

Gas Shale: Adsorbed component assessment



Jack Breig
Newfield Exploration

Outline

Geological Backdrop

Adsorption science

Measurement methodology

Key parameters for assessment

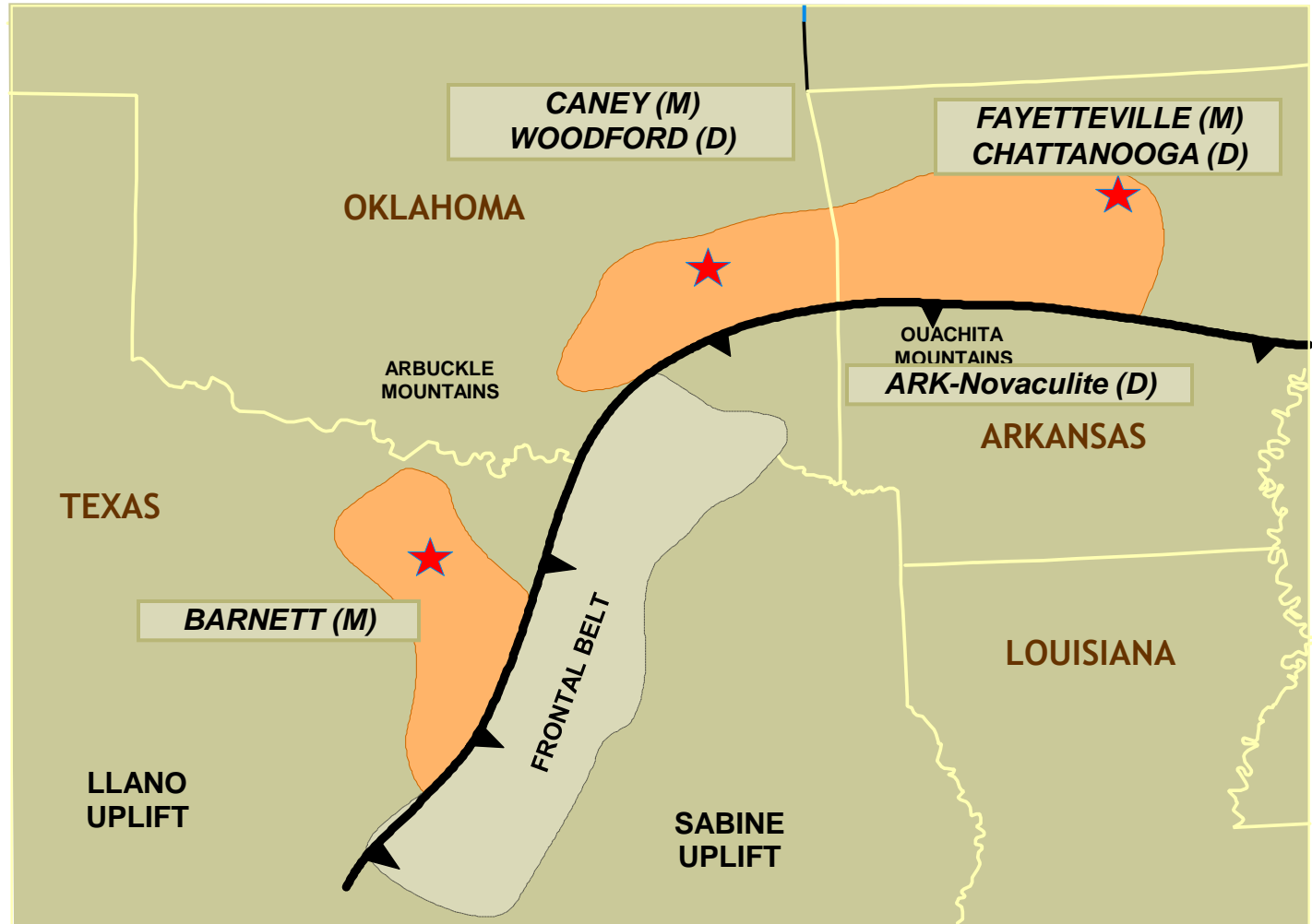
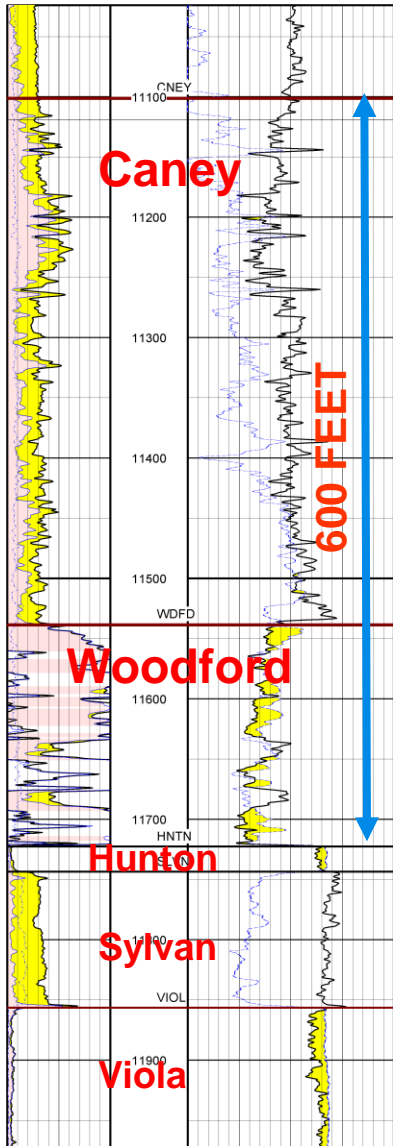
Petrophysical methods for TOC content

Source rock maturity & gas composition

Methodology to play analysis

Sorbed Gas in Place

Mississippian-Devonian Black shales



Woodford formation in outcrop



- Lightly colored facies caused by biodegradation of organic component of 'shale'

Woodford formation in core



Black color caused by elevated organic carbon component

Woodford: Chert facies

$\phi = 2.49\%$

$k_e = 5.93E-06$ md

$S_w = NA$

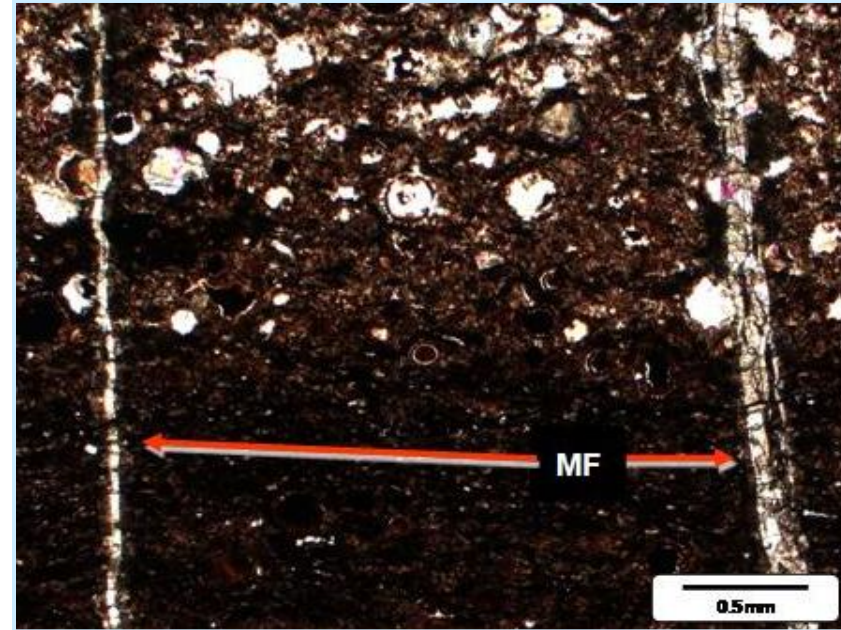
$S_g = NA$

$S_o = NA$

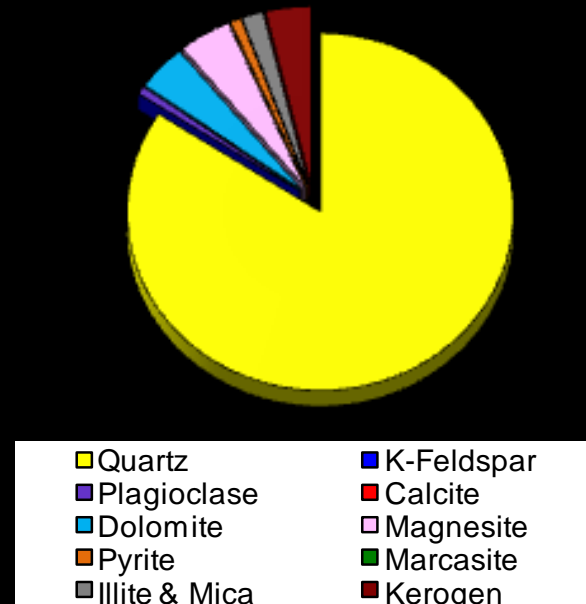
GD = 2.61 g/cc

TOC = 1.70%

Ro = 2.15

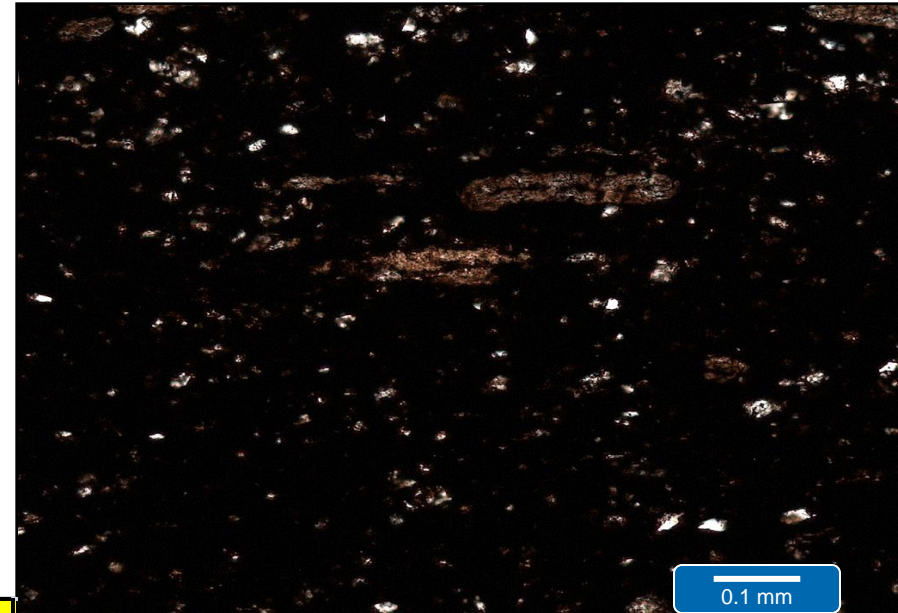


Chert Mineralogy (volume %)	Min	Max	Avg
Quartz	63.1	95.4	80.6
K-Feldspar	0.0	1.5	0.1
Plagioclase	0.0	11.6	1.6
Calcite	0.0	0.0	0.0
Dolomite & Fe-Dolomite	0.0	4.9	2.1
Magnesite	0.0	8.7	1.8
Pyrite	0.4	5.1	1.5
Marcasite	0.0	1.3	0.2
Illite & Mica	0.0	21.9	5.4
Kerogen	2.3	13.7	6.7
Vclay	0.0	21.9	5.4

