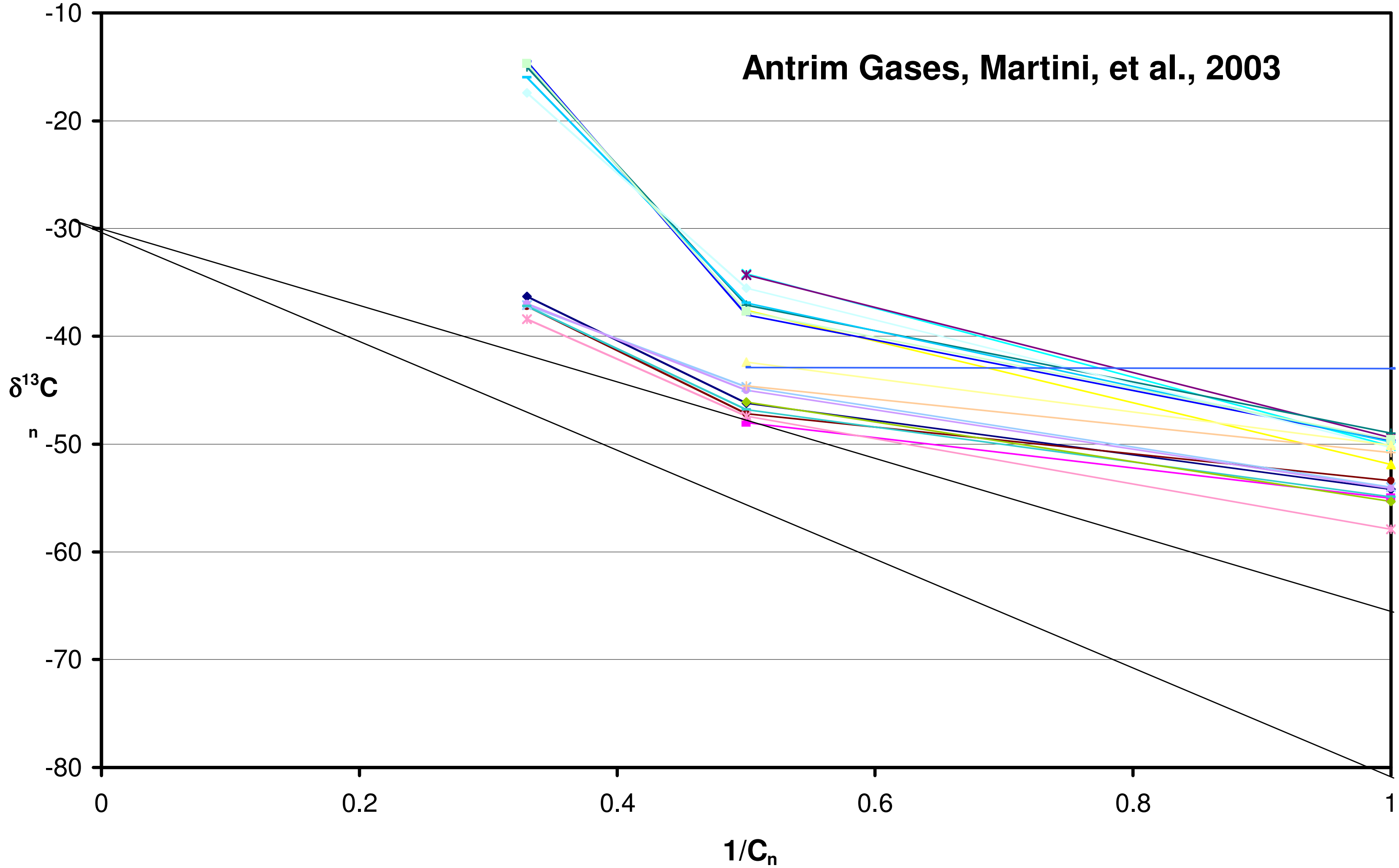
δ ^{13}C vs δ D for C_1 to C_4 hydrocarbons

