Serpentinization, Abiogenic Methane, and Extremophilic Archaea within the Seafloor

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Earth’s mantle is 68% of its mass and 83% of its volume. It is made of ultramafic rock: *peridotite*. 
### BULK COMPOSITION OF THE EARTH

<table>
<thead>
<tr>
<th>Element</th>
<th>wt.%</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>36.0</td>
<td>85 ± 4% is in the core.</td>
</tr>
<tr>
<td>O</td>
<td>28.7</td>
<td>(Upper) Mantle:</td>
</tr>
<tr>
<td>Mg</td>
<td>14.8</td>
<td>(Mg,Fe)&lt;sub&gt;2&lt;/sub&gt;SiO&lt;sub&gt;4&lt;/sub&gt; = olivine</td>
</tr>
<tr>
<td>Si</td>
<td>13.6</td>
<td>(Mg,Fe)SiO&lt;sub&gt;3&lt;/sub&gt; = pyroxene</td>
</tr>
</tbody>
</table>

**Subtotal:** 93.1%

#### Ordinary chondritic meteorite:

<table>
<thead>
<tr>
<th>Element</th>
<th>wt.%</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>2.0</td>
<td>46% olivine</td>
</tr>
<tr>
<td>Ca</td>
<td>1.7</td>
<td>24% pyroxene (mantle)</td>
</tr>
<tr>
<td>S</td>
<td>1.7</td>
<td>11% plagioclase feldspar (Ca, Al)</td>
</tr>
<tr>
<td>Al</td>
<td>1.3</td>
<td>8% metal</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7% FeS (core)</td>
</tr>
</tbody>
</table>

**TOTAL:** 98-99%

*What happens when we add H<sub>2</sub>O?*
## Serpentinization: 0-500°C

<table>
<thead>
<tr>
<th>REACTANTS</th>
<th>Mg:Si ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Mg end-members)</td>
<td></td>
</tr>
<tr>
<td>Forsterite: Mg$_2$SiO$_4$</td>
<td>2 : 1</td>
</tr>
<tr>
<td>(olivine)</td>
<td></td>
</tr>
<tr>
<td>Enstatite: MgSiO$_3$</td>
<td>1 : 1</td>
</tr>
<tr>
<td>(orthopyroxene)</td>
<td>= Harzburgite</td>
</tr>
<tr>
<td>Diopside: CaMgSi$_2$O$_6$</td>
<td>(depleted)</td>
</tr>
<tr>
<td>(clinopyroxene)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PRODUCTS</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Serpentine: Mg$_3$Si$_2$O$_5$(OH)$_4$</td>
<td>1.5 : 1</td>
</tr>
<tr>
<td>Brucite: Mg(OH)$_2$</td>
<td></td>
</tr>
<tr>
<td>Talc: Mg$_3$Si$<em>4$O$</em>{10}$(OH)$_2$</td>
<td>0.75 : 1</td>
</tr>
</tbody>
</table>

Chlorite: (Mg, Al, Fe)$_3$(Si, Al)$_2$O$_5$(OH)$_4$ (analog to serpentine)
Smectite: [(Ca,Na)(Al,Mg,Fe)]$_3$(Al,Si)$_4$O$_{10}$(OH)$_2$ (analog to talc)
**Serpentinization (hydration) Reactions**

Olivine to **Serpentine** (+ Brucite):  
\[ 2\text{Mg}_2\text{SiO}_4 + 3\text{H}_2\text{O} = \text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + \text{Mg(OH)}_2 \]

Enstatite to **Serpentine** (+ Talc):  
\[ 6\text{MgSiO}_3 + 3\text{H}_2\text{O} = \text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + \text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 \]

Olivine + Enstatite to **Serpentine**:  
\[ \text{Mg}_2\text{SiO}_4 + \text{MgSiO}_3 + 2\text{H}_2\text{O} = \text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 \]

**Addition of ~10 mol% Fe produces Magnetite and H\(_2\):**  
Fayalite (Fe end-member olivine): \(\text{Fe}_3\text{O}_4 = \text{Magnetite} = \text{FeO} \cdot \text{Fe}_2\text{O}_3\)  
\[ 3\text{Fe}_2\text{SiO}_4 + 2\text{H}_2\text{O} = 2\text{Fe}_3\text{O}_4 + 3\text{SiO}_2(\text{aq}) + 2\text{H}_2 \]

**Hydrocarbon production:**  
4\(\text{H}_2 + \text{CO}_2 = \text{CH}_4 + 2\text{H}_2\text{O} \text{ (Fischer-Tropsch rxn)} \)
(at high pH: \(4\text{H}_2 + \text{CO}_3^{2-} = \text{CH}_4 + \text{H}_2\text{O} + 2\text{OH}^-\))
Origin of CH₄ on Earth via:

**Biogenic processes:**

--thermal breakdown of complex C compounds in buried organic matter ("thermogenesis")

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

--microbial production ("methanogenesis")

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

\[ \text{CH}_3\text{COOH} \rightarrow \text{CH}_4 + \text{CO}_2 \]

**Abiogenic processes:**

--outgassing of juvenile CH₄ from the mantle

--inorganic synthesis at high T (Fischer-Tropsch rxn)
**Fischer-Tropsch process:**


--developed by the Germans in ~1940 to produce hydrocarbon fuels from inorganic precursors.

