

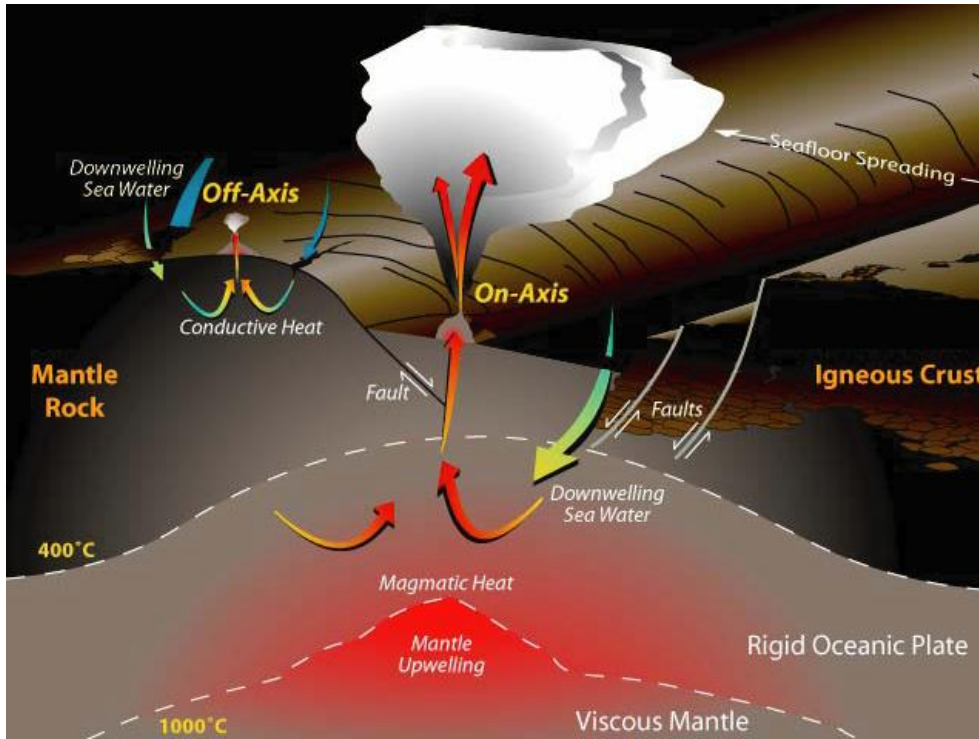
# **CH<sub>4</sub> Oxidation and Formation of Metastable Organics under Hydrothermal and Supercritical Water Conditions**

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# Hydrothermal Conditions



**P ~ 250 bars to 10 kbars**  
**T ~ 200°C-900°C**

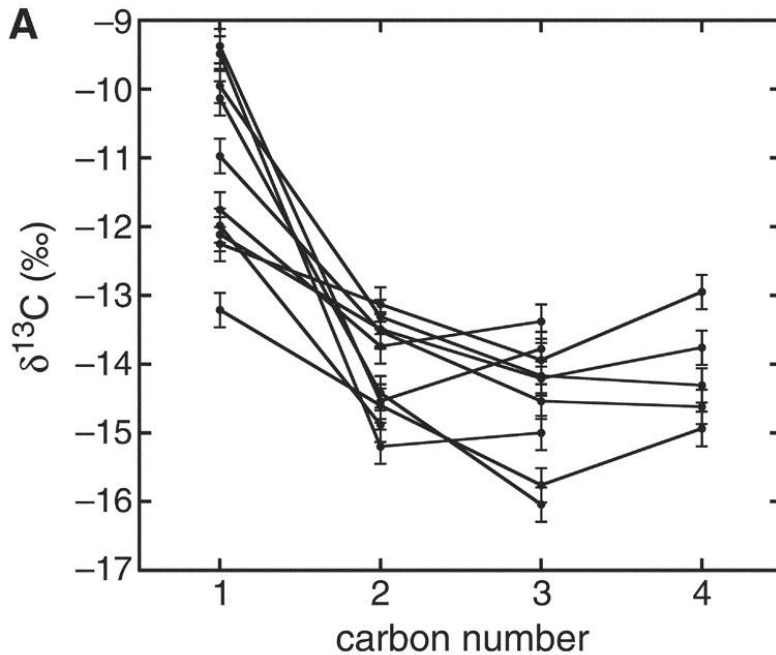
**Volatiles Dissolved in Water**  
**(e.g. H<sub>2</sub>, CO<sub>2</sub>, CO, CH<sub>4</sub>)**

# Abiogenic H/C in Hydrothermal/Volcanic Systems

1 FEBRUARY 2008 VOL 319 SCIENCE www.sciencemag.org

## Abiogenic Hydrocarbon Production at Lost City Hydrothermal Field

Glora Proskurowski,<sup>1,2\*</sup> Marvin D. Lilley,<sup>1</sup> Jeffrey S. Seewald,<sup>2</sup> Gretchen L. Früh-Green,<sup>3</sup> Eric J. Olson,<sup>1</sup> John E. Lupton,<sup>4</sup> Sean P. Sylva,<sup>2</sup> Deborah S. Kelley<sup>1</sup>

