“Carbon and hydrogen isotopic evidence for the origin of combustible gases in water-supply wells in north-central Pennsylvania”

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In cooperation with PADEP (Pennsylvania Department of Environmental Protection)
Natural Gas Migration Problem in Pennsylvania

The Pittsburgh Geological Society

[Diagram of gas migration process]

The Pittsburgh Geological Society
Northeastern United States of America
Tioga Junction Study Area – Tioga Gas-Storage Field

[Map showing geological features including shallow oil field, shallow gas field, deep gas field, and gas storage area.]
Storage fields are 3,500 - 4,100 feet below surface in Devonian rock.
Methane (CH₄) concentrations in well water

Uplands-- Fractured BEDROCK AQUIFER -- Lock Haven Formation of Devonian age

Valley-- GLACIAL OUTWASH AQUIFER of Quaternary age

EXPLANATION

A→A' Hydrogeologic section
- Anticline
\( \text{Faults} \)

- Water well in outwash aquifer and well number in Table A-2
- Water well in bedrock aquifer and well number in Table A-2
- Water well used for hydrogeologic section (Fig. 5) from Williams and others, 1998

Methane concentration in milligrams per liter

- \( \text{TI 606} \): \( \geq 2 \) to \( \leq 10 \)
- \( \text{TI 611} \): \( \geq 20 \) to \( < 25 \)
- \( \text{TI 577} \): \( > 10 \) to \( < 20 \)
- \( \text{TI 584} \): \( \geq 25 \)
\[ \delta^{13}C = \frac{R_{\text{sample}} - R_{\text{reference}}}{R_{\text{reference}}} \]

Where \( R = \frac{^{13}\text{C}}{^{12}\text{C}} \),

\( R_{\text{reference}} = \) VPDB (Vienna Pee Dee Belemnite)
Microbial Methane production

1. Near-surface environment, marsh etc.
   
   \[ \text{CH}_4 \text{ production by fermentation pathway:} \]
   \[ \text{CH}_3\text{COOH} = \text{CH}_4 + \text{CO}_2 \]
   
   Isotope change: Intra-molecular fractionation: \( \text{CH}_3 = \delta^{13}\text{C} \) in \( \text{CH}_3 \) depleted; \( \delta^{13}\text{C} \) in \( \text{COOH} \) is enriched.
   
   Product: \( \text{CH}_4 = \delta^{13}\text{C} \) depleted; \( \text{CO}_2 = \delta^{13}\text{C} \) enriched. (DIC)
   
   Concentration change: \( \text{CH}_3\text{COOH} \) decreasing
   
   \( \text{CH}_4 \) and \( \text{CO}_2 \) increasing (DIC)

2. Drift gas -old, covered by glacial drift deposit.
   
   \( \text{CH}_4 \) production by \( \text{CO}_2 \) reduction pathway:
   
   \[ \text{CO}_2 + 4\text{H}_2 = \text{CH}_4 + 2\text{H}_2\text{O} \]
   
   Isotope change: \( \text{CH}_4 = \delta^{13}\text{C} \) depleted; \( \text{CO}_2 = \delta^{13}\text{C} \) enriched (DIC);
   
   Concentration change: \( \text{CH}_4 \) increasing, \( \text{CO}_2 \) decreasing (DIC)

3. Minimal \( \text{C}_2 \) and \( \text{C}_3 \) production, \( \delta^{13}\text{C} = \) very depleted in \( ^{13}\text{C} \).
Thermogenic Methane production

– formed by thermal break down.

Higher hydrocarbon (C₂; C₃; etc.) present

δ¹³C isotope of CH₄ is closer to the isotope of substrate it is produced from (more enriched than microbial). δ¹³C of C₂ and C₃ are more enriched than microbial.
Methane oxidation
independent from production pathways

\[ 2\text{CH}_4 + 4\text{O}_2 = 2\text{CO}_2 + 4\text{H}_2\text{O} \]

Concentration change:
\( \text{CH}_4 \) decreasing, \( \text{CO}_2 \) (DIC) increasing.

\[ \delta^{13}\text{C} \] isotope change:
\( \text{CH}_4 \) becomes enriched; \( \text{CO}_2 \) (DIC) becomes depleted
Stable Isotope ranges of methanes from different sources

Whiticar, 1999:
Thermogenic Gas:
$\delta^{13}C = -50$ to $-20\%_\circ$;
$\delta D = -275$ to $-100\%_\circ$.

Microbial Gas:
$\delta^{13}C = -80$ to $-50\%_\circ$;
$\delta D = -400$ to $-300\%_\circ$.

$\delta^{13}C = -50$ to $-20\%_\circ$;
$\delta D = -350$ to $-100\%_\circ$.

