Differentiation of Biotic and Abiotic CH₄: Lessons from terrestrial analogs

B. Sherwood Lollar, U. Toronto
bslollar@chem.utoronto.ca
What can we learn from Earth analogs about differentiation?
Outline

- Overlapping Definitions and Signatures
- Success requires multiple lines of evidence, and contextual evidence
- New technologies (e.g. clumped isotopologues, PSIA) enabling a renaissance in the field
- For Mars - helps to consider the Parsimonious approach
- Test case from Earth analogs for differentiating biotic and abiotic CH$_4$
- Conclusions
Methane On Earth

BIOTIC
- Microbial
- Thermogenic

ABIOTIC
- Mantle-derived
- Crustal-derived

Many overlapping definitions
Overlapping $\delta^{13}C$ Signatures - *Biotic*

*Diagram showing overlapping $\delta^{13}C$ signatures between Thermogenic and Microbial sources of methane, according to Schoell (1988).*
Overlapping $\delta^{13}C$ Signatures - Abiotic

- Thermogenic
- Microbial
- Mantle carbon
- Experimental and field abiotic CH$_4$

$\delta^2$H$_{\text{CH}_4}$ (‰)

$\delta^{13}C_{\text{CH}_4}$ (‰)
Biotic vs Abiotic CH$_4$

- $\delta^{13}$C (or $\delta^2$H) value alone not diagnostic
- Abiotic CH$_4$ will have a $\delta^{13}$C value that reflects the local carbon source
- Enriched – if mantle-derived
- Wide possible range of $\delta^{13}$C values in crustal environments
- Mantle-derived = abiotic
- Abiotic is not necessarily mantle-derived
Methane on Earth

**BIOTIC**
- Microbial
- Thermogenic

**ABIOTIC**
- Mantle-derived
- Crustal-derived

$\text{CH}_4$

High $T$
Low to moderate $T$
processes of WRI or abiotic organic synthesis
• Overlapping Definitions and Signatures
• Success requires multiple lines of evidence, and contextual evidence
• New technologies (e.g. clumped isotopologues, PSIA) enabling a renaissance in the field
• For Mars - helps to consider the Parsimonious approach
• Test case from Earth analogs for differentiating biotic and abiotic CH₄
• Conclusions
Multiple Lines of Evidence

1. Isotopic signatures: including C & H source signatures and reaction products
2. Associated species (DIC, H₂O, H₂, higher hydrocarbons, N- or S- compounds)
3. Conservative tracers (e.g. noble gases)
4. Geologic and hydrogeologic context
5. Evaluate end-members and mixing
6. Post-genetic alteration and sinks
7. New breakthrough technologies (e.g. clumped isotopologues)
Researchers are developing instruments to determine where molecules come from — revealing everything from the origins of natural gas on Earth to whether there is life on Mars.

Shuhei Ono & D.T. Wang - MIT
A new geothermometer for methanogenesis based on $^{13}\text{CH}_3\text{D}$:

![Graph showing clumped isotope effect vs. temperature](image)

**Figure 2**: Methane clumped isotope thermometry scale.

The $\Delta_{18}$ value measures the deviation of the ratio $^{13}\text{CH}_3\text{D}/^{12}\text{CH}_4$ from that expected for a statistical (i.e., high temperature) distribution. For methane clumped isotope system, $\Delta_{18}$ equal to $(K-1)\times1,000$, where $K$ is the equilibrium constant for isotope exchange reaction (R2). Also shown in the figure are $T-\Delta_{18}$ relationships expected for various methane sources based on “typical” ranges of formation temperatures.
A new geothermometer for methanogenesis:
- Deeper levels of information available

3 complications and/or opportunities
- Low to moderate T Abiotic organic synthesis from water-rock reaction
- Mixing (e.g. $^{12}$CH$_2$D$_2$)
- Kinetic effects of microbial methanogenesis vs. equilibrium geothermometry (e.g. Wang et al., 2015)

**Figure 2:** Methane clumped isotope thermometry scale.

The $\Delta_{18}$ value measures the deviation of the ratio $^{13}$CH$_3$D/$^{12}$CH$_4$ from that expected for a statistical (i.e., high temperature) distribution. For methane clumped isotope system, $\Delta_{18}$ equal to $(K-1)\times1,000$, where $K$ is the equilibrium constant for isotope exchange reaction (R2). Also shown in the figure are T-Δ$_{18}$ relationships expected for various methane sources based on “typical” ranges of formation temperatures.
Outline

• Overlapping Definitions and Signatures
• Success requires multiple lines of evidence, and contextual evidence
• New technologies (e.g. clumped isotopologues, PSIA) enabling a renaissance in the field
• For Mars - helps to consider the Parsimonious approach
• Test case from Earth analogs for differentiating biotic and abiotic CH₄
• Conclusions
Origin of Methane On Mars?