--CO$_2$ and CO reduced to CH$_4$ by reaction with H$_2$ at 200-250°C and high pressure *in the gaseous phase*

--Became one of three leading hypotheses for the origin of *organic matter in meteorites*. The other two are:

--origin during accretion
--Miller-Urey process (electric discharges and UV).
Serpentinization and the hydration of ultramafic rocks are the proposed mechanisms for CH₄ and H₂ production.

Abiogenic processes of CH₄ production may be considerably more widespread than previously anticipated.
Reduction of \( \text{CO}_2 \) during serpentinization of olivine at 300 °C and 500 bar

Michael E. Berndt
Douglas E. Allen
William E. Seyfried, Jr.

Department of Geology and Geophysics, University of Minnesota, Minneapolis, Minnesota 55455

ABSTRACT

\( \text{CO}_2 \) reduction processes occurring during experimental serpentinization of olivine at 300 °C and 500 bar confirm that ultramafic rocks can play an important role in the generation of abiogenic hydrocarbon gas. Data reveal that conversion of \text{Fe(II)} in olivine to \text{Fe(III)} in magnetite during serpentinization leads to production of \( \text{H}_2 \) and conversion of dissolved \( \text{CO}_2 \) to reduced-\( \text{C} \) species including methane, ethane, propane, and an amorphous carbonaceous phase. Hydrocarbon gases generated in the process fit a Schulz-Flory distribution consistent with catalysis by mineral reactants or products. Magnetite is inferred to be the catalyst for methanization during serpentinization, because it has been previously shown to accelerate Fischer-Tropsch synthesis of methane in industrial applications involving mixtures of \( \text{H}_2 \) and \( \text{CO}_2 \). The carbonaceous phase was predominantly aliphatic, but had a significant aromatic component. Although this phase should ultimately be converted to hydrocarbon gases and graphite, if full thermodynamic equilibrium were established, its formation in these experiments indicates that the pathway for reduction of \( \text{CO}_2 \) during serpentinization processes is complex and involves a series of metastable intermediates.

First report of experimental Fischer-Tropsch synthesis of methane, ethane, and propane in aqueous solution (rather than in the gas phase). Shown to be \textit{bogus} by McCollum and Seewald (2001): dissolved hydrocarbons were already present in olivine at the start of the experiments!
Abiogenic Methane Formation and Isotopic Fractionation Under Hydrothermal Conditions

Juske Horita* and Michael E. Berndt

Recently, methane (CH₄) of possible abiogenic origin has been reported from many localities within Earth’s crust. However, little is known about the mechanisms of abiogenic methane formation, or about isotopic fractionation during such processes. Here, a hydrothermally formed nickel-iron alloy was shown to catalyze the otherwise prohibitively slow formation of abiogenic CH₄ from dissolved bicarbonate (HCO₃⁻) under hydrothermal conditions. Isotopic fractionation by the catalyst resulted in δ¹³C values of the CH₄ formed that are as low as those typically observed for microbial methane, with similarly high CH₄/(C₂H₆ + C₃H₈) ratios. These results, combined with the increasing recognition of nickel-iron alloy occurrence in oceanic crusts, suggest that abiogenic methane may be more widespread than previously thought.

Bonified Fischer-Tropsch synthesis of CH₄ (but no C-2 or C-3 HC’s) in aqueous solution, using a Ni-Fe catalyst.

“Abiogenic methane may be more widespread than previously thought.”

McCollum and Seewald (2001): CO₂ + olivine at 300°C, 350 bars
Although formate has been suggested to be a reaction intermediate in the formation of abiotic hydrocarbons from reduction of aqueous CO2, production of hydrocarbons was not observed in any of the experiments, except for trace amounts of methane, despite high concentrations of formate and strongly reducing conditions.
Hydrocarbons in Hydrothermal Vent Fluids: The Role of Chromium-Bearing Catalysts

Dionysis I. Foustoukos* and William E. Seyfried Jr.

Fischer-Tropsch type (FTT) synthesis has long been proposed to account for the existence of hydrocarbons in hydrothermal fluids. We show that iron- and chromium-bearing minerals catalyze the abiotic formation of hydrocarbons. In addition to production of methane (CH$_4$), we report abiotic generation of ethane (C$_2$H$_6$) and propane (C$_3$H$_8$) by mineral-catalyzed hydrothermal reactions at 390°C and 400 bars. Results suggest that the chromium component in ultramafic rocks could be an important factor for FTT synthesis during water-rock interaction in mid-ocean ridge hydrothermal systems. This in turn could help to support microbial communities now recognized in the subsurface at deep-sea vents.

Bonified Fischer-Tropsch synthesis of methane, ethane, and propane in aqueous solution, using an Fe-Cr catalyst (chromite).