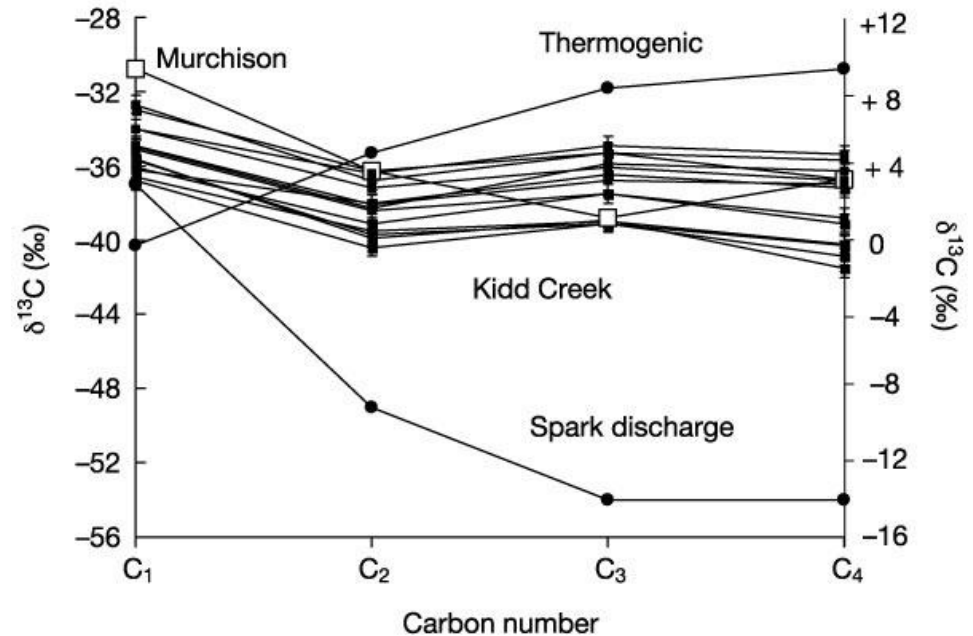


## letters to nature

## Abiogenic formation of alkanes in the Earth's crust as a minor source for global hydrocarbon reservoirs

B. Sherwood Lollar, T. D. Westgate, J. A. Ward, G. F. Slater & G. Lacrampe-Couloume

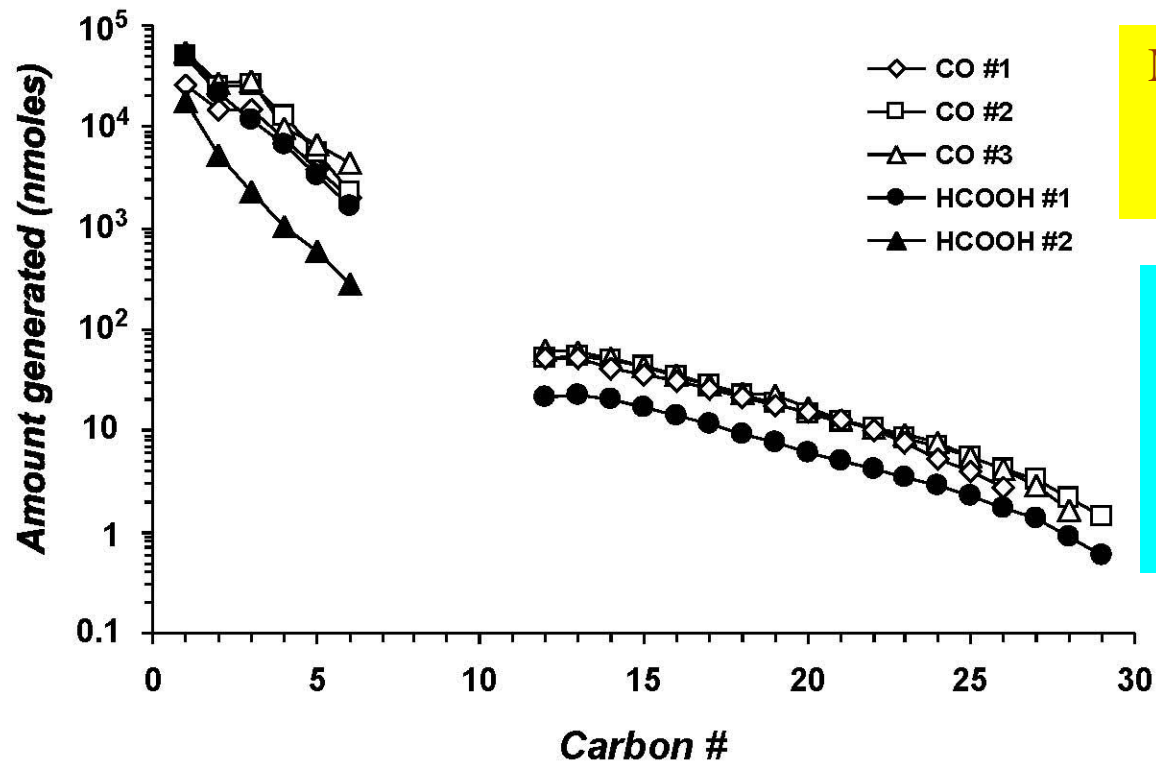
Stable Isotope Laboratory, University of Toronto, Toronto, Ontario, Canada M5S 3B1



Abiotic signature:  $\delta^{13}\text{C}$  depletion from  $\text{C}_1$ - $\text{C}_4$  (*inverse isotopic trend*)  
Main mechanism through  $\text{CH}_4$  polymerization –  $^{12}\text{C}$  reacts faster than  $^{13}\text{C}$ -bearing methylene groups.

