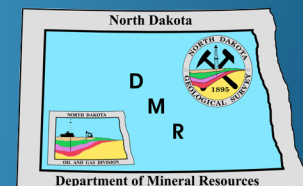


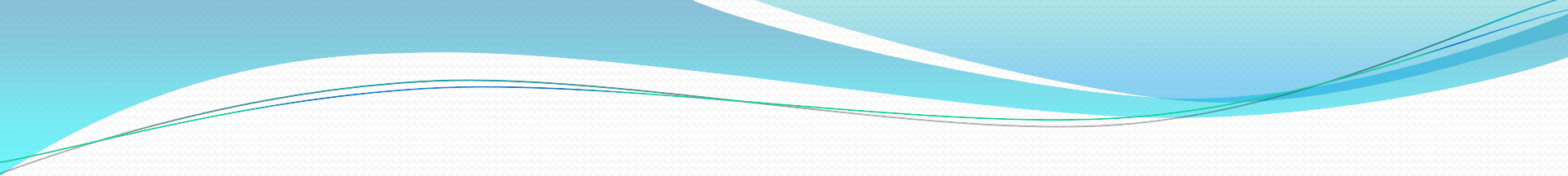
# Activation Energies and RockEval Analyses of Kerogenites in the Red River Formation in North Dakota

Stephan H. Nordeng  
North Dakota Geological Survey  
22<sup>nd</sup> Williston Basin Conference  
May 21, 2014



Geologic Investigations No. 178  
North Dakota Geological Survey  
Edward C. Murphy, State Geologist  
Lynn D. Helms, Director Dept. of Mineral Resources  
2014



- 
- Petroleum Systems
  - Role of Kerogen Kinetics and Permeability in accumulating “basin centered” petroleum.
  - Red River Petroleum System
    - Examples of accumulation
      - Oil Generation Rates
      - Oil Migration Rate

# Petroleum System

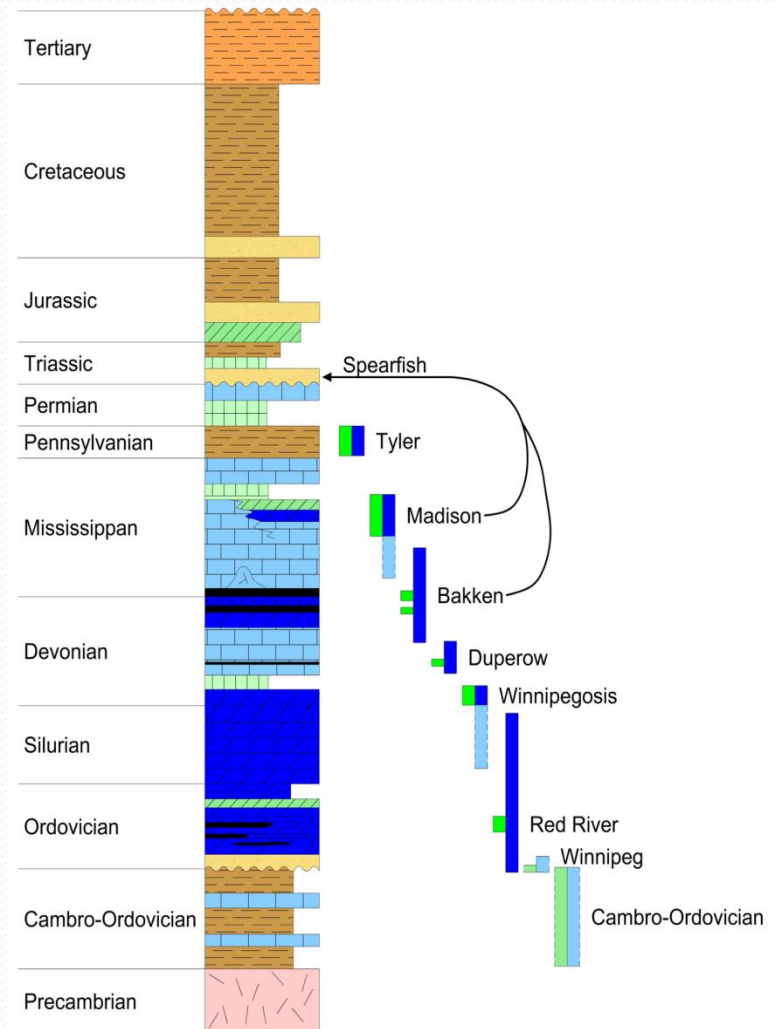
“A pod of **active** source rock and all genetically related oil and gas accumulations. It includes all of the geologic elements and processes that are essential if an oil and gas accumulation is to exist.” (Magoon and Beaumont, 1999)

Essential geologic elements:

- Petroleum sources – Organic Rich
- Reservoirs – Porous & Permeable
- Seals – Poorly Permeable
- Overburden – Thermal Insulation

Processes include:

- Trap formation
- Hydrocarbon generation
- Migration
- Accumulation



# Petroleum Systems

- Dow (1974) Open system
  - All of the oil expelled from source beds migrates.
  - Reservoir pressures are at or close to hydrostatic.
  - Trapping efficiency low
- Something in between.
- Meissner (1978) Closed system
  - None of the oil expelled from source beds migrates.
  - Reservoir pressures are significantly above hydrostatic.
  - Trapping efficiency high

# Closed Petroleum System

“A pod of **active** source rock and all genetically related oil and gas accumulations. It includes all of the geologic elements and processes that are essential if an oil and gas accumulation is to exist.” (Magoon and Beaumont, 1999)

Essential geologic elements:

**Organic Reservoir Seal Complex – Organic, Porous & Poorly Permeable**

Overburden – Thermal Insulation

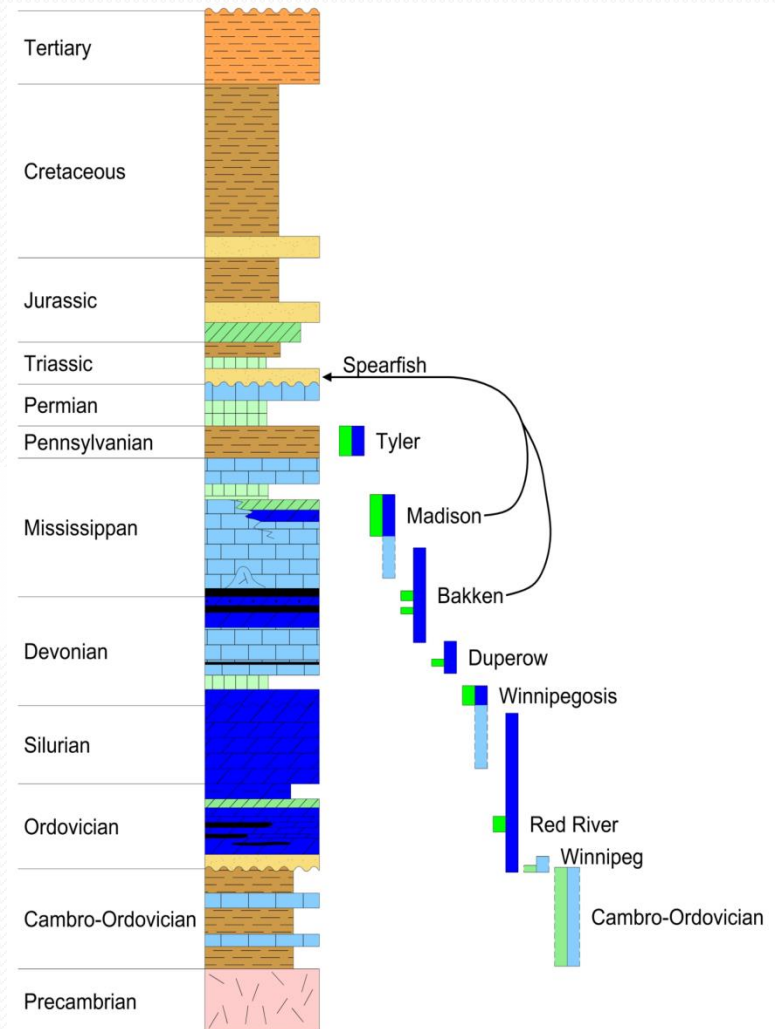
Processes include:

