APPLICATIONS OF STABLE ISOTOPE GEOCHEMISTRY IN THE PETROLEUM GEOSCIENCES

PTTC Workshop June 5, 2014
Pittsburgh, PA

Christopher D. Laughrey, Weatherford Laboratories, Golden, CO
Fred J. Baldassare, Echelon Applied Geosciences, Murrysville, PA
Welcome and introductions
Purpose of this workshop

• The purpose of this workshop is to acquaint petroleum industry and environmental professionals with the tools, methods, terminology, and interpretive techniques of stable isotope geochemistry used to understand the origin and fate of hydrocarbons and associated compounds in the earth’s subsurface.

• In practice, stable isotope geochemical data must be constrained by equally or more important geological, hydrological, and engineering data. A large portion of this workshop is dedicated to interpreting isotope data in conjunction with other earth science information.

• This workshop will provide a general overview of first principals concerning stable isotope geochemistry in the earth sciences, followed by in-depth discussions and exercises about natural gas and liquid hydrocarbon geochemistry, and stray gas investigation and mitigation.
Petroleum Isotope Geochemistry

**Natural Gas Geochemistry**
- Genetic origin of natural gas
- Thermal maturity of natural gas
- Correlating natural gas samples with their source rocks
- Vertical and lateral reservoir continuity
- Reservoir compartmentalization
- C and H isotopic fractionation of hydrocarbons and CO2 during gas desorption from coal and shale
- Gas leakage and hydrocarbon destruction
- Origin of non-hydrocarbon gases

**Stable Isotope Applications for Liquids**
- Correlation of whole oils, bitumens, and kerogen
- Quantitative estimates of oil co-sources
- Marine versus terrigenous organic input
- Compound Specific Isotope Analysis (CSIA)
- Reconstruction of paleoenvironment
- CSIA for correlation
- Distributed source rock sampling
- CSIA of carboxylic acids
**Workshop organization**

**Morning (Laughrey)**
- 9:00 AM: Petroleum systems and geochemistry.
- 9:20 AM: Introduction to stable isotope geochemistry:
  - What are stable isotopes?
  - How do we measure stable isotopes?
  - Isotope effects.
  - Isotope fractionation.
- 10:15 AM: Break
- 10:30 AM: Natural gas geochemistry:
  - The genetic origin and thermal maturity of natural gases – hydrocarbons and non-hydrocarbons.

**Morning to noon (Laughrey)**
- 11:15 AM: Break
- 11:30 AM: Natural gas geochemistry:
  - Correlating natural gases with their source rocks and each other.
  - Reservoir continuity and compartmentalization.
- 12:00 PM: Lunch
Workshop organization

Afternoon (Laughrey)

• 1:00 PM: Natural gas geochemistry:
  – Carbon and hydrogen isotope fractionation of hydrocarbons and CO₂ during gas desorption and diffusion.
  – Gas leakage and hydrocarbon destruction.
• 1:40 PM: Problem sets and exercise.
• 2:00 PM: Stable isotope applications for condensates and liquids-rich plays:
  – Correlation of whole oils, bitumens, and kerogens.
  – Quantitative estimates of oil co-sources.
  – Marine versus terrigenous organic input; environmental reconstruction.
  – Compound specific isotope analysis.
• 2:15 PM: Stable isotope applications in stratigraphy.
• 2:30 PM: Break

Afternoon (Baldassare)

• 2:50 PM: Stray gas migration and incident response:
  – Introduction and overview.
  – Physical and chemical properties of methane and light gases.
  – Sampling for dissolved and gas phase methane.
  – Stray gas origin and source correlation.
  – Potential impacts to groundwater geochemistry.
  – Stray gas case study.
  – Stray gas mitigation response protocol.
• 5:00 PM: Workshop summary and questions.
• 5:15 PM: Workshop adjourns.
Petroleum systems and geochemistry: Exploration risk (Hunt, 1996)

- The probability of spending exploration funds without economic success.
- Reducing risk depends on finding a *trap* and on determining how high the probability is that petroleum has migrated from a *mature source rock* into that trap and has not escaped or been destroyed.
- Successful exploration depends upon:
  - The existence of a trap (structure, reservoir, seal)
  - The accumulation of a petroleum charge (source, maturation, migration to the trap, timing)
  - Preservation of the entrapped petroleum (thermal history, meteoric water invasion)
- The probability of success is the product of the probabilities of all three of these factors.
Petroleum systems and geochemistry

- The **petroleum system** is a natural system that encompasses a pod of petroleum source rocks and all related oil and gas and which includes all the geologic elements and processes that are essential if a hydrocarbon accumulation is to exist.

http://home.hiroshima-u.ac.jp/er/Resources/Image267.gif
Essential Elements and Processes of a Petroleum System

• Essential Elements:
  • A petroleum source rock
  • A petroleum reservoir rock
  • A seal rock
  • An overburden rock

• Essential Processes:
  • Trap formation
  • Generation – migration – accumulation of petroleum

USGS SW Wyoming Province Assessment Team (2005) USGS DDS-69-D
Essential Elements and Processes of a Petroleum System

Essential Elements

• A petroleum source rock:
  – Generative potential
  – Kerogen type and petroleum product
  – Thermal maturity

• A petroleum reservoir rock.

• A seal rock.

• Overburden rocks.