Parsimonious approach – what measurement(s)?
Parsimonious approach

- Associated Gases
- 1. H₂ levels
- 2. Ethane (C₂H₆) levels
- 3. CH₄/H₂ and CH₄/C₂H₆ (CH₄/C₂⁺) ratios
- Conservative noble gases
  - constrain origin & sinks
  - constrain production rates & flux for reactive reduced gases (e.g. H₂/He)

Sherwood Lollar et al., 2014 Nature
Associated Gases (gas ratios)

- 1. Abiotic end-members from low T water-rock reaction (e.g. serpentinization) are characteristically H₂-rich
- 2. Microbial metabolisms (sulfate-reducers, methanogens) drive down H₂ concentrations
- 3. Abiotic end-members from low T water-rock reaction (e.g. serpentinization) are often rich in ethane in addition to CH₄ – resulting in low CH₄/C₂⁺ ratios (< 100)
- 4. Microbial methanogens produce little ethane and hence high CH₄/C₂⁺ ratios (>>1000)
Test case from an appropriate Earth analog?
Test Case: Ongoing reduced Gas production from billion(s) year old rock with (some) relevant minerology – the Precambrian Shields
Precambrian > 72% of surface area of Earth’s continental crust

14% Archean
86% Proterozoic

Data from Goodwin (1996); Condie (1993); Rudnick and Fountain (1995)
The contribution of the Precambrian continental lithosphere to global $H_2$ production

Barbara Sherwood Lollar$^1$, T. C. Onstott$^2$, G. Lacrampe-Couloume$^3$ & C. J. Ballentine$^3$
Analogs of ongoing processes of water-rock reaction relevant to Mars

- Water-rock reactions such as radiolysis (Lin et al., 2005) and serpentinization (Sherwood Lollar et al, 2006) producing $\text{H}_2$
- Drives the Deep Carbon cycle e.g. methanogenesis

**Abiotic Organic Synthesis**

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

**Surface catalyzed Fischer Tropsch–Type (Sabatier) Reactions**

**Microbial Methanogenesis**

\[
\text{CO}_2 + \text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}
\]

**CO}_2 reduction**
Test Case: Associated Gases

- Carry out this test for biotic vs. abiotic CH₄ on this global database
- 1. H₂ levels
- 2. Ethane (C₂H₆) levels
- 3. CH₄/H₂ and CH₄/C₂H₆ (CH₄/C₂⁺) ratios
- 4. Focus: South Africa where greatest contextual evidence gathered over past 20 years
Test Case: Wits Basin

Associated gases (H₂, C₂H₆) successfully identify sites with microbial CH₄

Consistent with sites where multiple lines of evidence (including culture and genomic data) support dominance of microbial methanogenesis
Multiple Lines of Evidence

1. Isotopic signatures: including carbon source and reaction products
2. Associated species (DIC, H₂O, H₂, higher hydrocarbons, N- or S- compounds)
3. Conservative tracers (e.g. noble gases)
4. Geologic and hydrogeologic context
5. Evaluate end-members and mixing
6. Post-genetic alteration and sinks
7. New breakthrough technologies (e.g. clumped isotopologues)
Conduits to Surface

Diffuse gas seeps over cratons

$\text{CH}_4$ gas from perennial springs in high Arctic permafrost
Reduced gases ($H_2$ and $CH_4$) exsolving from groundwaters above kimberlite pipes

Modified from Sader et al 2007
Acknowledgements

T.C. Onstott, C.-L. Lau, C. Magnabosco, Princeton
G. Holland, J. Fellowes Manchester
G.F. Slater, D. Simkus McMaster
E. Van Heerden, G. Borgonie, K. Olukayode, UFS
J. Lippmann-Pipke, Leipzig
T. Brisco, K. Wilkie, J. Moran, K. Chu
G. Lacrampe-Couloume, S. Mundle, Toronto
J. McDermott, C. Glein, Toronto