# Mechanism of Abiogenic H/C Formation

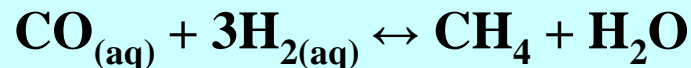
## Fischer-Tropsch Type Synthesis:



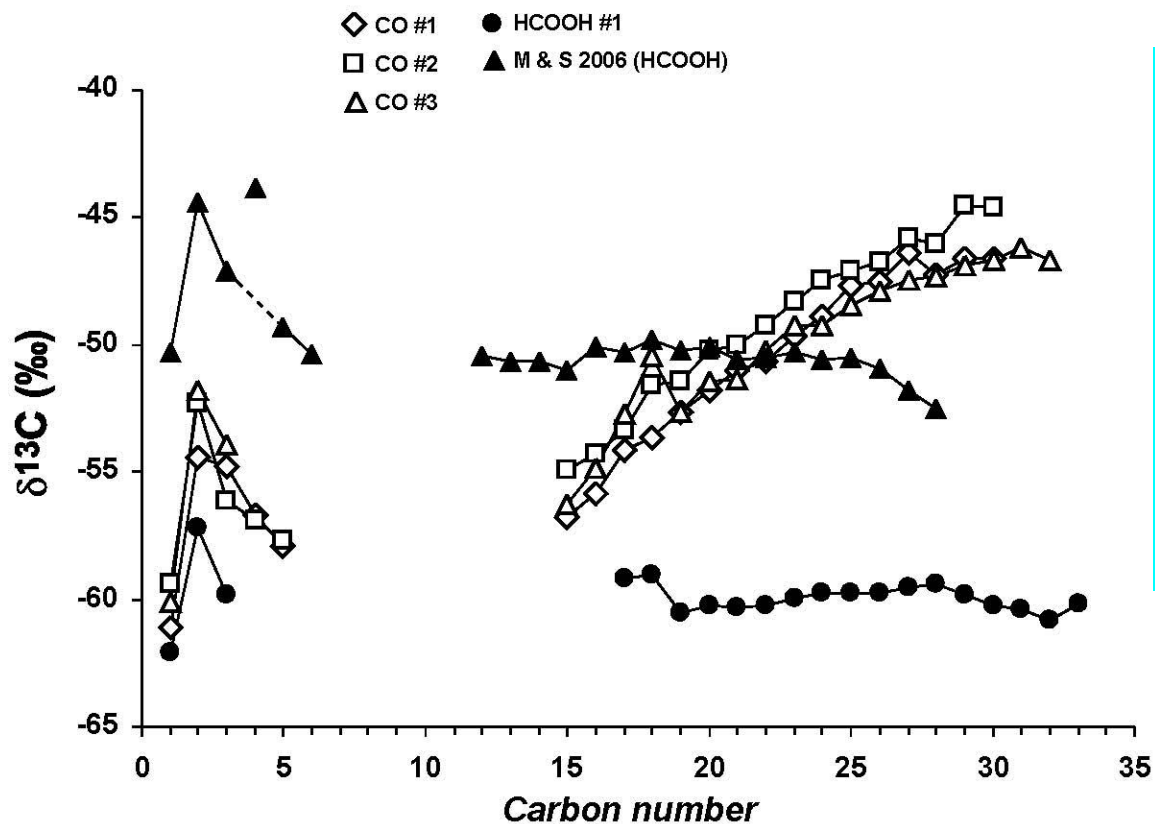
McCollom et al. (2010) *GCA*  
T = 250°C, P = 17 Mpa  
Native Fe

Absence of H/C in  
CO<sub>2</sub>-bearing experiments

Enhanced CO reduction to  
alkanes



# $^{13}\text{C}/^{12}\text{C}$ Isotope Ratios in Alkanes



1. Absence of  
“reverse isotopic trend”  
(Similar results from Fu et al.  
2007; Taran et al. 2007; Taran  
et al. (in press) *GCA*)

2. Initial step of chain  
formation:  
+7-10‰ on  $\text{CH}_4$

$\delta^{13}\text{C}$  isotopic fractionation between  $\text{CO}-\text{CH}_2$ :  $\sim -30\text{‰}$

$\delta^{13}\text{C}$  isotopic fractionation between  $\text{C}_2\text{H}_5-\text{CH}_2$ :  $\sim +7-10\text{‰}$

Very small fractionation with subsequent addition of  $-\text{CH}_2-$  to H/C growing chain