Essential Processes

• Generation of petroleum:
  – Kinetics
  – Transformation ratio

• Migration

• Petroleum accumulation
Screening for Generative Potential

Analysis

• Total Organic Carbon (TOC)
• Programmed pyrolysis:
  – S1
  – S2
• Bitumen
• Hydrocarbons

Tools

• Leco TOC analyzer/pyrolysis TOC
• Rock-Eval and Source Rock Analyzer (SRA)
• Extract analysis and gas chromatography
Screening for Organic Matter Quality

Analysis

• Programmed pyrolysis:
  – S2 versus TOC
  – Hydrogen Index
  – Oxygen Index
  – S2/S3

• Maceral analysis

Tools

• Rock-Eval and Source Rock Analyzer (SRA)
• Organic Petrology
Screening for Thermal Maturity Analysis

- Programmed pyrolysis:
  - $T_{\text{max}}$
  - Production Index (PI)
  - $T_{\text{max}}$ versus PI
  - $T_{\text{max}}$ versus HI
- Maceral analysis:
  - Vitrinite Reflectance
  - Thermal Alteration Index (TAI) and similar maturity scales
- Bitumen and Bitumen/TOC

Tools

- Rock-Eval and Source Rock Analyzer (SRA)
- Organic Petrology
- Extract analysis
Petroleum System Event Chart

Niobrara Total Petroleum System, Southwest Wyoming Province

From Finn and Johnson (2005), USGS Digital Data Series
DDS-69-D
Petroleum systems and geochemistry

• Modern isotope and biomarker analyses on the molecular level readily allow the identification and separation of multiple sources of oils in a petroleum system:
  – Oils inherit the molecular and isotopic character of the parent kerogen/oil.
• Natural gases do not inherit their molecular or isotopic properties from their parent kerogen/oil:
  – Bond-breaking processes that produce C1 – C4 hydrocarbon gases involve temperature-dependent isotope fractionations that vary with:
    • The number of carbons in the molecule;
    • Temperature;
    • Type of precursor (type of kerogen or oil).
  – Identification of the source of a gas requires a reconstruction and correction of the fractionations that occur during gas formation:
    • Simulation of gas-forming processes in laboratory experiments.

What about Appalachian basin petroleum systems?

From Schoell and others, 2014
Petroleum Formation: Reactions and Processes

Kerogen
Insoluble organic solid

Bitumen
Soluble organic tar

Crude Oil
Hydrocarbon-rich liquid

Natural Gas
Hydrocarbon-rich gas

Char/Pyrobitumen
Insoluble organic solid

Im immature

Mature

Over mature

Hydrogen Sulfide
Non-hydrocarbon-rich gas

Petroleum systems and geochemistry

Courtesy Michael Lewan
The Oil and Gas Windows

<table>
<thead>
<tr>
<th>MATURITY</th>
<th>%VR₀</th>
<th>Tmax °C</th>
<th>PI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Immature</td>
<td>0.20 – 0.60</td>
<td>&lt;435</td>
<td>&lt;0.10</td>
</tr>
<tr>
<td>Mature: Onset of oil generation</td>
<td>0.50 – 0.60</td>
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<td></td>
</tr>
<tr>
<td>Early</td>
<td>0.60 – 0.80 (0.60 – 0.65)</td>
<td>435 - 445</td>
<td>0.10 – 0.15</td>
</tr>
<tr>
<td>Peak</td>
<td>0.90 – 0.10 (0.65 – 0.90)</td>
<td>445 - 450</td>
<td>0.25 – 0.40</td>
</tr>
<tr>
<td>Late</td>
<td>1.0 – 1.4 (0.90 – 1.35)</td>
<td>450 - 470</td>
<td>&gt; 0.40</td>
</tr>
<tr>
<td>Post mature: Onset of the dry gas window</td>
<td>&gt; 1.35 -1.4 – 2.0 -2.0</td>
<td>&gt;470</td>
<td>Condensate/wet gas window Catagenesis/metagenesis</td>
</tr>
</tbody>
</table>

Sources:
- Killops and Killops, 2010
- Peters and others, 2007
- Huc, 2013
Introduction to stable isotope geochemistry

• What are stable isotopes?
• How do we measure stable isotopes?
• Isotope effects
• Isotope fractionation
What are stable isotopes?

- Reminders about the atomic nucleus:
  - Bohr model:
    - The atom is composed of two entities:
      - A central nucleus containing most of the mass;
      - An array of orbiting electrons.
    - The nucleus carries a positive charge (+Ze), which is balanced by the electron cloud’s charge of –Ze.
    - The number of protons, Z, is matched in an electrically neutral atom by the number of electrons. Each of these particles carries a negative electric charge e.
What are stable isotopes?

- The nucleus of any element is made up of two types of particle, neutrons and protons:
  - A neutron \((m_n = 1.67495 \times 10^{-27} \text{ kg})\) is slightly heavier than a proton \((m_p = 1.67265 \times 10^{-27} \text{ kg})\).
  - While similar in mass, the two particles differ above all in their charge:
    - Proton a positive charge \((+e)\).
    - Neutron is electrically neutral.
  - The number of protons \((Z)\) is the atomic number. \(N\) is the number of neutrons:
    - The sum of \(N + Z\) gives the mass number \(A\) \((A = N + Z)\).
    - This provides a measure of the mass of the nuclide in question if we take as our unit the approximate mass of the neutron or proton.
    - *However*, for a given \(Z\) (i.e., a given position in the periodic table), there are atoms with different mass numbers \((A)\) and therefore nuclei which differ in the number of neutrons they contain. Such nuclides are known as the *isotopes* of an element.
What are stable isotopes?

- Example:
  - There is one stable form of hydrogen whose nucleus is composed of just a single proton.
  - Another stable form of hydrogen (deuterium) whose nucleus comprises both a proton and a neutron.
  - A radiogenic form of hydrogen (tritium) whose nucleus comprises a proton and two neutrons.
What are stable isotopes?

• Notation for nuclides:
  – The symbol of the element, H for example, is completed by the atomic number (implied by the letter symbol of the chemical element) and the mass number:
    • $^1$H, $^2$H, $^3$H
    • $^2$H sometimes denoted as D
  – $^{12}$C, $^{13}$C, $^{14}$C
  – $^{16}$O, $^{17}$O, $^{18}$O
  – $^{32}$S, $^{33}$S, $^{34}$S, $^{36}$S
  – This notation leaves the right-hand side of the symbol free for chemical notations used for molecular or crystalline compounds:
    • $^2$H$_2$ or $^{16}$O$_2$
    • $^{13}$CH$_4$
What are stable isotopes?

