Gas Generation in Marine Shales 25° - 200°C

By
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Abstract

Marine shales generate two distinct gases in the laboratory, one at high temperatures (>300°C) from kerogen cracking and the other at low temperatures (<50°C) by a catalytic process probably promoted by transition metals. Low-temperature gas forms at reservoir temperatures, but only when there is gas flow under anoxic conditions. This is achieved in the laboratory by grinding the shales in pure argon to expose inner anoxic surfaces, and then passing a purified inert gas (e.g., helium) over the surfaces at constant temperature. In a typical example, a type II marine shale from the Black Warrior Basin generated 2.0 mg gas/(g shale) (C1-C5, 24% of its hydrocarbons) in three hours of anoxic helium flow at 50°C. The same shale generated 99% less gas in a closed reactor at the same temperature over 20 hours and 86% less gas under helium flow containing 10 ppm oxygen.

Low-temperature gas generation is unique in all respects. Generation rates are orders of magnitude higher than thermal cracking rates, product compositions are dynamic, kinetics of generation are non-linear, and gas generation terminates on exposure to trace levels of oxygen. Equally surprising, different shales generate gases having different compositions. Barnett Shale, Fort Worth basin, generates a gas enriched in methane and near thermodynamic equilibrium in C1-C3 (K = [(C1)(C3)]/[C2)2]), while New Albany Shale, Illinois basin, generates a gas with mainly propane; it is not at equilibrium, but it approaches equilibrium over time, consistent with catalytic gas metathesis.

Significant amounts of low-temperature gas could be generated during conventional gas production from marine shales. The reservoir conditions and shale properties conducive to such a process will be discussed.

Gas Generation in Marine Shales 25° - 200°C

Frank Mango, Daniel Jarvie, and Steven Garcia

Petroleum Habitats, LLC

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Major Points

- Catalytic gas is generated at 25°C
- Controlled by Pressure & Gas Flow, not time and temperature
- Five times more catalytic gas is generated at 25°C than thermogenic gas at 350°C
- Catalytic gas generation could be significant during production

Natural Catalytic Activity in Marine Shales

An Overview

$$\text{kerogen} \xrightarrow{k} \textbf{Gas} + \text{–C-}$$

$$\text{Rate} = \frac{a}{P}$$

At critical pressure P_c

$$\text{kerogen} \not\rightarrow \text{Gas} + \text{-C-}$$

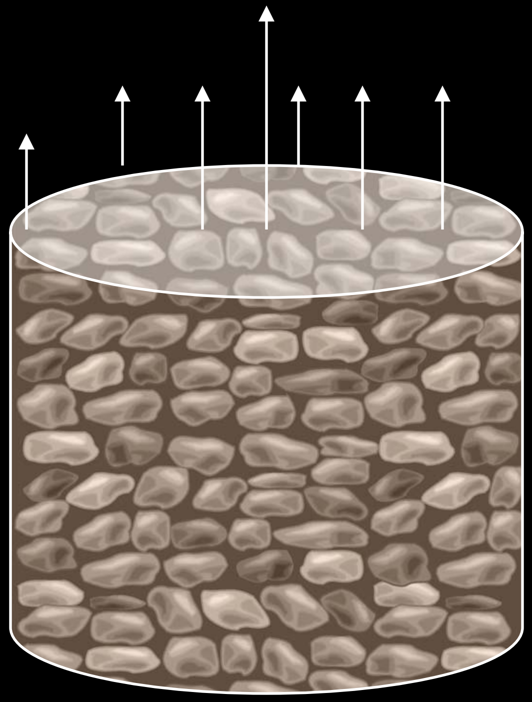
In principle, there is no minimum temperature for gas generation

One Example
Gas Generation, 25ºC

Lloyd Snowdon & R. G. McCrossan

Canadian Geological Survey, paper 72-36
1970

How much gas is lost from cuttings over time?



Fresh cuttings at well site

Uniform gas composition

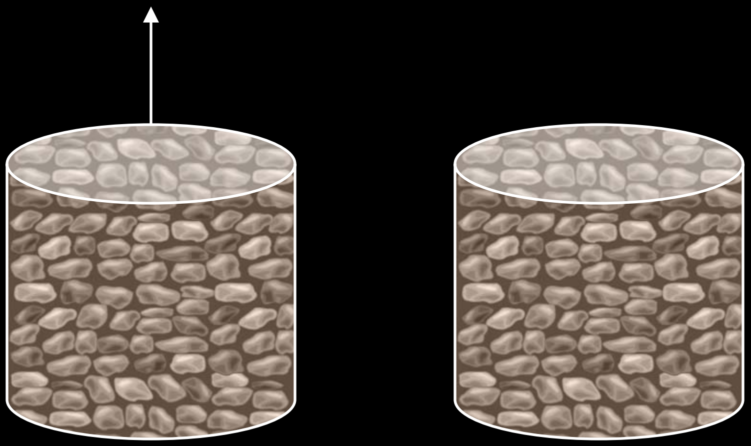
Sealed in air-tight metal containers

Stored in laboratory at room temperature

Measured the gas in the cuttings .. in first can

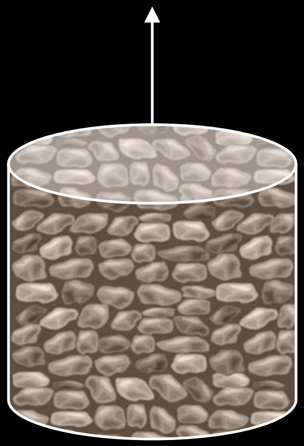
Month 1

Measured the gas in the cuttings .. in second can



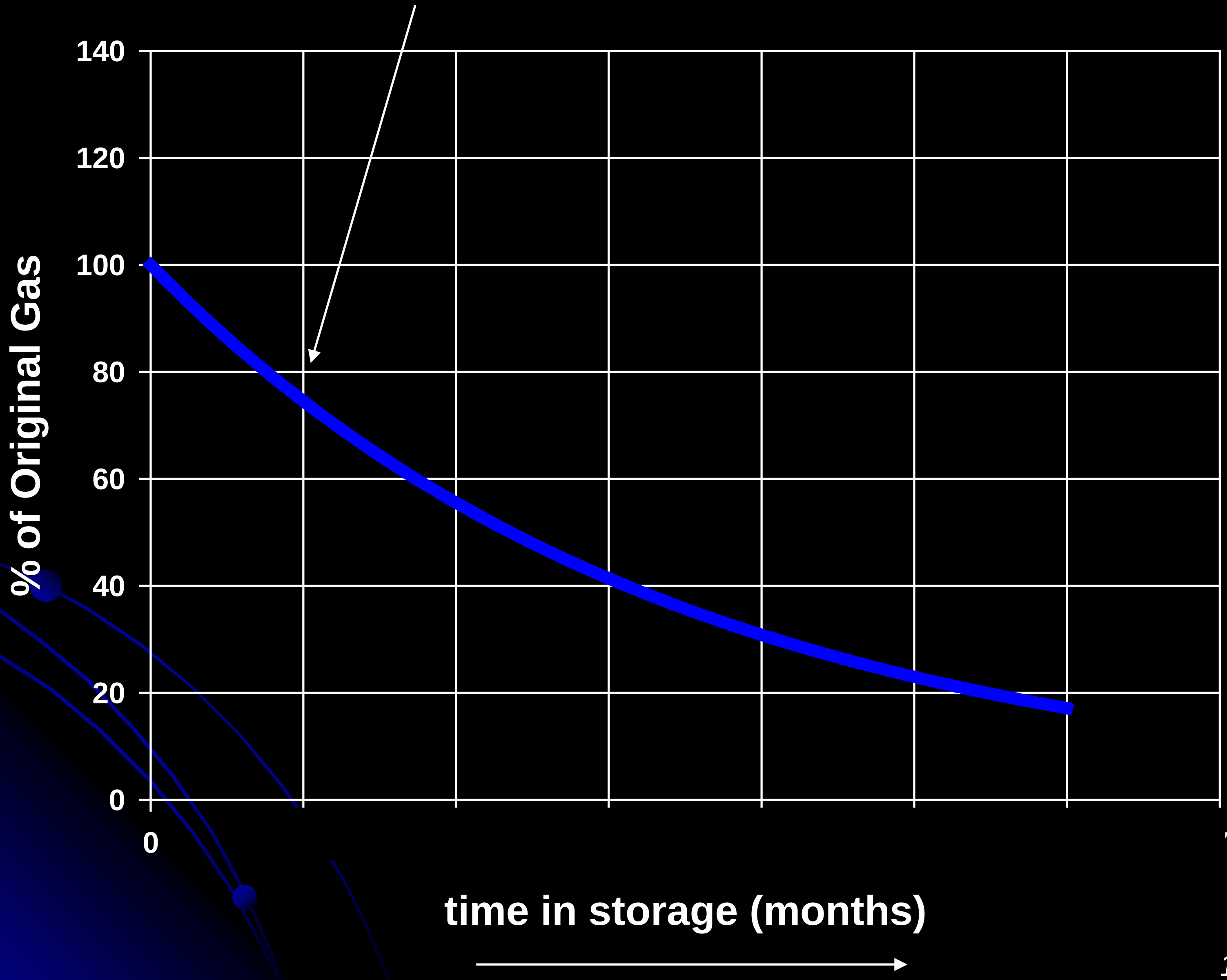
Month 5

Measured the gas in the cuttings .. in third can

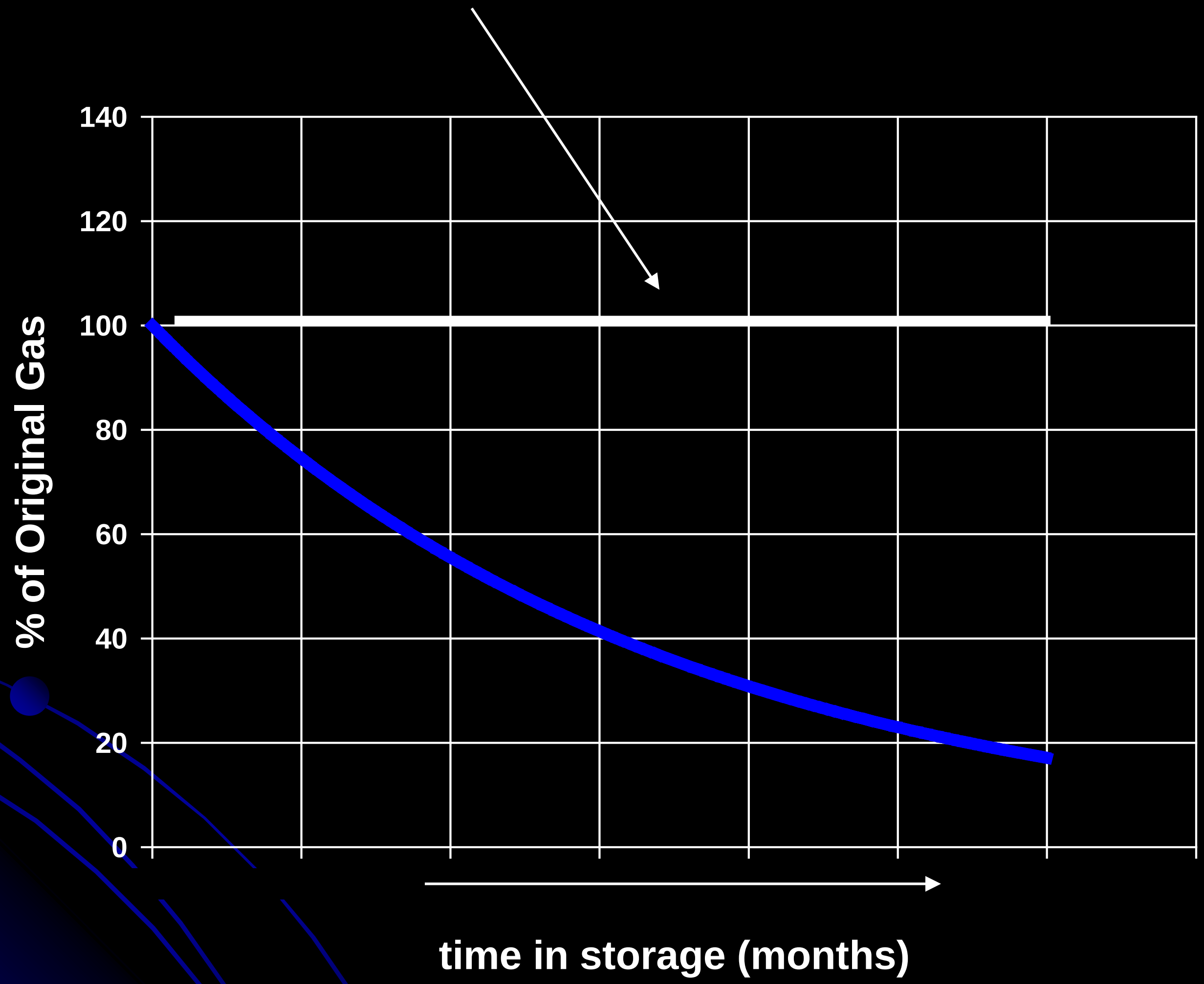


Month 15

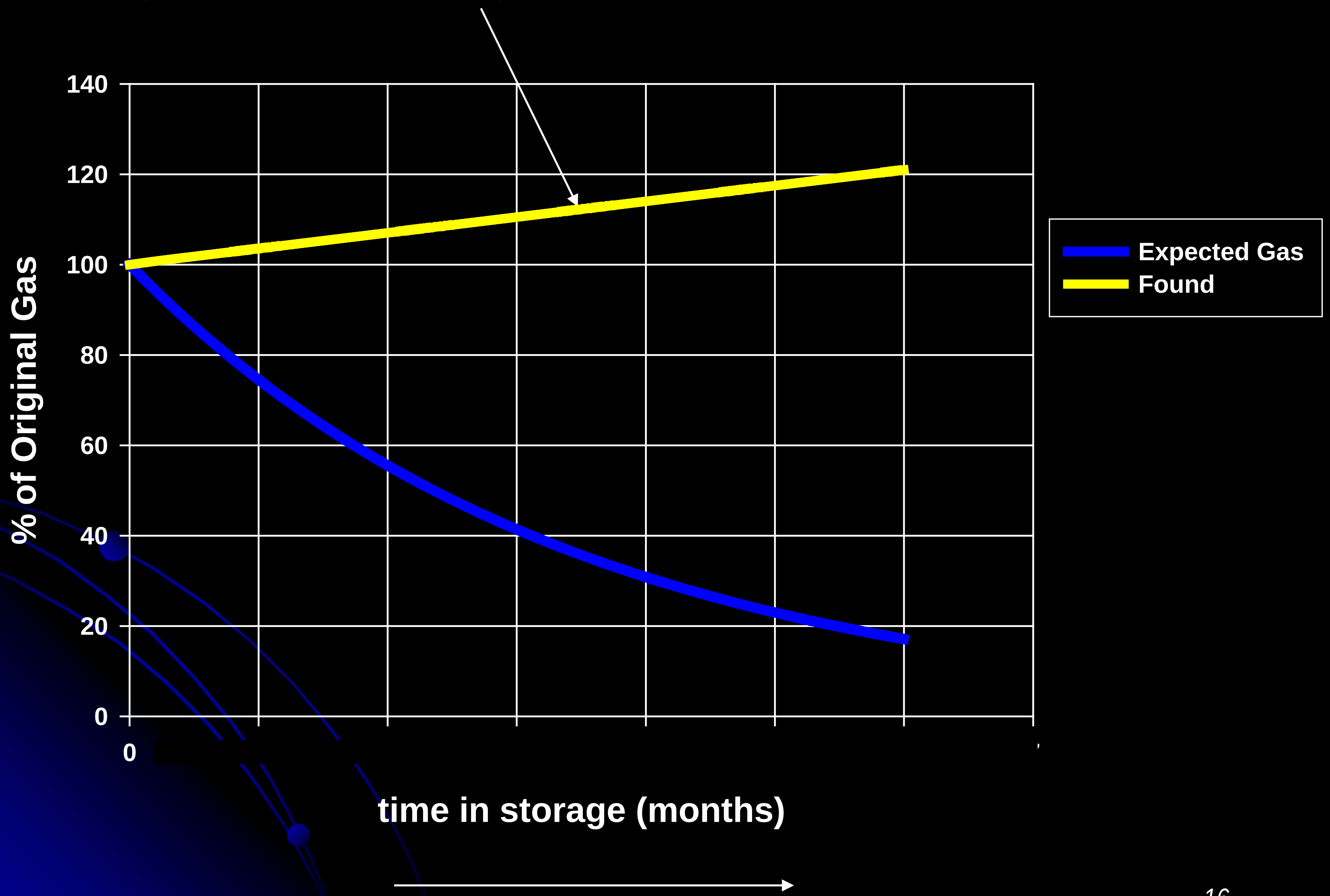
This is what they expected



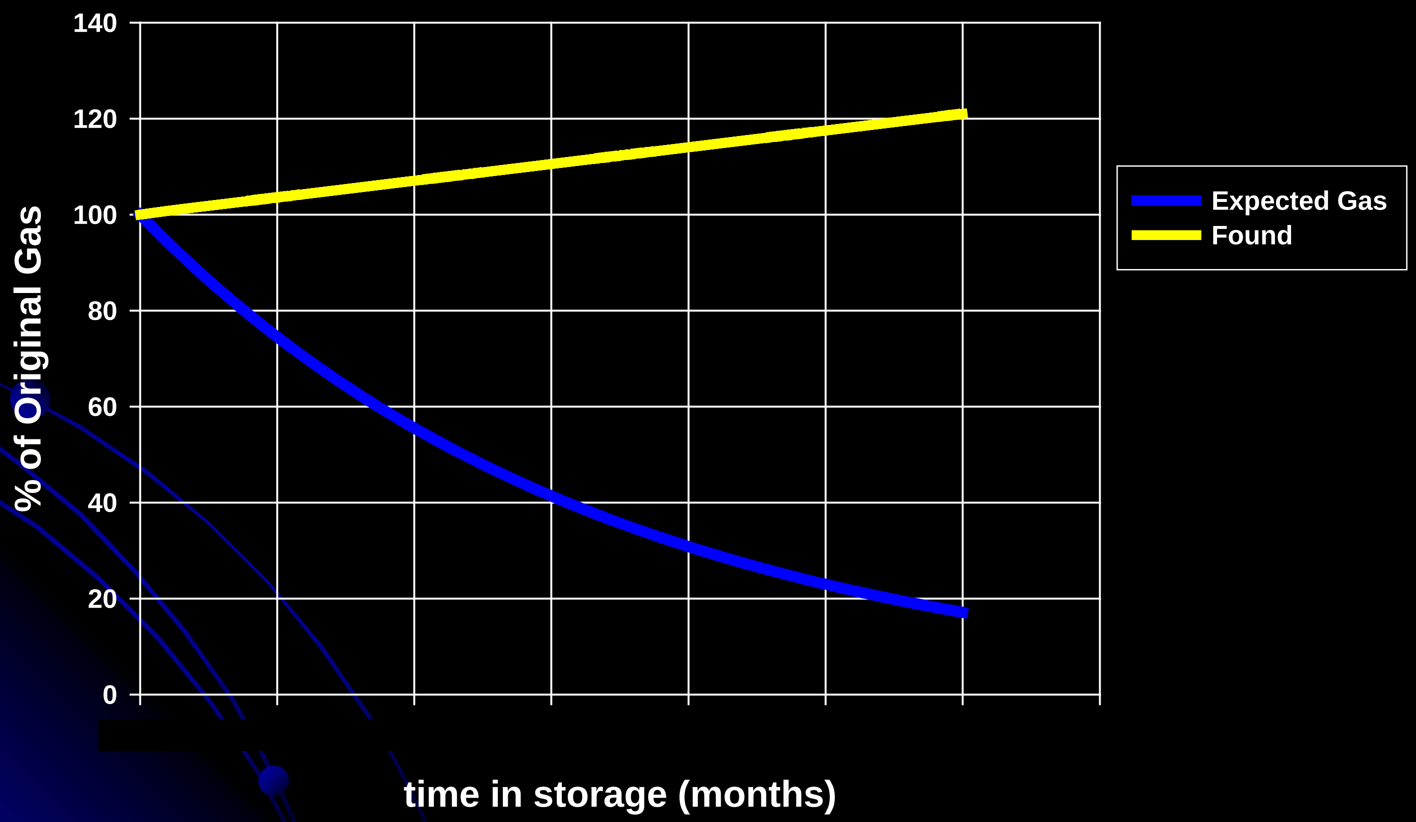
If no gas was released from the cuttings over time