**CONCLUSION:**
There is no doubt that the Fischer-Tropsch reactions takes place in aqueous solution at elevated T and in the presence of metallic catalysts, which are common in peridotite.
Mariana subduction zone
Mariana subduction system, Western Pacific Ocean:
remnant arc, backarc basin, active arc, forearc, trench, Pacific Plate
Forearc Types

Accretionary Convergent Margin

Non-accretionary Convergent Margin (IBM)

e.g., Mariana
Outer half of Mariana forearc (Fryer et al., 1999, *Geology* 27:103-106)
Mariana Forearc Seamounts: Serpentine Mud Volcanoes!

Cold Springs with chimneys

Sedimentary serpentine flows*

Core of serpentineite mud*

H₂O, Sulfur, Carbon
*both contain blocks of serpentinized harzburgite

Largest are 50 km across and 2-3 km high.
Conical Seamount, 90 km behind the Mariana Trench axis at 19°32.5’N, drilled in 1989 on ODP Leg 125

Chimneys of CaCO₃ (calcite and aragonite) (Chimneys at sites closer to the trench are brucite!)

Blocks of variably serpentinized harzburgite suspended in serpentinite mud
Shinkai-6500 Dive 351, Nov. 1996, summit of S. Chamorro Seamount
Shinkai 351 Vent Field, summit of South Chamorro Seamount, 2003
ODP Leg 195, Site 1200, summit of South Chamorro Seamount
Distance from spring: 7 m  20 m  80 m

vs. seawater:
0.94 x  1.3 x  1.9 x  8.0 x  7.8 x

One-dimensional advection (upwelling)-diffusion
Distance from spring: 7 m  20 m  80 m

Anaerobic Methane Oxidation: \[
\text{CH}_4 + \text{SO}_4^{2-} + 2\text{OH}^- \rightarrow \text{CO}_3^{2-} + \text{S}^- + 3\text{H}_2\text{O}
\]
Equilibrium of brucite with serpentine at low temperature keeps dissolved Mg and SiO$_2$ low and pH high: \(~10.7\) (11.1 at 2°C), as observed in springs near the trench.
The higher pH of 12.5 (13.1 at 2°C) for springs farther (≥70 km) from the trench results from serpentinization and methane generation at high pH:

$$4H_2 + CO_3^{2-} = CH_4 + H_2O + 2OH^-$$

This reaction converts carbonate alkalinity to hydroxyl alkalinity, thus raising pH. It occurs where there is an external source of carbon.
Mariana forearc: serpentinite mud volcanoes

1989: ODP drilling
   Leg 125, Site 780

1996: Shinkai-6500 dive

1997: 66 gravity cores
   from 13 sites
   on 10 mud volcanoes

2001: ODP drilling
   Leg 195, Site 1200

2003: 75 gravity cores
   from 13 sites
   on 12 mud volcanoes
Na, Na/Cl, and K increase with distance from the trench.
Mariana Forearc, 2003: 10 sites on 9 seamounts

With distance from the trench of 50-95 km:

--depth to the top of the subducting Pacific Plate = 15-29 km
--P, T = 5-9 kbars and ~100-300°C (?)
--alkalinity, sulfate, Na/Cl, K, Rb, Cs, B increase
--Ca, Sr decrease

Why? Carbon!
### Character of springs with distance from trench:

**Near (50-65 km)**

- **No C source:**
  - Low alkalinity
  - High Ca, Sr
  - Brucite chimneys
  - Low CH$_4$
  - pH 10.7 (11.1 at 2°C)

  \[
  \text{CO}_3^{2-} + 4\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O} + 2\text{OH}^-
  \]

- No S$^=\$
- No microbial activity(?)
- No macrofauna

**Far (70-90 km)**

- **C source:**
  - High alkalinity
  - Low Ca, Sr
  - CaCO$_3$ chimneys
  - High CH$_4$
  - pH 12.5 (13.1 at 2°C)

  \[
  \text{CH}_4 + \text{SO}_4^{2-} + 2\text{OH}^- = \text{CO}_3^{2-} + \text{S}^= + 3\text{H}_2\text{O}
  \]

- High S$^=\$
- Microbial activity
- Macrofauna
Summary: reactions relevant to extraterrestrial environments:

1. **Serpentinization**: peridotite + water produces OH\(^-\) and H\(_2\):

   \[
   2\text{Mg}_2\text{SiO}_4 + 3\text{H}_2\text{O} = \text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + \text{Mg}($\text{OH}$)_2
   \]

   \[
   3\text{Fe}_2\text{SiO}_4 + 2\text{H}_2\text{O} = 2\text{Fe}_3\text{O}_4 + 3\text{SiO}_2($\text{aq}$) + 2\text{H}_2
   \]

2. **Addition of C** (preferably as a flux) produces methane:

   \[
   \text{CO}_3^{2-} + 4\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O} + 2\text{OH}^-
   \]

3. **Anaerobic oxidation of methane** by *Archaea* produces sulfide:

   \[
   \text{CH}_4 + \text{SO}_4^{2-} + 2\text{OH}^- = \text{CO}_3^{2-} + \text{S}^- + 3\text{H}_2\text{O}
   \]