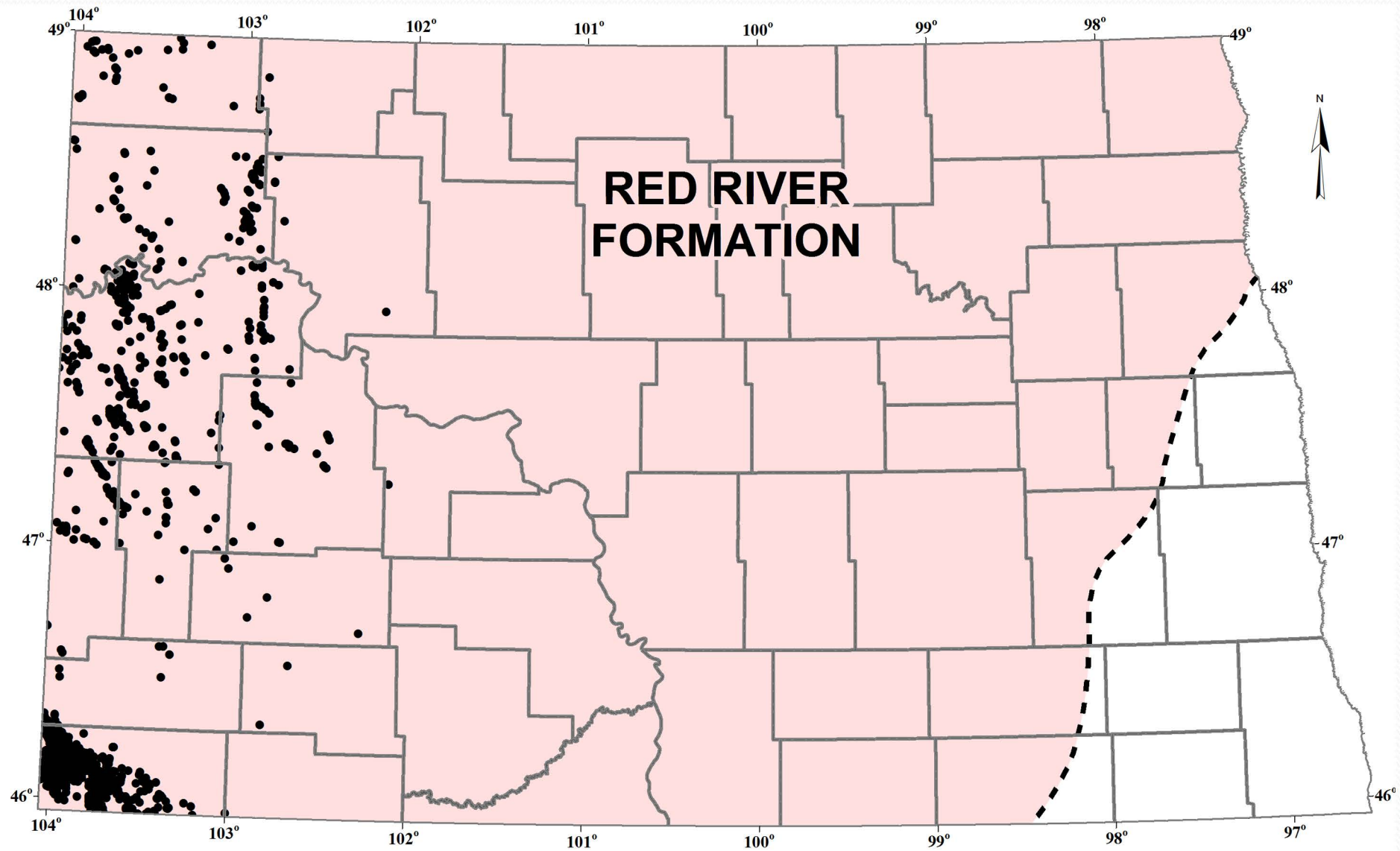
Trap formation

Hydrocarbon generation **rates**

Migration **rates**

Accumulation





Generation Rate < Migration Rate → Migration → Accumulation

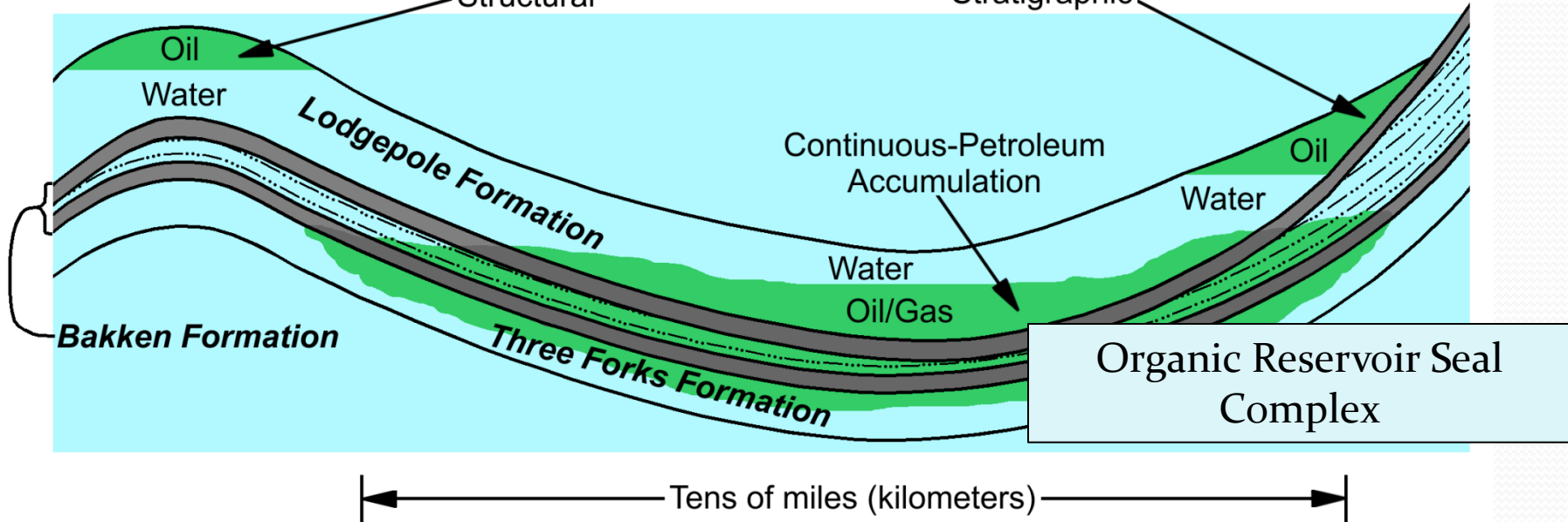
### "Bakken-Type" Continuous Petroleum Accumulation