- Variations in stable isotope composition are extremely slight, and are generally expressed in a specific unit, the δ unit:

\[ \delta = (\text{sample isotope ratio} - \text{standard isotope ratio}) \div \text{standard isotope ratio} \times 10^3 \]

In the case of carbon: 

\[ \delta^{13}C = (^{13}C/^{12}C_{\text{sample}} - ^{13}C/^{12}C_{\text{standard}}) \div ^{13}C/^{12}C_{\text{standard}} \times 10^3 \]

- Ultimately, δ is a relative deviation from a standard, expressed as the number of parts per thousand, or parts per mil (‰).
- Isotope ratios are expressed with the heavier isotope in the numerator:
  - If δ is positive then the sample is richer in the heavy isotope than the standard. If δ is negative then...
• Carbon:
  \[ \delta^{13}C = \left( R_s - R_r \right) \div R_r \]
  - \( R = \frac{^{13}C}{^{12}C} \)
  - Reported in parts per thousand (permil)
  - \( R_r = 0.01124 \) permil (VPDB)
  - Atmospheric CO\(_2\) ~ -8 permil
  - Plants, kerogen, coal ~ -8 to -55 permil
  - Oil ~ -22 to -55 permil
  - Natural gas ~ < - 25 to > - 90 permil
Measurement and Nomenclature

- **Hydrogen:**
  - $\delta D = (R_s - R_r) \div R_r$
  - $R = ^2H/^1H$
  - Reported in parts per thousand (permil)
  - $R_r = 155.76$ ppm (V-SMOW)

- **Nitrogen**
  - $\delta^{15}N$ (atm $N_2$ standard)

- **Sulfur**
  - $\delta^{34}S$ (CDT standard)
# Stable Hydrocarbon Isotopes

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Mass</th>
<th>Protons</th>
<th>Neutrons</th>
<th>Natural Abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{12}\text{C}$</td>
<td>12</td>
<td>6</td>
<td>6</td>
<td>98.89%</td>
</tr>
<tr>
<td>$^{13}\text{C}$</td>
<td>13</td>
<td>6</td>
<td>7</td>
<td>1.11%</td>
</tr>
<tr>
<td>$^{1}\text{H}$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>99.98%</td>
</tr>
<tr>
<td>$^{2}\text{H} \text{ (D)}$</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>0.0156%</td>
</tr>
<tr>
<td>$^{14}\text{N}$</td>
<td>14</td>
<td>7</td>
<td>7</td>
<td>99.64%</td>
</tr>
<tr>
<td>$^{15}\text{N}$</td>
<td>15</td>
<td>7</td>
<td>8</td>
<td>0.36%</td>
</tr>
<tr>
<td>$^{32}\text{S}$</td>
<td>32</td>
<td>16</td>
<td>16</td>
<td>95.02%</td>
</tr>
<tr>
<td>$^{33}\text{S}$</td>
<td>33</td>
<td>16</td>
<td>17</td>
<td>0.75%</td>
</tr>
<tr>
<td>$^{34}\text{S}$</td>
<td>34</td>
<td>16</td>
<td>18</td>
<td>4.21%</td>
</tr>
<tr>
<td>$^{36}\text{S}$</td>
<td>36</td>
<td>16</td>
<td>20</td>
<td>0.02%</td>
</tr>
</tbody>
</table>
How do we measure stable isotopes?

• Mass spectrometer:
  – Atoms of the chemical element whose isotopic composition is to be measured are ionized in a vacuum chamber.
  – The ions produced are then accelerated by using a potential difference of 3 – 20 kV producing a stream of ions, and so an electric current, which is passed through a magnetic field.
  – The magnetic field exerts a force perpendicular to the “ionic current” and so bends the beam of ions.
  – The lighter ions are deflected more than the heavier ones so the ions can be sorted according to their masses.
  – The relative abundance of each isotope can be measured from the relative values of the electron currents produced by each stream of ions separated out in this way.
How do we measure stable isotopes?

- Online combustion systems with a coupled elemental analyzer and isotope ratio mass spectrometer (combustion/IRMS):
  - Small sample sizes (≥1000 ppm for C and D in C₁; 250 ppm for C₂; 50 ppm for C₃)
  - GC can be coupled to the combustion system allowing carbon isotope ratios to be determined on individual organic compounds (GC/combustion/IRMS or compound-specific isotope analysis – CSIA)

- Cryogenic enrichment
- Offline preparation:
  - Offline purification/separation of gases
  - Large sample size
  - Sealed tube combustion to convert organic matter to CO₂ for isotope analysis
  - Dual inlet MS
Offline versus Online Preparation and Analysis

• Offline Method:
  – Offline purification/separation of gases
  – Large sample size
  – Direct inlet of sample gas
  – Pressure adjusts of both gases
  – Sample/standard changes (> 6 times)
  – D-value calculated from statistical mean
  – System calibration on a monthly basis
  – Dual inlet MS

• Online method:
  – Purification/separation of gases by GC column
  – Small sample size
  – Sample gas inlet via carrier gas
  – No pressure adjust: linearity and stability of the system are necessary conditions
  – One peak per sample
  – D-value calculated by peak integration and reference gas
  – System calibration on a daily basis
  – Continuous flow IRMS
Stable Isotopes - Review

- Isotope – atom contains same number of protons but different number of neutrons
- Isotope ratios determined by mass spectrometry
- Specified as a difference from a standard in parts per thousand
Isotope Effects

• Differences in chemical and physical properties arising from variations in atomic mass of an element:
  – Electronic structure/chemical behavior
  – Nucleus/physical properties
• Differences in the physicochemical properties of isotopes arise as a result of quantum mechanical effects.
• Bonds formed by light isotopes are weaker than bonds involving the heavy isotope.
Isotope Fractionation

• Partitioning of isotopes between two substances or two phases of the same substance with different isotope ratios:
  – Isotope exchange reactions
  – Kinetic processes
Stable Natural Gas Isotopes
Isotope Fractionation

• Fractionation is coupled to various geological processes ("tracers"):  
  – Gas generation (and alteration/destruction)  
  – Adsorption and desorption  
  – Migration and diffusion