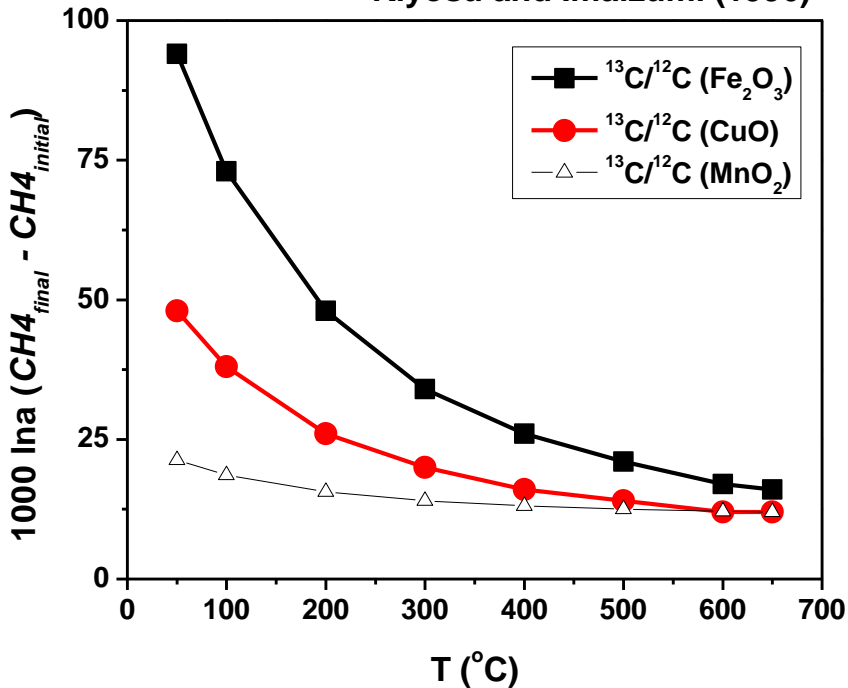
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So how can we produce the “inverse”  $\delta^{13}\text{C}$  isotope trend and establish a proxy for abiogenic H/C synthesis?

Is it possible to synthesize H/C through destruction of  $\text{CH}_4$ ?

# Partial Oxidation of CH<sub>4</sub> and Polymerization Reactions

Kiyosu and Imaizumi (1996)

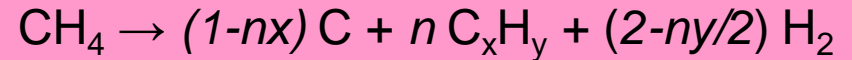


Methane Oxidation:



Formation of  $\delta^{13}\text{C}$  heavy CH<sub>4</sub> and light products (e.g. CO, C, -CH<sub>2</sub>- )

## Methane Polymerization



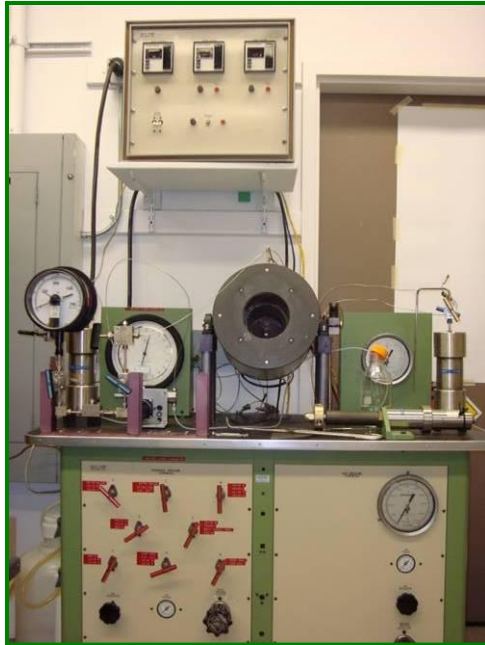
Benedetti et al. (1999) *Science*  
T = 2000 – 3000 K; P = 10 – 50 GPa

Hirai et al. (2009) *Phys. Earth Plan. Int.*  
T > 1100 K; P = 10 – 80 GPa

Kolesnikov et al. (2009) *Nat. Geosciences*  
T = 1000 – 1500 K; P = 2.2 – 6.5 GPa