Land surface

Conventional  
Accumulations

Structural

Stratigraphic



Generation Rate > Migration Rate → Local Accumulation

# Kerogen Kinetics and Rock Permeability are Critical

Source Rock

Adjacent Rock

Generation Rate < Transmission Rate → Migration

Kerogen Kinetics

Activation Energy  
Frequency Factor  
Temperature  
Kerogen Mass

Permeability

Fluid Viscosities  
Pore Space Texture  
Pressure Difference

Open

High Water Saturations  
Hydrostatic Fluid Pressure

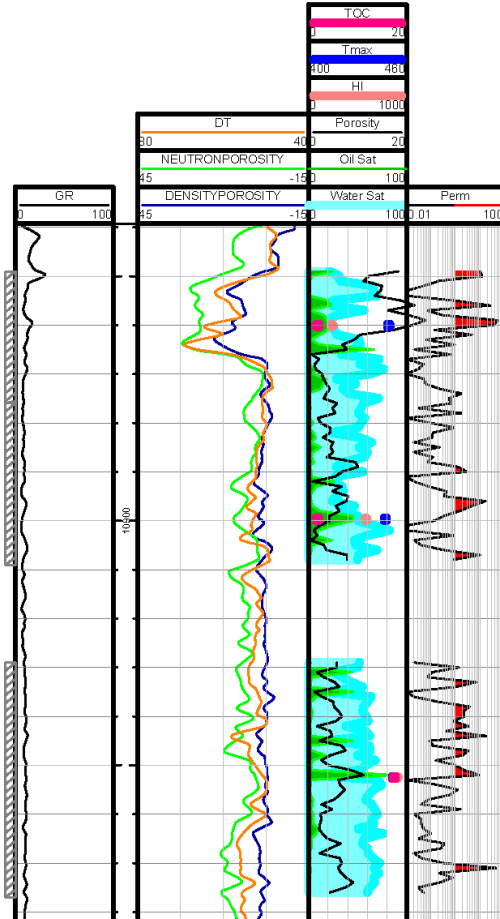
Generation Rate > Transmission Rate → Local Accumulation

Organic Reservoir Seal  
Complex  
Closed

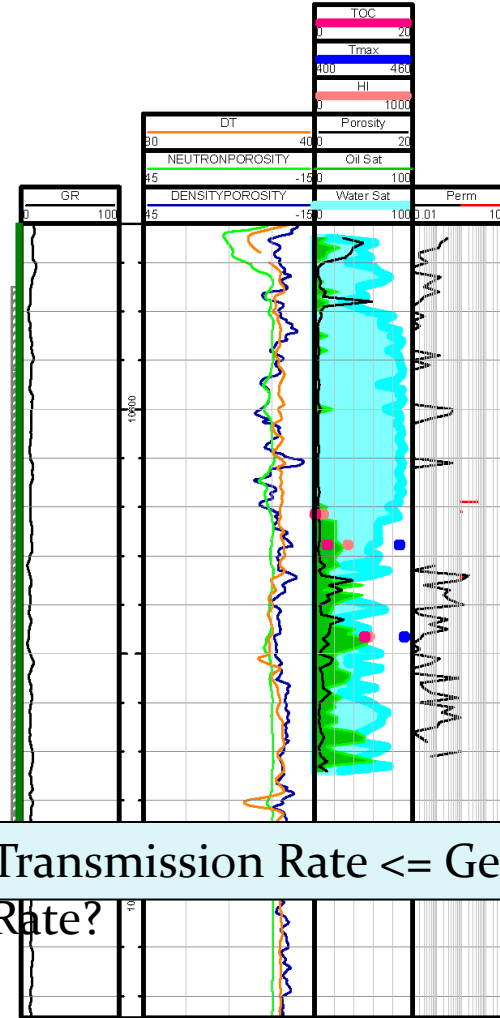
High Oil Saturations  
Elevated Fluid Pressure



33023003280000  
 SWAMPY-MOSSER 21-9  
 ENERPLUS RESOURCES USA CORPORATION



33033000440000  
 KREMERS 21X-22R  
 DENBURY ONSHORE, LLC



Transmission Rate <= Generation Rate?

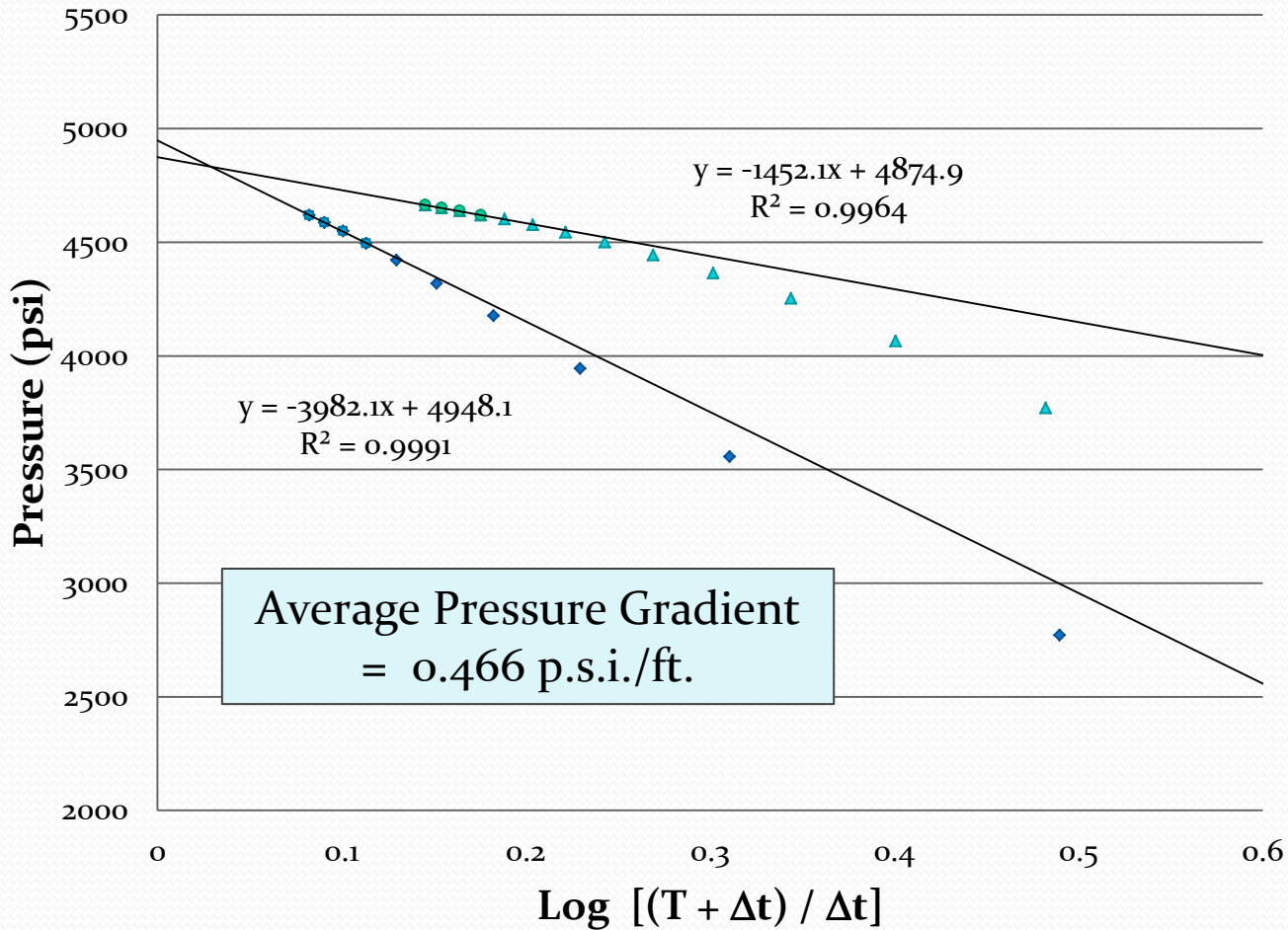
Rate?

