Creation of Porosity in Tight Shales during Organic Matter Maturation*

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Abstract

It has been suggested that porosity and permeability are created in tight shales during the organic matter maturation process; i.e., kerogen conversion to oil and gas followed by oil cracking to gas. We have tested this hypothesis by examining changes in porosity, using FIB-SEM and following our experimental protocol, as given here:

- Started with oil-window maturity samples of Woodford and Bone Spring shales
- Heated them into wet and dry gas window
- Measured the extent of oil cracking
- Observed changes in porosity microscopically

Artificial maturation (laboratory pyrolysis) was carried out on these samples by heating them in pressure vessels under argon for a sequence of times and temperatures to induce oil generation and oil cracking. Porosity was recorded at various stages of maturation. These experiments were compared with results from a variety of naturally-matured shales of varying maturities. Kerogen maturity and hydrocarbon generation were determined by Rock-Eval pyrolysis. The extent of oil cracking to gas was measured by diamondoid analysis; i.e., quantitative measurements of nanometer-sized hydrogen-terminated diamonds dissolved in the generated liquids. Our results show that the process of organic matter maturation can produce porosity in tight shales, with the amount of porosity creation varying from sample to sample. Further, pressure due to oil cracking may cause natural fracturing and/or aid in hydrofracing.

Reference

Loucks, R.G., R.M. Reed, S.C. Ruppel, and U. Hammes, 2010 Preliminary classification of matrix pores in Mudrocks: Gulf Coast Association of Geological Societies (GCAGS) Transactions, v. 60, p. 435-441.

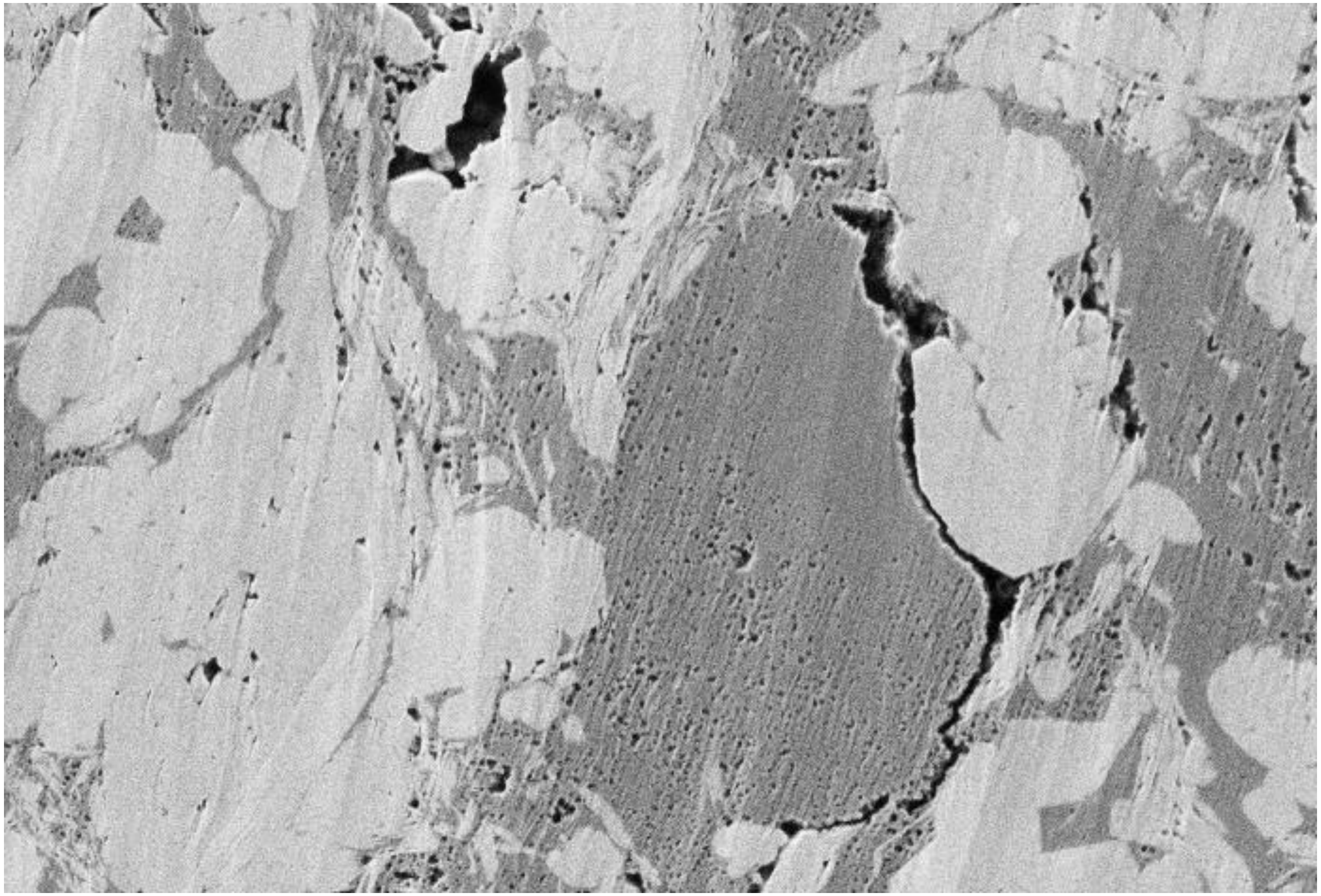
Creation of Porosity in Tight Shales during Organic Matter Maturation

By
Jeremy Dahl, J.M. Moldowan, Joel Walls, Amos Nur, Juliana DeVito

Stanford University, Ingrain Technologies

Porosity creation and destruction during maturation of organic matter

1. Kerogen conversion to gas and liquids and migration of those hydrocarbons out of pore space



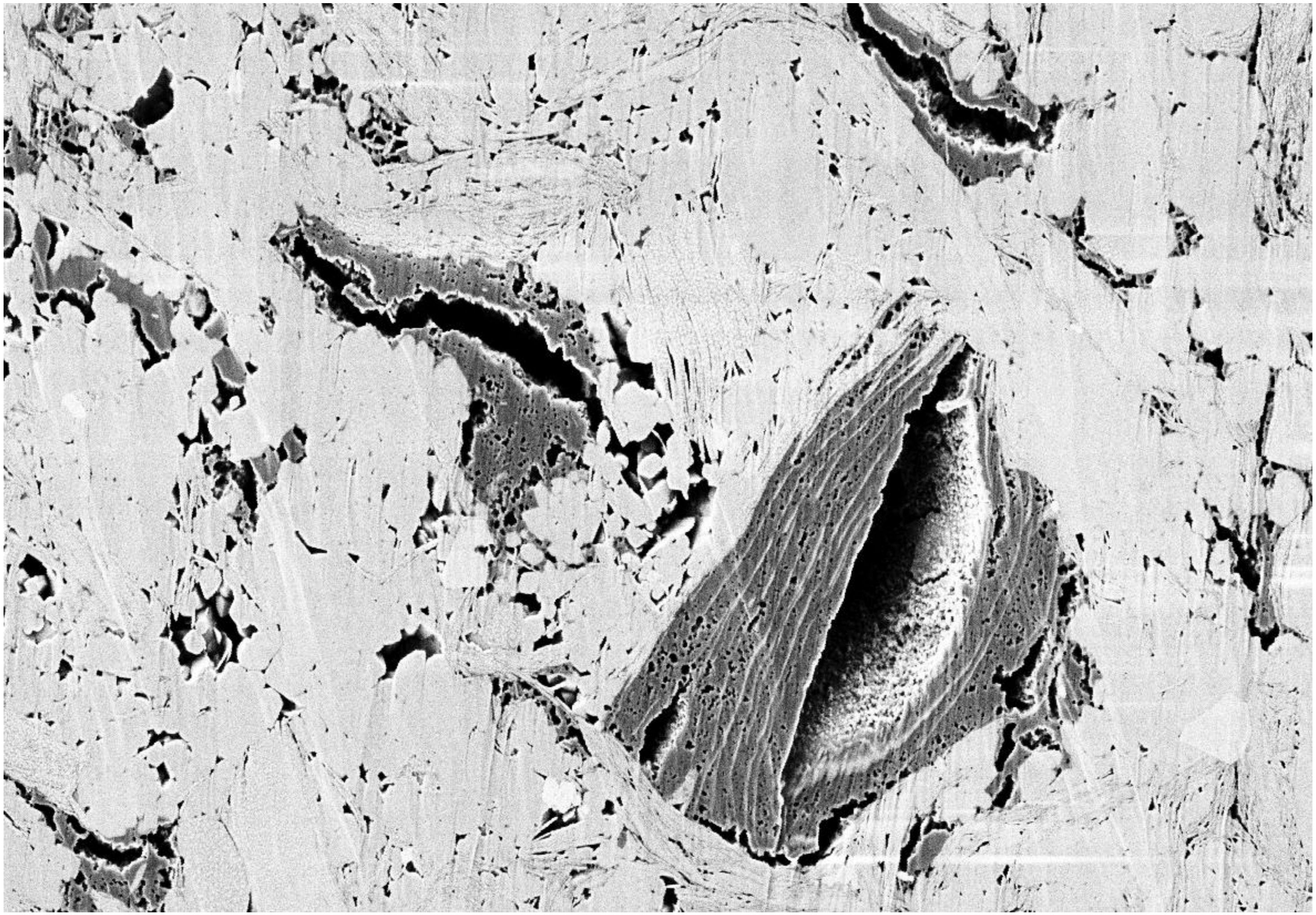
Porosity creation and destruction during maturation or organic matter

2. Oil conversion (cracking) to gas causing fracturing.

Porosity creation and destruction during maturation or organic matter

3. Formation of pyrobitumen (porosity destruction)

Conclusion: Porosity is created and destroyed during maturation but process shows wide variation from sample to sample.