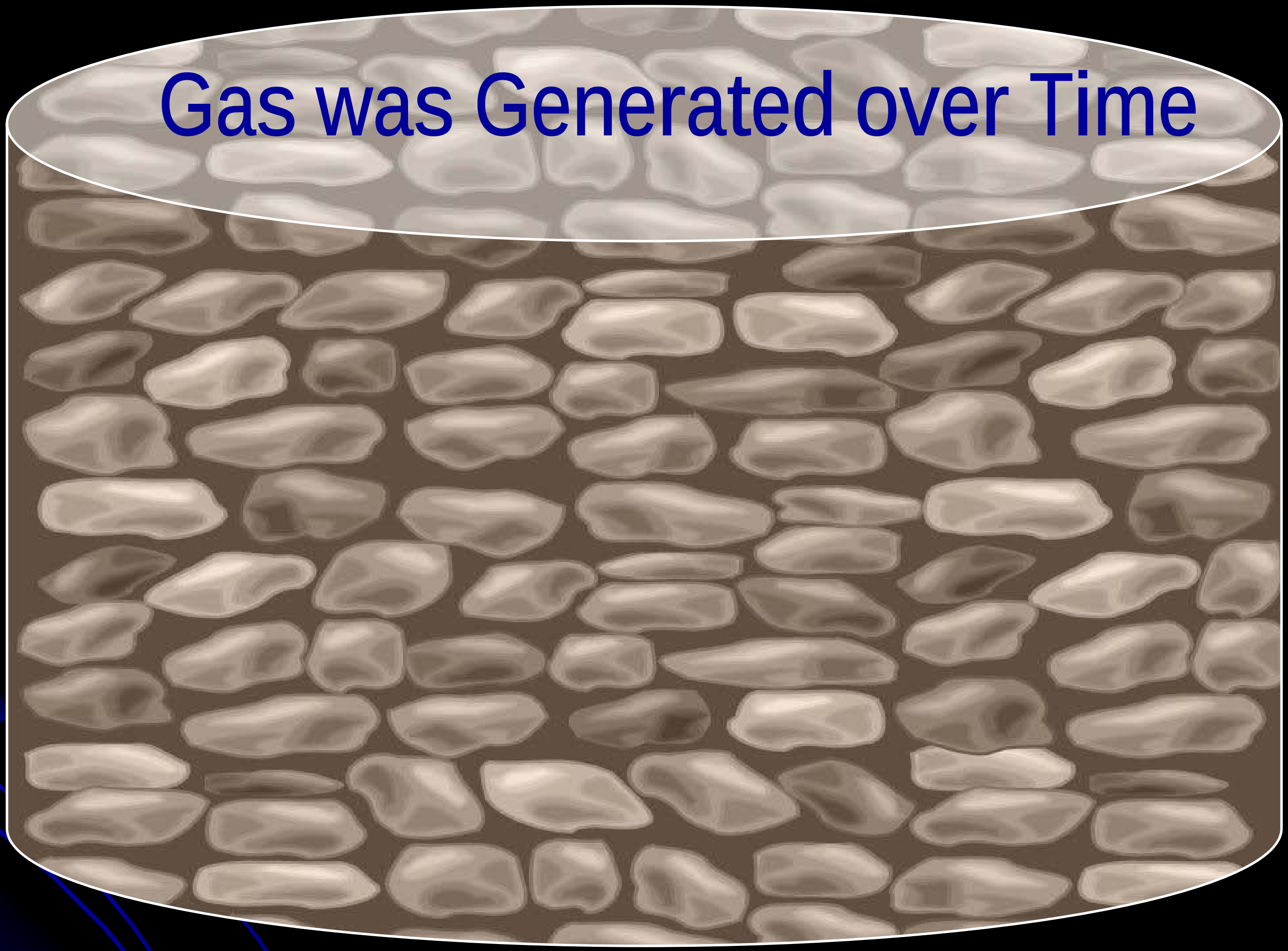
They saw something like this



“the sample actually yielded more gas as the length of the storage period increased”