Sokol et al. (2009) *GCA*  
T = 1673 – 1873 K; P = 6.3 GPa

# CH<sub>4</sub> Oxidation at Low-Pressure Conditions



$T < 400^{\circ}\text{C}$   
 $P < 500 \text{ bars}$

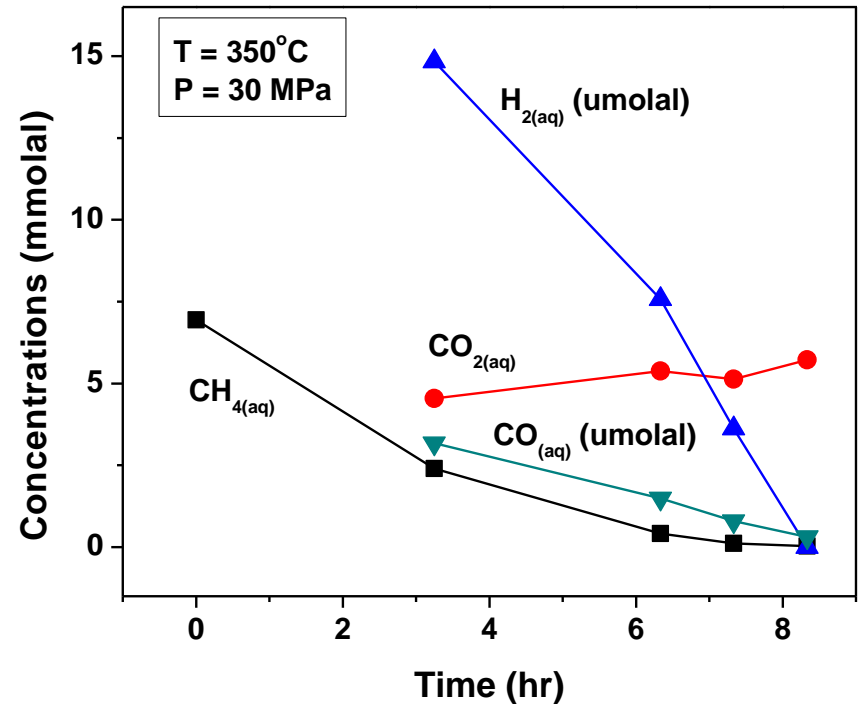
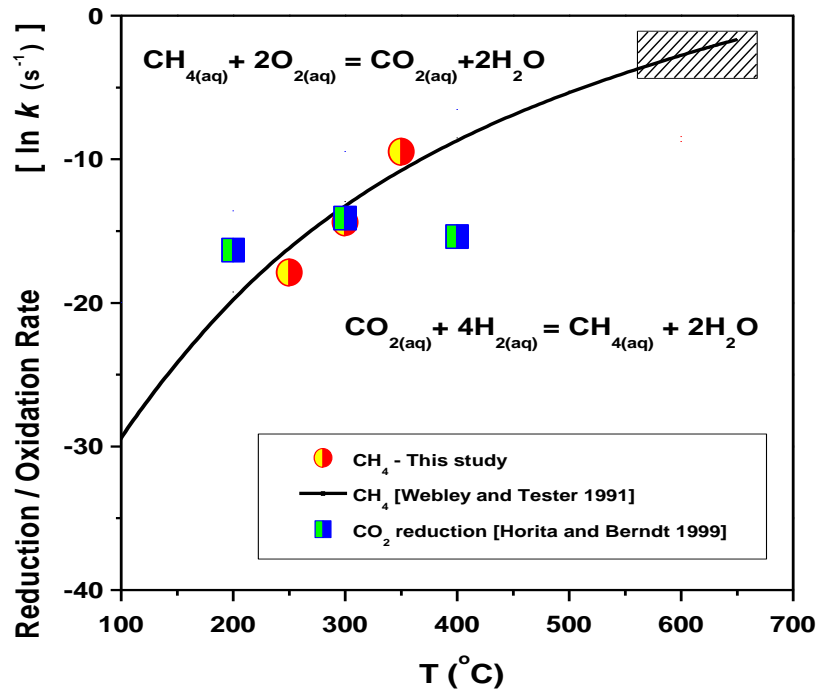
Conditions reflecting  
deep-sea hydrothermal  
systems

## Flexible Ti/Au-Cell



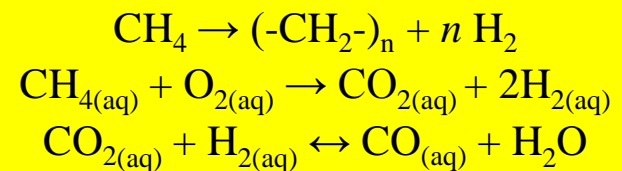
$T = 250^{\circ}\text{C} - 350^{\circ}\text{C}$   
 $P = 25 - 40 \text{ MPa}$   
 $\sim 10 \text{ mmol/kg CH}_{4(\text{aq})}$   
 $\sim 30 \text{ mmol/kg O}_{2(\text{aq})}$   
 $\text{pH}_{\text{in-situ}} \sim 5$

# Formation of Metastable Phases



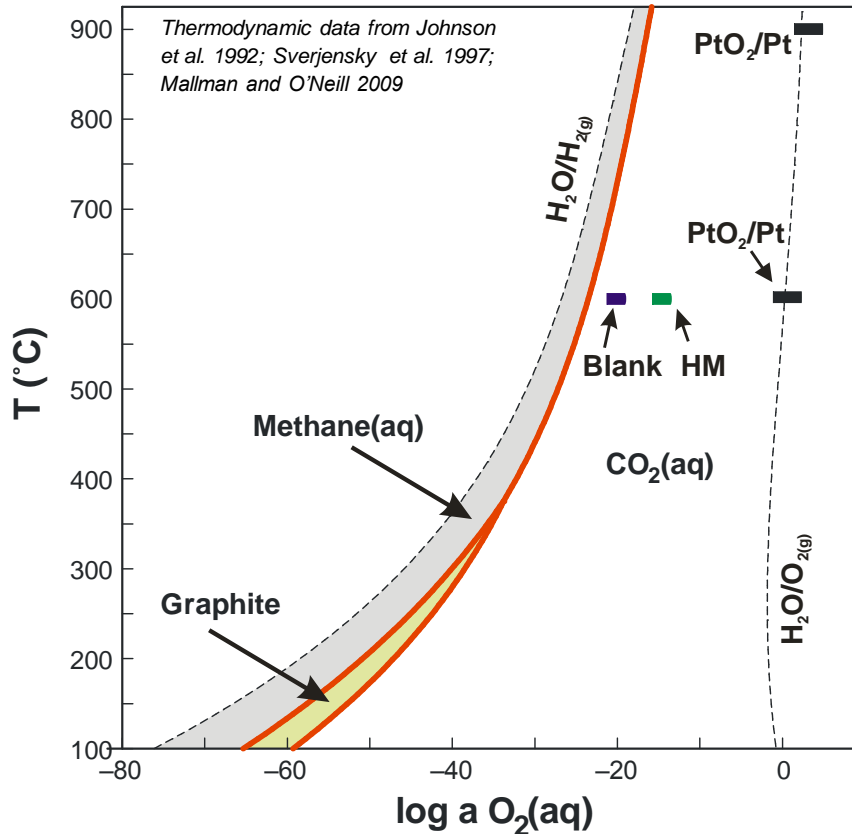
The rates of  $\text{CH}_{4(\text{aq})}$  oxidation approximate the extent of  $\text{CO}_{2(\text{aq})}$  conversion to  $\text{CH}_{4(\text{aq})}$  even when it's catalyzed at an ultimate rate by FeNi under highly reducing conditions.