Transmission Rate > Generation Rate?

# Horner Plot - Kremers 21X-22R

NDIC: 6272

DST Interval: 10528 - 10665' depth



# Kerogen Kinetics and Rock Permeability are Critical

Source Rock

Adjacent Rock

Generation Rate < Transmission Rate → Migration

## **Kerogen Kinetics**

Activation Energy  
Frequency Factor  
Temperature  
Kerogen Mass

## **Permeability**

Fluid Viscosities  
Pore Space Texture  
Pressure Difference

Open

High Water Saturations  
Hydrostatic Fluid Pressure

Generation Rate = Transmission Rate → **Local Accumulation**

Organic Reservoir Seal  
Complex  
Semi-Closed  
High Oil Saturations ?  
Elevated Fluid Pressure?

# Evaluating the Organic Component Generation Rate = Kerogen Kinetics

- How fast **ARE** HCs generated?

- Arrhenius Equation

$$dx/dt = A e^{-E_a/RT} x$$

Where:

T = Temperature (°K)

x = kerogen mass

t = time

$E_a$  = Activation Energy

A = Frequency Factor

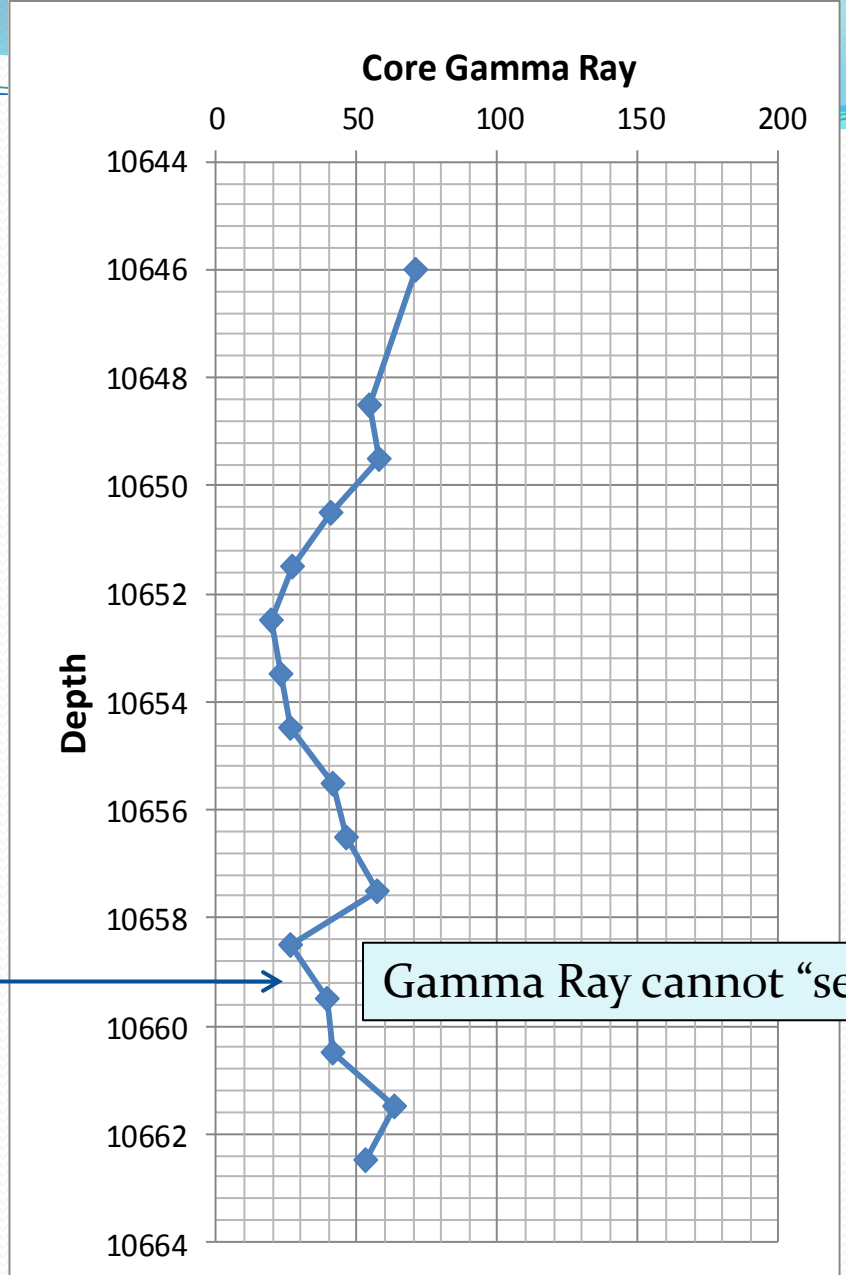
R = Gas constant

# Kremers 21-22

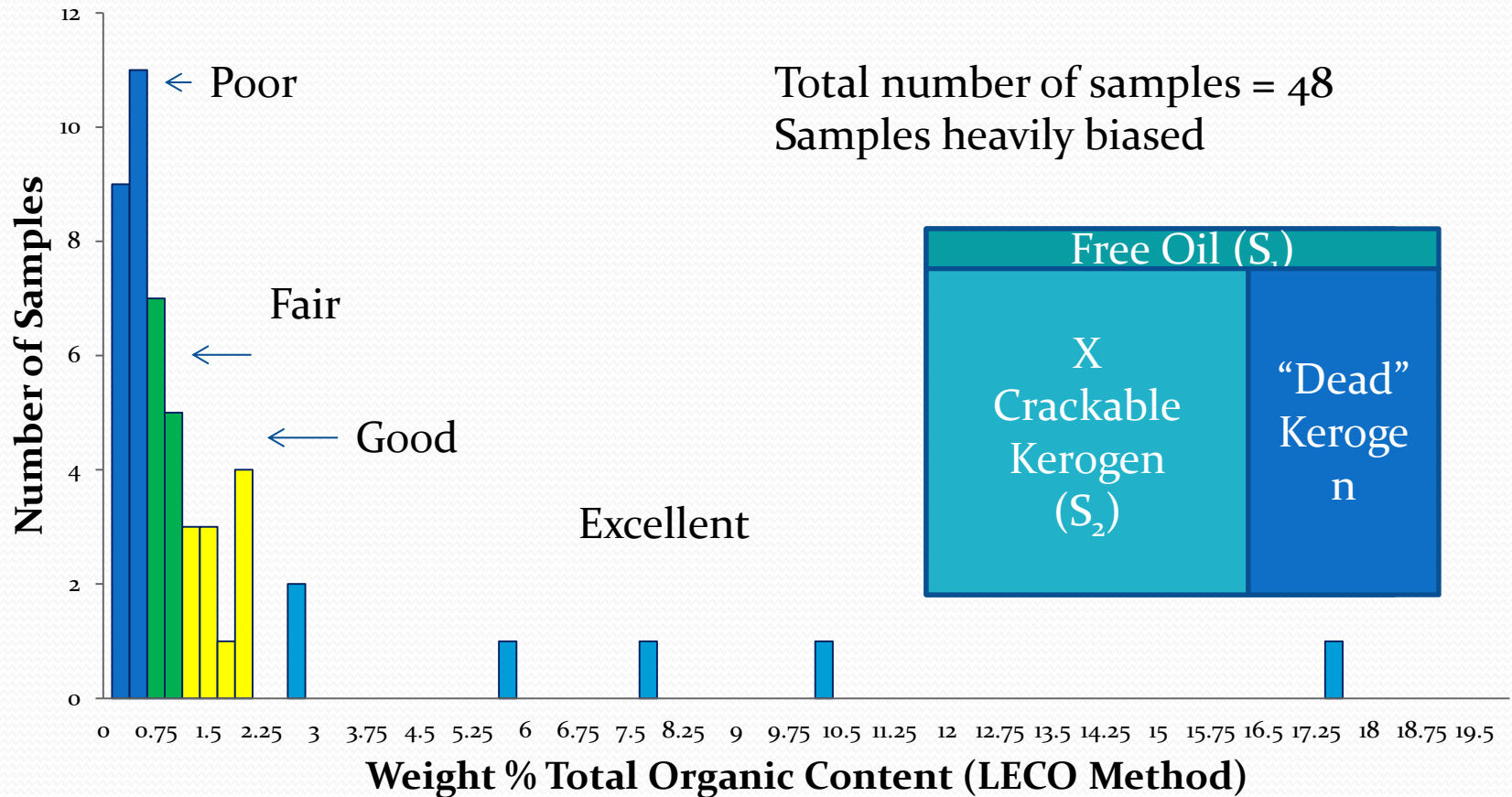
## Core Gamma Ray



Sample ID	6272-10659.1
Well Name	Kremers 21X-22R
Depth	10659.1
Formation	Red River
TOC (wt.%)	10.25
S <sub>2</sub> (mg/g)	57.65
T <sub>max</sub> (°C)	455
HI	562
OI	5



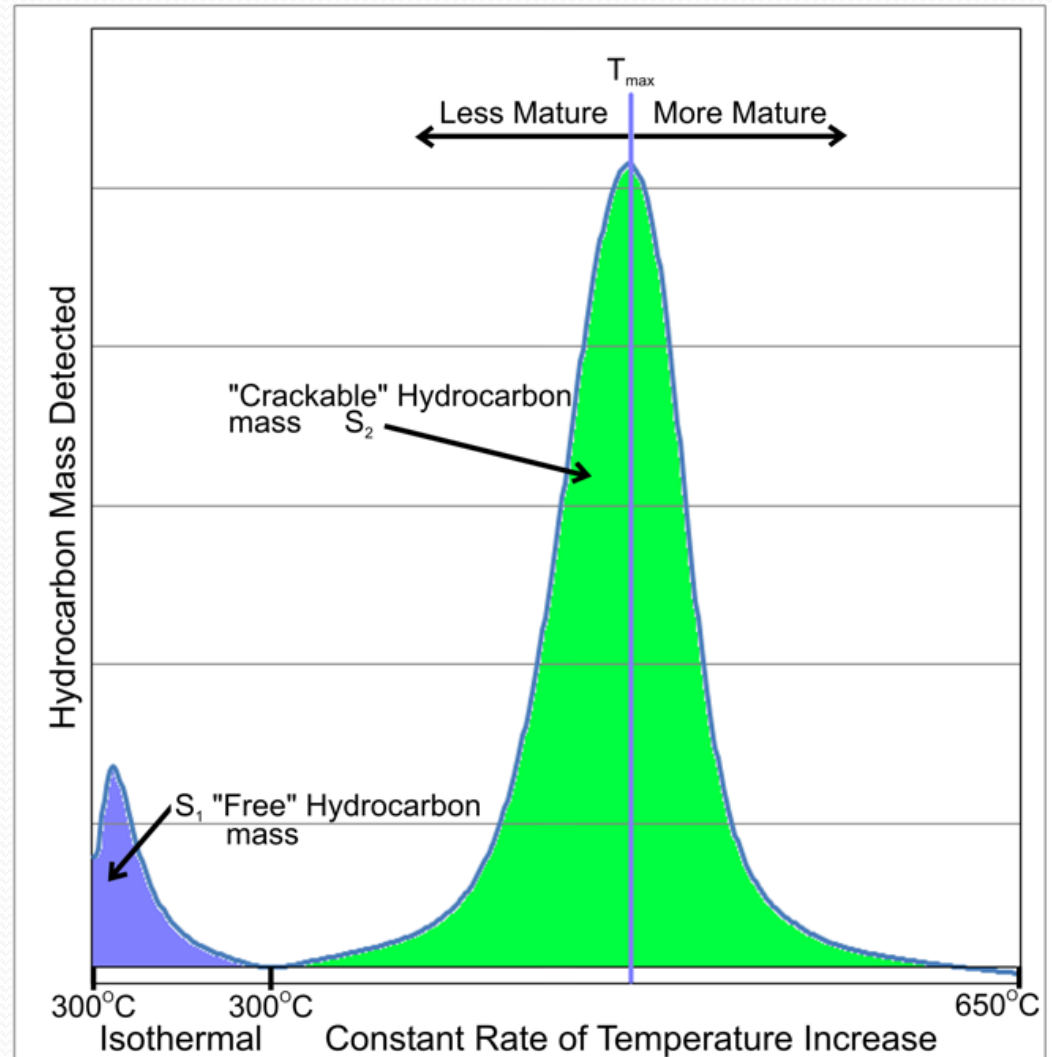
# How much reactive kerogen (x) is there?