• Fractionation is a result of different kinetics for $^{13}\text{C}$, $^{12}\text{C}$, D, $^{1}\text{H}$:  
  – Kinetically "easier" to break chemical $^{12}\text{C}$ and $^{1}\text{H}$ bonds  
  – Preferred rupture of these bonds during thermal maturation  
  – Results in $^{12}\text{C}$ enriched ("lighter") products (methane) and $^{13}\text{C}$ enriched ("heavier") residue ($C_{2+}$, kerogen, coal)
Fractionation Factor (α)

• An expression of the relative magnitudes of isotopic offset between two substances or phases:
  – $\alpha_{A,B} = \frac{R_A}{R_B}$, where $\frac{R_A}{R_B}$ are isotopic ratios referenced relative to a standard.
  – $\alpha_{\text{org,hc}} = \frac{\delta^{13}\text{C}_{\text{org}} + 10^3}{\delta^{13}\text{C}_{\text{hc}} + 10^3}$, where $\alpha_{\text{org,hc}}$ is the fractionation factor for carbon in hydrocarbon or CO$_2$ gases and their precursor organic matter.

• Microbial versus thermogenic gases:
  – Carbonate reduction: $\alpha_{\text{CO}_2-\text{CH}_4} = 1.05 - 1.10$
  – Acetate fermentation: $\alpha_{\text{CO}_2-\text{CH}_4} = 1.035 - 1.06$
  – Thermogenic gases: $\alpha_{\text{CO}_2-\text{CH}_4} < 1.03 - 1.001$
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Natural gas geochemistry

• Why is gas geochemistry important?
• The major sources of natural gas
• Sampling
• The genetic origin and thermal maturity of natural gases:
  – Principals
  – Applications and case histories
Why is gas geochemistry important?

- Genetic origin of natural gas
- Thermal maturity of natural gas
- Correlating natural gas samples with their source rocks
- Vertical and lateral reservoir continuity
- Reservoir compartmentalization
- C and H isotopic fractionation of hydrocarbons and CO₂ during gas desorption and degassing from coal and shale
- Gas leakage and hydrocarbon destruction
- Origin of non-hydrocarbon gases
- Predict fluid properties (GOR, saturation pressure)
- Prevention of “missed pay” and contingency for failed down-hole MDT sampling.
Major sources of natural hydrocarbon gases

- Methanogenic bacteria
- All types of kerogen
- Coal
- Oil in source and reservoir rocks
- “Special processes”
- Abiogenic gases

From Howell and others, 1993, USGS PP 1570, Figure 1, p. 2
Major Sources of Nonhydrocarbon Gases

• CO₂, H₂S, and N₂ are formed by both organic and inorganic processes.

• 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.
Gas Sampling

- Production gas
- Mud gas (from the gas trap)
- Headspace gas (evolved from cuttings)
- Flow line/seperator (field or laboratory sub-sampling)
- Drill stem test (“single stage flash” gas is separated from the fluid sample in the lab to a pressurized cylinder)
- Wireline Formation Test (MDT, RCI, RDT)
- Surface samples
Collecting Mud Gas Samples During Drilling
Headspace Gas

Gas Bag / Isotube “Mud Gas”

Gas Detector

Iso-Jars / GeoJars
The genetic origin and thermal maturity of natural gases

• Principals:
  – Microbial gases
  – Thermogenic gases
  – Other processes
• Applications and case histories
Methanogenic archaea ("methanogens" - a diverse group of anaerobic archaeabacteria) produce CH₄ by two primary pathways:

- **CO₂ reduction (dominate process)**
  
  \[ 2\text{CH}_2\text{O} + 2\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 8(\text{H}) \]
  
  \[ 8(\text{H}) + \text{CO}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \]

- **Fermentation (in some freshwater environments)**
  
  \[ \text{CH}_3\text{COOH} \rightarrow \text{CH}_4 + \text{CO}_2 \]
Microbial Gas

Methanogens can live in surface environments as well as subsurface environments

Obligate anaerobes

Not active at temperatures > ~80°C (175 °F).

- Optimal temperature ~25° - 65°C (75° - 150° F)
- Depending on the geothermal gradient, in offshore environments this may correspond with sub-seabed depths of 2 - 4.5 km.

“The Sydney Morning Herald, February 25, 2009

“New Research into Livestock Methane Emissions”
Microbial gas: primary and secondary

Primary microbial methane
- Generated from dispersed organic matter through CO$_2$-reduction or methyl-type fermentation pathways
- Very common in low – moderate temperature sediments
- Significant resource in some areas, e.g.,
  - Deep water Gulf of Mexico, Trinidad, Montana and Colorado Groups

Secondary microbial methane
- Formed from biodegradation of oil and C$_{2+}$ gases
  - Antrim, New Albany, and some Appalachian Devonian Shales
- Many dry gas caps associated with biodegraded oil rims, e.g.,
  - Troll and other North Sea fields
  - North Slope Alaska
  - Western Siberia (?)
Microbial Gases

- $C_1/(C_2 + C_3) > 100$
- $\delta^{13}C_1 < -60$ permil
- $\delta DC_1 < -150$ permil
- $\alpha_{CO2-CH4}$:
  - 1.05 – 1.10 (carbonate reduction)
  - 1.035 – 1.06 (methyl fermentation)
- Bacterial ethane, propane etc.
Microbial Gases

- Biogenic Zone
- Initial Produced Gas
- Older 12C-Depleted Gas
- MONTANA, COLORADO GROUPS
- NIOPRARA Mixing Zone
- ANTRIM, NEW ALBANY
- Thermogenic Zone

Higher Hydrocarbons Depleted During Migration

Weatherford Laboratories
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Secondary Effects

From Martini and others (2003), AAPG Bulletin, v. 87, Figures 6 and 11
Examples

Osborne and McIntosh, Applied Geochemistry 25 (2010), p. 456 - 471
Thermogenic Gases

- \( C_1/(C_2 + C_3): < 100 \)
- \( \delta^{13}C_1: >> -50 \) permil
- \( \delta DC_1: > -275 \) permil
- \( \alpha_{CO2-CH4}: \)
  - \(<1.03 - 1.001\)
Thermogenic gas: primary and secondary

Primary thermogenic gas:
- Generated from thermal cracking of bitumen and kerogen in maturing source rocks.
- Occurs between VR₀ ~ 0.5 to 2.5%:
  - Lewan (2002 and in press) shows hydrous pyrolysis data indicating that generation of hydrocarbon gas from kerogen and associated bitumen ends before VR₀ = 2.0%:
    - T_max ~ 555°C
    - HI ~ 35 mg/gTOC
    - H/C ~ 0.49
    - No remaining alkyl moieties to source HC gases.