Formation of metastable  $\text{H}_{2(\text{aq})}$  and  $\text{CO}_{(\text{aq})}$  in solution



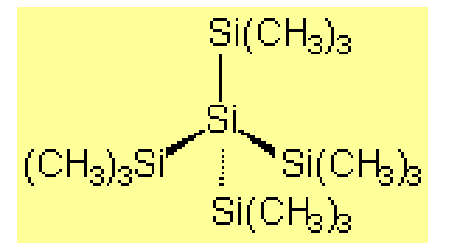
$$\log(Q/K) \sim 2.5$$

# Piston Cylinder Experiments



T = 600°C – 900°C  
 P = 1 GPa  
 Pt inner/outer capsules  
 “Blank” experiment in Au capsule

**f O<sub>2(g)</sub> Control:**  
 PtO<sub>2</sub>/Pt and Hmt - Mgt



Tetrakis(trimethylsilyl)silane

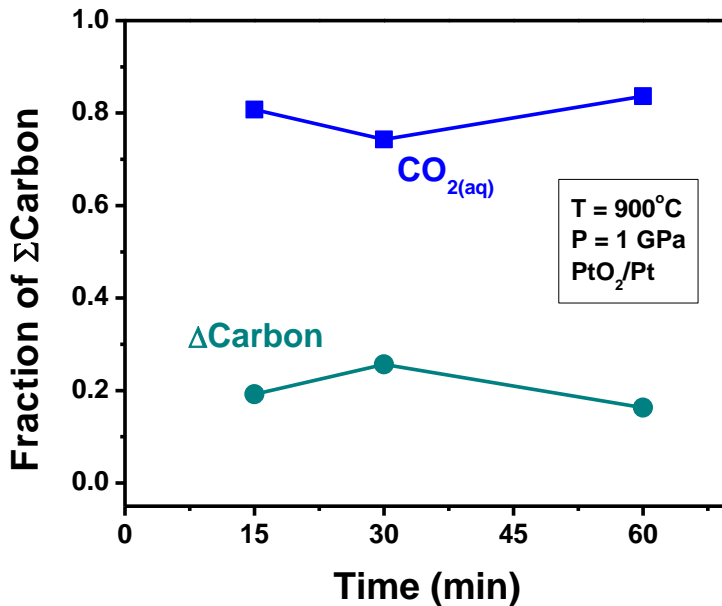
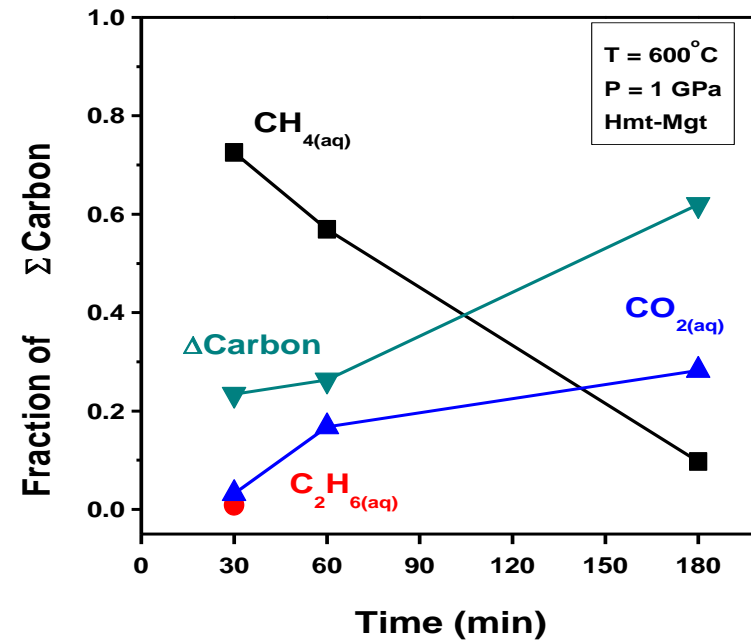
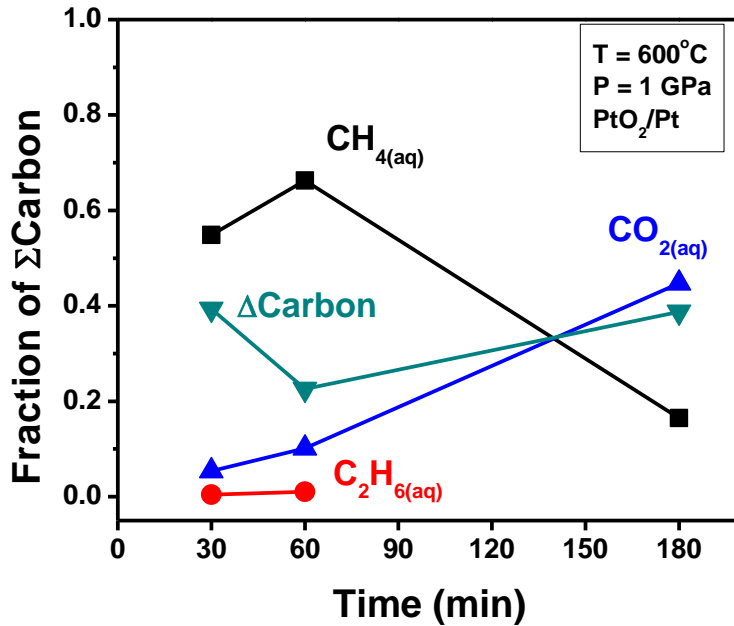