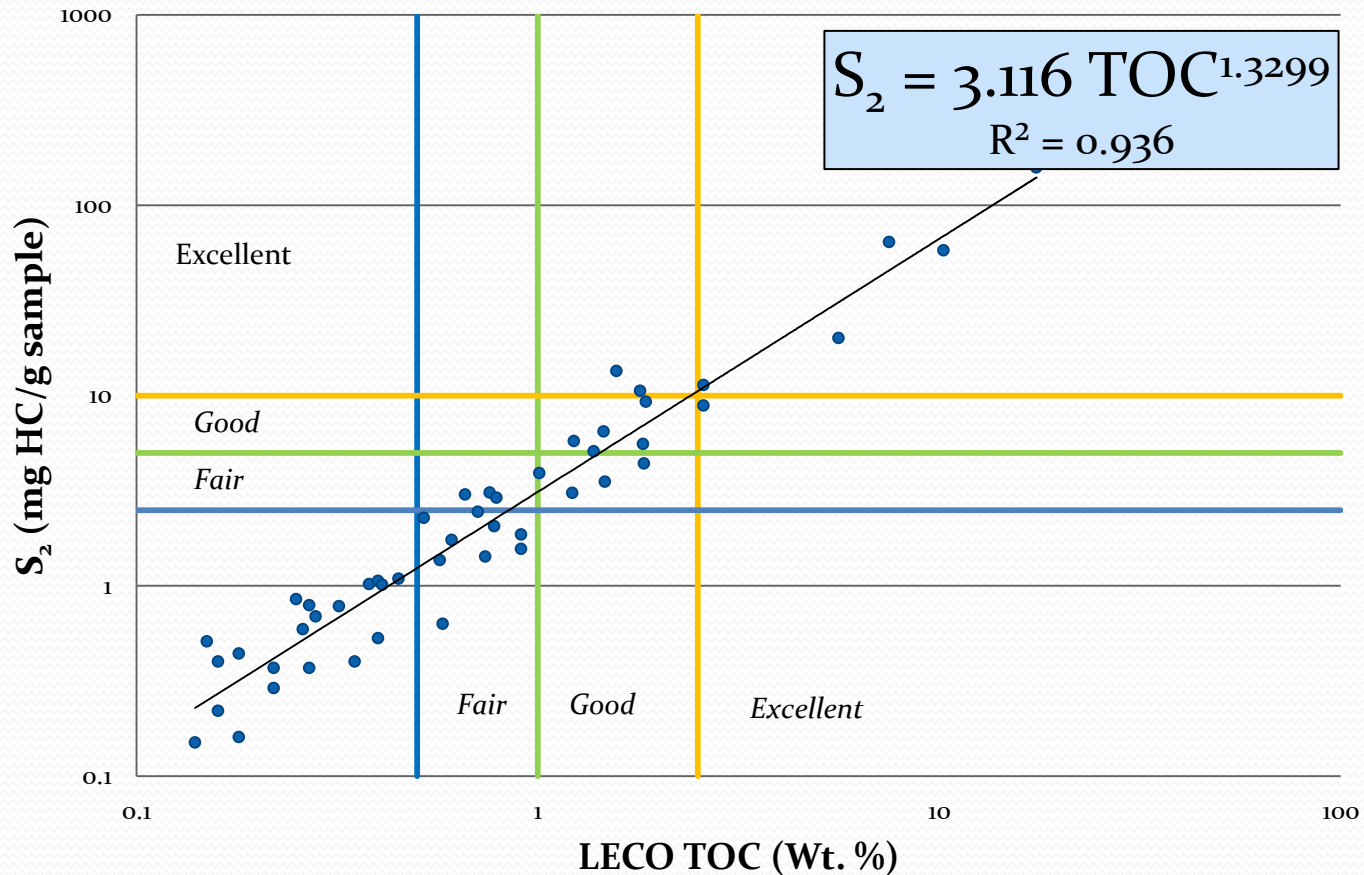
# Rock Eval Pyrogram

- Heating Rate – 25°C/min
- ~ 0.1 g sample
- **S<sub>2</sub> – Mass crackable kerogen (mg/g)**

Free Oil (S <sub>1</sub> )	
X Crackable Kerogen (S <sub>2</sub> )	?

