Locating Tight Shale Sweet Spots Using Diamondoid and Biomarker Analyses*

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Abstract

Mapping the extent of oil cracking is one of the most important factors in determining sweetspots for producing liquids from tight shales. This is because oil cracking:

1. Generates light oil and gas, which can solubilize oil and act as a carrier during production;
2. Can generate pressure within the formation to drive production and, in some cases, possibly even fracture the rock;
3. May create porosity and permeability through the conversion of liquid to gas which can then escape;
4. Can crack large oil molecules (such as asphaltenes) that can block pore throats to smaller molecules, allowing for mobility during production.

Because of the importance of oil cracking, thermal maturity measurements on tight shale organic matter is crucial, and maturity maps of most of the major tight shales in the United States have been made. The measurements generally include vitrinite reflectance and Rock-Eval. Although these analyses can be related indirectly to oil cracking, neither of these methods is a direct measurement. Furthermore, vitrinite reflectance and Tmax are made on the immobile organic matter which may or may not be of the same maturity as the fluids. We propose diamondoid and biomarker analyses on tight shale extracts as a means of supplementing Rock-Eval and/or vitrinite data. Diamondoid analysis, besides being a direct method of measuring oil cracking (Dahl et al., 1999), is made on the fluids within the rock. Comparing the maturity of the mobile and immobile phases, one can identify migrated fluids, and where fluids have migrated into the rock, one might expect that they can also be more easily extracted from these zones. Furthermore, although the maturity of the immobile phase should

change very little over a relatively small vertical section; e.g., 10s of meters, the maturity of mobile fluids can vary if migration of more mature fluids along bedding planes in certain zones within the section has occurred. Again, if fluids can migrate in, one might assume they will be more easily produced. An additional advantage of performing diamondoid and biomarker analyses on tight-shale extracts is that it can be difficult to get reliable vitrinite numbers and Tmax values can be confusing. Oil cracking and maturity determinations by biomarkers and diamondoids can obviously be used in conjunction with vitrinite and Rock-Eval results to provide more accurate oil cracking and maturity determinations.

References Cited

Dahl, J.E., J.M. Moldowan, K.E. Peters, G.E. Claypool, M.A. Rooney, G.E. Michael, M.R. Mello, and M.L. Kohnen, 1999, Diamondoid hydrocarbons as indicators of natural oil cracking: Nature, v. 399, p. 54-57.

EIA (U.S. Energy Information Administration), 2010, Eagle Ford Shale Play, Western Gulf Basin, South Texas (map, May 29, 2010). Website accessed July 28, 2014. www.eia.gov/oil_gas/rpd/shaleusa9.pdf

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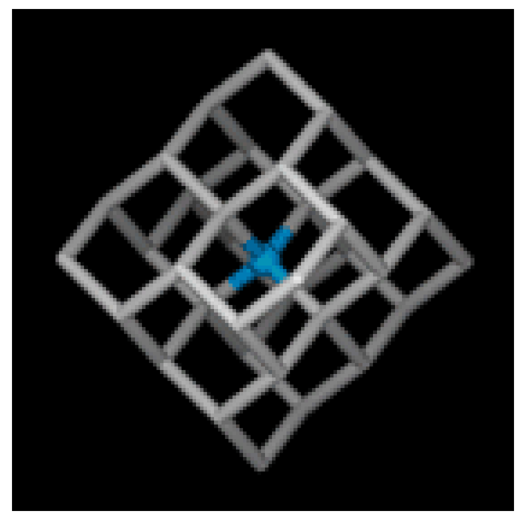
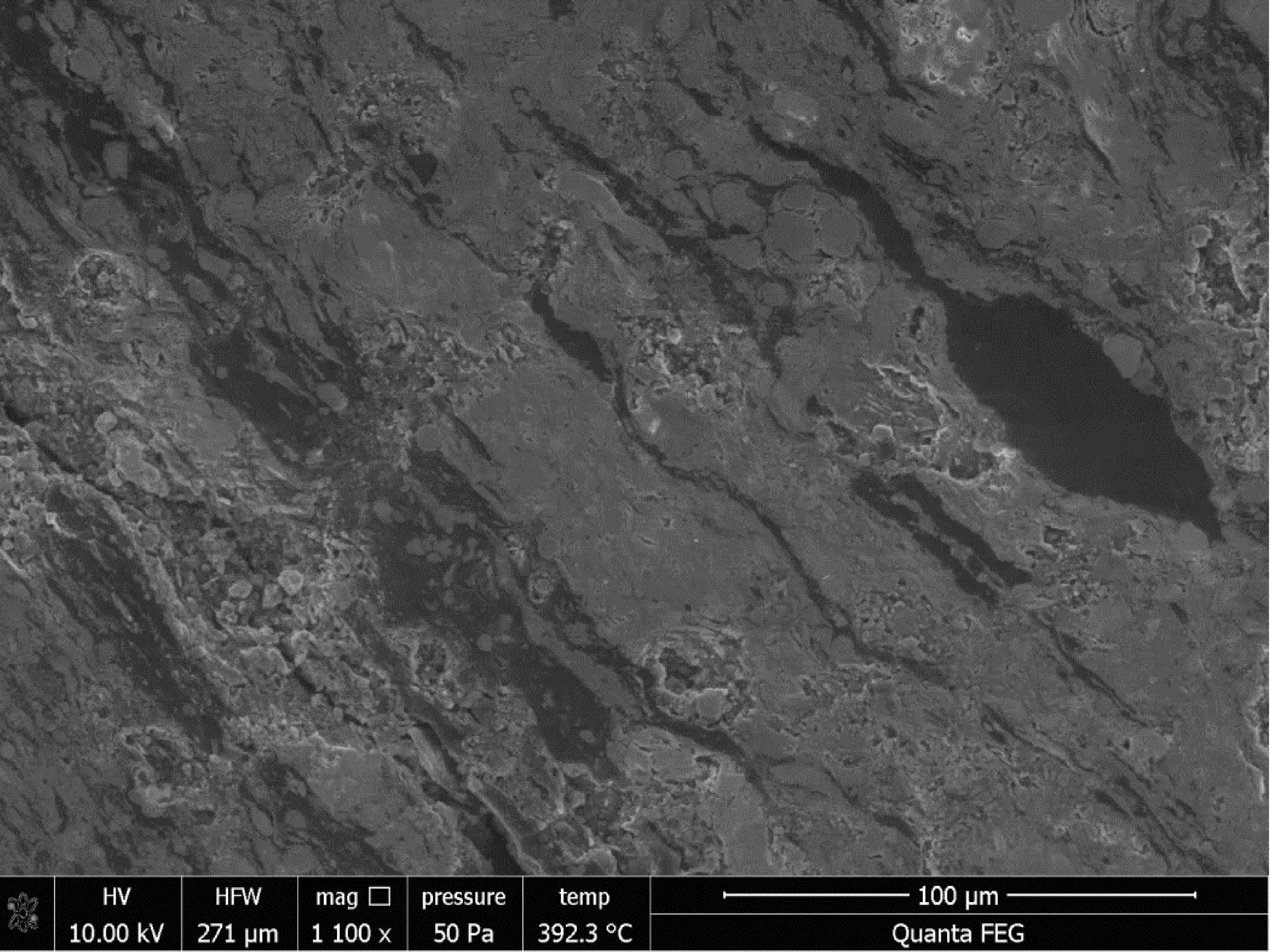


Crucial factors affecting the economics of a tight-shale play

- Carbon content; i.e., Total Organic Carbon (TOC)
- Generation potential of the organic matter
- Determination of how much gas and oil have already been generated from the kerogen
- Determination of the extent of oil cracking (thermal conversion of liquids to gas)
- Mineralogy, Structural Geology

Oil Cracking: Highly Important

- Generates reservoir pressure
- Generates gas to solubilize and carry liquids to well-head
- Cracks large molecules (asphaltenes and resins) which can plug nanopores to small molecules
- Creates porosity and permeability
- If too much cracking get dry gas
- **Sweetspot = Intermediate amount of cracking**