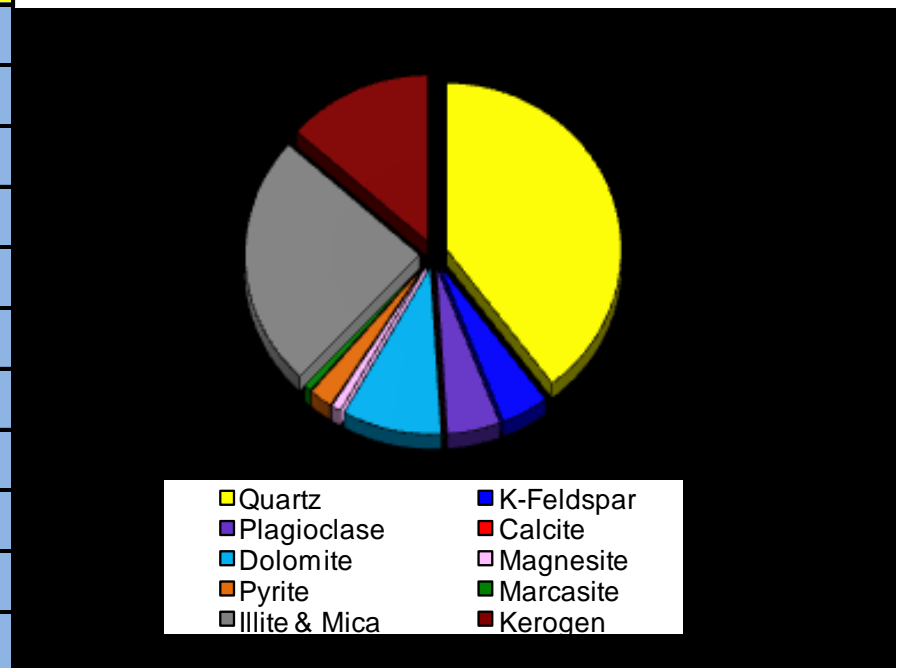


Woodford: Siliceous mudstone facies

$\phi = 4.75\%$ $k_e = 8.16E-06$ md
 $S_w = NA$ $S_g = NA$
 $S_o = NA$ $GD = 2.56$ g/cc
TOC = 4.16 wt% **Ro = 2.3**



Shale Mineralogy (volume %)	Min	Max	Avg
Quartz	25.5	68.5	50.0
K-Feldspar	0.0	5.7	2.3
Plagioclase	1.5	9.9	5.0
Calcite	0.0	14.0	0.7
Dolomite & Fe-Dolomite	0.0	31.8	5.3
Magnesite	0.0	2.6	0.2
Pyrite	1.2	11.4	4.5
Marcasite	0.0	4.9	1.2
Illite & Mica	9.2	35.8	18.7
Kerogen	2.0	18.3	11.9
Vclay	9.2	35.8	18.7



Gas swollen Woodford cuttings bags— doubled plastic bags inside cloth bags



29 12 2005

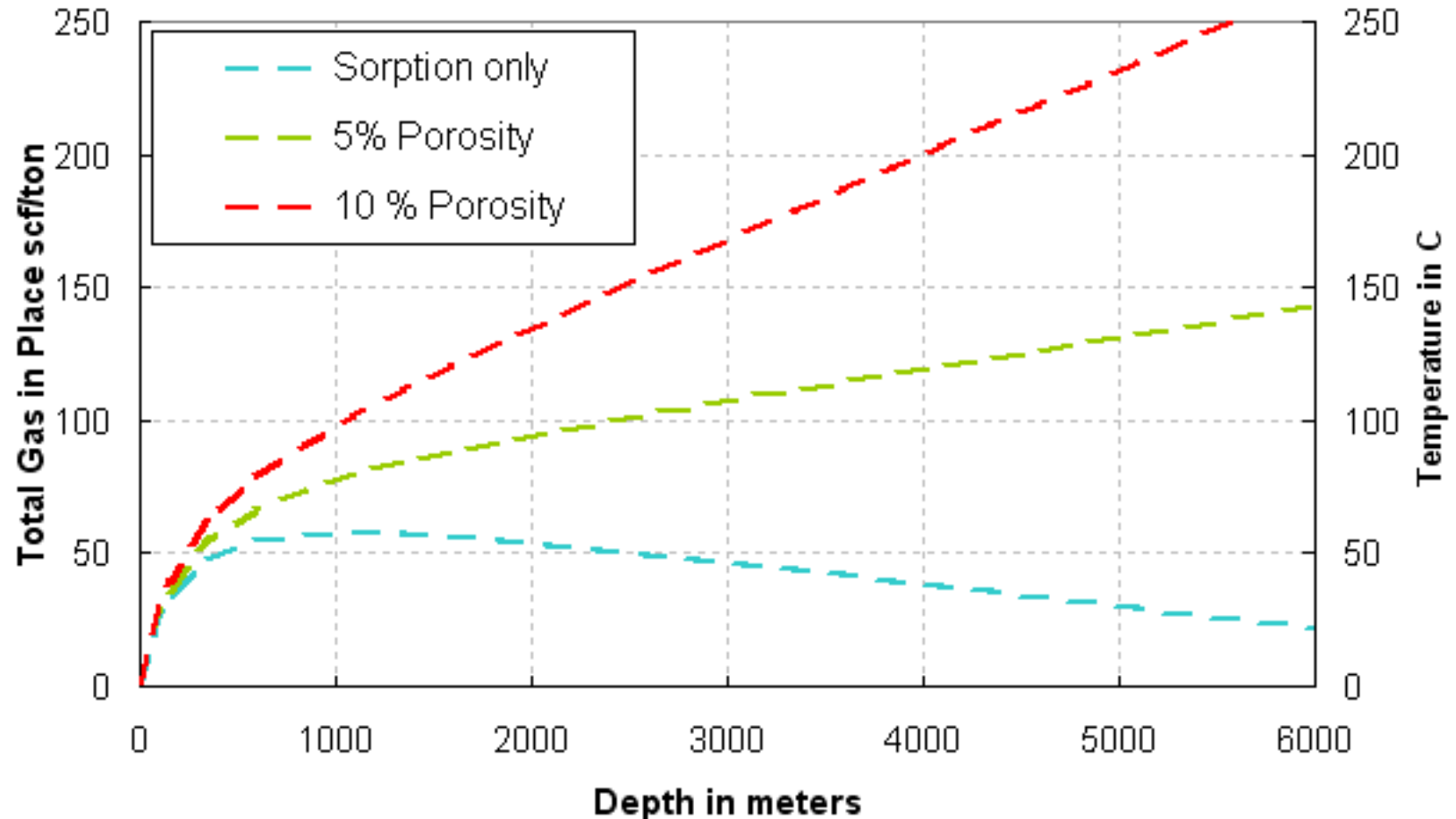
Cannister desorption test

Gas Composition Data (Continued)

Sample Number	Collection Point hours	As-Received Gas Content scf/ton	Incremental Gas Content ² scf/ton	Gas Analysis (O ₂ , N ₂ and H ₂ Mole Fractions Omitted) ¹					Dry Btu/ft ³	Saturated Btu/ft ³
				C ₁ mole %	C ₂ mole %	C ₃ -C ₁₀ mole %	CO ₂ mole %	Total mole %		
Average Depth (ft): 8,132.5				Lost Gas Content: 38.12%			Woodford Shale			
638-23-1	5.9	59.1	59.1	95.29	4.24	0.38	0.09	100.00	1,052.3	1,034.0
638-23-2	11.7	76.9	17.8	94.34	4.93	0.45	0.28	100.00	1,056.8	1,038.4
638-23-3	22.5	96.6	19.6	91.42	6.91	0.72	0.95	100.00	1,069.6	1,051.0
638-23-4	24.7	98.4	1.8	92.13	7.05	0.74	0.08	100.00	1,080.0	1,061.2
638-23-5	140.2	111.7	13.4	79.78	16.55	2.08	1.59	100.00	1,160.3	1,140.1
638-23-6	400.6	115.4	3.7	67.59	28.33	3.83	0.24	100.00	1,293.8	1,271.3
638-23-7	635.2	116.0	0.6	63.02	0.00	0.00	36.98	100.00	639.4	628.3
638-23-C ⁴	635.2	133.9	17.9	23.63	43.17	22.53	10.66	100.00	1,628.3	1,600.0
Apparent Gas Composition³				82.60	11.89	3.69	1.82	100.00	1,150.7	1,130.7
Average Depth (ft): 8,163.5				Lost Gas Content: 11.25%			Woodford Shale			
638-26-1	6.4	45.4	45.4	90.66	6.45	0.38	2.54	100.00	1,043.8	1,025.6
638-26-2	12.0	21.7	6.3	95.70	3.82	0.28	0.20	100.00	1,046.1	1,027.9
638-26-3	22.8	52.6	30.9	91.90	4.85	0.37	2.88	100.00	1,028.4	1,010.5
638-26-4	25.1	54.9	2.3	94.28	4.99	0.38	0.35	100.00	1,055.4	1,037.0
638-26-5	156.9	81.7	26.8	88.53	8.55	0.59	2.33	100.00	1,065.9	1,047.3
638-26-6	401.0	88.9	7.2	82.50	13.68	0.99	2.83	100.00	1,106.5	1,087.2
638-26-7	635.4	91.6	2.7	79.59	16.65	1.27	2.50	100.00	1,137.5	1,117.7
638-26-C ⁴	635.4	114.2	22.5	42.63	45.11	7.13	5.12	100.00	1,425.4	1,400.6
Apparent Gas Composition³				78.73	16.14	2.12	3.01	100.00	1,142.3	1,122.4

Note increasing contribution of C₂ and C₃-C₁₀ as sample desorption proceeds from high to low pressure (collection point time)

Sorbed gas capacity in relationship to free gas



Measurement methodology

- Determine the chemical composition of produced gas
- Derive storage capacity relationships for each chemical species for appropriate ranges of:
 - Temperature
 - Pressure
 - TOC content
 - Source rock maturity

Gas composition examples from western Arkoma Basin (Wet to dry gas transition)

THURMOND-McGLOTHLIN, INC.