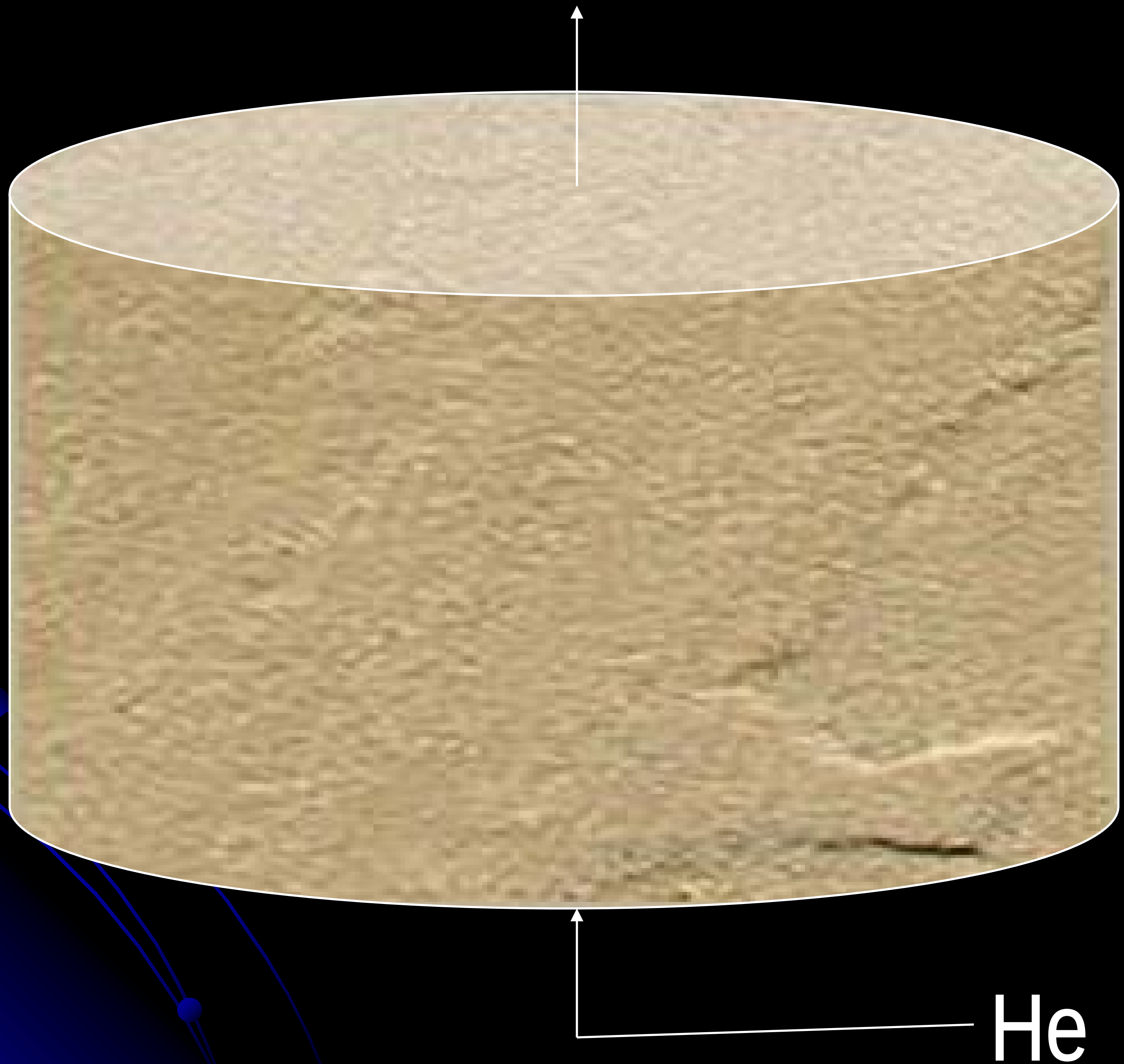
Gas was Generated over Time



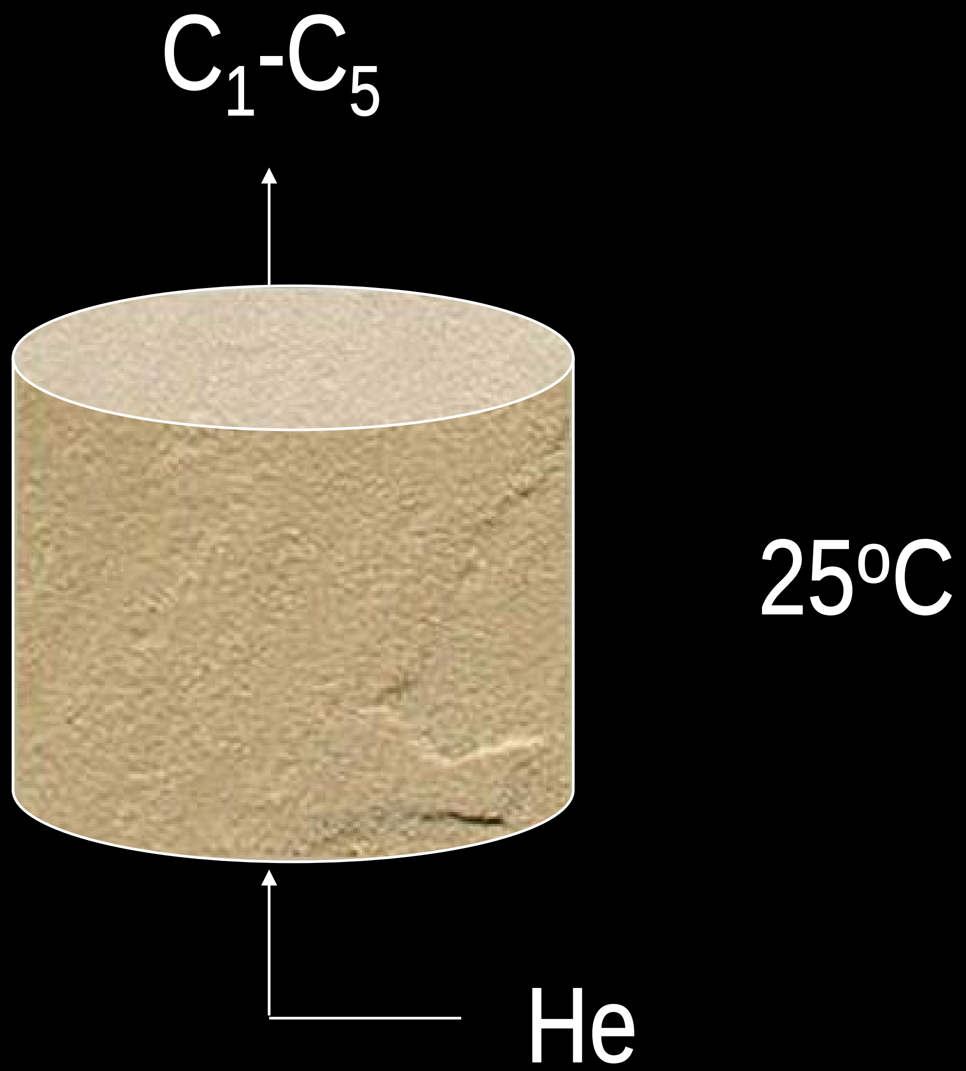
Month 15

Snowdon-McCrossen Experiment Repeated

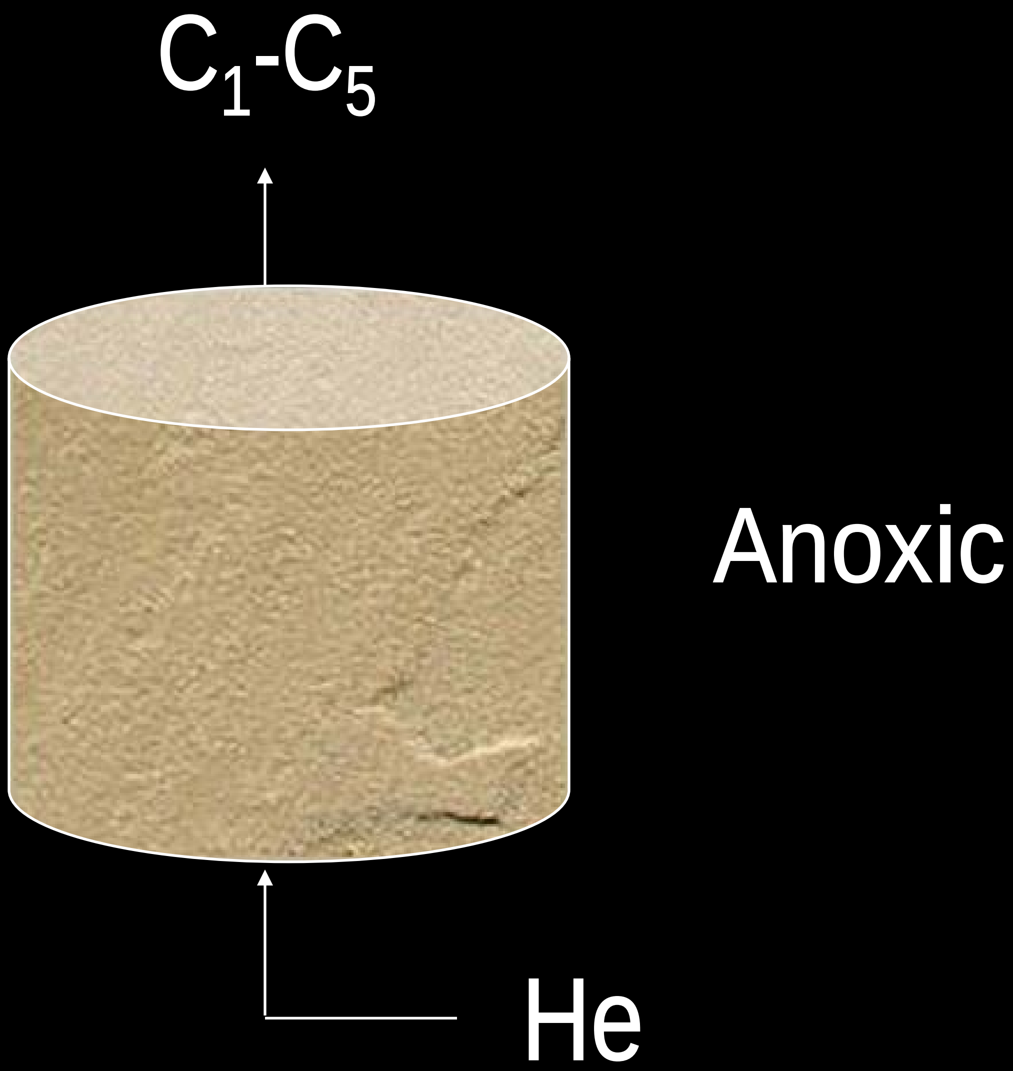
Open Reactor under Gas Flow

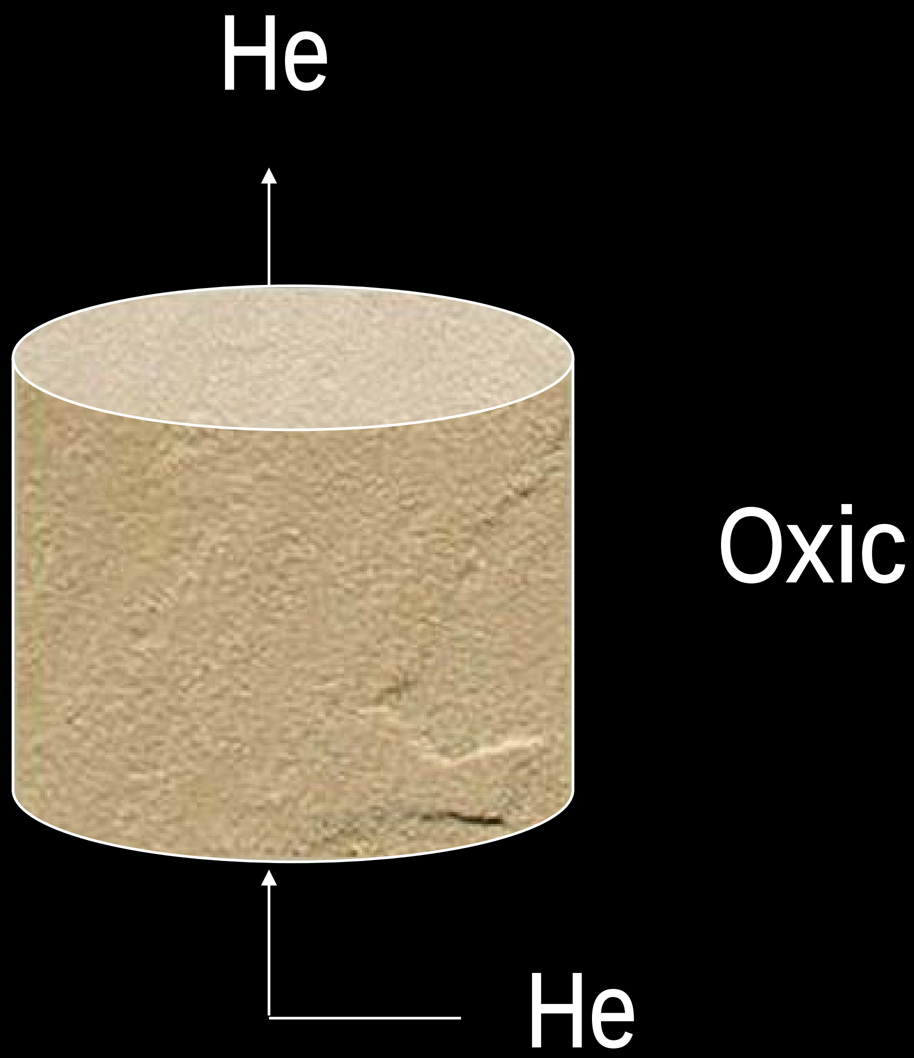

He

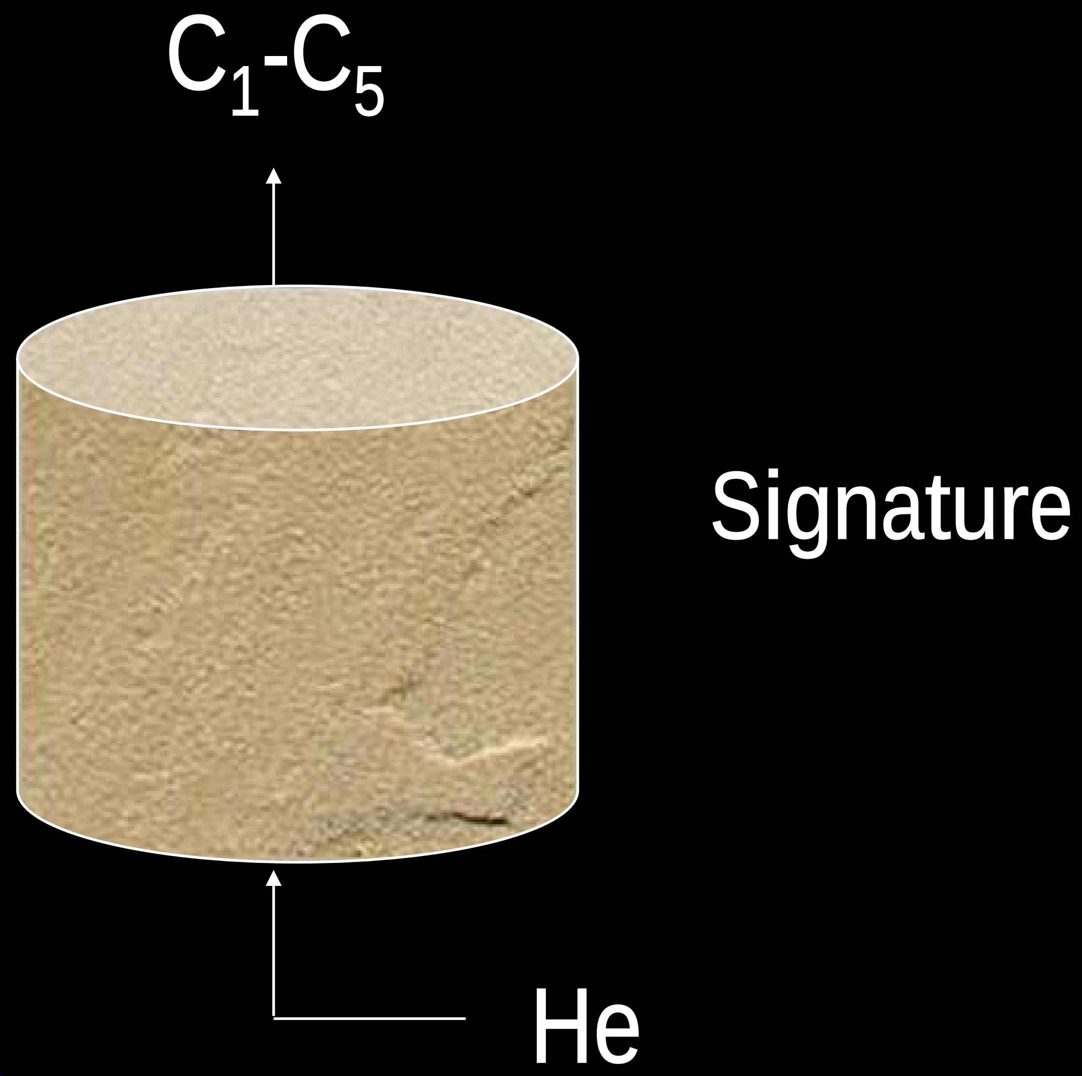
Significant Observations

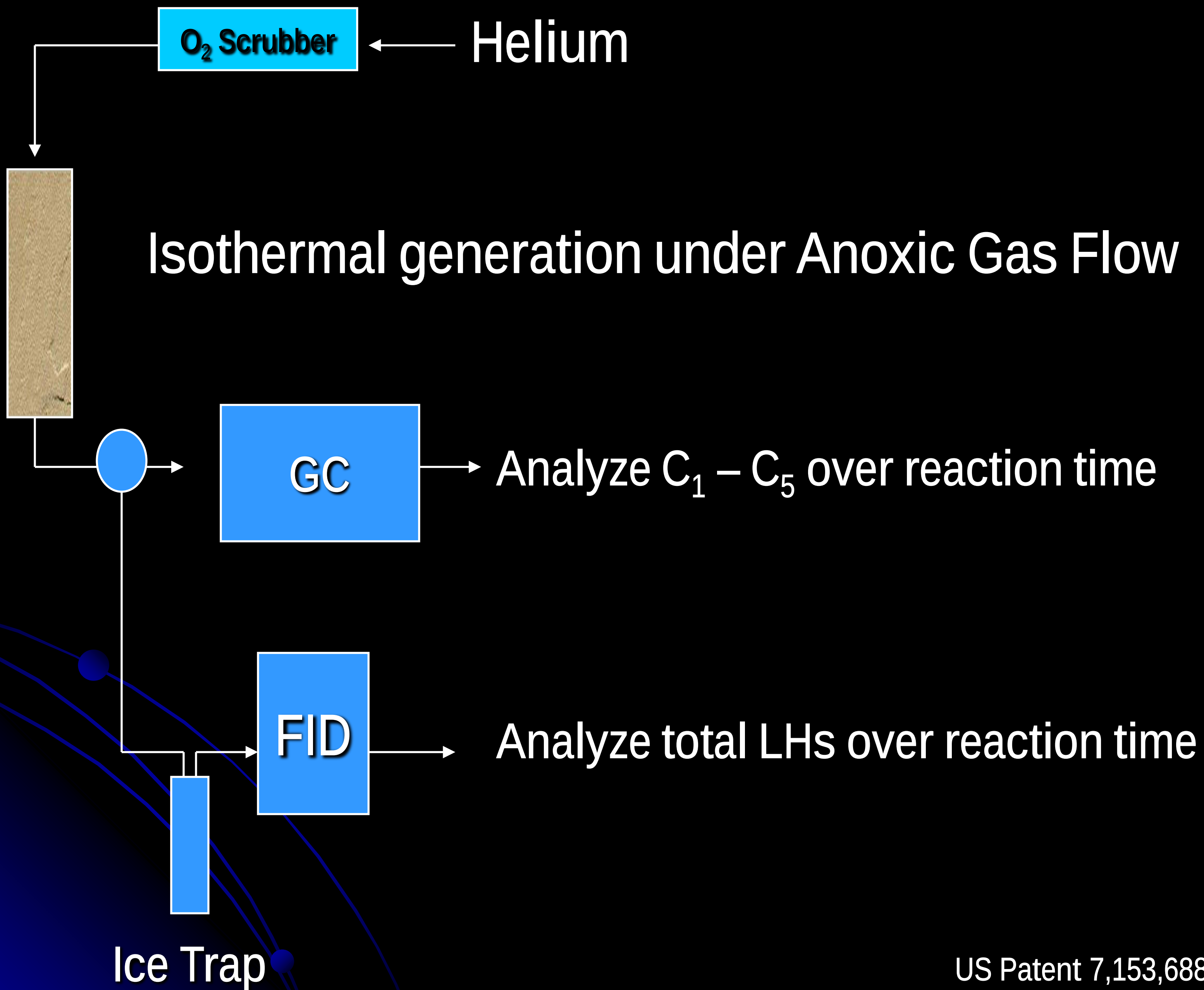

C_1-C_5
25^{o}C
He

Gas Flow Stimulates Rate of Generation

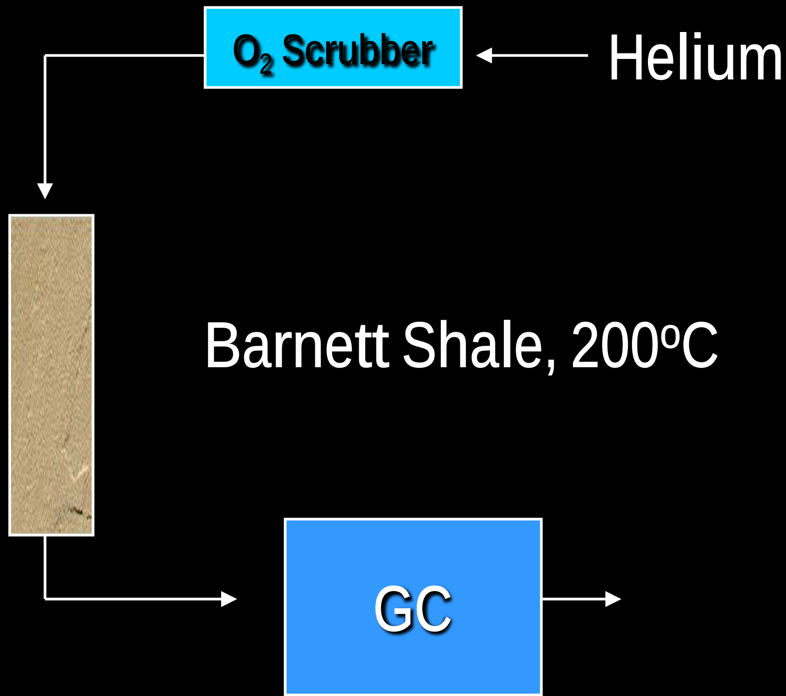

C_1-C_5
Anoxic
He


He
Oxic
He


C_1-C_5
Signature
He

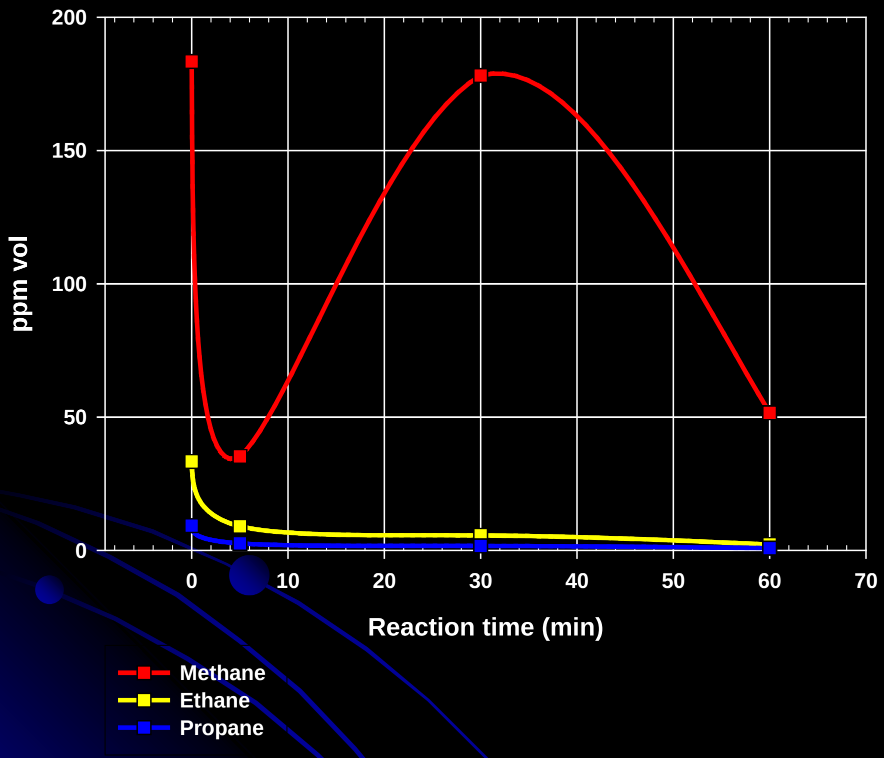


US Patent 7,153,688, Dec 06



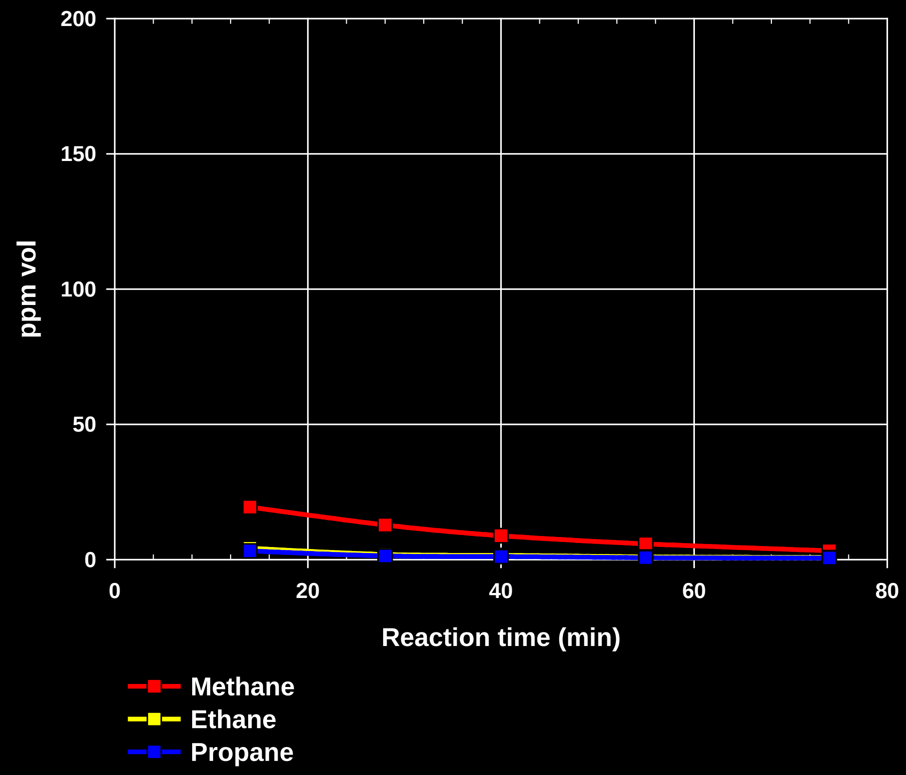
ANOXIC & OXIC conditions

Anoxic



No Olefins

Oxic

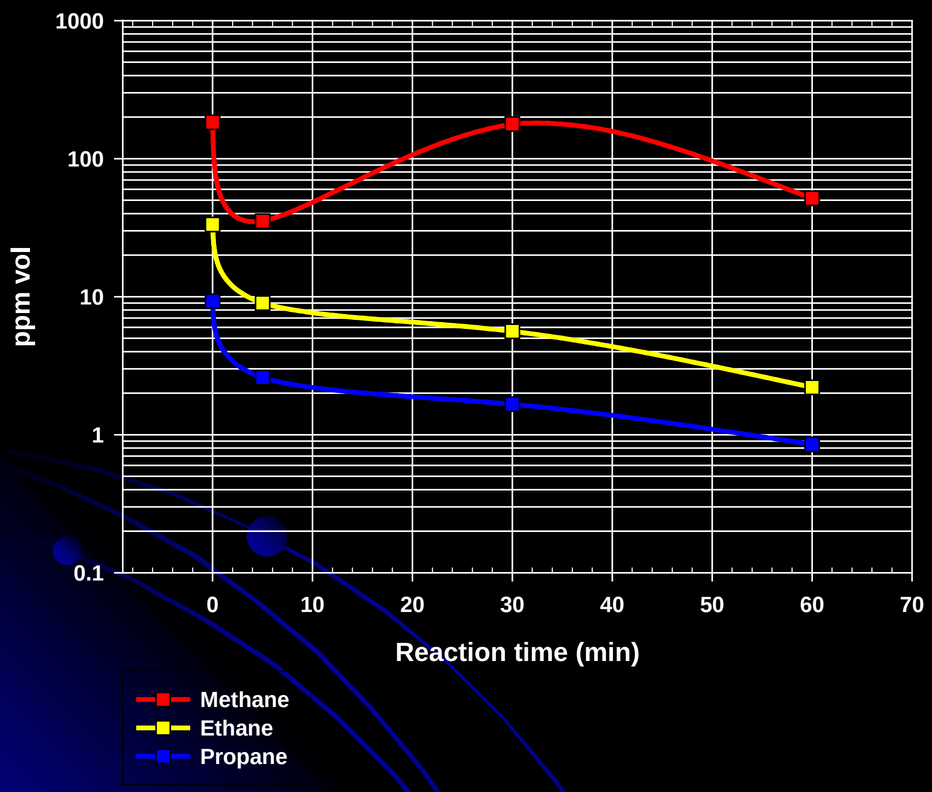


20% Olefins

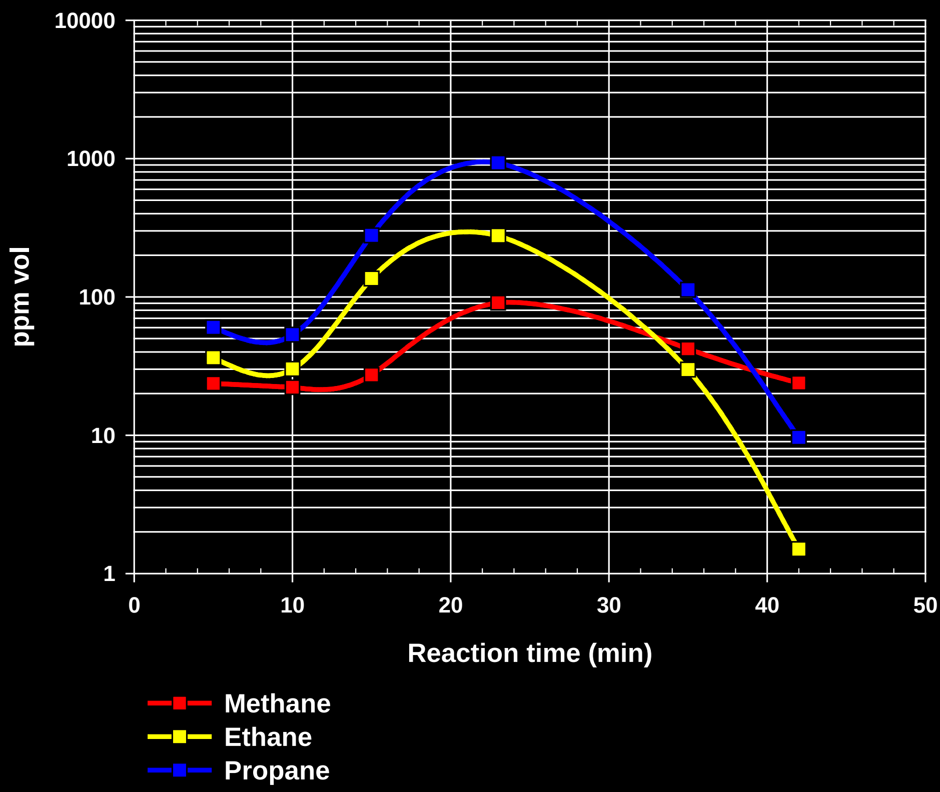
Different Shales give
Different Gas Compositions