HV
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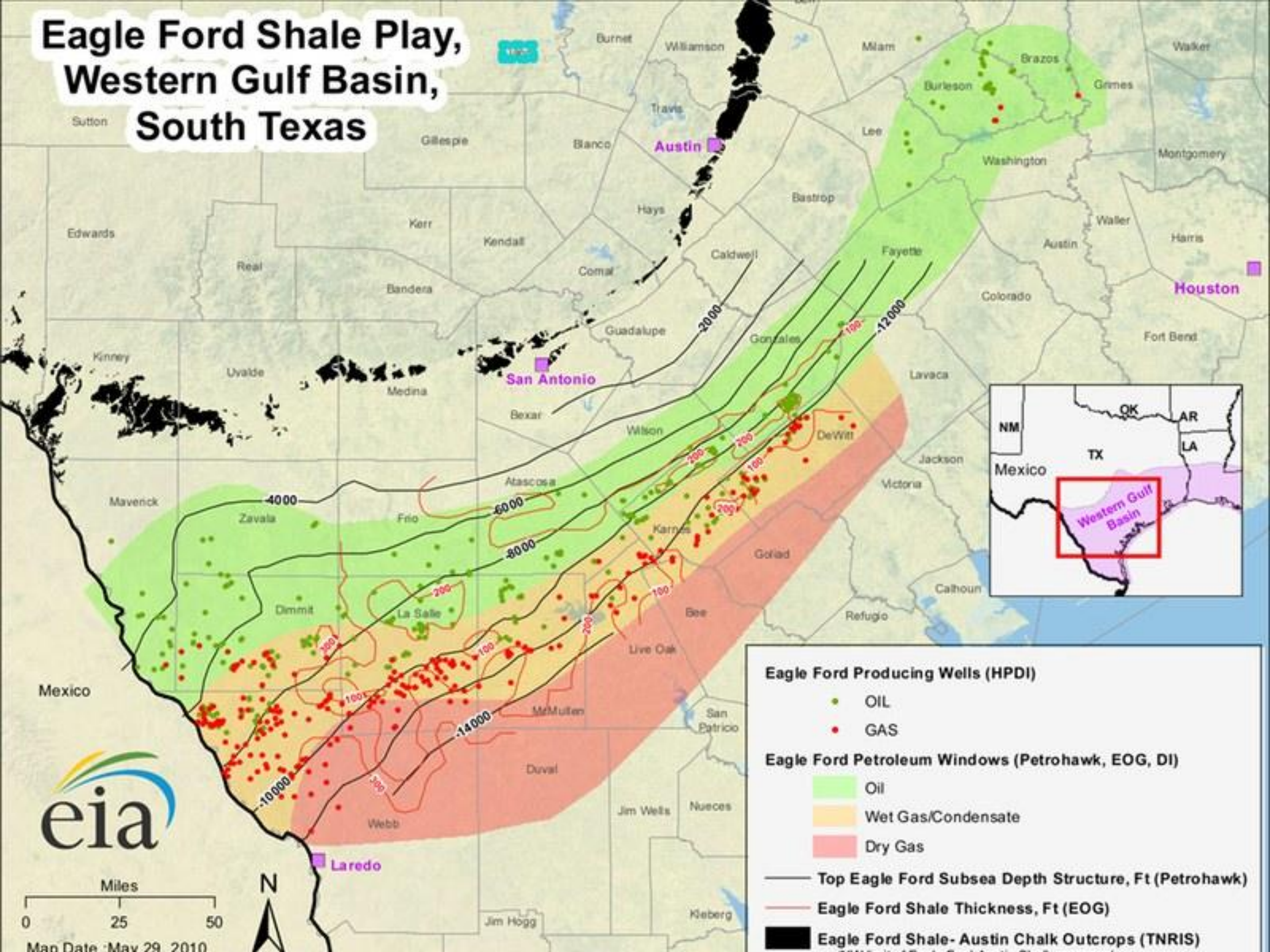
HFW
271 μm
mag ☐
1 100 x
pressure
50 Pa
temp
392.3 °C
100 μm
Quanta FEG

Fracture Orientation

- Are fractures predominantly parallel to bedding?
- Is migration predominantly parallel to bedding?
- Are source rocks with vertical fractures in tectonically active areas more prone to expulsion and therefore more prone to generate conventional plays?
- Are source rocks on stable cratons more likely to retain hydrocarbons, making them better unconventional plays?


Eagle Ford Shale Play,
Western Gulf Basin,
South Texas
Burnet
Williamson
Milam
Brazos
Walker
Burleson
Grimes
Travis
Sutton
Gillespie
Blanco
Austin
Lee
Washington
Montgomery
Bastrop
Hays
Kerr
Edwards
Kendall
Caldwell
Fayette
Waller
Austin
Harris
Real
Comal
Bandera
Colorado
Houston
Guadalupe
Gonzales
Fort Bend
Kinney
Uvalde
San Antonio
Lavaca
Medina
Bexar
Wilson
DeWitt
Jackson
Atascosa
Victoria
Maverick
Zavala
Frio
Karnes
Goliad
Dimmit
La Salle
Calhoun
Bee
Refugio
Live Oak
McMullen
San Patricio
Mexico
Duval
Jim Wells
Nueces
Webb
Laredo
Jim Hogg
Kleberg
2000
4000
6000
8000
10000
12000
14000
100
200
300
NM
OK
AR
TX
LA
Mexico
Western Gulf Basin
Miles
0
25
50
N
Map Date :May 29, 2010
eia
Eagle Ford Producing Wells (HPDI)
OIL
GAS
Eagle Ford Petroleum Windows (Petrohawk, EOG, DI)
Oil
Wet Gas/Condensate
Dry Gas
Top Eagle Ford Subsea Depth Structure, Ft (Petrohawk)
Eagle Ford Shale Thickness, Ft (EOG)
Eagle Ford Shale- Austin Chalk Outcrops (TNRIS)

Common methods used to determine thermal maturity and oil cracking

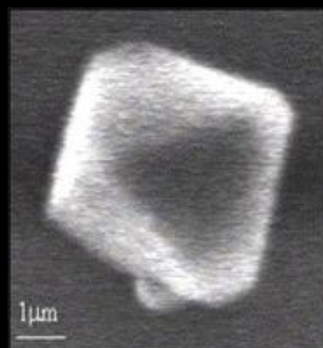
- Vitrinite Reflectance
- Rock-Eval
- Gas Isotopes
- Basin Modeling

Direct determination of oil cracking (thermal conversion of liquids to gas)

- **Diamondoids**

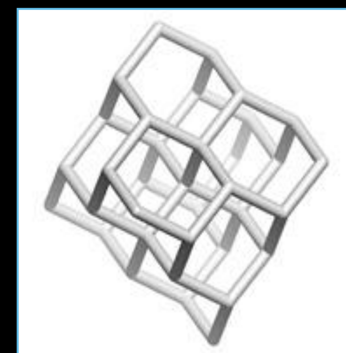
What are diamondoids?