THE NATURAL GAS MEASUREMENT COMPANY

501 East Main Street
 Wilburton, OK 74578
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 Website www.tm-ems.com

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FRACTIONAL ANALYSIS *		DATE RUN: September 21, 2006	
COMPONENTS	MOL %	GPM	
Carbon Dioxide	CO2	0.745	COMPANY: NEWFIELD
Nitrogen	N2	1.820	PURCHASER: CATTLE 1 H-21
Methane	C1	78.181	LEASE: CATTLE 1 H-21
Ethane	C2	12.608	STATION: 33
Propane	C3	4.523	PRESSURE: 1.239
iso-Butane	IC4	0.382	TEMPERATURE: 6033
n-Butane	NC4	1.044	CYLINDER: JW
neo-Pentane	neo C5	0.000	ANALYSIS BY: DS
iso-Pentane	IC5	0.223	SECURED BY: DS
n-Pentane	NC5	0.017	DATE SAMPLED: 9/21/2006
Hexane +	C6+	0.458	LEGAL:
		100.000	

FRACTIONAL ANALYSIS *		DATE RUN: July 25, 2005	
COMPONENTS	MOL %	GPM	
Carbon Dioxide	CO2	1.012	COMPANY: NEW FIELD
Nitrogen	N2	0.751	PURCHASER: REYNOLDS 1-11
Methane	C1	94.288	LEASE: REYNOLDS 1-11
Ethane	C2	3.135	STATION: 241
Propane	C3	0.592	PRESSURE: 0.833
iso-Butane	IC4	0.064	TEMPERATURE: 0.162
n-Butane	NC4	0.082	CYLINDER: 114
neo-Pentane	neo C5	0.000	ANALYSIS BY: BB
iso-Pentane	IC5	0.022	SECURED BY: LB
n-Pentane	NC5	0.015	DATE SAMPLED: 7/22/2005
Hexane +	C6+	0.037	LEGAL:
		100.000	

GASOLINE CONTENT @ 14.65 PSIA & 60 F

REMARKS:

	GPM
PROPANE & HEAVIER	1.777
BUTANE & HEAVIER	0.539
PENTANE & HEAVIER	0.087

Gross Heating Value	
BTU @ 14.65 PSIA & 60 F-REAL	
Dry	1206.3
Wet	1185.3

SPECIFIC GRAVITY- REAL	Z= 0.9988891
	0.7134
MOL WEIGHT	24.56

GASOLINE CONTENT @ 14.65 PSIA & 60 F

REMARKS:

	GPM
PROPANE & HEAVIER	0.222
BUTANE & HEAVIER	0.060
PENTANE & HEAVIER	0.014

Gross Heating Value	
BTU @ 14.65 PSIA & 60 F	
Dry	1027.6
Wet	1009.7

SPECIFIC GRAVITY	0.5917
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Western margin of gas play

Core area of gas play

Gas composition examples from eastern Arkoma Basin (elevated CO₂)

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FRACTIONAL ANALYSIS *			DATE RUN:	September 21, 2006
COMPONENTS	MOL %	GPM	COMPANY: NEWFIELD	
Carbon Dioxide CO2	0.745		PURCHASER:	
Nitrogen N2	1.820		LEASE:	CATTLE 1 H-21
Methane C1	78.181		STATION:	
Ethane C2	12.608	3.352	PRESSURE:	33
Propane C3	4.523	1.239	TEMPERATURE:	
iso-Butane IC4	0.382	0.124	CYLINDER:	6033
n-Butane NC4	1.044	0.327	ANALYSIS BY:	JW
neo-Pentane neo C5	0.000	0.000	SECURED BY:	DS
iso-Pentane IC5	0.223	0.081	DATE SAMPLED:	9/21/2006
n-Pentane NC5	0.017	0.006	LEGAL:	
Hexane + C6+	0.458	0.199		
	100.000			

FRACTIONAL ANALYSIS *			DATE RUN:	October 23, 2006
COMPONENTS	MOL %	GPM	COMPANY: NEWFIELD	
Carbon Dioxide CO2	5.642		PURCHASER:	
Nitrogen N2	0.558		LEASE:	JOHNSTON 3-24
Methane C1	93.342		STATION:	
Ethane C2	0.432	0.115	PRESSURE:	683
Propane C3	0.026	0.007	TEMPERATURE:	102.9
iso-Butane IC4	0.000	0.000	CYLINDER:	5376
n-Butane NC4	0.000	0.000	ANALYSIS BY:	JW
neo-Pentane neo C5	0.000	0.000	SECURED BY:	DS
iso-Pentane IC5	0.000	0.000	DATE SAMPLED:	10/23/2006
n-Pentane NC5	0.000	0.000	LEGAL:	
Hexane + C6+	0.000	0.000		
	100.000			

GASOLINE CONTENT @ 14.65 PSIA & 60 F

REMARKS:

	GPM
PROPANE & HEAVIER	1.777
BUTANE & HEAVIER	0.539
PENTANE & HEAVIER	0.087

Gross Heating Value
BTU @ 14.65 PSIA & 60 F-REAL

Dry	1206.3
Wet	1185.3

SPECIFIC GRAVITY- REAL Z= 0.9966691

0.7134
MOL WEIGHT
24.56

GASOLINE CONTENT @ 14.65 PSIA & 60 F

REMARKS:

	GPM
PROPANE & HEAVIER	0.007
BUTANE & HEAVIER	0.000
PENTANE & HEAVIER	0.000

Gross Heating Value
BTU @ 14.65 PSIA & 60 F-REAL

Dry	950.1
Wet	933.6

SPECIFIC GRAVITY- REAL Z= 0.9978636

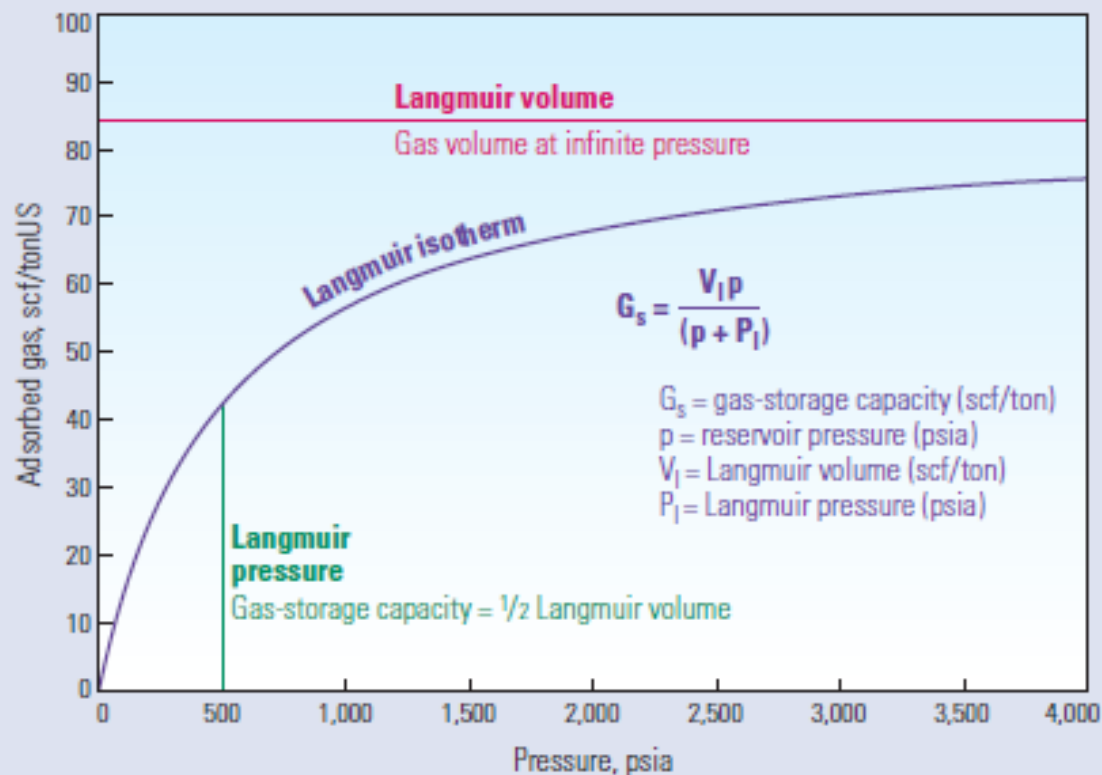
0.6144
MOL WEIGHT
20.43

RESULTS TO:
NEWFIELD

RESULTS TO:
NEW FIELD

Little CO₂ in western areas of gas play. This increases to > 10% in the deeper central parts of the basin. CO₂ can reach 75% in the south side of Red Oak field, where VRo reaches 5.0.

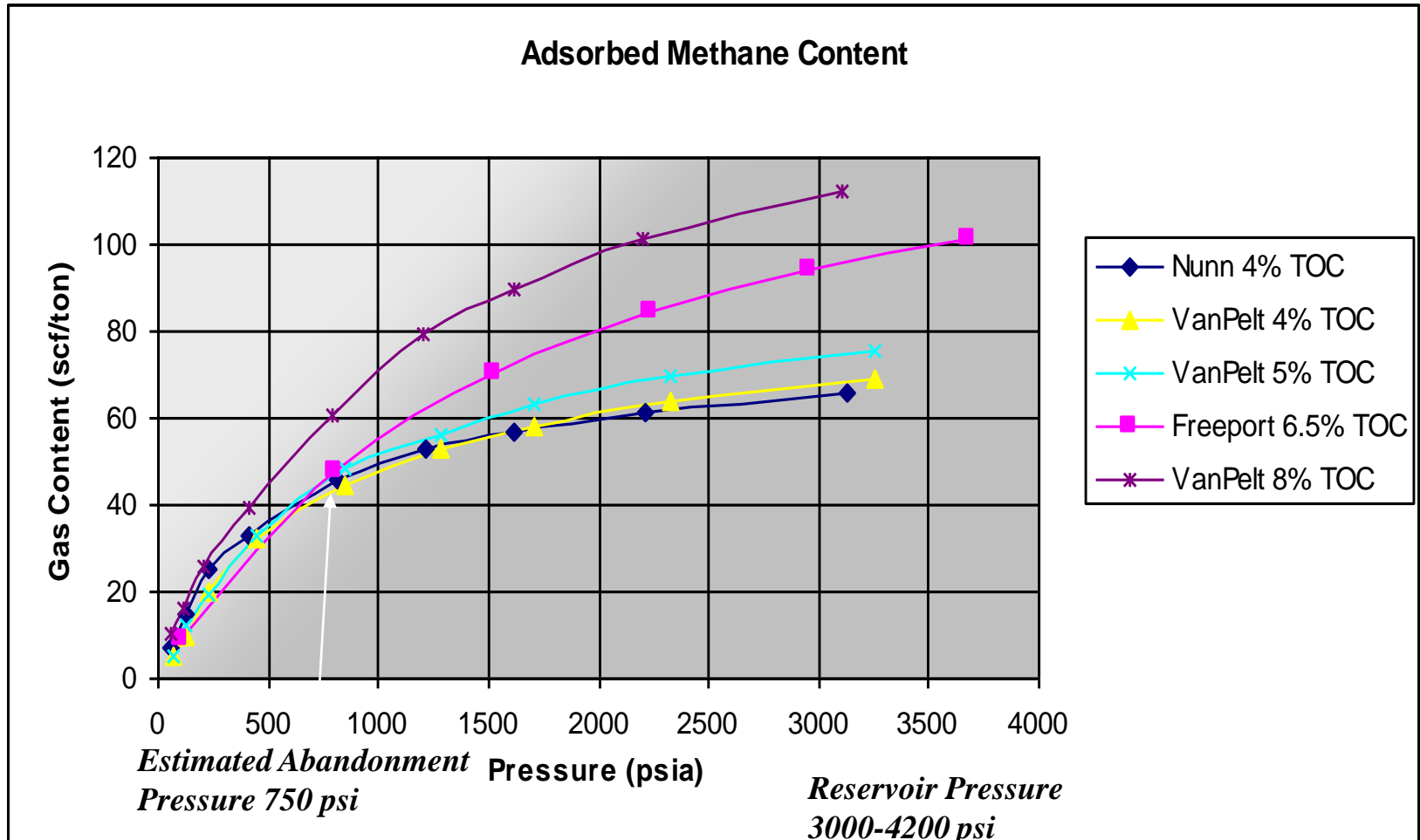
The Langmuir Isotherm



^ Adsorbed gas storage. The Langmuir isotherm (blue) shows the quantity of adsorbed gas that a saturated sample will contain at a given pressure. Decreasing pressure will cause the methane to desorb in accordance with behavior prescribed by the blue line. Gas desorption increases in a nonlinear manner as the pressure declines. Thus, in this example, a sample at 3,500-psi [24.2-MPa] pressure will have about 74 scf/ton adsorbed methane. As pressure first decreases from this point, the amount of gas desorbed is relatively small. Once the pressure has declined to 500 psi [3.4 MPa], one-half of the total gas that this shale could adsorb will have been desorbed. The remaining volume will desorb over the final 500 psi.

