Compound Specific Hydrogen and Carbon Isotopes as a Tool to Distinguish Abiogenic from Biogenic Hydrocarbons – Implications for the Terrestrial Deep Biosphere and Astrobiology

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Talk Outline

• Focusing on deep crustal brines present within Precambrian Shield regions of the world
• Origin of methane associated with the brines, and how we can tell if it’s abiogenic or biogenic
• Origin of hydrogen associated with the brines, and outline evidence that the hydrogen is supporting a deep terrestrial biosphere
• Relevance to astrobiology
Precambrian Shield Areas

- Fennoscandian Shield
- Canadian Shield
- African Shield
Canadian Shield Sites
South Africa: Witwatersrand deep gold mines

Witwatersrand Basin

South Africa
Geological settings

- **Kidd Creek Mine (Canada)**
  - 2700 Ma diorite, rhyolite, ultramafics
- **Copper Cliff Mine, Sudbury Basin (Canada)**
  - 1840 Ma norites, quartz diorites
- **Witwatersrand Basin - Kloof, Driefontein, Mponeng mines (S. Africa)**
  - 2700 Ma basaltic volcanics
Deep Shield Brines

• Saline groundwaters, with salinities of 100s g/L, chemistry often often dominated by Ca-Na-Cl

• Result from extensive water-rock interaction over tens to hundreds of Ma (based on *Lippmann et al. 2003*)

• Extensive water-rock interactions often mask the primary origins of the fluids

• Accessed by mining activity: mines provide *window into the deep Precambrian Shield subsurface.*
Deep Crustal Gases

Dissolved gases in sealed fracture systems (pressures > 5000 KPa)

By Volume

\( \text{CH}_4: \ 50-90 \% \)

\( \text{C}_2+: \ < 1-12 \% \)

\( \text{He:} \ < 1-10\% \)

\( \text{H}_2: \ < 1-58 \% \)

Dissolved gases in sealed fracture systems (pressures > 5000 KPa)
1) Microbial methanogenesis
2) Thermogenesis

1) Mantle derived
   a) Mid-Ocean Ridges
   b) Off-axis serpenination

2) Crustal derived
   a) Serpenination
   b) Fisher-Tropsch
   c) Metamorphism of carbonates
Stable Isotopes of Carbon

• $^{12}\text{C}$ (98.89%)
• $^{13}\text{C}$ (1.11%)

Stable Isotopes of Hydrogen

• $^{1}\text{H}$ (99.985%)
• $^{2}\text{H}$ (0.015%)
\[ \delta^{13}C = \left( \frac{^{13}C/^{12}C_{sample} - ^{13}C/^{12}C_{REF}}{^{13}C/^{12}C_{REF}} \right) \times 1000 \]

REF = International reference standard
Origin of CH₄: Conventional Conceptual Framework

Based on Schoell 1988

No δ²H data

Welhan & Craig 1983

Mantle carbon

Fermentation

CO₂ reduction

Thermogenic

δ²H(CH₄) (‰)

δ¹³C(CH₄) (‰)
Mixing Trend

Microbial end-member

Unknown end-member

$\frac{CH_4}{C_2^+}$

$\delta^{13}C_{CH4}$ (‰)
Crustal-derived Abiogenic CH₄

• Via water-rock interactions:
  – Serpentinization
  – Fischer-Tropsch synthesis
  – Metamorphism/reduction of carbonate

• Experimental studies have confirmed production of CH₄, C₂+ and wide range of δ¹³C values (Yuen et al. 1990; Berndt et al., 1996; Hu et al., 1998; Horita & Berndt, 1999; Foustoukos & Seyfried, 2004; Scott et al., 2004)
Cannot distinguish abiogenic from biogenic methane on the basis of the $\delta^{13}$C of methane alone.
The isotopic distribution pattern between methane, ethane, propane and butane is more diagnostic of reaction mechanisms and origin

(Des Marais et al., 1982, Yuen et al., 1990, Sherwood Lollar et al., 2002)
Isotopic Distribution Pattern for n-alkanes

Typical Thermogenic

$\delta^{13}C$ (%oo) vs. Carbon number
Thermal Cracking
(after Chung et al., 1988)

R – C – C – C - C
R – C – C – C
R – C - C
R – C

End product of cracking

Product more $^{12}$C rich

$\delta^{13}$C

$\Delta$ -50

$\Delta$ -20

Fractionation – preferential rate of reaction for $^{12}$C
Product = relatively more $^{12}$C (more negative $\delta^{13}$C)
Known Abiogenic Hydrocarbons

\[ \delta^{13}C \, (\text{‰}) \]