~0.3 mg Si<sub>5</sub>C<sub>12</sub>H<sub>36</sub> in 15 mg H<sub>2</sub>O

All species dissolved in H<sub>2</sub>O

CH<sub>4(aq)</sub> ~ 700 mmolal / H<sub>2(aq)</sub> ~ 250 mmolal

# Methane Oxidation at Supercritical Conditions



- Reaction time > 3 hr to reach equilibria at 600°C
- Formation of graphite (???)
- Increasing  $f_{O_2(g)}$  results to greater formation of CO<sub>2(aq)</sub> relative to graphite
- Presence of ethane only at early stages

Does this reflect CH<sub>4</sub> partial oxidation and -CH<sub>2</sub>- polymerization?

# Methane Polymerization in the “Blank” Experiment

600°C – 1 GPa - 30 min

$\text{CH}_4 = 0.78$

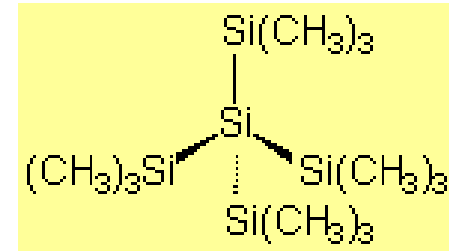
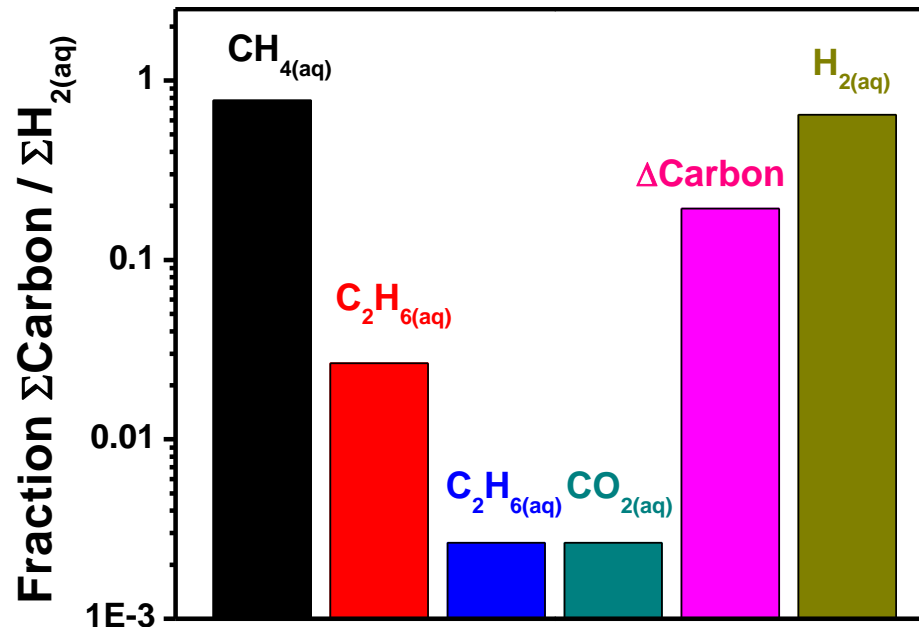
$\text{C}_2 = 0.03$

$\text{C}_3 = 0.003$

$\text{CO}_{2(\text{aq})} = 0.003$

$\Delta\text{C} = 0.19$

$\text{H}_{2(\text{aq})} = 0.65$



Formation of  $\text{C}_2$ - $\text{C}_3$  is linked to  $-\text{CH}_3$ - release and polymerization during  $\text{Si}_5\text{C}_{12}\text{H}_{36}$  decompositions

Potential to study  $\delta^{13}\text{C}$  isotope fractionations between  $\text{C}_1$ - $\text{C}_2$ - $\text{C}_3$  and constrain the abiotic signature of  $-\text{CH}_3$ -polymerization reactions at supercritical water conditions