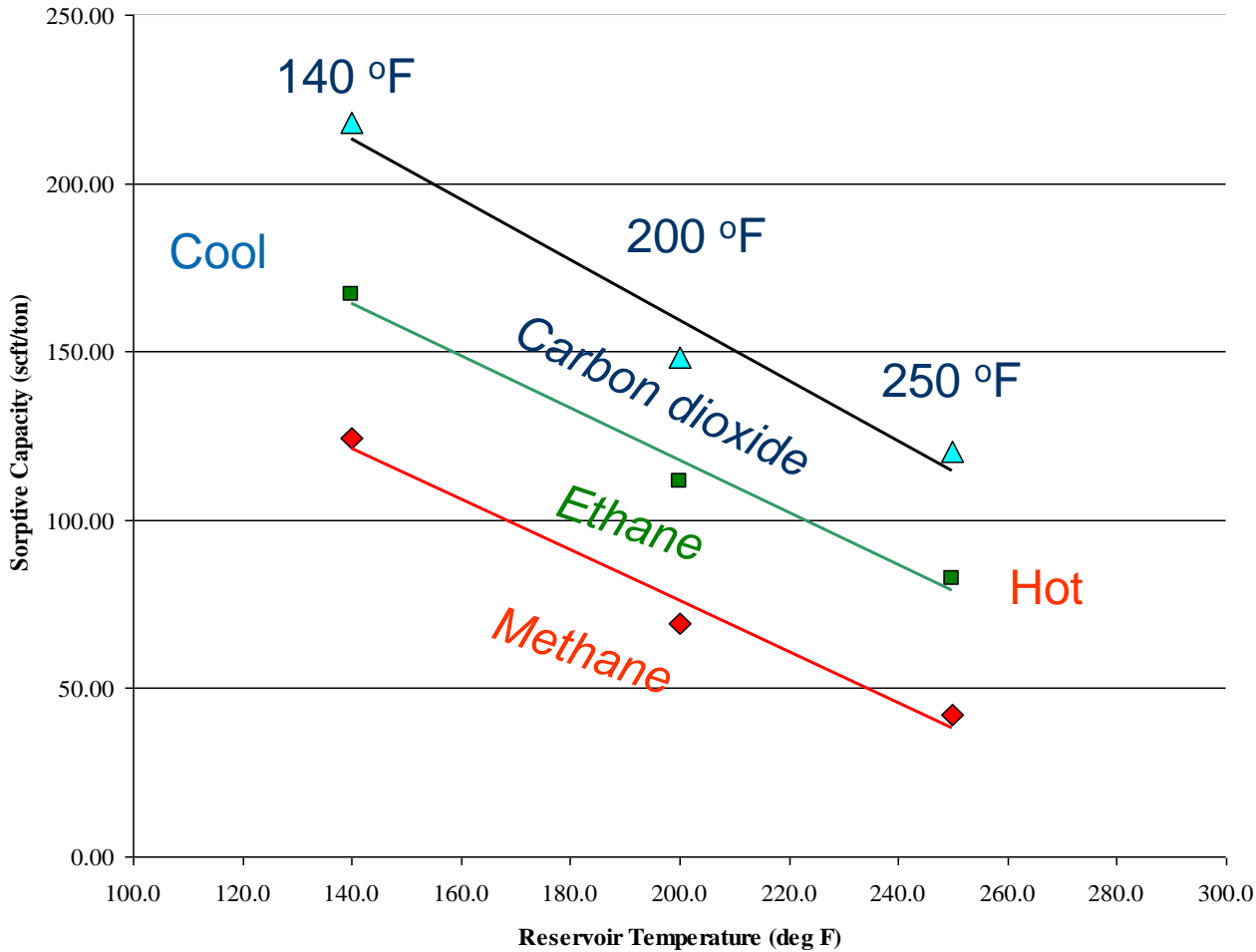
Adsorbed Gas Content

experimentally determined from core samples



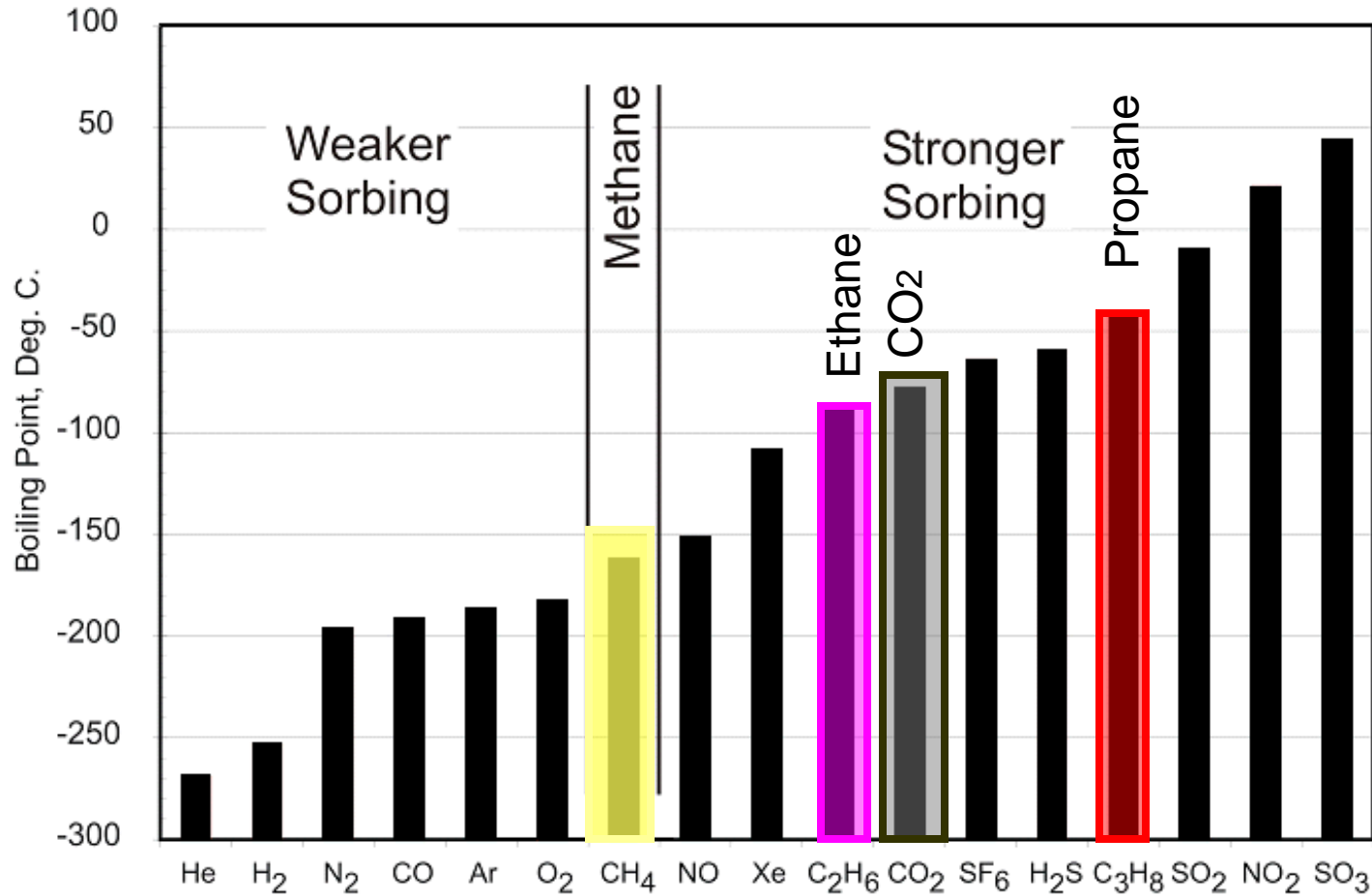
Sorptive capacity of methane, ethane, and CO2 at 3 temperatures

Sorptive Capacity at 4660 psi vs. Reservoir Temperature: Methane, Ethane, CO₂



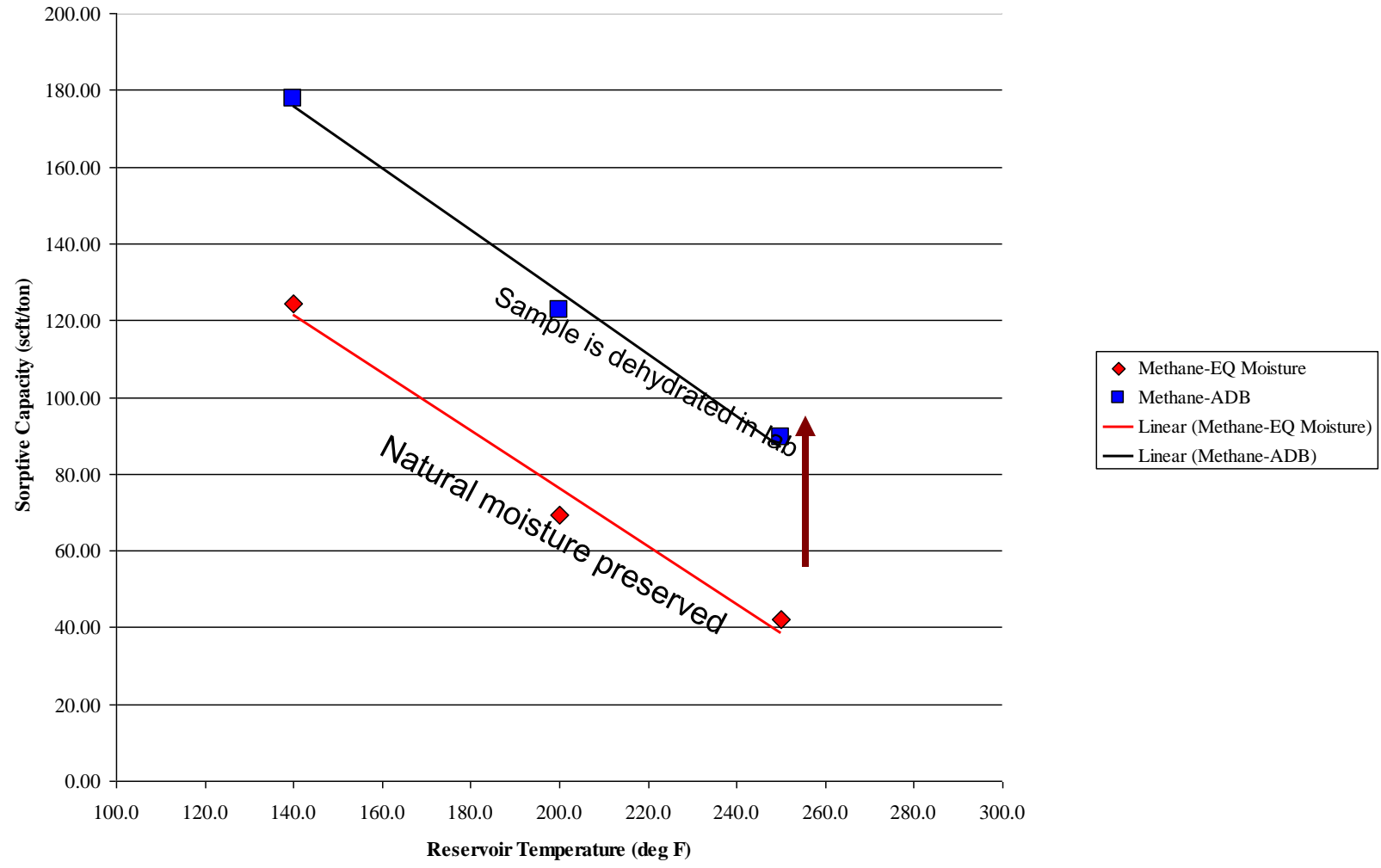
- ◆ Methane-EQ Moisture
- Ethane-EQ Moisture
- ▲ CO2-EQ Moisture
- Linear (Methane-EQ Moisture)
- Linear (Ethane-EQ Moisture)
- Linear (CO2-EQ Moisture)