Diamond



Micro-cyrstalline

CVD

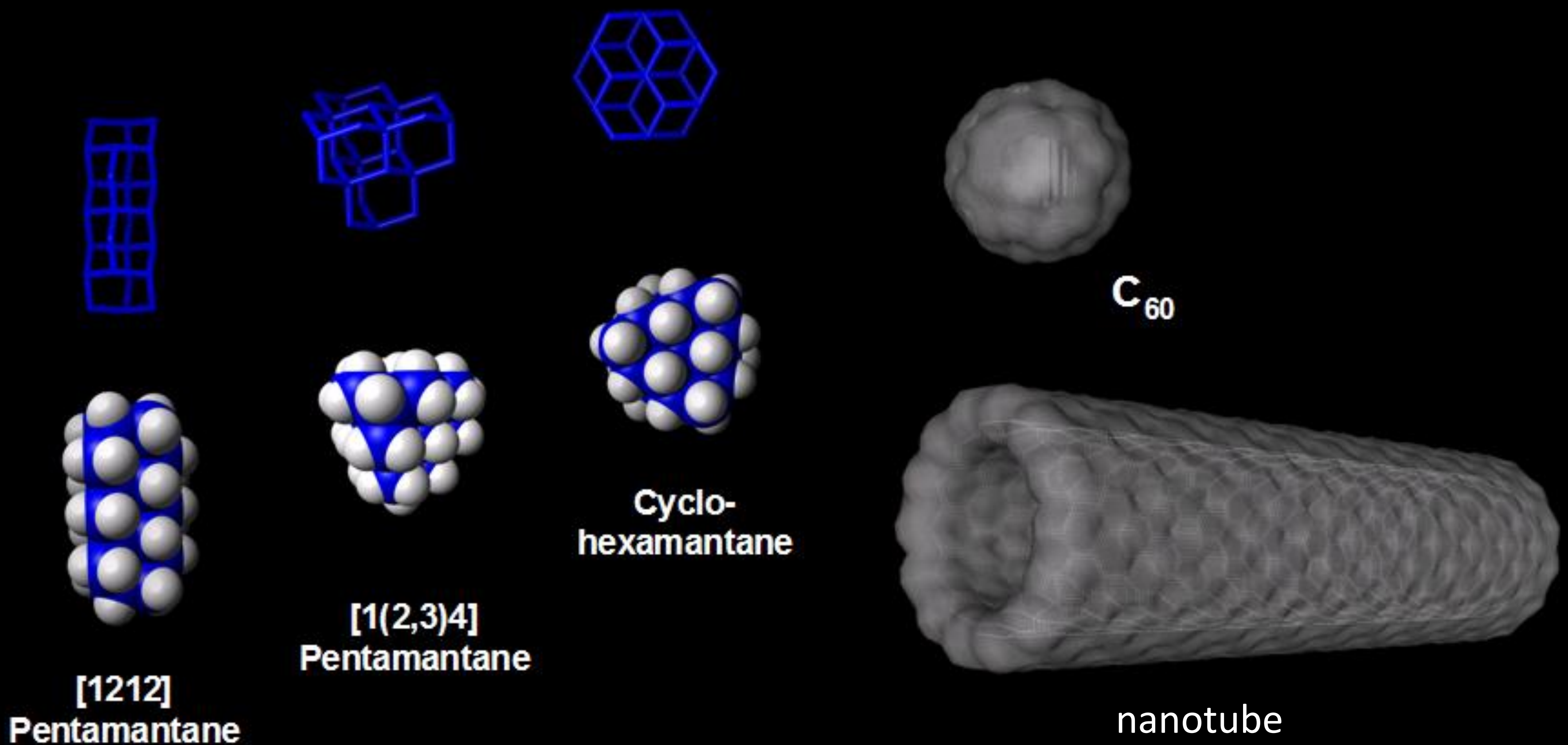


Higher Diamondoid 0.5-2nm

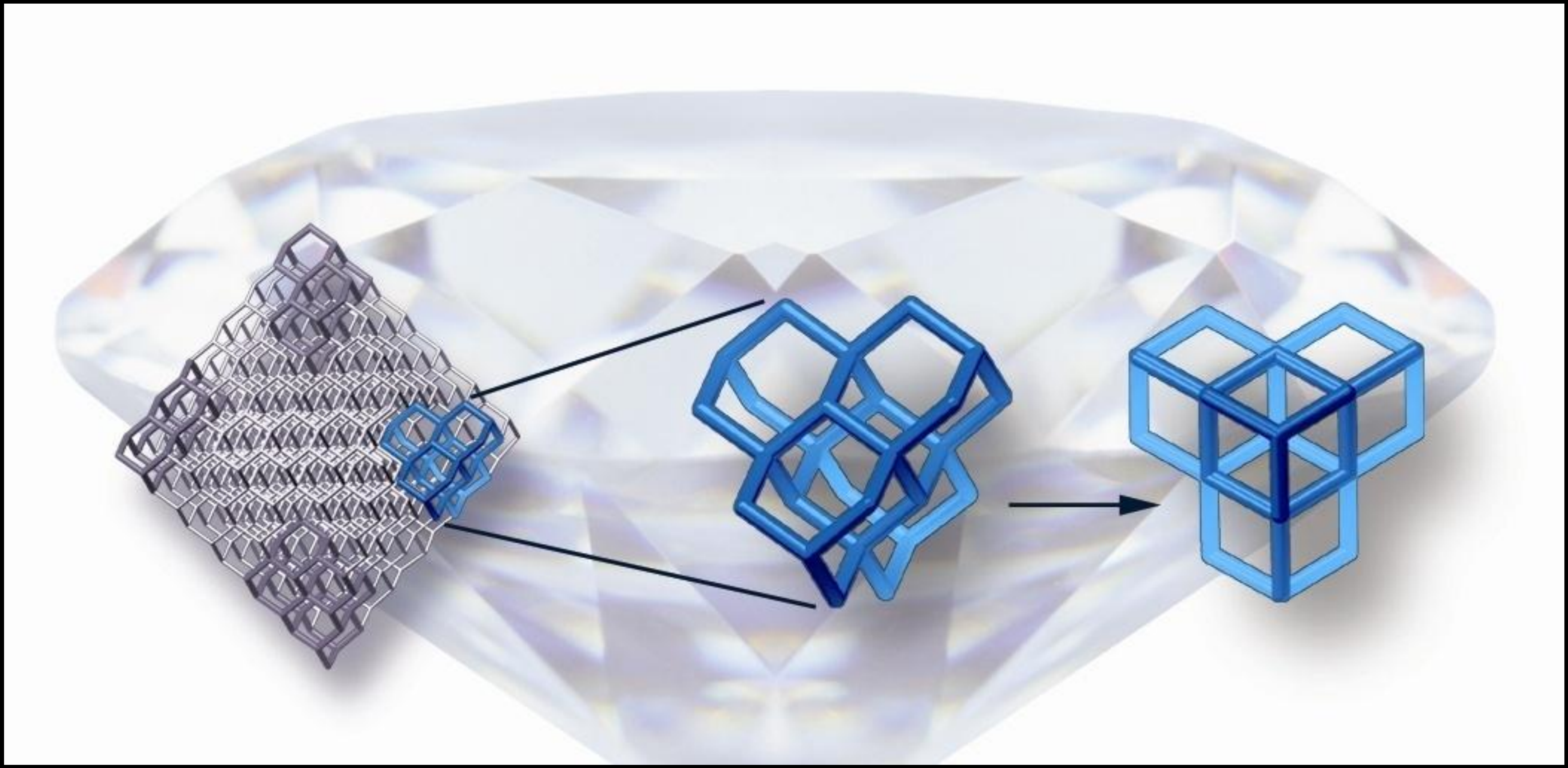
Adamantane

They are nanometer-size, hydrogen-terminated diamonds

They are about the same size as other nanomaterials

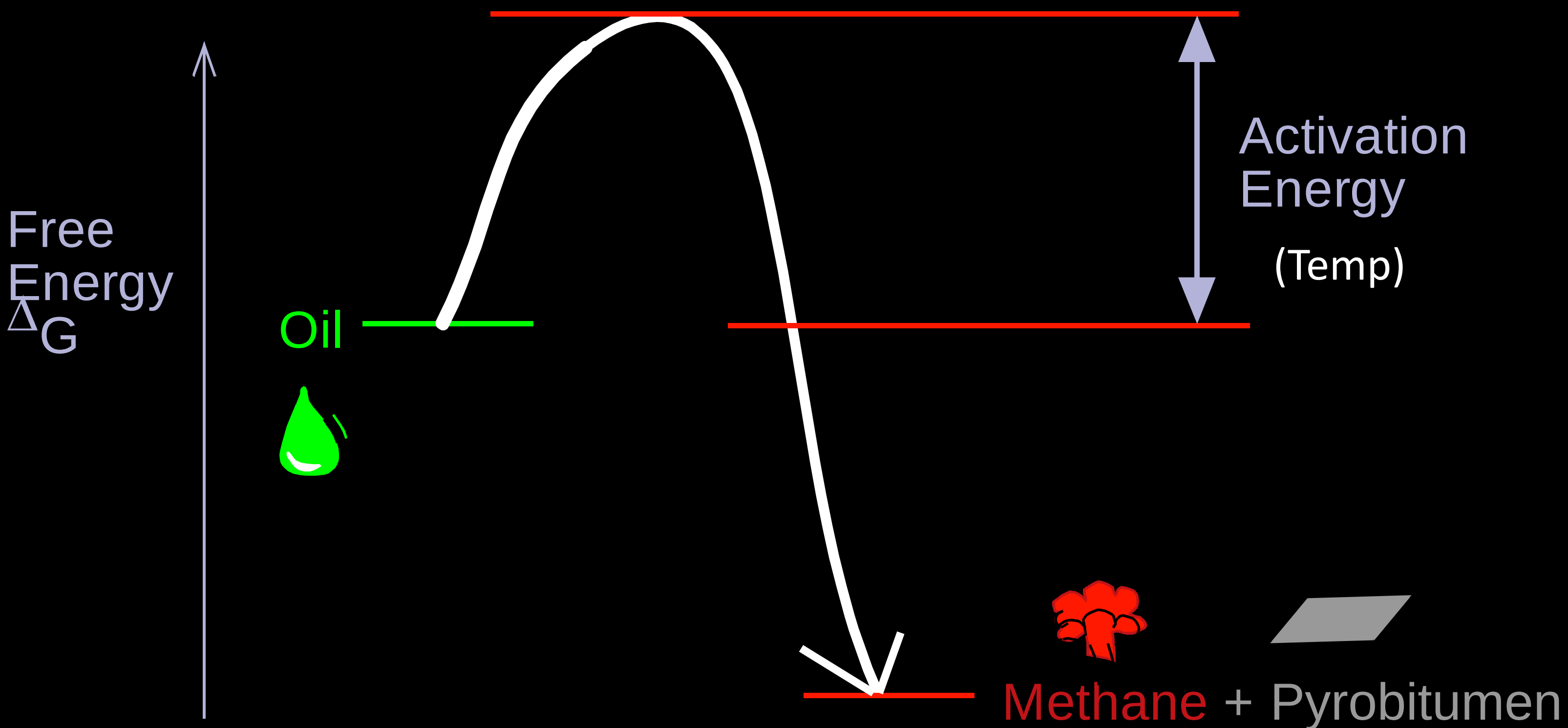