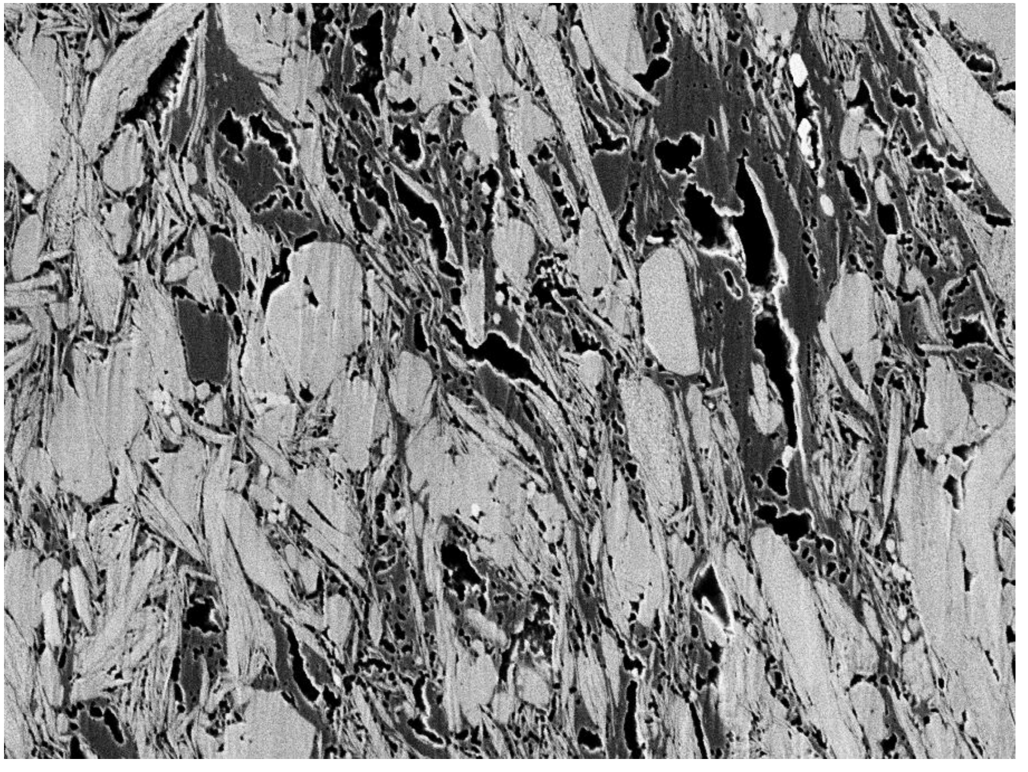


Considerations: Natural Samples

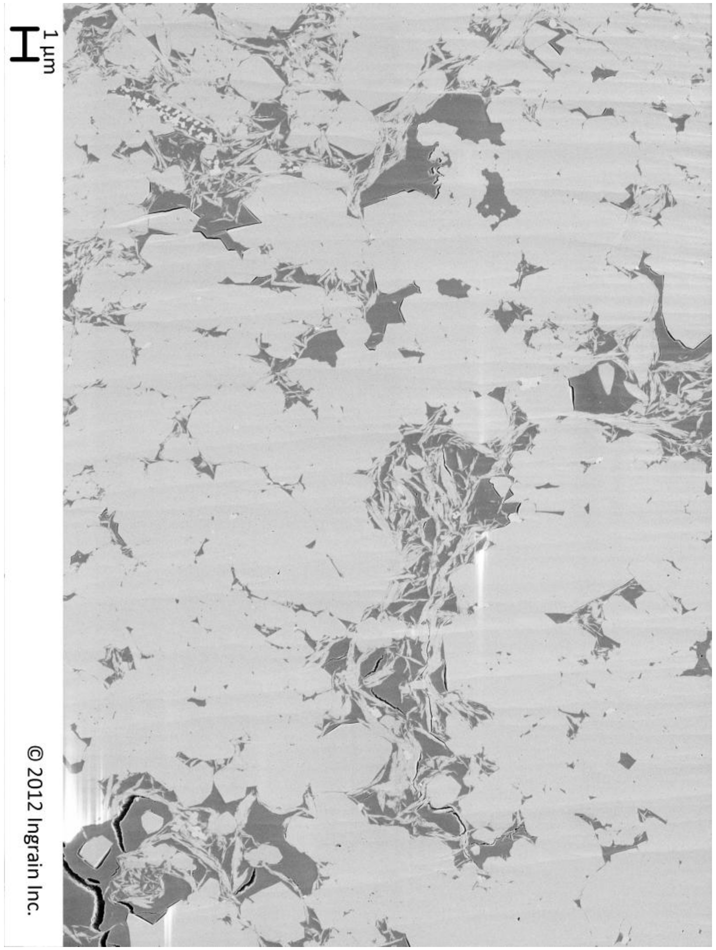
- With natural samples you don’t know if porosity creation is related to heating or facies (could be comparing apples and oranges).
- Therefore we did heating experiments to see if we see same trends and features that you do in natural situations.

Experimental Protocol

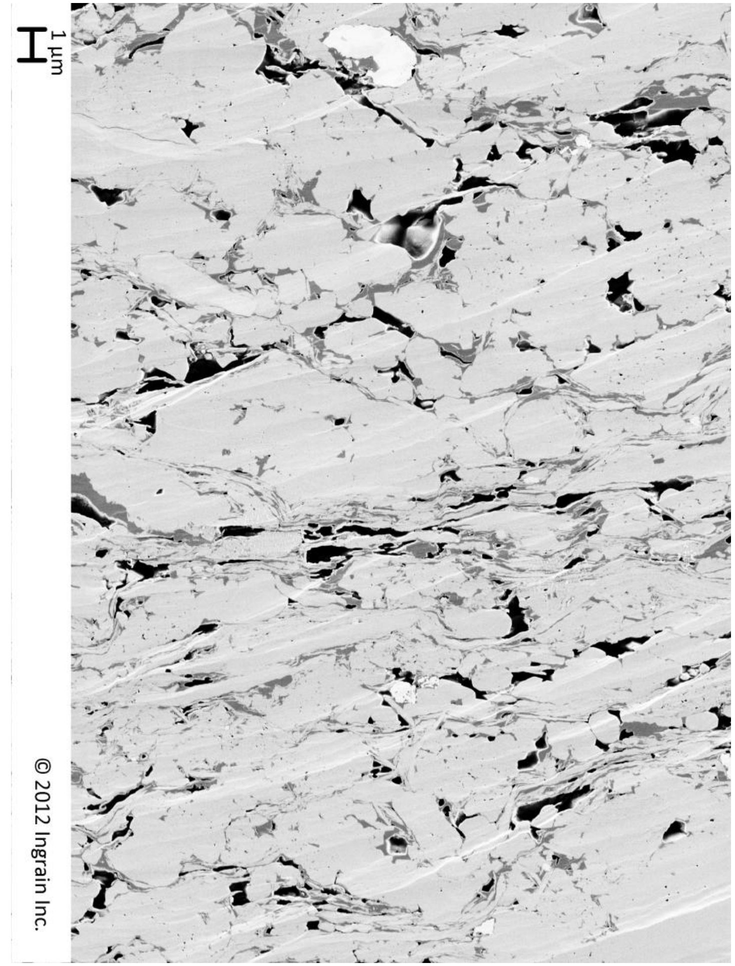
- Started with oil-window maturity samples
- Heated them into wet and dry gas window
- Measured the extent of oil cracking
- Observed changes in porosity microscopically



Samples



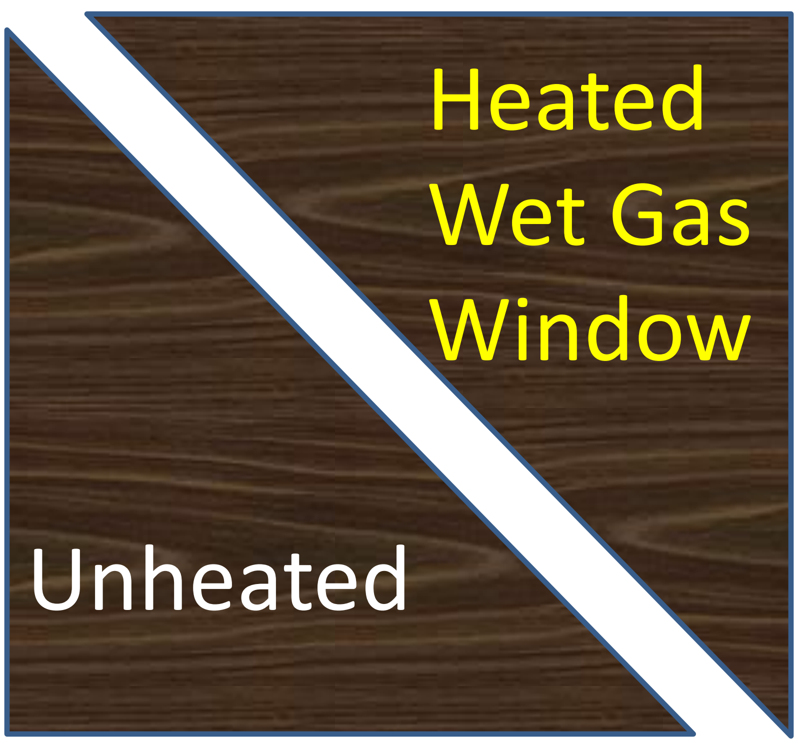
Woodford Shale
Ro = 0.9



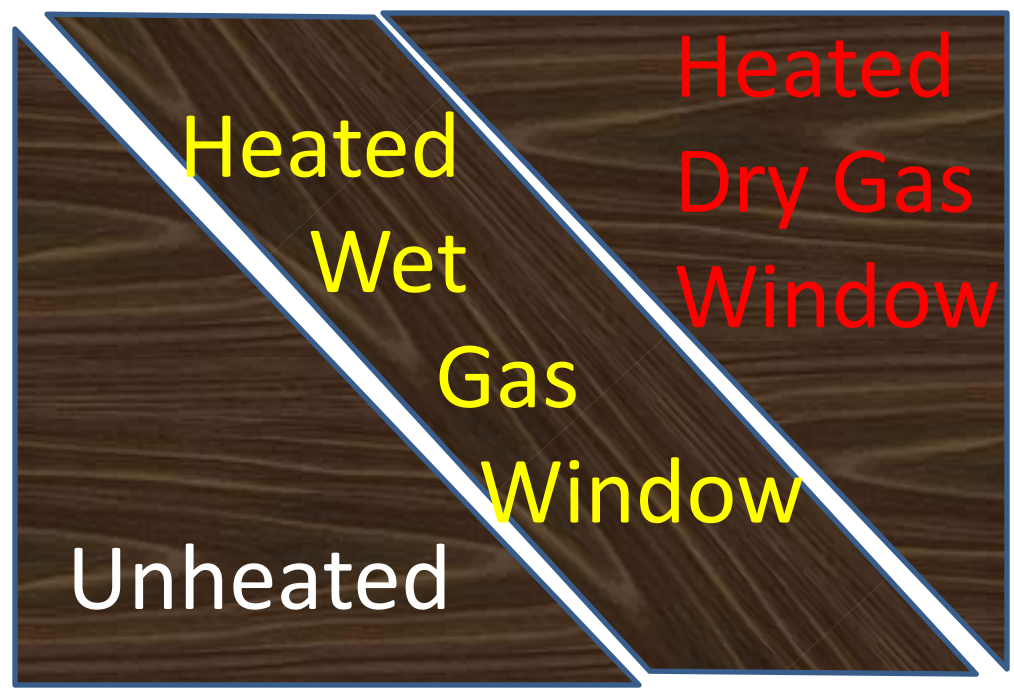
Bone Spring
Ro = 1.06

Heated samples in sealed pressure vessels
(no confining pressure)