Adsorption tendency in relationship to Fluid boiling point



Sorptive capacity of methane in moisture equilibrated and dried samples

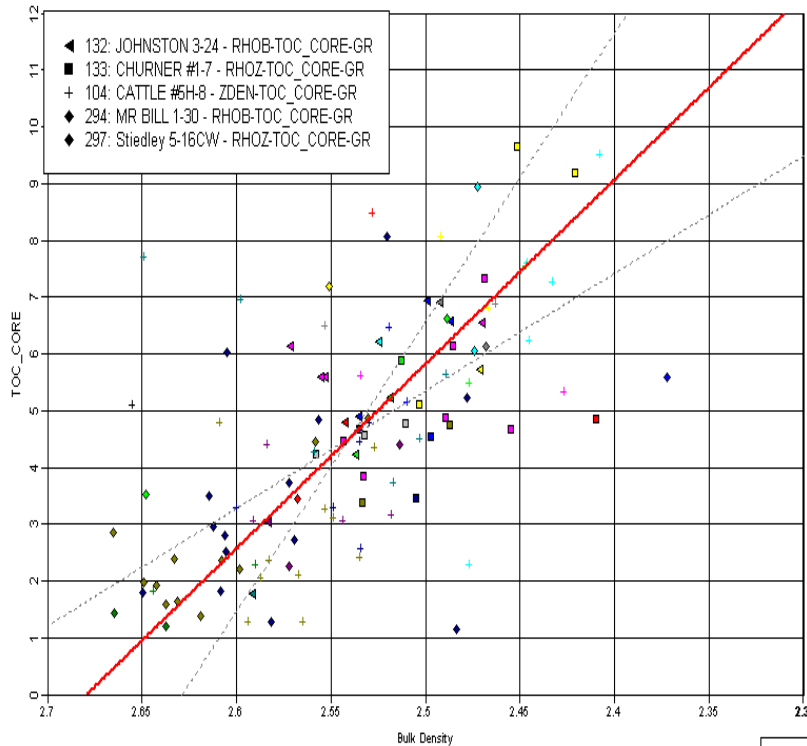
Sorptive Capacity at 4660 psi vs. Reservoir Temperature: Methane



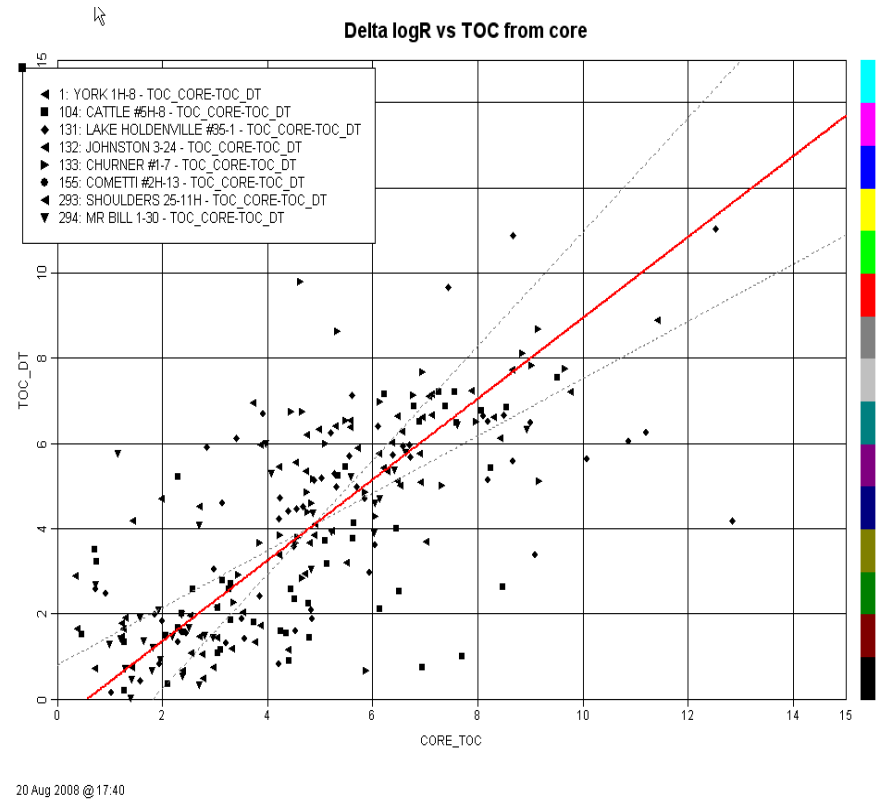
Key Parameters for assessment

- Map of Organic matter content
- Maps of reservoir temperature and pressure
- Map(s) of free gas composition
- Component storage capacity relationship, as specified in extended Langmuir isotherm relationships

TOC estimation from RHOB and DeltaT- log(Rt) Caney & Woodford shales



TOC = 87. - 34.5 * RHOB
Correlation Coefficient: r-square = 0.40

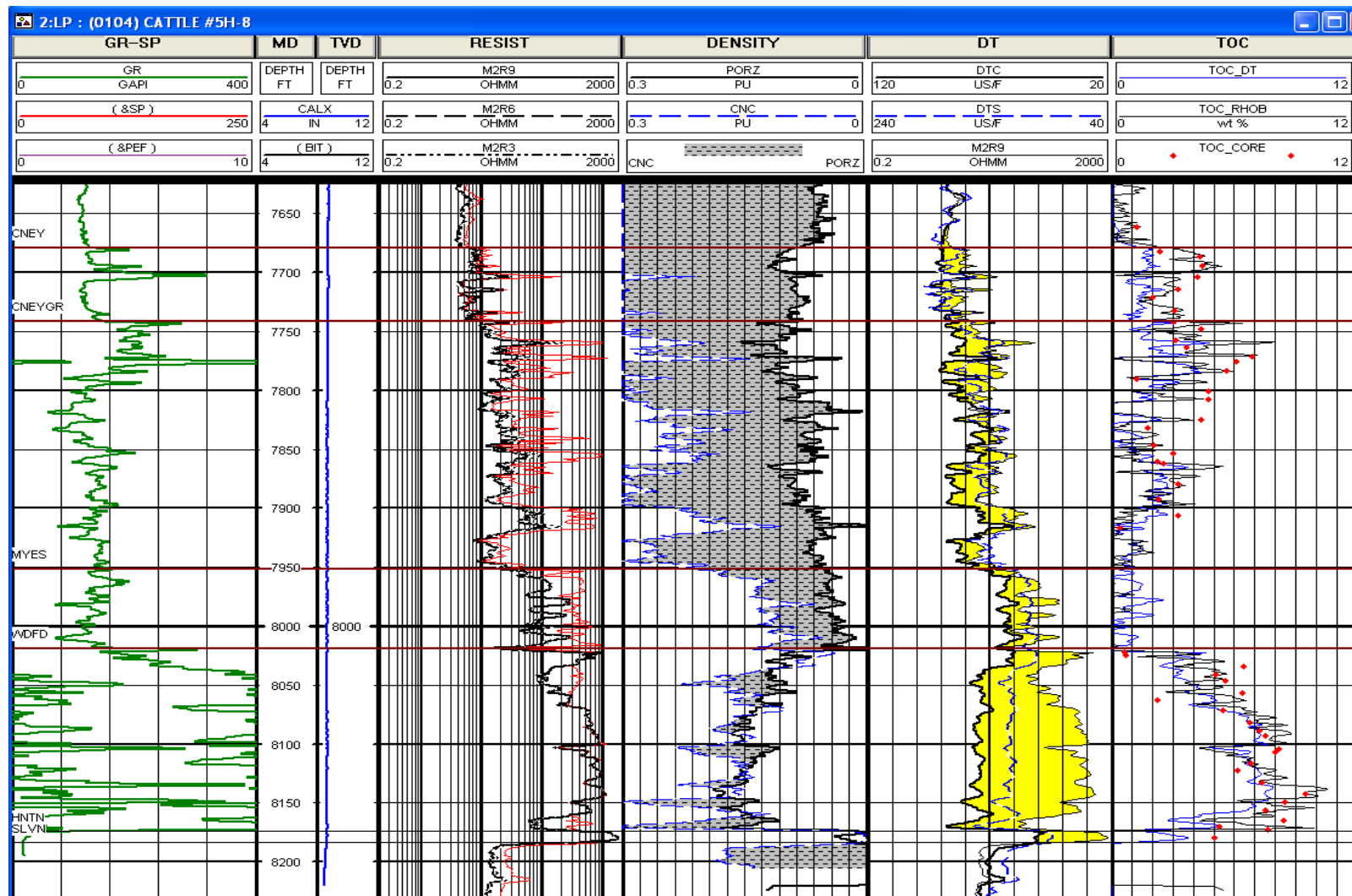


20 Aug 2008 @ 17:40

Regression : TOC = .82 * X - .57
Correlation Coefficients: r-square = 0.50

Newfield 5H-8 Cattle

TOC is approximated by petrophysical techniques



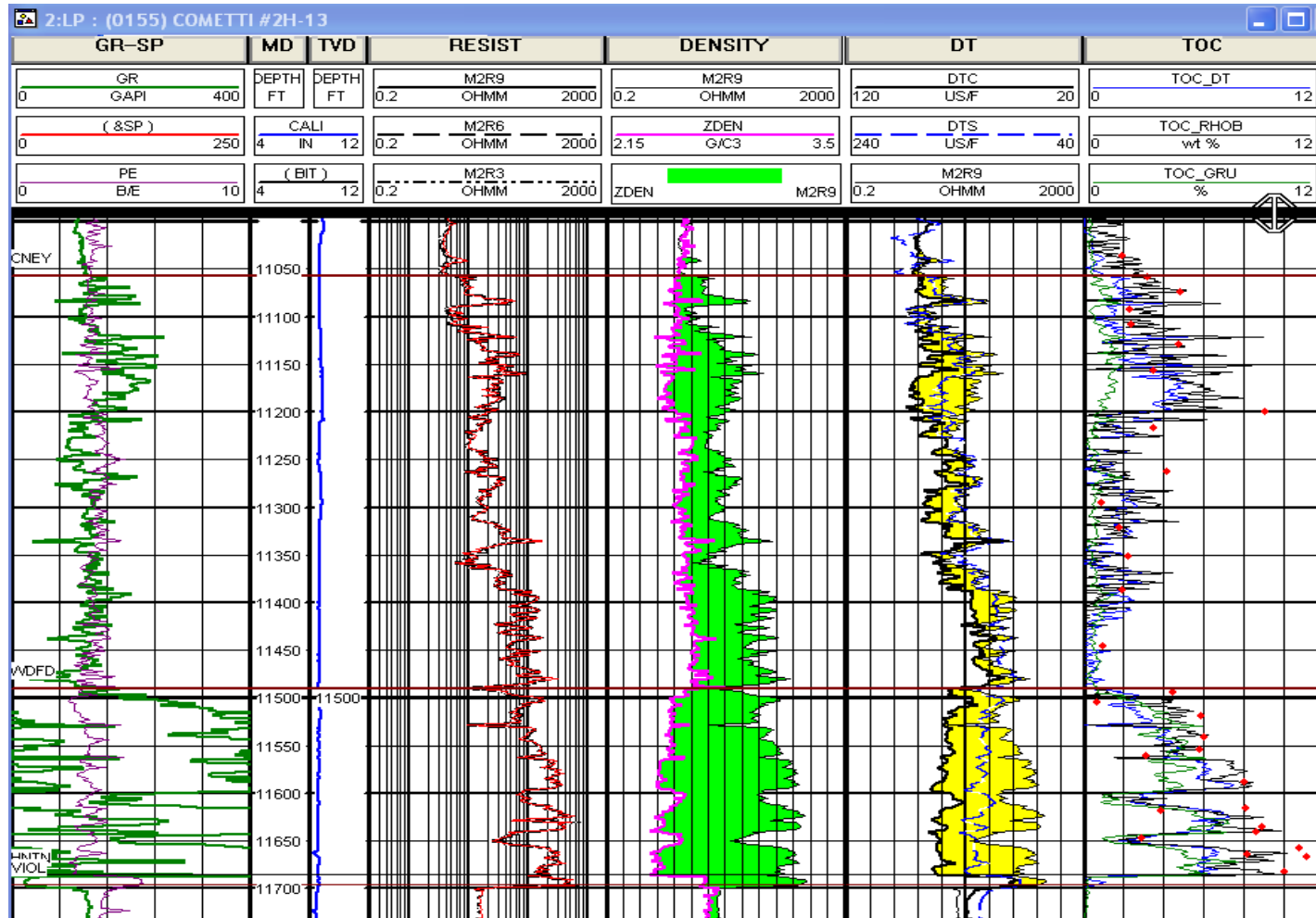
CANEY

Woodford

Calculated TOC curves from Density (black) and DTlogR (blue) are calibrated to core TOC measurements (red points);