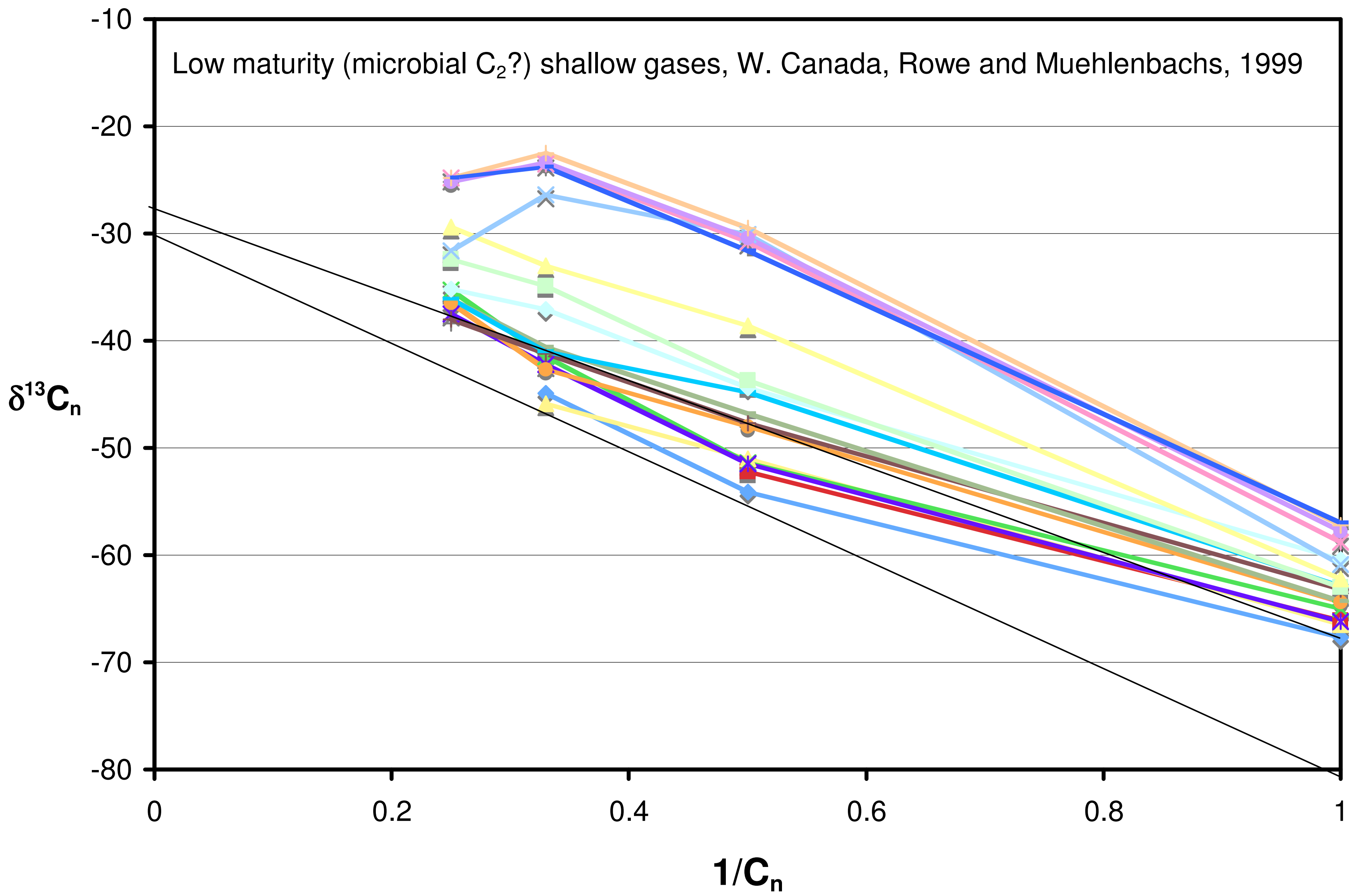


Low thermal maturity gases

- Are there thermogenic gases with $\delta^{13}C$ methane < <-55 ‰ ?
- What is the impact of microbial oxidation?
- Can consortia of methanogens and methanotrophs produce gases with $\delta^{13}C$ methane > -50 ‰ ?