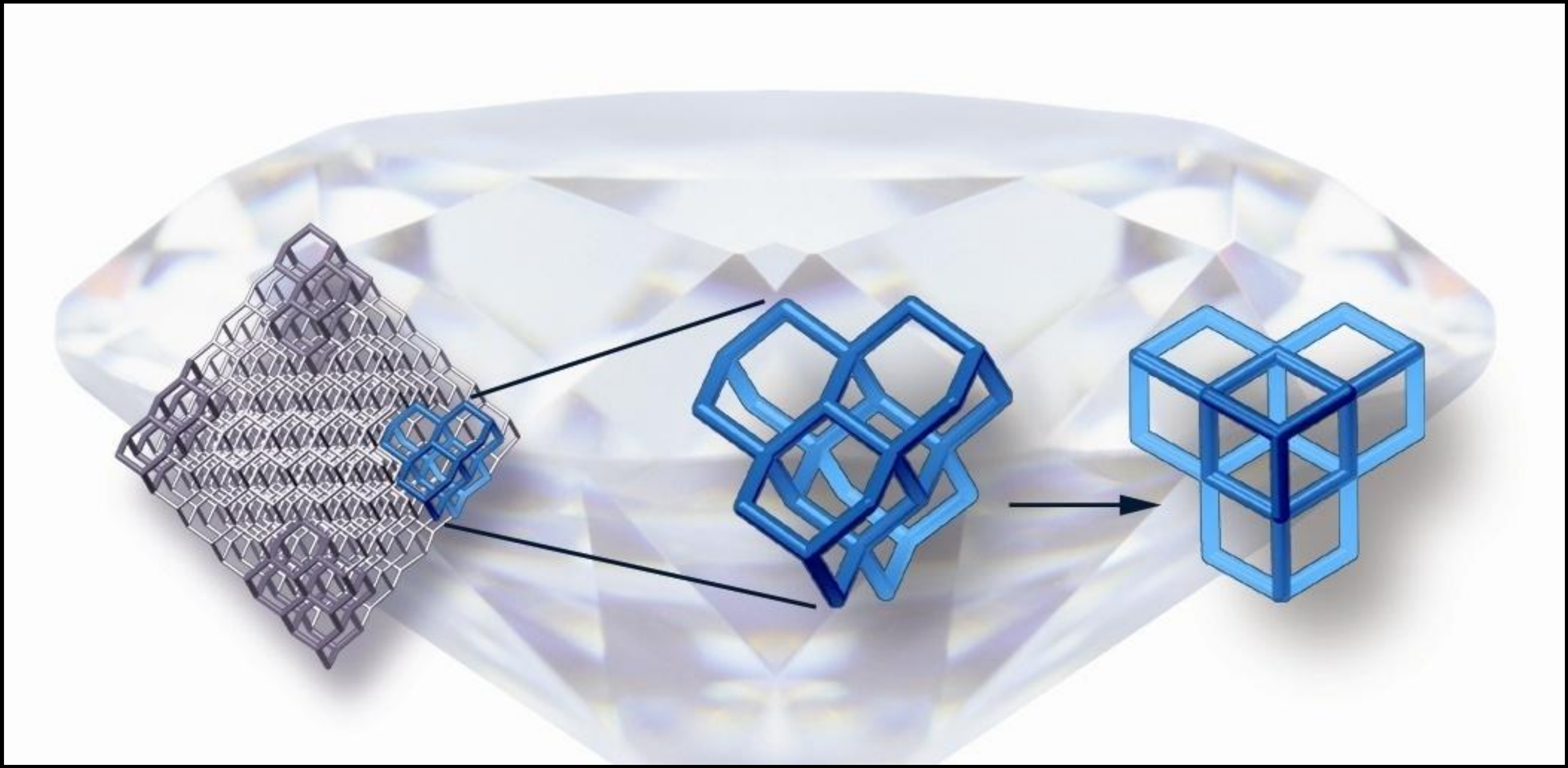
Woodford



Bone Spring

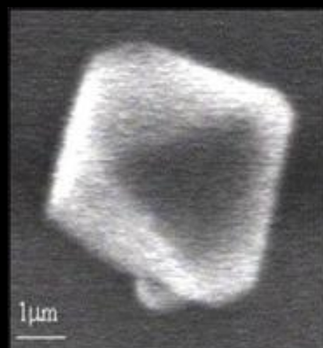


Measure Maturity (Oil Cracking) Using Diamondoids



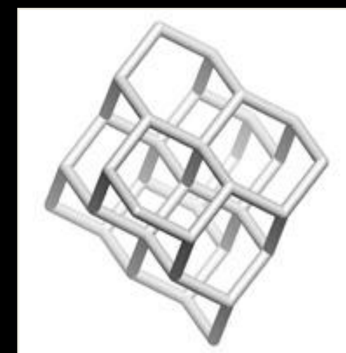
What are diamondoids?

Diamond



***Micro-
cyrstalline***

CVD

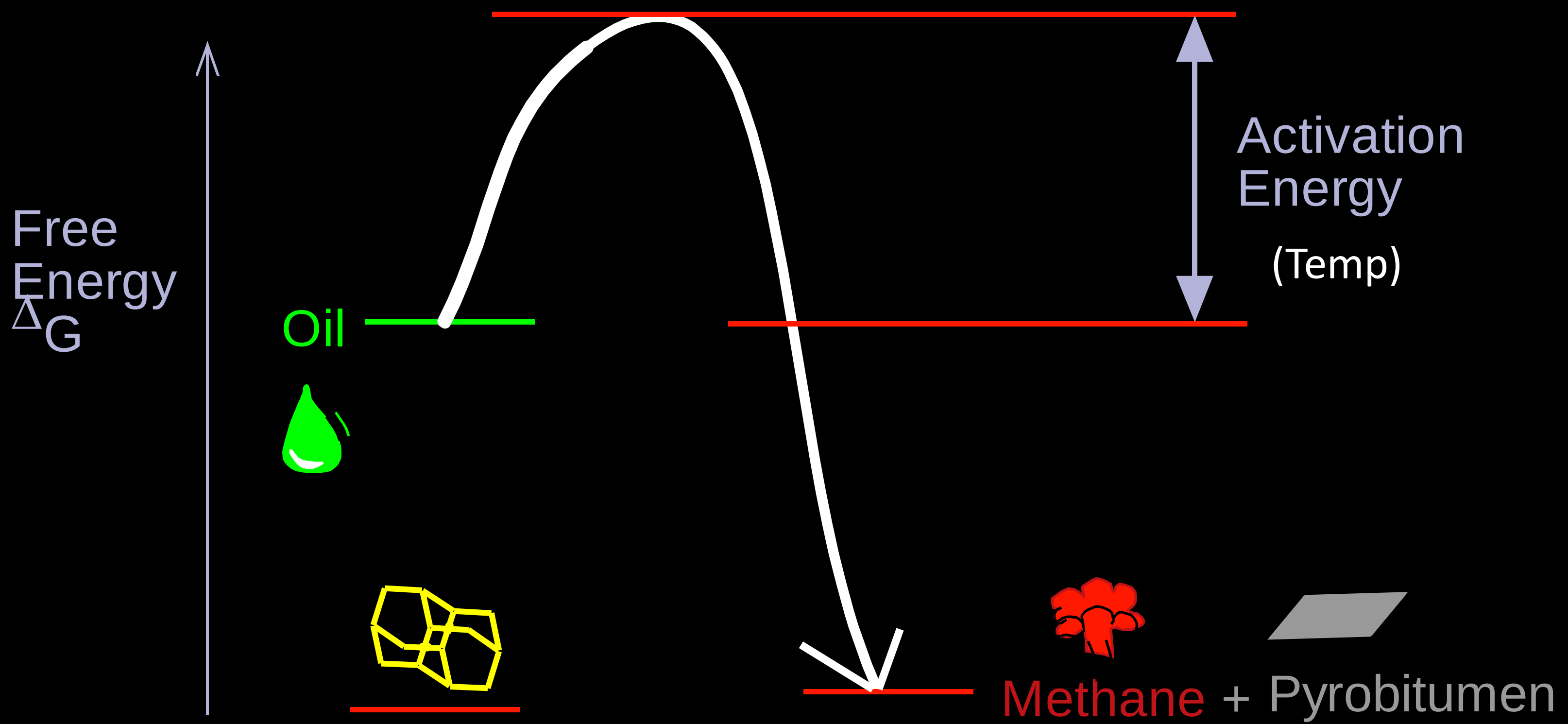


***Higher
Diamondoid
0.5-2nm***

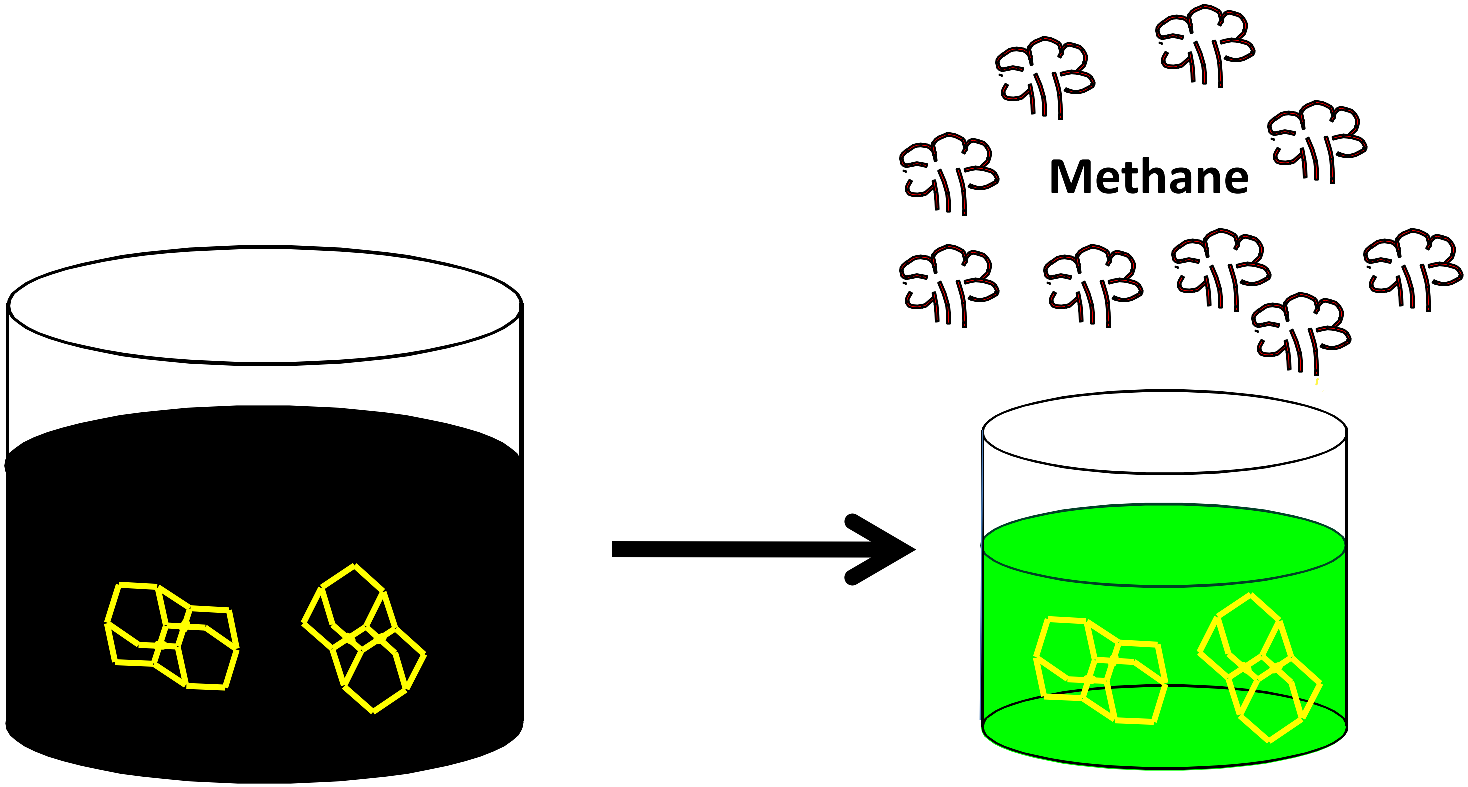
Adamantane

They are nanometer-size, hydrogen-terminated diamonds

What happens to diamondoids when we crack an oil?