NFX 2H-13 Cometti

TOC is approximated by multiple techniques



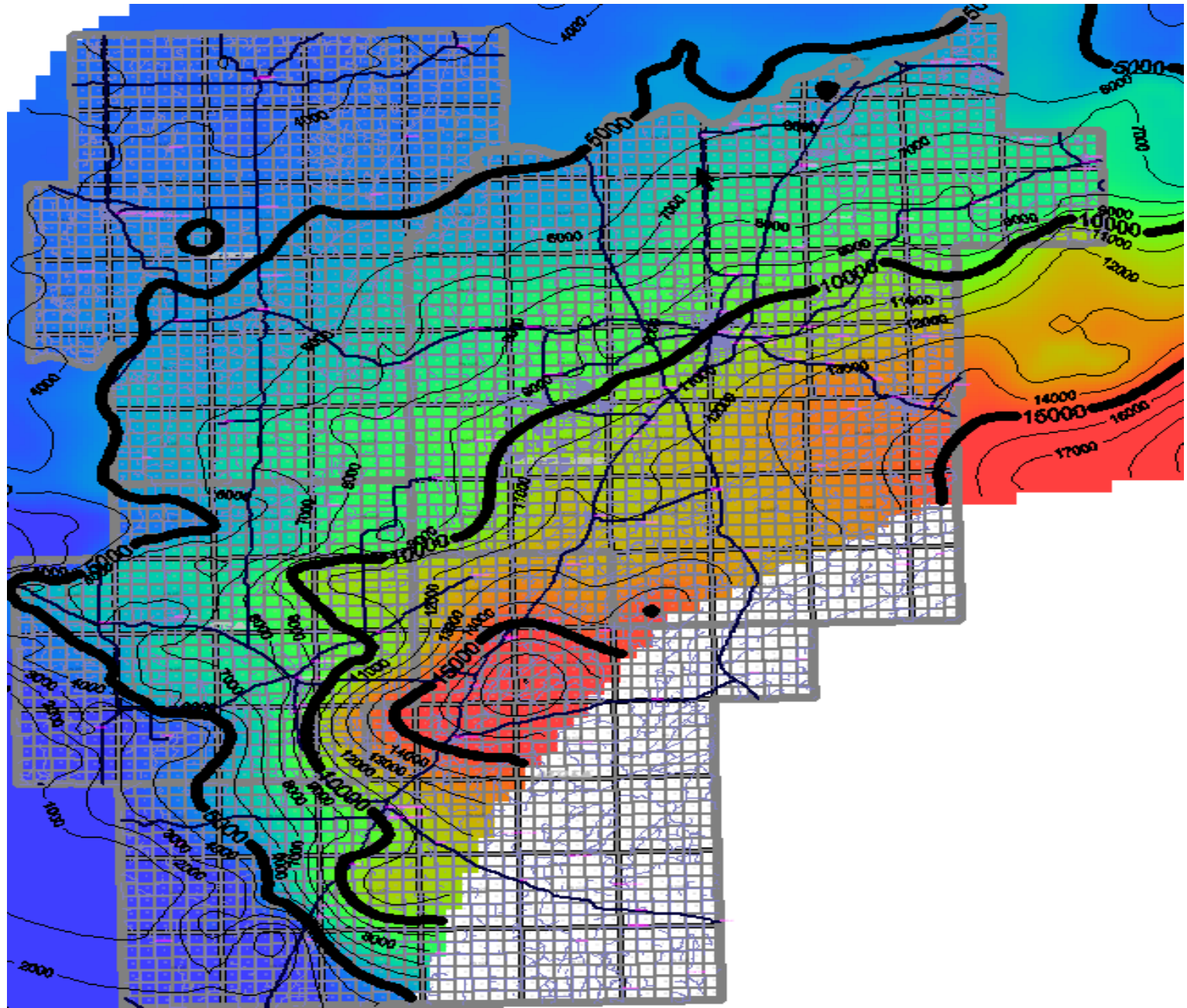
CANEY

Woodford

Calculated TOC curves are calibrated to core TOC measurements (red points);

Calibration: Goddard shale (top of picture) (TOC = 0%). Limestone & sandstone units excluded from evaluation.

Woodford structure



Woodford Temperature map

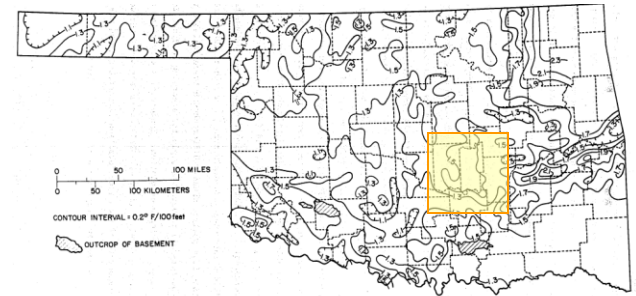
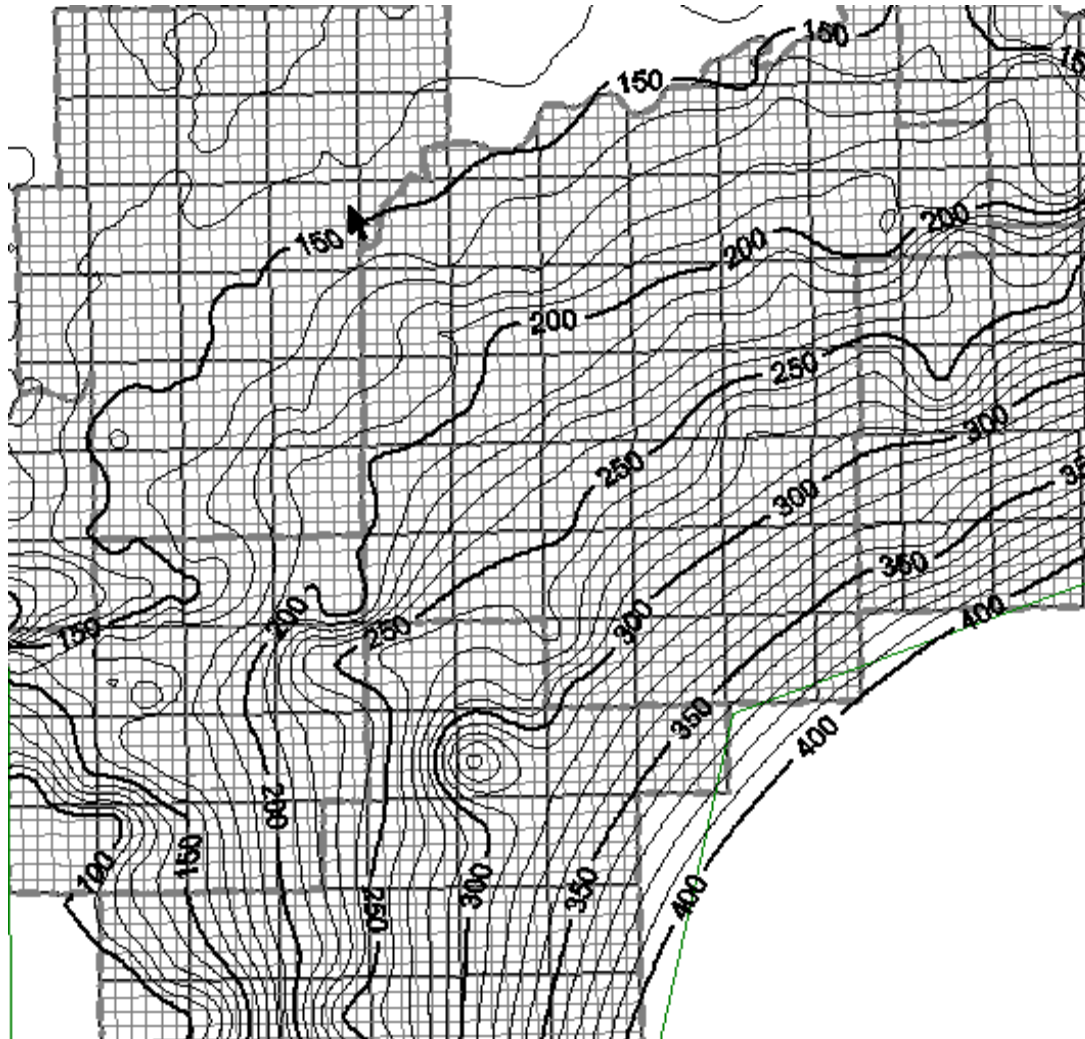
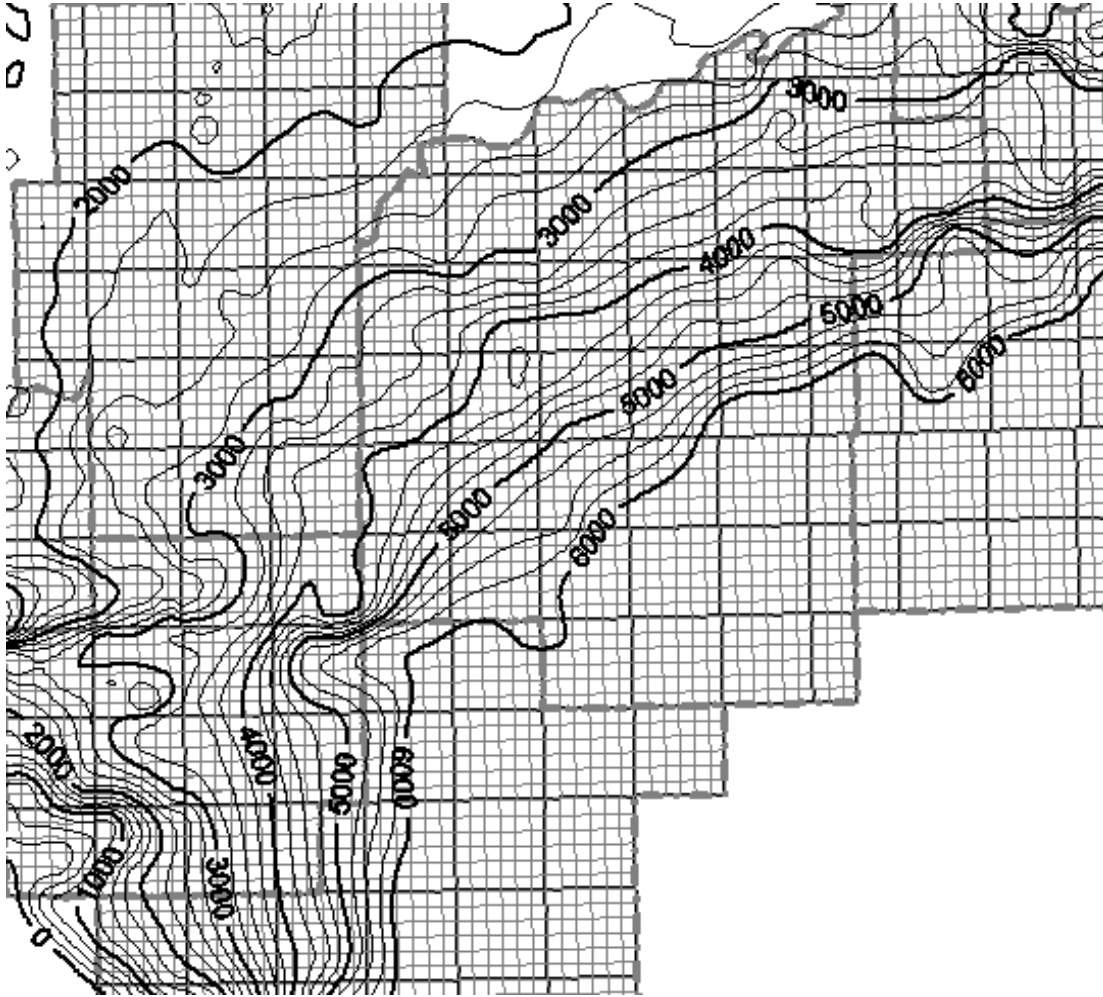