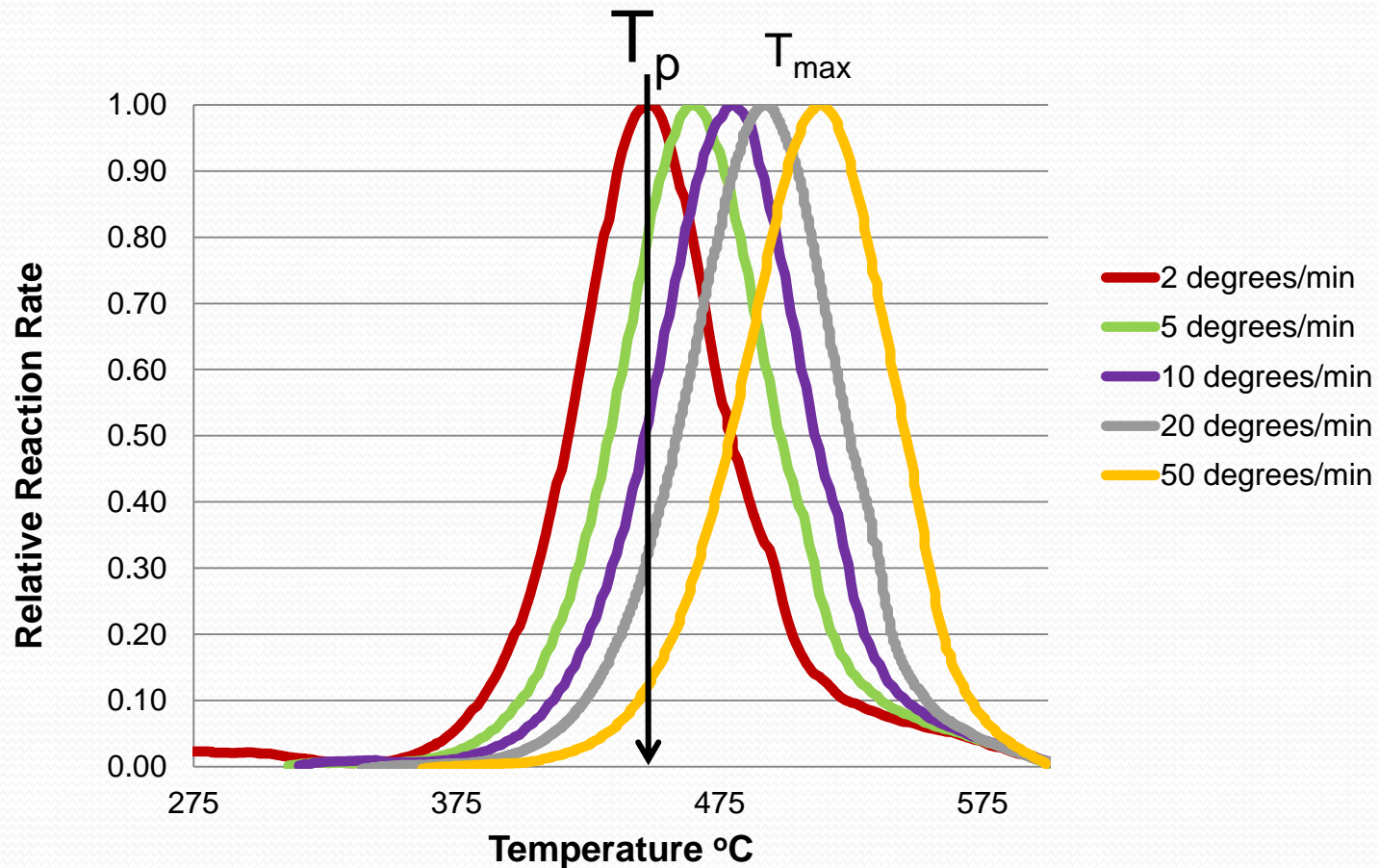


# Red River % TOC to S<sub>2</sub> Conversion (Provisional)



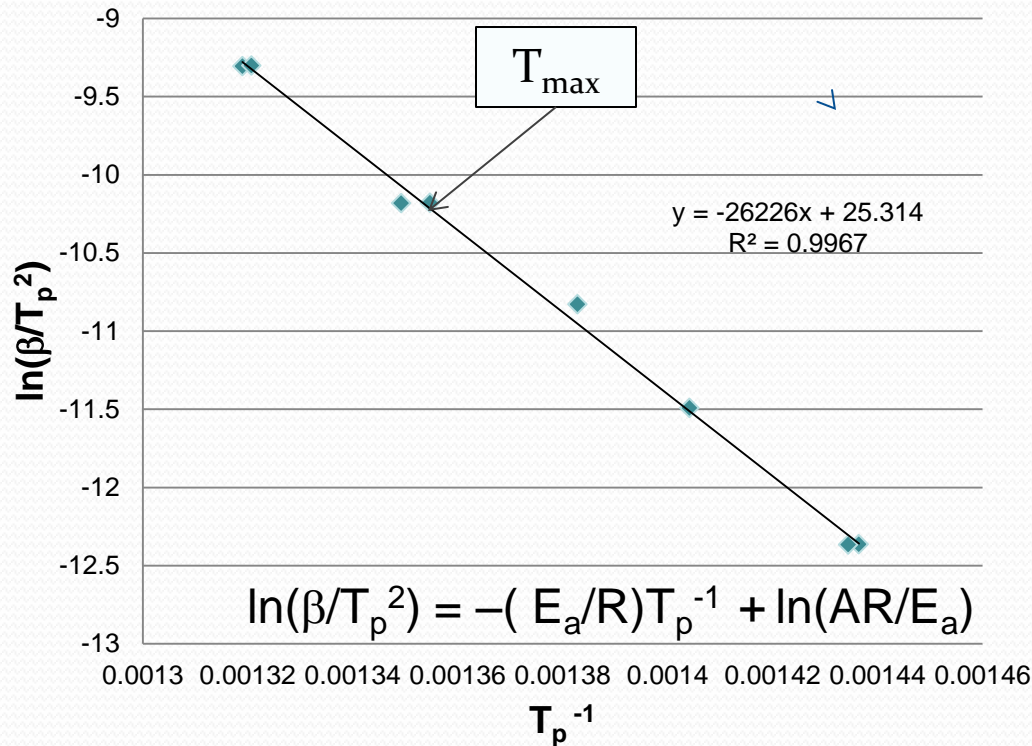


# Oil Generation Rates from Non Isothermal Pyrolysis



# Experimental Determination of $E_a$ and A. How $T_{max}$ Fits In

N&D 1-05H 9469

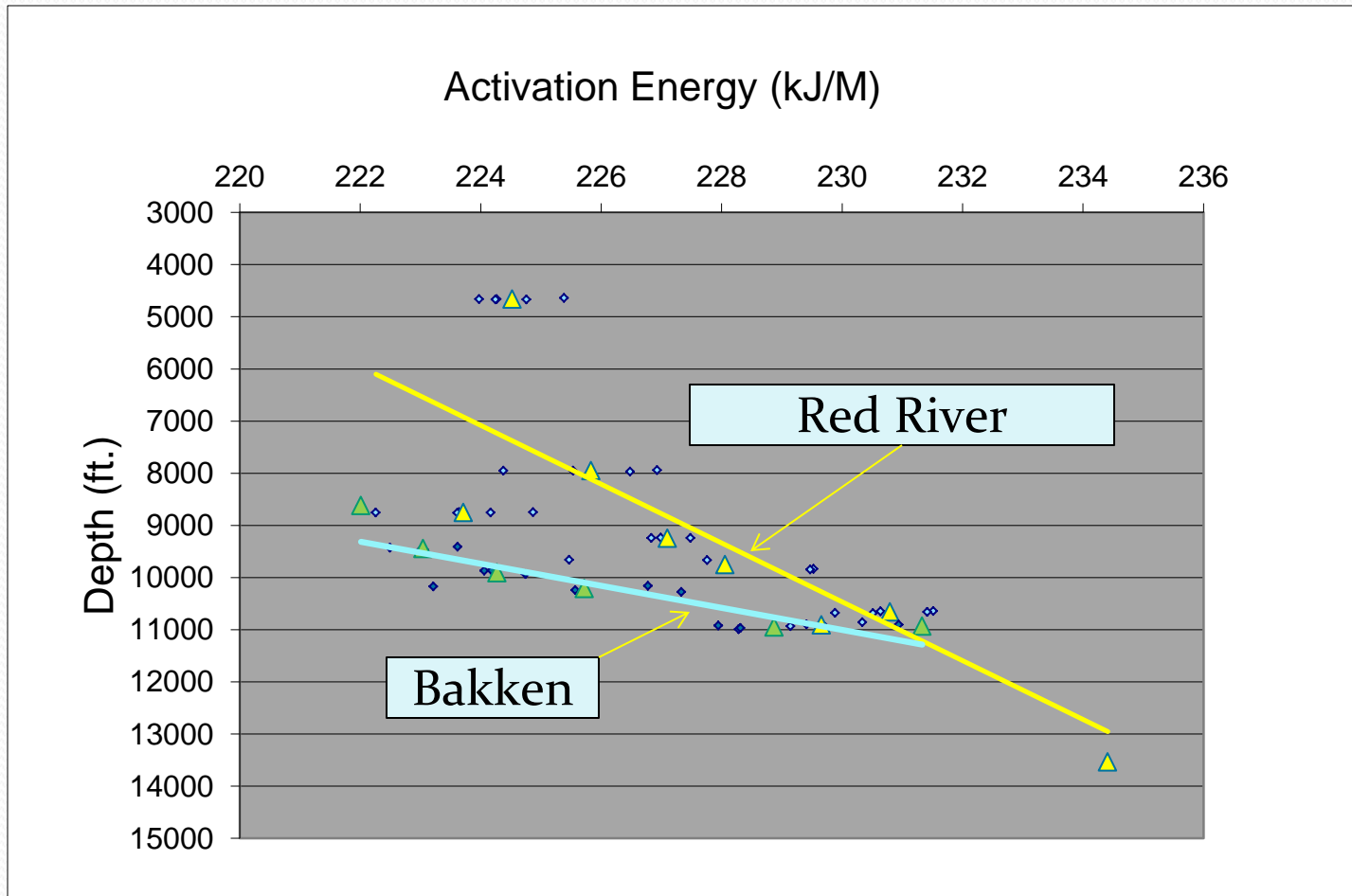


- $\beta$  = Heating Rate ( $^{\circ}\text{K}/\text{Min}$ )
- $T_p$  = Peak Reaction Temp. ( $^{\circ}\text{K}$ )
- $E_a$  = Activation Energy
- A = Frequency Factor (1/min)
- R = Gas Constant (kJ/ $^{\circ}\text{K}$ -mole)