Diamondoids are the Ultimate Oil-Field Nanosensors

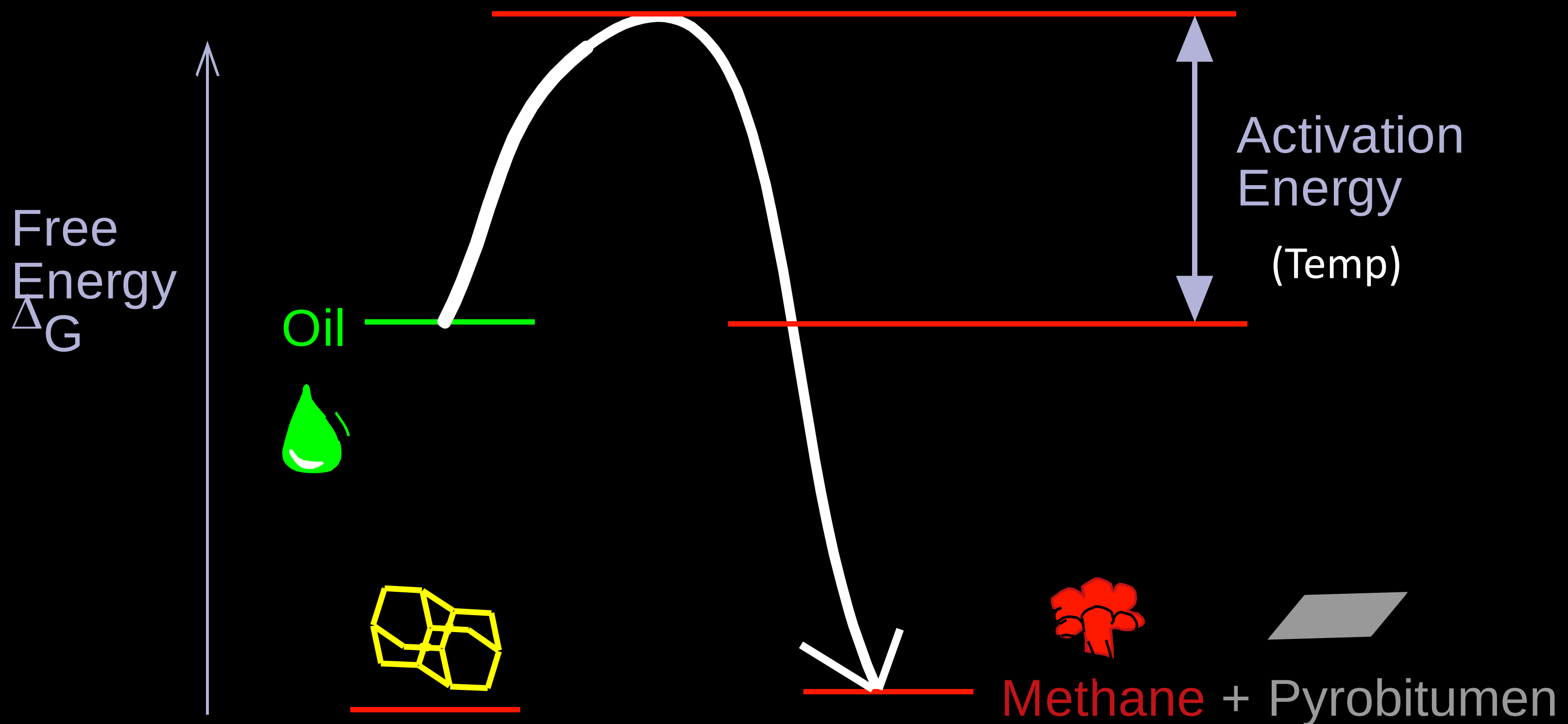


They are Extremely Stable Oil Components.
All Petroleums Contain Diamondoids.

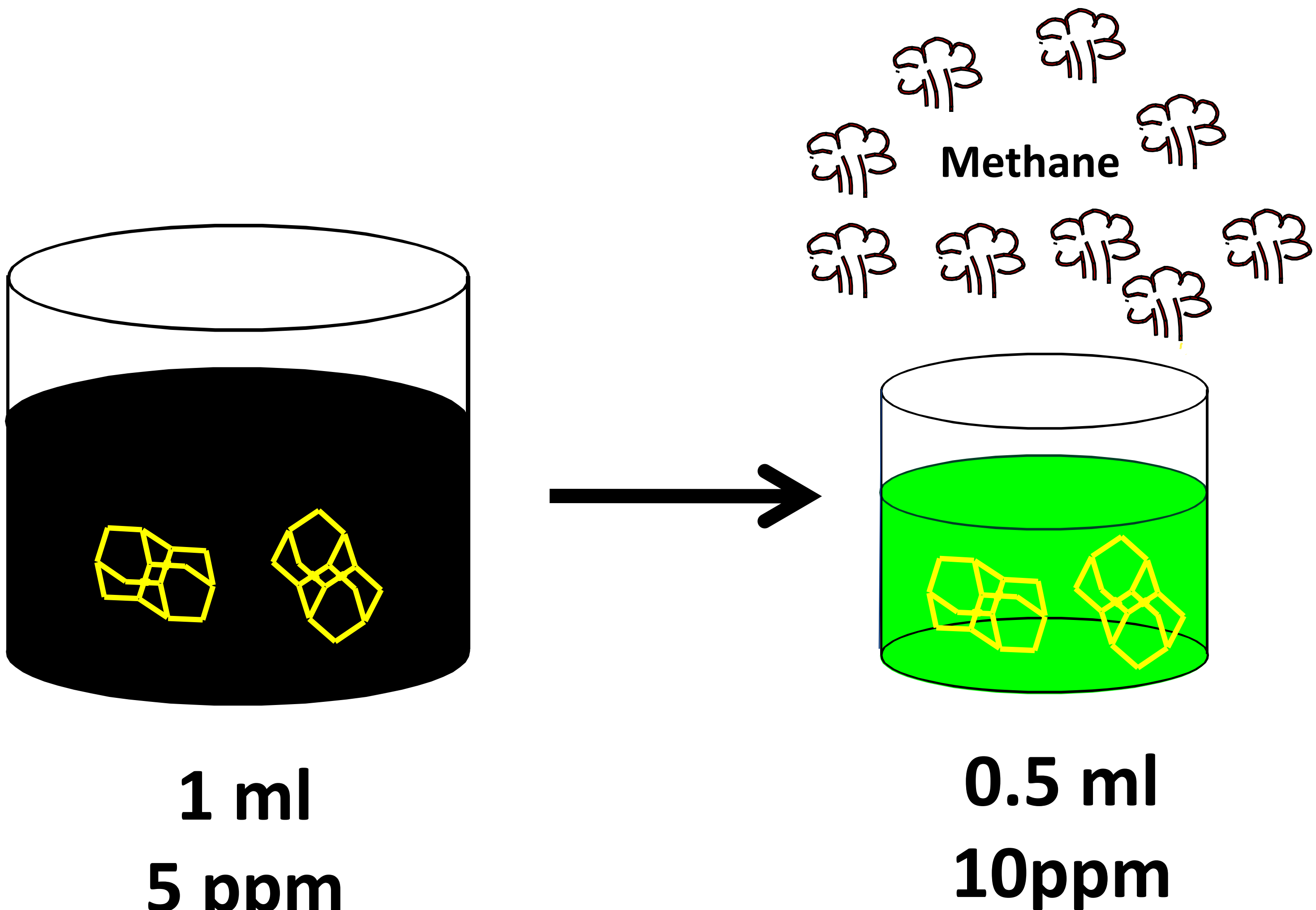
Oil Cracking



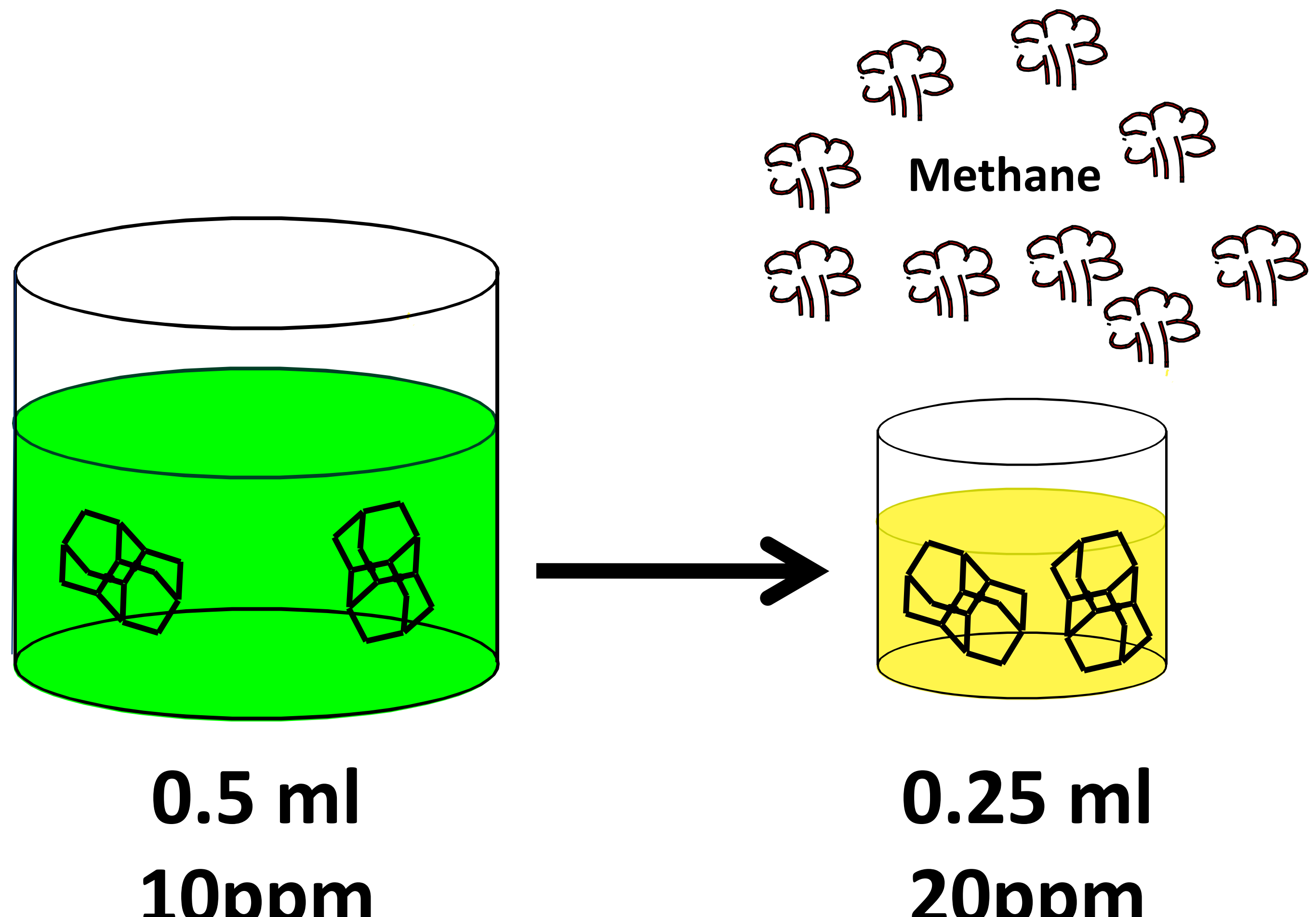
What happens to diamondoids when we crack an oil?