Fig. 3. Geothermal gradient map of Oklahoma (modified from Cheung, 1979).

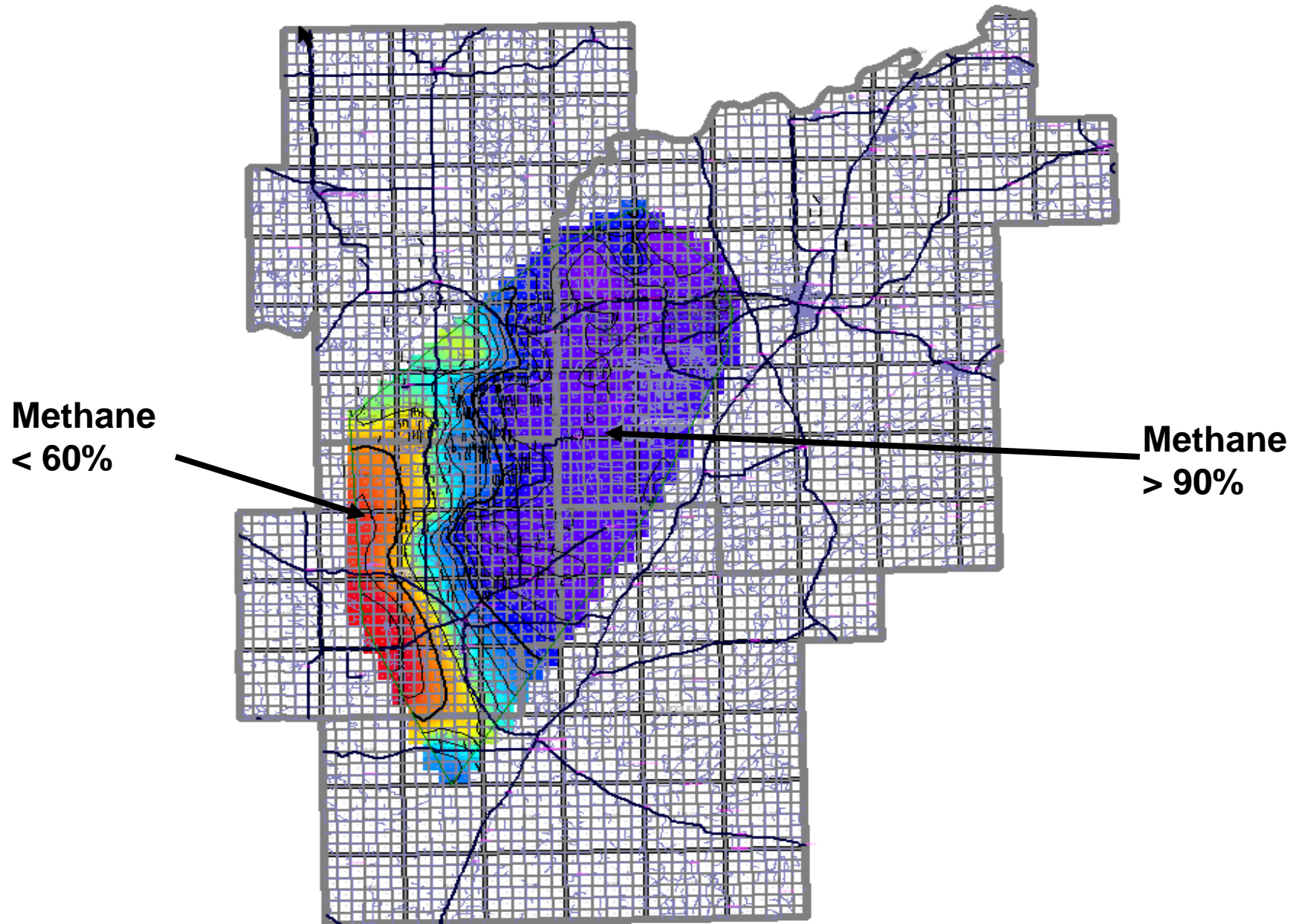
Geothermal gradient of
1.3 – 1.5 deg F / 100 ft.
Mean surface
temperature is 72 deg F
across study area.

Woodford Pressure map

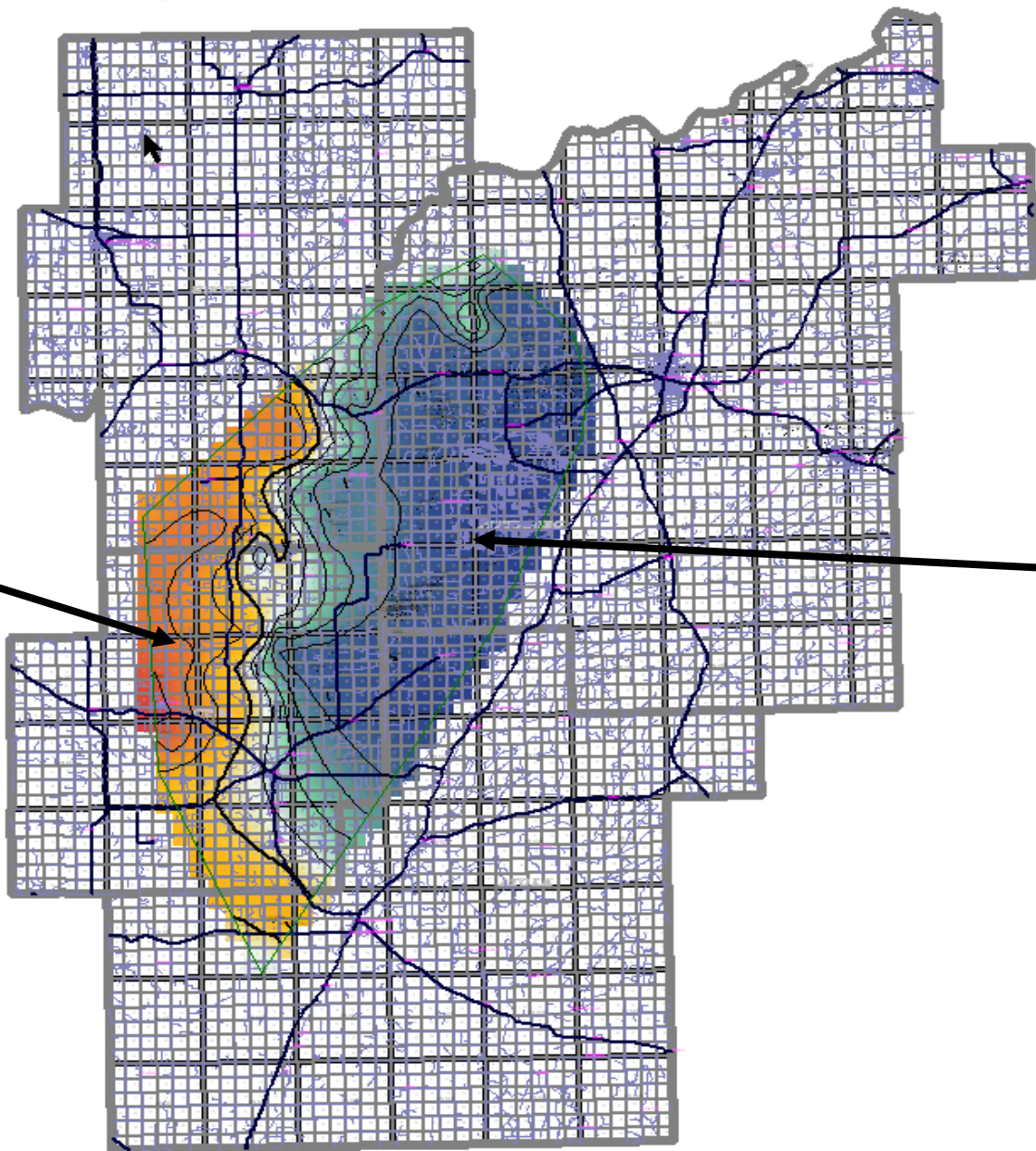


Geopressure Gradient:
.47 psi / ft (TVD)