Secondary thermogenic gas:
- Formed from cracking oil, condensate, and heavy gases to light gas.
  - Oil cracking likely complete by VR₀ ~ 3.5%
  - Condensate/wet gas cracking VR₀ limits?
  - Residual gases in source rocks and conventional reservoirs?

From Lewan, 2002
Thermogenic gas: primary and secondary
Gas from Oil Cracking in Reservoirs

Above temperatures of ~160°C oil begins cracking to natural gas and pyrobitumen:

\[
\text{Oil} \rightarrow \text{Gas} + \text{Pyrobitumen}
\]

\[
\text{CH}_{1.8} \rightarrow 0.41 \text{CH}_{3.8} + 0.59 \text{CH}_{0.4}
\]

About 50% yield as natural gas
Thermal stability depends on oil composition
NSOs < C_{14+} aromatics < C_{14+} saturates < C_6- C_{14} saturates
Empirical interpretations

[Diagrams showing various gas types and isotopic compositions.]
Empirical interpretations
Empirical isotope plots – “gas fingerprints”? 

Not really...
The Chung plot (natural gas plot)

Theoretical kinetic isotope effects during cracking of gases from kerogen:

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

where \( \varepsilon = \delta^{13}C_{KER} - \delta^{13}C_i \)

References:
Support from ab initio calculations:

Hexane precursor

- 300 K
- 400 K
- 500 K
- 600 K
Clayton (1992) plots

From Clayton (1991)
Thermogenic gas interpretation
A Simple Conceptual Model of Thermogenic Gas Generation from Kerogen

<table>
<thead>
<tr>
<th>Initial Petroleum</th>
<th>Kerogen</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Reactive</td>
</tr>
<tr>
<td></td>
<td>Labile (Oil Generative)</td>
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</table>

**Generation**

- Oil
- 2° Gas
- 1° Gas
- Graphite

**Expulsion**

- Pyrobitumen

- Expelled Oil
- Expelled Gas

**Primary Migration**
Water Reforming and Fischer-Tropsh Processes in Post-Mature Shales?

• Proposed by Tang and Xia, 2010. Bear in mind that considerable published work on so-called abiogenic gases is relevant (see Katz and others, 2008 and Glasby, 2006)

• Water Reforming:
  \[ \text{CH}_x + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + (2+x/2) \text{H}_2 \]

• Fischer-Tropsh:
  \[ \text{CO}_2 + m \text{H}_2 \rightarrow x \text{CH}_4 + y \text{C}_2\text{H}_6 + \ldots + z \text{H}_2\text{O} \]
Abiotic gas generation mechanisms

- Fischer – Tropsch synthesis
- Thermal metamorphism of carbonates at > T and in the presence of water
- Thermal metamorphism of carbonates and graphite
- Serpentinization reactions
- Experimental work at elevated T and P relevant to the earth’s deep crust and mantle conditions points to the possibility of deep abiotic hydrocarbon synthesis.
Applications and case histories

From Zumberge and others, 2011

From Laughrey, 2014
Upper Cretaceous Colorado Group, Alberta

- Initially a microbial gas play.
- Apparent mix of microbial and thermogenic gas?

Average $\%R_o = 0.38$
- Recycled/Oxid. Vitrinite
Colorado Group (Alberta)
Colorado Group (Alberta)

Cooper and others (2012)
Colorado Group (Alberta)

Cooper and others (2012)
Colorado Group (Alberta)

Colorado shows residual structure and is, in this case, faulted due to the underlying channel.

Upper Mannville Channel shows substantial drape from differential compaction

Cooper and others (2012)
Thermal Maturity of Natural Gases

- Maturity of source material
- Onset of low-maturity and high-maturity thermogenic gas generation
- Recognition of gas alteration and gas destruction ("preservation basement")
Thermal Maturity from Stable Carbon Isotope Data

Modified after Faber, 1987
Thermal Maturity of Natural Gases

• Empirical approach (Types I and II organic matter):
  – $\delta^{13}C_1 = 15.4 \log_{10} %R_o - 41.3$
  – $\delta^{13}C_2 = 22.6 \log_{10} %R_o - 32.2$
  – $\delta^{13}C_3 = 20.9 \log_{10} %R_o - 29.7$
  – Most reliable using ethane and propane:
    • C2 and C3 never generated in significant quantities by microbial processes.
    • C2 and C3 less susceptible to secondary effects

See Whiticar, 1994
Thermal Maturity of Natural Gases – Marcellus
Example 1

- Great Lakes Renz #1 well, Washington County, PA:
  - $\delta^{13}C_1 = -42.19$ permil
  - $\delta^{13}C_2 = -33.15$ permil
  - $\delta^{13}C_3 = -28.46$ permil
  - Calculated $R_o \sim 0.9 - 1.1\%$ (Late Mature)

- You must calibrate isotope data and measured $R_o$ for each basin.

- Solving the equations for $R_o$:
  - $\log_{10} R_o = \frac{13C_1 + 41.3}{15.4}$
  - $\log_{10} R_o = -42.19 + 41.3 \div 14.4$
  - $R_o = 0.9\%$
  - $\log_{10} R_o = \frac{13C_2 + 32.2}{22.6}$
  - $\log_{10} R_o = -33.15 + 32.2 \div 22.6$
  - $R_o = 0.91\%$
  - $\log_{10} R_o = \frac{13C_3 + 29.7}{20.9}$
  - $\log_{10} R_o = -28.46 + 29.7 \div 20.9$
  - $R_o = 1.1\%$
Point Pleasant Fm: Thermal Maturity?