Signature

Barnett Signature



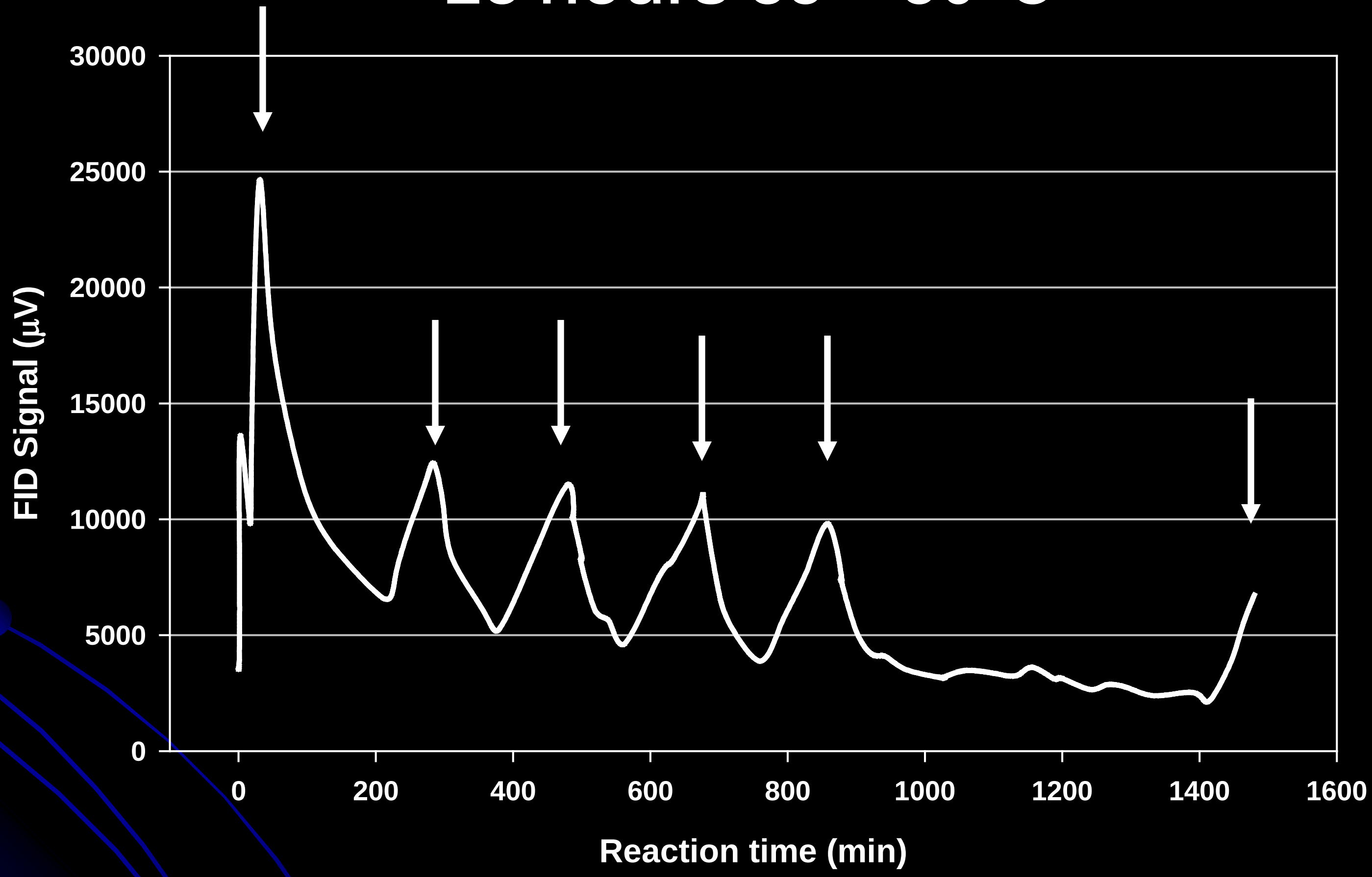
New Albany Signature



Mississippian Floyd Shale
Black Warrior Basin

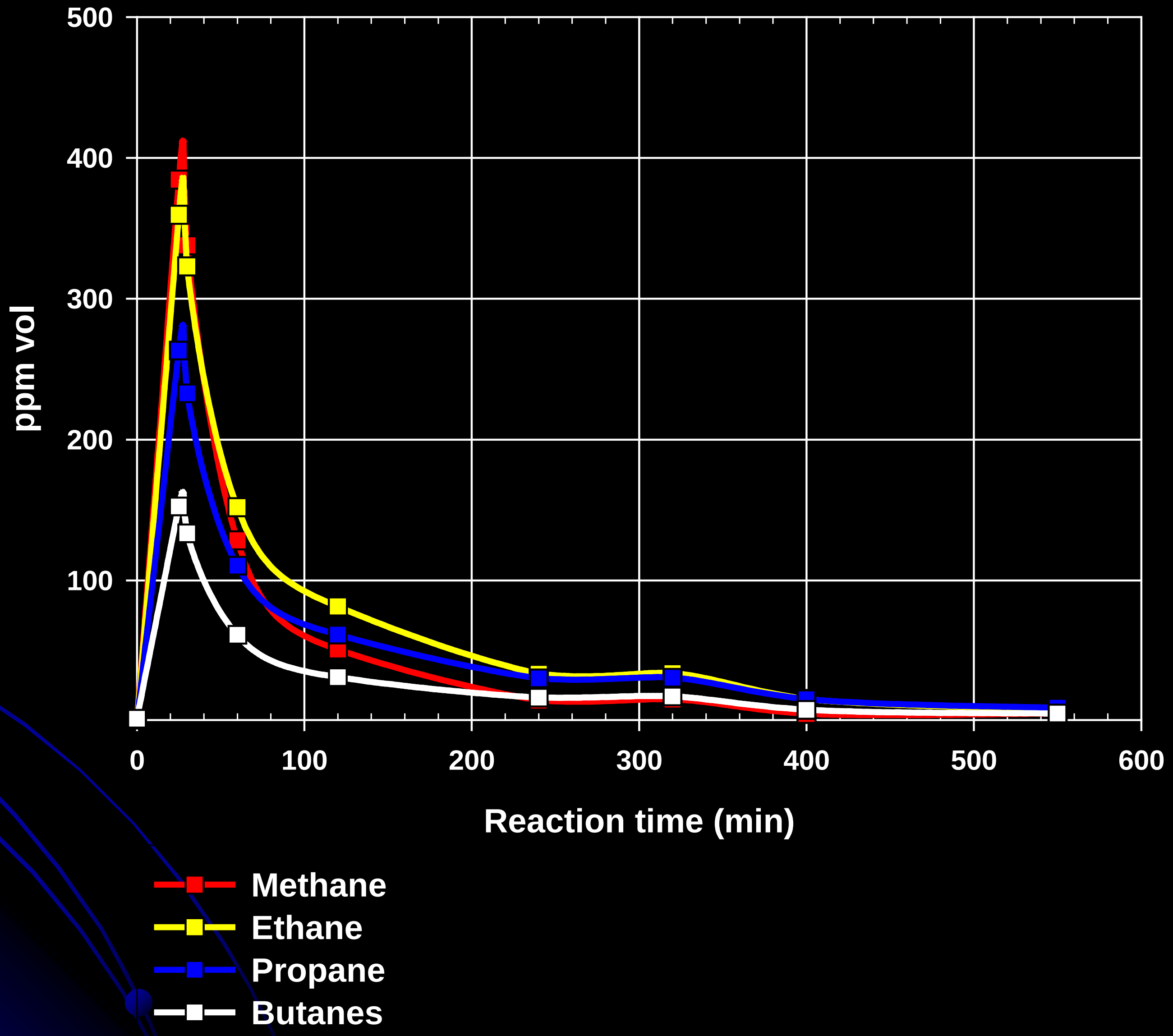
35 – 50^{o}C

Generation Episodes
23 hours 35 – 50ºC

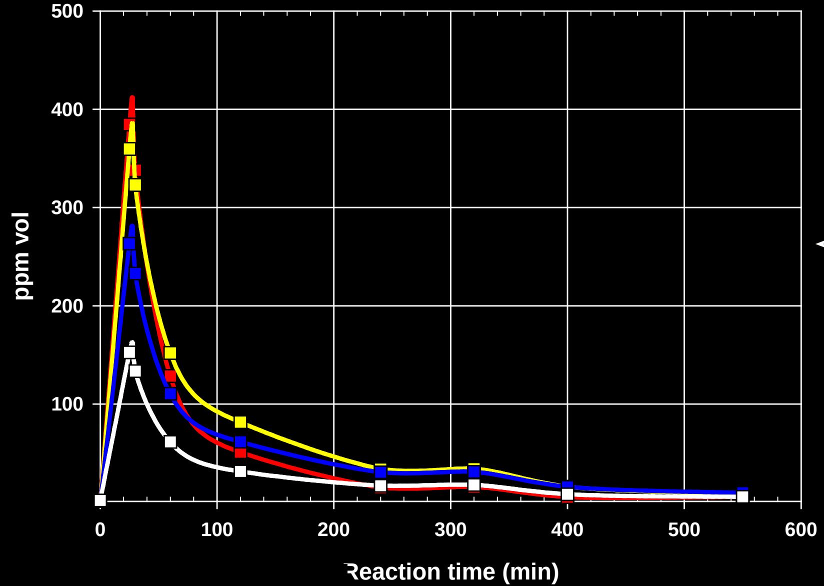


Floyd Shale

50^{o}C, Anoxic He Flow

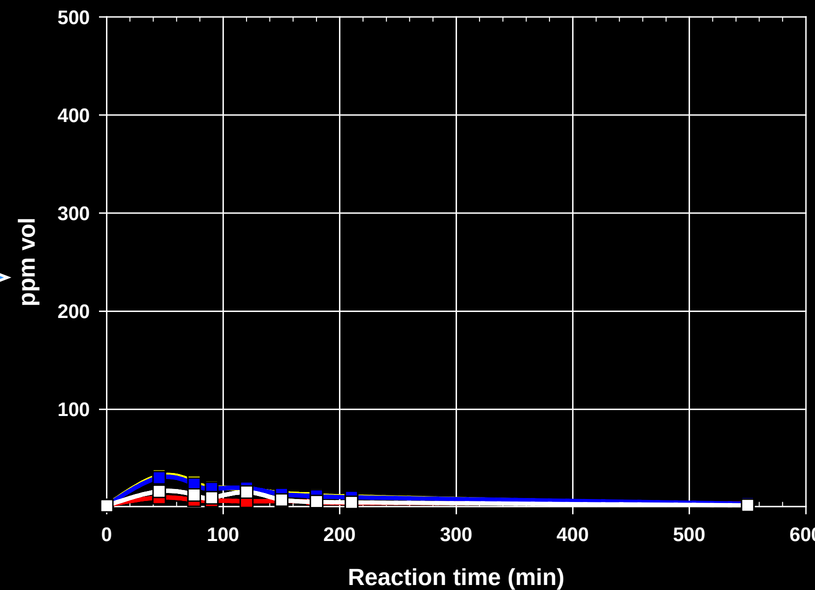


Repeat same experiment
oxic conditions



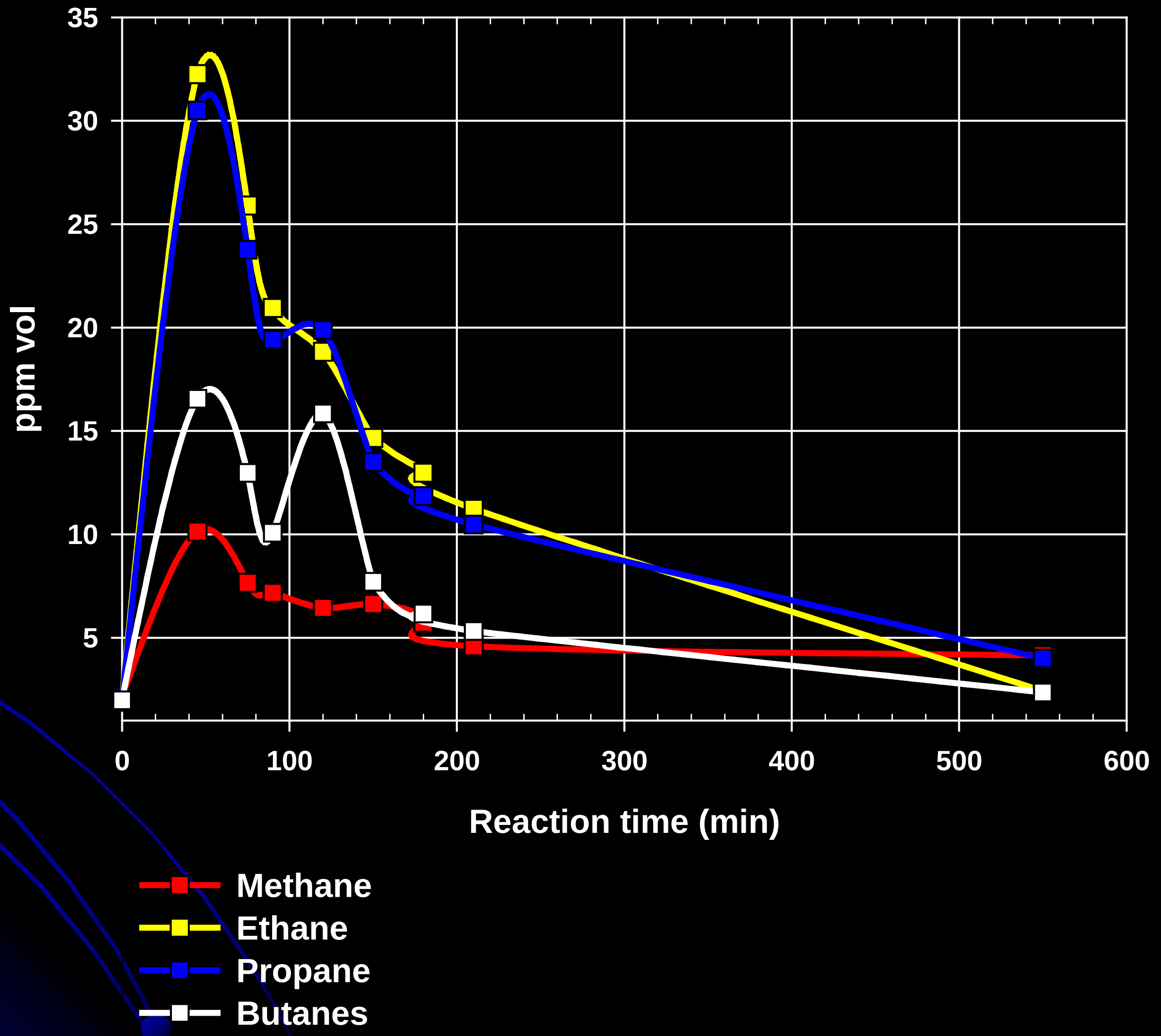
Anoxic He Flow
50ºC

10 1 ppm O_2
50ºC

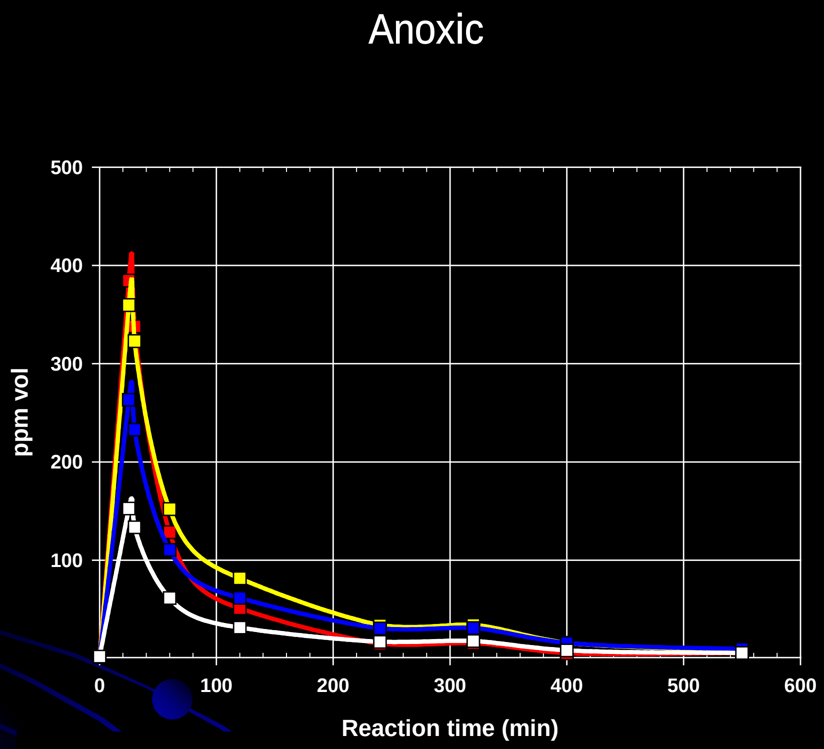


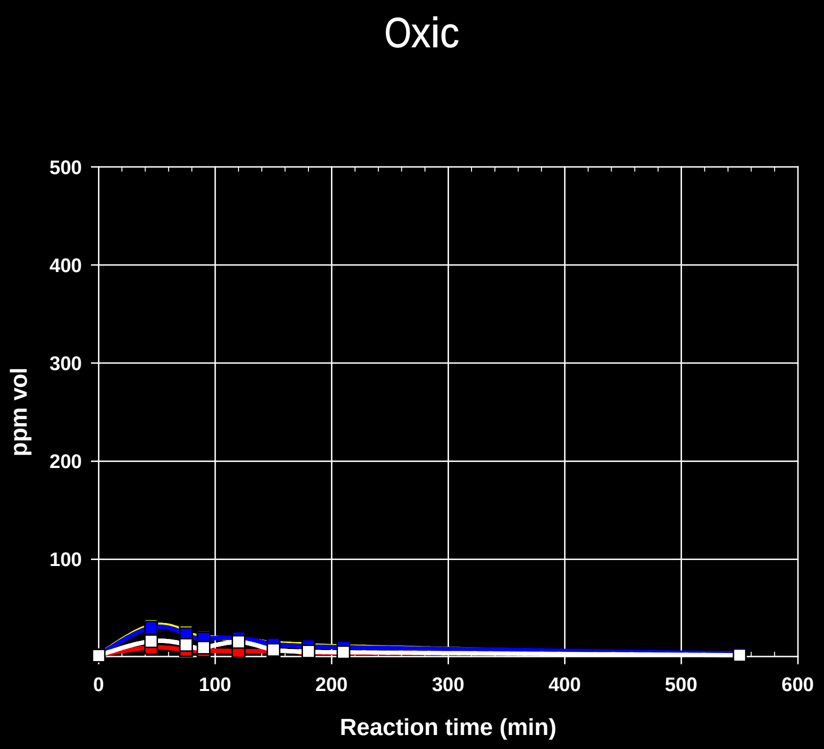
Floyd Shale

50^{o}C, Oxic He Flow (10 1 ppm O_2)



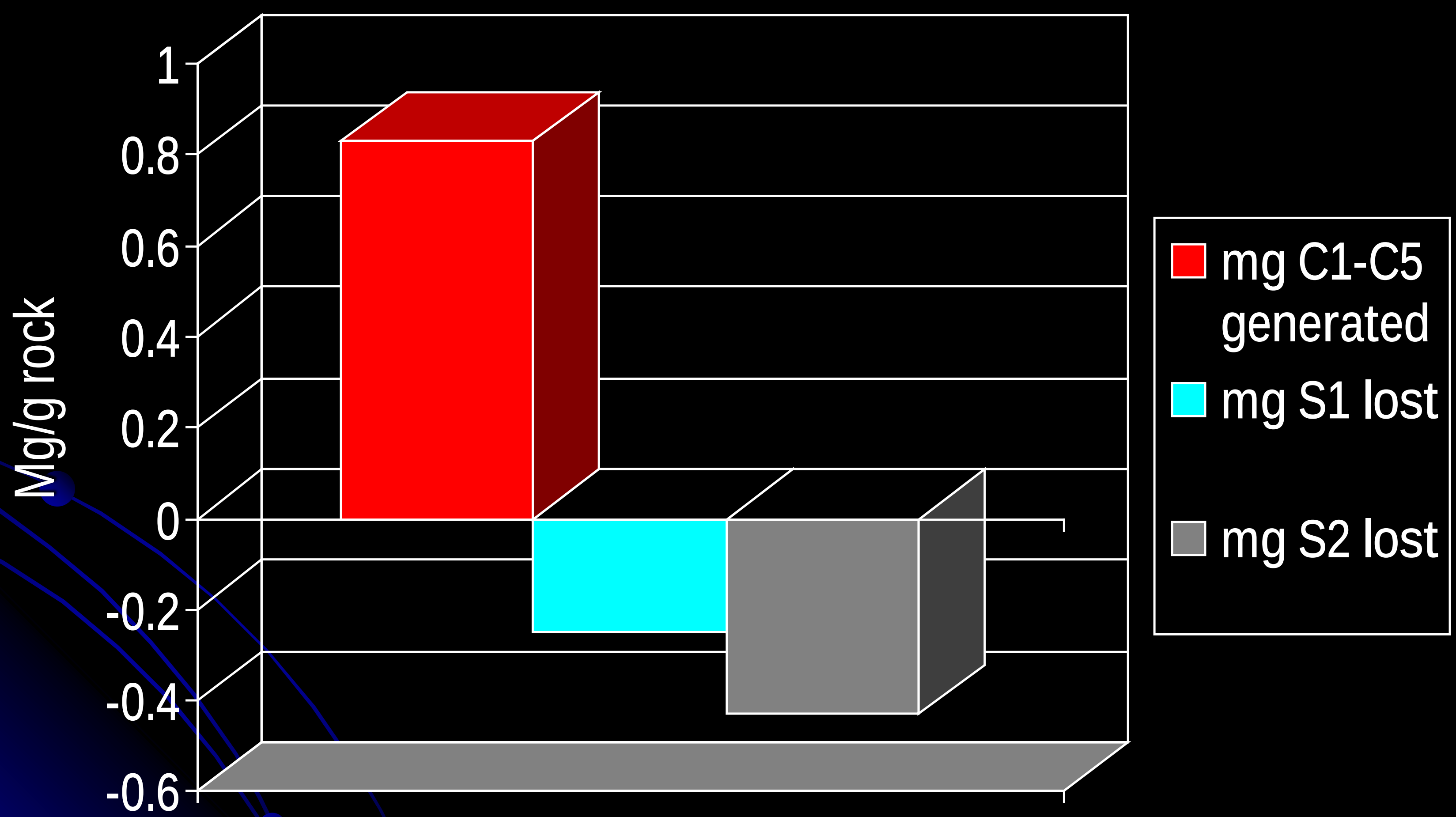
Yield


Anoxic
ppm vol
500
400
300
200
100
0
100
200
300
400
500
600
Reaction time (min)


Oxic
ppm vol
500
400
300
200
100
0
100
200
300
400
500
600
Reaction time (min)

Material Balance

Floyd Shale, He flow, 50°C



Comparative Results

Anoxic Isothermal Gas-Flow Generation 50ºC

Oxic Non-Isothermal Open-System Pyrolysis 350ºC

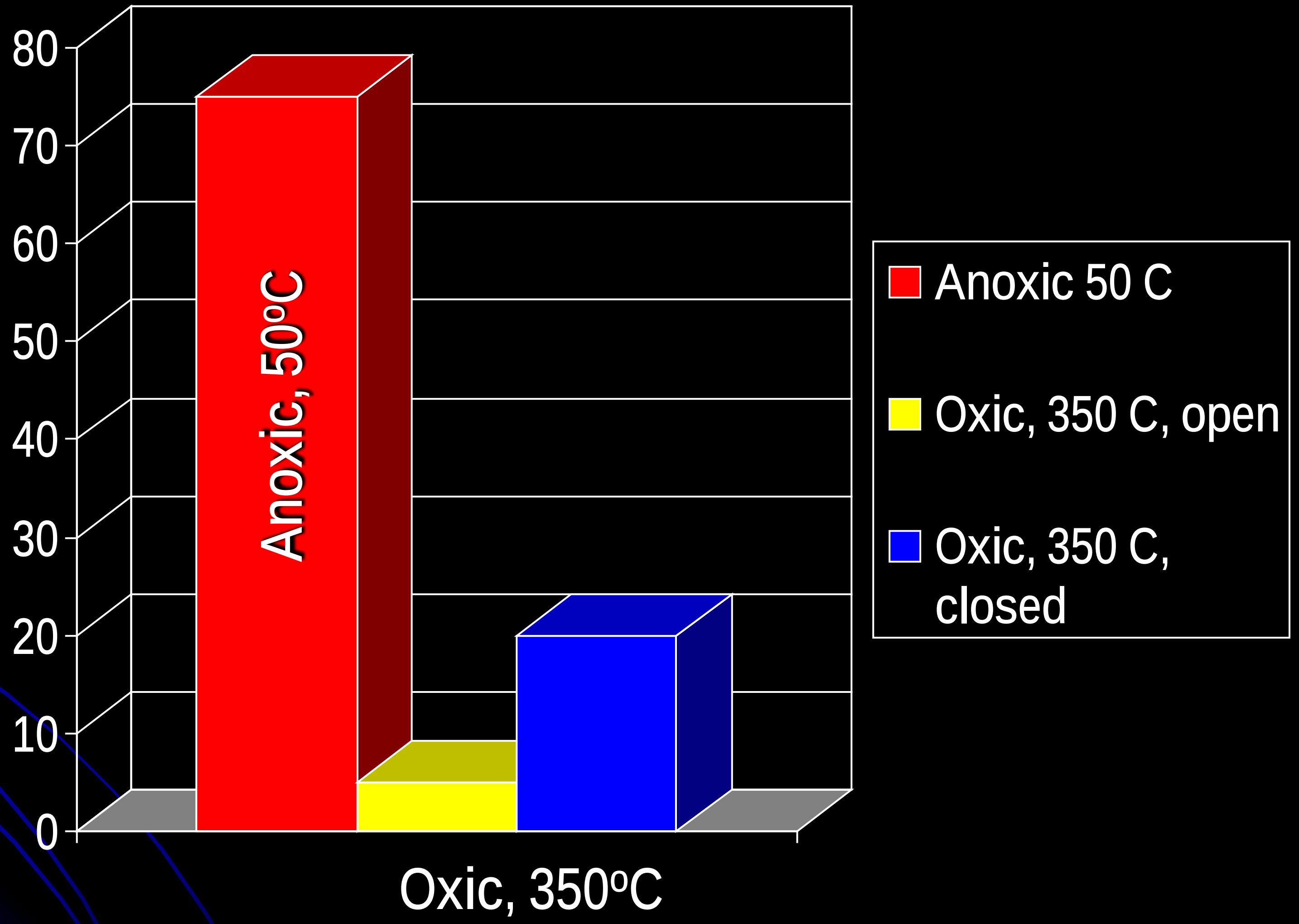
Erdman & Horsfield (2006) *GCA* 70, 3943.