50% Oil Cracking Doubles the Diamondoid Concentration

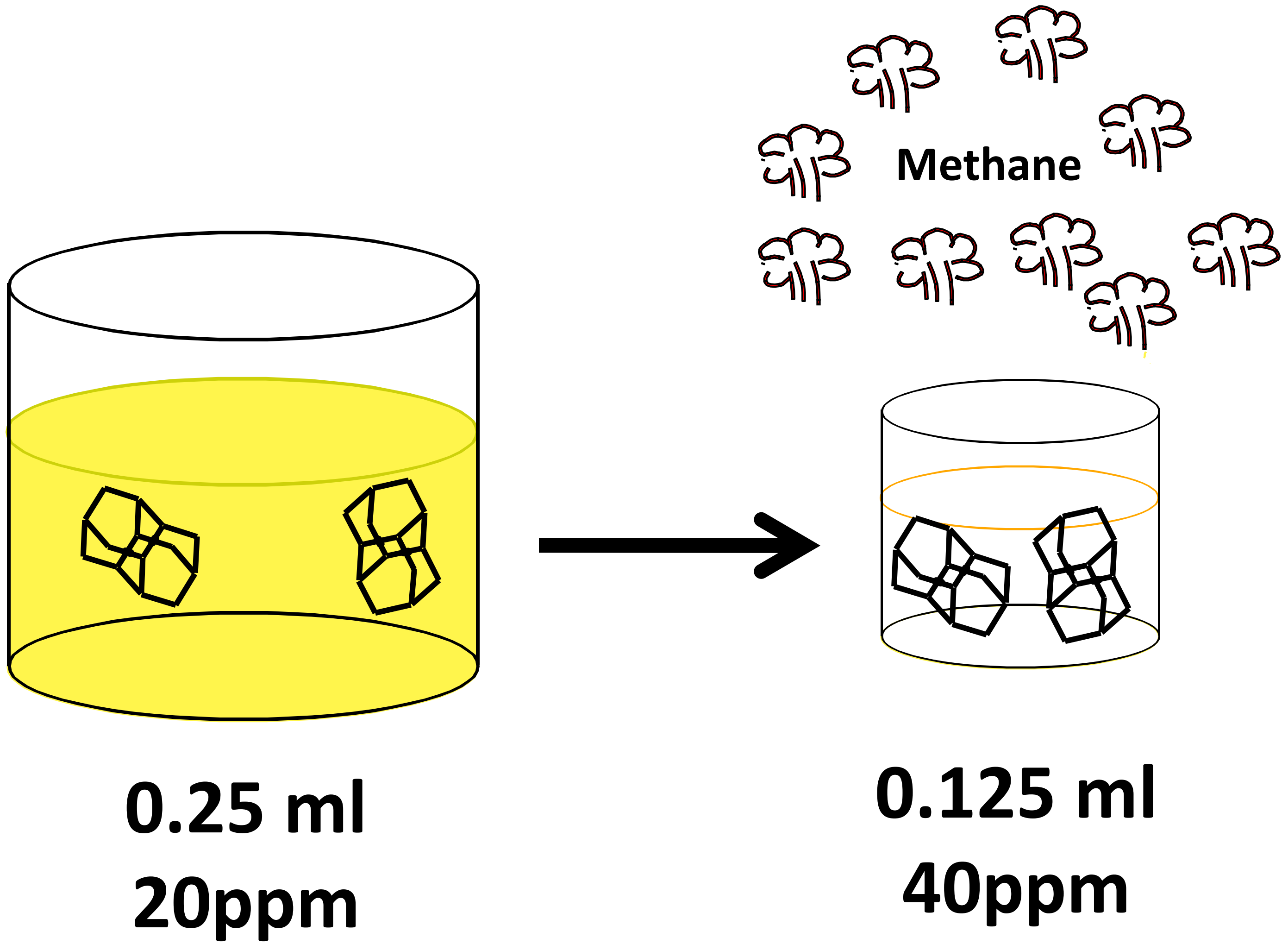


Crack Another 50% of the Oil and the Diamondoid Concentration Doubles Again



And So On According to the equation:

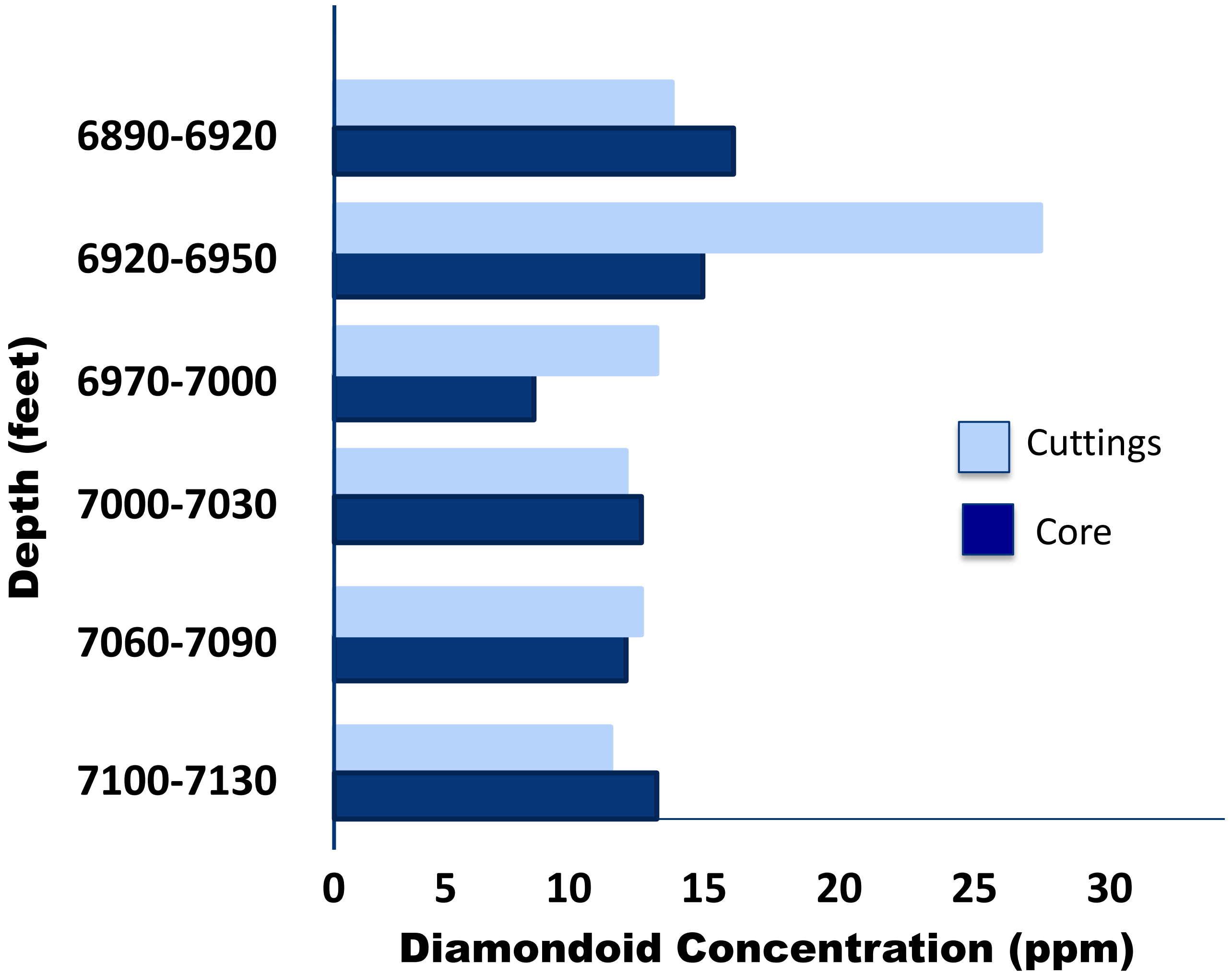
$$\% \text{ Cracking} = [1- (Co/Cc)] \times 100$$