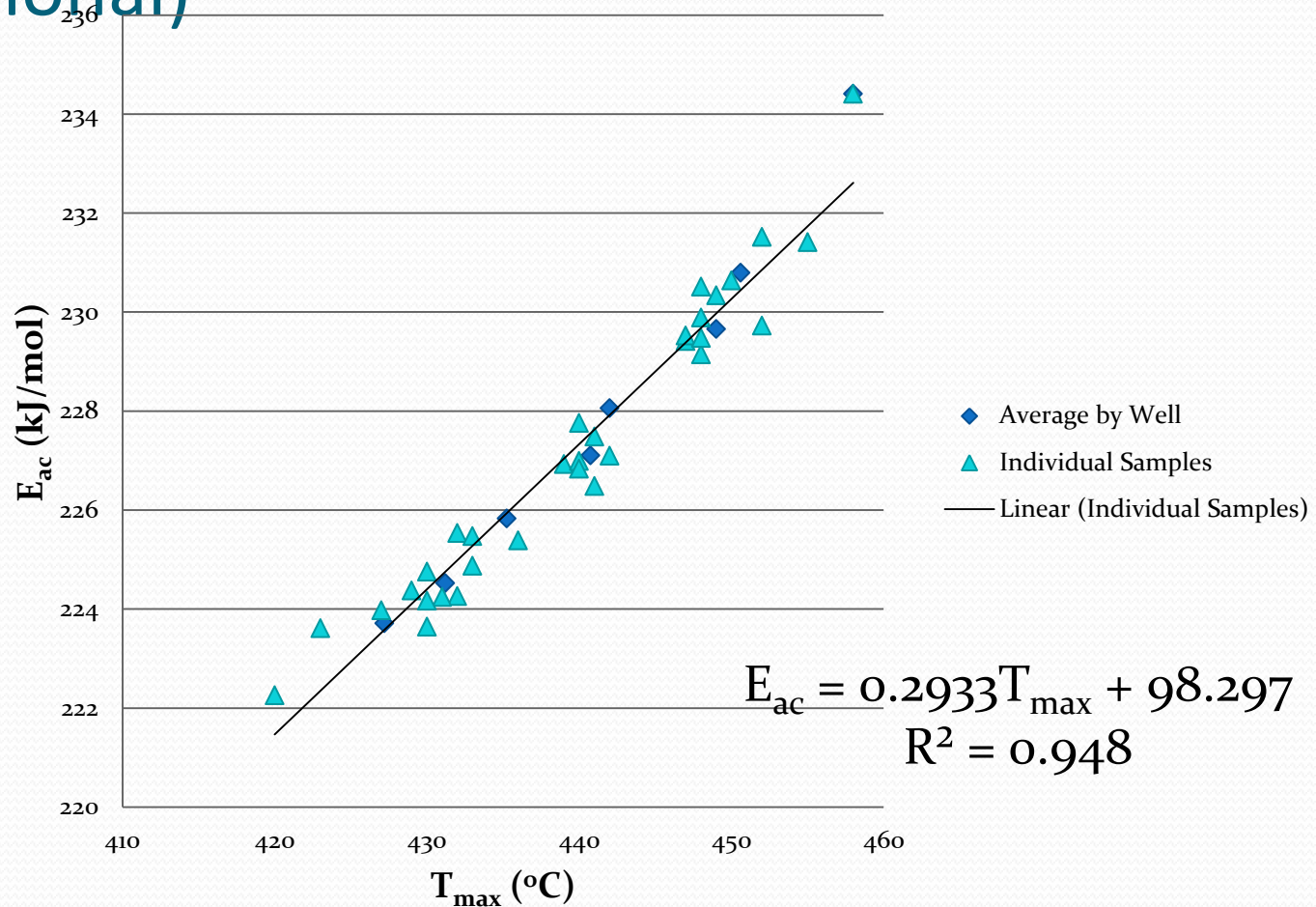
# Bakken Comparison

Well	E <sub>a</sub> kJ/mol	Est. Temp (oC)	k mol/my	Well	E <sub>a</sub> kJ/mol	Est. Temp (oC)	k mol/my
<i>Stenejhem HD 27-1</i>	229	138	2.54E-02	<i>Grant Carlson No.1</i>	234	160	1.90E-01
<i>Federal DG-1</i>	231	134	7.28E-03	Miller 1-21	228	121	1.92E-03
<i>Texel 21-35</i>	226	121	3.53E-03	Kremers 21X-22R	231	124	1.31E-03
Braaflat 11-11H	224	109	7.59E-04	Swampy-Mosser 21-9	230	122	1.24E-03
N&D 1-05H	223	106	5.97E-04	E-M Leland 10-15	227	116	1.07E-03
Dobrinski 18-44	222	100	2.64E-04	Karch 1	224	100	1.39E-04
				Little Boot 15-44	226	87	5.25E-06
				Naaden No.1	225	66	6.98E-08

# “Maturation” of the Red River is not the same as the Bakken



# Red River $T_{\max}$ to $E_{ac}$ conversion (provisional)



# Estimating Reaction Rates from RockEval6

$$dx/dt = A \exp^{-E_{ac}/RT} x$$

$$dS_2/dt \sim A \exp^{-E_{ac}/RT} S_2$$

$$S_2 = \text{mg Hydrocarbon} / \text{g Sample}$$

$$A = 3.15 \times 10^{27} \text{ m.y.}^{-1}$$

$$R = 0.008314 \text{ kJ/mol}$$

$$E_{ac} = 0.29 T_{max} + 98.3$$

$$T = \text{Formation Temperature (}^\circ\text{K)}$$

$$t = \text{time (m.y.)}$$

$$dS_2/dt = A e^{-(0.29 T_{max} + 98.3)/RT} S_2$$

# Conclusions

- Assaying the organic carbon content of the Red River is difficult without core.
- Activation energies of Red River kerogenites increase with maturation.
- Maturation induced variations in activation energies for the Red River Fm. are not the same as for the Bakken Fm.
- It may be possible to estimate an “index” that is proportional to the oil generation rate in the Red River using experimentally determined relationships between RockEval data and nonisothermal kinetic data.