Oxic Isothermal Closed-System Pyrolysis 350ºC

Behar et al., (1992) *Org. Geochem.* 19, *173*.

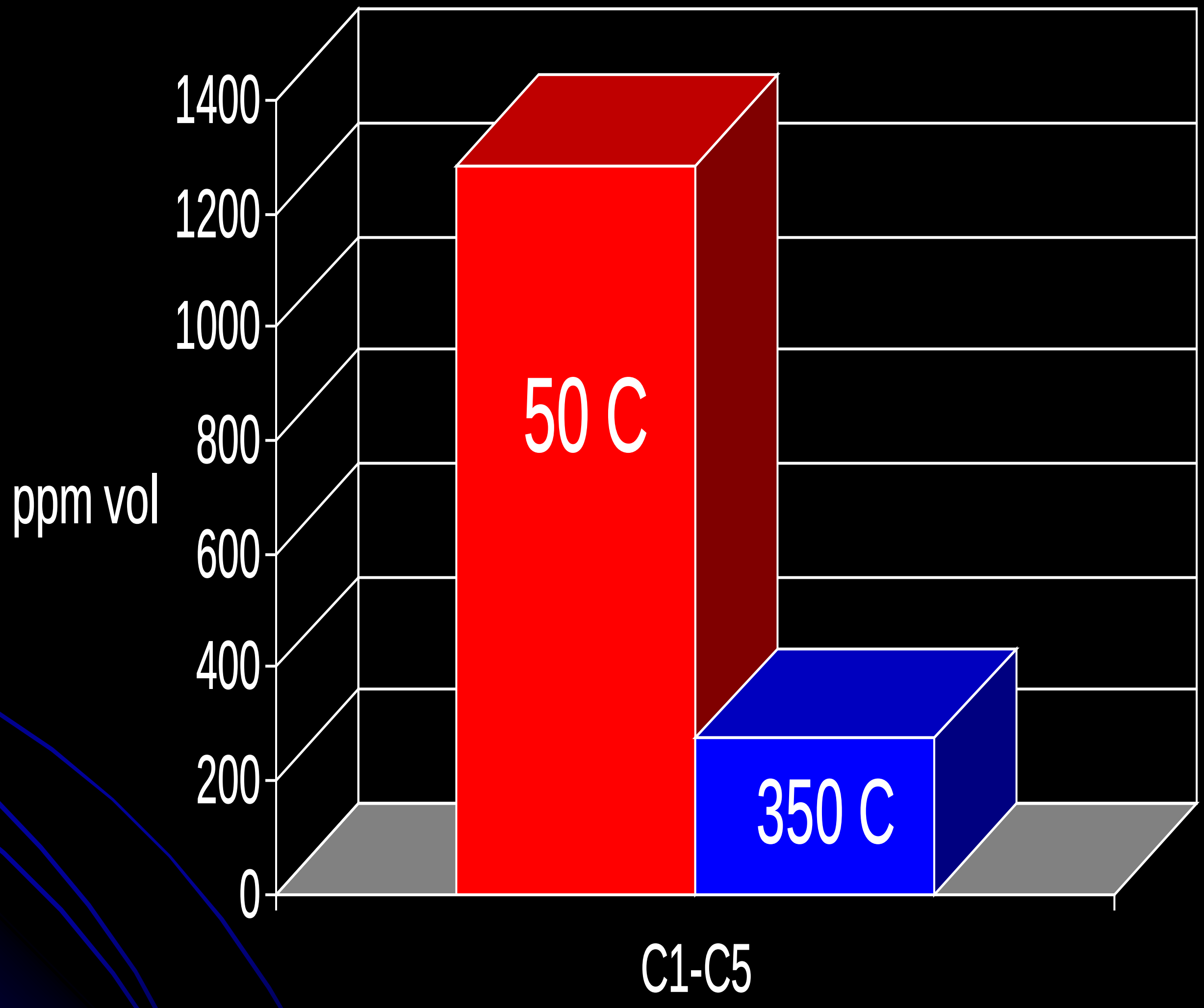
Active shales generate five times more catalytic gas at 50°C than thermogenic gas at 350°C

mg gas/g kerogen



Anoxic Isothermal Degradation

Floyd Shale



How can gas form at 25ºC?

Oil $\rightarrow$ **Gas + -C-** + Heat

Catalytic Degradation

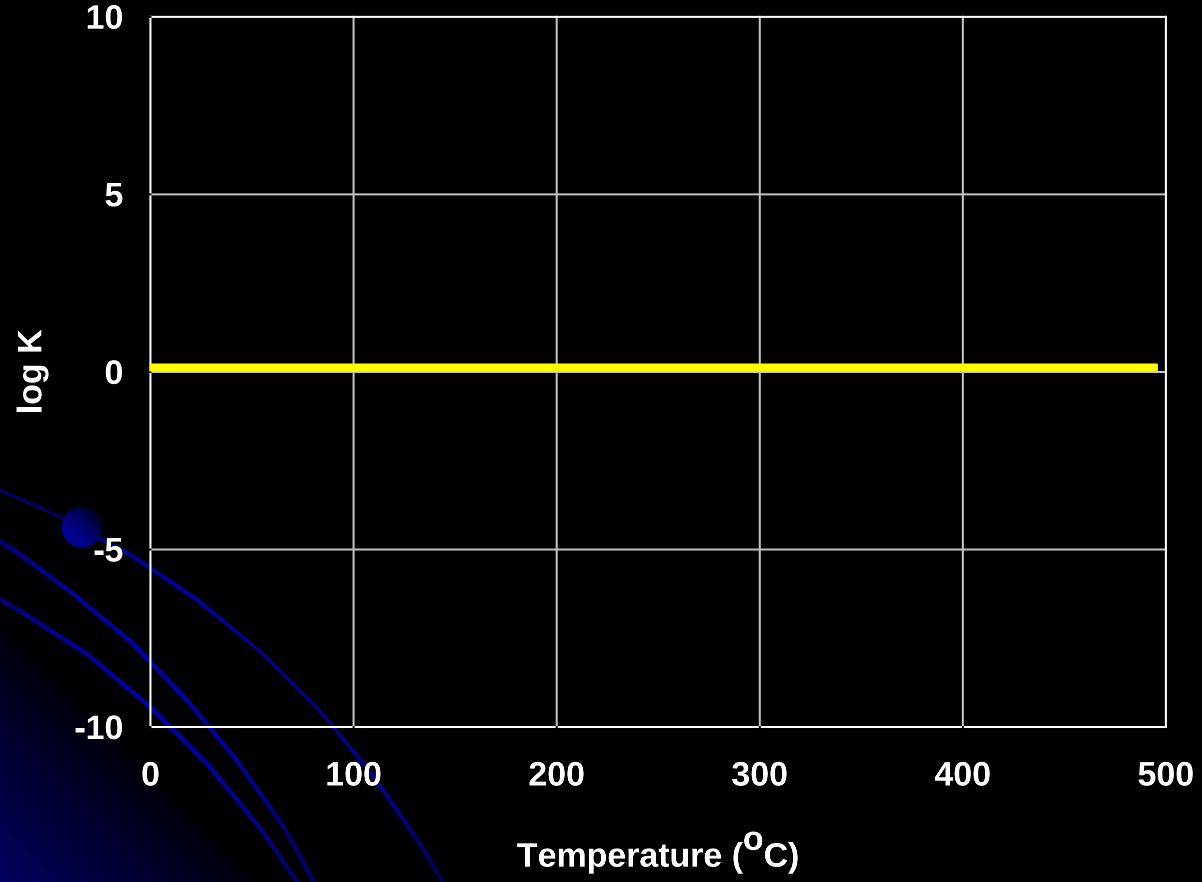
Heat + Oil $\rightarrow$ **Gas + Olefins**