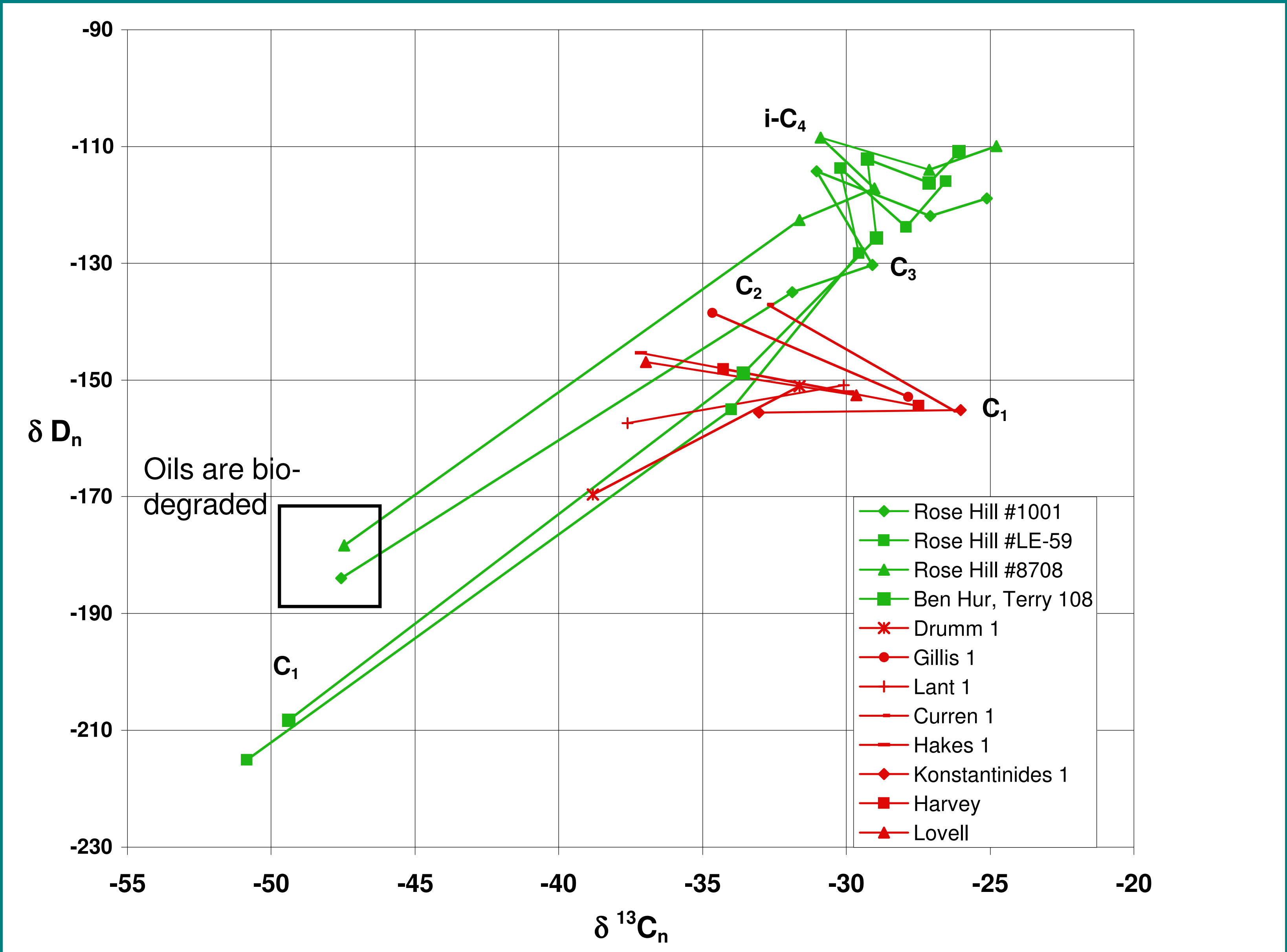
If the CH_4 is microbial, what is the source of ethane and propane ?





Low maturity (microbial C2?) shallow gases, W. Canada, Rowe and Muehlenbachs, 1999
-10
-20
-30
-40
-50
-60
-70
-80
δ13Cn
0
0.2
0.4
0.6
0.8
1
1/Cn

Covariation δ ^{13}C and δ D



So, what does it mean?

- Carbon isotopic reversals and increasing ^{13}C enrichment with depth imply destruction of HC leaving “heavy” residual components.
- H/D in methane from deepest samples suggests exchange with formation water

  $\delta\ ^{13}C$ in methane and ethane (and propane) in deepest samples suggests isotopic exchange

  $\delta\ ^{13}C$ in methane and CO_2 in deepest samples suggests isotopic exchange
- Apparent H/D exchange in CH_4-H_2O and $^{12}C/^{13}C$ exchange in CH_4-CO_2 is consistent with fractionations at T = 200 to 250 ^{o}C
- THE LEAP: Isotopic exchange is most efficient when molecular components undergo chemical reactions, therefore I suggest that all the gas components are linked through redox reactions, probably involving Fe^{2+}/Fe^{3+}, for example:
  - Combine $CO_2 + 4H_2 = CH_4 + 2H_2O$ with

    $2Fe_3O_4 + H_2O = 3Fe_2O_3 + H_2$ to get

    $8Fe_3O_4 + 2H_2O + CO_2 = 12Fe_2O_3 + CH_4$

OK, so maybe we are wrong and this has nothing to do with redox reactions

- We would welcome suggestions of other mechanisms to generate the isotopic variations we see.

The End