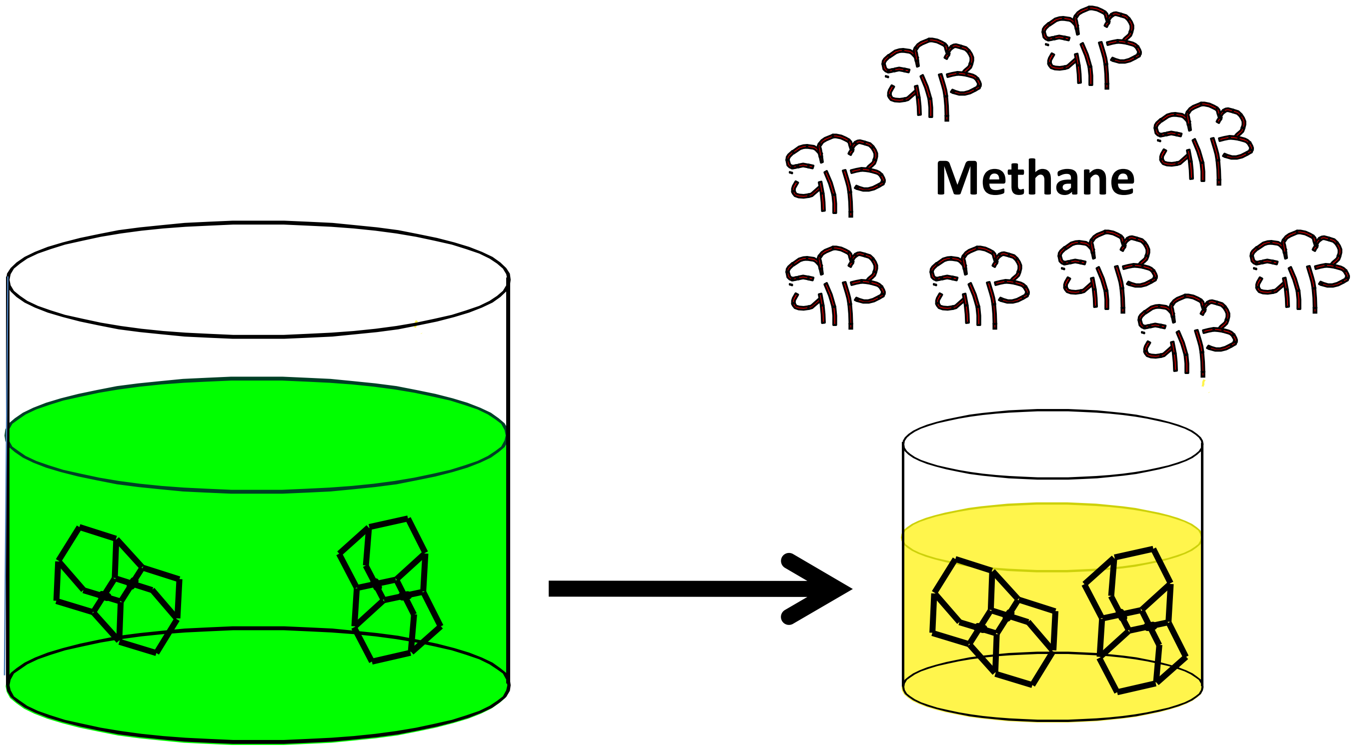
50% Oil Cracking Doubles the Diamondoid Concentration



1 ml
5 ppm

0.5 ml
10ppm

Crack Another 50% of the Oil and the Diamondoid Concentration Doubles Again

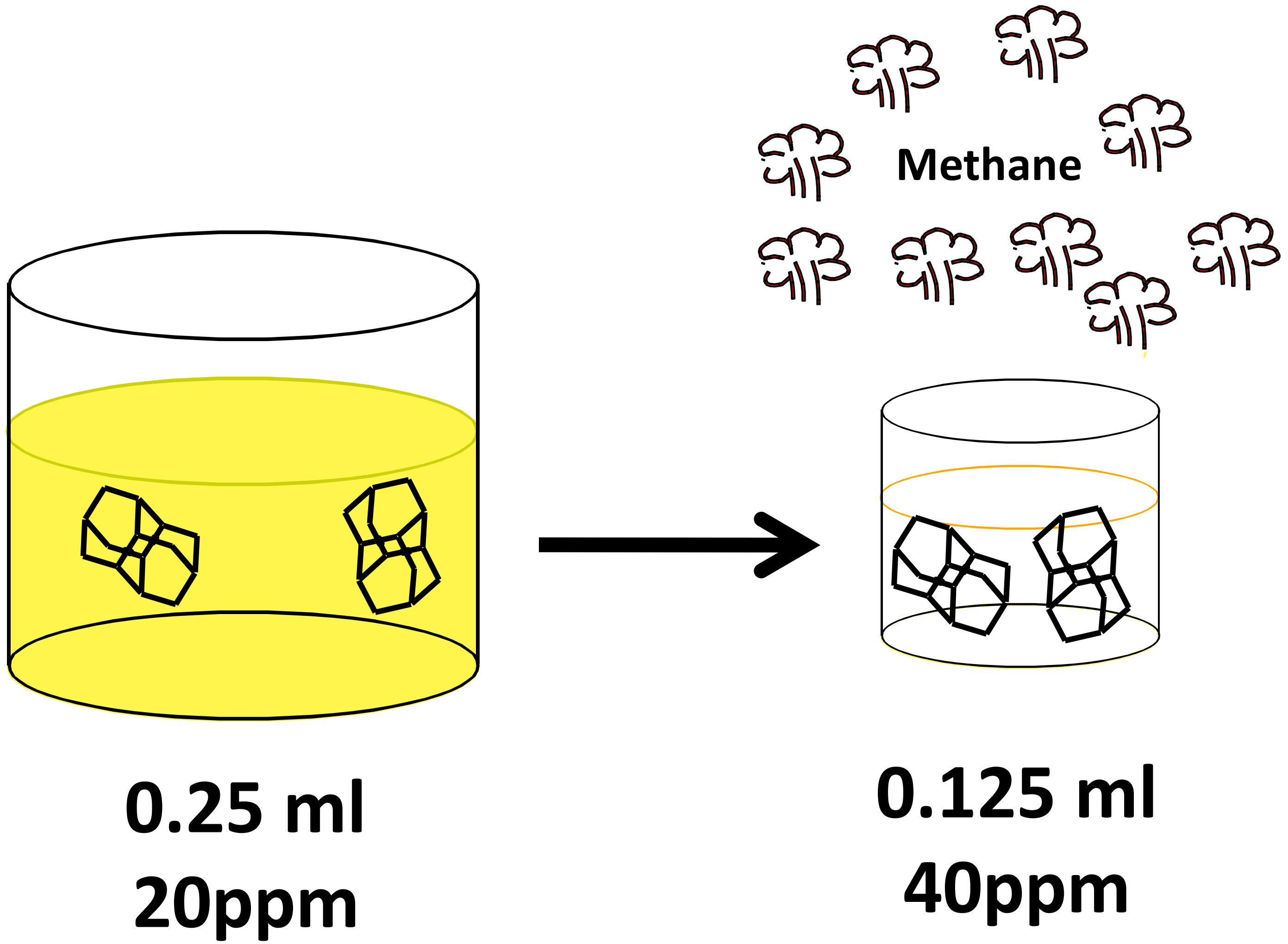


0.5 ml
10ppm

0.25 ml
20ppm

And So On According to the equation:

% Cracking = [1- (Co/Cc)] X 100



Results of Heating Experiments

Sample	Ro	Diam Conc. ppm	% Cracking
Woodford Unheated	0.9	2.6	0
Woodford Heated		3.8	32%
Bone Spring Unheated	1.06	3.9	0
Bone Spring Wet Gas Window		11.6	66%
Bone Spring Dry Gas Window		69.5	95%

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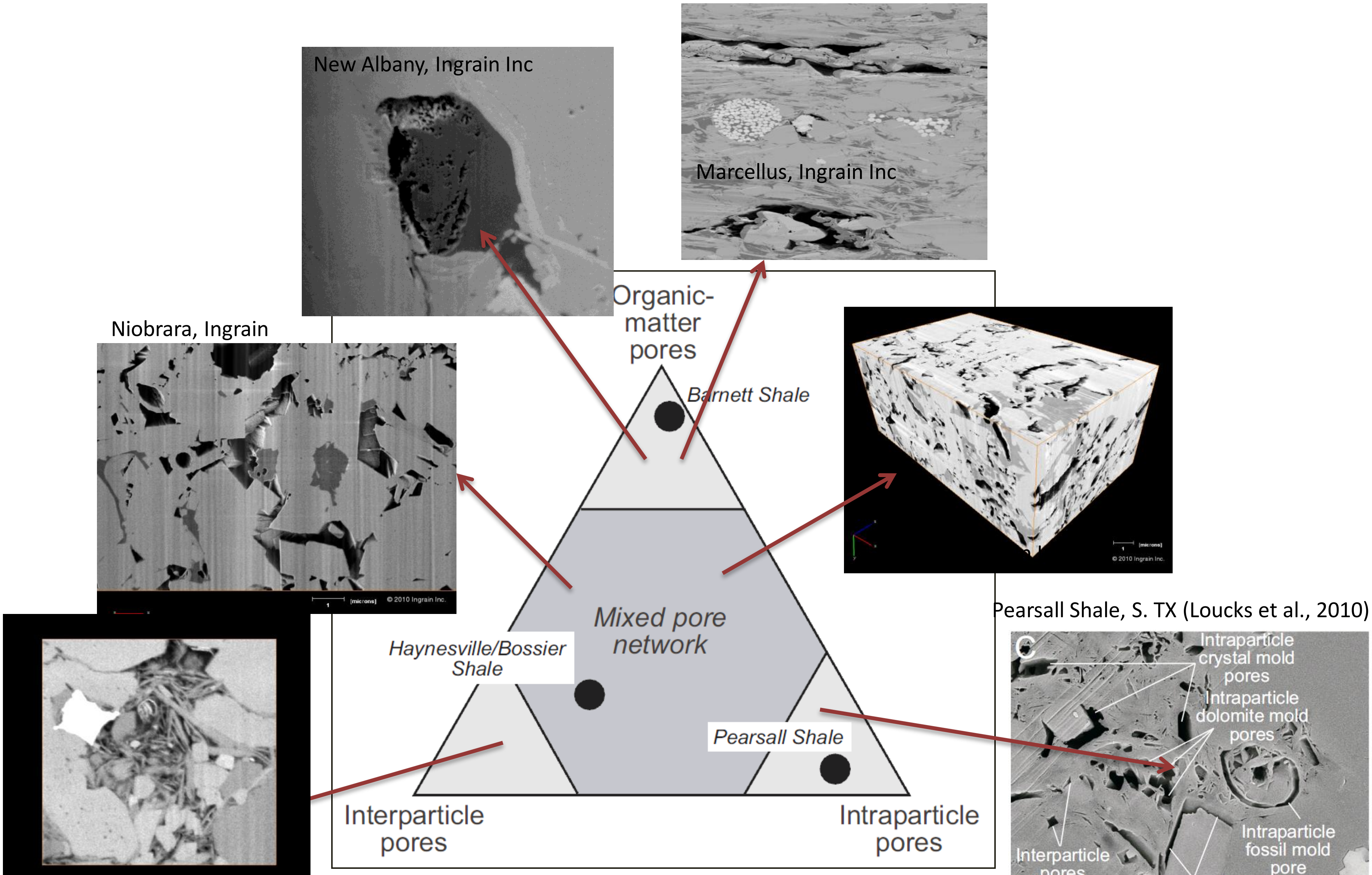
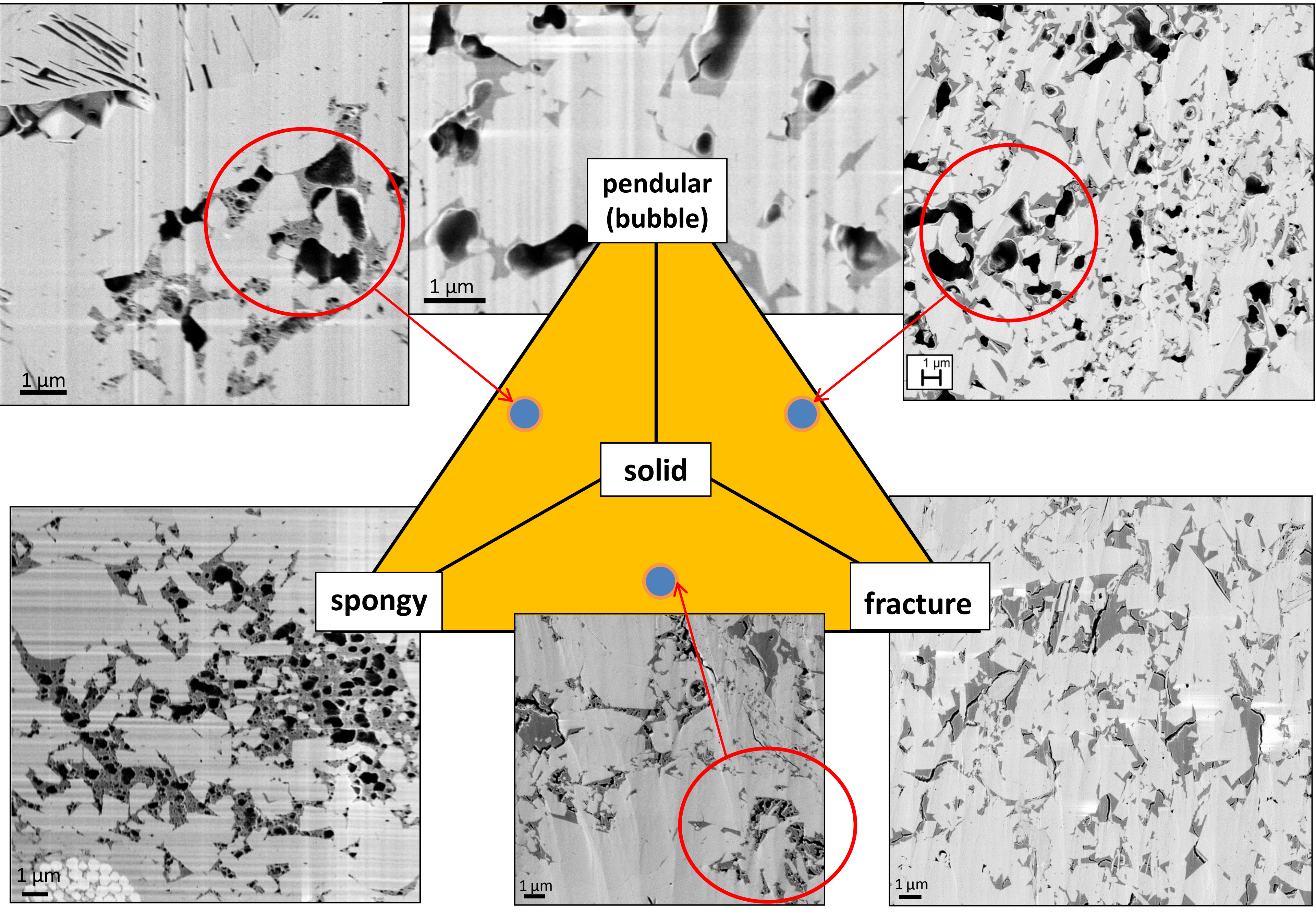
Tight Shale Porosity