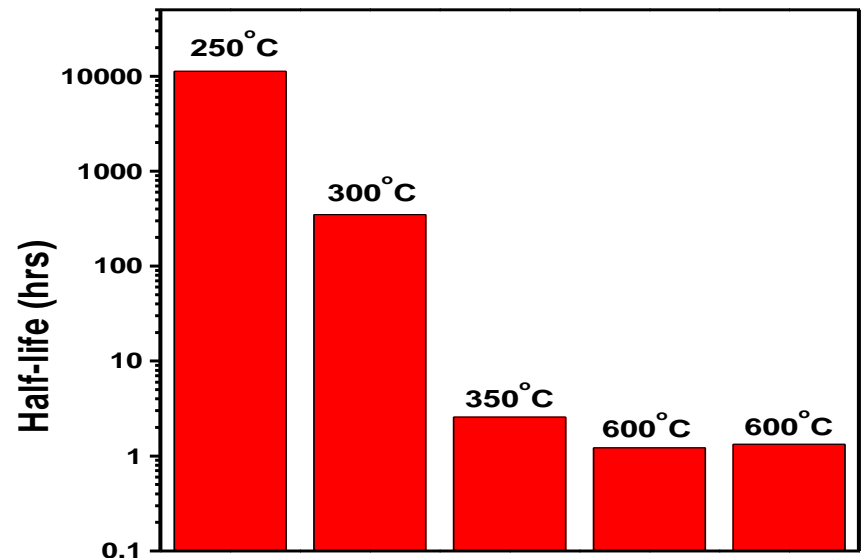
# Future Steps

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- Study CH<sub>4</sub> stability and oxidation rates at 600-900°C, 1 GPa and as a function of O<sub>2(g)</sub> fugacity: Use of reducing and oxidizing mineral assemblages (IW, QFM, HM, PtO<sub>2</sub>/Pt)
- Evaluate rates of CH<sub>4(aq)</sub> polymerization in Si<sub>5</sub>C<sub>12</sub>H<sub>36</sub>-H<sub>2</sub>O experiments
- Investigate the δ<sup>13</sup>C isotope fractionation during CH<sub>4(aq)</sub> oxidation and polymerization to higher chain alkanes – Evidence for “inverse isotopic trend”?
- Evaluate the catalytic role of Fe-bearing oxides in the CH<sub>4</sub>-H<sub>2</sub>O-CO<sub>2</sub> system

## Acknowledgments:

- Deep Carbon Observatory
- NSF-OCE 0928443 and 0752221
- Shell
- Dr. Bjorn Mysen
- Dr. Roxane Bowden
- Dr. G. Cody and Dr. R. Hemley



# Role of Fe-bearing Oxides / Formation of FeC/Fe(CO)<sub>5</sub>

## Internal-Heated PV

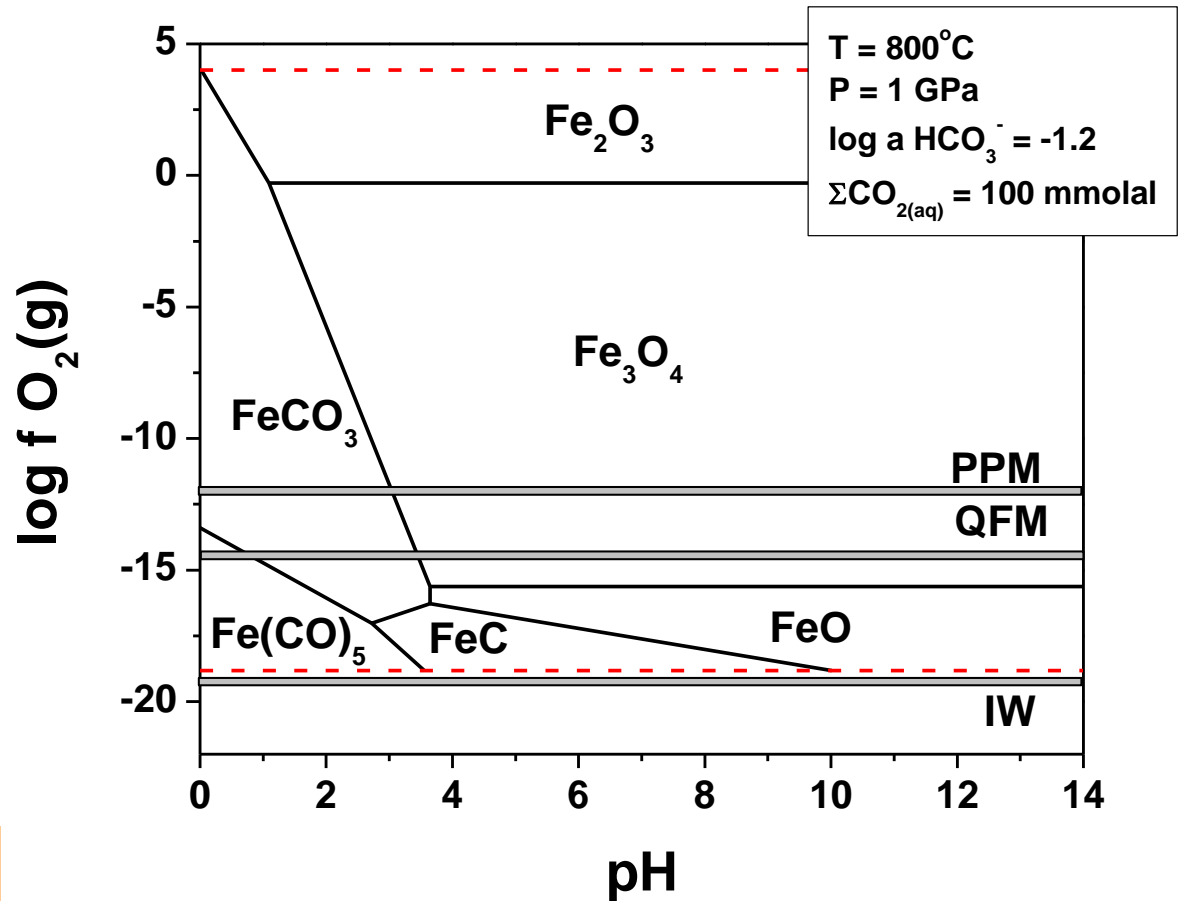


T = 600-900°C

P = 1 GPa

Supercritical Water Conditions

Lower Crust – Upper Mantle



- Abiotic H/C formation in presence of FeC, Fe(CO)<sub>5</sub>
- Fe-bearing C phases stable at reducing and acidic conditions