Thermal Cracking

A → B

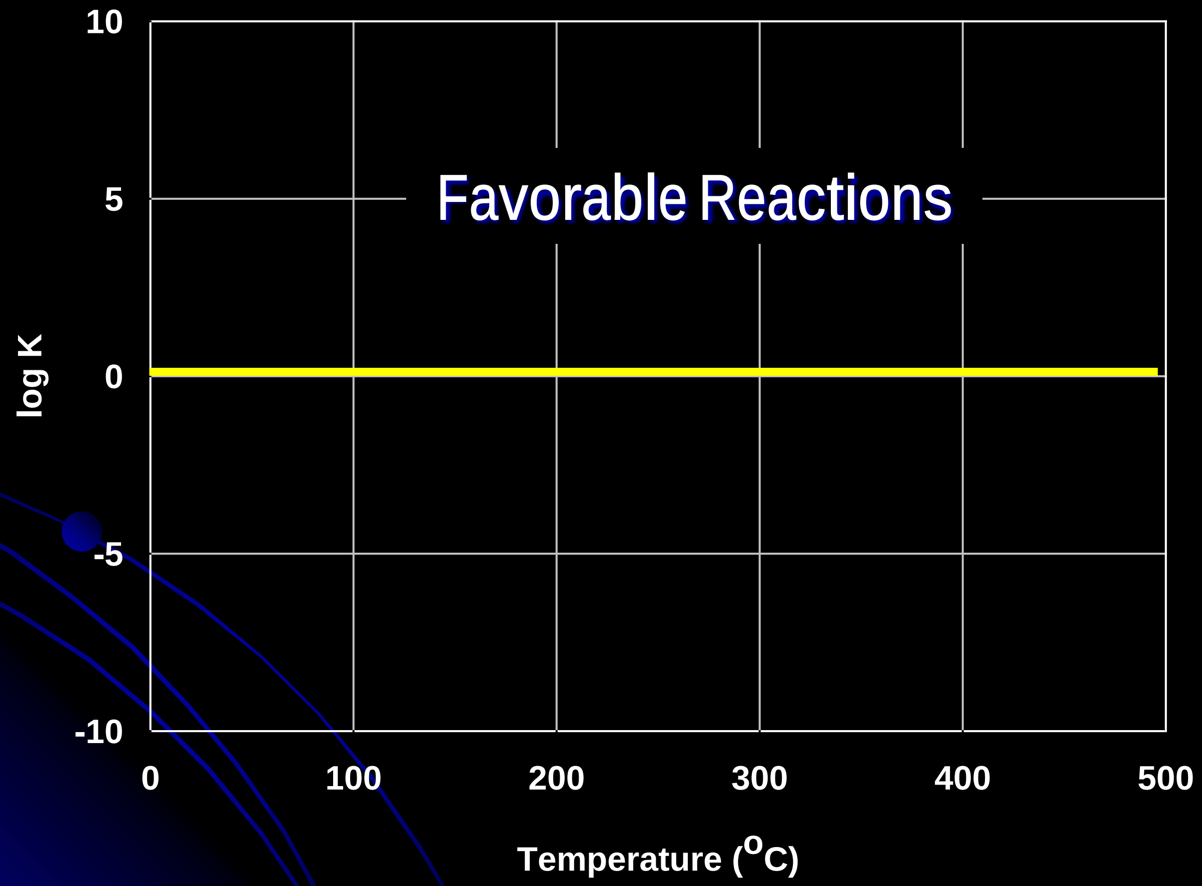
$$k = \frac{B}{A}$$

A & B at Equilibrium



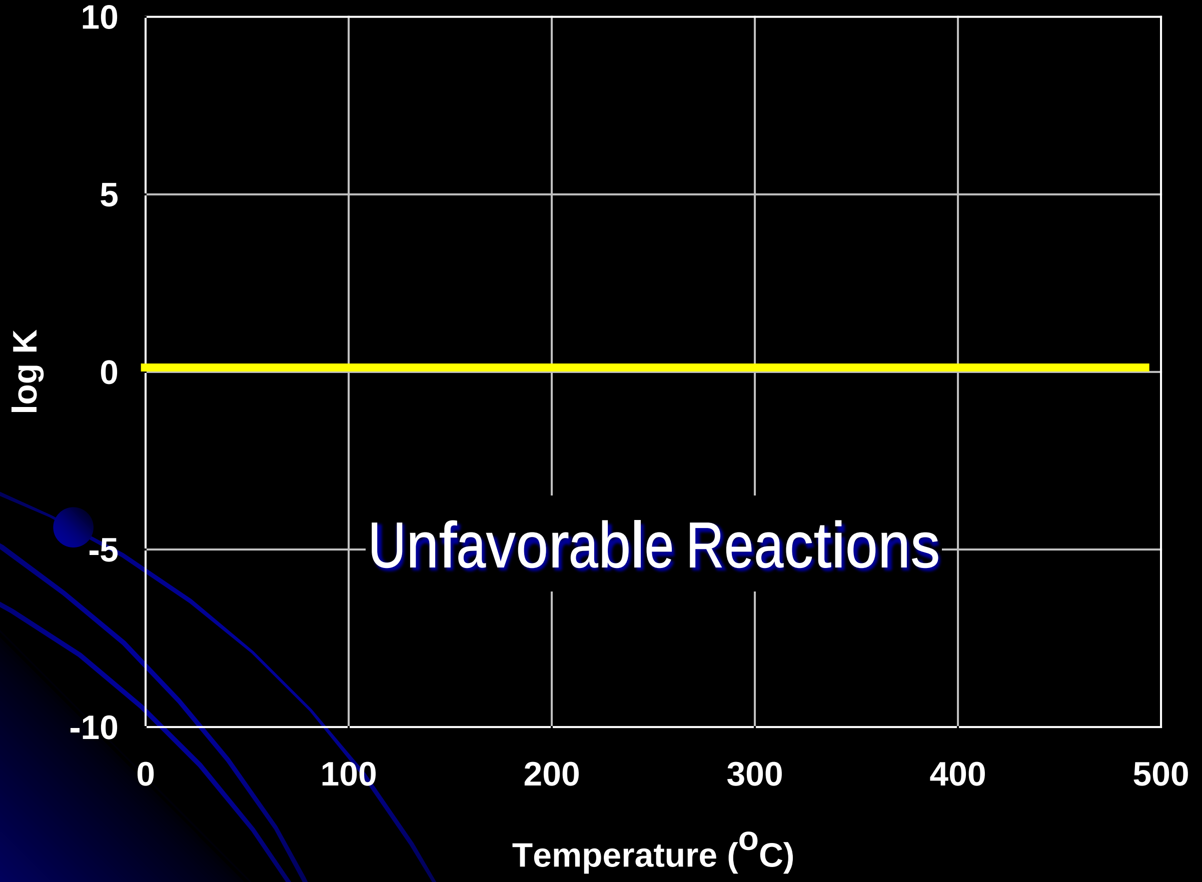
$$\frac{B}{A} = 1$$

A & B at Equilibrium



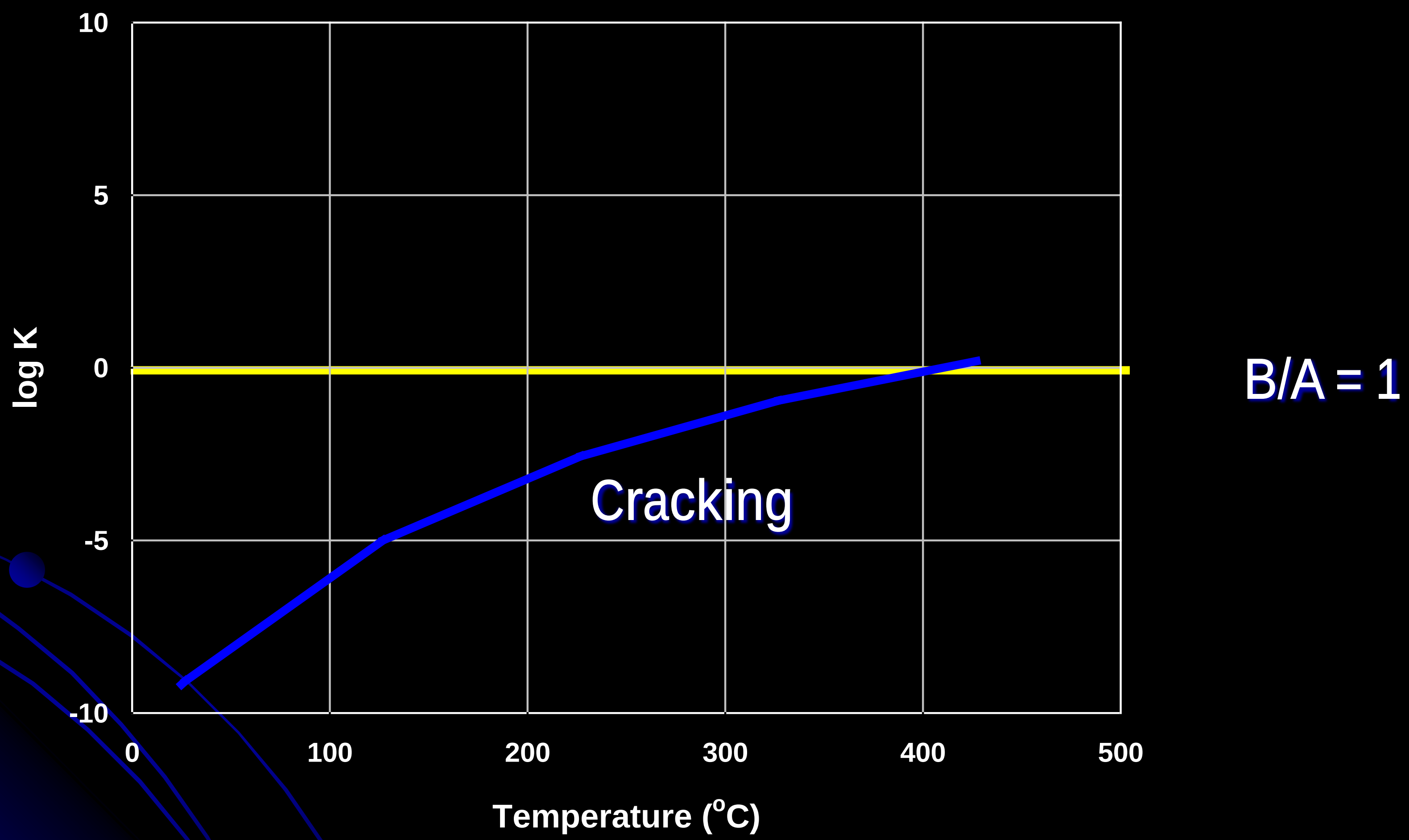
$$\frac{B}{A} >> 1$$

A & B at Equilibrium

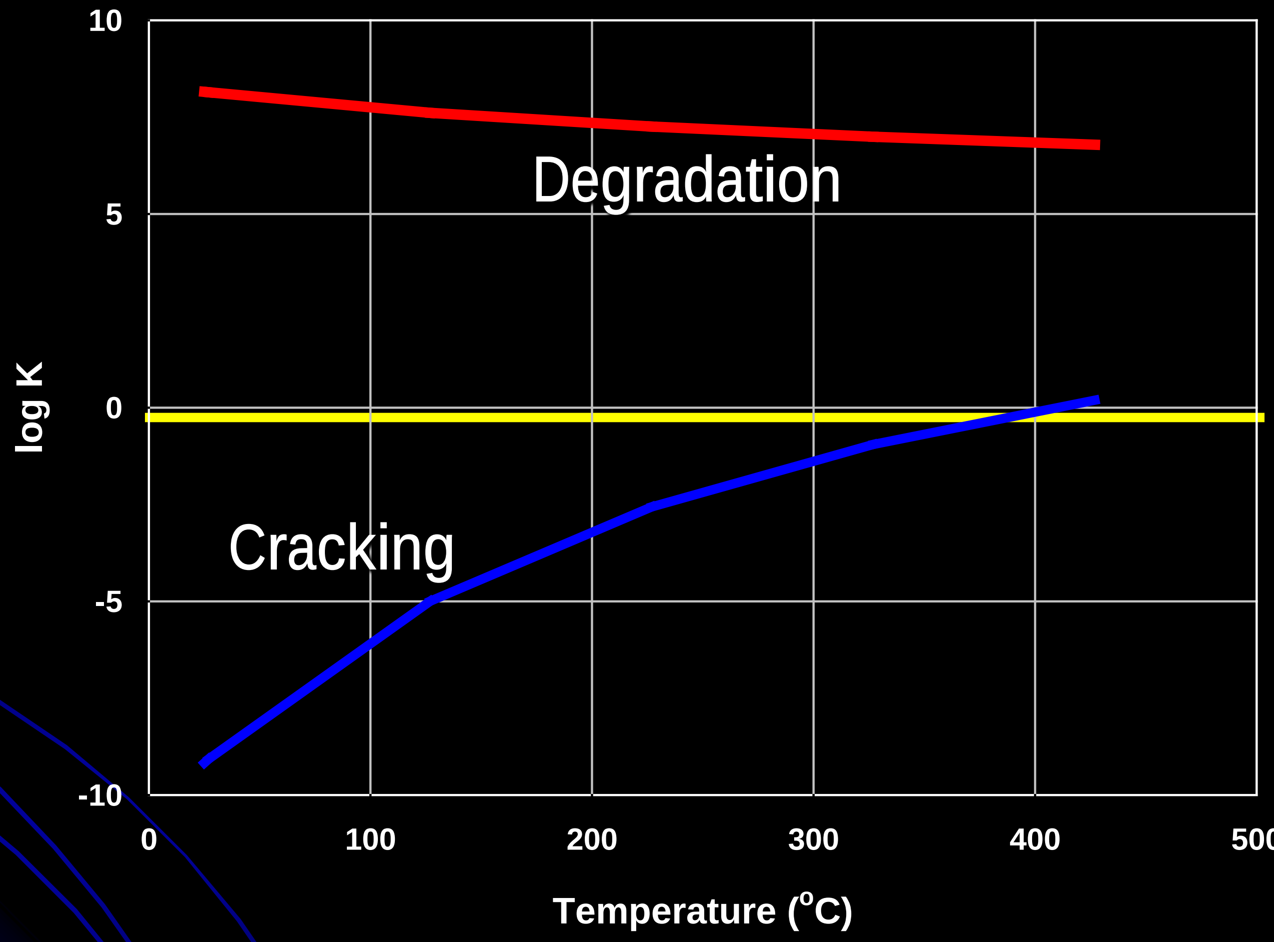


$$\frac{B}{A} \ll 1$$

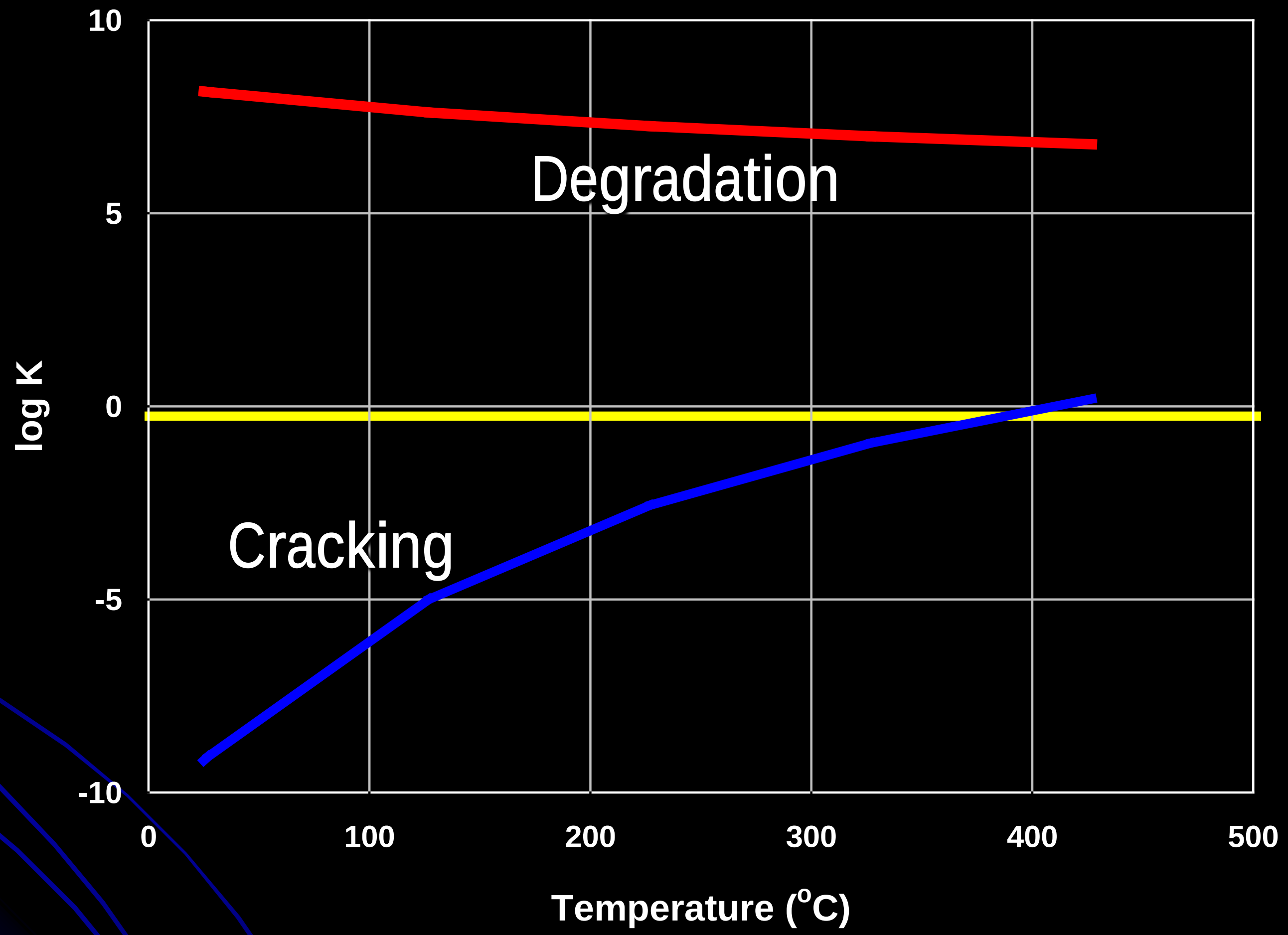
Thermal Cracking

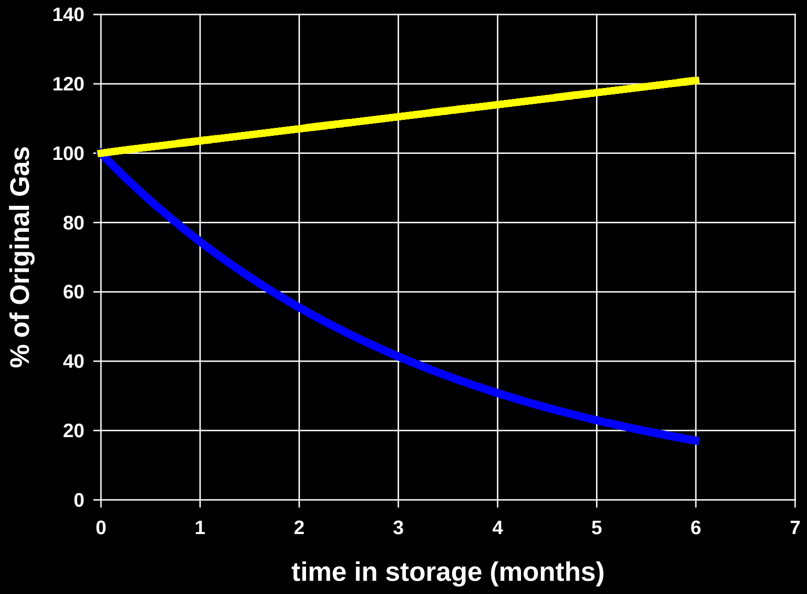


Catalytic Degradation



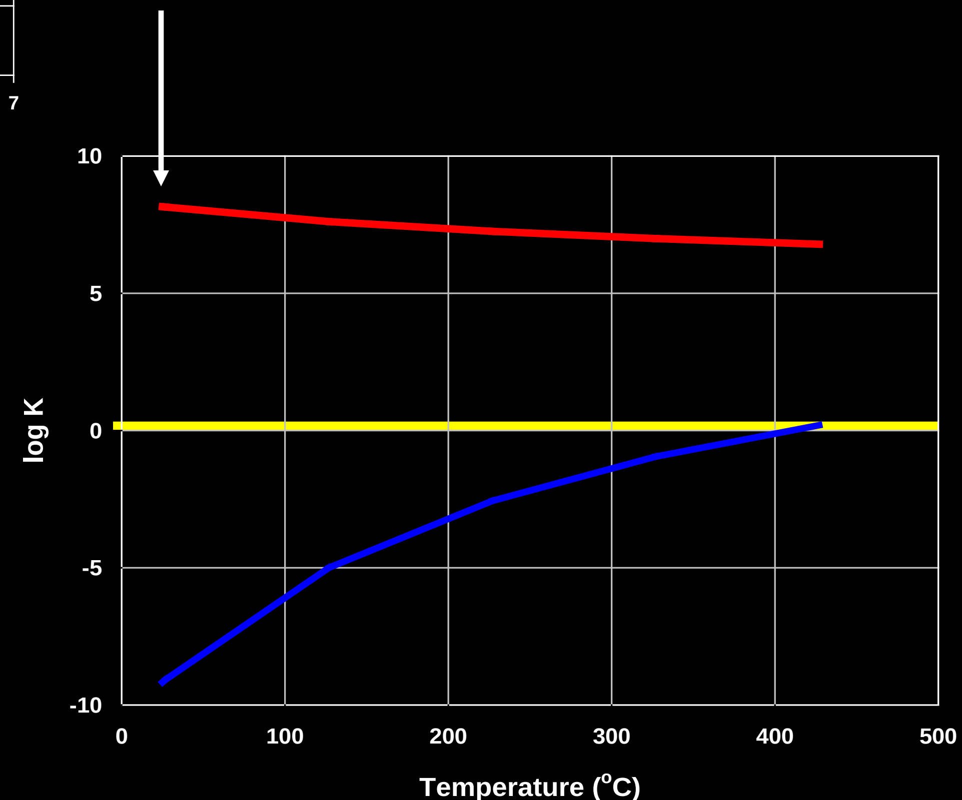
Kerogen → Gas at 25^{o}C

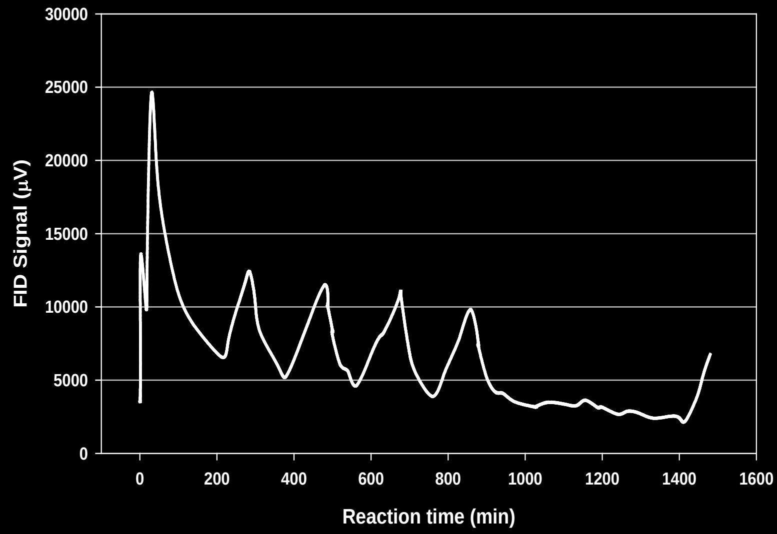




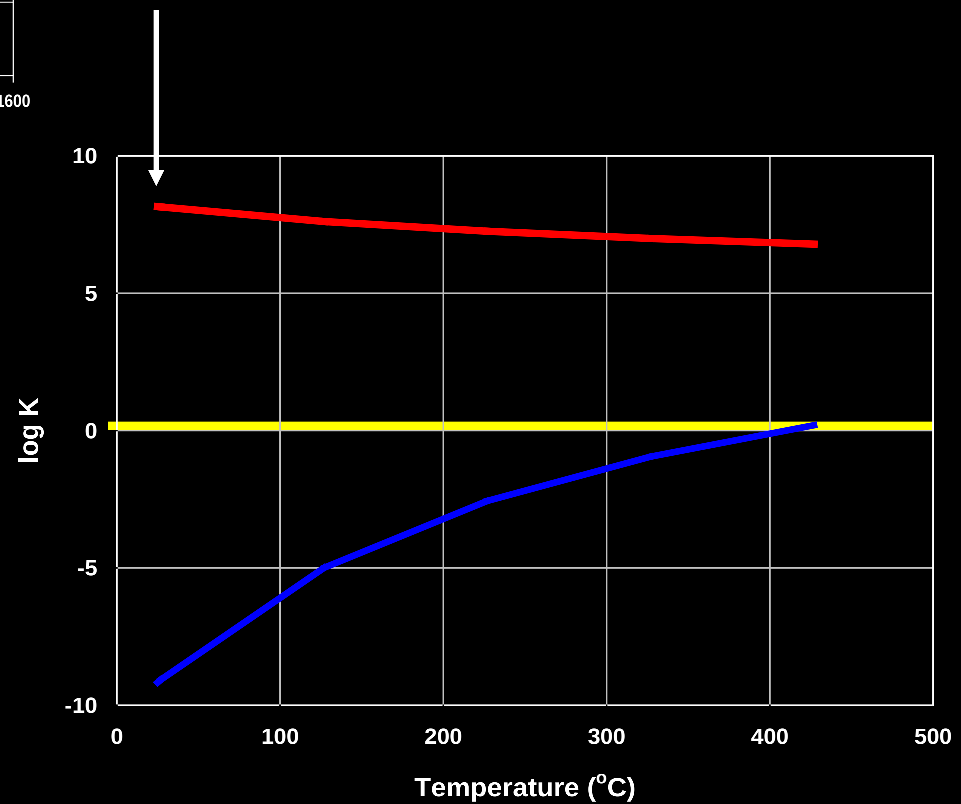
Snowdon & McCrossen

Oil → Gas + -C-



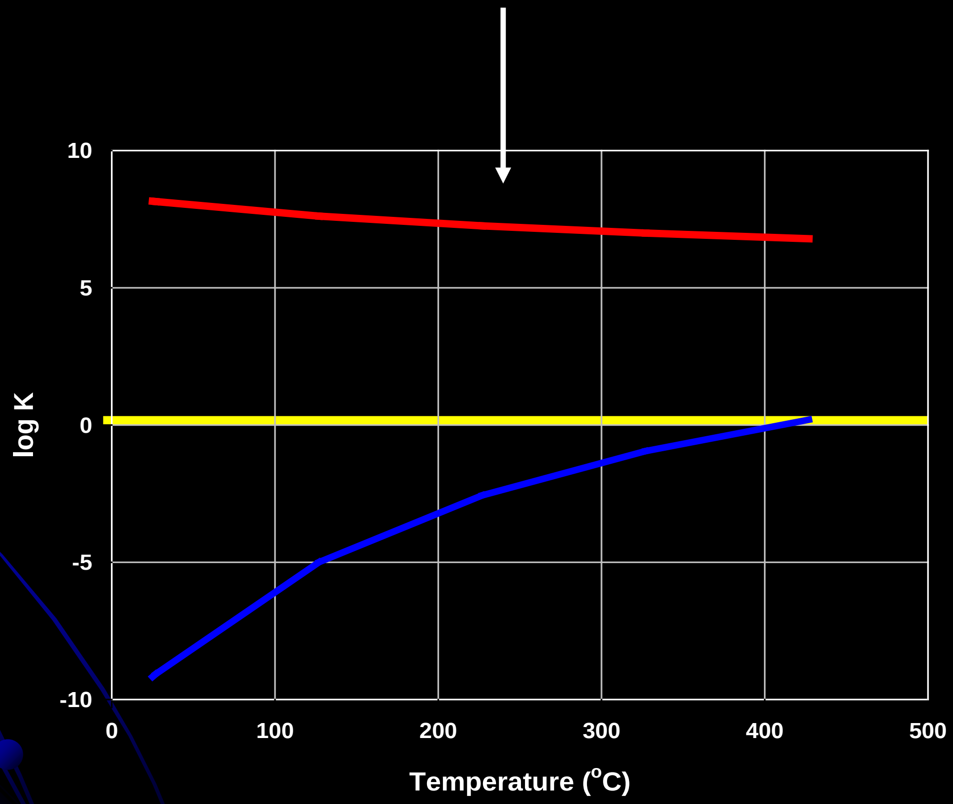


Oil $\rightarrow$ Gas + -C-



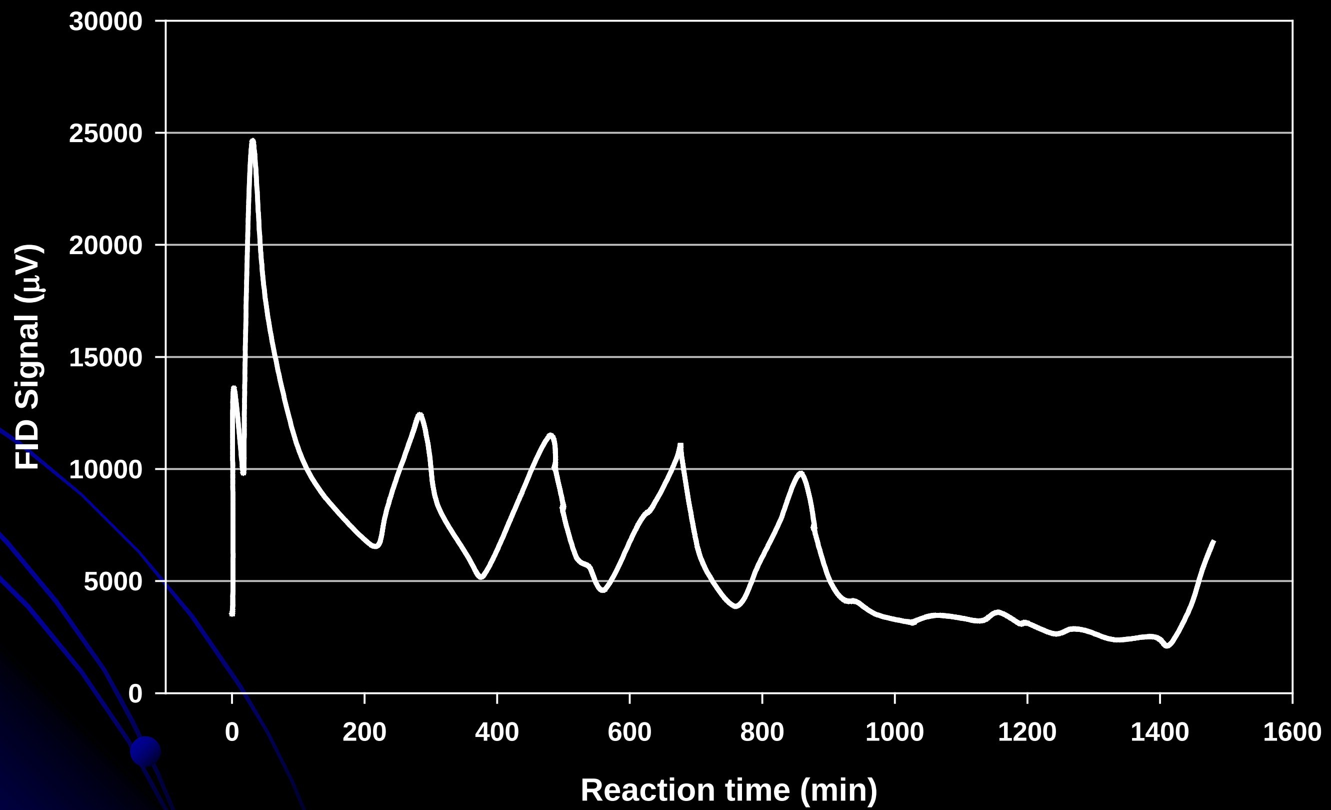
Catalytic Gas Generation during production

In Situ conversion of bitumens to gas

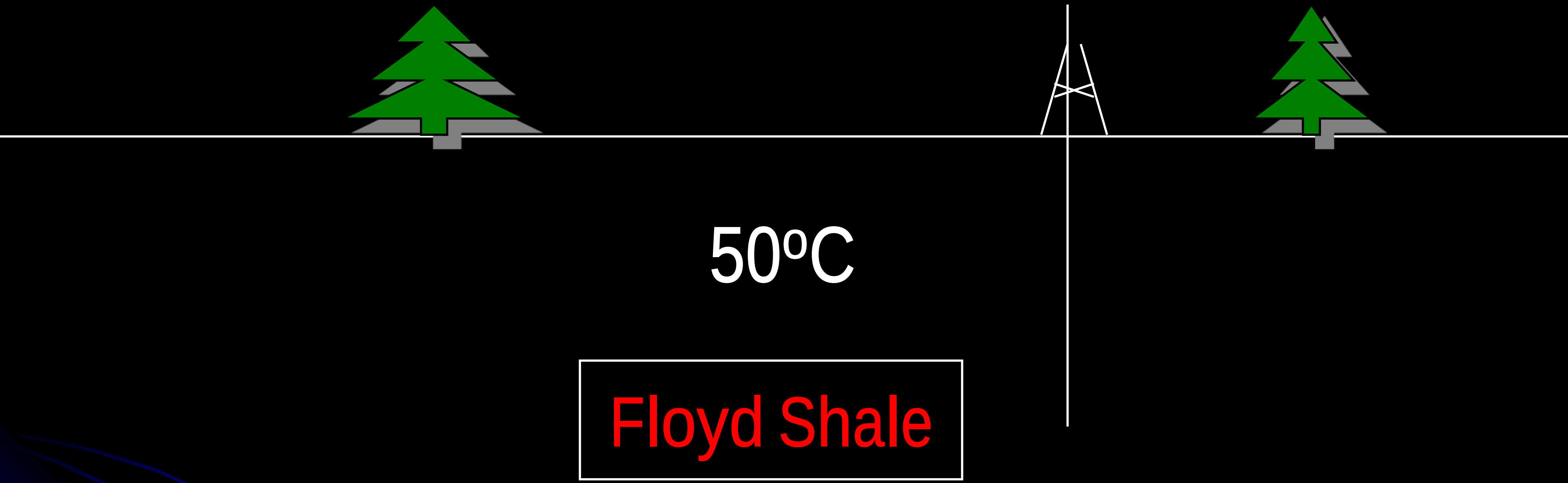


Catalytic Gas Generation in Production

Does this occur during production?