TOC = 3.27 wt.%
S1 = 3.12 mg hc/g rock
S2 = 2.43 mg hc/g rock
T_{max} = 470°C
HI = 74 mg hc/g TOC
PI = 0.56

R_{oe} = 1.3 (from T_{max}): “Late Oil”
• All aromatic biomarkers at equilibrium values ($\geq R_{oe}$ of 1.3%)

• $R_{oc} = 1.47$ (from MPI):
  - “condensate/wet gas”
C₇ Hydrocarbon Analysis
(Thompson parameters)

Oils thermally cracked

High maturity oil/condensate

Supermature oils

> Mature oils

Utica
C₇ Hydrocarbon Analysis
(Mango parameters)

• C₇ hydrocarbon ratios based on Mango’s (1987; 1990) steady-state kinetic model of light hydrocarbon generation are useful for oil-oil and oil-condensate correlations and to determine the temperature of generation (see Peters and others, 2005, p. 179 – 190):
  
  $°C_{\text{temp}} = 140 + 15(\ln[2,4\text{-DMP}/2,3\text{-DMP}])$

  • 2,4-DMP/2,3-DMP – 2,4-dimethylpentane ÷ 2,3-dimethylpentane
  • $\ln[2,4\text{-DMP}/2,3\text{-DMP}]$ Utica extract = -0.87
  • $\ln[2,4\text{-DMP}/2,3\text{-DMP}]$ Point Pleasant extracts = -1.14 to -1.22
  • $°C_{\text{temp}} = 153°$ to $158°$ (wet gas zone/oil cracking)
Point Pleasant Fm: Thermal Maturity

\[ \delta^{13}C_{\text{kerogen}} = -29\% \]

Gas maturity \( \sim \) \( VR_{oe} \) of 1.5

Model and figure from Xia and Tang (2012) with field data from Burruess and Laughrey (2010)
Thermal Maturity of Natural Gases – Marcellus Example 2

- **API** = 56.9° - 58°
- Unimodal distribution of predominant n-alkanes maximized at C$_7$ – C$_8$
- Maximum temperature of generation = 131° - 133°C
  - 140 + 15[$\log_e(2,4\text{DMP}/2,3\text{DMP})$]
  - Mango, 1994
  - **Late oil/generation of lighter oil**
  - Isoheptane values > 2.0 and Heptane values > 30 (protracted thermal transformation and cracking to gas)
Macerals in Oil-Prone Cretaceous Source Rocks (WIS)
Dual Maturity from VRo

Primary Vitrinite: $VR_o = 0.58\%$

Recycled Vitrinite: $VR_o = 0.87\%$
Dual Maturity from Alginite Fluorescence

Primary Alginite

Reworked Alginite

Onset of oil generation

Mid-oil window
Recycled Vitrinite Reflectance vs. $T_{\text{max}}$

$T_{\text{max}} = 430^\circ\text{C}$

Mean $\text{VR}_0 = 0.92\%$
Recycled Vitrinite Reflectance vs. Calibrated Gas Isotopes

Mean $VR_o = 0.92\%$
“Roll over”

From Zumberge and others, 2011 and Tilley and Muehlenbachs, 2012
Thermal Maturity and “Rollover” (slide courtesy of Wally Dow)

Mud Gas Ethane Isotope “Reversals” (Haynesville Example)

Bossier / Cotton Valley

Haynesville

Top of Overpressure

“Normal” maturity isotopic trend.
Gas Isotope Reversals

from Laughrey and Kostelnik, 2007 and Burruss and Laughrey, 2010.
Gas Isotope Reversals

Fig. 4. Scheme showing $\delta^{13}C$ reversal due to mixing of primary and secondary gas.

From Xia and others, 2012
The Marcellus Formation Gases Exhibit Carbon and Hydrogen Isotope Reversals with Respect to Carbon and Hydrogen Number

This study: NE PA; Reversed gas plot

\[ \delta^{13}C_1 > \delta^{13}C_2 > \delta^{13}C_3 \]

\[ \delta^{13}C_{KEROG} = -28.8\% \]

SW PA: Range Resources Marcellus Wells; Normal gas plot

\[ \delta^{13}C_1 < \delta^{13}C_2 < \delta^{13}C_3 \]

1From Laughrey (2014 and in review), Applied Geochemistry. Data courtesy Pennsylvania Geological Survey. Reported distribution of Devonian \( \delta^{13}C_{KEROG} \) values in the Appalachian basin (green arrow) from Maynard, 1981.

\[ \updownarrow \] Marcellus \( \delta^{13}C_{KEROG} \) from Werne and others, 2002
The Marcellus Formation Gases Exhibit Carbon and Hydrogen Isotope Reversals with Respect to Carbon and Hydrogen Number

• Proposed Explanations
  – Mixing:
    • Mixing of gases from different sources and of different thermal maturities (Jenden and others, 1996).
    • **Mixing of primary and secondary gases in source rocks** (Xia and others, 2012).
  – Rayleigh fractionation of the isotopic compositions of $C_2$ and $C_3$ during redox reactions of gases combined with:
    • the isotopic exchange of $C_1$ hydrogen with formation water;
    • Mixing with late-stage generation of CH$_4$ from super mature organic matter (Burruss and Laughrey, 2010).
  – Reforming/Recombination Reactions:
    • Organic matter/water reforming and Fischer-Tropsch synthesis (Sherwood Lollar and others, 2002; Tang and Xia, 2010).
    • **Gas-phase radical recombination reactions in deep-seated thermogenic hydrocarbon deposits** (Telling and others, 2013).
  – Isotopic fractionation introduced from gas adsorption/desorption and diffusion (Xia and Tang, 2012).
Marcellus Fm Gases: Primary Cracking of Carbonaceous Residual Type II Kerogen

- $\delta^{13}\text{CH}_4 = -28.69$ to $-24\%\text{o}$
- $\delta^{13}\text{C}_{\text{KEROGEN}} = -28.8\%\text{o}$
- $\text{H/C} = 0.4$
- $\text{O/C} = 0.06$

This study: NE PA

Range Resources Marcellus discovery: SW PA
Marcellus Fm Gases: Secondary Cracking of C$_2^+$ Hydrocarbons

$\delta^{13}$C$_{\text{KEROGEN}} = -28.8\%$
Lower Marcellus Fm Pressure Core: GIP = 329.03 scf/ton

CUMULATIVE DEGASSING VOLUME (% OF TOTAL)

δ^{13}C₁ (%)

Reflectance @ 546nm

3-50G

mean VR_o = 3.64%

PC-2 canister (9:00 – 20:35)

Crushed sample gas

δ^{13}C₁ of mud and production gases
What about shale gas “desorption”?