-28

-32

-36

-40

-44

-48

-52

-56

-16

\[ \delta^{13}C \, (\text{‰}) \]

\begin{align*}
\text{Murchison (Yuen et al., 1984)} \\
\text{Spark discharge (Des Marais et al., 1981)}
\end{align*}
Isotopic Distribution Pattern

$\delta^{13}C$ ($‰$)

Carbon number

$\delta^{13}C$ ($‰$)

Kidd Creek

Spark discharge

Murchison
Abiogenic polymerization from CH$_4$

C addition - preferential rate of reaction for $^{12}\text{C}$
$=^{13}\text{C}$ depleted ethane (Des Marais et al., 1981)

H elimination – preferential rate of reaction for $^1\text{H}$
$=^{2}\text{H}$-enriched ethane (Sherwood Lollar et al., 2002)

Diagram showing the relationship between δ²H and δ¹³C for Thermogenic Kidd Creek C1-C4.
Experimental Objectives

• Carry out spark discharge experiments to look at combined $\delta^2$H and $\delta^{13}$C of higher hydrocarbons polymerized from $\text{CH}_4$

• Why? To confirm the abiogenic origin of $\delta^2$H and $\delta^{13}$C patterns seen in Precambrian Shield sites
Spark Discharge Experiments –
Pure CH$_4$
Spark Discharge Results

Spark discharge

Kidd Creek

Thermogenic

δ²H (%o)

δ¹³C (%o)
Crustal Hydrogen

BIIOGENIC
Fermentation → H₂ ← ABIOGENIC
(rock-water interactions)

Serpentinization
Moody, 1976; Sherwood Lollar et al. 1993

Radiolysis
Lin et al. 2005
ABIOGENIC (rock-water interactions)

Serpentinization
Moody, 1976; Sherwood Lollar et al. 1993

Radiolysis
Lin et al 2005

Crustal Hydrogen

BIIOGENIC
Fermentation

Maximum of 50 nM
(Hoehler et al., 1998; Lovley and Goodwin, 1988)
Correlation between $\delta^{13}$C of methane and H$_2$ concentrations (based on 65 boreholes, 3 different continents)
Hydrogen driven autotrophic ecosystem?

- Geologically old, most saline groundwaters. Abiogenic gases ($^{13}$C enriched CH$_4$ and H$_2$) are released when fractures open.
- Redox gradient drives rapid utilization of H$_2$ via subsurface autotrophs.
- Coupled methanogenesis produces second CH$_4$ component - $^{13}$C-depleted microbial CH$_4$ that mixes with pre-existing $^{13}$C-enriched abiogenic.
- Correlation of decreasing H$_2$ concentrations and more negative $\delta^{13}$C values for CH$_4$.
<table>
<thead>
<tr>
<th>Depth Range</th>
<th>Groundwater Type</th>
<th>Methanogenesis Evidence</th>
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</thead>
<tbody>
<tr>
<td>&lt; 1.6 kmbs</td>
<td>Paleometeoric groundwater</td>
<td>Isotopic and microbial evidence (cultures and PCR) for methanogenesis.</td>
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<tr>
<td>30 to 40°C</td>
<td></td>
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<tr>
<td>&lt; 1.6 to 3.4 kmbs</td>
<td>Saline groundwater</td>
<td>No methanogens detected by PCR/enrichment culture, gases largely abiogenic in origin, large amounts hydrogen (mM)</td>
</tr>
<tr>
<td>45 to 59°C</td>
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Methane on Mars

Recent measurements indicate that methane is present in the atmosphere of Mars – average of 10 ppb, with local maxima of 30 ppb (Formisano et al 2004; Krasnopolsky et al 2004; Mumma et al 2003).

Suggests a subsurface origin for the methane.
Isotopic studies on methane alone cannot provide definitive proof of abiogenic versus biogenic origin. However, the relative $\delta^2H$ and $\delta^{13}C$ of methane compared to ethane provide a far more powerful tool.
Theoretical modeling indicates brines may be present at 2 km depth at equator, maybe shallower in areas with thermal anomalies (Clifford, 1993).
Detecting subsurface brines using radar

Mars Express MARSIS subsurface radar – due for deployment later in year

Mars Reconnaissance Orbiter SHARAD subsurface radar – due for deployment September 2006
Future drilling missions on Mars

Further research into microbiology of deep crustal brines on Earth can act as both analogue studies and training grounds for the detection of life on future deep drilling projects on Mars.
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