Haynesville, E.TX, Ingrain

From Loucks, et al, GCAGS, April 2010

Three Classes of Organic Matter Texture



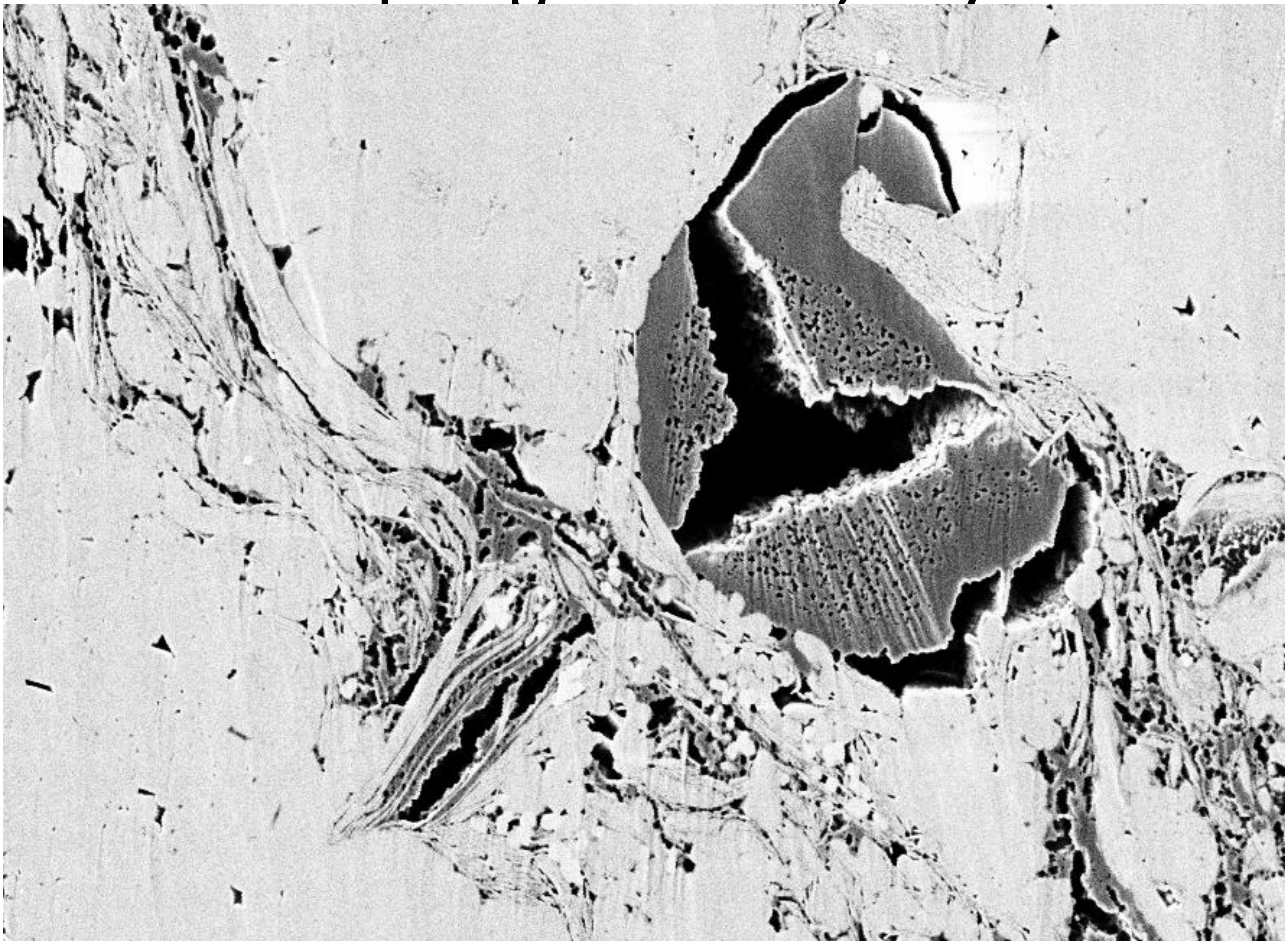
Porosity and Organic Matter

Interpretation of SEM image:

- White: High density material (e.g., iron rich)
- Shades of Gray: Minerals with densities of 2-3 g/cc
- Dark Gray: Organic Matter
- Black: Pore space

•Phi_OM: The percentage of space within the organic matter bodies that is classified as porosity

Bone Spring- Heated, Dry Gas



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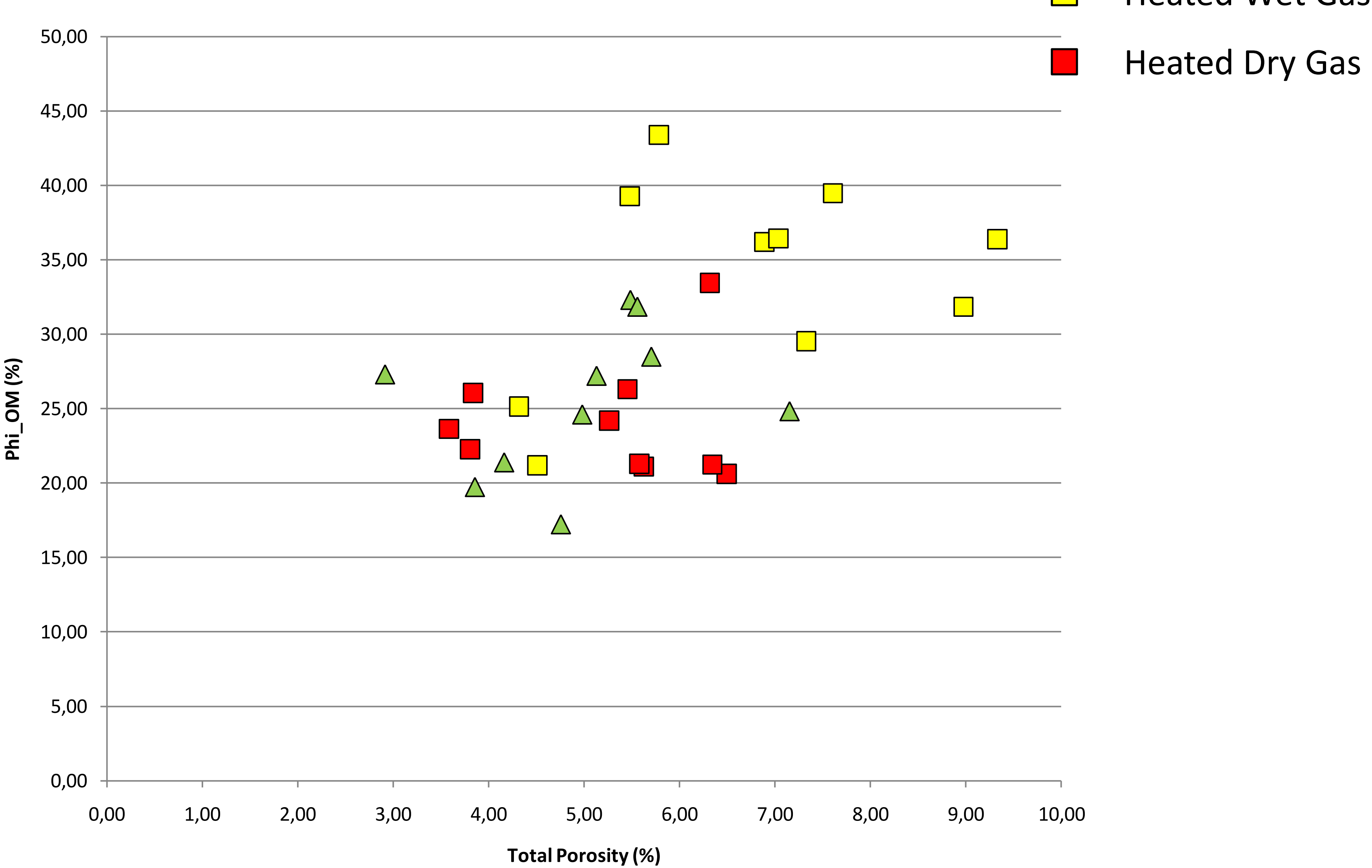
Heated Wet Gas Window