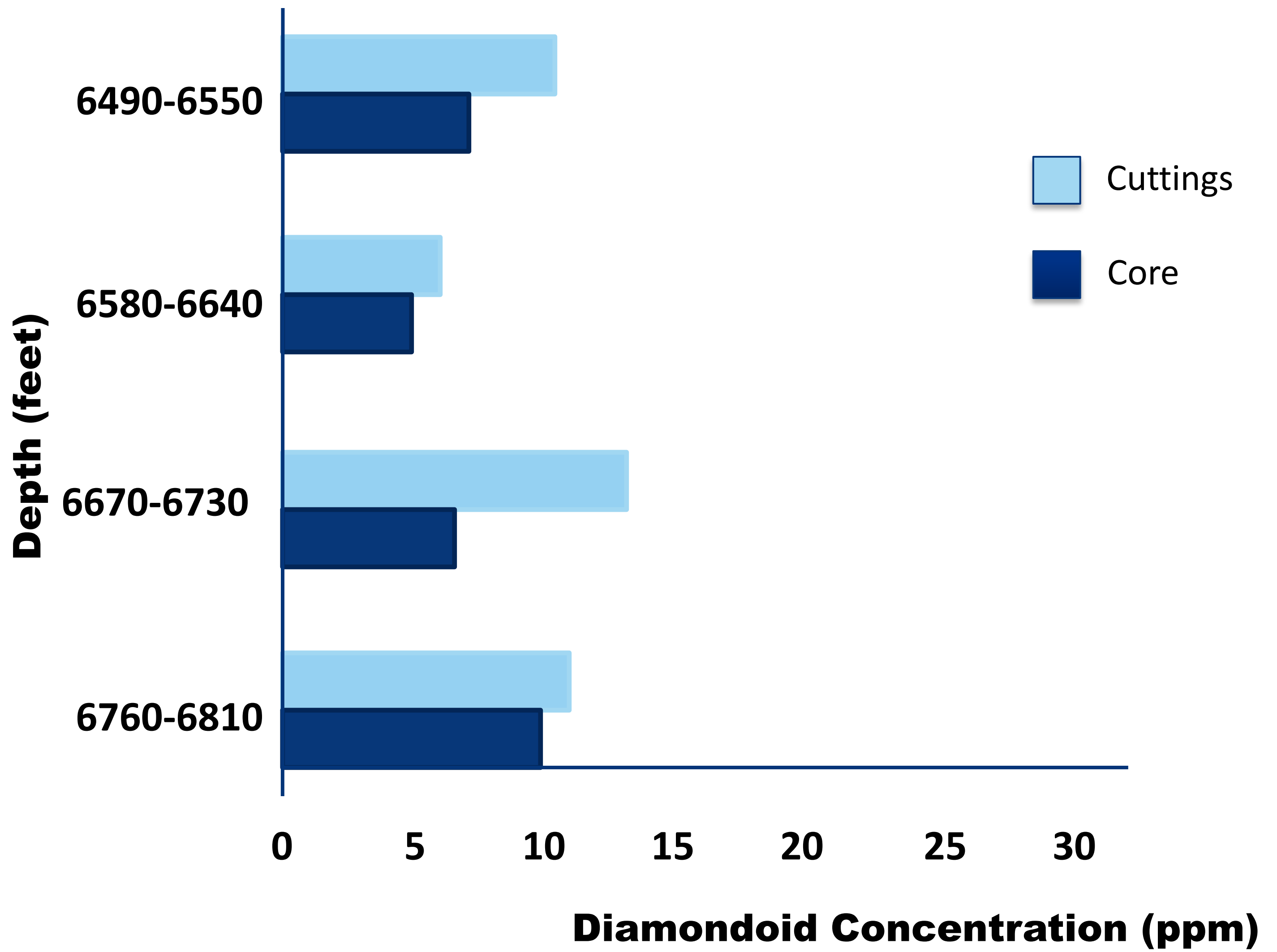
Diamondoid concentrations show oil cracking in tight shales.

Sample	Ro	Diam Conc. ppm	% Cracking (baseline of 5 which is worldwide average)
Woodford	0.9	1.6	0
Woodford	0.9	3.2	0
Tight Shale B	1.06	2.9	0
Tight Shale B	1.06	6.4	0-22
Bossier	1.75	457	99
Bossier	1.75	187	97
Bossier	1.75	131	96
Bossier	1.75	516	99
Barnett	3.0	>>1385	99.9

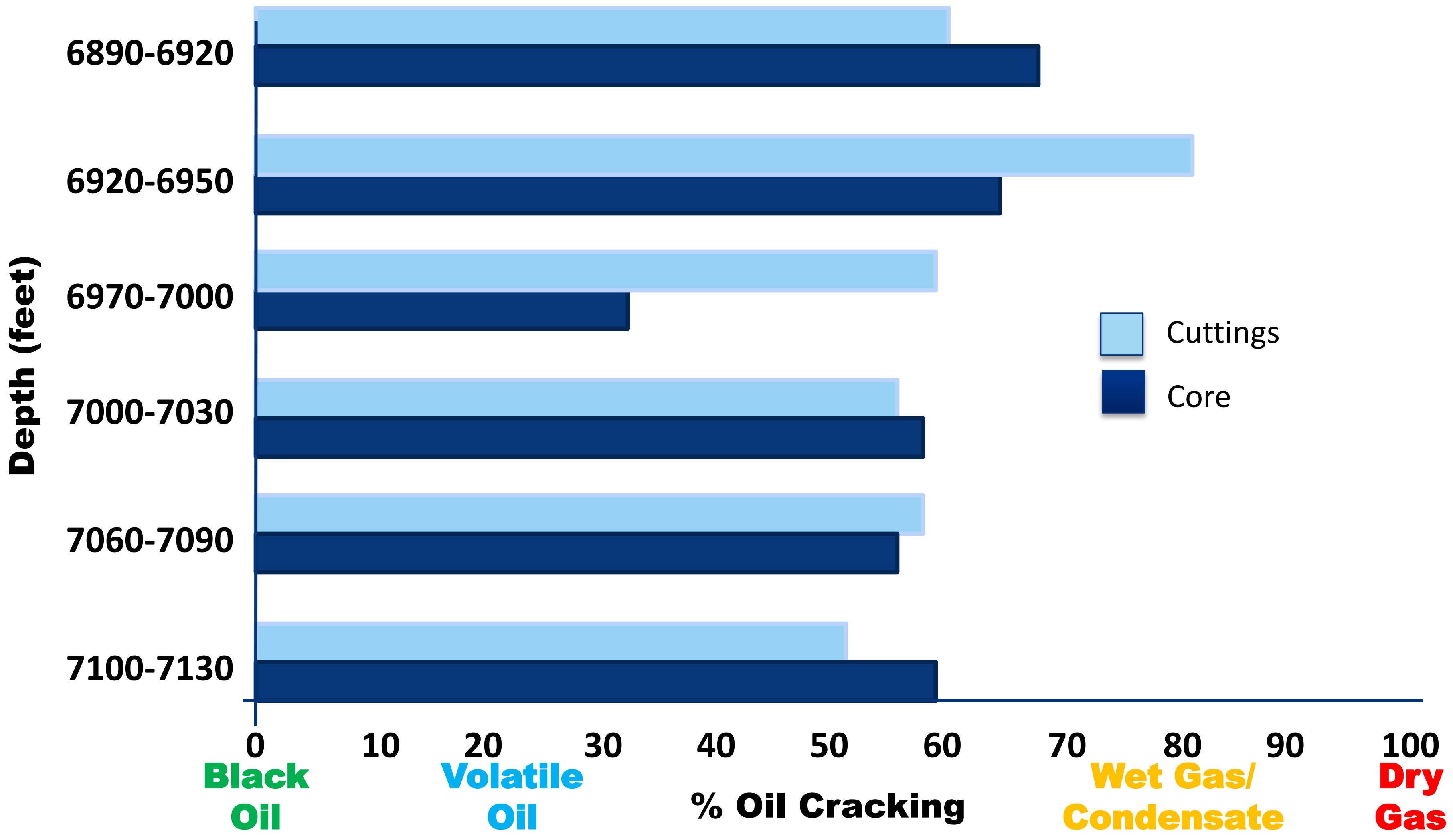
We can use cuttings as well as core samples: X Well Diamondoid Concentration (ppm)