- Unlike CBM core where desorption accounts for gas production, in shales diffusion trumps gas desorption. Shale gas moves by diffusion through the nanopore system. Isotopically light molecules diffuse faster resulting in observed fractionations. Possible proxy for organic porosity interconnectedness/permeability.
Correlating natural gases with their source rocks and each other
Reservoir Compartmentalization Principle

Flow Units

Geochemical Flow Unit Definition

Courtesy of Martin Schoell
York Field, Trenton-Black River Group reservoir gases

δ¹³C, Methane isotopic composition

δ¹³C₁, δ¹³C₂, δ¹³C₃, δ¹²nC₄, δ¹²/C₄

C₁-C₄ Hydrocarbons

Downes #1 well
Rifle #1 well
Dain #1 well
Downes #3 well
Mantell #1 well
York #1 well

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Non-hydrocarbon Gases in Shales

• Carbon dioxide:
  – Organic matter
  – Decarboxylation of organic acids (diagenetic remineralization)
  – Microbial degradation or oxidation of hydrocarbons
  – Inorganic dissolution of carbonates in the catagenetic stage (release of oxygen-bearing groups)
  – Magmatic CO$_2$
Variations in $\delta^{13}$CO$_2$ from Different Sources (Hunt, 1996, Table 7-7)

- Thermal degradation of organic matter: -8 to -12 ‰
- Thermal destruction of carbonates: +4 to -5 ‰
- Bacterial oxidation of CH$_4$: -20 to -59 ‰
- Volcanic degassing: -8 ‰
- Atmospheric CO$_2$: -8 ‰
Mancos Shale, Piceance Basin

- CH₄: 90.6%
  - δ¹³CH₄ = -34.3‰
- CO₂: 9.4%
  - δ¹³CO₂ = -1.7‰
- α₂CO₂-CH₄ = 1.033
- Thermogenic gas (%VR₀ = 1.7) with deep-seated CO₂ component derived from the thermal destruction of carbonates heated by magma
Caution: ranges of $\delta^{13}C$ in crustal and magmatic CO$_2$ are not unique!

- Useful to constrain interpretations with noble gas data:

From Ballentine and others, 2001
Non-hydrocarbon Gases in Shales

- Nitrogen:
  - Release of nitrogen-bearing groups from organic matter
  - Release of ammonia from clays at elevated temperatures
  - Influx of mantle nitrogen
  - Atmospheric nitrogen and dissolved meteoric nitrogen
Isotopic Composition ($\delta^{15}\text{N}$) of Nitrogen Observed in Natural Gases

- Thermally immature/early mature organic matter: $-19\permil \leq -10\permil$
- Mature to post mature organic matter: $-10\permil \leq -2\permil$ ($%VR_o = 0.6$ to 2)
- Deep crust or mantle: $-2\permil$ to $+1\permil$
- Atmospheric $\text{N}_2$: $0\permil$ and $\text{N}_2/\text{Ar} = 38$ - 84
- $\text{N}_2$ from ammonium in clay minerals: $+1\permil \leq +4\permil$
- Post mature ($%VR_o > 2$): $+4\permil \leq +18\permil$
- Overlapping range of $\delta^{15}\text{N}_2$ for respective end members and uncertainty in the range of $\delta^{15}\text{N}_2$ of these end members: *best to constrain with noble gas data*
Isotopic composition ($\delta^{15}N$) of nitrogen observed in natural gases

- Thermally immature/early mature organic matter: $-19\%_o \leq -10\%_o$
- Mature to post mature organic matter: $-10\%_o \leq -2\%_o$ (%VR$_o$ = 0.6 to 2)
- Deep crust or mantle: $-2\%_o$ to $+1\%_o$
- Atmospheric $N_2$: $0\%_o$ and $N_2/Ar = 38 - 84$
- $N_2$ from ammonium in clay minerals: $+1\%_o \leq +4\%_o$
- Post mature (%VR$_o$ > 2): $+4\%_o \leq +18\%_o$
- Overlapping range of $\delta^{15}N_2$ for respective end members and uncertainty in the range of $\delta^{15}N_2$ of these end members: *best to constrain with noble gas data*
Utica Shale, Central Pennsylvania

- $C_1$: 96.88%; $\delta^{13}C = -26.97‰$
- $C_2$: 1.22%; $\delta^{13}C = -34.68‰$
- $C_3$: 0.07%; $\delta^{13}C = -37‰$
- $N_2$: 0.66%; $\delta^{15}N = -9.2‰$
- $CO_2$: 1.8% $\delta^{13}C = -0.39‰$
- R/Ra: 0.021
- $^{40}Ar/^{36}Ar$: 312
- $^{40}AR^*/^{4}He$: 0.029
- $^{20}Ne/^{36}Ar$: 0.735
Non-hydrocarbon Gases in Shales

• Hydrogen Sulfide:
  – Thermal decomposition of high-sulfur oils deeper than the oil window
  – Thermochemical reduction of sulfate in pore waters accompanied by the oxidation of hydrocarbons
  – Thermal degradation of kerogen
  – Typically sequestered by iron minerals in shales, but a potential problem in carbonate source rocks (Niobrara, Point Pleasant/Trenton)
Hydrogen Sulfide and Nitrogen in Trenton/Point Pleasant Reservoir, PA

- Wolpert #1 well, Bradford County, PA
  - 0.51 mole percent H₂S
  - 14.14 mole percent N₂
- Limits to deeper Ordovician gas?
What is the Source of the $\text{H}_2\text{S}$?