After Coleman and others (1993) based on the data set of Schoell (1980)
Stable Isotope ranges of methanes from different sources (Whiticar, 1999)
$^{14}\text{C pMC (percent modern carbon)}$ in methane from different sources

- **Natural gas and coalbed gas** (no detectable $^{14}\text{C}$)
- **Glacial drift gas**
- **Swamp and marsh gas** (expected range)
- **Landfill gas**

Coleman and others (1993)
Possible Origins of Methane in the Area

• **Oriskany gas** - *thermogenic*, used up long time ago.
• **Pipe Line gas** – *thermogenic*.
• **Microbial** from possible landfill, or natural decay of organic matter.
• **Devonian gas (shallow)** - *thermogenic*.
• **Mixture** of all above.
Sample collection and analyses

- **Collections:**
  - End member Gases: Oriskany, Pipe Line; Storage gas.
  - Groundwater, containing methane (C1).

- **Analysis:**
  - \(^{13}\)C of C1 and C2; Deuterium of C1; \(^{14}\)C of C1 of some samples, Dissolved gas concentration, Water isotopes, \(^{13}\)C of DIC, Alkalinity.
$\delta^{13}$C and $\delta$D of CH$_4$ in sampled end members of natural gas
$\delta^{13}C$ of CH$_4$ and C$_2$H$_6$ in end member gas wells
\( \delta^{13}C \) of CH\(_4\), collected by USGS and Dominion Gas Co.
Whiticar, 1999:
Thermogenic Gas: $\delta^{13}C = -50$ to $-20\%_\circ$; $\delta D = -275$ to $-100\%_\circ$
Microbial Gas: $\delta^{13}C = -110$ to $-50\%_\circ$; $\delta D = -400$ to $-150\%_\circ$
$^{14}$C concentrations in methane samples from different sources.

- Natural gas and coalbed gas (no detectable $^{14}$C)
- Glacial drift gas
- Swamp and marsh gas (expected range)
- Landfill gas

Coleman and others (1993)
Relationship between $^{13}$C of CH$_4$ and conc. of C$_2$H$_6$ in wells

![Graph showing the relationship between $^{13}$C of Methane and Ethane concentration in Vol %]
δ¹³C of CH₄ and C₂H₆ for gas and ground-water (GW) samples
Bernard Graph
Bernard and others 1976

Type of Wells:
- ▲ Rock wells (GW)
- ○ Outwash wells (GW)
- ♠ Oriskany gas well
- □ Storage wells (gas)
- ▼ Non-native Storage Inj. wells (gas)

Biogenic End Member

Thermogenic End Member

\[
\frac{C_1}{(C_2+C_3)} \text{ concentration}
\]

\[
\text{delta } ^{13}\text{CVPDB of CH}_4 \text{ in per mil}
\]
Modified Bernard Graph
Taylor and others, 2000

Microbial CH₄

Thermogenic CH₄

$\delta^{13}C_{vPDB}$ of C2 in per mill

$\frac{CH_4}{(C_2+C_3)}$
Meteoric Water Line in GW

All GW data fall on the same MW-line.

\[
\delta^2 \text{H}_{\text{H}_2\text{O}} = 7.56 \times \delta^{18}\text{O}_{\text{H}_2\text{O}} + 8.57
\]

R-squared = 0.84

Well Origin

Rock

Outwash
Relationship between CH$_4$ and coexisting water

What else could make the DIC -4‰ than CH$_4$ production? Background is around -14 ‰.
Relationship between microbial CH$_4$ and coexisting water

This indicates a CH$_4$ production; the higher the DIC conc. the more enriched in $^{13}$C isotope. In case of CH$_4$ oxidation depleted $^{13}$C-of DIC should correlate with higher conc. of DIC.
Microbial Methane production and Consumption (Whiticar, 1999)

This indicate an acetate fermentation pathway CH₄ production; DIC conc. is increasing, and its isotope is enriched in C-13. There could be CH₄ oxidation as well, where DIC conc. increasing, its ¹³C is depleted, CH₄ conc. decreasing, ¹³C of CH₄ is enriched.
$\delta^{13}C$ and $\delta^2H(\delta D)$ of CH4 and $\delta^{13}C$ of DIC in sampled water wells
Methane (CH₄) concentrations in well water

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Methane Signatures in Groundwater from Wells

**Thermogenic with >0.1 percent ethane**

**Microbial**

Methane Signatures in Groundwater from Wells
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Relationship between $^{14}\text{C}$ and $^{13}\text{C}$ isotopes of $\text{CH}_4$ in GW wells
Relationship between $^{14}\text{C}$ and D isotopes of CH$_4$ in GW wells

![Graph showing the relationship between $^{14}\text{C}$ of CH$_4$ in PMC and delta D of CH$_4$ vsSMOW in per mil.](image)
Relationship of Ar and Methane concentration in water wells

Solubility of gases at 15 oC
Ar = 0.07 g/kg
CH4 = 0.028 g/kg
C2H6 = 0.08 g/kg