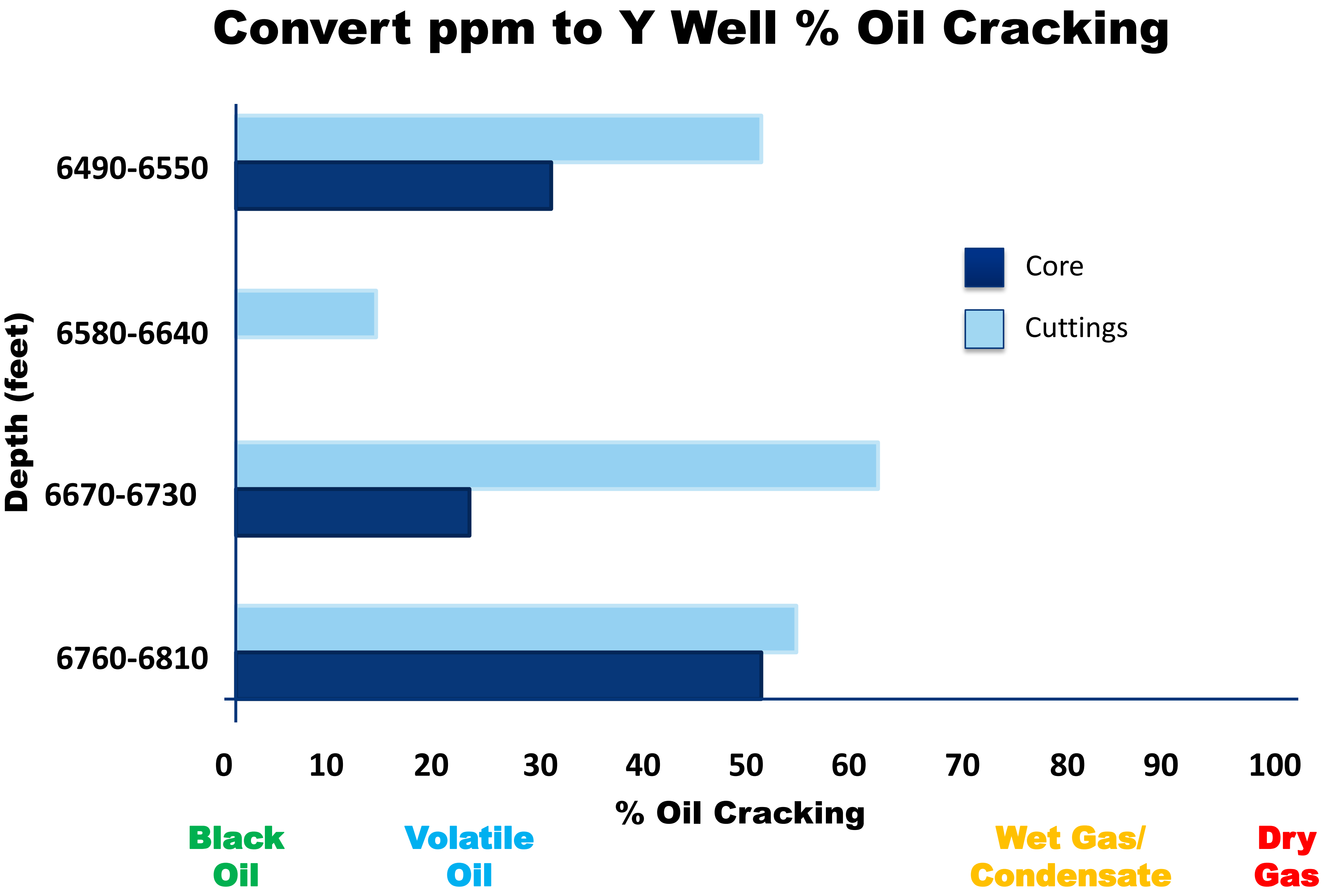


Cores versus Cuttings: Y Well Diamondoid Concentration (ppm)

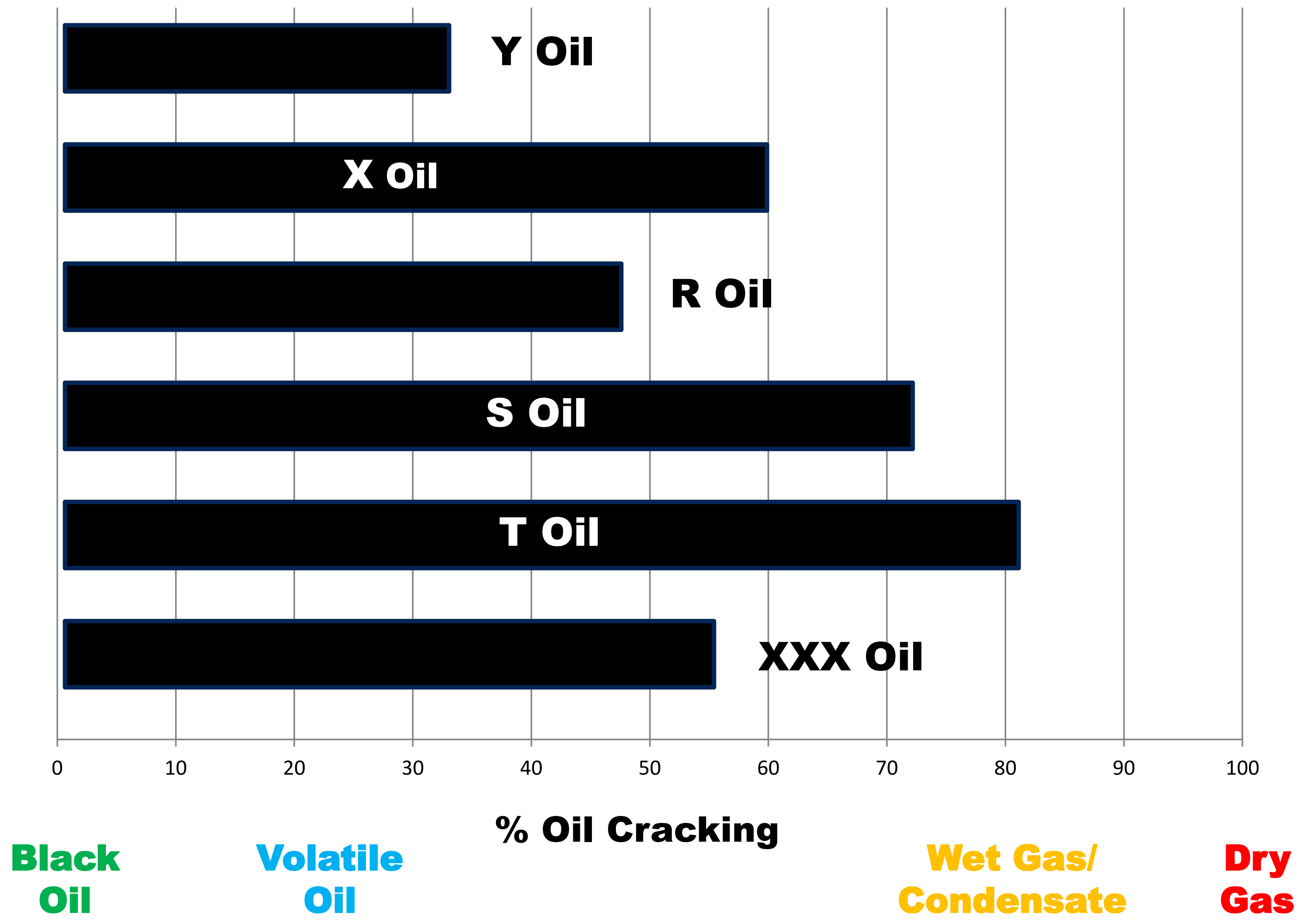


Convert ppm to X Well % Oil Cracking




Convert ppm to Y Well % Oil Cracking
Depth (feet)
6490-6550
6580-6640
6670-6730
6760-6810
Core
Cuttings
0
10
20
30
40
50
60
70
80
90
100
% Oil Cracking
Black Oil
Volatile Oil
Wet Gas/ Condensate
Dry Gas

All Oils Analyzed have Intermediate Amounts of Cracking!



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):

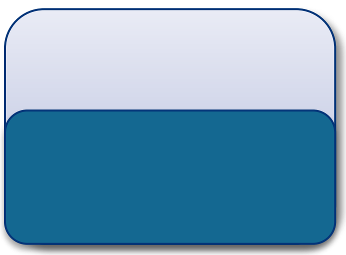
$$P=ZnRT/V$$

Calculating Pressures due to Oil Cracking

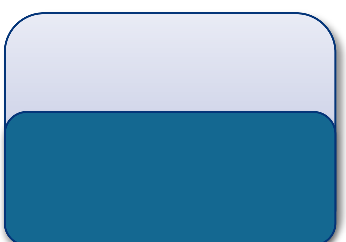
Example

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

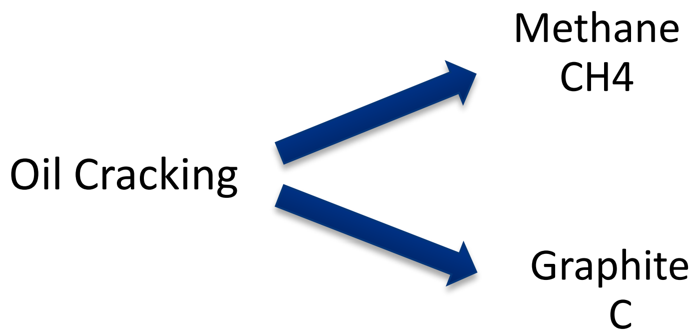
We have Type II organic matter (e.g., Barnett) so the specific gravity should be about 1.5 g/ml



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. We can use the amount of Hydrogen plus the extent of cracking 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 grams 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 =Z nRT or **P = ZnRT/V**

$$P = ZnRT/V$$

n = 0.025 mols of methane
R = 0.082 liter atmospheres/mol degree K
T = 200 + 273 = 473
V = .001 liter
Z near 1.0

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 hydrofracking pressures are 8000 psi at 10,000 ft. Pressure due to oil cracking may cause natural fracturing and/or aid in hydrofracking.