Phi_OM- Bone Spring



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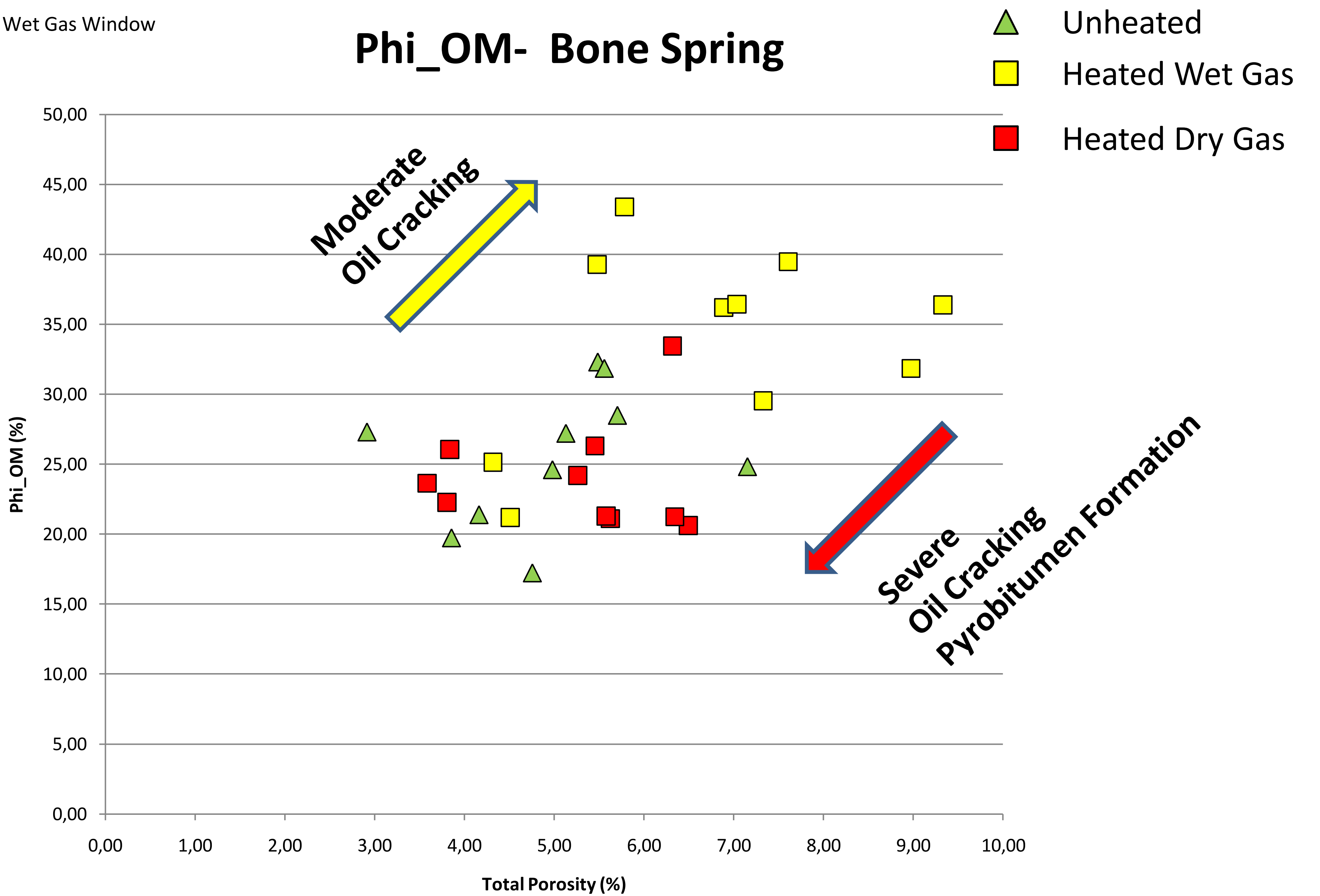
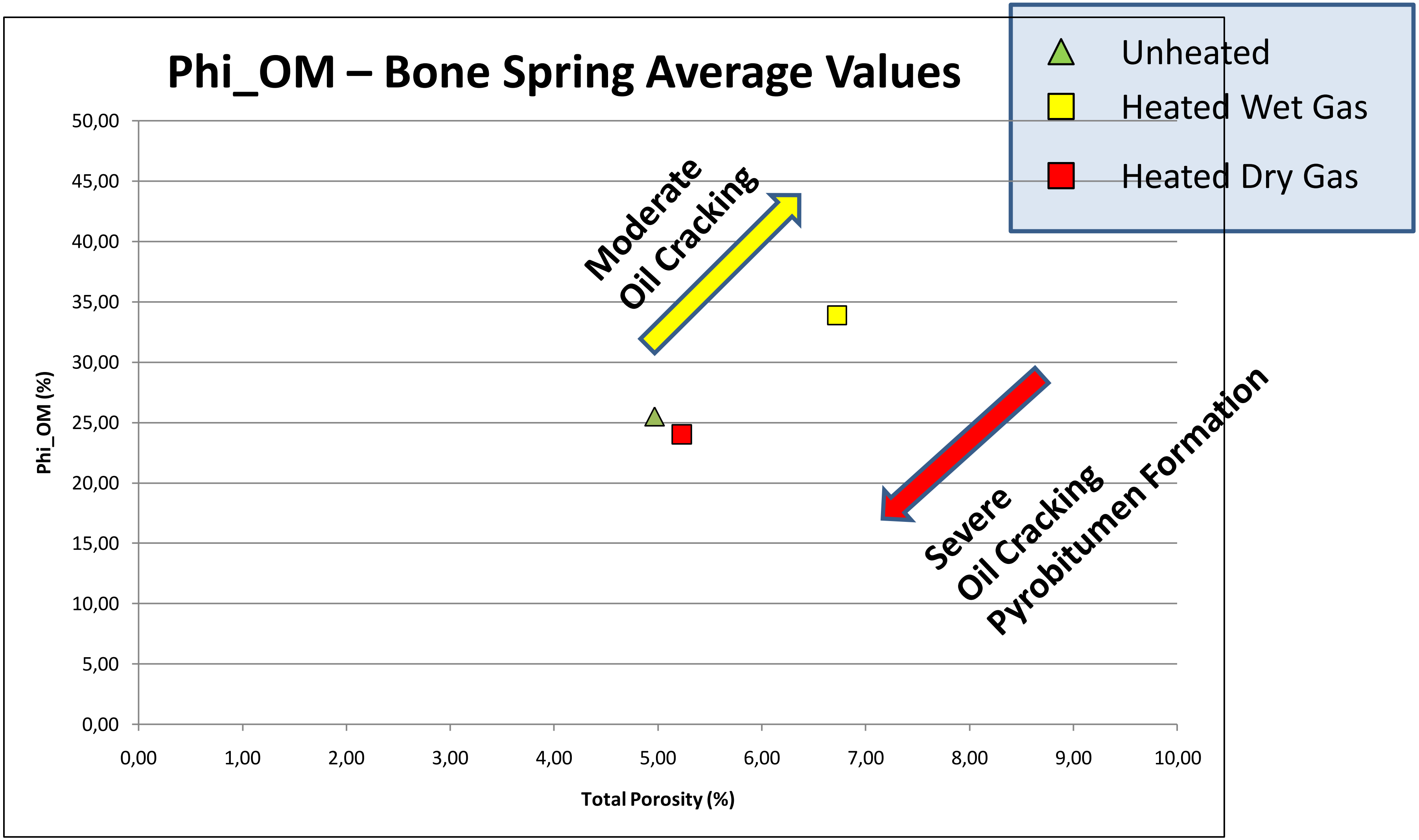
Heated Wet Gas Window




Phi_OM – Bone Spring Average Values
Unheated
Heated Wet Gas
Heated Dry Gas
50,00
45,00
40,00
35,00
30,00
25,00
20,00
15,00
10,00
5,00
0,00
Phi_OM (%)
0,00
1,00
2,00
3,00
4,00
5,00
6,00
7,00
8,00
9,00
10,00
Total Porosity (%)
Moderate
Oil Cracking
Severe
Oil Cracking
Pyrobitumen Formation

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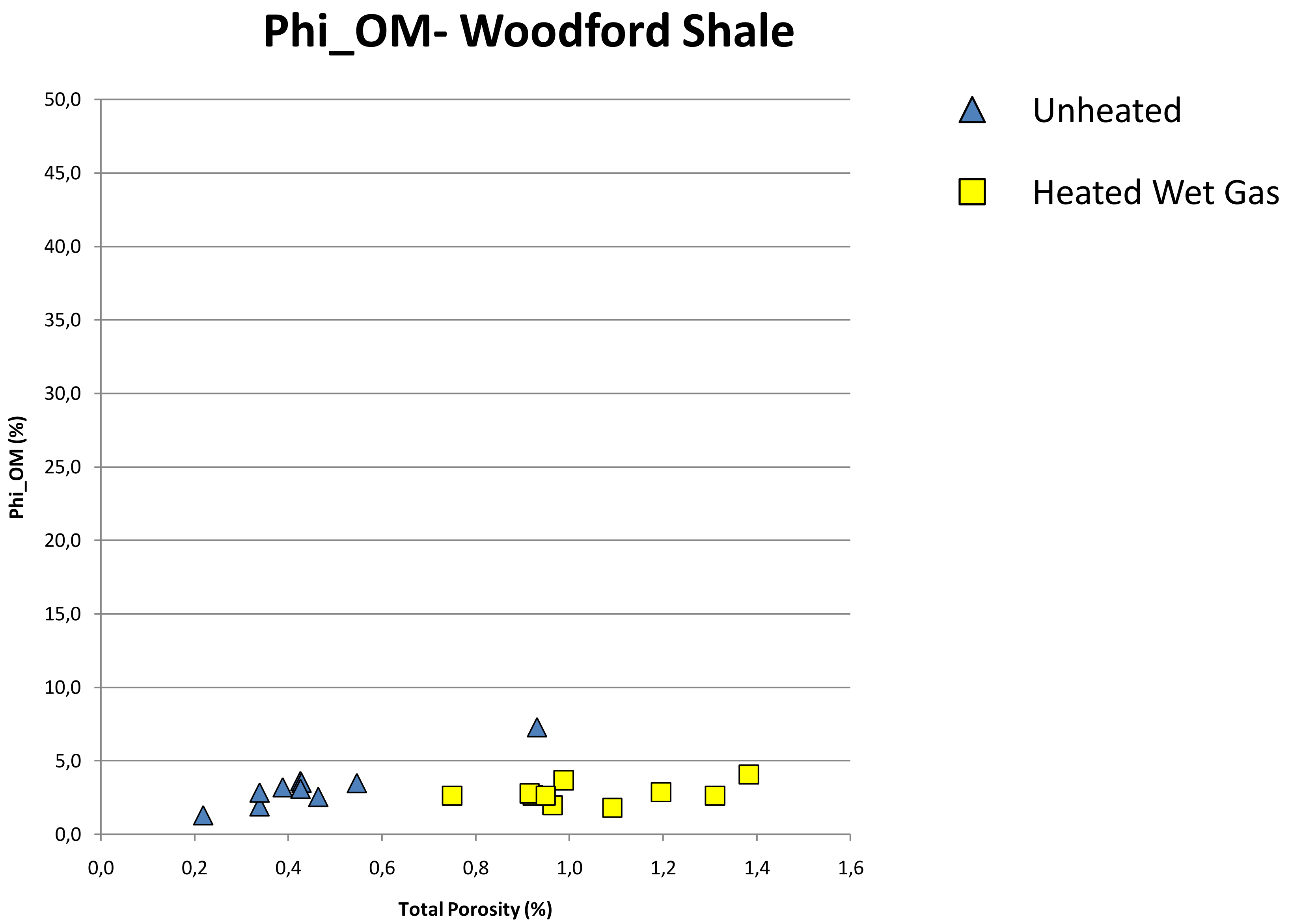
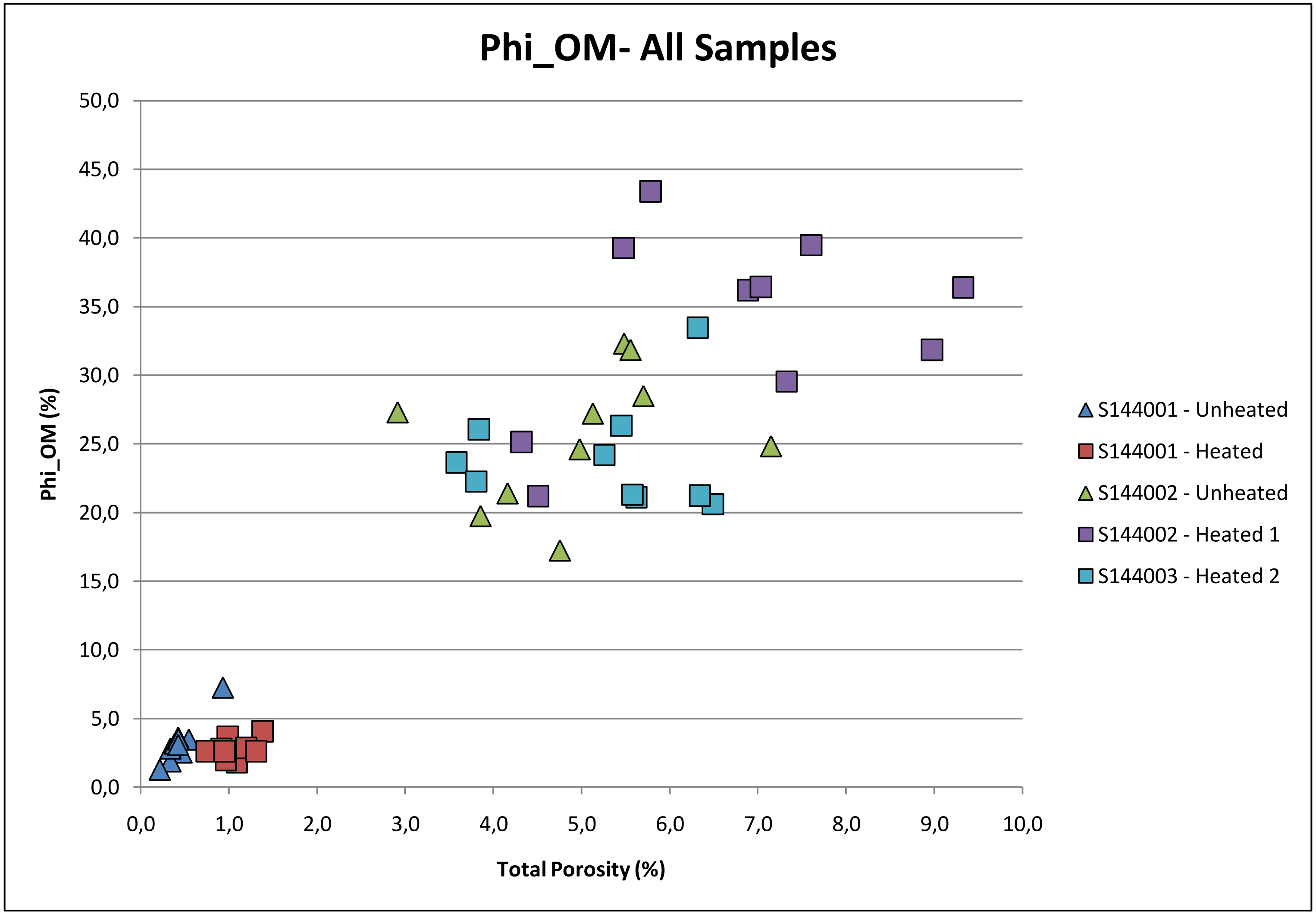
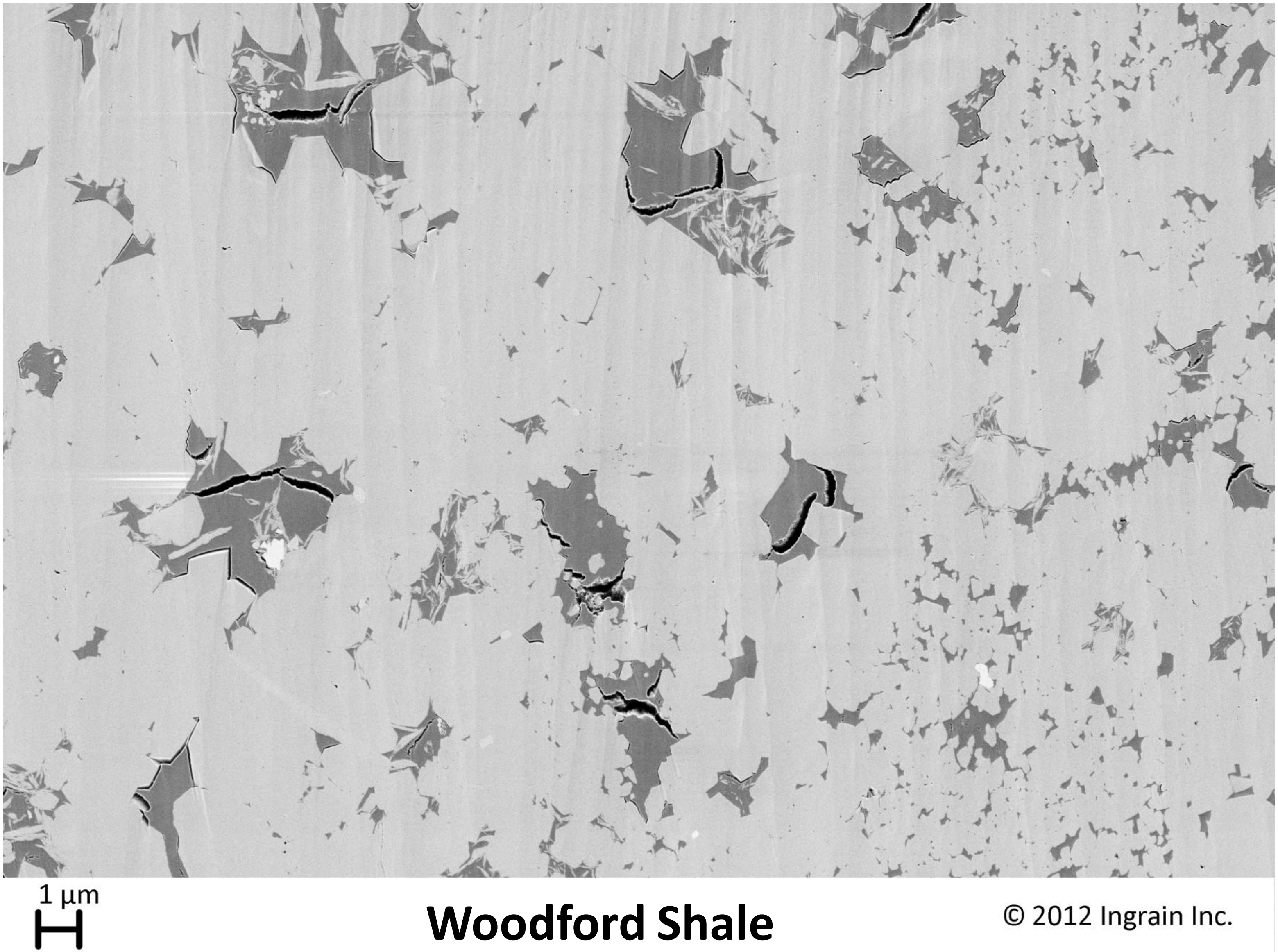
Woodford displays different behavior