Map of initial Methane



Map of initial Ethane



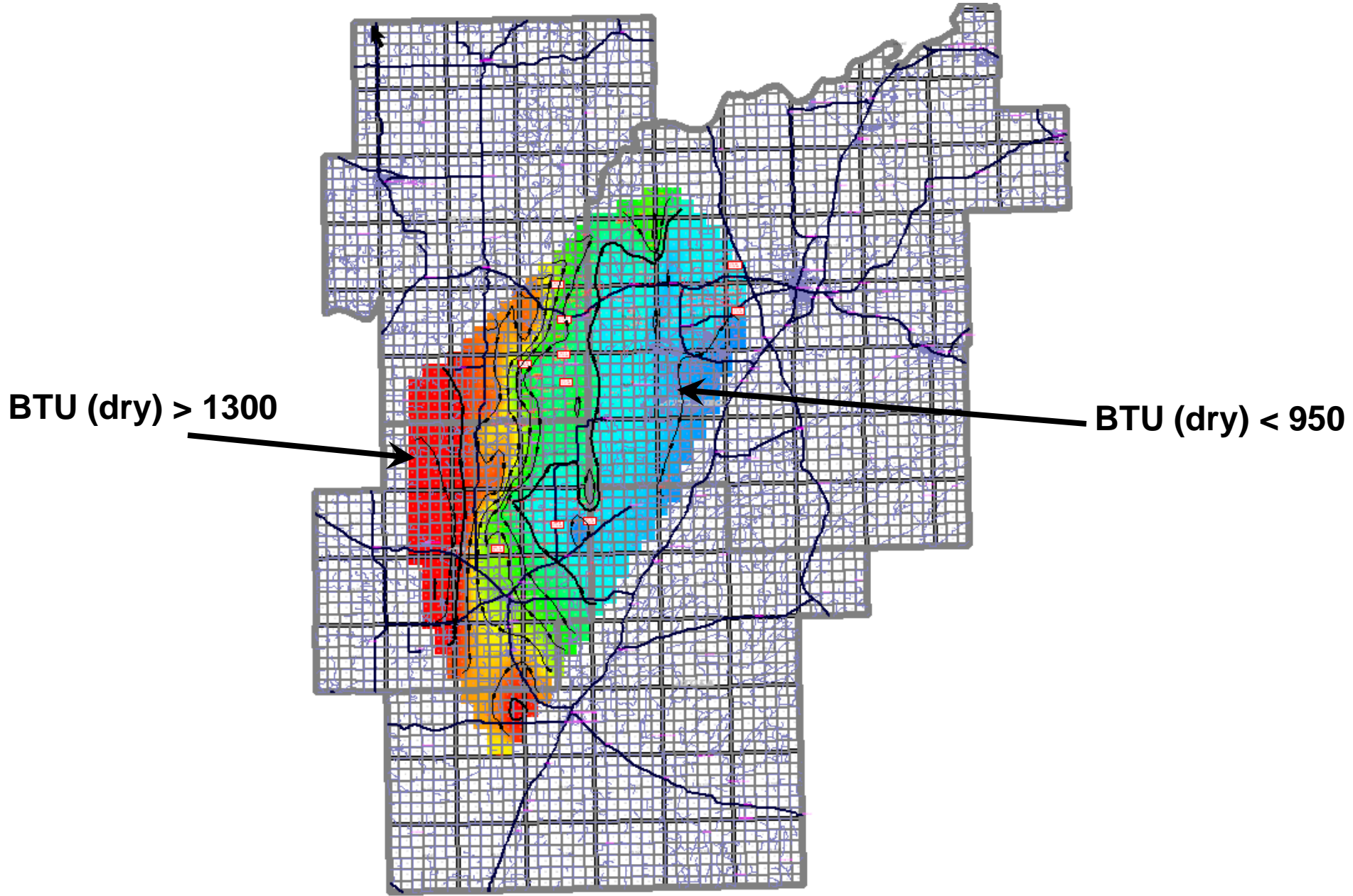
Ethane > 10%

Ethane < 2%

Map of initial CO₂



Produced gas (BTU content)



Extended Langmuir relationship

Multi-component isotherm relationships can be computed from single component data by use of extended Langmuir theory.

$$G_{si} = G_{sLi} \frac{\frac{py_i}{P_{Li}}}{1 + p \sum_{j=1}^{nc} \frac{y_j}{P_{Lj}}}$$

where:

G_{si} multi-component storage capacity of component i , scf/ton

G_{sLi} single component Langmuir storage capacity of component i , scf/ton

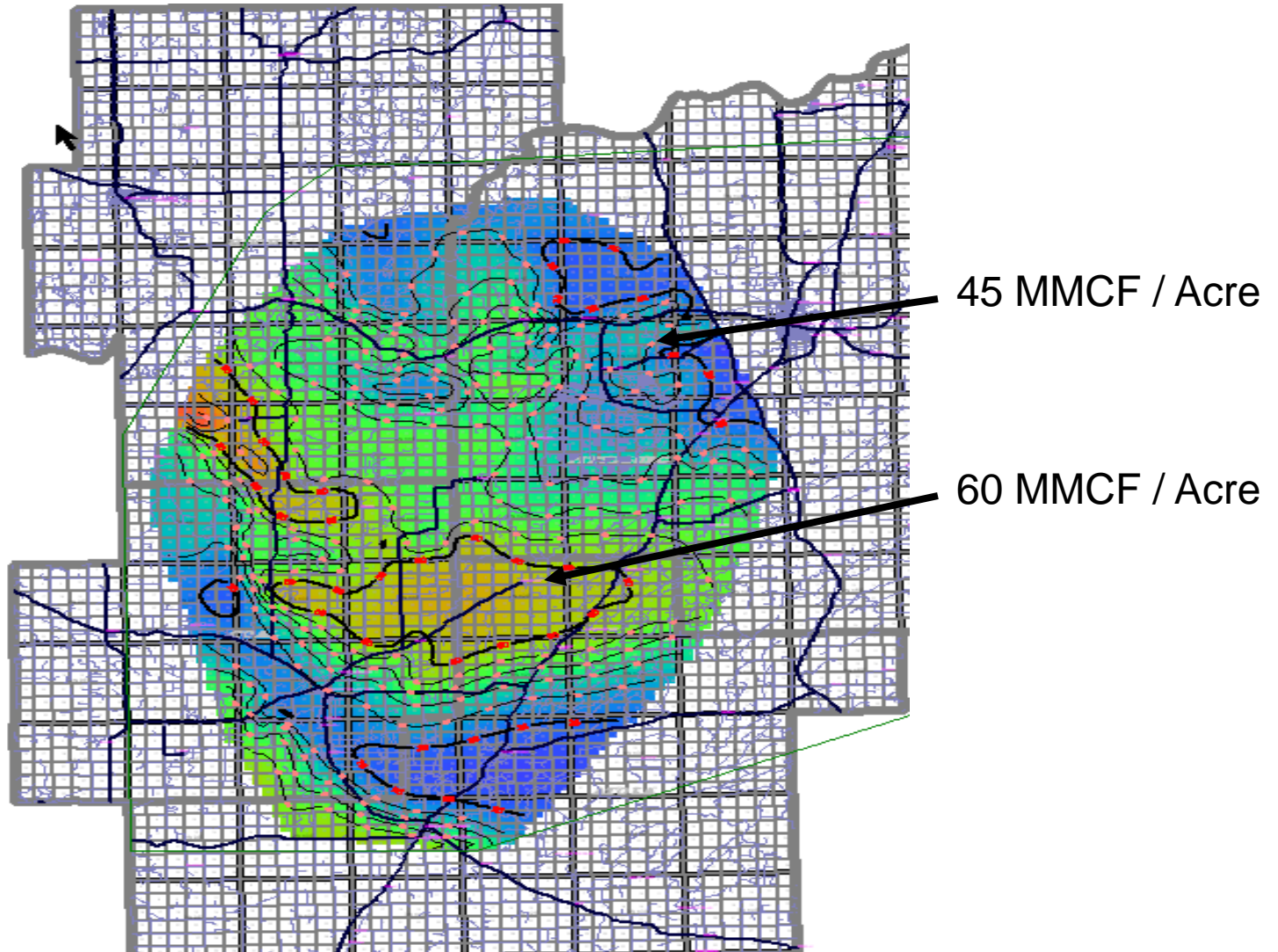
p_{Li} , p_{Lj} single component Langmuir pressure of component i or j , psia

y_i or y_j mole fraction of component i or j in the free gas (vapor) phase, dimensionless

nc number of components

p pressure of the free gas phase, psia

Adsorbed Gas in Place Woodford



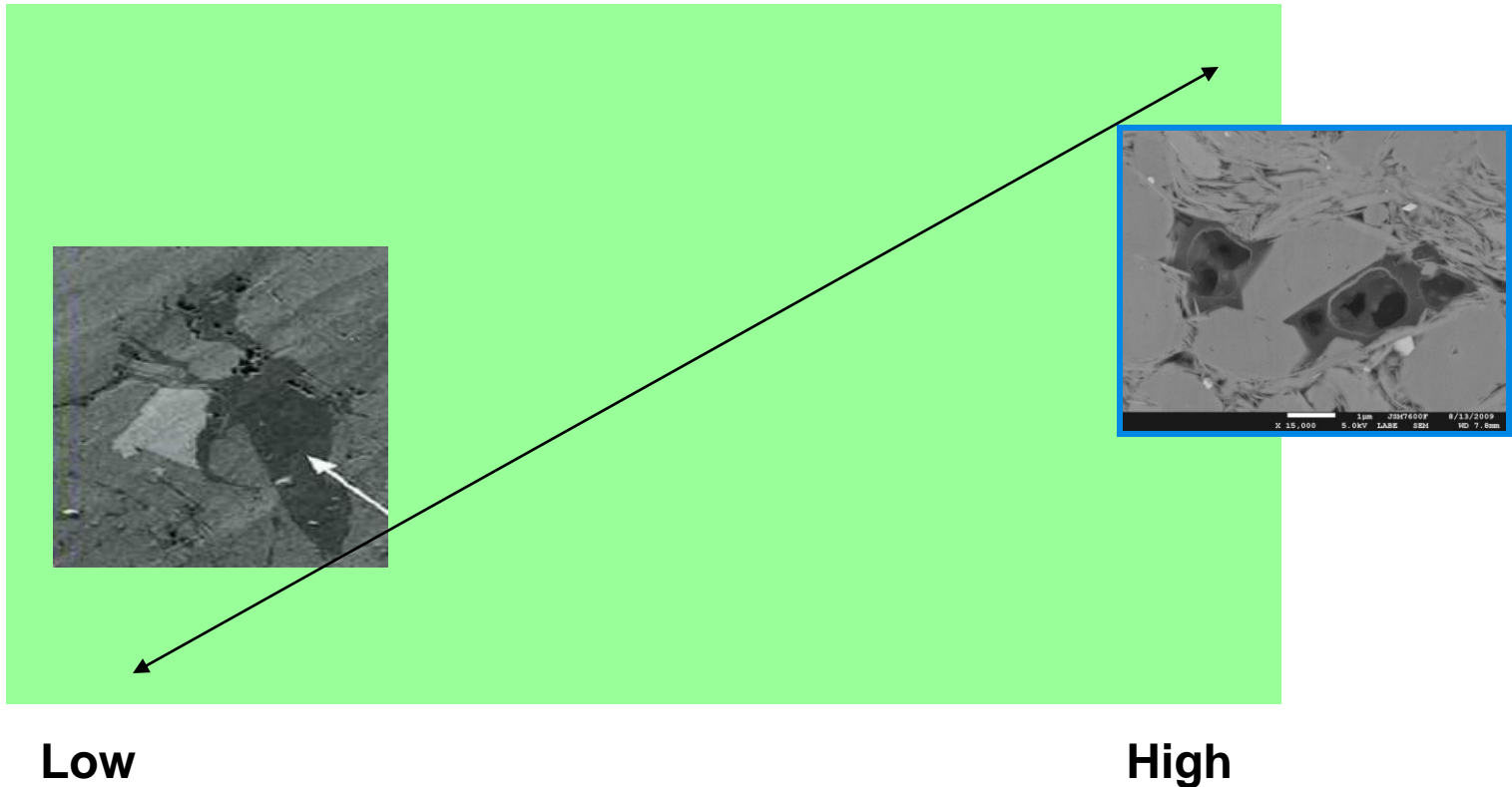
Acknowledgements

Significant contributions are recognized by:

- **Ciro Perez (Newfield Exploration)**
- **Brian Cardott (OGS)**
- **Randy Miller (Core Laboratories)**
- **The staffs of Weatherford Geochemical group (Humble Geochem & Ticora),**
- **Marc Bustin**

Kerogen adsorptive capacity related to thermal maturation

Degree of thermal maturation (VRo)



Effective surface area of Kerogen, based on observed nanoporosity level, using Field Emission SEM on Argon milled samples)

THIS IS STILL IN RESEARCH

Thermal maturity of Woodford Fm. organic matter (VRo) – western Arkoma Basin