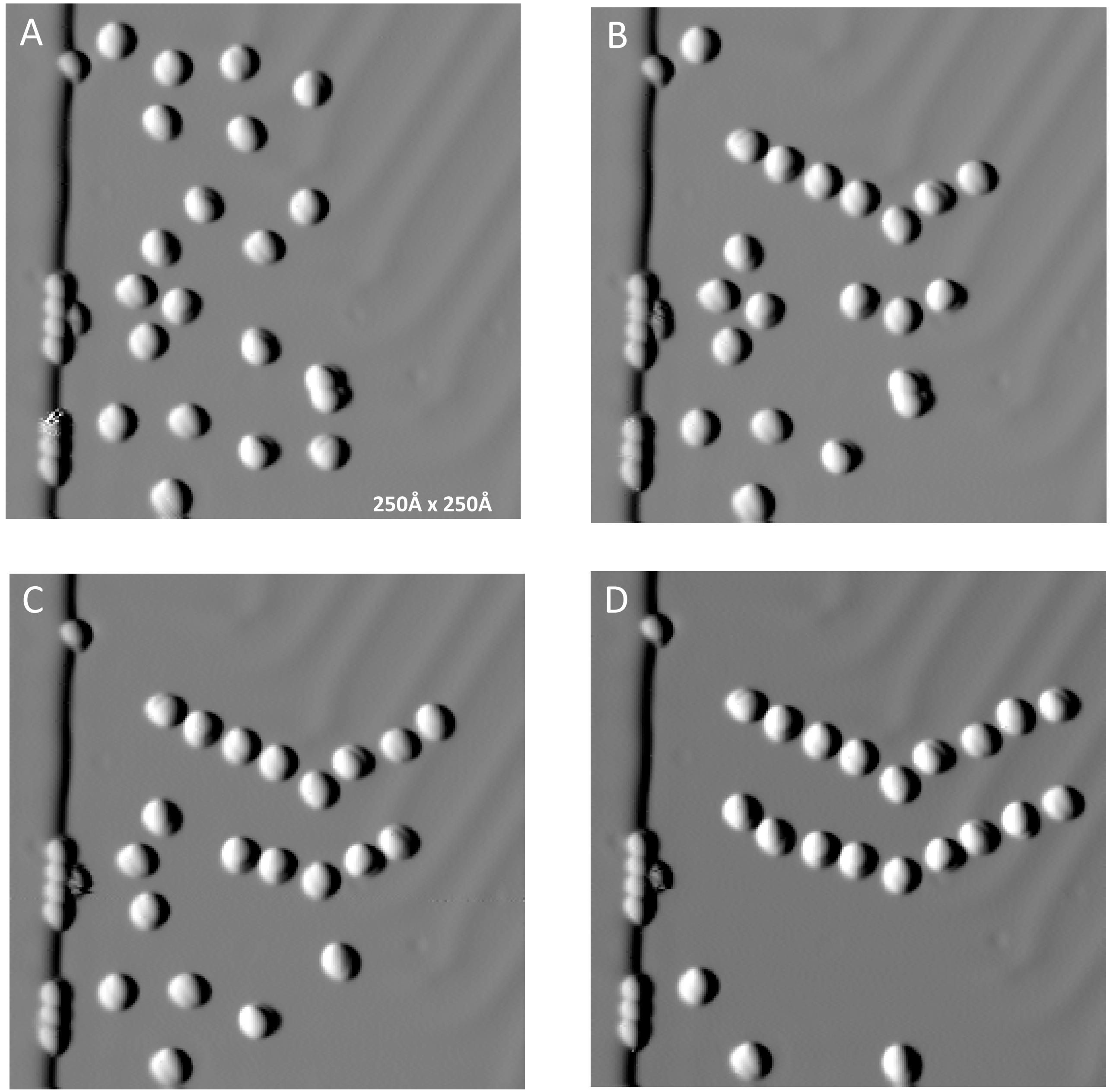
Oil Cracking: Highly Important

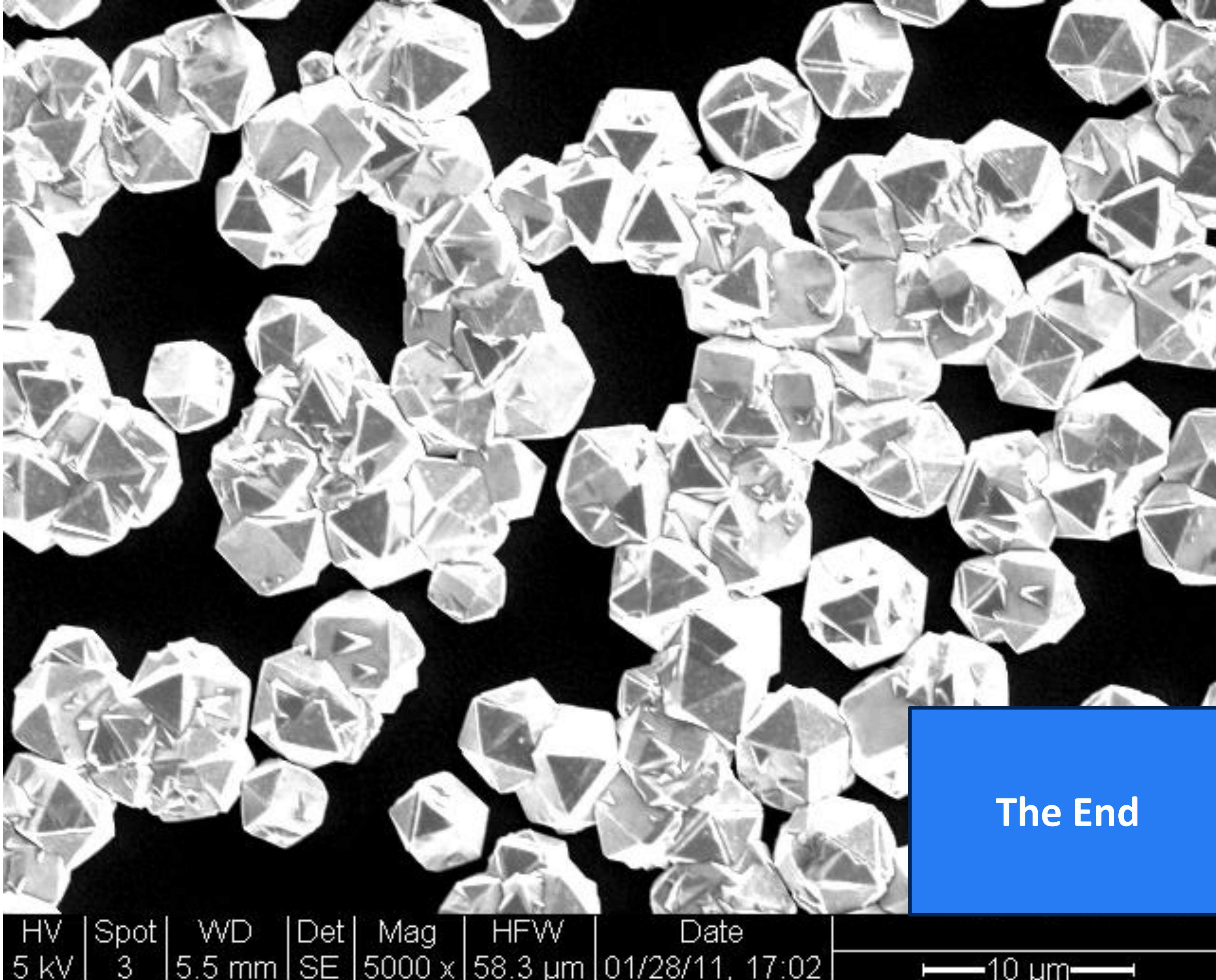
- Generates reservoir pressure
- Generates gas to solubilize and carry liquids to well-head
- Cracks large molecules (asphaltenes and resins) which can plug pores to small molecules
- Creates porosity and permeability
- If too much cracking get dry gas
- **Sweetspot = Intermediate amount of cracking**

Conclusions: Diamondoid/Biomarker Analysis of core and cutting extracts

- Direct measurement of oil cracking
- Performed on mobile phase (complementary to Vitrinite and Rock-Eval)
- Useful where vitrinite and/or Tmax are ambiguous
- Covers entire fluid-maturity range

Creating the Chevron Logo Using Tetramantane Diamondoids

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The End