Phi_OM- All Samples
50,0
45,0
40,0
35,0
30,0
25,0
20,0
15,0
10,0
5,0
0,0
0,0
1,0
2,0
3,0
4,0
5,0
6,0
7,0
8,0
9,0
10,0
Phi_OM (%)
Total Porosity (%)
S144001 - Unheated
S144001 - Heated
S144002 - Unheated
S144002 - Heated 1
S144003 - Heated 2

What if kerogen converts to liquids and liquids to gas and there is no escape route?



Woodford Shale

Fracturing?

Gasoline Explosions

We can Estimate Maximum Pore Pressure Generated by Oil Cracking

1. Estimate the volume of pore space occupied by organic matter (TOC, microscopically, etc.)
2. Determine kerogen type to estimate H/C ratio
3. Determine the amount of cracking using diamondoid methodology
4. Calculate pressure using ideal gas law (correct for non-ideality of methane):

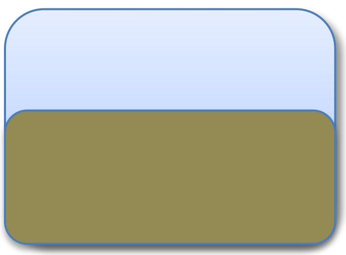
$$P=nRT/V$$

Calculating Pressures due to Oil Cracking

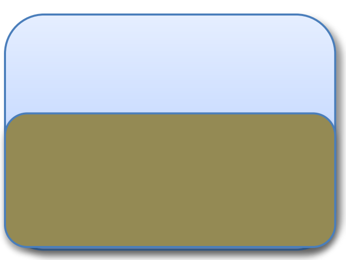
Example

Let’s say that the pore space is 75% full of organic matter

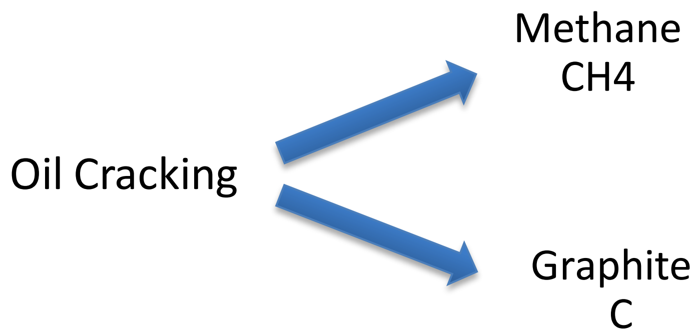
We have Type II organic matter (e.g., Barnett); so
the specific gravity should be about 1.5 g/ml



So there is .75 ml X 1.5 g/ml or
1.12 grams of organic matter in the pore



We also need to estimate original
Organic matter H/C ratio.
For Type I kerogen H/C >1.25
For Type II kerogen H/C <1.25 Let’s use 1.20



Hydrogen goes to methane production. The amount of Hydrogen plus the extent of cracking is used to calculate total amount of methane produced.

Then we can calculate the wt% H of organic matter with formula $C_1H_{1.20}$ (the C/H ratio is 1.20)
Carbon 12 (mol wt) X 1 is 12
Hydrogen 1 (mol wt) X 1.2 is 1.2 Total weight = 13.2
So weight percent hydrogen = 1.2/13.2 = 0.091 X100 = **9.1% H**

In our example we have 1.12 g of organic matter of which 9.1 wt% is Hydrogen
So we have 1.12 X .091 = **.10 grams of hydrogen**

To calculate pressure produced by cracking oil to methane
we will use the ideal gas equation

We have 0.1 g of hydrogen which is equal to 0.1 mols of Hydrogen.
To make 1 mol of CH_4 we need 4 mols of hydrogen. So in our example we can make 0.1/4 or **.025 mols of methane.**

PV = nRT or **P = nRT/V**

$$P = nRT/V$$

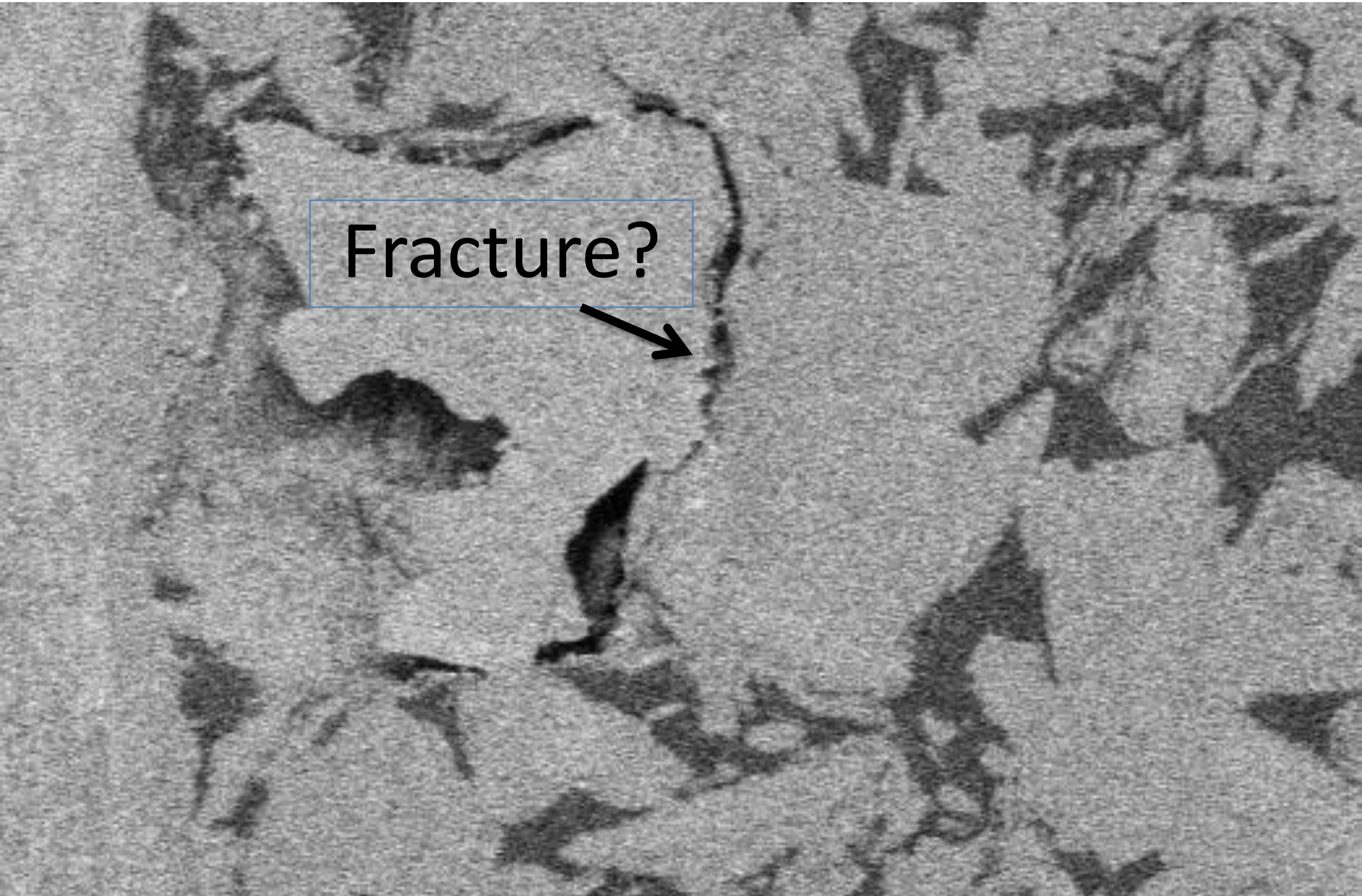
n = 0.025 mols of methane
R = 0.082 liter atmospheres/mol degree K
T = 200 + 273 = 473
V = .001 liter