- $\delta^{34}\text{S} = 14.7$ permil
- Stable isotope composition suggests a sulfate source for the $\text{H}_2\text{S}$:
  - Dissolved sulfate in brine
  - Anhydrite
- $\text{H}_2\text{S}$ formed in the reservoir at high temperatures (> 140°C) through thermochemical sulfate reduction (TSR)
What is the Source of the Nitrogen?

- $\delta^{15}N_2 = 0.4$ permil
  - Deep crust or mantle source
  - Further constrained by noble gas data:
    - No fractionation due to diffusion
    - Highly mature organic matter source; possibly metamorphic
- Nitrogen concentration increased at the expense of hydrocarbons destroyed by TSR
Nitrogen in deep Trenton/Black River reservoirs?

δ₁⁵N (‰) vs. N₂ mol% for
- Wolpert #1
- Glodes Corners/Langdon Hills
- Utica Shale source rocks

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• He, Ne, Ar, Kr, Xe isotopes provide useful tracers in fluid system studies:
  – Noble gases from the crust, mantle, and the atmosphere (dissolved in groundwater) all have a unique isotopic fingerprint
  – Resolve and quantify the contribution of fluids from these different sources

• Noble gases partition between water, gas, and oil phases as a function of solubility and relative volume of the different phase.
Helium Data

- Glodes Corners field:
  - $^{3}$He/$^{4}$He: 1.53 – 2.74 x $10^{-7}$
  - R/R$_{a}$: 0.019 – 0.196
    - Modestly elevated – possible mantle component
    - 1.2 – 2.3% mantle-derived $^{4}$He
  - Most He crustal in origin, but mantle He flux in the field is significant compared to other Ordovician carbonate reservoirs in the region.
  - Reflects the association of deep-seated basement faulting and fracturing at the northern margin of the play
Helium Data

- Other NY and PA fields:
  - $^{3}\text{He}/^{4}\text{He}$: $1.48 - 3.08 \times 10^{-8}$
  - $R/R_a$: $0.01 - 0.022$
  - He of crustal origin

$R/R_a$: $0.01 - 0.022$

$R/R_a$: $0.019 - 0.196$
CH$_4$/$^3$He in the Glodes Corners gases ($4.45 \times 10^6$ to $11.6 \times 10^6$) indicate a crustal methane source; minor mantle $^4$He component is present.

Crustal production ratio: closed system conditions
Mass fractionation Gas/Water at relatively cool temperatures

Atm loss in reservoir with 40Ar production possible early oil fm and loss

Black River
Original
Marshlands
Difference Between Mud Gas and Headspace Gas

• Mud gases are the “free” gas that comes out of the formation that has been circulated up in the mud
  — Gas isotopes usually compare well with “true” formation gas
  — Gas molecular composition usually drier (e.g., excess $C_1$) than true formation gas
  — Gas recycling can be a problem

• Headspace gases are the gases liberated into the headspace volume that have evolved out of the cuttings
  — Gas isotopes usually heavier than true formation gas
  — Gas molecular composition usually wetter (e.g., excess $C_{2+}$) than true formation gas
  — Used mainly in source rock evaluation, show detection and surface geochemistry
Mud gases suggest a flow barrier at about 5250 m MD

Produced gas isotopes indicate the toe section was not contributing to production

From Rein and Schultz (2003)
Assessment of Reservoir Continuity
Assessment of Reservoir Continuity

Stable Carbon Isotopic Composition

δC¹³ (‰)

Measured Depth (feet)

Well #2
Well #1

SL-2
SL-2B
SL-3
SL-4
SL-5
SL-6
SL-6B
SL-7
SL-8
SL-9

C1
C2
C3
Normalized isotopic composition of produced gases showing pronounced differences between N1, N4 and N5 gases and other gases

A significant degree of compartmentalization is suggested by gas and condensate geochemistry

After Mueller and Scholz (2004)
Predicting Saturation Pressures

From Weissenburger and Borbas (2003)
Introduction to Petroleum Isotope Geochemistry

Stable Isotope Applications in Liquids:

- Correlation of whole oils, bitumens, and kerogen
- Quantitative estimates of oil co-sources
- Marine versus terrigenous organic input
- Compound Specific Isotope Analysis (CSIA)
- Reconstruction of paleoenvironment
- CSIA for correlation
- Distributed source rock sampling
- CSIA of carboxylic acids
### δ\(^{13}\)C of hydrocarbon extracts from the Niobrara Formation

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<td>Series 1</td>
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<td>-29.8</td>
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Marine versus Terrestrial Input
$\delta^{13}C$ of hydrocarbon extracts from the Niobrara Formation

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Marine versus Terrigenous Organic Input – Niobrara Fm Extracts

TERRESTRIAL

MARINE

d$_{13}$C Aromatics

d$_{13}$C Saturates
Petroleum Geology and Geochemistry

From Keith, 1988

Utica
Point Pleasant
Trenton
GICE
Wantz well
## Related Applications of Geochemistry

Geochemistry solves problems throughout the lifespan of a field

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<th>PRODUCTION</th>
<th>FIELD ABANDONMENT</th>
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<td>Characterizing charge Risk (source, maturity, timing, gas vs oil potential)</td>
<td>Assessing reservoir compartmentalization</td>
<td>Oil/gas property prediction (API, viscosity)</td>
<td>Identifying completion problems (tubing string leaks, poor cement jobs, ineffective stimulations)</td>
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<td>Identifying missed pay</td>
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<td>Identifying induced fracture geometry</td>
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<td>Flood monitoring – Assessing sweep</td>
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<td>Flow Assurance: Prevent Sludge/Asphaltenes/ Wax Deposition</td>
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