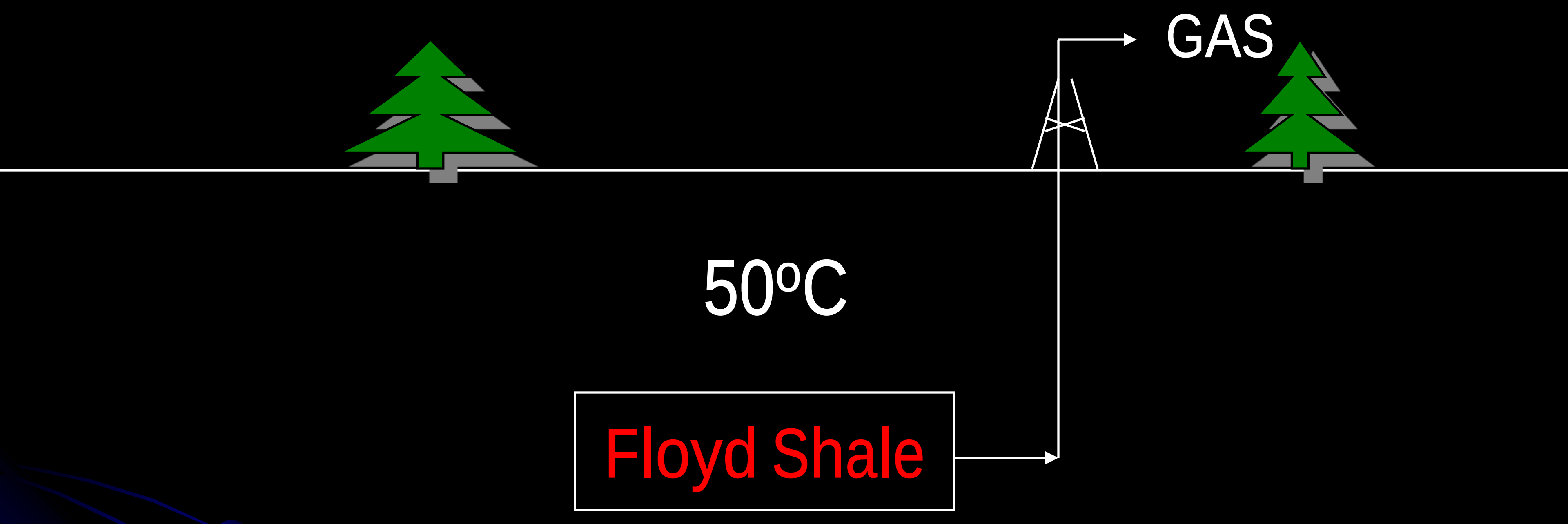
GAS GENERATION DURING PRODUCTION



CLOSED REACTOR

P_c

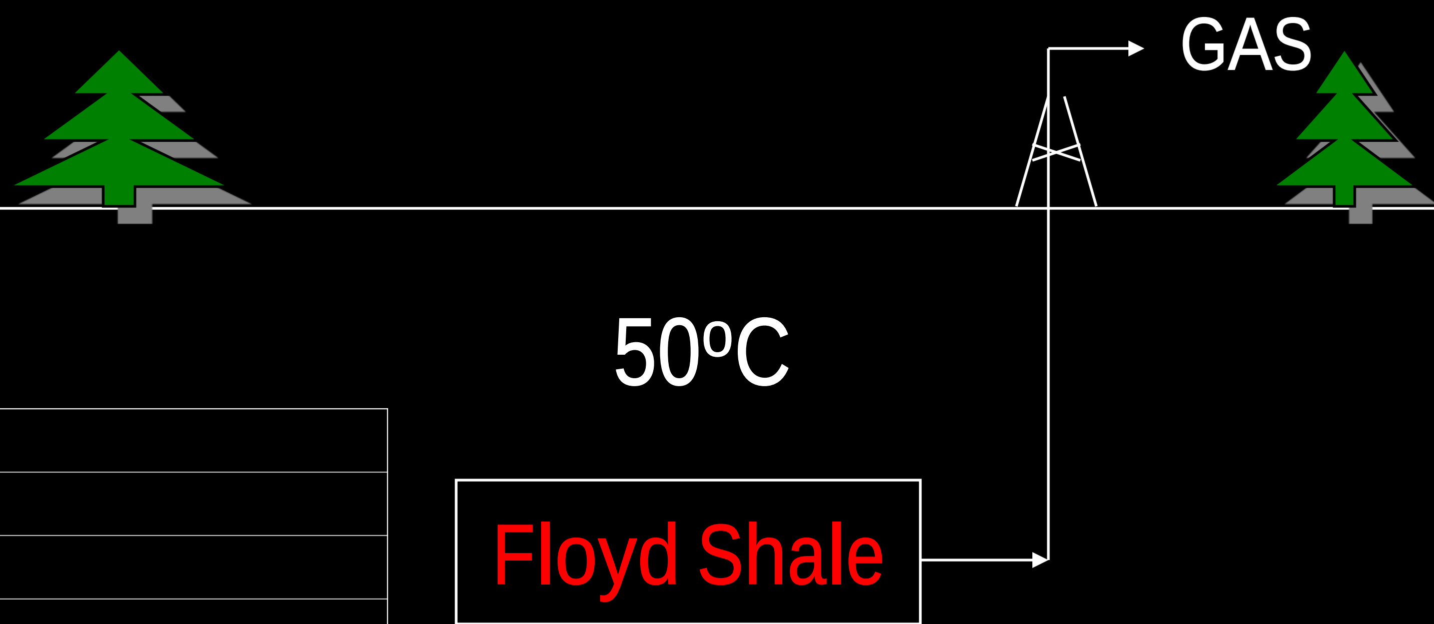
GAS GENERATION DURING PRODUCTION

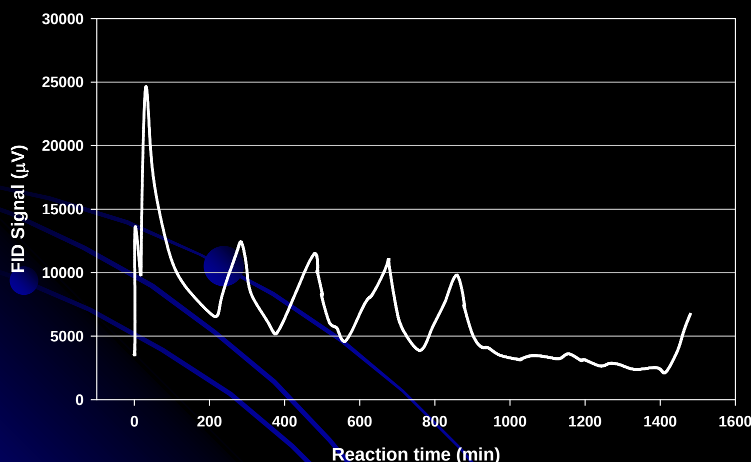


OPEN REACTOR

$P < P_c$

GAS GENERATION DURING PRODUCTION





OPEN REACTOR

$P < P_c$

GAS GENERATION DURING PRODUCTION

Native Gas
+
Catalytic Gas

50^oC

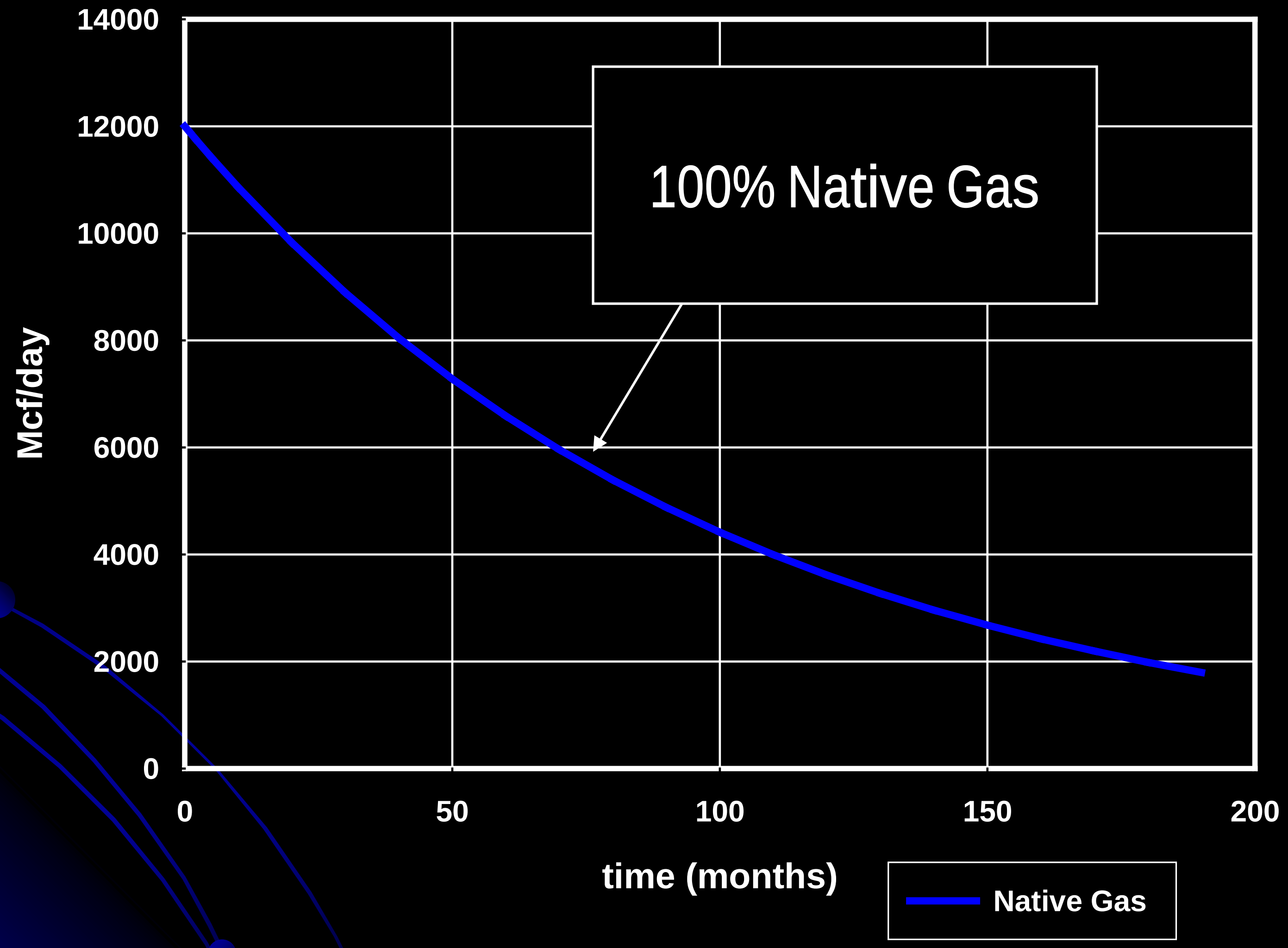
Production Flow

Floyd Shale

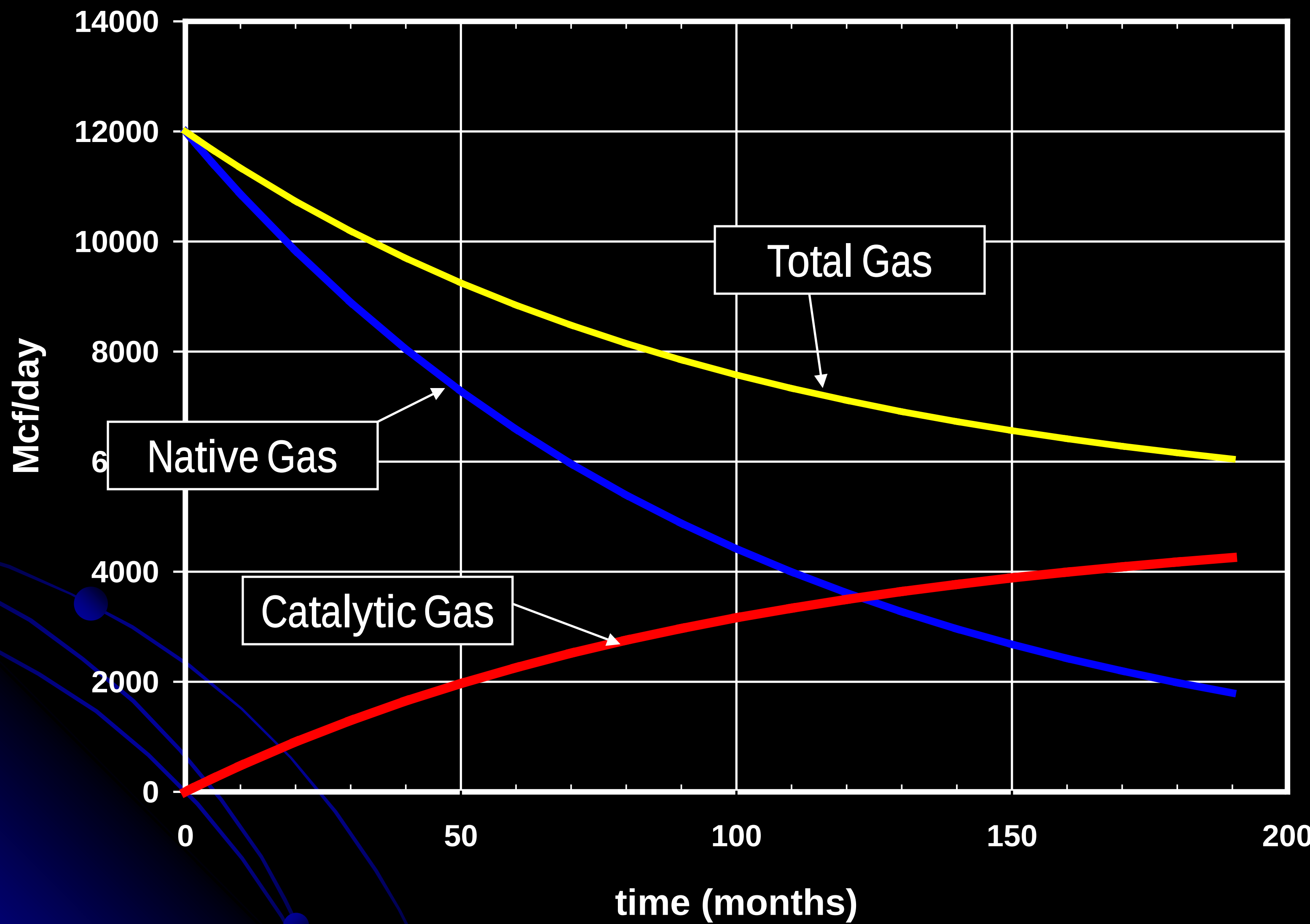
OPEN REACTOR

$P < P_c$

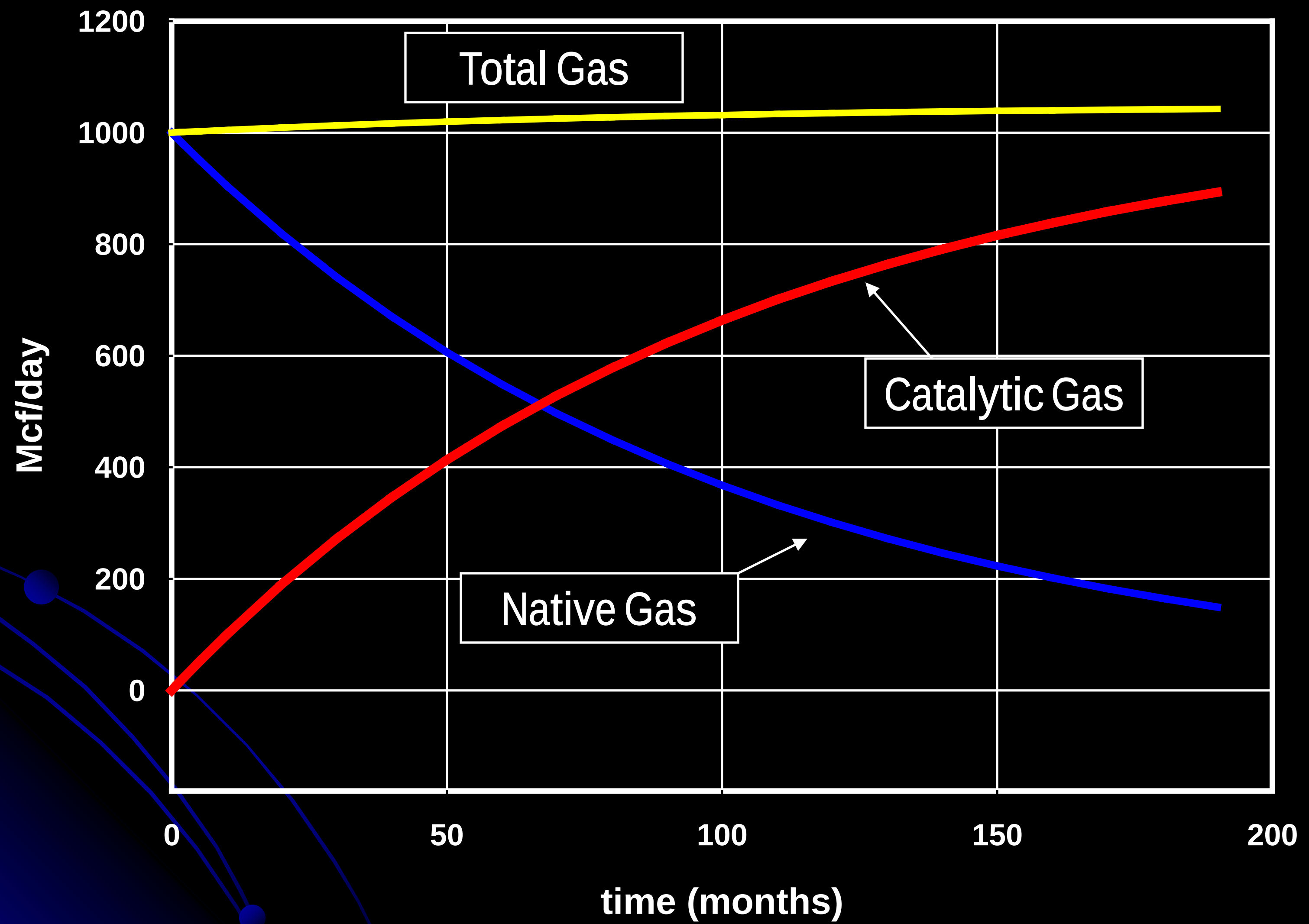
Exponential Decline Curve
Native Gas



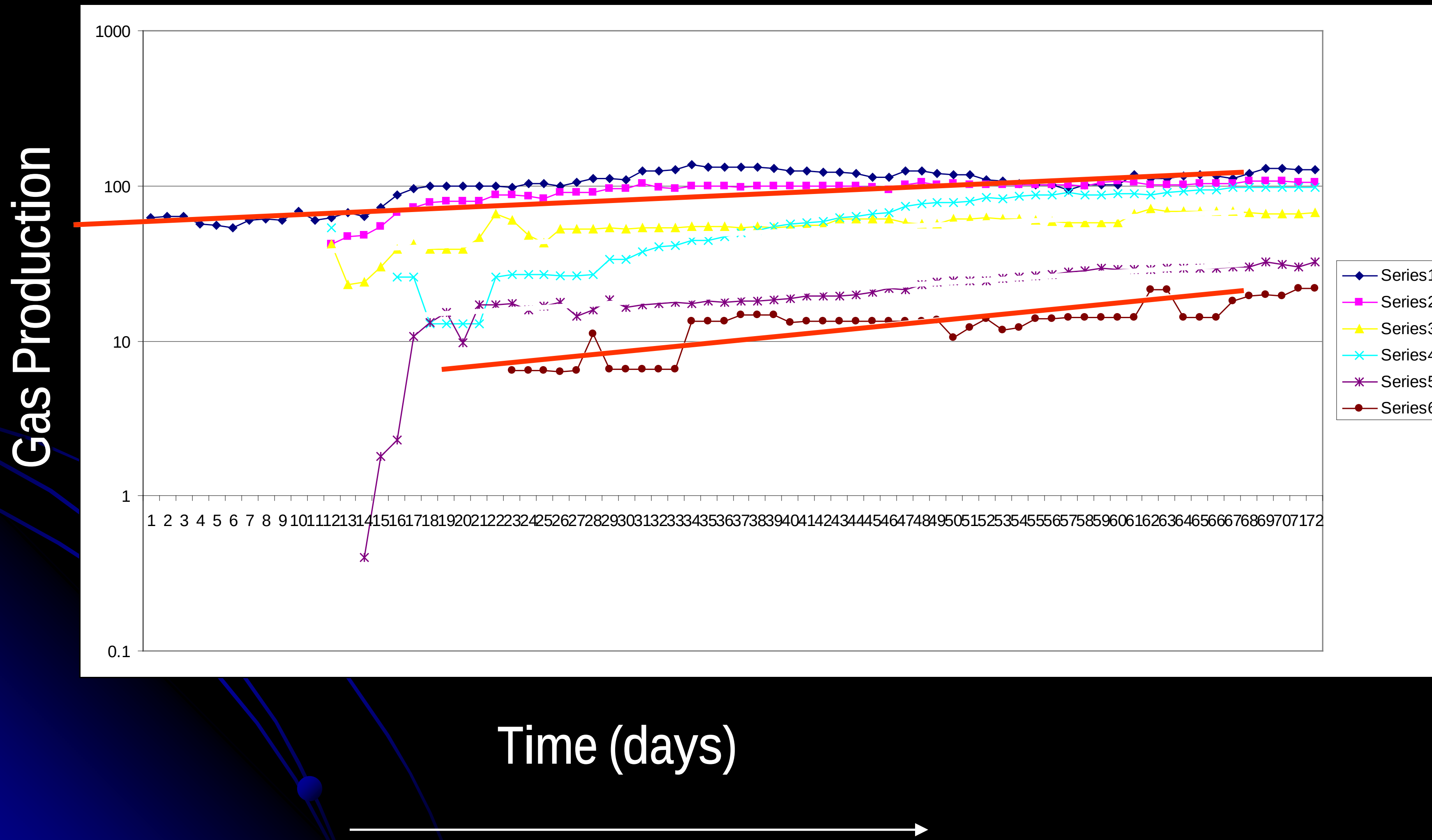
Moderate Activity Shales



High Activity Shales

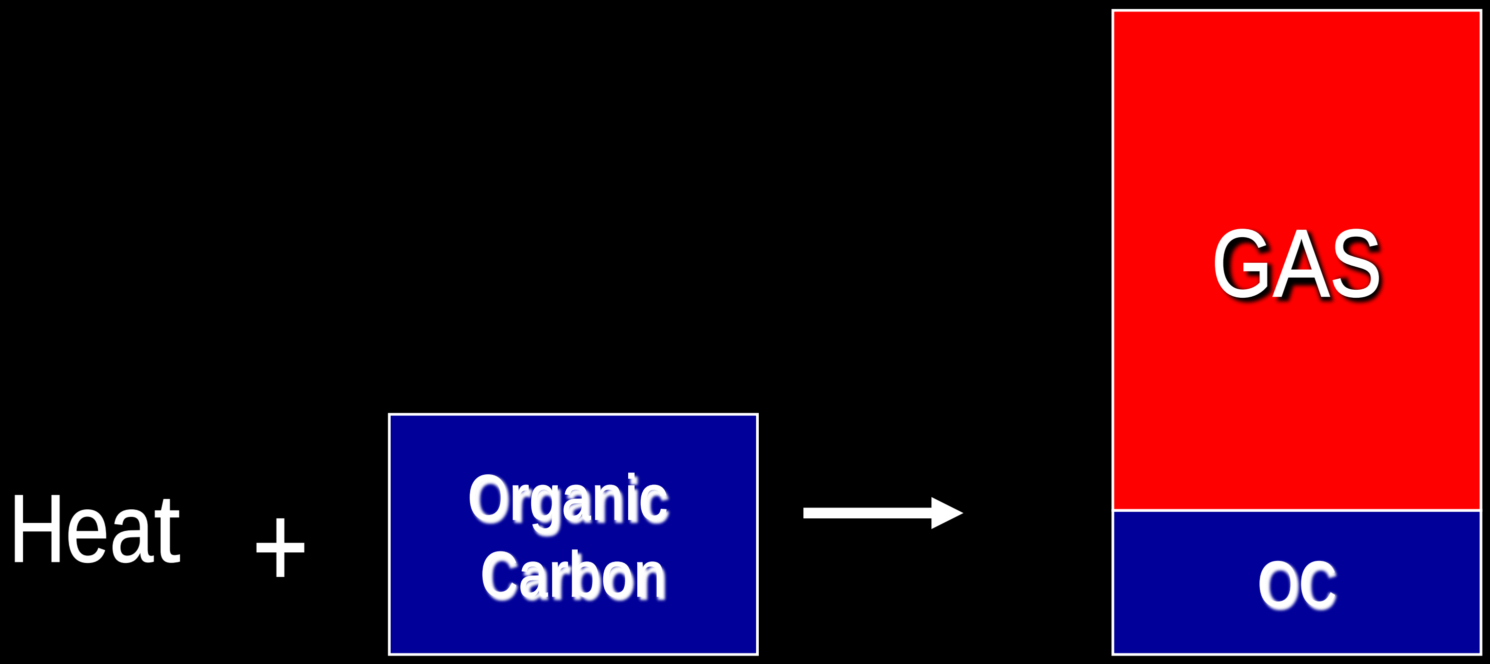


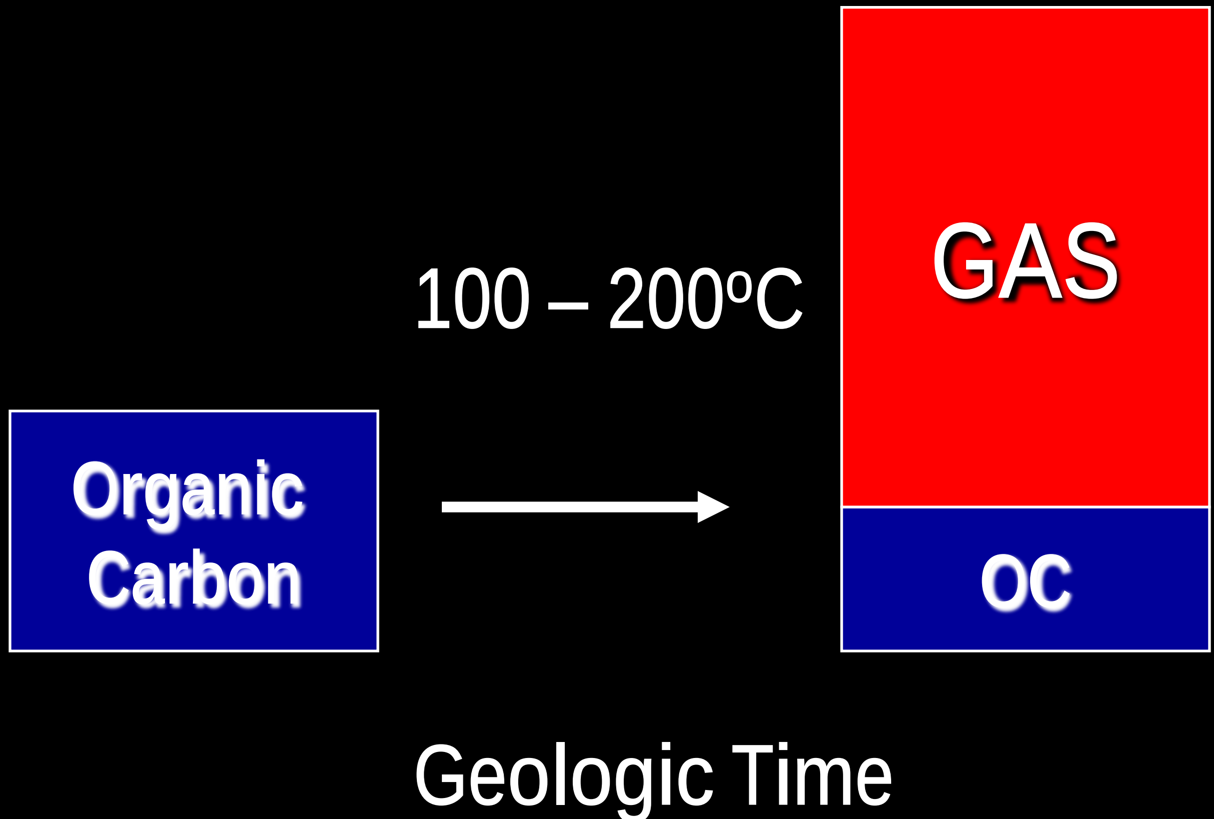
Six wells producing from high-activity Woodford shale

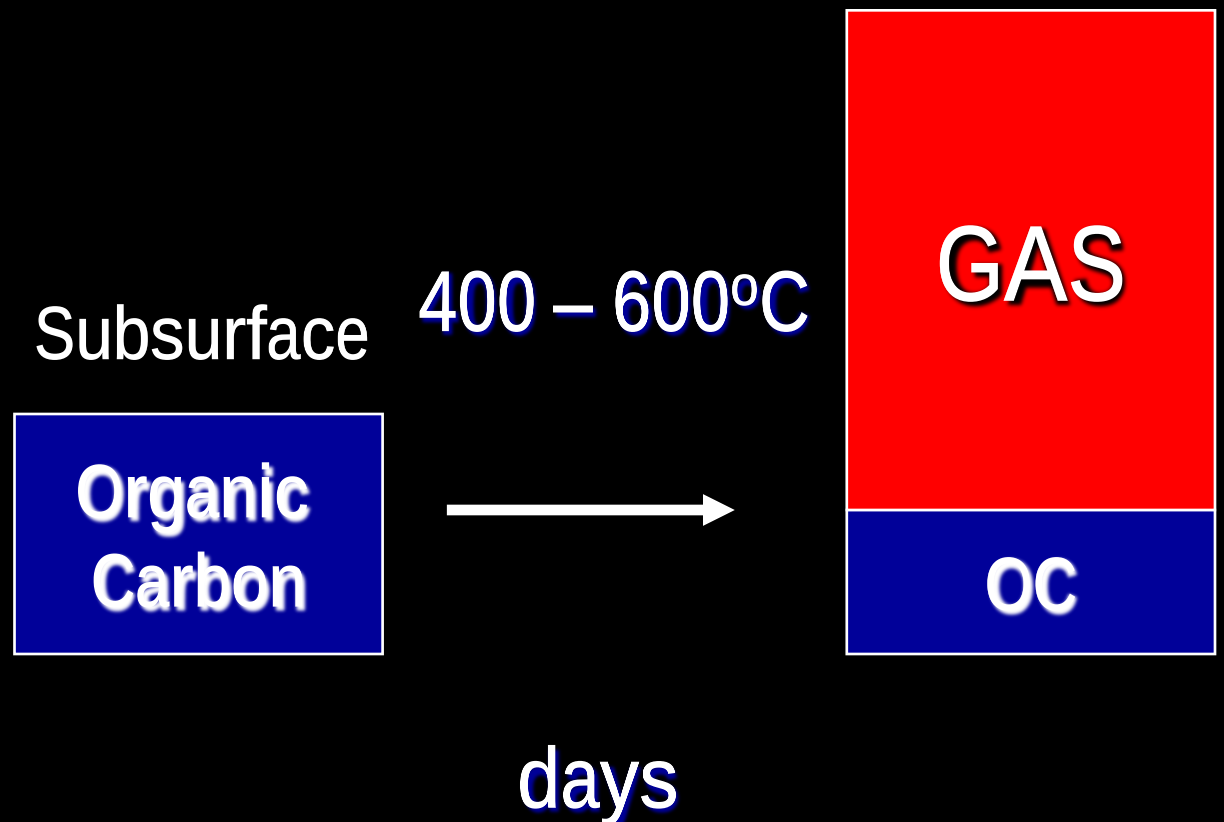


IMPLICATIONS

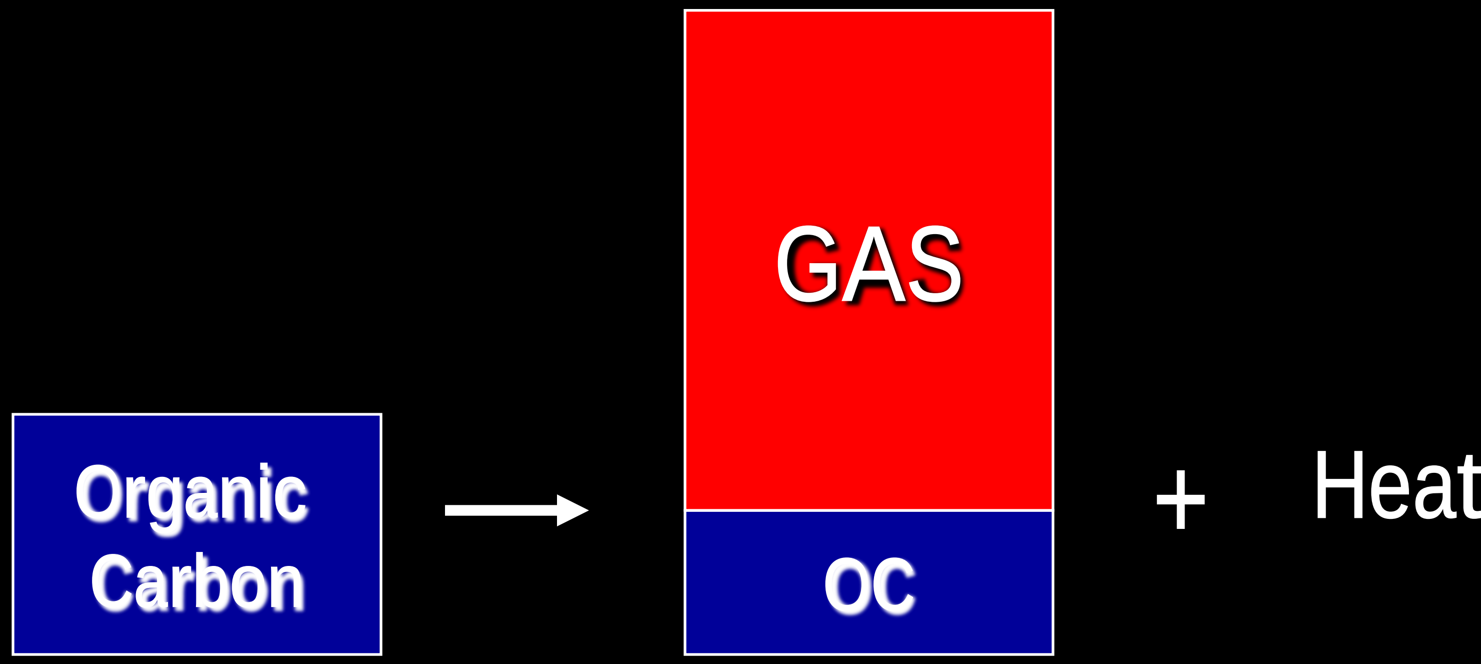
If Thermal Cracking is the source of natural gas

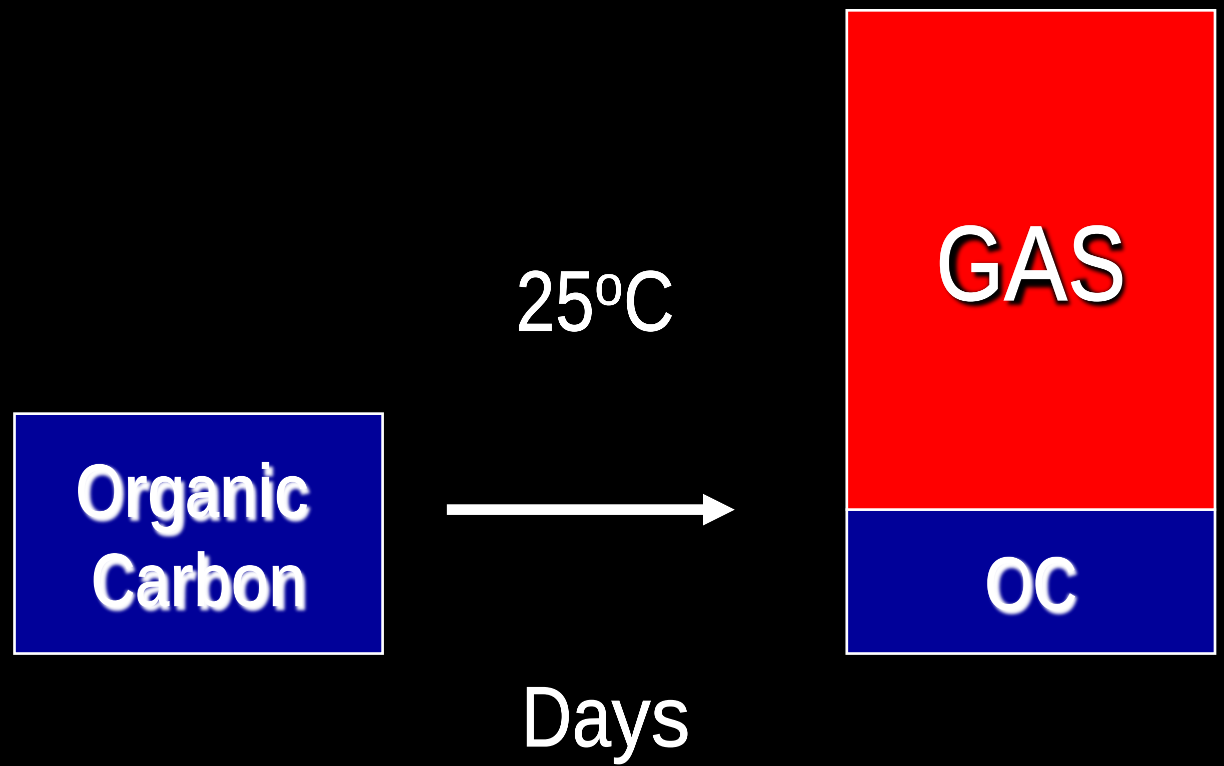