P = (.025) (.082) (473) / (.001) = **970 atm**

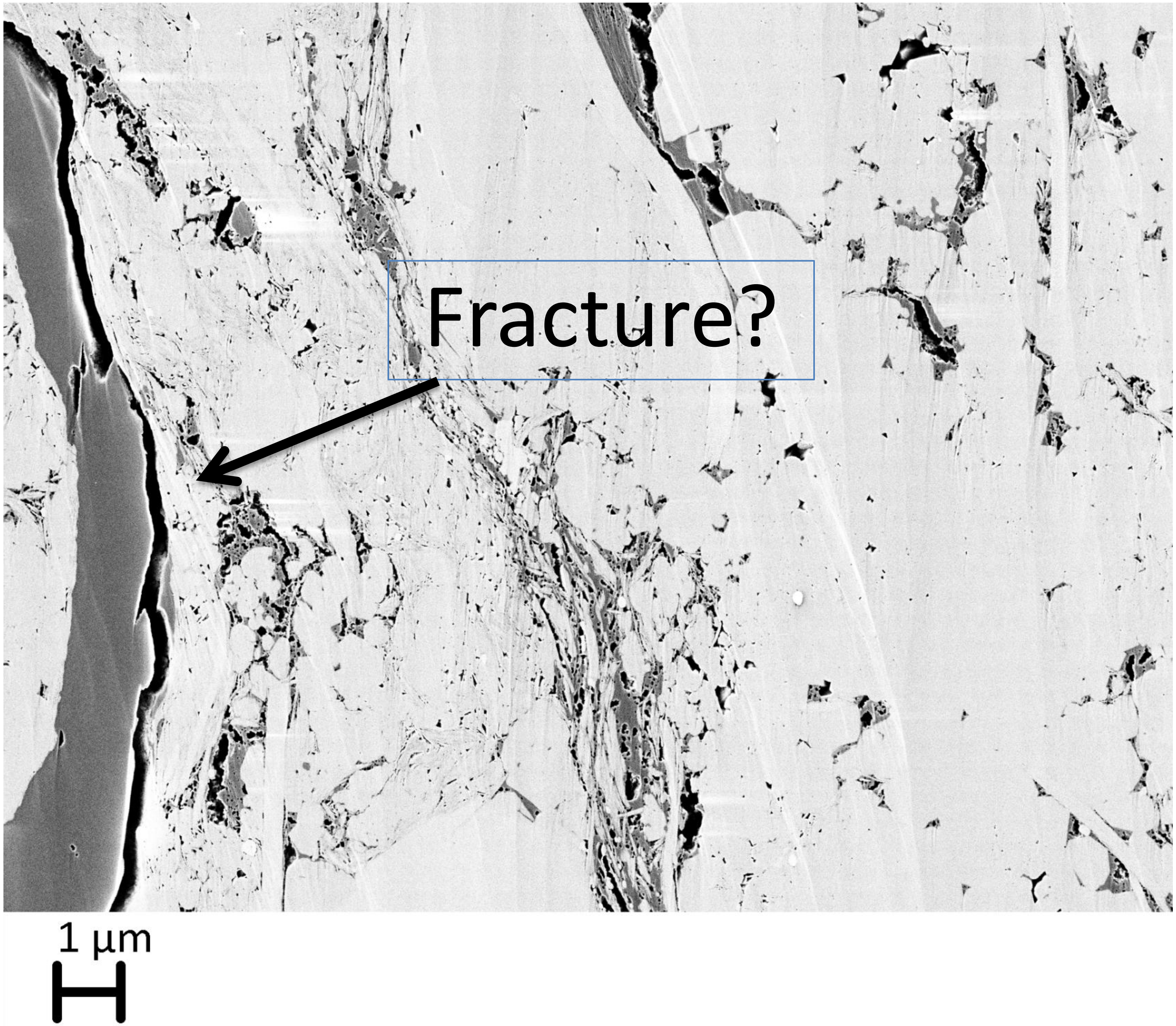
14.7 psi/atm X 970 atm = **14,260 psi**

This is for 100% cracking. We can adjust calculation to measured amount; e.g., 50% cracking generates about 7000 psi for this example with 75% pore space organic matter. Typical hydrofracing pressures are 8000 psi at 10,000 ft. Pressure due to oil cracking may cause natural fracturing and/or aid in hydrofracing.

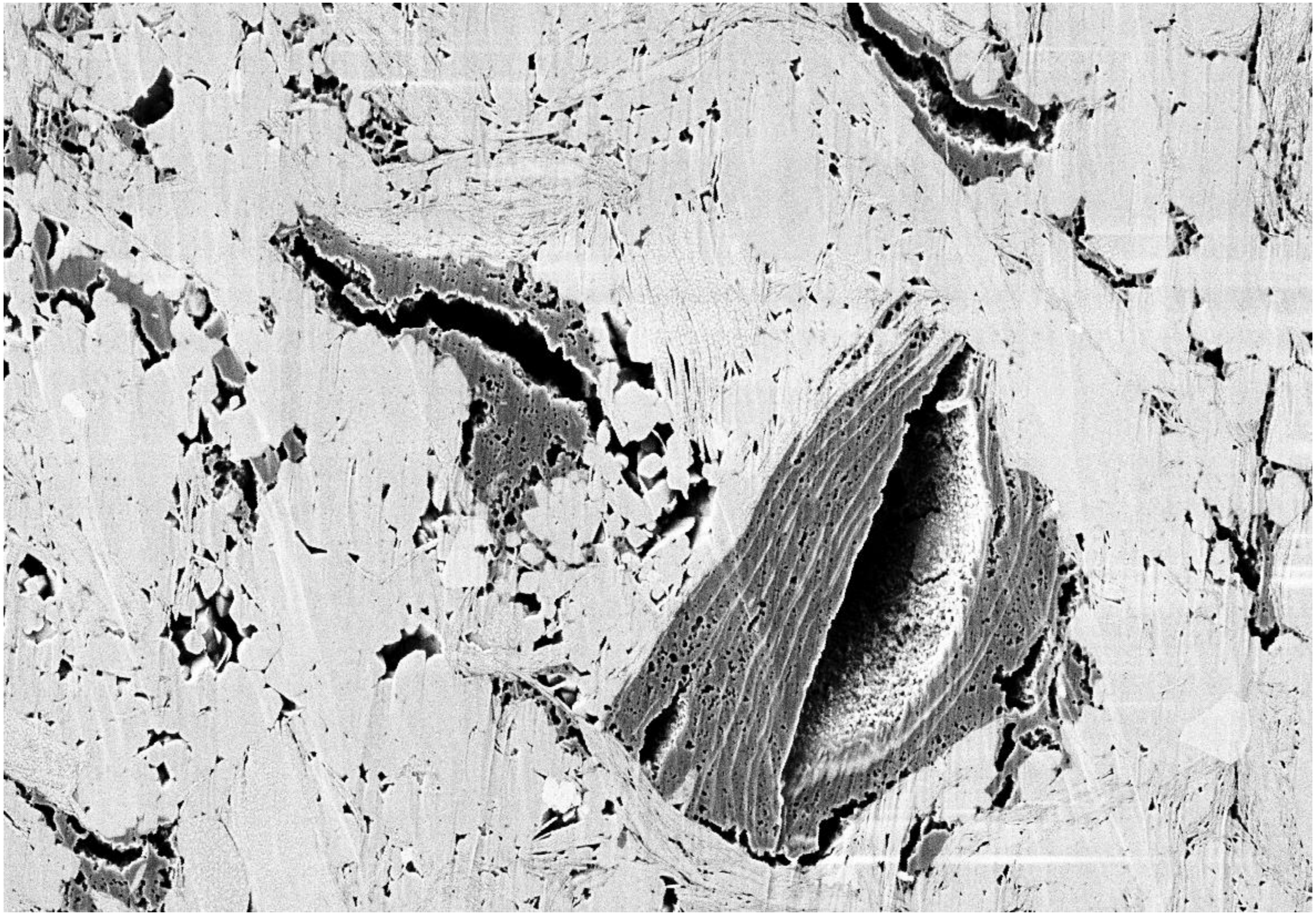
Heated Woodford

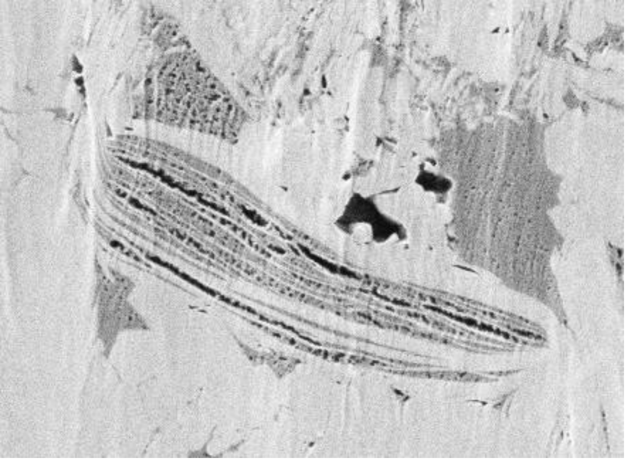


Heated-Dry Gas, Bone Spring

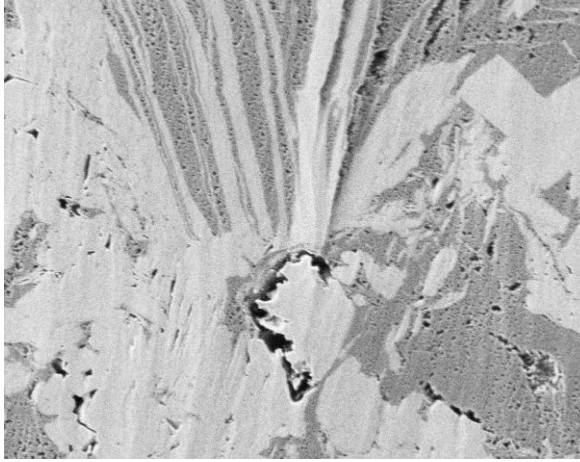


Conclusion: Porosity is created and destroyed during maturation but process shows wide variation from sample to sample.





Future Work



- *More samples, different shales, different mineral facies, different organic facies, different TOC's.*
- *Study process through entire oil window*
- *Compare lab results with natural samples*
- *Pyrolysis under pressure*
- *Continue to look for fracturing. Document extent, direction, size, etc.*
- ***dahl@Stanford.edu***