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: $^{13}\text{C}$ and $^2\text{H}$ on all HC gases yield more information, and therefore stronger interpretations
\[ \delta = \left( \frac{R_x - R_{std}}{R_{std}} \right) \times 1000 \]  
\( \delta \) units: parts per thousand, per mil or ‰.

Where:
\( R_x = ^{13}\text{C}/^{12}\text{C} \) or \(^2\text{H}/^1\text{H} \) (also D/H) in sample and
\( R_{std} \) = ratio in standard: \(^{13}\text{C}/^{12}\text{C} \), PDB; \(^2\text{H}/^1\text{H} \), VSMOW

\[ \alpha_{A-B} = \frac{R_A}{R_B} \]

\[ \alpha_{A-B} = K^{1/n} \]

Where \( K \) is the equilibrium constant for the exchange reaction for \( n \) atoms exchanged.
Organic Reaction Facies
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$_2$S, 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.
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
- $\frac{C_1}{(C_2 + C_3)} >> 100$
- $\delta^{13}C_1 < 60$ permil
- $\delta^{13}C_1 < 150$ permil
- Covariance of $\delta$D 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: \[ \text{CH}_3\text{COOH} \rightarrow \text{CH}_4 + \text{CO}_2 \] (reaction 1)

\[ \text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \] (reaction 2)
Schematic of Oil and Gas Generation:
why is there more gas at higher thermal maturity?

Organic Matter

Bitumen
Primary Cracking

Oil

Secondary Cracking

Wet Gas

Dry Gas

Dead Carbon

Biodegradation
CHO Reactions in Crustal Rocks

Cracking of sedimentary OM:
\[
[(C_xH_y)-CH_3]_{\text{Kerogen}} \rightarrow CH_4 + C_xH_{(y-1)}
\]
\[
[(C_xH_y)-C_2H_5]_{\text{Kerogen}} \rightarrow C_2H_6 + C_xH_{(y-1)}
\]

Anthracite grade:
- \( C_{20}H_4 \rightarrow 19C + CH_4 \)
- \( C_{20}H_4 + 2H_2O \rightarrow 17C + 2CH_4 + CO_2 \)

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

Molecular and Stable Carbon Isotope Characterization of Natural Gases

- Predominantly CO₂ reduction
- Bacterial
- Predominantly methyl-type fermentation

C₁ / (C₂ + C₃)

δ¹³C-methane (‰)

Migration

Oxidation

Microbial oxidation

Mixing

Thermogenic

Kerogen Type III and N. German coals
\[ \delta^{13}C \text{ Methane vs Gas Dryness} \]

- **Microbial**
- **Thermogenic**

**Gas hydrate drying effect**

**Locations**: 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

**USGS**
Bernard plot

\[ \frac{C_1}{C_{2+}} \]

\[ \delta^{13}C_1 \]

Legend:
- TBR
- LSRA
- Lee Cty, VA
- Rome Trough/Homer
- Swan Crk, TN
- L&B, 98
- J,D, &K, NYS
Lower Paleozoic gases compared to sources

\[ \delta^{13}C, \text{methane} \]
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

Isotopic composition of $C_n$

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

Rearranging:

$$\delta C_n = \frac{-1}{n} (\delta C_p - \delta C_m) + \delta C_p$$

Where:
- $\delta C_p$ is $\delta^{13}C$ of parent
- $\delta C_m$ is $\delta^{13}C$ of link C
- $\delta C_n$ is $\delta^{13}C$ of gas molecule
Theoretical kinetic isotope effects during cracking of gases from kerogen:

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

where

$$\varepsilon = \delta^{13}C_{KER} - \delta^{13}C_1$$

References:


Support from ab initio calculations:


$\varepsilon$ - $-15\%$
Ab initio calculations, Y. Tang, et al., 2000, GCA, assuming non-cleaved C is 0 per mil

\[ \delta^{13}C_n \] vs. \[ 1/C_n \] for different temperatures (300 K, 400 K, 500 K, 600 K). The lines represent the relationship between the isotopic ratio and the inverse concentration for each temperature, with markers indicating specific data points.

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

Greater Prudhoe Bay area fields

Prudhoe Bay Area Gases

δ\textsuperscript{13}C, C_n

δ\textsuperscript{13}C_n

West Sak
Tarn
Kalubik
Kuparuk River
Pt. MacIntyre
Alpine
Prudhoe Bay G.C.
Prudhoe Lisburne

methane
n-pentane
n-butane
propane
ethane
Reservoir intervals and distribution of gas reservoirs
Natural gas plot samples from basin-center LSRA

Theoretical cracking pattern

\[ \delta^{13}C_n \]

\[ \frac{1}{C_n} \]

\( n \)-butane  \( C_2 \)  \( C_3 \)  \( C_4 \)

Patterson #2
Bruno #1
Grandview - Johnson #2
Hissa #2
Detweiler #1
D. French #2
H. Griffin #3
Clemens #2
Krantz #2
Governor #1
Oris #8
Gibson #2
Brown #5
Velasaris #1
Mathews #2
Natural Gas Plot
Natural Gas Plot

Abiogenic, Kidd Creek gases.

Data sources:
Laughrey, et al. 2006, TBR Consortium
Figure 5a

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

\[ \delta^{13}C \text{ organic matter range: } -34 \text{ to } -24 \% \]
Mixing between OAG and Sil. NAG

Raleigh fractionation in Ord. NAG
Possible H/D exchange between CH$_4$ and H$_2$O

Possible range of $\delta D$ for formation water

Magnitude of fractionation at about 200 to 250 °C

Possible range of $\delta D$ for formation water

$\delta$ D methan

$\delta ^{13}$C methane

Lee Cty, VA
Swan Creek
Rome Trough, KY
Silurian, OH, PA
Kukersite
L&B, Cambrian, OH
TBR
$\delta^{13}\text{C}$ vs $\delta^D$ for C$_1$ to C$_4$ hydrocarbons

- Cretaceous Petroleum Systems
- Offshore, Angola C$_1$
- Lower Paleozoic Appalachian Basin NY
- Teapot Dome, WY
- Kidd Creek VMS Ontario, CA
- Abiogenic
Low thermal maturity gases

- Are there thermogenic gases with $\delta^{13}C$ methane $< -55 \%o$?
- What is the impact of microbial oxidation?
- Can consortia of methanogens and methanotrophs produce gases with $\delta^{13}C$ methane $> -50 \%o$?
If the CH$_4$ is microbial, what is the source of ethane and propane?
Low maturity (microbial C_2?) shallow gases, W. Canada, Rowe and Muehlenbachs, 1999
Covariation $\delta^{13}$C and $\delta$ D

Oils are biodegraded
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$_2$O and $^{12}$C/$^{13}$C exchange in CH$_4$-CO$_2$ is consistent with fractionations at $T = 200$ to 250 °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 $\text{CO}_2 + 4\text{H}_2 = \text{CH}_4 + 2\text{H}_2\text{O}$ with
    $2\text{Fe}_3\text{O}_4 + \text{H}_2\text{O} = 3\text{Fe}_2\text{O}_3 + \text{H}_2$ to get
    $8\text{Fe}_3\text{O}_4 + 2\text{H}_2\text{O} + \text{CO}_2 = 12\text{Fe}_2\text{O}_3 + \text{CH}_4$
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