Heat
+
Organic Carbon
GAS
OC


Organic Carbon
100 – 200ºC
GAS
OC
Geologic Time

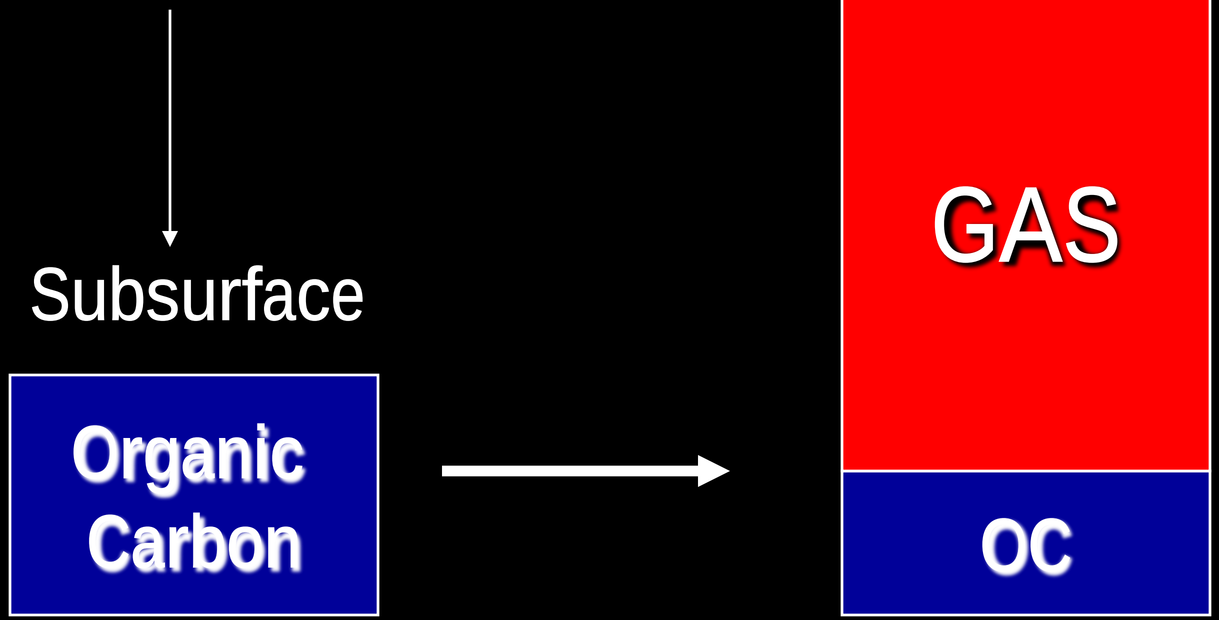

Subsurface
Organic Carbon
400 – 600°C
days
GAS
OC

If Catalytic Degradation is the source of natural gas


Organic Carbon
GAS
OC
+ Heat


25°C
GAS
Organic Carbon
OC
Days

Energy Resource



In Situ Conversion

Organic Carbon

25^{o}C

Days

GAS

OC

Shales

Coals

Tars

Residual Oil

The Source of Natural Gas

Thermal Cracking

- Recoverable hydrocarbon resources – require geologic time
- In situ conversion – requires extensive energy input

Catalytic Degradation

- Significant unrecognized resources exist – residual organic carbon
- In situ conversion – clean with no energy input

We thank Petroleum Habitats for permission to present this work

FDM thanks U.S. Department of Energy for Grants DE-FGO3-95ER14552 and DE-FGO5-92ER14295

Mango, Jarvie, and Garcia (2008). A new type of gas generated from marine shales at low temperatures. *Geochim. Cosmochim. Acta,* in review